Dr. Amita Somya
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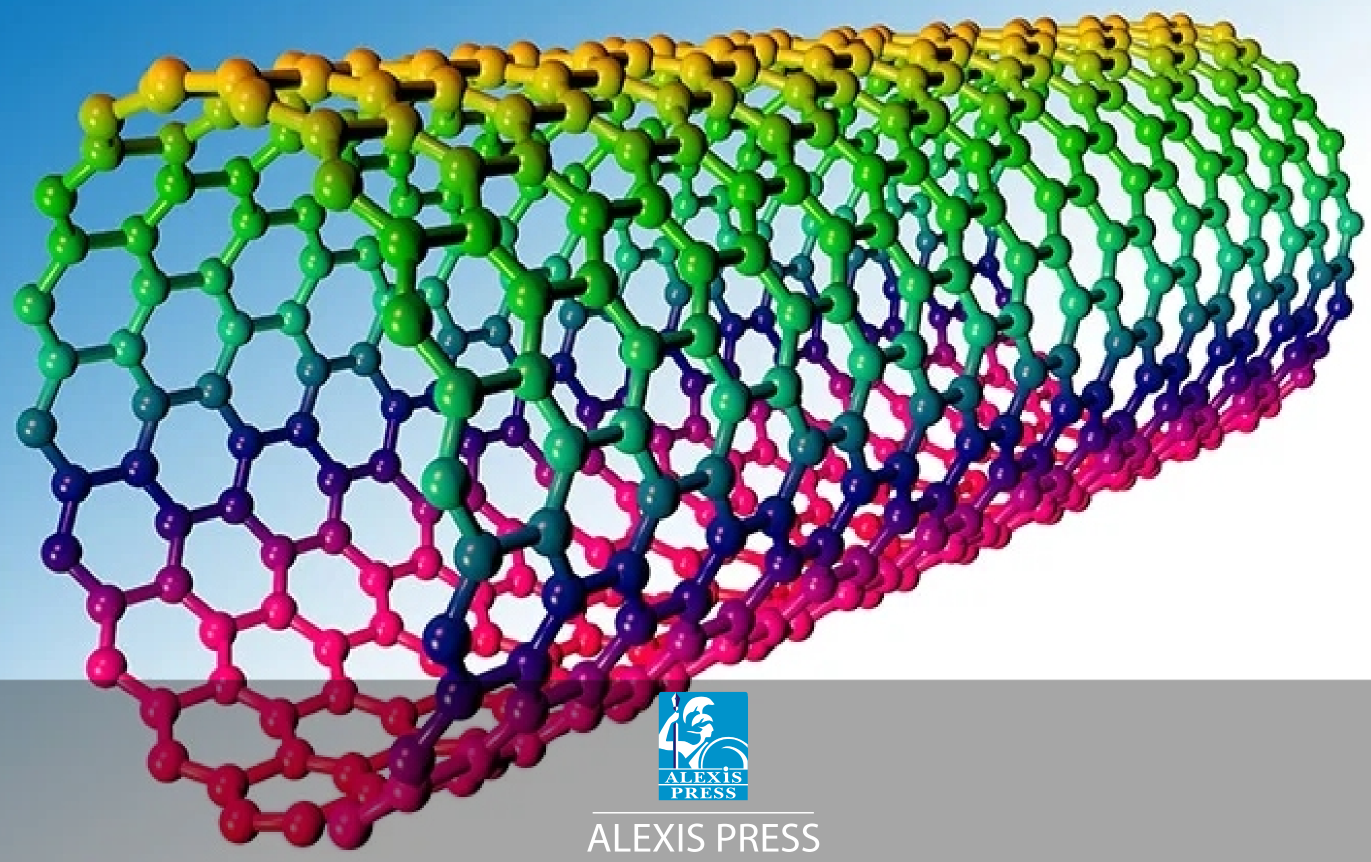
ADVANCES IN CARBON NANOTUBES



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CHAPTER 1

INTRODUCTION CARBON NANO TUBES

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Nanotubes are one of the substances that have undergone the most extensive research and are credited with helping to launch the nanotechnology revolution. Nanotubes have continued to amaze scientists and engineers throughout the last several decades. Even though they were first widely recognized as continuous hollow tubes in the core structure of carbon fibres in the 1970s, the discovery of nanotubes on the cathode of a carbon arc used to create fullerenes marked the beginning of the Nanotube Rush period. Nanotubes, especially those made of carbon, draw both basic scientists and engineers interested in applications due to the remarkable combination of their characteristics. To begin with, these molecular structures have an unmatched and superior length to diameter aspect ratio, being up to centimeters long but with a diameter of a few nanometers. A continuous tube consisting of long, thin sheets of graphene is one way to think about carbon nanotubes. They effectively and spontaneously produce nested multiwall nanotubes or single-wall nanotubes (SWNTs) under specific conditions (MWNTs). The atomic perfection of adjacent carbon nanotubes is clearly seen. Due to their close resemblance to graphene and this, nanotubes are rendered chemically inert. When under stress, nanotubes are thousands of times stronger than steel and only weigh a sixth as much as graphene. The melting point of nanotubes is higher than that of any metal, coming close to that of graphite at about 4000 K in a "ideal vacuum." Based on their atomic structure, including their diameter, single-wall nanotubes may behave either as semiconducting materials or as ballistic transporters of electrons.

Throughout the beginning of time, various kinds of carbon have been used in both art and technology. Charcoal and soot were used to create some of the earliest cave paintings at Lascaux, Altamira, and other locations. Since then, drawing, writing, and printing materials have included charcoal, graphite, and carbon black (a pure form of soot); photocopier toner is largely made of carbon black. Of course, coal and charcoal have been used as fuels for thousands of years, and charcoal was crucial to the development of what might be regarded as humankind's first technology the smelting and processing of metals. This method of using charcoal persisted until the seventeenth century, when it started to be replaced by coke, a change that sparked the Industrial Revolution. A need for graphite emerged in the late nineteenth century with the growth of the electrical sector. The first synthetic graphite was created in 1896 by an American named Edward Acheson. The use of activated carbon for cleaning air and water supplies increased gradually during the 20th century, while the development of carbon fibers in the 1950s gave engineers a brand-new, ultra-strong, lightweight material. Similar to graphite, diamonds have been known since ancient times but have only lately been employed for ornamental purposes. Diamond usage in industry was made possible by General Electric's invention of a commercial synthetic process in the 1950s.

Several famous names may be found throughout the history of the study of carbon. In a well-known experiment from 1772, Antoine Lavoisier established that diamonds are a kind of carbon by showing that when they burn, all that is produced is carbon dioxide. Prior to Carl Wilhelm Scheele doing a similar experiment with graphite in 1779, it was believed that graphite was a kind of lead as shown in Figure 1. At the Royal Institution, Humphrey Davy and Michael Faraday conducted in-depth research on combustion. Although Faraday used a burning candle as the beginning point for a comprehensive dissertation on natural philosophy in his renowned series of lectures on "The chemical history of a candle," Davy accurately attributed the yellow incandescence of a flame to blazing carbon particles. William and Lawrence Bragg determined the structure of diamond using X-ray diffraction in 1913, while John D. Bernal solved the structure of graphite nine years later. Rosalind Franklin distinguished between graphitizing and non-graphitizing carbons in 1951, and Kathleen Lonsdale made significant contributions to the study of diamonds, both natural and manufactured, around the same period. However, by the early 1980s, carbon science was widely regarded as an established field that was unlikely to produce any significant surprises, much less Nobel Prizes.

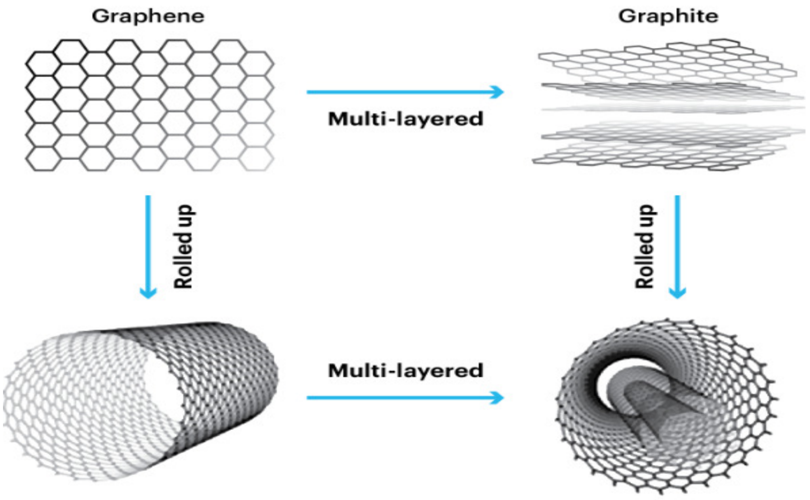

Figure 1: Illustrate the different types of Carbon Nano Tube.

History of Carbon Nanotubes

There is some controversy on who really discovered carbon nanotubes. The Japanese electric co.,LTD. (NEC) employee Lijima is credited by the majority of scientists with discovering the CNT. In In 1991, Lijima released a paper detailing his finding, which sparked a scientific frenzy and motivated numerous researchers to investigate the usage of carbon nanotubes. Notwithstanding the fact that carbon nanotubes were first reported in 1991, Lijima is really credited with their discovery. In 1952, Radushkevich and Lukyanovich, two bright researcher, who presented a crisp photograph of 50 carbon nanotubes in the Soviet Union in the Journal of Physical Chemistry. The political climate caused a major portion of this conclusion to be disregarded. In reality, the discovery of carbon nanotubes—the finding that carbon filaments may be hollow and have nanoscale diameters—is attributed to Radushkevich and Lukyanovich.

During the 14th Carbon Conference, held every two years at Pennsylvania State University, John Abrahamson presented data in support of carbon nanotubes. According to the conference report, carbon nanotubes are carbon fibers created on a carbon anode after an arc discharge. It also lists the fibers' characteristics and the theory that they develop in a low-pressure nitrogen environment.

Multi-walled carbon nanotubes have been found by Lijima in the insoluble component of graphite rods that are burning in an arc. According to predictions made by Mintmire, Dunlap, and White, single-walled carbon nanotubes will exhibit outstanding conductivity and lead to a discussion regarding the origins of carbon nanotubes in the future. Japanese electric company and IBM Bethune In a different work, Lijima added carbon to the arc discharge procedure together with transition metal catalysts to substantially speed up the creation of nanotubes for use in future research. He also used the arc discharge approach to make buckyballs. Mass manufacturing is a hallmark of Munster fullerenes.

These findings seem to broaden the use of fullerenes' accidental discovery. There is still much debate on who really discovered nanotubes. Several people see the Lijima paper from 1991 as being essential since it informed the whole scientific world of the existence of carbon nanotubes.

CNT application

Since Lijima's study on carbon nanotubes in 1991 brought them to the attention of scientists, they have been developed for a variety of applications owing to their exceptional mechanical and electrochemical characteristics, and they still have a broad range of potential uses. In order to include carbon nanotube technology in bike parts including riser handlebars, forks, cranks, seat bars, and air bars, Easy-Bell Sports collaborated with Zyvex Performance Materials. Hyperite Carbon Nanocup Hydrogen Resin, which is produced by Amory Europe Oy, contains carbon nanotubes that have been chemically activated and bound to acyclic hydrogen resin to create composites that are 20% to 30% stronger than conventional composites. It may be applied in this fashion to wind turbines, maritime paint, and a range of sporting goods. It is important to note that due to their electrochemical characteristics, carbon nanotubes have limitless potential in biological applications. Nowadays, tissue engineering uses carbon nanotubes as a scaffold for bone formation. This is due to the neutral electric charge carried by carbon nanotubes, which supported the maximum cell growth and creation of plate-shaped crystals. With osteoblasts cultivated on multi-walled nanotubes, there is a striking charge in the cell morphology, which is connected with alterations in the plasma membrane. In the future, carbon nanotubes may potentially be utilized to repair neurons, which would be beneficial for the research of the brain and neurological disorders.

In 1976, CNRS researcher Morinobu Endo discovered hollow tubes made of graphite sheets that had been created using a chemical vapour-growth method. Single-walled carbon nanotubes were later known to be the first specimens to be seen (SWNTs). Endo also recalled that he had seen a hollow tube, linearly stretched with parallel carbon layer faces towards the fiber core, in his early examination of vapor-phase-grown carbon fibers (VPCF). The presence of multi-walled carbon nanotubes in the fiber's core seems to be the cause of this. The VPGCF created by Endo has a close relationship to the MWCNTs that are mass-produced today. In fact, they refer to it as the "Endo-process" in honor of his early research and patents [1], [2]. Carbon nanotubes in 1979 at the Pennsylvania State University's 14th Biennial Conference on Carbon. The conference article defined carbon nanotubes as carbon fibers created during arc discharge on carbon anodes. These fibers were described, and theories on how they may have grown in a nitrogen atmosphere at low pressures were also provided.

The findings of the chemical and structural characterisation of carbon nanoparticles created by a thermocatalytical disproportionation of carbon monoxide were reported in 1981 by a team of Soviet scientists. The scientists proposed that their "carbon multi-layer tubular crystals" were made by rolling graphene layers into cylindrical shapes using TEM pictures and XRD patterns. They hypothesized that several distinct configurations of graphene hexagonal nets may be achieved by this rolling. They proposed two such potential arrangements: a spiral, helical layout and a circular arrangement (armchair nanotube) (chiral tube). A U.S. patent for the creation of "cylindrical discrete carbon fibrils" with a "constant diameter between about 3.5 and about 70 nanometers..., length 102 times the diameter, as well as an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core" was granted to Howard G. Tennent of Hyperion Catalysis in 1987.

Iijima's 1991 discovery of multi-walled carbon nanotubes in the insoluble material of arc-burned graphite rods and Mintmire, Dunlap, and White's independent prediction that if single-walled carbon nanotubes could be made, they would exhibit remarkable conducting properties both contributed to the initial excitement surrounding carbon nanotubes. After the separate discovery of single-walled carbon nanotubes and ways to specifically create them by adding transition-metal catalysts to the carbon in an arc discharge and Bethune et al. at IBM, nanotube research significantly increased [3], [4]. The famed Buckminster fullerene was well known to be produced on a preparative scale by the arc discharge technique and these results seemed to continue the trend of unintentional fullerene discoveries. By vaporizing the carbon/transition-metal combination in a high temperature furnace, improved this catalytic process. The production and purity of the SWMTs were considerably increased as a result. The finding of nanotubes is still a hotly debated topic. Many consider Iijima's study from 1991 to be especially significant since it made the scientific world as a whole aware of carbon nanotubes [5].

As carbon nanotubes also seem to be potent heat conductors, it is projected that they will beat the isotopically pure diamond's record thermal conductivity. Moreover, like the related substance graphite, carbon nanotubes seem to be biocompatible in a number of contexts. While the bulk of media coverage has focused on nanotube applications, nanotubes themselves provide a unique chance to look into the fundamental properties of quasi-one-dimensional (1D) conductors and semiconductors. For instance, any phase shift, such as the onset of superconductivity or permanent magnet ordering, should be suppressed in strictly one-dimensional systems. Moreover, it has been suggested that rather than acting, free carriers from one conductor behave like a Luttinger solvent [6], [7].

The screening behavior of these 1D systems significantly alters the optical properties of nanotubes. A notable example is the high exciton binding energy, which is comparable to their band gap in traditional semiconductors and is two orders of magnitude greater in semiconducting nanotubes than in 3D semiconductors. Some of the early problems have been fixed since the beginning of the Nanotube Rush era. Particularly in the field of single-wall nanotubes, close coordination between theory and experiment proved crucial for the rapid progress that has continued to the present. In one of the many cases, it was possible to remove observed differences in nanotube conductivity testing by developing a reliable method for making top-notch connections. Moreover, superconducting activity in nanotubes was only detected after the formation of strong connections between leads and nanotubes. The controlled production of carbon nanofibers with a clearly defined atomic (n, m) structure is one of the many problems that still needs to be addressed. This is crucial information for figuring out if a particular SWNT is metallic or semi-conductive and whether it will achieve the required performance standards.

Every theoretical and experimental method that has been developed to define low-dimensional systems, from nanoparticles to surfaces, has been used to study nanotubes. Nanotube metrology has established itself as a field that not only influences quality control but also provides guidance on the typical behavior of certain samples. The most direct experimental information on the radius and interlayer spacing of certain single- and multi-wall nanotubes has come from a high-resolution scanning electron microscope. By analyzing the surface area of the radial breathing mode, Raman spectroscopy has proved especially helpful in determining the distributions of nanotube diameters and the amount of amorphous carbon in the sample. Using photoluminescence spectra is a powerful technique for determining the substituent concentration among semiconducting nanotubes. These methods are often used with scanning-probe microscopy and certain other spectroscopic techniques to analyze nanotube materials for symmetry, purity, chemical changes, and defects. A carbon tube with a diameter commonly measured in nanometers is known as a carbon nanotube (CNT).

One kind of carbon allotrope, single-wall carbon nanotubes (SWCNTs), are nanometer-sized tubes that are midway between fullerene cages and flat graphene. Single-wall carbon nanotubes may be envisioned as cuttings from a two-dimensional hexagonal lattice of carbon atoms that have been rolled up along one of the Bravais lattice vectors to create a hollow cylinder, even though they are not really manufactured in this manner. A helical lattice of flawlessly connected carbon atoms is produced on the cylinder surface in this construction by imposition of periodic boundary constraints throughout the length of this roll-up vector.

Nanotubes with a Single or Two Walls

The kind of nanotubes Iijima first identified in 1991 almost often feature more than one graphitic layer and have inner diameters of around 4 nm. The synthesis of single-walled nanotubes was separately reported in 1993 by Iijima and Toshinari Ichihashi of NEC and Donald Bethune and colleagues of the IBM Almaden Research Center in California. The single-walled tubes looked to exhibit structures that are close to those of the "ideal" nanotubes, which proved to be a very significant breakthrough. Due to their amazing qualities, single-walled tubes are now the subject of more studies than their multiwalled counterparts. Smalley's team's description of the laser-vaporization-based synthesis of single-walled tubes in 1996 marked a significant advancement [8]. Moreover, as will be covered later, they may be produced catalytically. An illustration of a single-walled nanotube (SWNT). It is clear that the appearance differs significantly from samples of multiwalled nanotubes (MWNTs). The individual tubes are often bent rather than straight and have extremely tiny sizes (usually 1 nm). Moreover, they often form bundles or "ropes." Arc-evaporation techniques for making large yields of double-walled carbon nanotubes (DWNTs) have also been developed recently.

Multi-wall carbon nanotubes (MWCNTs) are tree-ring-like structures made of stacked single-wall carbon nanotubes that are weakly interconnected by van der Waals interactions. These tubes are extremely similar, if not identical, to the long straight and parallel carbon layers cylindrically stacked around a hollow tube proposed by Oberlin, Endo, and Koyama. Double- and triple-wall carbon nanotubes are also sometimes referred to as multi-wall carbon nanotubes. Tubes having an unknown carbon wall structure and sizes under 100 nanometers are also referred to as carbon nanotubes.

While it is often unreported, the length of a carbon nanotube created by standard manufacturing techniques is generally substantially more than its diameter. As a result, end effects are often disregarded and the length of carbon nanotubes is thought to be unlimited. Although some carbon nanotubes are semiconductors, others may display extraordinary electrical conductivity. Because of their nanostructure and the strength of the connections between the carbon atoms, they also exhibit outstanding tensile strength and thermal conductivity. They may also undergo chemical modification. These characteristics are anticipated to be useful in a variety of technological fields, including electronics, optics, composite materials (replacing or enhancing carbon fibers), nanotechnology, and other materials science-related applications. A hexagonal lattice may be rolled up in a variety of ways to create indefinitely long single-wall carbon nanotubes, and it turns out that each of these tubes has nontrivial rotational symmetry around its axis in addition to helical and translational symmetry [8]–[10]. Moreover, the majority are chiral, which prevents superimposing the tube and its mirror copy. Moreover, single-wall carbon nanotubes may be identified by a pair of integers thanks to this structure.

All but a tiny subset of achiral single-wall carbon nanotubes are semiconductors with modest to moderate band gaps. Yet, these electrical characteristics are the same for the tube and its mirror counterpart regardless of whether the hexagonal lattice is rolled from its front to rear or from its back to front. SWCNTs were anticipated to have amazing capabilities, but there was no way to make them until 1993, when Bethune et al. at IBM and Iijima and Ichihashi at NEC separately found that co-vaporizing carbon and transition metals like iron and cobalt could particularly promote SWCNT creation. These findings sparked research that considerably improved the effectiveness of the catalytic manufacturing method and resulted in a huge increase in the amount of effort done to describe and use SWCNTs.

Carbon nanotubes generated catalytically

Even before Iijima found carbon nanotubes linked to fullerene, catalysis was known to produce filamentous carbon. P. and L. Schultzenberger noticed the development of filamentous carbon during studies involving the passage of cyanogen over very heated porcelain as early as 1890. (1.26). A variety of hydrocarbons and other gases might interact with metals, the most efficient of which were iron, cobalt, and nickel, to generate filaments, according to research done in the 1950s. The Russian Journal of Physical Chemistry published a 1952 report by Radushkevich and Lukyanovich that likely included the first electron micrographs to depict tubular carbon filaments. As it became evident that filament development may pose a severe issue for the functioning of nuclear reactors and several chemical processes, substantial study into the catalytic synthesis of carbon filaments started in the 1970s. Terry Baker and his colleagues at the United Kingdom Atomic Energy Authority's laboratory in Harwell, and subsequently in the USA, conducted the most comprehensive research effort in the 1970s. This group was worried about the development of filamentous carbon in the cooling systems of nuclear reactors that use gas cooling. Hence, the need to prevent filamentous carbon formation in these cooling pipes served as the main driving force behind Baker's research. Yet, a few employees realized that catalysis may be used to generate valuable carbon nanofibres. Morinobu Endo of Shinshu University in Japan stands out among them for suggesting in 1988 that catalytic carbon nanotubes may serve as an alternative to ordinary carbon fibers, which are made by pyrolyzing strands of polymer or pitch [11]–[13]. With Iijima's study in 1991, interest in carbon nanotubes created by catalysis skyrocketed. Now, catalysis may also be used to create single- and double-walled nanotubes in addition to multiwalled nanotubes. Many benefits make the catalytic synthesis of nanotubes appealing. Most notably, it is far more scale-up-friendly than arc-evaporation. Many procedures have been developed recently for the catalytic bulk synthesis of single-walled tubes. Moreover, catalytic processes enable the controlled development of tubes on substrates for use in display technology and other fields. The fundamental disadvantage is that the quality of tubes generated in this manner is worse than that of tubes produced by arc-evaporation, at least for multiwalled nanotubes.

Multi-walled

Concentric tubes of graphene are the numerous wrapped layers that make up multi-walled nanotubes (MWNTs). The architectures of multi-walled nanotubes may be modeled using one of two different approaches. In the Russian Doll model, graphite sheets are placed in cylinders that are concentric to one another, for example, a smaller (0, 8) single-walled nanotube (SWNT) within a bigger (0,17) SWNT. In the Parchment model, a single graphite sheet is wrapped inward and over itself to resemble a scroll of parchment or a rolled piece of newspaper. The interlayer spacing in multi-walled nanotubes, which is around 3.4, is comparable to the separation between graphene layers in graphite. More often, the Russian Doll structure is seen. SWNTs, which may be metallic or semiconducting, can be used to characterize each of its constituent shells. Because to limitations on the relative sizes of the various tubes and statistical likelihood, one of the shells, and so the whole MWNT, is often a zero-gap metal.

Due to their comparable appearance and characteristics to those of single-walled carbon nanotubes (SWNTs) but greater resistance to chemical assaults, double-walled carbon nanotubes (DWNTs) constitute a unique class of nanotubes. This is crucial when it's essential to functionalize nanotubes (add characteristics to them) by grafting chemical functionalities onto their surfaces. When SWNTs are covalently functionalized, some C=C double bonds will be broken, producing "holes" in the nanotube's structure and changing both its mechanical and electrical characteristics. With DWNTs, just the outside wall is changed. It was initially suggested in 2003[30] to use the CCVD method to selectively reduce oxide solutions in methane and hydrogen to produce DWNT on the gram-scale.

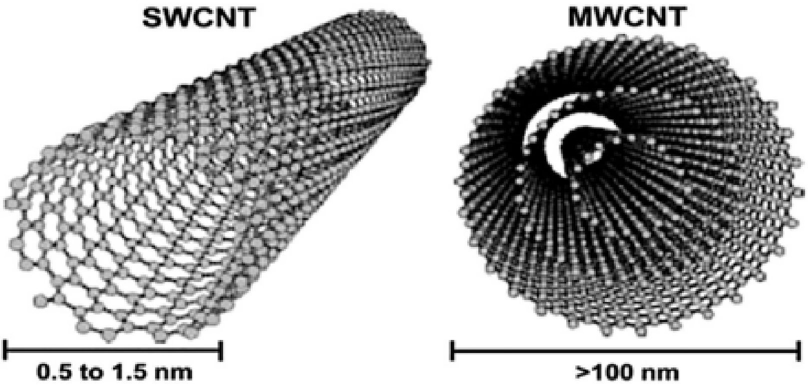

Figure 2: Illustrate Typical MWNT and SWNTs.

The usage of multi-walled nanotubes as the primary moveable arms in forthcoming nanomechanical systems will be made possible by the telescopic motion capability of inner shells and their distinct mechanical properties. The Lennard-Jones contact between shells is what causes the telescopic motion's retraction force, which has a magnitude of roughly 1.5 nN. Theoretical discussions about junctions between two or more nanotubes are quite common. Both samples made by chemical vapor deposition and by arc discharge typically include these connections. When originally theorized about the electrical characteristics of such junctions, they noted that a connection between two semiconducting tubes would be an example of a nanoscale heterojunction. So, a junction like this might be a part of an electrical circuit built using nanotubes. A junction between two multiwalled nanotubes may be seen in the photograph next to it. Nanotube-graphene junctions have been thought of theoretically and investigated experimentally. The building blocks of pillared graphene, which consists of parallel graphene sheets separated by brief nanotubes, are nanotube-graphene junctions. A group of three-dimensional carbon nanotube topologies are represented by pillared graphene.

Lately, a number of studies have emphasized the potential for creating three-dimensional macroscopic >100 nm in all three dimensions all-carbon devices employing carbon nanotubes as building blocks. In order to create macroscopic, free-standing, porous, all-carbon scaffolds, Lalwani et al. proposed a unique radical-initiated thermal crosslinking technique employing single- and multi-walled carbon nanotubes as building blocks. These scaffolds have holes that are macro, micro, and nanostructured, and the porosity may be adjusted for different uses. The next generation of energy storage, supercapacitors, field emission transistors, high-performance catalysis, photovoltaics, and biomedical devices, implants, and sensors may be made using these 3D all-carbon scaffolds and architectures.

A newly developed substance called carbon nanobuds combines two previously identified carbon allotropes, fullerenes and carbon nanotubes. The outside sidewalls of the underlying carbon nanotube are covalently bound to fullerene-like "buds" in this novel material. Both fullerenes and carbon nanotubes are present in this hybrid material in practical amounts. They have been discovered to be particularly excellent field emitters. The mechanical qualities of composite materials may be improved by the linked fullerene molecules acting as molecular anchors to stop the slippage of the nanotubes.

A unique hybrid carbon substance called a carbon peapod captures fullerene within a carbon nanotube. With heating and radiation, it may have fascinating magnetic characteristics. In theoretical analyses and forecasts, it may also be used as an oscillator. A carbon nanotube twisted into a torus is, in principle, a nanotorus doughnut shape. Many distinctive characteristics, such as magnetic moments 1000 times bigger than those previously anticipated for certain particular radii, are predicted for nanotori. The radius of the torus and the radius of the tube have a significant impact on properties like the magnetic moment and thermal stability, among others.

A relatively recent hybrid known as graphenated carbon nanotubes includes graphitic foliates formed on the sidewalls of multiwalled or bamboo-style CNTs. Depending on the deposition circumstances such as temperature and time, the foliate density may change. Its structure can range from a few layers of graphene less than 10 to thicker, more graphite-like layers. The large surface area three-dimensional framework of the CNTs combined with the high edge density of graphene is the primary benefit of an integrated graphene-CNT structure. As comparison to other carbon nanostructures, the total charge capacity per unit of nominal area may be greatly increased by depositing a high density of graphene foliates along the length of aligned CNTs. Other quasi-1D carbon structures, which often act as quasi-metallic conductors of electrons, are different from cup-stacked carbon nanotubes (CSCNTs). Because of the stacking architecture of the graphene layer, CSCNTs behave semiconductingly.

Raman spectroscopy, photoluminescence (fluorescence), and absorption are all advantageous characteristics of optical carbon nanotubes. A rather substantial quantity of carbon nanotubes may be quickly and non-destructively characterized using spectroscopic approaches. From an industrial perspective, there is a significant need for such characterisation since many nanotube synthesis factors may be altered, either consciously or unconsciously, to affect the nanotube quality. The following illustration demonstrates how to quickly and accurately characterize this "nanotube quality" in terms of non-tubular carbon concentration, structure (chirality) of the generated nanotubes, and structural flaws. Almost all other qualities, including optical, mechanical, and electrical ones, are determined by these traits.

The singular "one-dimensional entities" known as carbon nanotubes may be thought of as coiled graphite sheets (or more precisely graphene). Several rolling angles and curvatures may be used, resulting in various nanotube characteristics. The length-to-diameter ratio for nanotubes, which is as high is unmatched by any other material. As a result, all of the carbon nanotubes' characteristics are exceedingly anisotropic and adjustable in comparison to those of conventional semiconductors.

The actual use of the carbon nanotubes' optical qualities is not yet obvious, but their mechanical, electrical, and electrochemical (supercapacitor) capabilities are widely known and have immediate applications. Optics and photonics might benefit from the aforementioned tunability of characteristics. In particular, single nanotube-based light-emitting diodes (LEDs) and photo-detectors have been manufactured in the lab. Its distinctive quality is not their efficiency, which is still rather poor, but rather their tight selectivity in the light's emission and detection wavelengths and the potential for fine-tuning those wavelengths through the nanotube structure. Furthermore, single-walled carbon nanotube ensembles have been used to create bolometer and optoelectronic memory devices. The electrical characteristics of the tube are also impacted by crystallographic flaws. Reduced conductivity across the affected area of the tube is a frequent outcome. Single monatomic vacancies provide magnetic characteristics, and defects in armchair-type tubes which may conduct electricity can lead the surrounding area to become semiconducting.

Arc discharge, laser ablation, chemical vapor deposition (CVD), and high-pressure carbon monoxide disproportionation are some of the synthesis methods that have been developed to manufacture nanotubes in significant numbers (HiPCO). Arc discharge, laser ablation, chemical vapor deposition (CVD), and HiPCO are batch-by-batch processes, respectively. The majority of these procedures need process gases or a vacuum to operate. Because of its high yield and degree of control over diameter, length, and shape, the CVD growing process is well-liked. These techniques can synthesis enormous amounts of nanotubes using particulate catalysts, but they have significant problems with reproducibility when used with CVD growth. [84] CNTs are becoming more economically feasible because to improvements in catalysis and continuous growth made by the HiPCO technique. The HiPCO technique aids in the increased production of high purity single walled carbon nanotubes. The HiPCO reactor runs at high pressures of 30 to 50 bar and high temperatures of 900 to 1100 °C.

It employs iron pentacarbonyl or nickel tetracarbonyl as a catalyst and carbon monoxide as the carbon source. The nucleation location for the growth of the nanotubes is provided by these catalysts. Thermal chemical vapor deposition is another method for growing arrays of vertically aligned carbon nanotubes. A catalytic metal (Fe, Co, Ni) layer is applied to a substrate (quartz, silicon, stainless steel, etc.). Usually, that layer is made of iron and is sputtered to a thickness of 1 to 5 nm. Alumina underlayers between 10 and 50 nm are frequently also applied to the substrate first. Controllable wetting and good interfacial properties are imparted by this. The continuous iron film separates into small islands when the substrate is heated to the growth temperature (roughly 700 °C), and each island then initiates a carbon nanotube. The island size is governed by the sputtered thickness, which in turn affects the diameter of the nanotube. The diameter of the islands and the diameter of the produced nanotubes are both decreased by thinner iron layers. Due to their mobility and ability to combine into bigger (but fewer) islands, metal islands can only stay at the growth temperature for a certain length of time. The site density (number of CNTs/mm2) is decreased as the catalyst diameter is increased by annealing at the growth temperature. Impurities such as amorphous carbon, fullerene, and other forms of carbon as well as non-carbonaceous impurities are always present in the carbon nanotubes as-prepared (metal used for catalyst). For the carbon nanotubes to be used in applications, these contaminants must be eliminated.

Functionalization

Strong intermolecular p-p interactions cause CNTs to exhibit poor dispersibility in many solvents, including water. This makes CNTs more difficult to process for use in industrial applications. Several methods have been developed to change the surface of CNTs in order to increase their stability and solubility in water in order to address the problem. Insoluble CNTs may now be processed and handled more effectively, making it possible to create novel CNT nanofluids with amazing characteristics that can be tailored for a variety of applications. Covalent functionalization, which involves oxidizing CNTs with strong acids (such as sulfuric acid, nitric acid, or a mixture of both), has been studied extensively. This method leaves the CNTs with carboxylic groups on their surface, which can then be further modified through esterification or amination. Alkyl or aryl peroxides, substituted anilines, and diazonium salts are the starting ingredients for the promising covalent functionalization approach known as free radical grafting.

Compared to conventional acid treatments, which entail the attachment of tiny molecules like hydroxyl onto the surface of CNTs, free radical grafting of macromolecules (as the functional group) onto the surface of CNTs may increase the solubility of CNTs. Free-radical grafting may dramatically increase the solubility of CNTs because the large functional molecules make it easier for CNTs to disperse in a range of solvents, even at low functionalization levels. Clove buds have recently been used in an inventive, ecologically friendly method for covalently functionalizing multi-walled carbon nanotubes (MWCNTs). This method is novel and environmentally friendly since it avoids the use of dangerous and poisonous acids, which are often utilized in conventional methods for functionalizing carbon nanomaterials. With the aid of a free radical grafting reaction, the MWCNTs are functionalized all at once. After dispersion in water, the clove-functionalized MWCNTs form very stable multi-walled carbon nanotube aqueous suspensions (nanofluids).

Modeling microstructures with aggregation zones that were simulated by computers. Similar to conventional composites, which include a matrix phase encircling a reinforcing phase, carbon nanotubes are modeled in this way. Idealized models like cylinders, hexagons, and squares are widespread. The examined mechanical characteristics have a significant impact on the micromechanics model's size. In order to create a computer model that accurately represents the behavior of CNT reinforced nanocomposite, the representative volume element (RVE) idea is applied. One RVE may be able to forecast a material's desired attribute (thermal, electrical, modulus, or creep) better than the alternatives. While the ideal model's implementation is computationally efficient, it does not correspond to the microstructural characteristics of real nanocomposites that can be seen using scanning electron microscopy. Computer models are also created to include variability, such as waviness, orientation, and aggregation of multiwall or single wall carbon nanotubes, in order to add realistic modeling.

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CHAPTER 2

SYNTHESIS AND PURIFICATION OF MULTI-WALLED AND SINGLE-WALLED CARBON NANOTUBES

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Since the carbon nanotube (CNT) was discovered by lijima, numerous researchers have become interested in it, and as a result, a sizable body of research has amassed. Currently, CNT are produced using a variety of techniques, such as arc discharge, laser ablation, and catalytic hydrocarbon breakdown. CNT were initially produced as a by-product during the synthesis of fullerenes using the arc-discharge technique. It has also been proposed to utilize solar energy and electrolysis. Recent developments in the application of CNT have been remarkable, such as the field electron emitter, for instance. CNT is anticipated to rank among the most important materials of the twenty-first century due to its rapid growth in so many sectors. In line with the application of CNT, this chapter provides a description of the present situation and the possibilities for its synthesis. Single-walled CNT and multi-walled CNT (MWCNT) are two types that CNT may be categorized into (SWCNT). In contrast to the latter, the former had already been located [1], [2].

There have been substantial efforts placed towards the synthesis and purification of MWCNT in order to evaluate its physical properties. In spite of this, the moment is gradually expanding in anticipation of its industrial use. SWCNT was first tough to get, and in addition, both its purification and evaluation of its physical characteristics were problematic. Since SWCNT was initially effectively synthesized in 1996, it has been intensively investigated, mostly from scientific vantage points. The next sections will list each step in the production and purification of MWCNT and SWCNT.

MWCNT MWCNT was first identified as a by-product of the above-described synthesis of C60. In the electric arc-discharge process utilizing pure carbon, the yield of MWCNT is 30 to 50%. From an academic perspective, however, many academics seem to be working on SWCNT at the moment, possibly exhausted by the laborious process of purifying MWCNT, especially when it was produced using the arc-discharge technique. MWCNT is still appealing, however, since it has a wide range of industrial applications that may make use of its great chemical stability and high mechanical strength. For example, MWCNT possesses inherent characteristics that make it a good choice for field emitters, such as a sharp tip with a radius of curvature on the order of nanometers, high mechanical rigidity, chemical inertness, and high electrical conductivity. It also features the distinctive coaxial form, which will provide strong opportunities for application to a variety of industrial industries, in addition to these outstanding qualities [3], [4].

Cylindrical deposit formed on the surface of the cathode when the arc-discharge is continued while maintaining the distance between the carbon electrodes at around 1 mm. Its cathode deposit's diameter is the same as the anode stick's. The cathode deposit expands at around 2-3 mm per minute when the anode carbon is 8 mm in diameter, the arc-electric current is 80 A (voltage is about 23.5 V), and the He pressure is 300 Torr. The center of this cylindrical cathode deposit is a dark, brittle core, while the exterior is a hard shell. Nanotubes and polyhedral graphitic nanoparticles are present within the cathode-deposit cylinder, which is the inner core and has a fabric structure expanding along its length. Graphite crystals make up the outer-shell portion. A rotating-cathode arc-discharge technique that permits long-term operation is shown in Figure 1. MWCNT does not exist outside of the cathode deposit and only develops there. The most crucial parameter, the pressure of the He atmosphere in the reactor, determines how much MWCNT is produced. When the pressure of He is at 500 Torr, the most MWCNT is produced. There is essentially little MWCNT growth when this value falls below 100 Torr. In contrast, the maximum concentration of fullerene is produced at pressures of 100 Torr or less. The electric current for discharge is a further crucial factor. If the current density is too high, MWCNT production declines and hard shell production rises. In order to improve the output of MWCNT, it is beneficial to maintain a consistent arc discharge and keep the electrode cold. Even under the ideal conditions for the synthesis of MWCNT, the cathode deposit produces a significant amount of graphite. Using ethanol as the solvent, the bundle of MWCNT may be freed in an ultrasonic cleaner.

As neither nanoparticles nor amorphous carbon are present in MWCNT produced by catalytic breakdown of hydrocarbon, this process is appropriate for bulk manufacturing. Nevertheless, the geometry of MWCNT created in this way is not always straight compared to MWCNT created by the arc-discharge approach. The absence of pentagons and heptagons in the graphene sheet of the MWCNT, which would have an impact on its electric conductivity and electron emission, might be attributed to this discrepancy. Controlled manufacture of MWCNT with respect to length, diameter, and alignment is key to this approach. New catalyst techniques have been developed to solve these issues. The approach described by the author uses Fe particles on meso-porous silicon to produce aligned CNT nanotube brushes grown on silicates. Using a thin coating of Co catalyst imprinted on a silica substrate, the author has established a controlled way of producing aligned-MWCNT bundles [5], [6].

The use of laser ablation in the synthesis of CNTs

High intensity lasers are used to heat a graphite block in a quartz tube in a furnace to 1200°C in an argon environmen. Here, the quartz tube containing the graphite target is vaporized by the laser, and the presence of metallic catalysts causes the formation of SWCNTs. As a function of laser power, the diameter of manufactured carbon nanotubes is changed; for example, the diameter of the tube decreases when the laser pulse strength is increased, and vice versa. According to several other investigations, single walled carbon nanotubes may also be produced in huge quantities using ultrafast sub-picosecond lasers. It is further claimed to create carbon nanotubes up to 1.5 g/h by laser ablation technology.

One should keep an eye on the impact of various laser properties (oscillation wavelength, peak power, frequency, cw versus pulse), chamber pressure, distance between graphite target and substrate, ambient temperature, and the flow and pressure of the buffer gas in order to harness CNTS with the desired structural and chemical characteristics. This method allows for the production of significant amounts of high grade (purity) SWCNTs. Arc-discharge and laser ablation work in exactly the same ways mechanically. Here, a laser strikes a pure graphite pellet containing catalyst material, such as cobalt and nickel, to provide the necessary energy Figure 1. The presence of fewer metallic impurities and a better yield of CNTs are this method's main benefits. Nevertheless, the carbon nanotubes made using the laser ablation technique are not entirely uniform and straight. Due to the need for high purity graphite rod and the availability of two laser beams to create CNTs, this process is expensive. The daily yield of nanotubes produced by this method is much lower than that of the arc discharge method.

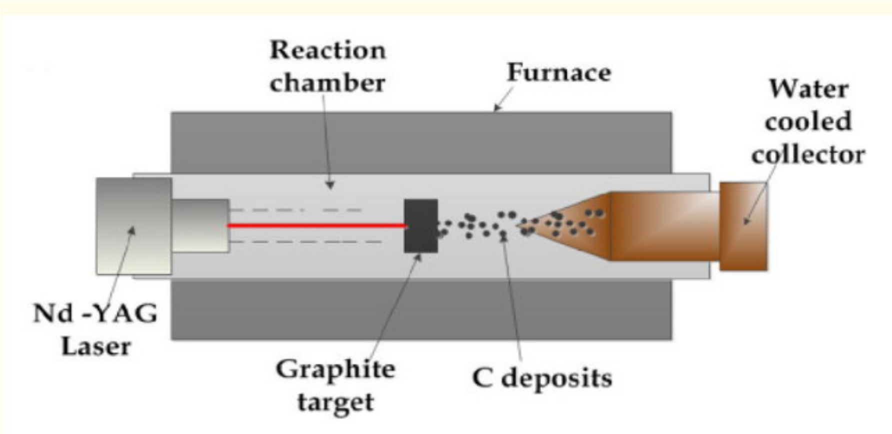

Figure 1: Illustrate the laser ablation process.

MWCNT isolation the removal of nanoparticles and fragments of graphite is the first step in the separation of MWCNT. Executing the isolation of MWCNT is really challenging, in fact. The primary cause of this is that although standard separation techniques like filtering and centrifugation are good at removing large bits of graphite, they are less successful at doing so with regard to removing nanoparticles. Thus, a technique to remove everything except MWCNT after removing large bits of graphite has been suggested. This involves burning nanotubes in an oxidizing environment. This technique makes use of the fact that nanoparticles burn out more quickly than MWCNT. Starting at the periphery of the nanoparticles and moving toward their centers, the reaction with oxygen begins. Since that MWCNT is significantly longer than nanoparticle, it takes more time for it to burn out fully. So, when burning is stopped after the required amount of time, all which is left is MWCNT, although the amount produced is extremely little [7], [8].

The raw cathode sediment is treated with CuCl2 to produce the graphite-Cu compound before burning in order to speed up the oxidation rate of graphite at lower temperatures and enhance the crop amount after burning. Due to the lower burning temperature of this chemical, MWCNT consumption that is not desired is prevented. A tube without seam is created by enrolling graphene in the structure of SWCNT. The kind of metal catalyst utilized in the synthesis determines the length and diameter. The diameter ranges from 1 to 3 nm, and the longest length is several lLim. The smallest diameter is similar to that of C60 (i.e., ca. 0.7 nm). SWCNT's structure and properties seem to be distinct from those of MWCNT and more similar to those of fullerenes. Being the one-dimensional material between molecules and bulk, SWCNT is thus predicted to have unusual physical characteristics. On the other hand, MWCNT's physical characteristics are virtually identical to those of bulk graphite. SWCNT is made using a process that is essentially identical to that used to make MWCNT. The remarkable distinction is that the synthesis of fullerenes is impossible without the use of a metallic catalyst. Benzene can be broken down into SWCNT using an iron catalyst, according to a very recent research.

Establishing the controllability of the diameter and helical pitch in this kind of SWCNT synthesis will be crucial for the creation of innovative types of electronic devices like single molecule transistors. One may say that this sector is rife with dreams.

Chemical vapor deposition for the production of CNTs

CNT manufacturing via chemical vapor deposition is one of the finest methods (CVD). There are several CVD methods, such as hot filament CVD, plasma enhanced oxygen aided CVD, and catalytic chemical vapor deposition with heat and water assistance (HFCVD). Catalytic chemical vapor deposition is the CVD technique for the manufacturing of CNTs that is most widely used. This method entails the chemical breakdown of a hydrocarbon on a predetermined substrate, which aids in the expansion of CNTs on various types of materials. As with the arc discharge process, the metallic catalytic particles include intact carbon atoms. Following that carbon atoms are permitted to come in touch with metal particles and implanted with in the holes, commencing the development of carbon nanotubes as shown in Figure 2.

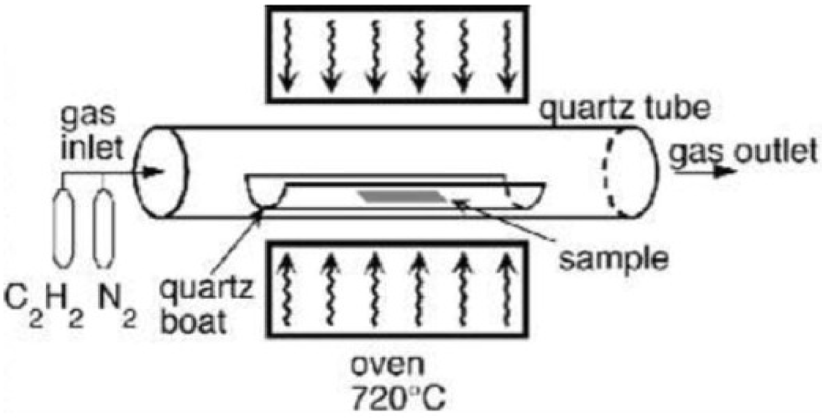

Figure 2: Illustrate the Chemical vapor deposition.

Using this method, long carbon nanotubes can be manufactured with good alignment and a coating of metallic catalyst particles can be created at 700 °C. The most popular catalyst metals are nickel, cobalt, iron, and mixtures. Using a fluidized bed reactor, carbon-containing gases like ethylene, acetylene, and methane as well as process gases like hydrogen, neon, or ammonia are utilized to expand nanotubes. The catalyst particles and process gas interact, causing the catalyst to break down. When CNTs are produced, carbon atoms become more noticeable at the edges of nanoparticles. In comparison to the laser ablation approach, CVD is a highly practical and affordable technology for producing fairly pure carbon nanotubes on a big scale. The primary benefits of CVD are its simplicity and ability to produce materials with a high degree of purity.

Purification

SWCNT is more quickly oxidized than MWCNT, hence the burning procedure used in certain purification processes cannot be used for that purpose. But have been successful in doing so by using the water-heating treatment; moreover, the centrifuge and micro-filtration techniques may also be used. According to a recent publication, SWCNT might be purified using the size-exclusion chromatography technique, allowing for separation based on length. This approach seems efficient for obtaining SWCNT with a high level of purity. It is still an issue to develop the differentiation technique of SWCNT with its diameter.

MWCNT was originally identified using the arc-discharge method of pure carbon, while SWCNT was later identified using a similar technique in which carbon is co-vaporized with a metallic element. Such a metallic catalyst has lately undergone optimization. While these electric arc techniques may provide grams of MWCNT and SWCNT, the raw material needs a time-consuming purifying step. The electric arc-discharge approach and the laser-ablation method both allow for the co-evaporation of metals, which may result in SWCNT. Fe, Co, or Ni play a crucial role as metallic catalysts, and their combination with or addition of a third element, such as Y, effectively creates SWCNT. Nevertheless, producing gram quantities of SWCNT via the laserablation approach is still challenging. Nonetheless, this synthesized SWCNT has made incredible strides in the study of its physical characteristics. Also essential to the catalytic breakdown of hydrocarbons are Fe, Co, or Ni. Having sufficient knowledge of the chemical interactions between carbon and these metals is essential and required in order to properly generate CNT and regulate its structure.

Scaling up CNT manufacture using the catalytic synthesis approach is rather simple. This approach is seen to offer the greatest potential for mass manufacturing in this regard. In order to further enhance the catalytic synthesis procedure, it is crucial to clarify the mechanism of CNT development in order to regulate the synthesis. Fortunately, a chemical process may produce CNT at a relatively low 11 temperature. In general, there are a variety of options for regulating chemical reactions between 1000 and 1500 °C. It is quite interesting to follow the progress of research in this area. The research on CNT started in Japan, and now, many researchers from across the globe take part in the study. In the sense that the research phase should go from fundamental to applied science, including greater improvement in the efficiency of the synthesis, separation, and purification, it is thought that it is now high time for the turning point in the study of CNT. Being involved in CNT science and technology is the most exciting thing for us since it is anticipated that CNT will be one of the most significant materials in the 21st century [9], [10].

For the past 15 years, there has been a flurry of research on carbon nanotubes, but in recent years, focus has shifted more and more toward the many applications of these strange materials. Because of the enormous interest in carbon nanotube applications, the book's editors chose to showcase implementations in the chapter. To further understand this topic, we first consider the commercial applications for which carbon nanotubes are now made accessible. These applications are growing fast in certain cases. There are now several applications being developed in laboratories throughout the world, some in university settings and others in national research organizations where a wealth of specialized resources are available, that show promise for commercialization in the next ten years. As one would expect, there is a lot happening in industrial research laboratories, ranging from small start-ups to substantial corporations, and everything in between. Not to mention, there are a ton of longer-term programs that are applications-focused that are emerging from fundamental findings at one end of the spectrum or from needs-driven R&D at the other. Many additional chapters in the book, including those on doping nanotubes, carbon nanohorns and nanocones, organometallic nanotubes, and structures that resemble fullerenes, as well as the chapter on the chapter, describe intriguing uses.

To have a substantial impact on society, applications must be based on metrology, standardization, and production tool control. For the study of nanometrology, which is essential for the development of nanomaterials in general, single-wall carbon nanotubes (SWNTs) are especially important. As a unique review article feature for this collection, the chapter provides an overview of nanotube spectroscopy in support of these applications. Despite the fact that many of the chapters in this book explore various techniques and approaches for improving nanotube metrology, the headline metrology chapter in this book focuses mostly on the research aspects of metrology. The particular challenges in nanotube metrology are caused by a number of variables. the inability of equipment with sufficient resolution to measure accurately and repeatedly the unique features of objects on such a tiny length scale due to the incredibly small diameter of nanotubes the diverse features of several (n, m) tubes, which just slightly vary from one another in terms of diameter or chiral angle. The difficulty in regulating the chirality of nanotubes (n, m) during synthesis the nanotubes' very tiny diameter. On the one hand, researching carbon nanotube metrology seems to be a challenging intellectual endeavor that should advance. The broad revolution in nanotechnology and nanoscience was announced. Such research is crucial for creating the measurements, standards, and industrial quality control required for the mass production of products that meet predefined requirements. Safety and public health issues are also essential for the widespread commercialization of nanostructures such as carbon nanotubes.

It may show out that the function of nanotubes in compounds is different from what was first believed; rather of serving as active heap fibers, nanotubes may operate as matrix additives, providing the composite multidimensional properties. Notwithstanding these challenges, a number of companies in the USA and Japan are striving to develop nanotube-infused polymers that will enhance sporting equipment, and some of these products are now available. They utilise MWNTs and Nano fibrils produced using CVD as its nanotube additives. Once again, nanotubes are only matrix enhancers and not the principal load-bearing structures in these products. Recently, it was shown using a quite different way that nanotubes may improve the properties of 3D composites. While nanotubes are not the main load-bearing fibers in this case, they do enhance the composite in the direction opposite to the fiber direction. Conventional particle matrix composites, which are made of layers of oriented fiber implanted in a polymer, have excellent in-plane properties, but the design for maximum linked to the towers and fiber direction qualities suffers. Many techniques have been used, including cutting-edge fiber packing designs, but none of them have proven to be particularly successful. Aligned interfibrillar carbon-nanotube arrays give enhanced multifunctional properties in the thickness direction. The carbon nanotube arrays, which contribute crucial interlinear resilience and strength under various loading conditions, enable the 3D composite to bond nearby plies together. The developed 3D composites containing nanotubes showed noticeably better interfibrillar yield stress, abrasive wear resistance, through-thickness mechanical properties, and damping.

Also, the enplane properties of the composites were not concurrently changed. Nanotube applications in structural biodegradable polymers that provide such value-added benefits by adding them in innovative geometries to traditional composites are encouraged. The interfacial weakness changes from being negative to being positive when nanotubes are introduced to polymer matrices, making it more useful for vibration damping. Recently, the effectiveness of using nanotubes for vibration damping has been shown, and absorption abatement is a key issue in both automotive and aerospace applications. The nanotube-matrix sliding energy-dissipation technique has the potential to boost SWNT fillers (1-2%) by around three orders of magnitude. With epoxy and other high-temperature resins, SWNT fillers have shown substantial damping improvements. If large-scale production of composite materials based on nanotubes can be done in a scalable way, nanotube fillers as dampening components in composites may become a practical bulk usage. While it was assumed that nanotubes will be used in composites, research on these applications is still in its infancy. It will take some time to discover if nanotube composite systems are superior to traditional fiber-reinforced composites in terms of effectiveness. It would be excellent if nanotubes in composites could serve as mechanical reinforcement as well as other purposes.

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CHAPTER 3

MECHANICAL AND ELECTRICAL PROPERTIES OF SINGLE WALLED CARBON NANOTUBES

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The characteristics of carbon nanotubes have recently been the focus of computational nanoscience study via numerical modeling and computer-based simulation. We offer computational analyses of the mechanical and transport characteristics of armchair-shaped and zigzag-shaped single-walled carbon nanotubes in this study (SWCNT). Carbon nanotubes are so tiny compared to other materials that variations in their structure may have an impact on their Young's modulus. Using an atomistic method and density functional theory, the Young's modulus for a zigzag single-wall carbon nanotube and an armchair single-wall carbon nanotube are computed (DFT). Atomistix's Virtual NanoLab (VNL) and ToolKit (ATK) software is used to calculate the atomic forces and total energies for strained carbon nanotube segments. Elastic moduli are computed utilizing both force-strain and energy-strain data up to a maximum strain of 1%. Depending on the cross-sectional area of the carbon nanotube employed and the calculation technique, the average values for Young's modulus were found to vary from 1.8 to 4.17 TPa. The results of recent experiments are in strong accord with this. The structural and electrical characteristics of the single walled carbon nanotube (SWCNT), including electronic band structure, density of states (DOS), and transmission spectrum, are examined using ab initio density functional theory (DFT) and non-equilibrium green function approach (NEGF). The findings point to a broad variety of real-world uses, including NEMS, acoustic sensors, and nano actuators.

Carbon nanotube (CNT) structures are a relatively new phase of carbon that were initially created at Sumio Iijima's lab at Tsukuba in 1991. They have a broad range of known electrical characteristics. They might be semiconducting or entirely metallic. Particularly intriguing are the possible industrial uses of semiconductor nanotubes. CNTs are intriguing because of their durability and nanoscale size, which make them perfect for a variety of uses in materials science, electronics, optics, and nanotechnology. While the carbon bonds in CNTs are comparable to those in graphite, their structure allows for bonding that are stronger than those in diamonds, giving CNTs their special strength. The CNTs' electronic characteristics also enable the existing micro scale in electronic devices to be reduced in size. One electron may be used to switch a CNT-based transistor, for instance, which runs at room temperature. As a result, high speed switches would use a small fraction of the current that computers do today and would occupy far less space than the electrical components on CPU chips.

Moreover, since CNTs are capable of being downsized to sizes considerably below those of present technologies, they may lead to high density storage for RAM applications. Also, it is anticipated that these electrical components would turn on and off at a rate of around one terahertz, which is 10,000 times quicker than the current generation of computers. The breakthrough technology made possible by CNT-based transistors will lead to faster and orders of magnitude smaller computers in the future. Due to their low resistance, CNTs are excellent heat conductors. Nanotubes with a smaller diameter may fit closer together and carry more current without overheating. They may also be utilized as heat sinks to divert heat away from CPU chips since they are excellent thermal conductors. Other potential uses include flexible nanotube films for use in computers and mobile phones, mechanical memory components, and nanoscale electronic motors. Nanomaterials with tunable band gaps may one day produce projectors with full color holograms that are no larger than postage stamps. As CNTs are exceptionally flexible, these projectors will provide a touch screen that is very dependable. Tunable band gaps may also result in lasers with a changing spectrum since they allow for the adjustment of the laser's color. Moreover, it has been suggested that CNTs may be used to transfer genes in conjunction with radiofrequency fields to kill cancer cells. Additionally, CNTs can be used to create strain gauges in materials that are doped with CNTs. These strain gauges are able to detect minute variations in internal strain in materials and transmit that information optically, enabling incredibly quick failure detection in bridges, buildings, and other public infrastructure settings. The CNTs would transmit the information about the stresses while also strengthening the steel utilized in the structure. Even commonplace things like clothing and sporting equipment, which aim for minimal weight and great strength, may be revolutionized by CNTs. Molecular Dynamics Simulation Techniques Using Computational Approaches of the many-body systems under examination lies at the core of the approach.

As a result, these potentials must be built beforehand before an MD simulation is attempted. They may be divided into two-body, three-body, and many-body contributions, each of which has functional forms designed for certain kinds of materials. Although there is no denying that the classical MD simulation method, which is based on the use of prescribed potentials, has an overwhelming success in the fields of condensed matter physics and materials modeling, for problems in which several different types of atoms, or molecules, are present and therefore a large set of inter-atomic potential energy parameters has to be parameterized, and for problems in which the electronic structure, and thus the bondi coefficient [1], [2].

Ab initio molecular dynamics simulation methods are quantum-mechanically based, potentialfree methods in which the forces experienced by the atoms are computed, not from inter-atomic potentials fixed in advance, but from the electronic-structure calculations while the simulation is running and the particle trajectories are unfolding in the phase space of the system under consideration. Because of this, the emphasis in these approaches has changed from creating approximation potential energy functions to picking approximation strategies for computing the many-body Schrodinger equation. The benefit of using these techniques is that they allow for the possibility of situations that were not anticipated before to the simulation's commencement to materialize.

A technique for solving difficult quantum many-body Schrodinger equations using numerical methods is called the ab initio or first-principles approach. While the system size is now just a few hundred atoms, the ab initio technique nonetheless offers a more precise description of the quantum mechanical behavior of material characteristics. The density functional theory provides a solid mathematical basis for the current ab initio simulation techniques (DFT). This is a result of the system's density being a function of the ground-state total electronic energy. Using a pseudo potential approximation and a plane-wave (PW) basis expansion of single-electron wave functions, the DFT-LDA approach has been created for use in real applications. These approximate solutions turn the electrical structure problem into a self-consistent matrix diagonalization issue. Atomistix Virtual Nanolab is one of the most well-known DFT packages (ATK).

Nanotubes' molecular structures

Carbon atoms make up the cylindrical molecule known as CNT. The hexagonal pattern that regularly repeats in space is one of the main characteristics of the construction. Each atom is bound to three adjacent atoms as a consequence of the periodicity. This structure is mostly the result of the sp2 hybridization process, in which one s-orbital and two p-orbitals unite to generate three hybrid sp2 orbitals that are spaced 120 degrees apart from one another (shown in Figure 2 for part of a graphene sheet). This covalent link, often known as the "-bond," is a strong chemical bond that contributes significantly to the remarkable mechanical capabilities of CNTs. Moreover, the interaction between the layers in MWCNTs and between SWCNTs in SWCNT bundles is facilitated by the comparatively weak out-of-plane link (the -bond). Once the graphene sheet is bent into a tube, the and orbitals undergo re-hybridization and produce an admixture, thus the bonding in nanotubes is obviously not entirely sp2 in nature. Ab Initio Molecular Dynamics Simulation Techniques, a Computational Method.

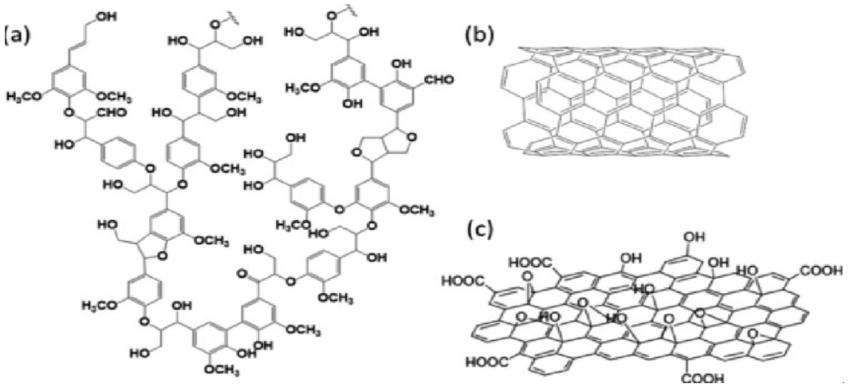

Figure 1: Illustrate the Lignin, carbon nanotubes, and graphene oxide molecular structures.

The use of predetermined inter-atomic potential energy functions to simulate the energetics and dynamics of the many-body systems under study is at the very core of the traditional molecular dynamics (MD) simulation approach, as we have shown in the section on the method. These potentials must thus be built beforehand before an MD simulation is attempted. They may be divided into two-body, three-body, and many-body contributions with functional forms that are designed for various kinds of materials. Although there is no denying that the classical MD simulation method, which is based on the use of prescribed potentials, has an overriding success in the fields of condensed matter physics and materials modeling, for problems where several different types of atoms, or molecules, are present and therefore a large set of inter-atomic potential energy parameters has to be parameterized, and for problems where the electronic structure, and thus the bonding, are important, the use of quantum mechanical simulations (QM) is recommended. Ab initio molecular dynamics simulation techniques are quantum-mechanically based, potential-free techniques where the forces experienced by the atoms are computed from the electronic structure calculations made as the simulation is running and the particle trajectories are unfolding in the phase space of the system under consideration rather than from interatomic potentials fixed in advance.

As a result, in these techniques, the emphasis is now placed on choosing approximation strategies to solve the many-body Schrodinger equation rather than on building approximate potential energy functions. So, the benefit of these methodologies is that situations that weren't anticipated before the simulation may arise during the simulation [3], [4]. The ab initio or first-principles method uses numerical algorithms to solve difficult quantum many-body Schrodinger equations. Even though the system size is currently restricted to just a few hundred atoms, the ab initio method offers a more precise description of the quantum mechanical behavior of material properties. The rigorous mathematical underpinnings of density functional theory serve as the foundation for current ab initio simulation techniques (DFT). This results from the fact that the total electronic energy in the ground state depends on the system density. The plane-wave (PW) basis expansion of single-electron wave functions has been used to build the DFT-LDA approach for use in practical applications. The electronic structure problem is reduced by these approximations to a self-consistent matrix diagonalization problem. Atomistix Virtual Nanolab is a well-known DFT package (ATK).

Computational Modeling of the SWCNT's Electrical Characteristics

Two theoretical methods for estimating the electrical structure and transport characteristics of carbon nanotubes will be discussed in this section. These two techniques are Non-Equilibrium Green's Function (NEGF) and Density Functional Theory (DFT). In this part, we'll talk about these two techniques. These techniques are used by Atomistix software to extract the electrical structure and compute current-voltage curves for various devices. We'll talk about a few DFT and NEGF-related parameters and underline how they affect the computations.

Theory of Density Functions (DFT) The electronic structure of carbon nanotubes is calculated using several assumptions derived from quantum mechanical techniques. Two excellent examples of techniques that do not explicitly address the electron-electron interaction are the tight-binding method and the Nearly Free Electron (NFE) model. The Hartree technique is another way that takes into account the electrostatic interaction between the electrons. The Hartree-Fock approaches, where the exchange effects are significant, expanded on this strategy. The "correlation energy" is the system energy mistake that still exists in the Hartree Fock method. In order to include the correlation effects without employing very expensive wave function approaches, the density functional theory (DFT) was developed. The density functional theory (DFT), which serves as the foundation for many atomistic-scale simulations in physics, was originally implemented by the author as an effective computing approach. For creating DFT, Walter Kohn received the 1998 Nobel Prize in Chemistry. The Hohenberg-Kohn Theorem, which derives energy as a function of ground-state electron density, is a fundamental DFT theorem. By adjusting the density to find the least energy, the ground-state energy may be discovered. The Kohn-Sham method is used to implement DFT, and it defines a non-interacting electron reference system with an effective potential and eigenvalues that are identical to those of the multi-electron system. The many-body issue can be solved by solving this single electron Schrodinger equation, although the effective potential in this equation relies on the electron density.

A self-consistent calculation is required because determining the electron density necessitates solving for the Eigen functions. The level of convergence of this self-consistent computation influences the accuracy of the DFT calculation in part. DFT is utilized in the project's software to compute the energy, electron density, and other physical parameters of molecules and many-atom systems. The computation of total energy and the atomic forces that are obtained from total energy are of special importance for this study. The total energy is made up of the sum of the exchange-correlation energy of the electrons, the mean-field electrostatic energy of the ions and the electron gas, and the kinetic energy of the non-interacting electron gas. Using an analytical differentiation of the total energy terms, atomic forces are discovered. The Kohn-Sham DFT treats exchange-correlation, and users may choose between the local density approximation (LDA) and the generalized gradient approximation

(GradApp). (GGA). Standard norm-conserving pseudopotentials in their non-local form may also be used with this program. To carry out precise computations, minimal basis sets are used; for instance, it employs single or multiplezeta polarized basis sets. The application of these and other characteristics is covered in more depth below. Density functional theory is discussed in further depth, along with the pertinent equations and techniques, in the literature and online. To employ the DFT technique, a set of approximations and computation parameters must be specified [5], [6].

Pentagons, heptagons, vacancies, and dopants are common defects in carbon nanotubes that significantly alter their electrical characteristics. Of course, faulty nanotube-based structures exhibit more complicated electrical characteristics than those of infinitely long, flawless nanotubes. So, it is intriguing to adjust the fundamental features of the carbon network to suggest new possible uses for nanotubes in nanoelectronics as well as to construct new prospective nanodevices. Carbon nanotubes may be utilized to create metal-semiconductor, semiconductor-semiconductor, or metal-metal junctions since they can be either metals or semiconductors, depending delicately on their geometrical configurations. Due to their nanoscale size and construction out of only one chemical element, these junctions offer a wide range of possible uses. Nanoscale metal-metal junctions, metal-semiconductor Schottky barrier junctions, or semiconductor intra molecule junctions may all exhibit unique behaviors in nanotube junctions, and these many kinds of junctions can be used as the foundation for nanoscale electronic devices.

Benefits and Drawbacks CNT

Carbon nanotubes, in contrast to the families of graphite and diamond, are said to belong to the fullerene family of carbon molecules. These carbon-based cylinder-shaped devices fall into two primary categories. Two of the categories are single-walled nanotubes and multi-walled carbon nanotubes (SWCNTs and MWCNTS). According to the uses it is put to, each of the two primary categories has benefits and cons. Yet, bucky sheets and double-walled carbon nanotubes may be studied at a different level where multi-walled carbon nanotube research is conceivable, as this work will accomplish [7], [8].

A single layer of carbon atoms "rolled into a seamless tube and capped at each end with half-spherical nanocrystal complexes" is how the single-walled carbon nanotubes may be conceptualized. The fact that they are covalently connected networks of all the atoms that make up each one sets them apart from multi-walled carbon nanotubes. The optical and electrical properties of single-walled carbon nanotubes are enhanced as a result. Following the discovery of multiwall carbon nanotubes in 1991 and their identification as single-walled tubes two years later, the physics of these tubes has rapidly advanced in the scientific community. Since then, studies have concentrated on the basic physical properties of the nanotubes as well as their prospective uses in a range of experimental and theoretical fields, including electronics, mechanics, and optics. Much progress has been achieved in every area of study during the last 10 years.Nanotubes are used in many fields, and there are now commercially available applications. Carbon nanotubes are useful materials for a range of applications, including sensors, catalysts, energy storage, and conversion, because to their unique properties. It is difficult to use this class of materials since they are insoluble in many common solvents, including water. The advantages and prospective applications of the various kinds of carbon nanotubes, such as single-walled, multi-walled, double-walled, and bucky sheets, will be covered in this chapter. Nevertheless, it is first vital to consider the solubility of the carbon nanotubes, especially in water, a common solvent, since this would considerably boost the usability of these materials.

Water Carbon Nanotubes' Solubility

By increasing the solubility of nanostructures in water, it is simpler to chemically modify them, purify them, and separate them from persistent pollutants. The solubility of carbon nanotubes was improved using a unique polymer wrapping method. One of the surface polymeric polymers employed for this was polyvinyl pyrrolidone, or PVP. The strength of the polymer's adherence was evaluated using the field flow fractionation technique, and the results showed that the polymer was firmly encircling the carbon nanotubes. The amount of polymer in solution was measured using NMR spectroscopy, and the total concentration of polymer was discovered using techniques for absorption spectroscopy. The variation in concentration determines how much polymer surrounds the nanotubes. After an investigation of the components linked to the tightly wrapped process's thermodynamic considerations, the polymer helical wrapping and surrounding of carbon nanotubes was suggested as a potential occurring mechanism [9], [10].

Making nanotubes liquid therefore makes it easier to sort and purify them. The current approaches for solubilizing nanotubes employ synthetic polymers. The usage of those similar polymers is constrained by the fact that they are not very biocompatible. Since natural polymers are biocompatible and take into consideration the utilization of starch together with other organic chemicals like glucosamine and gum Arabic to make the carbon nanotubes soluble, they may be utilized to wrap nanotubes. According to, when carbon nanotubes came into touch with a starch solution, they particularly failed to dissolve. Unfortunately, they decomposed when exposed to a solution containing the starch-iodine mixture.

These results were attributed to the formation of a helix that wraps around carbon nanotubes by the combination of the cornstarch amylase component and the iodine particles. Amylopectin, a branching component of starch, increases the amount of starch's solubilizing ability that is wrapped around carbon nanotubes, while amylase, a linear component of starch, was demonstrated to be the major component that assists in the dissolving of carbon nanotubes. Nanotubes may precipitate out of the liquid once saliva has been added. Salivary amylase is responsible for precipitating the tubes out of the solution and aids in the breakdown of amylase chains. Individual carbon nanotubes outperform ropes in terms of their mechanical and electrical properties.

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CHAPTER 4

OPTICAL RESPONSE OF CARBON NANOTUBES

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A great interest in mesoscopic carbon structures was sparked by the production of molecular carbon structures like €50 and other fullerenes. In this regard, the finding of carbon nanotubes (CNTs) in an arc discharge deposit was a significant advance. Early theoretical work concentrated heavily on these unique quasi-one-dimensional objects' electrical characteristics. These mesoscopic structures are fundamentally sp-bonded, much like graphite. Yet, compared to flat graphite, the curvature and cylindrical symmetry result in significant alterations. The underlying graphite band structure's folding when azimuthal periodic boundary conditions are applied to the tube determines whether it is a metal or a semiconductor. The CNTs' rolling technique has a significant impact on the boundary conditions. To provide one specific example, Mintmire et al. estimated the electronic structure using a technique known as allelectron Gaussian-orbital based local-density-functional, while also accounting for the electron-lattice interaction using a Frohlich Hamiltonian [1], [2].

According to their findings, fullerene tubules appear to have the advantages of a carrier density similar to metals as opposed to graphite and a simple metallic phase i.e., zero band gap at 300 K as opposed to poly acetylene, with a concomitant relatively high conductivity as a result of the small diameter. With the advent of well-aligned CNT films, extensive experimental study was also initiated, with a focus on the optical response, transport, and magnetic characteristics in particular. When measured parallel to or along the tubes, transport properties, conduction electron spin resonance (ESR), and static magnetic susceptibility measurements exhibit anisotropic behaviors. In addition to the inverse resistive scattering time obtained from ESR measurements, the resistivity of the tubes measured parallel to and perpendicular to the axis is also shown. When the temperature of the tubes is reduced using the traditional four-point method, their resistivity rises in both directions solid and dotted lines. Temperature affects the anisotropy between the two orientations.

For the study of materials, carbon nanotubes' optical characteristics are very important. Those materials' peculiar absorption, photoluminescence (fluorescence), and Raman spectra are proof of how differently they interact with electromagnetic radiation. Carbon nanotubes are special "one-dimensional" materials that may be manufactured in a variety of sizes and feature hollow fibers (tubes) with a distinctive and highly organized atomic and electronic structure. The diameter normally ranges by 100 times, or between 0.4 and 40 nm. The length, on the other hand, may be as long as 55.5 cm (21.9 in), which indicates a length-to-diameter ratio of up to 132,000,000:1, which is unmatched by any other material. As a result, the carbon nanotubes' whole range of electrical, optical, electrochemical, and mechanical characteristics may be controlled and are highly anisotropic. Compared to other fields, photonics and optics applications for carbon nanotubes are still in their infancy. Tunability and wavelength selectivity are two qualities that could have practical applications. Bolometers, optoelectronic memory, and light emitting diodes (LEDs) are a few potential uses that have been proven [3], [4].

The optical characteristics of carbon nanotubes may be highly helpful in their production and utilization in various domains in addition to their direct uses. A relatively large amount of carbon nanotubes can be quickly and non-destructively characterized using spectroscopic methods, allowing for precise measurements of the non-tubular carbon content, tube type and chirality, structural flaws, and a variety of other properties that are important for those other applications.

As compared to optical absorption in normal 3D materials, carbon nanotubes exhibit abrupt peaks (1D nanotubes) rather than an absorption threshold followed by a rise in absorption (most 3D solids). Electronic transitions from the v2 to c2 (energy E22) or v1 to c1 (energy E11) levels, etc. are the source of absorption in nanotubes. The relatively abrupt transitions may be utilized to distinguish between different kinds of nanotubes. Due to the fact that many nanotubes have E22 or E11 energies that are very comparable, there is a substantial amount of absorption spectrum overlap. This overlap is eliminated via photoluminescence mapping measurements, which instead of identifying individual (E22, E11) couples through a mixture of overlapping transitions.

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With the advent of well-aligned CNT films, extensive experimental study was also initiated, with a focus on the optical response, transport, and magnetic characteristics in particular. When measured parallel to or along the tubes, transport characteristics, conduction electron spin resonance (ESR), and static magnetic susceptibility tests exhibit anisotropic behaviors. The inverse resistive scattering time, calculated from ESR data, and the resistivity of the tubes, measured parallel to and perpendicular to the axis. Using the traditional four-point measurement technique, the tubes' resistivity shows that it rises with falling temperature in both directions (solid and dotted lines)

Bundling and other interactions between nanotubes expand optical lines. Bundling has a significant impact on the photoluminescence, although it has far less of an impact on optical absorption and Raman scattering. As a result, sample preparation for the latter two methods is not too difficult. It is common practice to measure the quality of the carbon nanotube powders using optical absorption. The pi-carbon peak, background, and nanotube-related peaks are all measured in terms of intensity. The latter two peaks mostly come from non-nanotube carbon in contaminated samples. Nevertheless, it has recently been shown that the absorption background may be ascribed to a free carrier transition resulting from intertube charge transfer hotoluminescence by packing virtually single chirality semiconducting nanotubes into dense Van der Waals bundles [5], [6].

Fluorescence and photoluminescence are two terms used interchangeably to describe the near-infrared light that semiconductor single-walled carbon nanotubes release upon photoexcitation (PL). An electron in a nanotube absorbs excitation light through the S22 transition, producing an electron-hole pair, which is how PL is typically excited (exciton). Via phonon-assisted processes, the electron and hole both quickly relax from their respective c2 to c1 and v2 to v1 states. After their recombination, light is released as a consequence of the c1 to v1 transition. Metallic tubes cannot create excitonic luminescence. While the optical absorption caused by their excited electrons may occur, the holes are quickly supplied by other electrons from the metal's abundant supply. As a result, no excitons are created.

Salient Features

1. Raman scattering, optical absorption, and photoluminescence from SWNT are all linearly polarized along the tube axis. This makes it possible to monitor the orientation of the SWNTs without doing a direct microscopic examination.
2. PL is quick: relaxing normally takes place within 100 picoseconds.
3. While PL efficiency was first determined to be modest (0.01%), subsequent research reported far greater quantum yields. The isolation and structural quality of nanotubes were improved, increasing emission efficiency. When the process of isolating individual nanotubes in solution was optimized, the quantum yield of 1% in nanotubes sorted by diameter and length by gradient centrifugation was enhanced to 20%.
4. The PL spectral range is rather broad. Depending on the structure of the nanotube, the emission wavelength may change between 0.8 and 2.1 micrometers.
5. As the photoluminescence spectrum shows a splitting compatible with intertube exciton tunneling, excitons seem to be delocalized throughout many nanotubes in single chirality bundles.
6. PL may be quenched or increased by interactions between nanotubes or between a nanotube and another substance.

Multi-walled carbon nanotubes show no PL. The emission of double-wall carbon nanotubes (DWCNTs) from both the inner and outer shells may be seen in CVD produced DWCNTs. DWCNTs made by enclosing fullerenes in SWNTs and annealing them, however, only exhibit PL in the outer shells. Just a few investigations have found the very weak PL that is shown by isolated SWNTs that are laying on the substrate. The PL is greatly increased when the tubes are separated from the substrate. The (S22, S11) PL peaks' positions are modestly (within 2%) influenced by the nanotube environment (air, dispersant, etc.). The complete PL map, however, shifts and warps as the CNT medium changes since the shift is dependent on the (n, m) index.Raman scattering Raman spectroscopy is a somewhat in-depth technique that provides strong spatial resolution (0.5 micrometers) and sensitivity (single nanotubes). Thus far, Raman spectroscopy has emerged as the method of choice for characterizing carbon nanotubes. Since only those tubes are examined that have one of the bandgaps equivalent to the exciting laser energy, Raman scattering in SWNTs is resonant. As will be covered below, a number of scattering modes predominate in the SWNT spectrum.

In Raman measurements, the energy of the excitation light may be scanned, creating Raman maps, similar to photoluminescence mapping. These maps additionally include oval-shaped elements that serve as (n, m) indices' distinctive identifiers. Raman mapping, in contrast to PL, is less sensitive to nanotube bundling and may identify metallic as well as semiconducting tubes. A significant technological barrier is the need for a tunable laser and a special spectrometer, however. We addressed the open question and contentious issue of CNTs' potential metallic character from an optical standpoint. Under the framework of the Maxwell-Garnett and Bruggeman models for the effective medium, we have interpreted our optical findings for oriented CNT films. With the use of this research, we were able to prove that CNTs are intrinsically metallic, with their intrinsic properties correlating with those deduced by other contactless methods like ESR and theoretical calculations [7], [8].

Yet, resistivity tests on single CNTs show that the conductivity measured by optical techniques may be up to two orders of magnitude more. Moreover, the optical findings point to a striking anisotropic conductivity between an, a, and p. Our results support the idea that contact effects and intertube hopping have a significant impact on dc resistivity measurements. It would be very important for the future if it were possible to gradually increase the inherent conductivity of CNTs. The most recent advancement in alkali metal intercalated CNTs seems to be rather promising in this regard. In reality, Chauvet et al. recently succeeded in potassium doping of aligned CNT and discovered that the Pauli susceptibility rises by a factor of 3 after doping, demonstrating that K-doped tubes are still effective conductors. To wrap off this project, we'd like to ramble on about some potential uses for the materials we looked at. As shown by W A. de Heer and colleagues, the extraordinarily excellent electron field emission properties of CNTs make them potentially highly interesting for use in devices like screens or electron microscopes.

A single CNT might be used as an electric line or they could be used in nanoscale devices. The technology used in microchips has likely reached its maximum degree of miniaturization at this point. Collins et al. recently had success using a scanning tunneling microscope to measure the conductivity of SWCNTs, to provide just one example. When the CNT's active length is extended, the conductivity shifts, which suggests that various CNT segments have distinct electrical characteristics. The foundational component of a future nanotechnology looks to be carbon due to its extensive spectrum of sp bond hybridization. The creation processes, however, are now nearly completely uncontrollable, and the structures of interest cannot be erected at will. One would want to have more elegant tools to manage the carbon structures in tubes, for example, which are formed under the very virulent circumstances of a plasma discharge; this work will likely remain challenging in the future.

Grouping into Fibers

Carbon nanotubes with one or more walls both have alluring axial properties. Mechanically, they are very strong and rigid. Structure and Synthesis In the case of single-wall tubes, the method used to join the graphene sheet to form the tube, especially its chirality, has a substantial impact on the kind of conductivity, which may vary from metallic to large-band-gap semiconductivity. They have promise as heat conductors as well. It is challenging to combine these separate nanoparticles into a substance that will translate their distinctive properties into a material form that can be employed in industry. The most obvious material form for the axial properties of carbon nanotubes is a fibre in which the nanocrystals are packed as tightly as possible and are exactly aligned with the axis. One of the key problems in materials science is how to organize atomic, molecule, nano, and microscale structures to accomplish desired properties at the macroscale. A variety of research have been done to determine the best ways to transfer properties from the nano to the macroscale. As it is very improbable that these traits would improve during fiber creation and are more likely to deteriorate, the final properties of the fiber rely largely on the characteristics of the individual nanotubes that comprise the fibre.

This section focuses on the cutting-edge technologies that are creating new opportunities for the production of fibers made of carbon nanotubes. However it is possible to include various amounts of a second substance typically a polymer into the fiber in a number of ways. The compositions covered here, of course, cover a broad range, from pure nanotube fibers to those with changed characteristics, to composites, to what are basically simply nanotube-filled polymer fibers, and finally to the pure polymer fibers themselves. Only fibers containing more than 20% carbon nanotubes are discussed in this section, and when the nanotubes are a small component, descriptions of processes that may also make reasonably pure nanotube fibers are used. As a result, coagulation spinning of composite fibers is also included. However, melt extrusion and drawing of a polymer containing carbon nanotubes as a filler are not, as the latter case's increased melt viscosity caused by the nanotubes makes such processing difficult above concentrations of 10–20%. Another concentration is on continuous fibre spinning processes, which are getting much of the attention [9], [10].

Processing Principles

The goal is simple: we must start with nanostructures in some way, organize them into a fiber, and, to the extent that is practicable, perfectly align them with the fiber axis. Single-wall carbon nanotubes are long and thin, and their diameter is similar to several polymer molecules. For instance, the PMMA molecule has a diameter of around 0.7 nm. They are incredibly stiff, stiffer than even the stiffest polymer molecules.

The persistence length of even a single-wall carbon nanotube with a small diameter is several tens of micrometers, making it 100 times stiffer than DNA, according to computer modeling. Although such a figure would seem surprising, it should be remembered that bending carbon nanotubes requires stretching and compressing the thick carbon-carbon bonds and that thin-walled tubes are among the stiffest engineering constructions, per unit mass. Carbon nanotube assemblies are not expected to melt or produce any free-flowing phases due to their stiffness. In the case of nanotubes, the S term is vanishingly small on two counts.

They are practically as rigid in the disordered state as when they are packed parallel on a hexagonal net due to their intrinsic stiffness, to start. Moreover, since they are bigger than individual atoms, mixing entropy is also quite low. As a consequence, there are no available techniques for treating melts, and the glass transition temperature is almost "off the scale." It is crucial to take into account extra options as a consequence. One involves using mechanical fields to settle free-flowing sedimentation in a low-molecular-weight liquid, while the other involves applying mechanical fields to diluted assemblies of nanotubes in a gas phase. Due to their dilution, the nanotubes will be able to be oriented by the field as it develops the fiber in each gas. These two processes, which may be categorized as "wet" and "dry," constitute the foundation of all successful process strategies for the production of carbon nanotube fibers. A last method that is now being used to extend an existing fiber involves the continuous manufacture and deposition of carbon nanotubes onto its end. In the descriptions that follow, wet trails will be investigated first, followed by dry trails.

Applications

In the lab, single nanotube-based light emitting diodes (LEDs) and photo-detectors have been created. Its distinctive quality is not their efficiency, which is still rather poor, but rather their tight selectivity in the light's emission and detection wavelengths and the potential for fine-tuning those wavelengths through the nanotube structure. Furthermore, single-walled carbon nanotube ensembles have been used to create bolometer and optoelectronic memory devices.

For characterisation reasons, photoluminescence is utilized to calculate the concentrations of various semiconducting nanotube species present in a sample. In order to minimize intertube quenching, nanotubes are segregated dispersed using the proper chemical agent. A PL map is then created by measuring PL after scanning the excitation and emission energies. The map's ovals designate the (S22, S11) pairings that uniquely identify a tube's (n, m) index. Typically, identification is done using data from Weisman and Bachilo.

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CHAPTER 5

NANOTUBE FLUORESCENCE USED IN BIOMEDICAL APPLICATIONS, FOR IMAGING AND SENSING

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Sensitization

Organic dyes (such lycopene and beta-carotene) may be encapsulated within the tubes to change the optical characteristics, including the PL efficiency. The encapsulating dye and nanotube effectively transmit energy; light is efficiently absorbed by the dye and transferred to the SWNT with little loss. Therefore it's possible that adding a certain chemical within a carbon nanotube may change its optical characteristics. Encapsulation also enables the isolation and characterisation of organic compounds that are unstable in natural environments. For instance, because to dyes' great PL (efficiency near to 100%), Raman spectra from these materials are very challenging to detect. Nevertheless, dye PL is entirely quenched when dye molecules are enclosed in SWNTs, making it possible to detect and analyze their Raman spectra.

Cathodoluminescence

The process of cathodoluminescence (CL), which is light emission stimulated by an electron beam, is often seen on TV displays. The substance under study may be scanned by an electron beam that has been carefully focused. This method is often used to examine flaws in semiconductors and nanostructures with spatial precision down to the nanoscale scale. It would be advantageous to use this method with carbon nanotubes. Nevertheless, no consistent CL, or sharp peaks corresponding to certain (n, m) indices, has been found in carbon nanotubes as of yet [1], [2].

Computer chips, photovoltaic systems (also known as solar cells), optical sensors, and optical communications devices are just a few examples of the many electrical and opto-electronic devices that depend on the amazing material properties of semiconductors for their performance. Because to its abundance (approximately 28% of the earth's crust contains silicon) and non-toxicity, silicon has so far been the most prominent material in this category. While arsenic is exceedingly dangerous and both are expensive, gallium-arsenide and germanium are used less often. Another frequently used element is carbon, however in its pure form it is found in amorphous organic phases with oxygen as coal or oils, or as crystalline graphite, a semi-metallic substance. While none of these phases can be used to fabricate semiconductors, breakthroughs in nanotechnology over the last 15 years have led to the identification of a number of novel forms of carbon (or carbon allotropes) that can only exist at the nanoscale.

These substances have exceptional physical characteristics that make them both metals and semiconductors. One of the most significant of these is graphene, which is a sheet of carbon atoms in a hexagonal lattice that is just one atomic layer thick. Another is carbon nanotubes, which are sheets of graphene that have been "rolled up" into cylindrical shapes. Today, methods based on the fundamental and computationally simple tight-binding approximation, employing empirical parameters or the more difficult density functional theory (DFT), which is itself a true ab initio method, are primarily used to study the electronic properties of carbon-based materials. In the tight-binding scheme, it is assumed that a basis of wave functions localized on the sites of the lattice atoms may adequately describe the density of electrons (shown as a cloud rather than distinct particles) inside a particular material [3], [4].

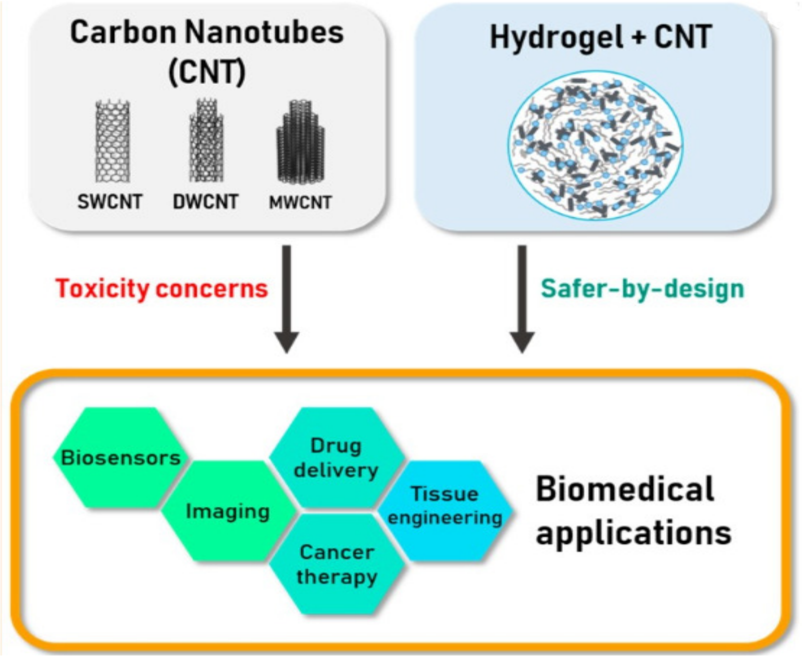

Figure 1: Topics covered in this review are organized as follows: While carbon nanotubes (CNTs) are ideal materials for many biological applications, their toxicity is a subject of some debate.

A crucial component of medical devices is biomaterials. Nanoparticles have gradually being included into biomaterials due to their unique nanoscale-related features. The large ratio of surface atoms to those in the bulk increases their chemical reactivity and significantly alters their physico-chemical characteristics generally (modified photocatalytic activity or even transparency for example in the case of nano TiO2, faster dissolution in most cases, modified electronic properties, etc.), which can be extremely helpful in biomedical applications. Their size also makes it possible for a much quicker dispersion throughout the body if they are intended to be released. Carbon nanomaterials, in particular, have intriguing qualities that distinguish them from other nanoparticles, including a very strong chemical resistance (no dissolving even in harsh settings), outstanding mechanical capabilities, and a very low weight. Nanodiamonds (ND), carbon nanotubes (CNT), and graphene and its related materials (GRM: few-layer graphene (FLG), graphene oxide (GO), and reduced graphene oxide (rGO)) are the most often utilized carbon nanomaterials. Also, the morphologies of carbon nanomaterials varied widely, from 0D (nanodiamonds) to 1D (carbon nanotubes), and from nanosheets to nanoplatelets (2D: GRM). CNTs are among the most promising nanomaterials for biomedical applications because they display a rare mix of mechanical, electrical, and optical capabilities. They may also be filled with various substances, including pharmaceuticals. The present method favors the use of nanomaterials in nanocomposite materials (Figure 1), as load in a biocompatible matrix (safe(r) by design approach), due to possible toxicity risks for nanomaterials in general when employed as free particles. In this study, we have placed a specific emphasis on hydrogel matrices, which are now the subject of active biomedical research.

Uses of Carbon Nanotubes (CNT) in Medicine

Since their discovery in 1991 by Iijima, carbon nanotubes have been extensively studied and used for a wide variety of purposes, including material reinforcement, electrode materials, components for nanoelectronics (biosensors), and even (which in some circumstances could be remotely activated) drug carriers in biomedicine. They may be made using a variety of processes, including the traditional electric-arc discharge, laser ablation, and the large family of catalytic chemical vapour deposition (CCVD) techniques, which will not be covered in depth here. CNT may be thought of as a graphene sheet that has been rolled up and is sometimes sealed at the end by fullerene caps. If a CNT has more than one concentric wall, the number of them makes up the CNT and is a crucial characteristic that affects several features. Whereas the outside diameter of multi-walled CNT (MWCNT) may reach around 100 nm, the outer diameter of single-wall CNT (SWCNT) is typically between 1 and 2 nm. MWCNTs that have more layers always have more flaws, which makes them simpler to change and functionalize, usually at the expense of losing some of their physical features. Due to the existence of a second exterior wall, double-wall CNTs (DWCNT) may be covalently functionalized like MWCNT without significantly affecting their electrical conductivity [5]–[7].

They have many features with SWCNT, such as an extremely thin diameter and outstanding mechanical properties. In fact, CNT are not an exception to the norm when it comes to the importance of the function performed by the surface chemistry of nanoparticles in general. It is generally recognized that a nanoparticle's inherent chemical makeup and crystal structure determine its surface characteristics, including charge, hydrophobicity or hydrophilicity, potential for dissolution, (photo)catalytic activity, and other qualities. This will influence how the nanoparticle interacts with its surroundings, particularly when it comes to the adsorption of proteins (corona). Yet, it has also been shown that any nanoparticle's surface decorating may change its surface characteristics, which in turn alters its biological behavior and significantly affects its biodistribution. Comparable outcomes have been reported for CNT as well, which will be covered in more depth in the last section. The grafting of oxygen-containing functional groups (hydroxyl, carboxylic acid) at the surface of the outer wall as well as the opening of the CNT occur often when CNT are covalently functionalized by oxidation (HNO3 alone or coupled with H2SO4). Yet in many other instances, the functionalization is non-covalent and is accomplished by the straightforward adsorption of various molecules, such as polymers, DNA, as well as carbohydrates and their derivatives.

There are a few difficulties that must be overcome for CNT to be used in the biomedical area. The first is safety-related and suggests using extremely high purity CNT to prevent the emission of potentially harmful ions while operating in any biological environment. This presents a significant issue since high purity CNT samples are often difficult to manufacture on a large scale, necessitating trade-offs between number and quality. The other major difficulties are more formulation-related, not only in the biological sector. One of the key ones is being able to successfully disperse CNT in solvents, particularly in water. Because of their high hydrophobicity, CNTs are challenging to sustain the suspension as well as separate or identify in a solvent. As was previously said, this may be done by functionalization (covalently, for example, by chemical oxidation, or more often, non-covalently, by the addition of a dispersion agent or a surfactant). Another tactic is to restrict or prevent drying processes during the production of CNT since they are always challenging to scatter when beginning from a dry powder. It may be challenging to generate nanocomposite materials with a large volume proportion of well-dispersed CNT because of the normal viscosity increase associated to the correct dispersion of CNT in a fluid, even at low concentration.

SWCNT exhibit either semiconductor or metal behavior depending on their electronic structure. A random SWCNT population has a statistical distribution with two thirds semiconducting and one third metallic. Inter-wall interactions cause the population of metallic MWCNT to gradually grow as the number of concentric walls rises. When it comes to mechanical properties, they may have a big surface area—up to 1000 m2 g1 in the case of DWCNT—a very high aspect ratio, a low density, great mechanical resistance (better than steel along their axis), and outstanding flexibility when there aren't many barriers (this is especially true for CCVD CNT). CNT are increasingly employed for biomedical applications because of their reasonably strong biocompatibility, whether for disease diagnosis or therapy [6]–[8].

Diagnostic Usage of CNT

The development of detection technologies is particularly important since early diagnosis is a prerequisite for effective therapy. Due to the ability to identify immune complexes, in vitro examination of biomarkers is currently achievable with reasonable precision; however, utilizing conventional dosing procedures may be time-consuming and need the use of significant quantities of biological materials. Several teams have examined employing CNTs as the primary component of electrochemical sensors due to their electrical capabilities, and numerous label-free CNT-based biosensors have been created as a result. With a variety of bio imaging techniques, CNT may also serve as a contrast agent [15]. When functionalized and coupled with different biomarkers, they may effectively and precisely identify the presence and location of targeted cells.

Biosensors Based on CNT

In the realm of biosensors, CNT has been suggested as a sensing component to identify and track a number of illnesses, including diabetes but also bacterial infections. As an example, Punbusayakul et al. employed electrochemical monitoring of immune complexes for salmonella detection, which decreased the detection time and sped up sample preparation in comparison to other approaches. Also, by grafting directed antibodies onto the surface of DWCNTs in order to immobilize them, an immunosensor for adiponectin—a biomarker for obesity—was created. A second antibody, coupled with horse radish peroxidase (HRP)-streptavidin binds to adiponectin and interacts with the substrate during cyclic voltammetry monitoring, enabling hence quick detection and quantification.

In general, the presence of CNT at the electrode surface speeds up the transport of electrons and increases the sensitivity for electrochemical detection. Field-effect transistor (FET)-based sensors have been found to exhibit high sensitivity, sometimes as low as attomole. Recent research has shown the enormous value of resistive sensors, specifically differential resistive pulse sensors (RPS) based on MWCNT in achieving the single molecule detection threshold.

From a strictly qualitative standpoint, this supports the conventional theory that some kind of Coulomb force is responsible for binding (i.e., localizing) negative electrons to positive atomic nuclei. Since these almost exclusively define the electronic properties in the energy region under consideration here, only the so-called -electrons are modelled in the most basic model of conjugated carbon systems (UV or X-ray radiation will affect the -electrons involved in carbon-carbon covalent bonding and the tightly bound electrons near the atomic nuclei). A photon in the visible spectrum is absorbed by a substance when an electron in the material absorbs a quantum of energy from the optical field, pushing the electronic system out of its ground state and into an excited state with greater energy.

This can be modeled using a one-electron approximation, where the excitation of a single molecular orbital is taken into account, or using a many-particle formulation, known as the exciton formulation, which takes into account the full rearrangement of the electronic system due to the absorbed energy. The latter may easily be integrated into a tight-binding formulation and is known to be significant for modeling optical spectra. The one-electron, tightbinding theory can also take into account the application of an electric field perpendicular to the long CNT axis, which results in a modulation of the electronic energy spectrum and, consequently, affects optical absorption spectra that are modelled using the one-electron framework [Correa This study was written because, as far as the authors are aware, no work has been done on the incorporation of excitonic effects into the theory of optical excitations under transversally applied dc-electric fields.

This topic has important aspects, such as the potential to resolve CNT band structural characteristics and provide a better tool for CNT-type identification. Instead, this study may be seen as a straightforward model of the optical consequences of placing CNTs on a substrate that has electrical polarization. This research presents a thorough investigation of the optical characteristics of semiconducting CNTs in a transverse dc electric field. Three stages will be taken to show the applied theoretical model: Initially, the transversally applied electric field is included in the one-electron or band theoretical tight binding model of optical excitations. Many-body effects are only taken into account in this case at the so-called "scissor shift" level. The theory of many-body excitations will next be discussed, along with the Bethe-Salpeter equation. In the third section, a formula for determining the optical absorption spectrum is presented. The findings for two members of the (n, 0) and (2n, n) CNT families are then shown, followed by a discussion and a conclusion. Instead of a real electric field, a voltage differential across the CNT is used in this scenario.

Electroluminescence

Electron-hole pairs (excitons) may be produced by injecting electrons and holes from electrical contacts that are properly connected to a nanotube. Electroluminescence is produced as a consequence of later exciton recombination (EL). Single nanotubes and the macroscopic assemblies of these tubes have been used to create electroluminescent devices. There are discrete peaks that correspond to the E11 and E22 transitions, suggesting that recombination seems to happen by triplet-triplet annihilation.

Carbon nanotubes with many walls

Multi-walled carbon nanotubes (MWNT) may be made from a single graphene strip that has been rolled up several times, much like a scroll, or from numerous nested single-walled tubes. They are challenging to analyze since the contributions and interactions of each individual shell, which has a distinct structure, dictate their characteristics. Also, the processes utilized to create them are not very selective and lead to a greater frequency of faults [9], [10].

Degenerate points, where many electronic states have the same energy, are known to exist in the electronic energy spectrum of CNTs. This is primarily because both states reflect symmetrically similar circumstances inside the CNT's atomic landscape, leading to the creation of two physically different configurations with the same amount of energy. Several of these symmetries are broken by applying a static electric field, dividing the analogous degenerate states. The excitation energies are altered, which has a significant impact on the optical spectra, but it also affects the optical transition laws. When considering, for example, the optical response of CNTs deposited on a strongly polarized surface or dissolved in a strongly polar medium, the effects shown in this paper should be taken into account because relatively strong static electric fields can be found on molecular length scales and can affect the optical spectra. A more intriguing way to test for CNT chirality may be to experimentally apply dc electric fields. Higher order optical phenomena like second harmonic production will also be influenced by the selection rules' sensitivity to the applied fields owing to symmetry breaking. Scientists have developed several intricate methods using magnetic or laser traps to enclose atoms and molecules. An alternative approach that involves some clever chemistry involves enclosing molecules, such carbon buckyballs (C60), within the confined interior of a carbon nanotube and examining how this confinement affects the molecule's motion and properties.

Optically spectroscopic analysis may be used to study such confined molecules, albeit it is unclear how the carbon atoms in the nanotube can affect the light's intensity. Using simulations on Japan's Earth Simulator supercomputer, Hong Zhang of Sichuan University in China and Yoshiyuki Miyamoto of NEC in Japan1 have looked at how the electric field of light is enhanced inside of various types of carbon nanotubes. The researchers utilized a method known as time-dependent density functional theory to examine how electrons in carbon nanotubes with varying chiralities how the tube is rolled react to electric fields pulsating at high frequencies, as they do in light. Their simulations of the behavior of the electrons in the "cross-polarized" geometry, in which the electric field of the light is polarized perpendicular to the long axis of the carbon nanotube, mark a significant advancement in their research.

Liquid suspensions of carbon nanotubes

Because dispersing nanotubes in a liquid medium yields so little entropy, this can only be accomplished by modifying the system in a manner that lowers the heat of mixing, or, in other words, encourages the creation of bonds between the nanotube surface and the molecules of the liquid. To create such a favorable mixing temperature, carbon nanotubes' surfaces may be treated to make them compatible with the suspending liquid, or surfactants, which are small molecules containing a component that is compatible with liquid and a portion that is compatible with carbon nanotubes, can be utilized. These strategies are always evolving. Two distinct arrangements are possible for long stiff rods floating in liquid.

They may initially be arranged in haphazard ways, much like a bag of nails, but this packing is very ineffective and makes such structures connected to considerable dilutions. Although still having solvent molecules in between them, the rods may also be packed parallel to one another. The concept of such a phase a liquid-crystalline, solvent-stabilized, exactly lipotropic phase was first put out by Flory. It represents the relationship between stiff rod concentrations in a suspending medium and either the heat of mixing or the temperature. The first demonstration of the liquid crystallinity of nanotubes was accomplished using aqueous suspensions of multiwall nanotubes. They broadened the study to include topological imperfections in the production and organization of carbon nanotubes.

The picture does not depict the chance of the rods crystallizing at high concentrations. In order to link these ideas to the basic ideas of liquid-crystal physics, the picture is shown below as a function of temperature and Hmix direction fields, a variable related to the heat of mixing. It has also been shown that for concentrations within the "Flory chimney" or two-phase region, the longer, straighter tubes grouped into the liquid-crystalline phase, with the poorer information being rejected into the isotropic phase, where there is a distribution of lengths and elegance among any suspension of carbon nanotubes. As will be discussed in more depth below, it is known that the longer, straighter nanotubes produce stronger fibers, therefore this division has recently been exploited in a fractionation process, which is important. The most noteworthy example of liquid crystallinity, which serves as an illustration of self-organization, is the synthesis of aramid fibers, which is depicted. Such phases are known to be a wonderful precursor for getting high orientation in fibres spun from the liquid.

Nanoparticles used as reinforcement to traditional fiber-reinforced polymers have a lot of potential for usage as cutting-edge structural materials. The purpose of this work is to use electrophoretic deposition (EPD) to create hierarchical carbon fiber (CF)-multi-walled carbon nanotubes (MWCNTs). In order to maximize the advantages of the water-based EPD technique, the stability of MWCNTs in distilled water (DW) was studied in relation to the effects of voltages and deposition timeframes. The UV-Vis and stability test data quickly showed improved MWCNT dispersion and greater colloidal stability in DW solution. MWCNTs-DW suspension had little sedimentation when there was an applied voltage and good dispersion. Flexural characteristics of laminate composites and Field Emission Scanning Electron Microscopy (FESEM) pictures indicated that a deposition duration of 5 min and an applied voltage of 20 V were the ideal EPD conditions for the deposition of the MWCNTs onto the CF.

Due to its superior performance and favorable strength-to-weight and stiffness-to-weight ratios, carbon fiber-reinforced plastic (CFRPs) composites have been extensively employed as advanced structural materials, notably in the aerospace, automotive, and marine sectors. The compatibility between CF and the matrix is intimately tied to certain limits with the advanced composites, however. Weak adhesion and poor bonding between CF and matrix are caused by a non-polar, stable, and smooth graphitic surface of CF [2]. Lately, a lot of focus has been placed on enhancing the characteristics of composite materials by creating hierarchical (or hybrid, nanostructured, or multiscale) composites based on carbon nanotubes (CNTs). According to earlier research, the composite materials that arise from the hierarchical fiber-CNT architectures have the capacity to boost interfacial strength, strain/damage monitoring, humidity and temperature sensitivity, UV and curing sensing, as well as energy storage. As a result, it is anticipated that adding nanoscale reinforcements, such as CNTs, to traditional fiber-reinforced polymer (FRP) composites would result in the creation of hierarchical fiber-CNT structures, which will considerably improve the performance of the composite.

Hierarchical fiber-CNT structures have been made using a variety of approaches, including dip coating solution mixing and CNT surface interactions chemical vapour deposition (CVD) growth coating and electrophoretic deposition (EPD). Although the CVD approach comprises in situ development of CNTs directly onto the fiber surface, the dip coating, solution mixing, and EPD procedures generally rely on physical interactions between CNTs and the fiber surface. Because to their gentle operating conditions, the earlier approaches that used liquid phase media retained the CF structure. The second method, which utilised a gas phase medium, degraded the CF structure and consequently reduced its strength as a result of the harsh operating circumstances. Yet, the adjustable growth size and repeatability of the CVD process are advantages. EPD has shown to be the most successful method for depositing CNTs onto fiber surfaces among them, maybe as a result of its affordability, ease of use, uniformity of deposits, microstructural homogeneity, and reduced electric potential needs.

For controlling individual nanoparticles in colloidal suspensions in order to create sophisticated nanostructured coatings and nanoscale films with better characteristics, EPD continues to draw attention in the area of carbonaceous materials. It is a commonly used method for creating free-standing items and coating different particles on conducting surfaces. EPD is often thought of as a two-step process in which the colloidal charged particles are transported and drawn towards an electrode that is oppositely charged by an applied electric field, and then they are deposited onto the electrode surface to form a compact deposit. The particle surface charge, where the positively charged particles are deposited onto the cathode and the negatively charged particles are deposited onto the anode, affects the movement direction of the charged particles in the colloidal suspension during EPD. There has been a lot of work done on the EPD of CNTs in liquid solutions. Optimization of suspension-related parameters, including particle size, liquid dielectric constant, zeta potential, viscosity, conductivity, and stability, is necessary for successful EPD. Additional significant factors related to the process include the deposition duration, applied voltage, solid in suspension concentration, and substrate conductivity.

Stable colloidal suspensions are often made using the EPD medium, such as organic and water-based EPD. Researchers and business are beginning to adopt water-based EPD due to environmental concerns about the toxicity of organic solvents. As compared to organic solvents, water-based EPD offers advantages such as cheaper cost, less electrical field needs, better process temperature control, and more environmental compatibility. Yet water-based EPD induces hydrolysis, which leads to the creation of gaseous bubbles at the electrodes. At the cathode and anode, respectively, the impact of hydrogen and oxygen gas evolution takes place, and high voltages cause joule heating. According to a previous research, the aforementioned issues may be reduced by adding chemicals, decreasing the voltage, lowering the water ionic conductivity, employing a porous membrane electrode, and using an alternating current during EPD. The techniques described in earlier investigations, it may be inferred, are still unable to produce a uniform deposit and provide adequate control of the thickness and microstructural homogeneity.

The influence of applied voltages and deposition periods on MWCNT suspension stability in distilled water (DW) suspension were examined in this research in order to achieve a uniform deposit of the MWCNTs on the CF surface. By evaluating the zeta potential and electrophoretic mobility (EM) of the MWCNT colloidal suspension at various pH levels, a quantitative assessment of the stability of the MWCNT suspension in DW was carried out. The stability of the suspensions with and without applied voltages was used to evaluate the behavior of the MWCNTs distributed in a DW suspension. Using the use of ultraviolet-visible (UV-Vis) spectroscopy, the findings were further validated. More research was done on the connection between applied voltages and deposition time, and the shape of the MWCNTs as they deposited on the CF surface was also linked. The CNT particles employed for EPD in this work have a surface charge of 14.8 mV.

Suspensions for spinning carbon nanotube fibers that are liquid-crystalline

The first faultless production of a continuous single-wall carbon nanotube fiber from a liquid-crystalline solution was documented by Rice University researchers in 2004. Using the method, a single-wall nanotube with an 8% dispersion was produced from carbon monoxide and suspended in 102% sulfuric acid with 2% more SO3. A charge-transfer complex was created when the acid protonated the nanotubes, stabilizing the solution. The combination, which required constant dryness, was extruded into an intermittent coagulation bath, where the sulfuric acid evaporated, leaving a fibre with a diameter of around 50 m. An azimuthal scan yielded a peak width of 31 nm at half-maximum, and the pattern exhibits perfect nanotube alignment with the fiber axis. The fibers are stiff at 120GPa and have a strength of 0.16GPa.

Two further research investigated how to create fibers in a manner similar to the Rice work but using more friendly solvents. Arc-grown single-wall nanotubes were spun in a liquid medium of either ethylene glycerol or ethylene glycol that also included 1% SDS as a surfactant to create a stable aqueous suspension. The surfactant was then removed from the fibers by emulsifying spun multiwall nanotubes in an ether coagulation bath after they had been ultrasonically stabilized in a suspension in glycol. The techniques produced fibers with corresponding strengths of 0.20GPa and 0.1GPa. The elastic moduli, however, were 2GPa and 130GPa for the two processes. The electrical conductivities, which varied greatly and fell between 700S/m and 8000S/m, were also quite different. Furthermore evaluated was the alignment quality in order to contrast it with sulfuric acid spinning. The number, 20 width at fifty for the azimuthal peak, suggested that the multiwall nanotube specimen had a little better alignment.

Hydrogels Based on CNT for Biomedical Uses

The materials may be divided into two categories based on the kind of interactions that cross-linking produces. The cross-linking in chemical hydrogel, which is made, for example, by radical polymerization or UV irradiation, is covalent in nature and is permanent. Electrostatic interactions have a role in physical cross-linking, which introduces the possibility of reversibility. Not all polymers are utilised in the manufacture of CNT-based nanocomposites, including hydrogels. For instance, Mamidi et al. assessed the cytotoxicity of CNT in ultrahigh molecular weight polyethylene on fibroblasts, while Martinelli et al. produced cardiac tissue scaffolds made of polydimethylsiloxane. Nonetheless, the CNT-Hydrogel nanocomposites will be the exclusive subject of the next sentences.

Hydrogels made of biopolymers

Because of their biocompatibility and the minimal inflammatory reactions they cause, hydrogels are frequently employed in the biomedical industry. Its hydrophilicity and porosity enable the loading of cargo molecules for the administration of drugs or for biosensing, and their mechanical characteristics may be excellent for use in tissue engineering. Physical hydrogels' ability to be reversed is also highly intriguing since it may be the cause of phase transitions that may be used for in situ injection. Many hydrogels may react to various stimuli, such as changes in temperature or pH, exposure to light, or the introduction of an electric field. They thus provide intriguing materials for controlled and targeted medication delivery, particularly as some of them can also be controlled remotely.

Many polymers may be used to create hydrogels, but as most natural polymers are biocompatible and renewable, they are more often used for biomedical applications. Moreover, certain synthetic polymers meet biocompatibility standards (nontoxic and inducing low inflammation). Since polymers or monomers are typically employed together with others, Table 1 compiles the major monomer/polymer families utilized for the production of hydrogels. The ultimate characteristics of the gel are determined by the reticulation of those polymers. The inherent features of hydrogel matrices are constrained, notwithstanding their promise for the diverse uses mentioned in the preceding sentence. Hence, the use of additional polymers or the addition of nanoparticles like CNT were examined as ways to improve them.

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CHAPTER 6

QUANTUM PHYSICS OF NANO TUBES

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The dispersed wave function in quantum physics is a spherical wave that is far from the scattering center and has the form f (q) eik0r/r, where k0 is the de Broglie wave vector of the entering particles. When an electron interacts with an atom, U = eV, where V is the atomic number 134 Ph, the amplitude of the spherical wave is f(q) =. Electrostatic potential shows the atomic scattering factors for B, C, and N atoms for 200-keV electrons (left) and X-rays (right) (nucleus plus electron screening). On a graph of the electron scattering factors for B, C, and N, the relativistic correction m/m0 to the electron mass is represented by the factor (1+ E0 m0c2), where E0 is the electron energy. Since the length unit is the Bohr radius a0, the electron scattering power is 108 times stronger for electrons than for X-rays. An electron beam may be diffracted in a detectable way by a single nanotube as opposed to X-rays and neutrons, which need a huge number of nanotubes. Despite this, the firstborn approximation for nanotubes with up to a few tens of layers may be supported by the electron scattering factor for light materials like carbon [1], [2].

Neutrons

Although the neutron wavelength may be roughly approximated by a Dirac delta function, the nuclear interaction between neutrons and non-magnetic materials is significant. Considering these facts, it is obvious that the scattering factor resulting from them is a (complex) constant known as the neutron nuclear scattering length. Maybe, depending on the isotope. The average value of natural carbon is |b| = 6.648 1015 m. The scattering factor is of the same order of magnitude as X-rays (f(0) = 6re = 15.6 1015 m). Neutrons offer an advantage over X-rays in structural research using elastic scattering methods because the constant nuclear scattering factor does not affect the intensity for large scattering wave vectors. For q up to 20, neutron-diffraction profiles may be measured [3], [4].

The lattice positions are normally occupied by the majority of an element's stable isotopes with probability equal to their respective abundances. Because it depends on the isotope, the neutron scattering length varies in the lattice around the average value of b. This fluctuation leads to incoherent scattering, much as how the blue sky is produced by the incoherent Rayleigh scattering of solar light by variations in air density. Similar to how the blue sky provides a continuous background for the diffraction pattern, the isotropic incoherent neutron scattering cross section does the same. It has a ratio of |b b|. Carbon has a relatively small ratio of 0.0018 between coherent and incoherent scattering cross sections.

Moving beyond the simple kinematic theory of diffraction is necessary for the interpretation of images from fast electron transmission through a crystalline film. It is really quite difficult to describe the electron-atom interaction of the sample as a succession of single-scattering occurrences. It is far more straightforward to consider the electrons as being distributed by the total electrostatic potential of the sample, which causes a continuous change in the phase and amplitude of the wave functions as they move through the specimen. To do this, we consider a piece of crystalline material that is subjected to a monokinetic electron beam of energy E0 (a few hundred keV) that arrives at normal incidence (z-direction). The de Broglie wave vector, k0, which is situated above the film, is the electron wave function, which is represented by the plane wave 0 = eik0z. We only consider the elastic interactions of the electrons with the crystalline material in order to guarantee that the energy E0 is retained. Since the crystal exhibits translational symmetry in directions perpendicular to the surface, the momentum parallel to the surface is maintained inside a two-dimensional reciprocal vector g of the crystal film. Because 2(g2 + K2)/2m = E0, where m is the relativistic mass of the electron, the wave function that is elastically transmitted through the film may be divided into numerous plane waves as a consequence. High energies induce a simplification since we can substitute k for k0 thanks to k0 g. The beams that correspond to the set of g vectors will make up the crystal film's diffraction pattern, with the intensity of the spots being inversely proportional to the square of the amplitude |Ag|. Contrary to common perception, additional scattering in magnetic nuclei is specified by a q-dependent scattering factor. Moreover, this part does not address the Debye-Waller factor attenuation, which explains the thermal vibration of the atoms [5]–[7].

Wave Function

The expected electromagnetic potentials for one graphene sheet, one graphite sheet, and one Ni crystal are used to estimate the wave function at the sample's exit face. These electromagnetic potentials are caused by interference between the diffracted beams and the transmitted beam. After the regular intervals potential is known, the modulus ag and phase g of the amplitudes Ag = ag eig of the transmitted and refracted beams may be calculated. When the crystal is positioned such that dense atomic sections are horizontal to the electrical current, only two Bloch states, one of which is located within each atomic column, normally contribute to the wave function, according to the Bloch wave approach. The "multislice approach" is an optical method that has been suggested and is often used, especially when analyzing large cells (including, for example, extensive faults). In the latter technique, the specimen is cut into thin slices with a thickness of zi. I The phase object approximation is applied, and it is hypothesized that a propagation in vacuum will take place between two slices. At the departure of the I + 1) Th slice, the resulting wave function is. We used three Miller indices connected to the unit vectors a1, a2, and c with = (a1, a2) = 120. As the two a1 and a2 unit vectors of the graphene sheet form a 60° angle, this foundation is not often employed for nanotubes.

Ψi+1(ρ) = ψi (ρ) The propagation function, pi (), is equal to i/zi exp(i2/zi), and the wave component transmission factor, q(), is equal to eiVp()zi. A convolution product is represented by the symbol. After N repetitions, the exit wave function is determined, accounting for the sample's overall thickness. For graphite (001), graphite (210), and Ni (110), all treated to 400 keV electrons, the differences in the transmitted and diffracted beams' amplitudes and phases are presented. The high permeability limit of graphite, graphene, is the actual weak phase object with g 0 = /2 and ag a0. In contrast to the 110 beams (u = 1/0.1235 nm), which oscillates rapidly with a 20 nm extinction distance, the 100 diffracted beam in the graphite (001) instance does not change much with thickness (with a Pendell-osung distance4 of more than 70 nm). This results in the transmitted beam having two frequencies, as was previously observed in Fig. 3.5. The similar behavior is seen in the phase variation. The fundamental idea is that once graphite's thickness exceeds 10 nm (at 400 kV), it can no longer be considered a weak phase object. This restriction is much more stringent for Ni, as evidenced by the amplitudes and phases fluctuations in Ni(110), where the phase varies significantly with thickness. All simulations were performed using P. Statesman's EMS code [8]–[10].

Since the exit wave function is complex, it can be written as (,d) = A(,d) exp[i(,d)], where is the phase difference between the sample's entry and exit sides, and A2 is the intensity of the wave function in the specimen's exit plane at thickness d. Graphene, graphite, and nickel can all be seen along with variations of the A2 with d. In the graphene scenario, A2 remains in the vicinity of 1 and 0. (With just one slice by definition). Due to the phase shift between the transmitted and diffracted electrons of g 0 = /2, (,d)=1+i, where I is a fictional component. A weak phase object is compatible with the wave function intensity of I = 1+ 2, which yields a contrast that is virtually zero.

For thicknesses smaller than 10 nm, the intensity maxima for graphite along 001 are found on the atomic columns with a weight corresponding to V 2 p, but for thicknesses larger than this, A2 simply reflects the locations of the doubled columns in the ABAB hexagonal sequence. A quick phase fluctuation is present along with this phenomena, which is principally due to the fact that the projection distances between the atomic columns are just 0.142 nm. This tendency is correlated with the relative weight of the Bloch states as demonstrated in and is amplified with a lower accelerating voltage. Even though the atoms in Ni are heavier, their projection distance from one another is only around 0.2 nm, allowing the A2 and variations in thickness to follow the channeling behavior up to 5 nm.

Quantum, quantum sizes, and biomolecules

The study of nanostructured materials has made it feasible to comprehend and control events, manipulate elements at the biomolecule, quantum, and quantum scales. By making it feasible to produce nanoparticles, this innovation expands the range of applications for materials and improves their properties. Research on nanomaterials in a variety of fields, including as biomechanical, sensing, and military systems, has enlarged the scientific field. Carbon nanostructures are becoming essential for many industrial applications. Yet, only graphite and diamond were acknowledged as unique carbon structures until to the 1980s. The situation changed at that time with the discovery of C60 and other carbon fullerenes. This incredible discovery has since propelled the study of Nano science. The discovery of fullerene stimulated investigation into new architectures. Carbon nanotubes were discovered in the next ten years (CNTs).

Theoretically, CNTs are produced when tubes are made by wrapping graphene sheets around one another. In the x-y plane, each carbon atom in the layers of these tubes is sp2-bonded to two other carbon atoms. The three main types of CNTs that are often classified are single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), and multi-walled carbon nanotubes (MWCNT), which incorporate multiple concentric tubes. Due of their multiple applications in biosensors, drug transport, and electrochemistry, CNTs have generated a great deal of interest since their discovery in 1991 and have become a hot study subject. Nanowires, magnetic fluids, and nanoelectronics

The remarkable mechanical, electrical, and thermal properties of the CNT structure, with nanometer-sized diameters and lengths, enable a wide range of applications. CNTs might have Young's moduli between 270 GPa and 2 TPa. The degree of precision with which the CNT properties are measured, however, depends on the type, diameter, length, and chirality of the material. The chirality of the CNTs is a result of the manufacturing process.

A Different Approach to Functionalizing Carbon Nanotubes

The hunt for functionalization optimization to fill the gaps left by covalent and non-covalent functionalization led to the development of click chemistry functionalization, one of the most successful methods used in the production of CNTs for biosensing applications. Moreover, employing the above-mentioned CuAAc procedure between arylazido-decorated N3-SWCNTs and alkyne-terminated organic/organometallic compounds, biological sensing components may be immobilized on CNTs. The click chemical functionalization of CNTs has been the subject of other articles. In Sahoo's paper, click coupling was used to attach a variety of unique functionalization agents to CNTs, including gold nanoparticles-N3.

Defect functionalization is a method of functionalization that results from the oxidation process. Oxygen functionalities like carboxyl, phenolic hydroxyl, ketonic carbonyl, lactone, and others transform CNT from a hydrophobic material to a hydrophilic one, improving the dispersion in solvents and the chemical reactivity. This method of functionalization often entails immersing CNTs in a number of strong oxidizing agents, such as KMnO4, H2SO4, HNO3, and H2O2. Gas-phase oxidation, on the other hand, is a speedier and cleaner process. In comparison to other oxidants, ozone is an oxidant gas that offers a number of advantages, including price, accessibility from ozone producers, and sustainability. Additionally, due to ozone's higher reactivity and the ability to functionlize at room temperature. The covalent functionalization of CNTs destroys the ordered structure of CNTs for a number of purposes, including adsorption, an electrode for electric double-layer capacitors (EDLC), catalyst support, energy storage, and fuel cells. Electrochemical techniques may be used to control the functionalization's accuracy.

Gonzalez-Gaitán asserts that the Carbon Nanotube 45 method had no effect on the CNTs' wall structure. This process may be carried out with small quantities of samples and reagents at room temperature and atmospheric pressure. Moreover, it is simple to halt the reaction and duplicate the reaction conditions, enabling exact reaction control. The wide variety of methods, such as defect functionalizations, click chemistry, electrochemistry, and covalent and non-covalent functionalizations, increase the relevance of CNTs in technological applications and open up new markets for nanomaterials based on CNTs.

Uses for Carbon Nanotubes

CNTs have been the focus of several investigations due to their exceptional mechanical, electrical, and structural qualities, which make them very attractive materials. The excellent mechanical and electrical capabilities of CNTs, in addition to other multi-functional qualities, enable an entirely new class of composite materials with tremendous promise for structural and functional applications. Recent scientific research has focused a great deal on functionalized CNTs and their applications. Research, health, and engineering have all recognized potential applications. A number of industries, including the reinforcement of high-performance composites, electronic and optoelectronic devices, chemical sensors, optical biosensors, energy storage, field emission materials, catalyst support, nanoprobes for meteorology, and biomedical and chemical research, have benefited greatly from the use of CNTs and CNT-based materials. These are but a handful of the scenarios that have been researched; further work will be done in the next years that will result in the creation of new applications.

Polymer and CNT-based composites

Optical components, electronic packaging, insulating materials, semiconducting materials, tubing, and liquid crystal displays are just a few examples of the advanced technical applications for polymers. Despite their advantages (lightweight, easy molding, and low cost), polymers have a number of disadvantages, such as low melting point, weak strength, and time-dependent liquid-like flow. The discovery of CNTs paved the way for polymers to be given better mechanical, electrical, and other crucial characteristics, leading to the emergence of a new class of functional materials for sensors, energy storage, structural, and biological applications.

In 1999, Shaffer and Windle conducted the first study on the incorporation of CNTs as reinforcement in the polymer matrix. They looked at the electrical and thermomechanical properties of polymer nanocomposites. Applications of functionalized carbon nanotubes. While the stiffness of the nanocomposites was relatively low at room temperature, they discovered that it was substantially greater at higher temperatures. Moreover, these nanocomposites displayed the same percolation behavior as previous fiber-filled systems. They came to the conclusion that nanotubes may be used, particularly at high temperatures, to change polymers.

CNT-based hydrogels for targeted therapies

While the use of CNT-based hydrogels for drug administration is relatively new, it has been looked into by several authors, as noted in Comprehensive. It has been shown that the porous nature of biocompatible hydrogels and the superior mechanical and electrical characteristics of CNTs have promoted the stability of drug molecules and enabled long-lasting therapeutic effects. Also, this type of material enables the creation of other delivery systems, including transdermal administration patches.

Drug delivery through CNT-based hydrogels

Various groups looked into the potential for drug delivery using hydrogels based on electro-responsive CNTs. For example, using sodium methacrylate and N,N'-ethylenebisacrylamide, Spizziri et al. Microspheres were formed by polymerizing gelatin containing MWCNTs. The microspheres were loaded with the drug, diclofenac sodium salt, by soaking them in a concentrated solution. Scientists have shown that applying a pressure of 9V to the beads causes them to shrink, thereby promoting the release of the drug. Furthermore, his team revealed that the drug release behavior varies depending on the drug charge. The results of experiments on covalent films polymerized by UV excitation of acrylamide and N,N′-ethylenebisacrylamide and containing MWCNT showed that whereas cationic drugs were retained and released more rapidly without electrical stimulation The anionic drugs were released more slowly under 12V excitation. This was explained by the formation of negative charges on the CNTs under 12 V excitation. For remote electrically controlled delivery, Naukar et al. investigated the use of implantable CNT-based hydrogels. They demonstrated methacrylic acid free-radical polymerization in the presence of pristine MWCNTs to enable pulsatile drug release. The electrical pulses speed up drug release, although studies have shown that the rate of administration returns to normal sooner when the pulse ends, providing greater accuracy.

With regard to pH-controlled drug delivery systems based on CNT/hydrogel nanocomposites, they were also taken into account. According to Peng et alfindings, the MWCNT/chitosan hydrogel swells differently depending on the pH of the buffers that mimic two different gastrointestinal environments, which affects the release rate [96]. Ye et al. It has also been shown that the wettability and swelling of vertically aligned CNTs with poly(methacrylic acid-co-ethylene glycol diacrylate) (P(MAA-co-EGDA)) was affected by pH, and this may result in controlled release .A dual release carrier using a CNT/polycaprolactone (PCL)-PEG-PCL thermosensitive hydrogel in which Rhod was encapsulated inside the hydrogel and DOX was loaded onto the CNT. The reason for the observed release rate is identified as variation in drug loading. In addition, pH dependence was also found. To load pharmaceuticals such as curcumin and facilitate cellular absorption of the drug, Hindumati et al. in their research on CNT-based hydrogels contained CNTs within a PEG cocoon.

Application of CNT-based hydrogels to the skin

The limited drug release rate and poor skin penetration of current transdermal administration patches are their main limitations. CNT-based nanocomposites may provide a novel solution to both difficulties due to their inherent characteristics. As previously shown, this type of hydrogel may provide better control over the release rate while increasing drug stability over time. By electrospinning a polyethylene oxide/pentaerythritol triacrylate/MWCNT hydrogel, they were able to create such a patch, and they observed a relationship between drug release and applied voltage. The release performances of both diltiazem and diclofenac membranes, fabricated from PVA and carboxy-functionalized MWCNTs made from 2-hydroxyethyl methacrylate grafted carboxymethyl guar gum and functionalized MWCNTs, were promising.

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CHAPTER 7

AUTOMOTIVE APPLICATIONS

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The extraordinary mechanical properties of CNTs, with a Young's modulus as high as TPa and mechanical properties ranging from 50 to 200 GPa, are widely recognized in the field of mechanics. Due to their superior characteristics, low density, significant surface area, and high aspect ratio, CNTs are great choices for nanocomposite reinforcing materials. Nevertheless, the success of adding CNTs to polymers depends significantly on the dispersion state of the nanofillers. A suitable dispersion increases the CNT surface area that is available for interfacing with the polymer while minimizing stress concentration. SWCNTs and MWCNTs are used as reinforcement in thermosetting and reversible polymer nanocomposite fabrication. The most popular polymer matrices are epoxy, polyurethane, phenol-formaldehyde resins (thermosetting), polyethene, polypropylene, polystyrene, and polyamide [1]–[3].

Several authors have studied composites reinforced with CNTs that have been functionalized. In their 2013 work, the authors used micrographs of the cryogenically cracked surfaces of composites made of epoxy resin and carbon nanotubes to draw the conclusion that non-functionalized CNTs were poorly dispersed in the epoxy matrix and had poor adhesion with epoxy. Acid functionalization improved the adherence of the CNT to the resin and somewhat improved the CNT dispersion. Nevertheless, nanocomposites created utilizing CNTs that had undergone amino treatment exhibited the most uniform dispersion and the best interfacial contact between epoxy and CNT. They also asserted that CNTs, whether functionalized or not, increased the degree of healing in the samples.

According to various research, adding functionalized CNT to a polymer matrix improved the mechanical properties. CNT/epoxy nanocomposites that had been functionalized have better thermal and mechanical properties. CNTs were disseminated throughout a polymer containing epoxide groups after receiving carboxyl group functionalization. The elastic and storage moduli of the functionalized CNT/polymer nanocomposites were 100% and 500% greater than those of pure polymer. Moreover, compared to the original CNT/polymer nanocomposite, the functionalized version shows higher thermal stability. Shi et al. (2012) produced nanocomposites using high-density polyethylene (HDPE), SWCNT, MWCNT, and hydroxylated MWCNT. The interactions of the CNT with the matrix led to a 40–60% increase in mechanical properties. They also observed that CNT displayed antioxidant characteristics by increasing the oxidation induction temperature (OIT) and the oxidation induction time (OIt).

Ryu and Han employed a melt-compounding method to make nanocomposites. Polyamide was reinforced with non-functionalized CNTs and non-covalent functionalized CNTs (PA). The CNTs were functionalized by tetrahydrofuran (THF). The nanocomposite of PA/functionalized CNTs showed a much higher flexural modulus than the nanocomposite of PA/non-functionalized CNTs. Moreover, the electrical performance and CNT dispersion in the PA matrix were best for the functionalized CNT-containing nanocomposites [4]–[6].

Furthermore, elastomer reinforcing has been done. Produced samples of surface-modified CNT-reinforced vulcanized silicone rubber nanocomposites at room temperature. These CNTs were first given an acid functionalization treatment, and then they received a polyester-modified polydimethylsiloxane treatment (BYK-310). They observed that the CNTs were more equally distributed throughout the silicone rubber matrix after BYK-310 CNT treatment. The nanocomposite formed with unfunctionalized CNTs has noticeably lower mechanical properties. The nanocomposite created with CNTs that had been BYK-310-treated demonstrated an extremely higher mechanical property, while the nanocomposite made with acid-treated CNTs revealed a somewhat superior mechanical property. Composites constructed of CNTs and polymers may enhance the electrical properties of certain materials. CNTs provide significant advantages over traditional materials due to their exceptional electrical conductivity and high aspect ratio. By facilitating the formation of conducting networks, these properties transform insulating polymers into conducting polymers. CNTs and polymer-based nanocomposites are now generating a lot of attention due to their applicability in flexible electronics, electromagnetic interference shielding, and sensor applications.

Conducting networks start to form in the nanocomposites as a result of improved CNT dispersion brought on by CNT functionalization, which significantly affects their electrical conductivity. In performing the functionalization process, care must be taken to prevent introducing too many heterogeneous atoms into the network, which act as a barrier to electrons and reduce electrical conductivity. The process of acid functionalization may also weaken the walls of the nanotubes, resulting in defects and a decrease in aspect ratio.

CARBON NANOTUBES IN THE HYDROGEN FUEL CELL

Many people think that future cars will run on sustainable hydrogen, which emits clean water instead of harmful CO2 emissions. Hydrogen fuel cells are improving the dream came true. The hydrogen's explosive qualities must be handled by the fuel cell while still providing the customer with a reliable supply of renewable energy. Many developments in nanotechnology are raising the hydrogen fuel cell's efficiency and making it more accessible and inexpensive for people in underdeveloped countries. This article will concentrate on the use of carbon nanotubes in proton exchange fuel cells and provide information on how carbon nanotubes may be utilized to improve the safety, affordability, and accessibility of fuel cells in poor countries.

HYDROGEN FUEL CELL IMPROVEMENT USING CARBON NANOTUBES

Basically, hydrogen fuel cells "convert the molecules hydrogen and oxygen into water while producing power." Single-walled carbon nanotubes (SWCN) are being used to create more effective hydrogen sensors and safer fuel cells. Developing carbon nanotubes is superior than carbon powder because it increases efficiency and the catalyst's use. MWNTs, or multi-walled carbon nanotubes, effectively connect electrically to the substrate (carbon paper). While the platinum particles used in this study were quite big at the time, the researchers thought that future reductions in size will also improve fuel cell performance [7]–[9]. The CFE/CB/Pt electrodes are around 20% less efficient than the "Single-Wall Carbon Nanotube-Based Proton Exchange Membrane Assembly for Hydrogen Fuel Cells," which employs a platinum catalyst. The performance of h2-based PEM fuel cells, particularly at higher pressures, was enhanced by this technique. The fuel cell has become more affordable because to 2004 research on nano-structured hydrocarbon membranes. Nanocomposite materials based on conducting polymers and CNTs have attracted attention for their potential application in the development of sensitive and focussed sensors, particularly for the detection of hazardous substances. High CNT dispersion is necessary for excellent polymer matrix capabilities, however. Uses of Carbon Nanotube Functionalization Surface functionalization may result in a homogeneous dispersion by increasing the interaction between CNTs and polymer chains. The CNT functionalization may boost the intra- and interchain charge mobility in the polymer chains, change the electron-donor or gas-acceptor properties of the nanocomposites, or even increase the number of CNT sites that interact with the analyte.

Using in situ chemical oxidation polymerization, carboxyl (-COOH)-functionalized MWCNT and poly (m-aminophenol) were combined to form nanocomposite films (PmAP). They looked at the properties of aliphatic compounds to detect alcohol. The results showed a site-selective interaction between the conjugated PmAP backbone chains and the bonded surface of functionalized MWCNTs. Moreover, X-ray studies showed that adding a little quantity of functionalized CNTs to PmAP considerably increases the material's crystallinity and significantly improves the sensor's sensitivity to aliphatic alcohol vapour when compared to pure PmAP.

Due to the significant increase in power consumption, much research is being done in the area of solar cells, notably in organic solar cells. When CNTs are used as an electron transport channel, charges are quickly and effectively transported across the electrode surfaces. There is hence a substantial power conversion. Investigated functionalized nanocomposites incorporating octadecylamine on a bulk heterojunction of organic solar cells. Four solar panels with different CNT concentrations were produced using the same manufacturing parameters. Functionalized CNTs were added to the solar cells, which slightly increased the optical absorption of the active layer, but did not significantly alter the open-circuit voltage. Yet, current density potential curves from photovoltaic experiments revealed that the CNT-containing cell was 31.8% more effective than the cell without them. The reason, according to the researchers, is that the CNT within the device has nano-sized channels that boost electron mobility.

Studies on the topic have shown a connection between electromagnetic interference (EMI) and the increasing sensitivity of electronic equipment. CNTs may be incorporated to composite materials as nanofillers to give a cutting-edge way of EMI shielding because of their outstanding dielectric properties. The surface functionalization of CNTs enhances their electrical properties and compatibility with polymer matrices.

Functionalized Carbon Nanotubes

Raman-based spectroscopy

Raman spectroscopy, which examines the relative intensities of the D band and graphite G band (*1570 cm1) in the material, is one of the best approaches to evaluate the level of defect in carbon materials. The D band is caused by disorder-induced defects and non-hexagonal structures, while the G band is caused by the symmetric E2g mode of the hexagonal lattices in graphite. The Raman spectrum reveals the structural changes in the CNT, providing conclusive evidence of its chemical functionalization. Raman also reveals the nanotubes' surface chemistry, namely their fraction of carbon atoms with sp2 and sp3 bonds. G band displays just two lines at *1570 and *1590 cm-1 for isolated CNTs. A rise in the D/G intensity ratio (ID/IG) is always seen as an indication of successful covalent functionalization, including oxidation, which may exacerbate the structural faults of CNT. Peaks at lower wave numbers are no longer visible when the band G width moves. The sp2 structure of the CNTs was perturbed by the covalent attachment of functional groups during functionalization, resulting in an increase in the ratio (ID/IG) from 0.16 to 0.40 after an acid covalent functionalization. Nevertheless, a non-covalent Carbon Nanotube 51 functionalization with 1-aminopyrene did not appreciably change the ID/IG (from 0.16 to 0.2), maintaining the CNT structure.

We detected no changes in the ID/IG of non-covalent functionalized CNT (with dendrimeric cyclophosphazene) after the formation of nanocomposite material to show that non-covalent modification of CNTs has no effect on the CNT structure. Data of suspensions containing both functionalized and unmodified CNTs were shown, and they often showed three peaks. Three peaks at 1346, 1583, and 2697 cm1 in the neat MWCNTs correspond to the D, G, and G' bands, respectively. The G band, which is present in all graphite-like materials, is caused by the in-plane vibration of C-C bonds. The G' band, which is the D band's overtone, is brought on by anomalies in carbon systems. After functionalization, all bands shift in the direction of higher wave numbers, demonstrating that CNTs have been separated. SDS (sodium dodecyl sulphate) is added to CNT surfaces to shift these three bands to 1348, 1585, and 2701 cm1, along with bandwidth narrowing that shows enhanced dispersion.

Thermal Spraying is a kind of carbon Nano spraying.

Melted (or heated) materials are sprayed onto a surface during coating procedures. The "feedstock" (a coating precursor) is heated using either chemical or electrical (plasma or arc) methods (combustion flame). In comparison to other coating methods like electroplating, physical and chemical vapor deposition, thermal spraying may produce thick coatings (approximate thickness range is 20 micrometers to several millimeters, depending on the procedure and feedstock). Metals, alloys, ceramics, polymers, and composites are among the coating materials that may be thermal sprayed. They are supplied in powder or wire form, heated to a molten or semi molten state and propelled towards substrates in the form of micrometer-size \sparticles. Thermal spraying often uses electrical arc discharge or combustion as the energy source. The buildup of several sprayed particles creates the final coatings. The surface may not heat up much, permitting the coating of combustible chemicals. Typically, the porosity, oxide content, macro and microhardness, bond strength, and surface roughness of a coating are measured in order to determine its quality. In general, when particle velocities rise, coating quality rises as well [10].

Fragrance

Depending on the shape of the feedstock material—powder, wire, or rod—flame spray is split into three subcategories. Combustible gasses are used in flame spray to provide the energy required to melt the coating material. Considering that there isn't an extension nozzle where acceleration might take place, combustion is practically unconfined.

Fourier Transform Infrared Spectroscopy Analysis (FTIR)

None of the normal peaks connected to organic or inorganic chemical groups can be seen in the FTIR spectra of pure CNT. In other cases, the presence of OH groups, which are assumed to be the result of ambient moisture adsorption or the leftovers of different purification processes, causes peaks out at around 980 and 3430 cm1 to be seen. Peaks between 1550 and 1700 cm-1 are also conceivable; these peaks are ascribed to the aromatic ring C = C bonds on the nanotube walls.

The FTIR spectra for CNT functionalized with the H2NCH2CH2O group showed bands at around 1040, 1625, 2850, 2920, and 3410 cm1. The scissoring in-plane N-H of the free primary amine group and the C-N stretching vibration, respectively, are linked to bands at around 1040 and 1625 cm1. Bands at 2850 and 2920 cm1 are responsible for the stretching of -CH2, respectively. Lastly, the broad band at *3410 cm1 is caused by the stretching of NH2.

Peaks in the FTIR spectra of the sodium dodecyl sulfate (SDS)-dispersed CNT can be seen at around 1100, 1400, 2905, and 2980 cm1. The peak at 1400 cm1 is due to the scissoring and bending of the C-H bonds, whereas the peak at roughly 1100 cm1 is caused by the SO4 group. The peaks at 2905 and 2980 cm1 are thought to be induced by the stretching of C-H bonds. These peaks demonstrate that the SDS was successfully coated onto the CNTs.

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CHAPTER 8

FABRIC AND CARBON NANO TUBE

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Carbon nanotubes (CNTs) are cylindrical structures comprised of one or more graphene layers that are continuous. They are known as SWNTs or MWNTs and may have open or closed ends. Pentagons, heptagons, and other sidewall imperfections in mass-produced CNTs, on the other hand, often impair beneficial properties. Except for their ends, all carbon atoms in perfect CNTs are interconnected in a hexagonal lattice. SWNT and MWNT diameters are typically 0.8 to 2 nm and 5 to 20 nm, respectively, despite the fact that MWNT diameters may exceed 100 nm. CNT lengths range from a few hundred nanometers to several meters, spanning the molecular and macroscopic sizes [1], [2].

By just considering the cross-sectional area of the CNT walls, it has been shown that individual MWNTs have an elastic modulus close to 1 TPa and a tensile strength of 100 GPa. Its strength is more than five times more than that of industrial fibers. The majority of MWNTs are constructed of metal and can carry currents up to 109 A cm-2. Individual CNT walls may be metallic or semiconducting depending on the chirality or orientation of the graphene lattice with respect to the tube axis. A single SWNT may have a thermal conductivity of 3500 W m1 K1 at room temperature, which is higher than the thermal conductivity of a diamond and depends on the size of the wall.

There have been reports of hollow carbon Nano fibers since the 1950s, and the first industrial synthesis of what are now known as MWNTs occurred in the 1980s. In the early 1990s, considerable CNT research got underway as a result. Yet during the last 10 years, the business activity around CNT has grown the most. Since 2006, the ability to produce CNTs has increased by at least 10 times, and the number of CNT-related journal publications and issued patents is rising yearly. The majority of CNT production is used in bulk composite materials and thin films today, which rely on disordered CNT topologies with restricted properties. Organized CNT architectures like vertically aligned forests, yarns, and sheets show promise for scaling up the characteristics of individual CNTs and realizing new functionalities like shape recovery, dry adhesion, high damping, terahertz polarization, large-stroke actuation, near-ideal black-body absorption, and thermoacoustic sound emission. Despite the development of CNT macrostructures such sheets and threads, their mechanical, thermal, and electrical properties are still thought to be subpar compared to those of individual CNTs.

CNT powders have already been employed in a number of commercial applications, and with the backing of high-volume bulk production, they are now reaching the growth stage of their product life cycle. This study focuses on the most promising existing and possible commercial applications for CNTs in light of these advancements, as well as any challenges that may arise that may spur more research and development. High-purity SWNT particles may also be separated by chirality using density gradient centrifugation in combination with selective surfactant wrapping (24) or gel chromatography (25). While there are several commercially available CNT powders and suspensions, stabilizing CNT suspensions requires coating the CNT surface or adding surfactants. In processes including spin coating, printing, washing, and heat treatment, surfactants are often only removed after the solvent has been applied [3], [4].

Nevertheless, CVD synthesis of SWNTs requires far more stringent methods than MWNT synthesis, in addition to the legacy costs associated with research and process development, therefore the price of bulk SWNTs is still significantly higher than the price of MWNTs. MWNTs are therefore favoured for applications where CNT diameter or bandgap are not required, but for the majority of newly discovered applications that need chirality-specific SWNTs, the extra price reduction is required to establish commercial viability.

As an alternative, the creation of long, aligned CNTs that can be processed without the need for liquid dispersion raises the prospect of the economically beneficial realization of compelling bulk properties. In addition to the self-aligned development of horizontal and vertical CNTs on surfaces coated with catalyst particles, these approaches also involve the direct synthesis of CNT sheets and yarns from floating-catalyst CVD systems. In addition to being able to be immediately spun or drawn into long yarns and sheets, thick solids, aligned thin films, and intricate three-dimensional (3D) microarchitectures, CNT forests may also be used as a raw material.

Composite Materials

MWNTs were first used as electrically conductive fillers in polymers to take advantage of their high aspect ratio and create a percolation network at concentrations as low as 0.01 weight percent (wt%). With 10 weight percent loading, conductivities of disordered MWNT-polymer composites may surpass 10,000 S m-1 (34). Fuel lines, filters, and mirror housings may now be painted utilizing electrostatic aid thanks to conductive CNT polymers. Other products include electromagnetic interference (EMI)-shielding packaging and wafer carriers for the microelectronics industry.

For use in load-bearing applications, the addition of CNT particles to polymers or precursor resins may increase the materials' stiffness, strength, and toughness. Adding 1 wt% MWNT to epoxy resin raises stiffness and tensile characteristics by 6 and 23%, respectively, without changing other mechanical attributes. These enhancements are influenced by the CNT's diameter, aspect ratio, synchronization, dispersion, and interfacial contact with the matrix. Several CNT companies provide masterbatches and pre-blended resins with CNT loadings varying from 0.1 to 20% by weight. Moreover, the production of nanoscale stick-slip between CNTs and CNT-polymer contacts might enhance sports equipment like tennis racquets, baseball bats, and bicycle frames by enhancing material damping.

CNT resins are also used to enhance fiber composites. Current examples are the sturdy, light-weight hulls for maritime surveillance boats and composite wind turbine blades made of carbon fiber composite with CNT-enhanced resin. CNTs may also be utilized in place of the organic precursors that are used to make carbon fibers. The effect of the CNTs on the arrangement of carbon in the pyrolyzed fiber allowed for 1-mm diameter carbon fibers with over 35% greater strength and stiffness when compared to control samples without CNTs [5].

The Environment and Energy Storage

The widespread use of MWNTs in lithium-ion batteries for laptops and mobile phones has been a big commercial success. In these batteries, minute amounts of MWNT powder are mixed with active ingredients and a polymer binder, such as the 1% CNT loading in $LiCoO_2$

cathodes and graphite anodes. The improved rate capability and cycle life afforded by CNTs' greater mechanical and electrical connection. In articles, gravimetric energy storage and load parameters for prepacked batteries and supercapacitors are often described, with weights of the active electrode components being normalized. It is difficult to compare these gravimetric performance measurements to those for packed cells, since getting high performance based on total cell weight or volume necessitates high areal energy storage and power densities. This is a result of the widespread usage of active materials with low areal densities.

Supercapacitors made with additive- and binder-free forest-grown SWNTs performed very well in one of the few recent tests for packed cells. It was possible to attain an energy density of 16 Wh kg-1 and a power density of 10 kW kg-1 with a 40-F supercapacitor with a maximum voltage of 3.5 V. Based on accelerated testing at temperatures of up to 105°C, a lifetime of 16 years was estimated. Despite these remarkable achievements, the cost of SWNTs at the moment remains a major barrier to commercialization. CNTs have the potential to reduce the consumption of Pt in fuel cells by 60% when compared to carbon black, and doped CNTs may potentially enable Pt-free fuel cells. Inorganic solar cells, the features of CNTs are being used in ongoing research to reduce undesired carrier recombination and boost photooxidation resistance. Solar technologies could be able to make use of the effective multiple-exciton creation at p-n junctions created within individual CNTs and the long-term integration of CNT-Si heterojunctions [6]–[8].

In the near future, transparent SWNT electrodes may be used in commercial photovoltaics. Future applications for CNT include water purification. In this case, tangled CNT sheets may provide networks with controlled nanoscale porosity, which are robust in terms of both physical and electrochemical processes. They have been used to electrochemically oxidize organic contaminants, bacteria, and viruses. To purify contaminated drinking water, commercialized portable filters made of CNT meshes have been developed. Moreover, membranes built of aligned encapsulated CNTs with open ends may achieve previously unheard-of low flow resistance for both gases and liquids by permitting flow through the interiors of the CNTs. Its increased permeability may make reverse osmosis a less costly technique of desalinating water when compared to current polycarbonate membranes. Therefore, extremely small-diameter SWNTs are needed to reject salt in seawater proportions. CNTs continue to be a popular component for biosensors and medical devices because of their dimensional and chemical compatibility with biomolecules including DNA and proteins. At the same time, CNTs enable localized heating with near-infrared light, photo acoustic imaging, and fluorescence imaging.

SWNT biosensors may exhibit notable fluctuations in electrical impedance (80) and optical properties in response to their surroundings, which are typically affected by the adsorption of a target on the CNT surface. Functional groups and coatings, for example, may be utilized to tailor the CNT surface for low detection limits and high selectivity, and the appropriate sensor design, such as field effects, capacitance, Raman spectrum changes, and photoluminescence, should be employed (82, 83). NO2 and cardiac troponin sensors, microarrays for DNA and protein detection, and inkjet-printed test strips for the detection of oestrogen and progesterone are among the products now in development (84). Similar CNT sensors have been used to detect gases and poisons in the food industry, the military, and environmental applications.

By initially attaching the ends of CNTs to receptors on the cell membrane, cells may then internalize them for use in in vivo applications. As a result, molecular payload that is embedded within or attached to the CNT walls may be transfected. For instance, the cancer drug doxorubicin was loaded up to 60% weight on CNTs as compared to 8–10% weight on liposomes. To release cargo, near-infrared radiation may be employed. Nevertheless, it will be important to control CNT retention in the body and prevent undesired accumulation in order to utilize free-floating CNTs. This might be done by changing the surface chemistry of CNTs.

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CHAPTER 9

PROCESSING AND PURIFICATION

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Pure carbon nanotubes cannot be created using any of the methods covered in the preceding two chapters. For instance, nanoparticles and disordered carbon are always present when multiwalled nanotubes are created via arc evaporation. Nanotubes are polluted with catalyst and support material during catalytic production. Thus, it is often required to clean the nanotubes before using them. An overview of the current chemical and physical purification techniques for nanotubes opens this chapter. Afterwards, methods for processing nanotubes are examined. There are instructions for aligning tubes, shaping them into fibers and sheets, and sorting tubes by length and structure. The methods for increasing the solubility of nanotubes by functionalization are described, and discusses the insertion of nanotubes into composite materials [1]–[3].

Multiwall tube purification

Arc-evaporation-made MWNTs

Thomas Ebbesen and colleagues published the first detailed description of the first effective method for cleaning multiwalled tubes made by arc-evaporation in 1994. These researchers discovered that nanoparticles, with their defect-rich structures, may be oxidized far more rapidly than the comparatively flawless nanotubes when it was shown that the caps of nanotubes could be preferentially targeted by oxidizing gases (see Chapter 10). In the hopes that the nanoparticles would be preferentially oxidized away, they thus submitted raw nanotube samples to a variety of oxidizing processes. They discovered that using this method might result in a significant relative enrichment of nanotubes, but only at the risk of losing a significant amount of the original sample Hence, more than 99% of the raw sample has to be oxidized in order to eliminate all of the nanoparticles. Around 10- 20% of the residual sample had nanoparticles when 95% of the original material had been oxidized, while there had been no enrichment at all when just 85% of the original material had been oxidized. According to these findings, there is only a very little 'window' between the selective removal of nanoparticles and total oxidation of the sample. This suggests that the reactivities of nanotubes and nanoparticles towards oxidation are quite comparable [4], [5].About the same time, a Japanese group devised a different and slightly less harmful technique. This method took use of the comparatively "open" architectures of nanoparticles and other graphitic impurities, which may be intercalated with a range of materials more easily than closed nanotubes. The Japanese team used copper as an oxidation catalyst to selectively oxidize the nanoparticles away by intercalating with copper chloride and then reducing this to metallic copper. The Oxford Group reported a similar purification method that includes intercalation with bromine followed by oxidation. To purify arc-grown MWNTs, another Japanese team used wet grinding, hydrothermal treatment, and oxidation. In this manner, 850 mg of inner core material from the cathode yielded 16 mg of purified MWNTs.

Others have used solubilization techniques to accomplish the purification of arc-fabricated MWNTs (see Chapter 8, p. 211, for a discussion of solubilization by surfactants). In order to create a stable suspension of nanotubes and nanoparticles in water, a team from the École Polytechnique Fédérale de Lausanne in Switzerland first utilized sodium dodecyl sulphate (SDS), and then they allowed the nanotubes to flocculate, leaving the nanoparticles in suspension. The sediment might then be taken out, and further flocculation techniques could be used. This led to some separation in the length of the tubes as well as the removal of the nanoparticles. The purification and size selection of MWNTs generated by arcs may also be accomplished using chromatographic techniques, as shown by Georg Duesberg and associates. Because the focus has changed from catalytically generated tubes to multiwalled nanotubes, there has been a decline in interest in purifying arc-grown MWNTs, and there are currently no fully adequate methods for doing so.

MWNTs created via catalysis

MWNT samples made catalytically always include support material and any leftover metal catalyst particles. Compared to the carbon pollutants that come with arc-produced tubes, these impurities may be more dangerous. Yet, as shown by many groups, it is possible to remove this undesired material somewhat more simply than with arc-grown tubes (e.g. 4.7–4.11). The most effective techniques seem to entail high-temperature annealing. Purification of catalytically generated MWNTs was reported by Rodney Andrews and colleagues from the University of Kentucky by annealing at temperatures close to "graphitization" (1600–3000 °C) (4.7). This treatment has the additional benefit of improving the structural perfection of the tubes, as illustrated in Fig. 4.1, in addition to removing catalyst impurities [6], [7].

Purifying CVD-produced MWNTs has also included the use of acid treatments, often in conjunction with heat treatments. This method was utilized by researchers from Hunan University in China to purify MWNTs made using Ni-Mg-O catalysts (4.8). 510 °C air oxidation after intense HNO3 and HCl treatment allegedly produced 96% pure tubes. Acid treatments have the potential to harm the nanotubes' structural integrity, while heat treatments tend to strengthen them. Vacuum annealing and acid techniques were contrasted by Fei Wei and colleagues, they discovered annealing to be more efficient, having the potential to create tubes with a 99.9% purity. An efficient purification technique was disclosed by Hui-Ming Cheng and associates that included high-temperature annealing (at 2600 °C), followed by an extraction procedure using a dispersion agent (4.11). Metal particles were vaporized during the annealing process, while carbon nanoparticles were removed during the extraction process.

Single-walled tube purification

Much more difficult than purifying MWNTs are single-walled nanotubes. Early efforts to employ severe oxidation techniques, such as those used to purify MWNTs, failed with SWNTs, necessitating the development of more complex procedures. Depending on how the tubes were made, somewhat different techniques are required, much as with MWNTs. SWNTs are often present in mixtures containing significant quantities of amorphous carbon and metal particles, which are frequently also covered with carbon, when they are created using the arc-evaporation and laser vaporization techniques. It might be extremely challenging to eliminate these coated particles. While they typically include less amorphous carbon, samples of SWNT generated by catalysis do contain leftover catalyst material. A portion of the work that has gone into creating methods for purifying SWNTs will now be summarized. Several outstanding evaluations that go into further depth have been published [8], [9].

Oxidation and acid treatment

Most of the recipes for the purification of single-walled nanotubes that have been published include acid treatments and/or gas phase oxidation. This section will discuss two very efficient ways for the purification of SWNTs that were reported by Ivana Chiang and colleagues at Rice University rather than attempting to evaluate all of the known methods (4.15–4.16). Initially, some background information is provided.

It was discovered that the tubes were destroyed along with the contaminant when oxidation procedures were used on SWNT samples. There was some confusion as to why this occurred. However it is now understood that the metal catalyst particles in the soot are the source of the issue. The metal particles catalyze the indiscriminate low-temperature oxidation of carbons in the presence of oxidizing gases, destroying the SWNTs. Thus, procedures are required to get rid of the metal particles before using more intense oxidation treatments. As first described by Andrew Rinzler et al. in a 1998 study explaining the manufacturing of "buckypaper," the technique often utilized for this includes an acid reflux

The purification of SWNTs made using the laser vaporization approach was covered in the first Chiang article. In this instance, the soot had previously undergone treatment with nitric acid, which would have dissolved away the majority of the metal particles. The soot was provided as a toluene suspension. To get rid of any remaining soluble material from the original solution, this suspension was filtered and washed with methanol. As a result, "buckypaper," a black puffy paper that was refluxed in water, was left behind. The next stage included two oxidations, the first at 300 °C and the second at 500 °C, separated by an HCl extraction step. The authors speculate that this might lead to samples that are 99.9% SWNTs. Two images are used to illustrate the purification process. They subsequently explored the purification of the SWNTs produced by the HiPco technique [10], [11].

HiPco nanotubes often contain 14% by weight of Fe, which is a significant amount. Here, a wet Ar/O_2 oxidation process at a low temperature (225 °C) constituted the first step. It was found that the removal of carbon-coated metal particles was facilitated by opening the carbon shell and converting the metal into oxide or hydroxide. Following this procedure, stirring the material in strong HCl caused the iron to dissolve. After filtering the acid out and drying, the cycle of oxidation and acid extraction was carried out once again at 325 °C. After that, the material was heated oxidatively at 425 °C and then annealed in Ar at 800 °C. While the authors do not seem to provide the SWNT purity after this treatment, they do state that the final Fe level is close to 0.02%. Understanding that carboxylic acid and other groups may form at the tube ends and maybe at sidewall defects when applying acid and oxidative treatments for purification is critical. The introduction of these groups could alter the properties of the tubes. A complete analysis of acid and oxidative treatments for SWNT purification may be found in the review by Stanislaus Wong and colleagues.

Functionalization

The chemical functionalization of carbon nanotubes is addressed in detail. A few researchers have investigated the idea of functionalizing single-walled tubes for purification. The idea has been put out that organic functionalization, as opposed to treatment with acids or gas phase oxidants, renders SWNTs more controllable and, as a result, better for potential practical. Maurizio Prato of the University of Trieste and colleagues first revealed the functionalization of SWNTs with azomethine ylides in 2001. They showed that this method may be used to purify SWNTs produced utilizing the HiPco technology. The solubility of SWNTs in organic solvents was shown to be greatly increased by the functionalization, despite the fact that the metal particles remained insoluble. The metal atoms and nanotubes may then be easily separated from one another. By gradually adding diethyl ether to a SWNT solution in chloroform, the remaining amorphous carbon and nanoparticles were eliminated. As a consequence, it was found that the bulk of the tainted carbon precipitated, leaving the nanotubes in solution. The remaining functional groups were then thermally treated at 350 °C and then annealed at 900 °C as part of the last step of the purification operation. Transmission electron microscopy demonstrated that the resulting nanotubes were almost impure-free. Ozonolysis was used by Sarbajit Banerjee and Stanislaus Wong to functionalize SWNT sidewalls, as was indicated. Ozonelysis was found to purify the nanotube sample materials, as well. This seems to be caused by the severe ozonolysis that amorphous carbon and nanoparticles experience, which improves their solubility in the polar solvents used to wash the samples.

Physical techniques

Single-walled nanotube purification techniques that have been used physically include filtering, chromatography, centrifugation, and laser treatment. Theoretically, physical treatments offer an advantage over chemical ones in that they are less likely to harm tubes by causing chemical change. Microfiltration was probably used for the first time to purify SWNT compounds by Smalley and colleagues. In 1997, they described a technique that included cationic surfactant suspension of the nanotubes and related material in solution followed by membrane filter trapping of the tubes. In order to achieve a considerable level of purification, the procedure required repeated filtrations with sample resuspension after each filtration, making it slow and ineffectual. Large amounts of sample may reportedly be continually filtered by using ultrasonication to keep the material suspended during the filtration. This made it possible to purify up to 150 mg of soot in 3-6 hours, producing a result that included more than 90% SWNTs. The method of aloxidation-filtration’s was described above. Little quantities of SWNTs have been separated into fractions with a restricted range of length and diameter after being cleaned in single-walled tubes using size exclusion chromatography.

Claim that a method similar to that used for MWNTs, which were successful for SWNTs. Robert Haddon's team at Kentucky has published a technique for employing chromatography to purify soluble single-walled tubes. Haddon's group has also shown that SWNT soot treated with nitric acid may be effectively centrifuged to eliminate both amorphous carbon and carbon nanoparticles. Low-speed centrifugation preferentially suspended the amorphous carbon, leaving the SWNTs in the silt. High-speed centrifugation of evenly distributed preparations efficiently sediments carbon nanoparti- cles by maintaining the SWNTs floating in the aqueous solution. SWNT purification using laser treatments was shown by John Lehman of the National Institute of Standards and Technology in the United States in 2007. (4.25). Raman tests showed purity improvements after using a 248 nm excimer laser on arc discharge and CVD samples. Particularly resistant to the technique appears to be nano-crystalline graphite and amorphous carbon.

Assessing purity

The best feasible method for assessing the purity of single-walled nanotube samples is probably Raman spectroscopy. The use of this technique to nanotubes is comprehensively discussed in. In terms of purity, the so-called D line, which is thought to be caused by disordered graphitic material and is situated at a wavelength of around 1340 cm 1, is particularly important. The ratio of the D band intensity to the G band intensity at 1582 cm-1 (ID/IG) is a valid measure of sample purity. However, Raman spectroscopy cannot quantify the amount of metal contamination.

Near-infrared (NIR) spectroscopy has also been used to determine the purity of huge quantities of single-walled carbon nanotubes. The purity may be assessed by comparing the integrated intensity of the S22 transitions with the S22 intensity of a reference sample. While technique is less effective at distinctly discriminating between various carbonaceous species, thermogravimetric analysis (TGA) has been demonstrated to be beneficial in determining the quantity of metal catalyst particles in samples of SWNTs. The most accurate approach for measuring purity is, of course, transmission electron microscopy, but collecting a representative sample may be difficult since the raw material may be rather uneven. Haddon and colleagues found that solution-phase near-infrared spectroscopy and solution-phase Raman spectroscopy are the most effective methods for determining the purity of samples of bulk single-walled nanotubes.

Surface groups containing oxygen are often introduced as a consequence of acid treatment, including phenolic, carboxylic, and lactonic groups. According to Alan Windle and colleagues, they have the capacity to stable nanotube dispersions at far higher concentrations than are practical with the raw material. To learn more about these nanotube dispersions' properties, analogies between the dispersions and polymer solutions have been made. Optical bireflection demonstrated that aqueous dispersions of multiwalled tubes underwent a transition where the arrangement went from isotropic to liquid crystalline above a certain concentration. Schlieren texture, a characteristic of nematic liquid crystal phases in which the components exhibit long-range orientational order, was seen in the liquid crystal phase.

In rigid nanoscale rod systems, such as the tobacco mosaic virus, such a structure is often seen. Under the scanning electron microscope, the solid sample created by the solvent evaporation from the dispersions exhibited a microstructure that was surprisingly similar to that of the original dispersions. These may be identified by the nematic liquid crystal disclinations that are present here. The existence of these phases, according to Windle et al., suggests that carbon nanotubes may be handled using methods comparable to those used to stiff chain polymers like aramids. This has been difficult in reality because of the strong interactions between tubes and their inclination to bundle or rope together.

Positioning and alignment of MWNT

Even though there are documented methods for growing aligned MWNTs on substrates via catalysis, post-synthesis alignment of nanotubes. There are several ways to do this. It has been shown that aligned arrays of tubes may be spun into nanotube "yarns," which will be described in more detail in the section below. By incorporating nanotubes into a matrix and then extruding the matrix in some way, the tubes will be aligned along the direction of flow. This method is covered in the nanotube composites. One of the first methods for aligning multiwalled tubes was called dielectrophoresis, or the application of an electric field to a sample held between electrodes. Seiji Akita and colleagues from Osaka demonstrated considerable alignment of MWNTs suspended in isopropanol using this method. Experiments on single-walled tubes provided evidence in favor of the claim that when AC fields were used, the alignment degree increased with increasing frequency of the applied field. Most recently, the research team of Rodney Ruoff at Northwestern University used a variety of electrodes to align multi-walled tubes in solution. By using a biased AC field, which blends AC and DC fields, the results were determined to be ideal. With the use of functionalization, multiwalled nanotubes have been organized into aligned arrays. Researchers from China, using an oxidation-sonication procedure, created a method for shortening MWNTs before functionalizing them with acyl chloride in thionyl chloride (SOCl2). Substrates that had undergone multilayer polyelectrolyte film deposition were then immersed in a suspension of functionalized tubes in tetrahydrofuran.

After being partly oxidized to help with wetting, the tubes were submerged in a variety of liquids and allowed to evaporate at room temperature. The drying procedure led to the creation of haphazard, foam-like formations. Using patterned substrates allowed for the formation of ordered groupings as well. Created from a substrate with a collection of circular holes. It was shown that the nanotube foams could be transported to other substrates or elastically deformed. They could even be disengaged from the substrate to create free-standing "fabrics." The use of the foams as elastic membranes or shock-absorbing structural reinforcements was proposed. Lei Jiang and colleagues from the Chinese Academy of Sciences in Beijing created comparable patterns independently around the same time by adding water droplets on aligned MWNT films.

Pure MWNT fibers, the preceding chapter covered direct spinning of MWNT yarns utilizing catalytic synthesis. For the creation of continuous nanotube fibers, post-synthesis techniques have also been devised. The method that has shown to be the most effective includes plucking nanotube "yarns" from arrays produced on flat substrates. A team from Tsinghua University first mentioned this in 2002. Initially, they were trying to extract a bundle of nanotubes from a Si substrate-grown array. Instead, scientists were able to extract a continuous nanotube yarn, a feat they likened to extracting a thread from a silk worm's cocoon. The threads may be pulled to a length of 30 cm and often assumed the shape of thin ribbons. Originally, the threads were pulled by hand using tweezers, but subsequent research resulted in a more manageable technique that used an electric motor to pull the threads at a steady pace.

In 2004, Ray Baughman and his colleagues at the University of Texas at Dallas disclosed a further improvement to this procedure. In this piece, a twist was added as the yarns were pulled, using a method that has been used in the manufacture of textiles since ancient times. Displays scanning electron micrographs of a nanotube yarn being pulled and twisted at the same time the process was conducted outside the SEM and interrupted for SEM imaging. The yarns could be further twisted to create two- and four-ply MWNT threads, or they may be knitted together to create more intricate designs. Single yarns had recorded tensile values between 150 and 300 MPa, but two-ply yarns showed greater strengths between 250 and 460 MPa. By soaking single yarns in a polymer solution and then drying them, it was shown that single yarns may be contaminated with polyvinyl alcohol. As a result, the yarns' strength rose to 850 MPa. The MWNT yarns, according to Baughman and colleagues, may find use in a variety of products, including electronic textiles, protective apparel, artificial muscles, and structural composites.

Sheets of MWNT

Moreover, Baughman's team has shown that catalytically generated nanotube forests may yield MWNT sheets (4.44). Using an adhesive strip once again to start the drawing process, it was shown that sheets up to 1 m long and 5 cm broad could be produced. The translucent sheets might be used as electrodes or light-emitting diodes because of their extremely anisotropic electronic characteristics.

Cutting and breaking MWNTs

There are a number of reasons why MWNTs may need to be sliced into little lengths. Compared to immaculate MWNTs, broken or damaged ones are easier to functionalize. Tubes, for instance, because of the greater number of flaws. Moreover, cutting the as-made tubes into short lengths often makes it easier to incorporate catalytically generated MWNTs into composites. A variety of techniques have been developed for purposefully destroying MWNTs or shortening their length. The Oxford group published a description of one of the first techniques for cracking MWNTs in 1996. This study used an immersion horn to deliver high-intensity ultrasound to samples of the tubes that were suspended in CH2Cl2, cooled to 0 °C this method delivers much more energy to the tubes than the ultrasonic processing sometimes used to aid dispersion in solvents. After this treatment, a large percentage of the tubes had flaws including bending and buckling. While the exterior graphene layers were often stripped away, fully shattered tubes were very uncommon. Since then, it has become rather common to utilize high-energy ultrasonic processing to induce flaws into MWNTs in order to make it easier for catalytic metal particles to adhere to the tubes.

MWNTs generated by catalysis were broken down using ball-milling by Janos Nagy and associates from Namur, Belgium (4.47). The average length of the untreated tubes was 50 m, but after 12 hours of milling, it was around 0.8 m. Chinese researchers demonstrated in 2006 (4.48) that short lengths of MWNTs created by catalysis may be achieved by first coating them with NiO particles and then causing a localized reaction between the carbon and the oxide particles. A short while later, Milo Shaffer of Imperial College and colleagues demonstrated how short CVD-generated MWNTs may be made using a simple oxidizing procedure (4.49). The resultant short tubes shown improved organic solvent dispersibility and modest degrees of functionalization. Our team sliced arc-grown MWNTs precisely using a concentrated electron beam from a SEM. It was shown how to cut completely, partially, and to create hinge-like geometries.

Single-walled tube processing

SWNT alignment and layout

Our focus is on pure single-walled nanotube alignment and arrangement techniques. Nanotubes with functionalized tips may be joined together to form defined networks as one method of organization. The Smalley group presented the first instance of this in 1998. in this study, SWNTs were first sliced into short, and they then underwent two reactions, one with thionyl chloride and the other with NH2-(CH2)11-SH, to form an amide bond between the ends of the alkanethiol and the nanotubes. The tubes' thiol-derivitized tips were subsequently covered with gold particles. By connecting to a single gold particle, the scientists showed that nanotubes might be joined together in this manner. Masahito Sano and others have since completed fascinating work in this area. A 2001 Science article.They observed that esterification between the carboxylic acid and hydroxyl end-groups at the nanotube tips in the presence of a condensation reagent, 1, 3-dicyclohexylcarbodiimide, led to the production of rings from acid-oxidized SWNTs. The same team has created nanotube stars by grafting dendrimers or dendrons onto oxidized carbon nanotubes. Duesberg and colleagues have showed how amine connections cause junctions to develop between SWNTs. either an end-to-side or end-to-end arrangement of tubes might be used for the connection.SWNT arrays on surfaces have been created using similar techniques. SWNTs may be adhered perpendicularly to gold surfaces using a wet chemical method disclosed by Zhongfan Liu and colleagues from Peking University. The as-grown nanotubes were first chemically transformed into "pipes," and then the open ends were thiol-derivatized. The thio-functionalized nanotubes were then suspended in ethanol and applied to a gold crystal with a clean surface. As a result of spontaneous chemical adsorption to the gold surface through Au-S bonds, the SWNTs were assembled. An additional technique included dipping a pre-treated gold surface into a suspension of truncated, carboxyl-terminated SWNTs. Once again, this led to an organized assembly of SWNTs with perpendicular orientation. Similar techniques were utilized by Justin Gooding from the University of New South Wales and associates to create vertically aligned arrays of SWNTs on gold, which were subsequently functionalized using the enzyme microperoxidase MP-11. The arrays that are created might be employed as sensors.

Dielectrophoresis was suggested before as a method of aligning MWNTs. SWNTs have been successfully positioned and aligned using the method as well. Ralph Krupke of the Center for Nanotechnology in Karlsruhe and colleagues presented one of the most stunning demonstrations of placing nanotubes using this approach in 2007. (4.59). as shown in Fig. 4.8, nanotubes were deposited in this study from an aqueous solution onto a grid of electrodes. The tubes were deliberately placed between the two opposing needle-shaped electrodes, which produced an inhomogeneous electric field. The fact that just one nanotube or nanotube bundle was placed at the predetermined locations was a significant feature of the effort. This occurred as a result of the dielectrophoretic force field changing after the deposition of nanotubes, making further tubes repellent. According to the authors, this method might produce several million nanotube devices per square centimeter of substrate. As stated, dielectrophoresis has also been utilized to distinguish between metallic and semiconducting nanotubes.

Seunghun Hong and colleagues have provided yet another efficient technique for the construction of several single-walled tubes. They employed two kinds of surface regions, one patterned with polar groups like amino or carboxyl, and the other covered with non-polar groups like methyl, to produce patterns of self-assembled monolayers (SAM) of molecules on a substrate, which were then used to direct the self-assembly of the tubes. SWNTs were suspended in the substrate, and it was discovered that the tubes were drawn to the polar areas and aligned inside them.

Pristine strands of SWNT

As was previously established, nanotubes are far less processable than polymers, in part because of their propensity to bundle or rope together. It is required to separate the bundles in order to make it easier to apply techniques like extrusion to nanotubes. Researchers from Rice University demonstrated in 2004 that treating SWNT bundles with 102% sulfuric acid may efficiently separate them. This results in an aligned phase of 8% weight of positively charged nanotubes surrounded by acid anions. A technique for the mass manufacture of pure SWNT fibers was then disclosed by the Rice group in conjunction with researchers from the University of Pennsylvania as a follow-up to this study. HiPco tubes that had been purified using the Chiang technique were utilized for this project. The tubes were scattered among the sulfuric acid before being.

Extruded into a coagulant bath containing either diethyl ether, 5 wt% aqueous sulphuric acid, or water via a capillary tube with a diameter of less than 125 m. The coagulation conditions had an impact on the final structure of the carbon nanotube fibers. Diethyl ether-spun fibers exhibited a collapsed "dogbone" structure, but fibers spun in water or diluted sulfuric acid maintained their circular form and were denser. The researchers then heated the fibers to eliminate any remaining water and acid.

A significant degree of nanotube alignment was seen in the fibers using scanning electron microscopy (SEM), and tests made using X-ray diffraction and Raman spectroscopy supported this finding. The fibers' mechanical characteristics were respectable but not exceptional. Consequently, the fibers' Young's modulus was calculated to be 120 GPa and their tensile strength to be 116 GPa. After being annealed at a high temperature to eliminate any remaining acid, the fibers' electrical resistance was less than 2 milliohm cm. This is about two orders of magnitude greater than that of composite nanotube/polymer fibers, but comparable to that of SWNT-aligned mats.

SWNT Sheets

Using a straightforward technique, Rice University's Andrew Rinzler and colleagues published a description of single-walled nanotubes created by laser vaporization in vast numbers in 1998. (4.17). The process required centrifuging and rinsing the raw soot in deionized water for 45 hours, filtering, and vacuum baking. The final result was a thin, flexible film, held together by the tubes like the fibers in a piece of paper. Without realizing it, the authors had created buckypaper, a novel kind of nanostructured carbon material whose manufacture is comparable to the age-old craft of papermaking. Despite not being made of ultra-pure nanotubes, buckypaper has shown several intriguing features. Several SEM pictures of SWNT thin-film samples made by German researchers in Karlsruhe using a method similar. The images show how the paper can be bent into curved forms while maintaining its structural integrity. The same German group also investigated the mechanical characteristics and processes of buckypaper failure. Strengths between 10 and 20 MPa were recorded during tensile testing on a 14 m thick SWNT film. The films were adhered on 3 mm copper TEM rings in order to study failure causes. The adhesive contracted as it dried at room temperature, resulting in the films experiencing tensile stresses. Next, to cause ripping, a tiny hole was made with a sharp needle in the center of each specimen. Several pictures of the damaged films are shown. As can be tight SWNT strands that ended in branching structures were often discovered to span the narrow sections of the fissures. Andrew Rinzler, who is now at the University of Florida, and his coworkers reported a technique for creating ultra-thin buckypaper years after his first work. The use of a filter material cellulose ester that could be removed after the nanotube layer was deposited was essential for creating the thin film. This method allowed them to create films that were both electrically conductive and transparent to visible light, with thicknesses ranging from 50 to 150 nm. Several teams have looked at the use of these films in solar cells and light-emitting diodes, among other uses.

It has been shown that by using high magnetic fields during the filtration process, alignment may be partially induced in SWNT films. Researchers from Rice and the University of Pennsylvania proved this. The parallel components of both the electrical and thermal conductivity increased in comparison to unoriented material, demonstrating that this alignment produced anisotropic electrical and thermal transport capabilities.

There are more ways than filtering to create SWNT films. Sulphuric acid may help with the processing of SWNTs, as was before indicated. This method has been employed by researchers from Rice and the Georgia University of Technology to promote the production of films. SWNTs were mixed with oleum, transferred to a Petri plate, and then the acid was removed and the film was left to dry. The films seemed to possess buckypaper-like mechanical and electrical characteristics. Aqueous solutions may also be dried down to create thin SWNT films. By using single-walled tubes and water droplets containing surfactant to evaporate, Matteo Pasquali of Rice and colleagues created nanotube films on glass.

Multiple-purpose nanoparticles

By combining several functional agents, such as particular targeting molecules, imaging, and therapeutic agents, into a single nanoconstruct, multifunctional nanoparticles were created. One research shown that doxorubicin and magnetofluorescent carbon quantum dots might be combined to form multifunctional nanocomposites. Another multifunctional SWCNT nanocomposite with possible therapeutic application has been found by the same group. They proved that this nanocomposite performed the functions of a multimodal imaging probe, an NIR photothermal heater, and a doxorubicin carrier all at once. These nanocomposites may combine chemotherapy, photothermal treatment, and tumor imaging. Due to their nanostructure and biopersistence, CNTs may still be harmful, similar to asbestos, despite their promising promise in biomedical applications. We shall talk about CNTs' potential to cause pathologies resembling mesothelioma in the next section.

Animal Models Provide Experimental Proof of CNT-Induced Mesothelioma

Studying CNTs' negative effects in pulmonary models .They were able to cause respiratory tumors, fibrosis, granulomatous lesions, and oxidative stress/inflammation. Moreover, it has been shown that CNTs may facilitate angiogenesis and tumor invasiveness. Also reported CNT toxicity were reproductive and developmental harm and testicular injury. Animal tests are the only kind of study that has been done on CNT-induced mesothelioma carcinogenesis. Similar essential pro-oncogenic molecular processes are present in human MPM and MWCNT-induced mesothelioma.

CNTs' Fiber Pathogenicity Paradigm

High aspect ratios are shared by asbestos and CNTs. The fiber pathogenicity paradigm has been expanded to incorporate synthetic, high-aspect-ratio nanomaterials like CNTs, in which the length, diameter, and biopersistence of fibers are recognized as key toxicological features. Another criterion to be included to the toxicological profile of CNTs was the stiffness of nanofibers. Critical assessments have outlined the physical and chemical characteristics of asbestos and CNTs. Surface charge, hydrophilicity and hydrophobia, contaminants, tensile strength, and biopersistence are some of them. In contrast to asbestos, CNTs are a varied set of nanoparticles with a range of physiochemical properties, such as wall number, length, diameter, and surface modification. The lengths of SWCNTs and MWCNTs range from several hundred nanometers to several millimeters, while their diameters range from nanometers to tens of nanometers. Moreover, surface modification of CNTs modifies surface chemistry and boosts diversity, which ultimately modifies the protein-binding, cytotoxicity, and immunological response associated with CNTs in vivo.

The toxicity of nanomaterials is anticipated to be significantly influenced by the processes of absorption, biodistribution, metabolism, and excretion (ADME) of nanoparticles. The ADME and biological impacts of CNTs are unique physicochemical properties (length, diameter, surface modification, and exposure pathways). The most typical areas of exposure to CNTs are the gastrointestinal system, skin, and pulmonary tract. Localized dermal exposure to CNT caused dermal toxicity that was linked to the production of free radicals, oxidative stress, and inflammation. As an alternative, it has been shown in animal experiments that CNTs ingested orally enter the body as agglomerates and seem to be mostly eliminated in feces without causing any behavioral abnormalities, changes in body weight, or pathological abnormalities in the animals.

Once inhaled, long fibers and thin fibers with diameters less than or equal to 1 m were found to readily enter the ciliated airways. The deposited nanosized CNT particles first enter the alveolar space, travel through the lung parenchyma, and then exit into the pleural space. The precise transitional paths are yet unknown. Many theories have been developed. It is generally known that CNTs may penetrate alveolar macrophages, the alveolar wall, and the visceral pleura. Short fibers and particles may diffuse more broadly, but long fibers and particles may stay in the interstitium of the lung or the pleura due to their restricted mobility. Another crucial component of CNTs' carcinogenicity is their biopersistence. Certain SWCNTs and MWCNTs are susceptible to enzymatic degradation in vitro and vivo by macrophages. The biopersistence of CNTs in vitro is influenced by the type, length, surface modifications, contaminants, and dispersion state of the CNTs. Biodegraded CNTs and their by-products don't exhibit toxicity in both in vitro and in vivo experiments. Retained long

CNTs may cause an immediate inflammatory reaction, followed by an influx of inflammatory granulocytes and what is known as "frustrated phagocytosis" in which (pleural) macrophages release cytokines and oxidants. This mechanism causes persistent fibrosis, genotoxic consequences, and inflammation in the surrounding tissues. Asbestos is believed to cause mesothelioma by a similar process.

Inhalation, intratracheal intrapulmonary spraying, intrapleural injection, and intraperitoneal injection have all been linked to the development of mesothelioma in experimental investigations of CNT exposure pathways. Both asbestos and CNT fibers may be "aerospherized," with CNT inhalation being the most common method of fiber exposure in people.

In conclusion, MWCNTs are a possible new carcinogen that might cause MPM. Thus, the dangers of exposure to CNTs should be carefully assessed, and suitable precautions should be adopted. In the physicochemical characteristics of CNTs, exposure data, and research study findings are condensed.

Injections Given Intravenously or Intrascrotally

When CNTs are injected into the peritoneal cavity, equivalent injections into the pleural cavity have identical biological effects (58). A pilot investigation in mice revealed that intraperitoneal injection of two kinds of MWCNTs (MWCNT1 length (L) =13 m, diameter (D) =84 nm, and MWCNT2 L=56 m, D=165 nm) resulted in inflammation and granuloma lesions on the peritoneal side of the diaphragm. This study's lack of mesothelioma development is attributed to the study's brief and low-dose exposure. Another research revealed that after 84 days of intraperitoneal treatment of MWCNT-7 (L=less than 5 m, D=100 nm) at a dosage of 3 mg (1109 fibers)/mouse, 87.5% of p53 heterozygous mice developed mesothelioma. In p53 heterozygous mice, the cumulative incidence of mesothelioma caused by MWCNT-7 was shown to be correlated with the exposure dosage (300 g (1 108 fibers), 30 g (1 107 fibers), and 3 g (1 106 fibers). This study proved that MWCNTs, more especially MWCNT-7, may cause mesothelioma.

MWCNT-7 is more toxic and more likely to cause inflammation and mesothelioma in vivo when compared to the other two varieties of MWCNTs with comparable lengths (less than 10 m) and diameters of 150 nm and 2-20 nm (tangled). This is most likely because of its tiny diameter and high crystallinity. These properties enable MWCNT-7 to enter mesothelial cells and trigger a frustrated phagocytosis. Moreover, straight, acicular-shaped MWCNTs, such MWCNT-7, are more likely to cause mesothelioma when injected intravenously or intrascrotally. MWCNTs that are twisted and curved have less hazardous carcinogenic potential than their straight, needle-like counterparts. In conclusion, the properties of CNTs are thought to be important determinants of their carcinogenic potential. CNTs that are hard, needle-like, 5 m long, and 50 nm in diameter are more likely to promote the formation of mesothelioma.

Route Exposure

The inhaling route is the most significant way for humans to be exposed to CNTs, and in animal research, pharyngeal or intratracheal installation is the preferred approach for CNT delivery. For these experiments, a sophisticated lab environment is required. During inhalation and penetration into the lung parenchyma, those MWCNTs that can reach the subpleural tissue provide the groundwork for MPM formation. Recent research has shown that MWCNTs may cause pleural fibrosis in mice, as well as dose-dependent mesothelial hyperplasia in the rat parietal pleura. CNTs delivered through pharyngeal aspiration may potentially translocate into the pleural cavity, reach subpleural tissues, and deposit in the parietal pleura. MWCNTs trapped in the parietal pleura may thereafter, in a length-dependent way, result in pleural inflammation and the formation of (pre)malignant lesions.

MWCNTs are linked to pleural fibrosis, mesothelial proliferation, and inflammation via airway exposure in both the visceral and parietal pleura. Nevertheless, in one investigation, the brief experimental duration could have had an impact on the MWCNT-induced inflammatory responses in the pleural cavity and hyperplastic visceral mesothelial proliferation. Another study discovered that SWCNTs with a length of 0.5 m might have comparable inflammatory effects to those of MWCNTs.

During a year of exposure, MWCNT-7 and MWCNT-N may both cause mesothelioma development. Nevertheless, one research discovered that mice exposed to MWCNT-7 alone did not develop mesothelioma, however mice treated to MWCNT-7 with a co-treatment of a recognized carcinogen, methylcholanthrene, did. A larger amount of fiber dispersion in the pleura may be required for mesothelioma induction, according to other studies with 2 years of MWCNT-7 treatment or specific mice models may be resistant to the formation of mesothelioma. In conclusion, fiber length has a significant impact on how inflammation promotes the development of mesothelioma. Considered essential for malignant transformation are the persistent CNTs that made it to the pleura following inhalation and lung penetration. Inhaling CNTs is thought to cause the development of malignant mesothelioma in people as well. This disease has a protracted latency period before it is discovered.

Insertional injection

CNTs may also be given intravenously or intrapleurally (through the thoracic wall). According to studies, length-dependent retention of CNTs in the pleural cavity may cause mesothelioma development, persistent inflammation, and progressive fibrosis. When asbestos is exposed, the molecular pathways that lead to the formation of mesothelioma are thought to be similar. The relationship between fiber length and pleural inflammation was examined through the experimental use of a variety of nanoparticles of various sizes. The results revealed that the dimension threshold for pleural inflammogenicity was 5 m for mice, and the resulting data could be extrapolated to the human situation.

The stiffness of CNTs is a significant physicochemical factor that influences toxicity in addition to length. The bending ratio and static bending persistence length are used to define rigidity, a measure of fiber curliness. The threshold stiffness values for asbestos-like pathogenicity are bending ratio of 0.97 and static bending persistence length of 1.08. Moreover, a key element influencing the biological impacts of CNTs is surface modification. For instance, compared to pristine and alkyl-functionalized MWCNTs of the same effective length, MWCNTs with surface modification using ammonium-terminated tri (ethylene glycol) chains cause fewer granulomas on the mesothelial membrane, indicating that surface modification can lessen the adverse effects of CNTs.

According to studies using animal models, mesothelioma caused by MWCNT-7 may grow more quickly and at a higher incidence rate than mesothelioma caused by asbestos. These disparities might be explained by three factors. First, when MWCNT-7 or asbestos fibers pass cellular membranes of mesothelial cells, MWCNT-7 fibers are more likely to result in DNA damage than asbestos fibers because they are surrounded by vesicular membrane structures in the cytoplasm. Second, a protein corona surrounds CNTs, which interact with biological elements in physiological environments or cell culture conditions. The components of protein corona have an impact on how poisonous nanoparticles are. For instance, the protein corona of MWCNT-7 contains transferrin, while asbestos does not. Transferrin absorbed on MWCNT-7 surface induces mesothelial iron overloading, which may lead to mesothelial cell carcinogenesis and significant amounts of oxidative stress. Finally, compared to asbestos, CNTs may induce an immunosuppressive microenvironment that comprises more myeloid-derived suppressor cells.

There are several questions that need to be investigated further. For example, it is unknown if CNTs injected intravenously will finally reach the pleura. Additionally, it is still unknown what amount of fibers must be deposited in the pleural cavity in order to cause MPM. Just 103 MWCNT-7 fibers implanted in the pleura, according to a prior work, were able to cause mesothelial hyperplasia. The dosage was 106 times lower than what would have been needed to cause lung cancer. It is possible that toxicity will depend more on the number of fibers that may reach the pleura than on the physicochemical characteristics of CNTs.

Control of SWNT length

The initial method for controlling the length of single-walled nanotubes included breaking each tube at certain spots using a scanning tunneling microscope tip. Although this technology could be beneficial for building devices out of single tubes, there is also a need for techniques for shortening large samples of single-walled nanotubes. As was previously said, Smalley's team created such a technique. They demonstrated how samples of short tubes, or "fullerene pipes," could be made by repeatedly ultrasonically processing nanotube material in a solution of high sulphuric and nitric acids. Localized sonochemistry seems to create holes in the tube walls during this process, which are subsequently further attacked by the acids to leave the open "pipes." Smalley and associates demonstrated that the pipes could be divided into various length fractions using a technique called fractionating the field-flow. Other teams have also employed acid treatments to shorten single-walled tubes, often in conjunction with other techniques.

Because to the significant weight loss of SWNTs after acid treatment, it might be quite ineffective even if it produces small tubes. Fluorination has replaced cutting as a more often used option. Once again, the Rice group is in charge in this regard. They said in 2002 that sidewall-fluorinated SWNTs may be reduced to lengths of under 50 nm using pyrolysis at temperatures up to 1000 °C. In subsequent work, they proposed a two-step method for cutting SWNTs that involves fluorinating the sidewalls first and then subjecting them to powerful oxidants like H2SO5 (Caro's acid). 100 nm or shorter nanotubes were created as a result. Ozone (O3) has also been used to cut SWNTs in place of fluorine. In this instance, the tubes were suspended in perfluoropolyether, a suitable ozone solvent, and bubbled with a 9 weight percent O3:O2 combination. The length of the treatment had an impact on the cut nanotubes' lengths. As a result, the mean length at 1 hour was 92 nm, and at 8 hours it was 59 nm.

Risky Issues for Occupational Safety and Public Health

Since CNT-based nanotechnology is constantly improving, CNTs and the products they are related with have been employed in a wide range of industrial and commercial applications. The industry is quite concerned about the emission of CNTs into the air during product manufacture, shipping, and processing. Moreover, following abrasion, the CNTs used in sporting goods, battery electrodes, and coating may potentially emit dangerous particles to the general population. Additional evidence that CNT exposure may have an impact on human tissue comes from the discovery of CNTs in the bronchoalveolar secretions of asthmatic children from Paris as well as in the lung tissue of those who were exposed to the

World Trade Center dust. According to recent research, CNTs discharged from CNT-based goods dumped in soil, sediment, and aquatic habitats have shown potential toxicity. Investigations need to be done into how these goods' incorrect disposal affects species in the water and on land.

Many government rules have been developed as a result of the growing concern over the environment and human exposure to CNTs. The US National Institute for Occupational Safety and Health suggested an exposure limit of 1 g/m3, or an average concentration of CNTs over 8 hours, in 2013. Eventually, the MWCNT-7 was classed as "probably carcinogenic to people" (Group 2B) by the International Agency for Research on Cancer (IRAC), although other forms of CNTs were categorized as "not classifiable as to their carcinogenicity to humans." The International Agency for Research on Cancer (IARC) Monographs deemed MWCNTs a high priority for carcinogenicity investigation. Due to their carcinogenicity, probable reproductive toxicity, and persistency, CNTs were recently added to the SIN ("Substitute It Now") list and placed into the "extremely worrisome" classification by the Swedish non-profit group ChemSec.

Just six mineral fibers actinolite, amosite, anthophyllite, chrysotile, crocidolite, and tremolite out of 400 fibrous minerals are now controlled, leaving additional substances that can result in an asbestos-like sickness unregulated. Nations and areas have banned the use of asbestos completely or partially, according to the International Ban Asbestos Secretariat. Although being outlawed in many nations, asbestos is nonetheless widely utilized in a few of developing nations. Researchers have previously urged for an asbestos ban in China because of how widely used and produced asbestos is in developing nations. In fact, it is anticipated that China would reach its peak in MPM prevalence in the next decades.

In both industrial and non-occupational situations, humans may be exposed to CNTs by inhalation, cutaneous contact, and oral contact. The latency duration, mesothelioma cell types, and site of CNT-induced malignant growth in humans have received less attention from researchers. To prevent negative consequences, precautionary measures for workplace exposure should be implemented, and items containing CNTs should be marked. CNTs are thought to pose a significant health risk that has not yet received enough attention. The information now available on the effects of asbestos on cancer prevention may be very useful in preventing illnesses brought on by CNTs.

CNTs are among the most promising alternatives for a variety of applications because to their remarkable physical and chemical characteristics. Yet, recent in vivo animal investigations have shown that nanoparticles may be hazardous. Our comprehension of CNT-induced mesothelioma development may be aided by the present understanding of MPM caused by asbestos. The occurrence of MPM and lung damage brought on by CNT exposure have not been well studied. The development of malignancy by CNTs is more complex than asbestos-related MPM. Because of their distinct physicochemical traits, CNTs are more varied. A thorough understanding of CNTs is necessary to comprehend sickness that is associated to them. The health of employees who are routinely exposed to CNTs at work has to be monitored. Governmental Occupational Safety and Health Boards should develop the recommended exposure limit of CNTs and preventive actions to reduce the health hazards related to the usage of CNTs. The experimental results reported in this work further suggests that CNTs should be employed under close supervision and that the environmental discharge of CNTs should be monitored and governed by relevant legislation.

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CHAPTER 10

DISTINGUISHING SINGLE-WALLED NANOTUBES WITH METALLIC AND SEMICONDUCTING WALLS

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Strict eradication

The Phaedon Avouris team at IBM announced the first effort to distinguish metallic (m) and semiconducting (s) nanotubes. To get rid of metallic tubes, they used current-induced electrical breakdown. While carbon nanotubes can endure current densities surpassing 109 A cm2, with sufficiently high currents, the nanotubes will spontaneously burn away in the atmosphere. This enables the selective removal of metallic tubes from SWNT ropes. The IBM team started by depleting the electrical carriers (electrons or holes) from the semiconducting tubes within a SWNT rope using a gate electrode. The carrier-depleted semiconducting tubes, which carried no current, could thus be left intact while the metallic SWNTs in the rope were destroyed by current-induced oxidation. The team was able to create arrays of nanoscale field-effect transistors based just on the residual s-SWNTs after removing the metallic tubes, as explained in Chapter 6. They also demonstrated in the same work that identical methods could be used to extract individual shells from multiwalled tubes one at a time [1]–[3].

The Hongjie Dai group introduced a different strategy for the selective removal of metallic SWNTs in 2006. This was predicated on the hypothesis that m-SWNTs could be more chemically reactive than s-SWNTs. Between, the tubes were developed. Patterned catalytic islands in the manner mentioned on a silicon wafer. To selectively hydrocarbonate (i.e. turn into hydrocarbons) the m-SWNTs and tiny nanotubes of both kinds, the tubes were exposed to a methane plasma at 400 °C. The remaining semiconducting tubes underwent a second annealing process at 600 °C to eliminate undesirable functional groups. They were able to create a vast number of devices, each of which included a few tubes, in this manner.

Dielectrophoresis

Both multiwalled and single-walled nanotubes have been positioned and aligned using dielectrophoresis, as was previously mentioned. Ralph Krupke and associates demonstrated in 2003 that this method may be used to distinguish between metallic and semiconducting nanotubes. The reasoning for this is because differing electrical polarizabilities are predicted for metallic and semiconducting tubes. According to Krupke et alcalculations,'s the dielectric constant of s-SWNTs is on the order of 5, but the figure for m-SWNTs is at least 1000. In an aqueous suspension of the two tube types, it should be feasible to separate them by subjecting them to a strong and inhomogeneous electrical field since water has a dielectric constant that is between these two numbers, at around 80 [4]–[6].

HiPco tubes were suspended in D2O with 1 wt% SDS according to Krupke and colleagues' technique (D2O was used rather than H2O as it interferes less with the absorption spectroscopy of SWNTs). To further distribute and clean the tubes, the suspension was centrifuged and sonicated. Electron-beam lithography was used to produce the microelectrodes, which were then coupled to a function generator running at 10 MHz and 10 V peak to peak voltage. When a drop of the suspension was placed to this chip, it was discovered that the semi-conducting tubes stayed in the solution while the metallic tubes were drawn to the microelectrode array. The success of the separation was verified using Raman spectroscopy. Eleanor Campbell and colleagues from Gothenburg University in Sweden showed a similar process using multiple separation cycles in 2005.Semiconducting SWNTs were sorted by size in 2006 by Howard Schmidt and colleagues from Rice using a dielectrophoresis-based method. This is feasible because to the greater band gap and thus lower dielectric constant of smaller diameter semiconducting tubes. The Rice team used a technique known as dielectrophoresis field flow fractionation, which included injecting a suspension of SWNTs into a mobile phase that was passing through a chamber that had an array of gold electrodes installed at the bottom. The electrodes were subjected to a 1 GHz, 10 V peak-to-peak pulse that attracted the metallic tubes while keeping the semiconducting ones in solution. It was discovered that as the retention period rose, there were less smaller nanotubes when the tubes eluted from the chamber [5]–[7].

Selective functionalization

In order to distinguish between metallic and semiconducting materials, a team from the University of Connecticut employed a technique called non-covalent functionalization using octadecylamine (ODA). Based on the presumption that semiconducting SWNT sidewalls would physisorb ODA more forcefully than metallic ones, this was done. While there doesn't seem to be much direct proof, the authors mention a study by Kong and Dai that shows how the electrical characteristics of s-SWNTs are significantly altered whereas those of m-SWNTs are not. The tubes in this investigation were carboxy-functionalized by acid treatment before being treated with ODA. HiPco and laser-ablated SWNTs were both employed. Raman investigations seemed to confirm the prediction that the ODA treatment would preferentially solubilize the s-SWNTs while leaving the m-SWNTs in the solid phase.

DNA may be used to distinguish between metallic and semiconducting nanotubes, according to research done in 2003 by a team headed by Ming Zheng of DuPont. As mentioned in Chapter 8, preliminary research shown that single-stranded DNA interacts strongly with SWNTs to create a stable DNA-carbon nanotube hybrid that efficiently disperses carbon nanotubes in an aqueous solution . In a follow-up investigation, the team discovered that a certain single stranded DNA sequence self-assembles into a helical shape around individual carbon nanotubes. Significantly, it was shown that the DNA-nanotube hybrid's electrostatics were dependent on the tube's diameter and electrical characteristics, allowing the separation of the nanotubes using anion exchange chromatography. As a result, early fractions were concentrated in metallic tubes with a lower diameter, while late fractions were richer in semiconducting tubes with a greater diameter. Optical absorption and Raman spectroscopy were used to confirm this. Bibiana Onoa and coworkers have provided an overview of the interactions between carbon nanotubes and nucleic acids. According to Chapter 8's discussion of this topic, French researchers suggested that the covalent functionalization of SWNTs by azomethine ylides may be utilized to distinguish between metallic and semiconducting tubes in 2006.

DISCUSSION

Purification of nanotubes was the topic of this chapter's introduction. Many studies have been conducted in this field, and fresh purification techniques are often published. High-temperature heating, oxidative and acid treatments, as well as physical processes including filtration, chromatography, and centrifugation, have all been employed as approaches. A mixture of two or more of these techniques is often used. There are a few protocols that may be broadly advised, but which one to use will depend on the kinds of nanotubes and to some part on the planned application. The high-temperature annealing method of Andrews and colleagues (4.7) is a very efficient method of both eliminating catalyst impurities and enhancing the structural perfection of the multiwalled nanotubes generated catalytically. The techniques outlined by Chiang and others have shown to be quite effective for single-walled tubes. Next, techniques for processing nanotubes were taken into consideration, and some outstanding work has been done in this field. A particularly intriguing discovery is the creation of "buckypaper" using single-walled carbon nanotubes. This is a remarkable resource [8], [9].

The work of Baughman in spinning MWNT yarns from arrays produced catalytically on substrates is also noteworthy. The question of whether this method might be scaled up for commercial production is still open. Methods for assembling nanotubes, particularly single-walled ones, into specific configurations have been developed with a lot of imagination. While various strategies are continuously being investigated, dielectrophoresis-based techniques seem to be the most promising ones. Several organizations have said that they have organized millions of tubes in a certain manner using these approaches. Yet, we are far far from manufacturing useful nanoelectronic systems based on arrays of tubes.

Methods for distinguishing nanotubes based on their structure or other characteristics are crucial since it is now impossible to create nanotubes with a specific structure. Instead than isolating tubes with a particular structure, the majority of the research in this field has focused on separating metallic and semiconducting nanotubes. Metallic SWNTs have been successfully removed from mixes of tubes with some success, and promising outcomes using dielectrophoresis and selective functionalization have also been described. Naturally, none of these techniques would be necessary if it were possible to create tubes with a certain structure, therefore this must continue to be the major objective.

Structure

As soon as fullerene-related carbon nanotubes were discovered, it became obvious that a brand-new framework would be required to examine the structures and symmetries of these novel materials. While theoretical techniques for analyzing cylindrical arrays in biology have been established, they are inadequate for a thorough examination of the structure of nanotubes. Mildred Dresselhaus and colleagues, as well as Carter White and colleagues, among others, took on the problem of developing the new methodologies required for categorizing nanotube structure. As will be covered in subsequent chapters, the methods used by these organizations were crucial in figuring out the electrical and vibrational characteristics of nanotubes. The layer structure of multiwalled tubes, tube capping, and other facets of nanotube structure, such as elbow connections, have also been discussed theoretically.

The principal method used in experimental research of nanotube structure is microscopy. As samples of nanotubes invariably comprise tubes with a variety of various shapes, X-ray and neutron diffraction have often been of limited use. The method that has been employed the most often and has shown to be the most useful is high-resolution transmission electron microscopy (HRTEM). Recent advancements in HRTEM resolution have made it possible to examine both the layer structure and the atomic network that make up individual tubes directly, leading to a fuller understanding of their structure. It is detailed how spectroscopic methods may be used to examine the structure of nanotubes [10].

A short study of bonding in graphite and full-erenes opens this chapter. Next, a summary of carbon nanotube structural theories follows. The topic of experimental investigations of nanotube structure, mostly employing HRTEM, is next explored. Multiwalled tubes are discussed first, followed by single-walled tubes. Lastly, a short discussion is made on the use of neutron diffraction to analyze the structure of carbon nanotubes.

Carbon-based materials' bonding

The electrical configuration of a free carbon atom is 1s2 2s2 2p2. One of the 2s electrons is promoted to the 2p state and one of three orbital hybridizations occurs as a result in order to generate covalent bonds. In graphite, one 2s electron hybridizes with two 2p electrons to produce three sp2 orbitals arranged in a plane at an angle of 120° to one another, with the fourth orbital having a pz configuration and positioned at a 90° angle to the plane. The weak van der Waals bindings between the graphite planes are provided by the pz, or, orbitals whereas the strong bonds between the planes are formed by the sp2 orbitals. The electron bond network that gives graphite its comparatively high electrical conductivity is created by the overlap of orbitals on nearby atoms in a particular plane.

The stacking order of the layers in naturally occurring or high-quality synthetic graphite is typically ABAB, with an interlayer 002 spacing of around 0.334 nm. The name "Bernal graphite" refers to the 1924 proposal by John D. Bernal that gave rise to this structure. The space group is P63/mmc, and the unit cell has four atoms (D6h). The layer planes are arbitrarily rotated with respect to one another around the c axis in less perfect graphites, and the interplanar distance is found to be much higher than the value for single crystal graphite (usually 0.344 nm).

Turbostratic refers to these types of graphites. Each carbon atom in a diamond is connected to four of its neighbors via a tetrahedral structure. One 2s orbital and three 2p orbitals combine to form the sp3 bonding in this instance. Diamond is less stable than graphite, and under normal pressures, it turns into graphite at a temperature of 1700 °C. At high temperatures, disordered carbons with sp3-bonded atoms also quickly turn into graphite.

The C60 molecule is made up of 60 carbon atoms bound together in an icosahedral form with 20 hexagons and 12 pentagons. While there is a little degree of sp3 character owing to the curvature, each carbon atom in C60 is connected to three neighbors, making the bonding primarily sp2. According to theory, C60's hybridization is sp2.28. The strain is uniformly distributed across the molecule due to the 60 identical carbon atoms that make up the molecule. Carbon nanoparticles and nanotubes have mostly sp2 bonding as well, while high curved sections may once again exhibit some sp3 character.

Andre Geim of the University of Manchester and colleagues from Russia isolated individual sheets of graphene in 2004, opening a new chapter in the study of carbon. Amazingly, the method they used was as easy as rubbing one newly sliced graphite surface against another. Many flakes were left as a result. The surface, including individual graphene sheets. With the use of AFM, TEM, and optical microscopy, the sheets were characterized. Due to the amazing electrical characteristics of graphene and its potential in nanoscale devices, this discovery has drawn enormous attention, akin to that which enveloped nanotubes after Iijima's 1991.

Carbon nanotube vector notation

The terms "zigzag" and "armchair" refer to two potential high-symmetry configurations for nanotubes, provides an illustration of them. In reality, it's thought that most nanotubes have structures with the hexagons arrayed helically around the tube axis, rather than these extremely symmetric forms. Due to the fact that they may exist in two mirror-related forms, these structures are often referred to be chiral.

The easiest method to describe the construction of a single tube is in terms of a vector that joins two equivalent places on the initial graphene lattice. We call this vector C. The sheet is rolled up to create the cylinder such that the vector's two endpoints are overlaid. Many of the cylinders made in this manner will be equivalent due to the symmetry of the honeycomb lattice, but there is a "irreducible wedge" that makes up one-twelfth of the graphene lattice and is where distinct tube forms are created. A potential tube structure is represented by each pair of integers (n, m). As a result, the vector C may be written as C 14 na1 ma2, where a1 and a2 are the basis vectors for the unit cells of the graphene sheet, and n and m, respectively. A chiral tube is any other tube. The zigzag tube is represented by the numbers (9, 0) for the two "archetypal" nanotubes that may be capped by half of a C60 molecule.

Nanotube unit cells

The definition of a translational unit cell along the tube axis may be established if we consider a nanotube to be a "one-dimensional crystal." The translational unit cell is shaped like a cylinder in all nanotubes. The 'unrolled' cylindrical unit cells for both of the two typical tubes that may be capped by one-half of a C60 molecule. The width of the cell for the zigzag tube is p3a, while the width of the cell for the armchair tube is equal to the magnitude of a, the unit vector of the original 2D graphite lattice.

Unit cells in larger diameter armchair and zigzag nanotubes are merely extended variants of these. The decreased symmetry of chiral nanotubes leads to bigger unit cells. Jishi, Dresselhaus, and others have detailed an easy procedure for creating these cells. To do this, draw a straight line at the irreducible wedge's origin O, extend it until it passes precisely through an analogous lattice point, and then turn the line around.

Nanotube symmetry categorization

Following Mildred Dresselhaus and colleagues' previous research, we now take a look at how carbon nanotubes are classified based on their symmetry. First, the symmetry of zigzag and armchair nanotubes is taken into account. Symmorphic groups, or groups in which rotations can be handled by straightforward point group representations, may be used to represent such tubes. They vary from chiral tubes in that their symmetry operations don't entail either rotations or translations.

We use the assumption that the tube length is much bigger than the diameter for classifying the symmetry of nanotubes, allowing us to ignore the caps. All armchair and zigzag nanotubes belong to either the Dnh or the Dnd group because they all feature a rotational symmetry axis and may also have an inversion center or a mirror plane at an angle to this axis. We follow Dresselhaus and colleagues in assuming that all tubes contain an inversion center when choosing between these two categories. Inversion is now solely a component of Dnh for even n and only a component of Dnd for odd n. As a result, Dnh is the symmetry group for armchair or zigzag tubes with n even, whereas Dnd is the group for same shapes when n is odd.

The hexagonal lattice's flaws

The hexagonal carbon network that makes up the sidewalls of nanotubes has been taken for granted in the debate up to this point. This is never the case in reality, thus it's critical to take into account the many kinds of flaws that could arise. In samples produced by arc-evaporation, abrupt elbow-like bends in nanotubes are often seen. Several researchers have examined connections of this kind. It has been shown that elbow connections using a pentagonal ring on the outside and a heptagon on the inside of the elbow may unite armchair tubes to zigzag tubes. Using a link between an armchair tube and a zigzag tube as an illustration. Fonseca et al. explored the formation of nanotube tori and helices by the introduction of a number of pentagon-heptagon pairings in addition to analyzing single elbow connections. Experimental observation of nanotube tori, or "hoops," has now been made. In samples of nanotubes made catalytically, helical tubes are often seen.

Adjacent pentagon-heptagon pairs are a kind of defect that may appear in the hexagonal carbon network. The hexagonal network below is given positive or negative curvature by individual pentagons and heptagons. The effects cancel out in neighboring pairings, maintaining the network's shape.

The multiwalled nanotubes' layer structure

The most fundamental issue about the layer structure of multiwalled tubes is whether they have a scroll-like, or "Swiss-roll," structure, or if they are made up of a nested, or "Russian doll," arrangement of discrete tubes. Alternately, the structure may be made up of a combination of these two configurations, as various scholars have suggested. At least for MWNTs made via arc-evaporation, experimental findings typically support a Russian doll structure. Assuming that this presumption is true, we will now discuss the issue of the structural connection between succeeding cylinders. This cannot be done using zigzag tubes, since 2.1 nm is not an exact multiple of 0.246 nm, the width of a single hexagon. The inter-tube distance of 0.352 nm is achieved by separating two subsequent cylinders by nine rows of hexagons, which is the closest approach to the "proper" separation. This is a schematic cross-section through a three-layer zigzag tube. The 9 and 18 additional atom rows that have been added to the inner and outer tubes, respectively, are shown here by the bold lines. Similar to the insertion of a Shockley partial dislocation, these additional rows are included. Makes it obvious that concentric zigzag tubes mostly lack the ABAB stacking of perfect graphite. However there are brief patches with ABAB stacking that are close to each "dislocation" halfway between them. In the case of armchair tubes, multiwalled structures that preserve the ABAB layout and have an interlayer spacing of 0.34 nm may be put together. This is due to the fact that 2.1 nm is not far from the repeat unit's length of 5 0.426 nm, from which armchair tubes are made. It is tricky in the case of chiral nanotubes, but generally speaking, it is impossible to have two tubes with the exact same chiral angle separated by the graphite interplanar distance. Overall, it is doubtful that single-crystal graphite's ABAB stacking will be seen in cylindrical carbon nanotubes, with the possible exception of a few minor places.

Nanotube capping theory

It has been determined that a very large number of different cylindrical graphene configurations are conceivable. According to theory, all nanotubes bigger than the classic (5, 5) and (9, 0) tubes may be capped, and the number of potential caps rises sharply with diameter. The representation of nanotube caps and counting the number of caps that can fit on a given tube have both been approached in a variety of ways. We start by describing the strategy used by Fujita, Dresselhaus, and others, who provided the first extensive explanation.

All capped nanotubes must abide by Euler's law, much as fullerenes. According to this, only a hexagonal lattice with exactly 12 pentagons may create a closed structure, regardless of its size or shape. Six pentagons must thus be present in every nanotube cap, and strain concerns require that they be separated from one another neglecting, for the moment, caps containing heptagons. As previously mentioned, the two archetypal tubes are the smallest tubes that can be capped with isolated pentagons. For each of these tubes, there is only one conceivable cap, which corresponds to the C60 molecule split in two distinct ways. Using a technique called "projection mapping," Fujita et al. determined the number of potential caps for nanotubes bigger than these. Using this technique, a map is built on a honeycomb network that may be folded to create a specific fullerene or nanotube. A 60° triangular portion of the lattice is removed to create the pentagons, creating a conical flaw known as a 60° positive wedge disclination. The projection mapping of icosahedral fullerenes is first taken into consideration by the author, who then demonstrates how it may be used to nanotubes. The vector that joins two nearby pentagons may completely specify an icosahedral fullerene. Take the icosahedral fullerene C140 as an example. In this instance, we specify the defining vector. The whole C140 projection map. In this instance, the flaws are arranged in a regular triangular array. The non-shaded portion of the lattice is removed, and rings with the same number are then superimposed to create the fullerene.

When the diameter grows, the number of caps quickly rises. The number of caps, including those with neighboring pentagons, varied with d7.8, as shown by Stephanie Reich and colleagues. The frequency of isolated pentagon-rule-compliant caps decreased for lower diameters, but returned to its power-law behavior for bigger diameters. The reason for this is because the percentage of caps with neighboring pentagons decreases with high tube diameters. It should be noted that armchair and zigzag tubes have fewer caps than chiral tubes for a given tube diameter. This is because there are fewer options for caps owing to the achiral tubes' greater degree of symmetry. Moreover, Reich et al. have shown that although a given nanotube may have hundreds of different caps, the inverse issue is precisely the contrary: a given cap can only fit onto one specific nanotube. It is important to take into account the potential cone angles that are generated by the addition of pentagonal rings to a hexagonal network because experimental investigations of nanotube caps, as discussed, reveal that they commonly have conical geometries. A cone may be created by adding fewer pentagons than the six required to create a cylinder.

Experimental studies: arc-evaporation-produced multiwalled nanotubes

Experimental findings on the layer structure

There are two conceivable configurations for the layer structure of multiwalled nanotubes. The "Swiss-roll" structure or the "Russian doll" design. Preparing cross-sections of MWNTs and sectioning and imaging them using HRTEM would be the most straightforward technique to identify the multilayer structure, however this has proven to be quite challenging. As a result, we must extrapolate the structure from more ambiguous observations. A "closed" Russian doll structure would seem to be the result of taking nanotube reactivity into account. Much research has been done on the interaction of nanotubes with gas- or liquid-phase oxidants with the goal of opening the tubes. These investigations consistently demonstrate that the main body of the tubes is kept intact while the cap area of the tubes is selectively targeted. Due to the ending graphene layers, this seems to be incompatible with a scroll model, which would have a reactive surface down the whole length of the tube. Now let's look at high-resolution TEM photos of multiwalled nanotubes, which often have equally spaced lattice fringes on each side of the central core. The existence of interior caps or closed chambers in the tubes, as mentioned below, may provide greater proof of a Russian doll construction. Such elements are challenging to include inside a scroll framework. For all of these reasons, the Russian doll structure for MWNTs created by arc-evaporation is presently preferred by the majority of researchers.

While typically equal, there are several instances in which the lattice spacings on each side of the cavities in MWNTs are not. The fringes on one or both sides of the cavity often feature "gaps," or abnormally wide spacings, as depicted. The presence of one or more layers across the center core is a common finding in multilayered tubes. It's also extremely typical to observe interior structures that are more complex, sometimes forming isolated chambers. These characteristics may act as a deterrent to the insertion of foreign substances into nanotubes. These edge flaws signify a transition from a scroll-like configuration to a Russian doll configuration.

MWNT electron diffraction

As mentioned electron diffraction has been used to single-walled carbon nanotubes rather well, but it has been less successful when applied to multiwalled nanotubes. This is due to the fact that MWNT electron diffraction patterns are difficult to understand since they include spots from tubes with various chiralities. Given that a "scroll" nanotube would have uniform helicity throughout, this may be seen as more support for a Russian doll structure.

While there have been very few investigations of this kind since Iijima's initial Nature report , he presented electron diffraction patterns of certain MWNTs. Severin Amelinckx and colleagues' study in this area from 1993 to 1994 may be the most thorough. Who discovered proof of chiral, zigzag, and armchair tubes within a single multiwalled nanotube. References for the nanotube theory of electron diffraction.

The design of multiwalled nanotubes' cross-section

It has been quite challenging to make direct measurements of the cross-sectional shape of nanotubes with the electron microscope. Hence, conclusions concerning the cross-sectional Images captured perpendicular to the tube axis must be used to determine the form of multiwalled tubes. It should be noted that the expected cross-sectional forms may be influenced by cap construction. For instance, according to Ebbesen, a cap with fivefold symmetry would force the tube to have a faceted structure. This impact, however, is probably minimal and will disappear as one gets further away from the cap zone. For "asymmetric cone" caps, such as those covered in the next section, a bigger impact on nanotube shape is likely. This kind of cap will produce an "egg-shaped" cross-section, albeit, as before, the impact may be less pronounced in areas far from the cap.High-resolution electron micrographs of multiwall nanotubes sometimes exhibit irregularly spaced lattice fringes on one or both sides of the core, as was previously mentioned. Amelinckx and associates hypothesized that this may be caused by scroll-like components in the multilayer structure, however Mingqi Liu and John Cowley of Arizona State University have offered a different theory. These scientists conducted a thorough investigation of high-resolution photographs of multiwall nanotubes and came to the conclusion that the tubes often have polygonal cross-sections made up of flat portions connected by high-curvature regions. Liu and Cowley contend that fringes with spacings higher than 0.34 nm would be seen in photographs of the locations where the two flat sheets intersect. This scenario is schematically shown. The gaps that are seen are a result of bringing together idealized flat sections with the 0.34 nm spacing, which is important to keep in mind since their model assumes a reasonably "perfect" multilayer structure. This model predicts a maximum interlayer spacing of 0.41 nm. In practice, spacings far greater than this are seen. Under these circumstances, the multilayer structure is likely somewhat less perfect than Liu and Cowley had intended.

The existence of distorting forces brought on by interactions between neighboring tubes must also be taken into consideration when analyzing the cross-sectional forms of nanotubes. Rodney Ruoff and associates spoke about this impact. These researchers discussed TEM findings of nanotubes in touch along one edge at great resolution. There is a flattening of the tubes at the contact zone, as seen in micrographs of neighboring nanotubes where 002 fringes are denser around the inner region where the two tubes make contact than at the outside margins. Using a Lennard-Jones model for the van der Waals interaction, Ruoff et al. calculated the interaction of two double-layer tubes. They demonstrated a significant flattening in the contact region, which was consistent with the experimental findings. In addition, Ruoff and colleagues discovered that the '002' interlayer spacings on the sides of the tubes close to the contact zone were smaller than those on the outer sides by roughly 0.008 nm.

Cap structure of MWNT

Theoretical work on the capping of nanotubes was reviewed, where it was stated that there are several methods to cap tubes with diameters bigger than about 1 nm. Multilayer nanotube caps do actually have a large variety of various topologies, according to experimental research. The cap structures are often asymmetrical, however greater symmetry caps may sometimes be seen. Two exquisite micrographs of symmetrical tube caps by Iijima are shown with schematics demonstrating the approximate locations of the pentagonal rings in each instance. It is interesting to note that the amount of faceting rises from the inner to the outer graphene layers. This is generally in line with predictions made concerning the morphologies of larger fullerenes, which state that as size grows, the shapes become less spherical. According to Iijima, the left-hand tube's biggest cap is equivalent to half of the icosahedral fullerene C6000. The "asymmetric cone" form, as seen in the illustration, is a frequently seen variety of nanotube cap. This sort of structure is thought to be caused by the existence of a single pentagon where the arrow points, together with five other pentagons at the cone's tip. According to theory, five pentagons should generate a cone angle of 19.19°. The angles seen in asymmetric cone caps may really vary quite a bit from this figure. The angle is around 26° in the case of the cap. As mentioned before, this kind of cap forces the nanotube to have a non-circular cross-sectional form. Less often seen are caps with a "bill-like" shape, like the one a single pentagon at point "A" and a heptagon at point "B" combine to form this construction. Almost all multiwalled nanotubes in samples produced by arc-evaporation are closed, however sometimes specimens are seen that are fully open and lack any discernible cap structure.

Branching structures and elbow connections

As mentioned above, samples produced using the traditional arc-evaporation approach sometimes include nanotubes with abrupt elbow-like bends. The joints often have "internal caps," and the tubes on each side of the elbow are typically of different widths. According to certain theories, the existence of a pentagonal ring and a heptagon on the inner side of the elbow, respectively, causes this sort of structure. Yet, the layer structure on the inner side of the elbow joint often has discontinuities in experimental photographs. As a result, the connections' structure may not be as flawless as theoretically predicted. It is difficult to determine if the tube axis is perfectly perpendicular to the path of the electron beam, making accurate angle measurements on electron micrographs problematic. Even in cases when the joint is thought to be roughly perpendicular to the beam, measurements have shown angles that deviate quite a little from the 150° theoretically expected.

Dan Zhou and Supapan Seraphin of the University of Arizona discovered more intricate, branching nanotube structures in 1995 that also seemed to have negative curvature. These structures were created using standard arc-evaporation procedures, but with a graphite anode that had been hollowed down to leave a 0.32 cm-diameter core. 'L', 'Y', and 'T' configurations were used to characterize three different sorts of branching structures. Labeled a, b, c, and d are the points that are negatively curved. These connectors' angles varied greatly, just as the elbow connections' did. Currently, it is unclear why these formations occur, but Zhou and Chow contend that they support the "crystallization" theory of nanotube growth.

Experimental studies: catalysis-produced multiwalled nanotubes

A short summary of some of the structural characteristics of multiwalled tubes formed by catalysis is provided in this section. In general, MWNTs made using catalysis have less precise structural characteristics than those made through arc evaporation. As might be expected, the circumstances utilized, namely the temperature, have a significant impact on the structure of tubes formed during catalysis. The tubes usually take on an erratic shape and are defective when made at relatively low temperatures (below roughly 600 °C). The level of graphitization in these tubes is minimal. Higher temperatures enable the creation of almost straight and flawless nanotubes. In samples created catalytically, helical coiled tubes are often seen. Another often noted characteristic of catalytically produced nanotubes is their bamboo-like shape and abundance of "internal caps." Marc Audier and colleagues first described such structures in 1981 after seeing them in tubes created by the disproportionation of carbon monoxide at 400 °C on a Fe-Co alloy catalyst. The reasons for this are not yet entirely understood, but experimental data demonstrate that the bamboo tubes nucleate at greater carbon feedstock pressures than those needed for SWNT and MWNT nucleation. By using doped electrodes for an arc discharge, bamboo-like structures may also be created. The way that these structures evolve. On occasion, branching structures are seen in catalytically produced nanotubes. In his earlier writings, Baker described structures that resembled trees. In 2005, Patrick Bernier of the University of Montpellier and his colleagues used a technique in which an aqueous catalyst-precursor solution was sprayed into a furnace to manufacture branched MWNTs with a greater yield. They suggested a mechanism in which the catalytic particle remodelling into lobed forms caused the branching. Y-shaped nanochannel alumina has also been used as a template to create branched nanotubes.

Research investigations with single-walled nanotubes

Basic characteristics

Single-wall nanotube samples often have a significantly smaller range of sizes than multiwall nanotube samples, are much more homogeneous, and have less evident flaws. As compared to photographs of multiwalled nanotubes, high-resolution electron micrographs of single-wall nanotubes often display "featureless" thin tubes. Some of the common characteristics of single-wall nanotubes have been covered in earlier chapters. The tubes often group together to form bundles, and end-on pictures of these bundles show tightly packed arrays of tubes. The individual tubes as well as the tube bundles are typically coiled and looped. Nevertheless, single-walled nanotubes do not exhibit regular helical shapes like those seen in multilayer tubes made by catalysis. Although the majority of them seem to be simple domes, the caps of SWNTs, like those of multilayer tubes, may have a variety of forms. One example of an asymmetric cone cap may be seen in the lower left corner.

SWNT Electron Diffraction

Many writers have provided comprehensive theoretical analyses of electron diffraction from single-walled nanotubes. If the electron beam is not perfectly normal to the tube, a second disagreement also appears. The adjustment necessary to derive the real helicity from the observed rolling angle has been determined by Qin, Ichihashi, and Iijima. In their alternate method, Meyer et al. used the relative distances of the peaks to the equatorial line, denoted by d1, d2, and d3, to calculate the chiral angle. This approach has the benefit that these distances are unaffected by the electron beam's incidence angle.

It is very difficult to produce single-walled nanotube electron diffraction patterns experimentally. In addition to the few electrons that are diffracted by a single tube, there are issues with specimen drift and beam damage. The interpretation of diffraction data may also be made more difficult by the possibility that tubes are not perfectly straight or perpendicular to the electron beam. The fact that Iijima and Ichihashi were able to include a diffraction pattern of a single single-walled tube in the 1993 Nature publication announcing their synthesis of SWNTs is amazing given these issues. In terms of a chiral tube structure, this was understood. Between the grid bars, well-separated, long, and straight individual tubes that are perfect for diffraction may be created. Displays examples of the superb diffraction patterns they were able to capture using this technique. In all, 28 nanotubes that were created via the CVD technique had their diffraction patterns captured. These tubes' chiral angles weren't dispersed at random. There were six tubes with the armchair configuration and no zigzag tubes. The majority of the remaining tubes had chiral angles that were close to the 30° armchair value. Several investigations utilizing fluorescence spectroscopy have also revealed a tendency toward the armchair form.

SWNTs HRTEM

Single-walled nanotube atomic resolution TEM imaging is as challenging as, if not more so than, capturing electron diffraction patterns. It seems that Dmitry Golberg and colleagues from Tsukuba got the first such photos in 1999. These researchers presented pictures of fringes with a 0.21 nm spacing that were perpendicular to the tube axis. An interpretation of a zigzag construction was made with them. Another picture with a hexagonal pattern of dots was seen to be an armchair-like structure.

The Oxford Group provided an intriguing study of the kind of contrast that may be anticipated from SWNTs in 2001. In this study, improved pictures of filled tubes were created by digitally merging tilt- or focal-series photos with certain aberrations eliminated. They demonstrated that depending on the tube construction, the periodicities seen along the tubes' walls should vary fairly noticeably. This illustrates the contrast that would be seen in a tube that is perpendicular to the electron beam. The observable contrast on the two walls of achiral tubes is always the same. As the spacing of 0.125 nm is beyond of the experimental resolution of the majority of microscopes, there would typically be no wall contrast seen for the armchair tube. Due to the zigzag tube's 0.216 nm spacing, fringes on both carbon walls should be easily apparent. The chiral angle, affects the contrast that may be seen in chiral tubes. Fringes on one or both of the walls should be easily seen if this is tiny (less than roughly 10°). The impact of tilting on the apparent contrast was also modelled. The spacing of the fringes relies on the chiral angle. It was feasible to infer the structure of the tube from the contrast seen in the walls of certain filled tube pictures by calculating the tube's tilt in relation to the electron beam.

Suenaga, Iijima, and others have conducted TEM examinations of single-walled tubes. Graphs from an article they wrote that was published in Nature. It is easy to see atomic resolution difference between the two black lines that represent the vertical tube walls. The contrast from the top and lower walls is superimposed in this. The top and lower tube walls are represented by two regular hexagons in the Fourier transform (or optical diffraction pattern) of this picture. The chiral indices might be calculated by properly measuring the tube diameter and the angles that these hexagons form with the equatorial line. The indices in this instance were discovered to be. Moreover, intentionally introducing defects into tubes by electron bombardment and imaging the resultant formations. Demonstrates how a connection between two tubes with somewhat differing diameters was created. Iijima and colleagues were able to assign the indices by examining the Fourier transform of this picture.

SWNTs using scanning tunneling microscopy

Getting atomic resolution photographs with a scanning tunneling microscope (STM) is just as difficult as getting high-resolution TEM images of nanotube structure. The first issue is the practical one of securely securing the tubes to a flat support material. Highly oriented pyrolytic graphite (HOPG) has often been used as a substrate, although there is a chance of misunderstanding since HOPG has the same atomic structure as nanotubes. Alternative substrates like gold provide benefits for these reasons. Even when a nanotube's atomic resolution picture has been captured, it is not always easy to extract structural information. For example, distortions brought on by a torsional twist may have a significant impact on the observed pitch angle. The process used to create the STM picture itself may potentially cause distortions. The tunneling current, which flows perpendicular to the nanotube surface rather than vertically downhill from the tip to the nanotube, takes the shortest route, as noted by Meunier and Lambin and their colleagues. This has the result of extending the lattice in the direction normal to the tube axis, as shown in the picture.

As mentioned in the beginning of this chapter, the variability of the majority of nanotube samples has made diffraction methods less useful for studying carbon nanotubes than microscopic and spectroscopic approaches. The layer structure has been partially revealed by X-ray diffraction, as was explained, although nothing is learned from the (hkl) peaks in X-ray powder patterns. As neutron diffraction allows for a greater exploration of scattering vectors, Q, it has the potential to provide more precise data on the hexagonal network. In both single- and multi-walled nanotubes, Andrzej Burian and colleagues calculated the nearest-neighbor carbon-carbon distance using neutron scattering and found a value of 0.141 nm (5.84). This is much shorter than the value for fullerenes, which is 0.144 nm, and is fairly similar to that of graphite. The results from samples with a variety of tube structures would make it challenging to interpret the data from these samples, but calculations by this group (5.85) have suggested that, for the smallest tubes, it may be possible to distinguish between armchair, zigzag, and chiral structures using neutron diffraction.

DISCUSSION

Nowadays, a wide range of methods are being used to investigate the structure of carbon nanotubes. While there is still much to learn, these approaches are gradually helping us to understand the types of structures that are found in actual nanotube samples. How much about the structure of single-walled nanotubes can be predicted with certainty? We are aware that chiral structures are far more prevalent than achiral structures, but this is not unexpected given that there are many more chiral forms that might exist than there are zigzag and armchair configurations. More intriguing is the data that, at least for catalytically generated nanotubes, there is a preference for close to armchair architectures. Studies using spectrofluorimetry and electron diffraction (5.66) have both shown this tendency. It is unclear what may be the causes of this. Nevertheless, it should be noted that certain Raman spectroscopy experiments have discovered a random distribution of SWNT structures, therefore it cannot be argued with certainty that the predilection for near-armchair structures has been verified.

Transmission electron microscope pictures typically portray a high level of perfection; flaws like those in are uncommon. While defect-free structures are also shown by STM pictures that directly depict the atomic structure of the SWNTs, Inevitably, microscopic pictures only display brief tube lengths. There are additional reasons to think that SWNTs often display a high level of perfection. It appears reasonable to claim that multiwalled nanotubes are typically more flawed than their single-walled cousins. Even those made using arc-evaporation, the greatest process for creating high-quality MWNTs, are affected by this. These tubes often have characteristics such as ending lattice fringes and unevenly spaced gaps seen in transmission electron microscope pictures. Common elbow connections are seen, and the tubes often include interior chambers. While the quality of catalytically generated MWNTs may be increased by raising the synthesis temperature, they often have less ideal structural characteristics and are helically coiled or have bamboo-like architectures.

The types of applications that may be employed for single- and multiwalled nanotubes vary depending on their structural perfection. SWNTs may thus be used in nanoelectronic systems, where the presence of defects might have a significant impact on performance, due to their low defect density. Multiwalled tubes would be of limited value in such devices due to their more intricate and often flawed construction. On the other hand, compared to single-walled tubes, multiwalled tubes may have less of an impact on their mechanical characteristics when flaws are present. A single flaw in a SWNT would represent a vulnerability, but a flaw in a MWNT may be made up for by a more flawless construction in other levels.

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CHAPTER 11

PHYSICAL PROPERTIES: MECHANICAL, OPTICAL AND THERMAL

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Carbon nanotubes' mechanical qualities have generated almost as much attention as their electrical ones, and for good reason. Nanotubes are the stiffest and sturdiest fibers ever made, it is now widely accepted. The best nanotubes may thus have a Young's modulus of up to 1000 GPa, which is around five times greater than steel, and a tensile strength of up to 63 GPa, which is almost 50 times stronger than steel. Because to these characteristics and their low density, nanotubes have enormous promise in a variety of structural applications. The incorporation of the tubes into composite materials is often necessary to take use of their capabilities, and this is explored. The detailed discussion of carbon nanotube mechanical characteristics in this chapter starts with a review of theoretical predictions and is followed by a synopsis of actual results on both multi- and single-walled nanotubes. Then, the optical characteristics of carbon nanotubes are discussed, and several spectroscopic techniques are used to nanotubes. The thermal characteristics of nanotubes are next briefly discussed, and lastly some observations on the physical stability of nanotubes are made.

Aspects of carbon nanotubes' mechanics

Predictions based on theory

We can do some quick calculations to demonstrate the connection between a nanotube's diameter and stiffness before going into more depth about calculations of the mechanical characteristics of nanotubes. First, imagine a tube with a 1 nm inner diameter. Assuming a 0.34 nm wall thickness, the cross-sectional area is 1.43 10-18 m2 and the outer diameter is 1.68 nm. The tube experiences a stress of 7 1010 Nm-2 when we now add a tensile load of 100 nN to it. Assuming a Young's modulus of 1060 GPa, the resultant strain is roughly 6.6%. Think about a tube that has an exterior diameter of 10.68 nm and an interior diameter of 10.0 nm. In this instance, a 100 nN tensile load causes a stress of 9.05 109 Nm2, a 0.85% strain, and other physical changes. These graphs make it quite evident how stiffness rises with tube diameter. This is in line with the finding that multiwall nanotubes tend to be straight whereas single-walled nanotubes, which generally have diameters on the order of 1 nm, are frequently curly.

In this straightforward calculation, it was expected that the Young's modulus of nanotubes would be 1060 GPa, the same as that of a sheet of graphene. This can only be a rough estimate, and many organizations have made an effort to determine the modulus for nanotubes with different diameters and topologies using a range of methods. Jian Ping Lu of the University of North Carolina at Chapel Hill performed some of the first thorough calculations. He performed tight-binding calculations on single-walled tubes with diameters ranging from 0.34 to 13.5 nm and discovered a Young's modulus of 970 GPa. This was shown to be independent of tube construction or diameter and is comparable to the modulus for a graphene sheet. Shortly after, Angel Rubio of the University of Valladolid and associates discovered somewhat higher values for the Young's moduli of tubes with various topologies and diameters (usually 1240 GPa). Rubio et al. discovered, in contrast to Lu, that the moduli were affected by both tube diameter and structure. The idea that modulus is influenced by tube construction and diameter has typically been validated by subsequent research. According to a study of computational research, the expected values of Y fall between 0.5 and 5.5 TPa. This relatively broad range of projected values is partially caused by the fact that many writers selected various numbers for the single-walled tube's wall thickness. The majority of writers use the assumption that the wall thickness is 0.34 nm, which is the distance between neighboring walls in a multiwalled tube. Studies expecting significantly lesser values for the wall thickness discovered the high values of 5 TPa and more. The stiffness of tiny tubes will always tend to be lower than that of bigger tubes, as indicated by the naive estimate above, despite the fact that the modulus may change with tube diameter.

Researchers from North Carolina State University have researched the behavior of nanotubes under compression (NCSU). Molecular dynamics has been used to predict the impact of axial compression on an armchair-shaped nanotube in this case. Depicts the relationship between strain energy and longitudinal strain. This demonstrates that the strain energy varies with 2 at lower strains, as predicted by Hooke's Law; but, at greater strains, a number of discontin- uities are seen, and the strain energy curve roughly becomes linear. The four buckled configurations shown in the simulations are represented by the discontinuities labeled b-e. The bending of nanotubes was also modelled.

It has been extensively researched theoretically how nanotubes behave under high tensile stresses and ultimately shatter. Once again, the NCSU group took the lead. According to their estimates, a single-walled tube may elongate by a maximum theoretical tensile strain of about 20%. Several scientists think that the creation of Stone Wales flaws may be involved in the first phases of the fracture process [1] .

Observations from experiments: multiwalled nanotubes

Transmission electron microscopy general observations provide some helpful information on the stiffness and tensile strength of nanotubes. The fact that arc-grown multiwalled nanotubes often seem quite straight in TEM pictures is one sign of their stiffness. Despite the fact that samples for TEM are sometimes made by pulverizing the material in a pestle and mortar while submerged in a solvent, completely shattered nanotubes are rarely ever seen. Single-walled nanotubes often exhibit far greater curvature than multiwalled tubes, however this is likely due to the fact that they are typically quite thin (as noted in the previous section, stiffness increases with increasing diameter). These findings suggest that nanotubes have both a high Young's modulus and a high breaking stress. Broken nanotubes are very uncommon, however bent nanotubes are often encountered. As shown in the stunning photograph by Walt de Heer, Daniel Ugarte, and colleagues above, bent tubes with regularly spaced buckles are often seen. The remarkable lack of broken layers in the buckled regions demonstrates the incredible flexibility of graphene layers [2].

When a tube is under stress, it might unwind and take on its original straight shape. Nanotubes differ from other known fibers and regular carbon fibers in that they exhibit a behavior that makes them far less likely to shatter under stress that exceeds the elastic limit. Moreover, it presents the exciting potential that composite materials may be created that would rebound after deformation. Researchers from Ajayan's group and others have examined how compressed MWNT films behave. They discovered that the tubes joined together to create zigzag buckles. These compressed tubes could completely unfurl to their original length upon load removal, just as bent nanotubes could. Iijima and colleagues have reported buckled single-walled tubes in part of their work. In TEM grids, nanotube clusters were placed such that solitary tubes protruded into the void for a substantial distance. The specimens were then put in a unique container that allowed the TEM to do in situ heating. Next, at temperatures as high as 800 °C, pictures of several individual, freely vibrating nanotubes were captured. You may estimate the Young's modulus by analyzing the mean-square amplitude as a function of temperature. They had an average pressure of 1.8 TPa and varied from 410 GPa to 4.15 TPa. The wide range of values is due to both the existence of faults in the tube constructions and inaccuracies in the estimation of the lengths of the anchored tubes.

The mechanical characteristics of nanotubes were originally investigated using scanning probe microscopy by Charles Lieber and colleagues at Harvard. They provided instructions for attaching nanofibres at one end and calculating the fibers' bending force as a function of displacement in 1997. The fibers were initially spread out over a single crystal MoS substrate, and then they were pinned to it by deposition of square

As a result, many fibers had one end stuck beneath the pads and the other end free. The free nanofibres could then be found once the materials were scanned by AFM. It was then possible to capture lateral force vs. displacement (F-d) data by repeatedly scanning individual fibers. When a particular applied force was achieved while scanning, the tip may ride over the fiber, causing the fiber to spring back to its equilibrium position and allowing for more scans to be performed. Tests on arc-produced multiwalled nanotubes resulted in linear F-d curves for modest deflections, and the data suggested that the elastic modulus was around 1.28 TPa. The tubes were discovered to be capable of taking on significant deflections without cracking. The slope of the F-d curve, however, abruptly changed at deflections greater than 10°. This was explained by elastic buckling similar to that seen in TEM experiments.

Richard Superfine and colleagues at the University of North Carolina at Chapel Hill also discussed AFM tests of arc-synthesized MWNTs exposed to significant bending forces in a report that was released soon after the Harvard study . The tubes used in these experiments were supported on mica rather than being fastened at one end. For imaging purposes, friction was often enough to pin the tube in a stretched position. Once again, it was discovered that the tubes could be repeatedly twisted at extreme angles without breaking. A single tube that has been manipulated into a highly distorted structure is shown in Fig. 7.8. The nanotubes treated to this treatment exhibited no signs of plastic degradation after being bent repeatedly. The bent tubes showed evenly distributed buckles, much as in the TEM experiments, which vanished when the tubes were straightened. These tests provide more proof of carbon nanotubes' exceptional toughness.

Much more difficult than using AFM, manipulating carbon nanotubes within an electron microscope is possible, although only a few teams have done so. The reversible telescopic extension of arc-grown multiwalled tubes was proven in situ tests carried out within a TEM in 2000, according to a description by John Cumings and Alex Zettl. The usage of MWNTs in nanomechanical systems may be a realistic option since there didn't seem to be much friction between the layers and there was no sign of wear or fatigue. In a later investigation, the Zettl group put individual MWNTs through a series of tugging and bending tests using the same in situ technique. They were able to break the tubes in several of these tests, so they estimated the tensile strengths and discovered values of around 150 GPa. The tubes' Young's modulus was calculated from bending experiments to be 900 GPa. Rodney Ruoff and his colleagues have done very skillful work on the mechanical characteristics of nanotubes (7.37–7.39). This involves attaching individual arc-grown MWNTs to the opposing points of AFM cantilever probes using a micromanipulator within a SEM, as illustrated in Fig. 7.9. The tube ends were deposited with carbonaceous material and the probes were attached by the electron beam. After a tube had been securely fastened at both ends, a tensile force was applied by driving one of the cantilevers away from the other. The Young's moduli of the outermost layer might be calculated by analysis of the stress-strain curves for individual MWNTs. There were quite a few different values discovered, ranging from 270 to 950 GPa.

This variation's occurrence is most likely explained by faults. In contrast to some of the other techniques, which measured the moduli of whole tubes, it should be noted that just the exterior layers of the tubes were strained in these studies. A failure mechanism known as "sword-in-sheath" occurs when enough force is applied to cause the exterior layers to fracture while the inner ones remain intact. The outer layers' observed tensile strengths varied from 11 to 63 GPa. The Ruoff group also noted the phenomena of sliding shells in multiwalled tubes. The subject of every study that has been mentioned so far is multiwalled nanotubes made using arc evaporation. Measurements of the mechanical characteristics of MWNTs generated using catalysis by Forró and colleagues revealed that, in general, they were much worse than those of MWNTs developed through arcing.

The AFM technique was employed in the first investigation, which was published in 1999, to directly compare arc-grown and catalytically generated MWNTs. 870 GPa was determined to be the average Young's modulus for the arc-grown tubes, which is quite comparable to the value discovered in the prior research. Yet, the average pressure for tubes made via catalysis was just 27 GPa. It was shown in a subsequent work that heating CVD tubes to temperatures of up to 2400 °C did not considerably increase their elastic moduli. Even after heat treatment, the modulus' best value was remained below 100 GPa. This significant finding indicates the improved structural nature of MWNTs made via an arc. The number of 350 110 GPa was later generated through AFM research, which is somewhat higher but still falls well short of the values for arc-grown tubes.

It is obvious that the majority of catalytically produced tubes have imperfections that are almost hard to fix. Nevertheless, this may not apply to all tubes made via catalysis. The Forró group has shown that MWNTs made catalytically can have outstanding mechanical qualities even when they have a limited number of layers. Therefore, for tubes with 2 or 3 walls, moduli as high as 1 TPa were observed. This suggests a much lower fault density than in many-walled CVD tubes and may show that, as was previously said, "few-walled" nanotubes form via a distinct process.

Research findings: single-walled nanotubes

There have been relatively few measurements on individual single-walled tubes (SWNTs), and it is more difficult to quantify the elastic characteristics of SWNTs than it is for MWNTs. These measurements were initially reported in 1998 by Ebbesen, Treacy, and others. They discovered an average Young's modulus of 1.25 TPa by using techniques identical to those initially employed for MWNTs, i.e., watching the tubes' vibrations at room temperature in a TEM. This is rather comparable to the normal values discovered for MWNTs developed by an arc. Although doing studies on individual SWNTs is very challenging, studying the mechanical characteristics of SWNT "ropes" is much simpler. Ruoff and colleagues measured the Young's modulus and breaking strength of SWNTs created by laser ablation using the "nanostressing stage" mentioned in the preceding section.

They were able to calculate values for individual tubes using these data, and they discovered that the average strength and modulus were 30 GPa and 1.0 TPa, respectively. A single-walled tube's maximum elongation under tensile strain was discovered to be 6%, far less than the 20% expected by theory. Ropes hanging across 200 nm pores were employed in the AFM technique mentioned in the preceding section. In this approach, they discovered that the ropes' elastic and shear moduli were on the order of 1 TPa and 1 GPa, respectively. Shortly after, Thomas Tombler of Stanford and colleagues did a research on CVD-grown SWNTs. While the electromechanical characteristics of the tubes were the major focus of this study, the Young's modulus was also determined, and a value of 1.2 TPa was discovered. The tensile strength of single-walled nanotube ropes created by laser vaporization was assessed by a Rice University team using AFM (7.49). An estimated 45 GPa of tensile strength was discovered, with a maximum strain of 5.8%. When seen together, these findings demonstrate that SWNTs exhibit remarkable mechanical characteristics regardless of the technique of manufacture.

Nanotubes' optical features

The brilliant clarity of diamonds to the inky black of soot are all examples of the optical characteristics of carbon compounds. Diamonds are transparent because all of their electrons are linked to their sp3 bonds, which only absorb infrared light (IR), allowing visible light to pass through unimpeded. Due to their very high refractive index and capacity to separate visible light into its spectral components, they glitter. On the other hand, soot, like other finely split forms of sp2 carbon, is dark in color due to its high concentration of -electrons, which may absorb light of a variety of wavelengths. Compare the imprint left by a pencil to that left by a charcoal crayon to illustrate that graphite lacks the matte black color of more finely separated sp2 carbons. This is because graphite has reflecting qualities due to its metallic nature; they are especially noticeable in highly-oriented pyrolytic graphite, an exceedingly crystalline form of graphite. Nanotube samples often have a dark appearance. Tubes may have translucent layers, however, if they are exceedingly thin. This is due to nanotubes' relatively high penetrating depth. The depth to which a certain wavelength of electromagnetic radiation may enter a substance is known as the penetration depth. As nanotubes are a system with a low free carrier density, they have a considerable penetration depth for visible light, which varies inversely with the free carrier density. We discuss the use of optical spectroscopy methods to the investigation of carbon nanotubes in the next two parts [3].

Optical absorption spectroscopy

As optical absorption spectroscopy does not provide a lot of useful information, it has not been commonly employed to research carbon nanotubes. For instance, it is impossible to discern the structure of nanotubes using absorption spectra. Single-walled tubes have been used nearly entirely in the little research that have been done. In 1999, Hiromichi Kataura and colleagues at Tokyo Metropolitan University released one of the most significant of these. On top of the wide plasmon-induced absorption, three significant absorption peaks at around 0.68, 1.2, and 1.7 eV can be detected. Moreover, it was shown that the locations of these peaks in the spectra of SWNTs with various diameter distributions differed somewhat. This is predicted given that transitions between spikes in the densities of the states in the tubes' electronic structure are what cause the absorption bands [4], [5] . The structure and diameter of the tube affect how these singularities are positioned in the density of states, as we observed in the previous chapter. The graphic indicates where peaks in an absorption spectra for tubes with a certain range of diameters should be seen. For instance, 1 nm-diameter tubes would exhibit peaks at around 0.8, 1.6, and 2.3 eV (peak energies above this would be overwhelmed by the plasmon). The Kataura figure demonstrates why basic optical absorption spectroscopy is ineffective in determining nanotube structure because the absorption characteristics from nanotubes with various shapes often overlap, making a clear identification difficult. Nevertheless, a team from Rice University's discovery of fluorescence in single-walled nanotubes in 2002 paved the path for structure-assigned optical spectroscopy of SWNTs, which is covered in more detail in the next section.

Fluorescence spectroscopy

The first experiment to show fluorescence in single-walled nanotubes used spectroscopic measurements on materials where the bundles of nanotubes had been segregated into tubes by being enclosed in cylindrical micelles. When these materials were subjected to optical spectroscopy, a sequence of emission peaks in the near infrared (between 800 and 1600 nm) were discovered. These emission peaks were ascribed to fluorescence occurring across the band gap of semiconductor nanotubes. It is possible to comprehend the fluorescence, which schematically depicts the density of states for a semiconducting nanotube. These spectral characteristics haven't yet been connected to (n, m) structures, however. Resonance Raman spectroscopy was used on the same samples to determine these assignments. Each optical transition may be mapped to a particular (n, m) nanotube structure by combining these Raman findings with a thorough examination of the spectrofluorimetric data.

This research produced a potent new method for determining the structure of nanotubes. Nevertheless, it should be noted that only semiconducting nanotubes will show fluorescence, which means that about one-third of tubes will not be picked up by this kind of spectroscopy. The Rice researchers discovered a strong bias towards near-armchair configurations in the HiPco nanotube sample they were studying. No zigzag tubes were found, and as armchair tubes are all metallic, they would not be seen either. Fluorescence spectroscopy-based follow-up research have discovered more evidence that near-armchair configurations seem to be preferred. According to Resasco and colleagues, SWNTs made using the CoMoCAT approach seemed to have a significant percentage of tubes with the and architectures (around 50%).

Raman spectroscopy

For the identification of nanotubes in bulk materials and for the investigation of nanotube structure, Raman spectroscopy has shown to be a very useful instrument. Experimentally, the method is quite straightforward, at least when used with bulk materials, and the equipment is generally accessible. At room temperature and pressure, spectra may be captured using a rapid, non-destructive, and sensitive method. Raman may also be used on individual nanotubes, albeit the experimental requirements are significantly more difficult. The discussion that follows focuses mostly on single-walled nanotubes; multiwalled tubes haven't benefited as much from this method.

A low-frequency peak (200 cm1) attributed to the radial breathing mode with A1g symmetry (RBM). As will be detailed later, the tube's width affects the frequency of the peak. The so-called D line, a prominent feature at around 1340 cm1, is attributed to disordered graphitic material. The G band is a collection of peaks that are roughly in the 1550-1600 cm-1 range. The C atoms' tangential mode vibrations cause a single peak in the G band of graphite at a wavelength of 1582 cm1. A line with the designation G′ that is the second order harmonic of the D mode at around 2600 cm1. There are several second order modes between 1700 and 1800 cm1, however they are not very useful for describing nanotubes. the resonant vibrations that cause RBM and G-band vibrations [6] .

Being a special phonon mode that only appears in the spectra of single-walled carbon nanotubes, the radial breathing characteristic that appears slightly below 200 cm1 is highly helpful in establishing that bulk samples include SWNTs. Moreover, it may be utilized to infer structure and offer details on tube diameter. The first thorough explanation of this trait was provided in a classic study that appeared in Science in 1997. This report detailed a Raman analysis of samples of pure nanotube "rope," which was a joint project of researchers from five separate centers in the USA and Japan. There were many brand-new nanotube-related characteristics found, with the RBM peak being by far the strongest. Surprisingly, it was shown that the laser stimulation frequency affected both the intensity and location of this peak. These findings demonstrate that tubes of varying diameters connect to the laser field with varied efficiency and were explained in terms of a resonant Raman scattering mechanism. When a photon's energy matches that of strong optical absorption electronic transitions, resonant Raman scattering occurs [7], [8] .

Nanotubes' thermal characteristics

The greatest recorded thermal conductivities of any known material are found in crystalline carbons. At ambient temperature, graphite's in-plane conductivity may reach 2000 W m 1 K whereas that of pure diamond ranges from 2000 to 2500 W m 1 K. Much greater values are anticipated for carbon nanotubes; according to studies by David Tománek and colleagues, a single isolated (10, 10) nanotube at ambient temperature would give a value of 6600 W m1 K1.

Using ropes or bundles of tubes, early experiments on the thermal characteristics of nanotubes were conducted. SWNT mats, which are constructed of tangled bundles of rope, were tested for their heat conductivity by Alex Zettl's team at Berkeley (7.85). The first readings for the mats' thermal conductivity at room temperature ranged from around 2-35 W m1 K1, which were not very high numbers. Their calculations, however, did not account for how twisted the ropes were. When attempting to convert these figures into thermal conductivities for specific ropes, results in the range of 1750–5800 W m–1 K–1 were obtained. At temperatures as low as 7 K, SWNT mats' thermal conductivity was also measured. It was discovered that k's temperature dependency was significantly different from graphite's. The in-plane thermal conductivity of high-quality graphite, which is dominated by acoustic phonons, changes as T2-3 up to 150 K. Zettl and colleagues discovered that the low-temperature thermal conductivity of the SWNT samples varied linearly with temperature and projected to zero at T = 0. This result is in line with quantization of SWNTs' thermal conductivity.

It seems that no measurements of the thermal conductivity of specific single-walled tubes have been made to yet. Such trials would undoubtedly be a significant experimental difficulty. Nonetheless, measurements on certain multiwalled nanotubes have shown once again very high conductivities, at least for arc-grown tubes. Berkeley researchers led by Paul McEuen utilized a microfabricated instrument to measure the thermal conductivity of MWNTs made using arc evaporation. At room temperature, values of more than 3000 W m 1 K 1 were discovered. Yet, it seems that MWNTs created by catalysis have a substantially lower thermal conductivity. Using a technique termed pulsed photothermal reflectance, researchers from Singapore produced arrays of tubes on Si substrates and discovered values of around 200 W m K1. Heat conduction in nanoscale objects may become quantized, much as electrical conduction. This is due to the fact that in tiny devices, only a small number of phonons are still active at temperatures near to absolute zero (7.89, 7.90).

In 2000, Schwab et al. performed the first experimental observation of quantized thermal conductance using a device featuring Si3N4 "phonon wave guides. SWNTs are excellent candidates for the measurement of quantized thermal conductance due to their very tiny diameters and great stiffness. They have phonon mean-free paths that are enormous, on the order of 1 m. Takahiro Yamamoto and associates provided a theoretical study of quantized thermal conductivity in carbon nanotubes (7.92). It was shown that, regardless of the radius or atomic geometry, the phonon-derived thermal conductance of semiconducting SWNTs displays a universal quantization in the low-temperature limit. Experimental verification of this has not yet been made. Results from certain investigations, nevertheless, show quantum effects in only one dimension. Zettl's group's work on SWNT mats has previously been acknowledged. As mentioned in the previous chapter, researchers from the National Physical Laboratory used a temperature sensing scanning probe microscope to simultaneously test thermal and electrical properties of individual SWNTs and discovered some evidence for the ballistic transport of phonons.

Alex Zettl's team has employed carbon nanotubes to create a thermal rectifier, a device that controls the flow of heat, in addition to conducting thorough examinations of the thermal characteristics of nanotubes. Trimethyl cyclopentadienyl platinum, a substance with a high mass density, was loaded into one end of a tube to accomplish this. The system's asymmetric thermal conductance was shown, with more heat flowing in the direction of decreasing mass density. Such a "thermal diode" could help keep microelectronic devices from overheating.

Nanotubes' physical stability

Gary Tibbetts published the first theoretical study on the stability of carbon tubules as a function of diameter in 1983. Tibbetts discovered that the strain energy of a thin graphitic tube varied with 1/ using a continuous model (diameter). This suggests that the strain energy varies with 1/for each atom (diameter) 2. Many groups have conducted more thorough theoretical analyses of nanotube stability in the wake of the discovery of fullerene-related nanotubes. For all potential tubes with diameters smaller than 1.8 nm, John Mintmire and colleagues at the Naval Research Laboratory in Washington calculated the strain energies per carbon atom using empirical potentials. Also, they discovered that, roughly speaking, the strain energy per atom changed.The strain energy approaches that in planar graphite for tubes greater than roughly 1.6 nm in diameter. It's important to note that this diameter is about equal to the lowest yet recorded in multiwalled nanotube experiments. Strain energy was discovered by Mintmire and colleagues to be independent of tube structure. In order to ascertain the stability of nanotubes, some researchers have used a slightly different strategy. This entails weighing the energy obtained by the removal of edge atoms against the energy cost of bond-bending and seeing a nanotube as a graphene strip that has been rolled up. According to simulations of this kind, Sawada and Hamada discovered that tubes are more stable than strips above a threshold diameter of around 0.4–0.6 nm. Similar results were obtained by separate computations by Lucas, Lambin, and Smalley.Charlier and Michenaud have thought about the energetics of multiwalled carbon tubes. They discovered that the energy acquired by adding an additional cylindrical layer to the center one was on par with the energy gained by bilayering graphite. It was determined that 0.339 nm was the ideal interlayer separation between an inner (5, 5) and an outer (10, 10) nanotube. The turbostratic graphite's 0.344 nm 002 spacing is a little less than this. The interlayer spacings in nanotubes may vary quite a little, according to experimental observations, although they are normally about 0.34 nm. They discovered atomic-scale stability at temperatures nearing 3000 °C using a specifically built thermal platform capable of operating at severe temperatures and real-time TEM. This implies that carbon nanotubes are more durable than diamond or graphite.

DISCUSSION

Superlatives abound in a list of carbon nanotubes' physical characteristics. The best nanotubes, for instance, have mechanical qualities that are better to any other known fiber. As we've seen, several research have shown that arc-grown multiwalled tubes have Young's moduli of around 1 TPa and tensile strengths on the order of 50 GPa (although other studies have reported greater values for tensile strength). Comparable numbers for single-walled tubes were discovered. The only other materials that even closely resemble them in terms of characteristics are regular carbon fibers, which are made by pyrolyzing organic precursors. Nevertheless, carbon fibers only have either a high modulus or a high strength; they do not have both of the qualities seen in nanotubes. As was mentioned in the section above, carbon nanotubes have a very high thermal stability. The extraordinarily high electric current-carrying capacity of the tubes, as was described in the preceding chapter, is largely explained by this stability. Moreover, carbon nanotubes seem to have remarkable thermal conductivity. For arc-grown MWNTs, values of more than 3000 W m K1 at room temperature have been discovered.

The fervor around carbon nanotubes. It's crucial to note that not all nanotubes have these exceptional qualities, however. Because to the relatively large concentration of flaws in these tubes, catalytically generated MWNTs in particular fall short in a number of areas. Consequently, the research by László Forró and colleagues discovered that the elastic modulus of CVD-grown tubes was only 27 GPa on average. One may speculate that annealing the flaws out will increase rigidity. Nevertheless, the Forró group discovered that the greatest moduli were remained under 100 GPa even after heating to 2400 °C (7.32). Similar to how MWNTs generated by catalysis have substantially lower thermal conductivities than arc-grown tubes . Hence, it would seem that catalytically-grown MWNTs shouldn't be employed when the greatest qualities are needed, and that techniques for producing arc-quality tubes in large numbers still need to be developed.

This chapter has also covered the optical features of nanotubes in addition to their mechanical and thermal characteristics. While they don't lend themselves to applications as easily, fluorescence spectroscopy is proven to be a useful technique for determining nanotube structure (although it only applies to semiconducting tubes). Raman spectroscopy has also developed into a very significant and popular technique for analyzing both bulk nanotube materials and individual tubes.

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CHAPTER 12

CHEMISTRY AND BIOLOGY OF NANOTUBES

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Early 1990s attempts to open and fill the tubes led to the first understandings of the chemistry of carbon nanotubes. This experiment amply demonstrated one very fundamental property of nanotube chemistry: they are more reactive at the tips, as discussed in Chapter 10. In fact, the interaction of acids and other chemicals with nanotubes may be quite selective, attacking just the faulty areas. Since this pioneering study, there has been a sharp increase in interest in the functionalization of carbon nanotubes. By connecting hydrophilic species to these typically hydrophobic structures, functionalization in numerous experiments has been used to simply solubilize the tubes. Yet, as will be shown, the chemical modification of nanotubes is proving to be useful in a variety of applications, from the creation of sensors to the manufacturing of carbon nanotube composites. In addition to covalent functionalization, "non-covalent functionalization," or joining molecules to nanotubes without actually creating chemical bonds, is also of significant interest [1]–[3]. The benefit of this method is that it preserves the tubes' structural integrity, allowing for the retention of all of their qualities. Van der Waals bonds between planar groups and the tube walls or helically wrapping molecules around the tubes may also be used to create non-covalent functionalization. A review of the techniques for chemically functionalizing carbon nanotubes opens this chapter. A description of functionalization using biomolecules is then covered. The finding that functionalized nanotubes may traverse cell membranes has significantly increased interest in this field since it raises the possibility of using tubes to deliver drugs into cells. Of course, it is crucial to evaluate the possible toxicity of carbon nanotubes before any such uses can be considered, and a short survey of the work that has been done on this issue is presented at the conclusion.

Covalent functionalization

It would be impossible to provide a full assessment of the constantly expanding field of nanotube chemistry in this article; instead, the goal is to use a few chosen examples to demonstrate the numerous ways that nanotubes may be functionalized. A number of reviews are available for more thorough treatments, with the 2006 paper "Chemistry of Carbon Nanotubes" by Maurizio Prato and colleagues being especially noteworthy.

Functionalization of flaws and nanotube ends

As has previously been mentioned, the use of acids in the purification and opening of nanotubes causes the functionalization of their ends and flaws. HNO3 (8.7), HNO3 + H2SO4, and H2SO4 + KMnO4 are a few of the acids and acid combinations that have been used for this. At the acid-attacked sites, these processes cause the production of carboxyl and other groups. Reaction with these groups may be used to further functionalize a compound. The University of Kentucky's Robert Haddon and associates were among the first to use this strategy. They reported a technique for condensing long-chain alkylamines in 1998, using shorter SWNTs that had carboxyl groups appended to the ends of them. This was accomplished by first reacting with octadecyla-mine and activating the carboxyl groups with thionychloride. The tubes were highly soluble in dichloromethane, benzene, toluene, chlorobenzene, 1, 2-dichlorobenzene, chloroform, and CS2. Through "end-functionalization," shorter SWNTs have been effectively solubilized. The solubilization of whole SWNTs was then proven by Haddon and colleagues [4]. The procedure they used to do this split the SWNT ropes and created an octadecylammonium SWNT-carboxylate zwitterion. The Smalley group showed that single-walled nanotubes may be connected via end-functionalization in 1998. As was previously mentioned, this procedure first entailed sonicating the tubes in acid to cut them into small lengths. To create an amide bond between the ends of the nanotubes and the alkanethiol, the shorter tubes were first treated with thionyl chloride and then with NH2-(CH2)11-SH. The tubes were subsequently linked together using gold particles that had been attached to their thiol-derivitized tips.

Treatment in an oxidizing atmosphere resulted in the opening and shortening of multiwalled tubes. The tubes were then employed to detect particular interactions with functional groups on substrates when various functional groups were subsequently bonded to the carboxyl groups at the open tip ends. We talk further about the use of nanotubes as AFM tips. Polymers having amino terminal groups, such as polyn (propionylethylenimine-co-ethylenimine) (PPEI- EI), have been grafted onto oxidized nanotubes by the amide synthesis process by researchers at Clemson University in South Carolina. The resultant polymer-grafted SWNTs and MWNTs are very soluble in water and the majority of popular organic solvents. The aqueous suspensions' optical limiting qualities were advantageous. Covalent attachment of polymers, such as poly (vinyl acetate-co-vinyl alcohol) (PVA-VA), to oxidized carbon nanotubes was also accomplished using the same procedure. By treating oxidized tubes with elemental iodine and iodosobenzene diacetate, Karl Coleman and colleagues were able to create iodinated SWNTs [5]–[7].

In order to incorporate nanotubes into composite materials and maybe modify their electrical characteristics, it is interesting to add silyl moieties to their walls. Masami Aizawa and Milo Shaffer explained how different silyl sources react with polar groups that have been added to the surface of multiwalled tubes by acid oxidation. Multiwalled nanotubes' asymmetric end-functionalization was shown in 2004 by Liming Dai's team. This was accomplished by growing aligned MWNT films on substrates, removing them, and setting them on the surface of a liquid like water or alcohol. Just one end of the tubes could be functionalized since the films floated on the liquid surface due to the hydrophobic nature of the tubes. The films might then be reversed and the ends of a separate functional group joined. The process of functionalization was photochemical. This brilliant method has the potential to self-assemble a significant number of nanotubes.

Sidewalls that function

The functionalization of previously oxidized nanotubes was the major topic of the previous section. Typically, 'pristine' tubes must be directly treated in order to functionalize the sidewalls of nanotubes. Consideration of fullerene chemistry may provide some significant insights into the reactivity of nanotube sidewalls. Research on several fullerenes have shown that curvature has a significant impact on how reactive they are in addition reactions. The sp2 atoms become more pyramidalized as the carbon shell's curvature increases, which increases the likelihood that addition processes will occur [8]. The example of C70, whose polar bonds are much more reactive than those at the flatter equatorial area, serves as an illustration of this phenomenon.

The sidewalls of nanotubes cannot be functionalized without the application of a highly reactive chemical since their curvature is much less than that of tiny fullerenes like C70. Moreover, it follows that smaller-diameter nanotubes will probably exhibit greater reactivity than larger-diameter tubes. While there is no conclusive data, it has been hypothesized that metallic SWNTs may be more reactive than semiconducting tubes.

Fluorination

Researchers from Rice University identified fluorination as one of the first methods for functionalizing the sidewalls of SWNTs in 1998. Purified buckypaper served as the starting point for these studies, and it was exposed to elemental fluorine at temperatures ranging from 150 to 600 °C. The degree of fluorination for tubes heated to 600 °C was calculated to be 0.1–1. When the functionalized tubes were exposed to hydrazine at ambient temperature, defluorination occurred, seemingly returning the tubes to their initial structures. The fluorinated SWNTs might be dissolved in alcohols by ultrasonication, according to further research. Other groups have since employed elemental fluorine to fluorinate nanotubes, and the use of XeF2 has also been investigated. Nanotubes have been further functionalized utilizing fluorination as the foundation, for instance, by employing alkyl lithium reagents [9], [10].

Include carbenes

Haddon and colleagues showed the functionalization of nanotube sidewalls using a carbene about the same time as Rice's work on fluorination. It is widely known that 1,1-dichlorocarbene may dissolve C=C bonds bridging two neighboring six-membered carbon rings. By use of this reaction, Haddon and colleagues were able to derivatize both insoluble SWNTs and shorter SWNTs that were dissolved in toluene. The mercury combination PhCCl2HgBr was used to produce the dichlorocarbene. There are instances when a zwitterionic adduct is created from the substrate in place of the cyclo-propane ring that is typically formed when carbenes react with carbon double bonds. The carbene dipyridyl imidazolium is one that responds in this manner. In addition to being utilized to functionalize fullerenes, this carbene has also been used to do so with SWNTs. Andreas Hirsch of the University of Erlangen and colleagues in 2001. In dimethyl sulphoxide, the derivitized nanotubes were highly soluble (DMSO).

Addition of nitrenes

Hirsch and coworkers also used nitrenes to show how to functionalize nanotube sidewalls. Alkyl azides were used as the nitrene precursors, and it was discovered once again that the functionalized SWNTs produced were soluble in DMSO. After functionalizing MWNTs (8.28) using azide photolysis, Maxine McCall and associates from CSIRO Molecular Science in Australia attached DNA oligonucleotides to the tubes, as will be covered in more detail below.

Modification of azomethine ylides via 1, 3-dipolar cycloaddition

C60 may be functionalized via azomethine ylides and 1, 3-dipolar cycloaddition. The Prato reaction is the name given to this reaction, which was first seen in experimentation by Maurizio Prato & colleagues. In order to solubilize SWNTs and MWNTs, Prato, Hirsch, and colleagues exploited the process, which may also occur on nanotube surfaces.

According to an aldehyde and a -amino acid were condensed to create the ylides. Due to its strong solubilizing activity, the triethylene glycol group was selected as the N-substituent group of the -amino acid, and different aldehydes were used. These modifications to single-walled nanotubes resulted in a high solubility in chloroform (up to 50 g l1), other organic solvents, and even water.

SWNTs generated by the HiPco technique may be purified by functionalizing them with azomethine ylides, as shown by Prato and colleagues. Later research by the same team (8.32) showed that SWNTs functionalized in this manner may interact electrostatically with plasmid DNA, as covered. An alternate technique for the covalent functionalization of SWNTs by azomethine ylides was disclosed by French researchers in 2006. Their strategy was centered on producing a 1, 3-dipole from the appropriate trialkyl-N-oxide by double deprotonation. They said that their technology offered a way to distinguish semiconducting tubes from metallic tubes by selectively functionalizing semiconducting tubes.

Ozonolysis in the solution phase

The State University of New York at Stony Brook's Sarbajit Banerjee and Stanislaus Wong have functionalized SWNT sidewalls using ozonolysis. Ozonolysis was conducted in the solution phase at a low temperature. Via a 1,3-dipolar cycloaddition akin to the addition of azomethine ylides, ozone ($O3$) adds to the sidewall double bonds. As a result, an unstable ozonide is created, which may then be broken down to produce a variety of functional groups, such as aldehydic, ketonic, alcoholic, and carboxyl groups. In further research, they demonstrated that smaller tubes responded in the ozonolysis process more quickly than bigger tubes. Ozonolysis, as discussed, produces purified nanotube samples in addition to functionalized tubes.

Increase in radicals

Radicals have been used for nanotube functionalization rather often. This has been accomplished electrochemically in certain instances, as will be detailed below, and thermally and photochemically in other instances. In a 2003 work, the Rice group employed radicals created by thermally breaking down alkyl or aryl peroxides to create phenyl and undecyl sidewall functionalized SWNTs. About the same time, László Forró and colleagues reported a comparable technique. the photoinduced addition of perfluorinated alkyl radicals to tube walls. This was achieved by shining a mercury lamp over a solution of SWNTs and an alkyl iodide.

Silylation

Above, it was noted that Aizawa and Shaffer's work on the silylation of MWNTs was done. In this study, silylation was accomplished by combining silyl sources with tubes that had been acid-oxidized. Hemraj-Benny and Wong reported silylation of perfect single-wall tubes in 2006. Trimethoxysilane and hexaphenyldisilane, two distinct organosilanes, were utilized, and UV irradiation was employed to initiate the reactions. Examination electron microscopy and several kinds of spectroscopy revealed that the chemical treatment had not caused any structural damage to the functionalized tubes.

Electronic chemical processes

Since the degree of reaction can be directly controlled by an applied voltage, the electrochemical technique has the potential to be an effective strategy for chemically altering nanotubes. Researchers from Rice University have electrochemically reduced a number of aryl diazonium salts to derivatize SWNTs. As a consequence, a link was created between the surface of the nanotube and a benzene ring. The electronic characteristics of functionalized tubes seemed to have undergone a significant change, according to spectroscopic analysis.

In later research, a team from Stuttgart showed that using single-walled nanotubes as the cathode or anode in an electrochemical cell allowed for the oxidation or reduction of small molecules at the nanotube surface, resulting in radical species that could then attack the carbon lattice to form covalent bonds. As oxidative coupling led to the attachment of amines via an NH group whereas reductive coupling produced C-C bonds. It was shown that polymerized layers up to 6 nm thick might develop.

In a groundbreaking work, electrochemistry was employed by Philip Collins and colleagues from the University of California, Irvine to regulate and track the covalent functionalization of certain SWNTs. On oxidized Si wafers, the nanotubes were produced by CVD and linked to metal electrodes. Thereafter, the apparatuses were put within an electrochemical cell that contained an acidic electrolyte solution. An electrooxidation process might be generated by adding a voltage, leading to significant increases in conductance that could be ascribed to distinct oxidation events. With microsecond precision, the potential may be turned off, terminating the process after only one chemical occurrence. This method has a significant deal of promise for investigating functionalization and even creating molecular circuits.

Functionalization that is non-covalent

One kind of non-covalent functionalization is the use of commercial surfactants to increase the solubility of nanotubes. It was discovered that the commonly used ionic surfactant sodium dodecyl sulphate (SDS), which is used in goods like shampoo and shaving cream, was very useful in solubilizing both MWNTs and SWNTs. Although SDS's usage in suspending single-walled tubes for fluorescence spectroscopy was covered, its use in the purification of MWNTs was noted in Chapter 4. Ultrasonication is widely employed to aid in dispersion, and typically, around 1% of SDS is added to the aqueous solution. On the surfaces of the nanotubes, surfactant molecules may sometimes create orderly layers. Ionic surfactants function by introducing a charge to the nanotube surfaces. The behavior of the dispersion will be strongly influenced by pH once the nanotubes are dispersed by electrostatic forces. Since SDBS includes a benzyl ring, Arjun Yodh and colleagues from the University of Pennsylvania have shown that it can be more successful than SDS at dispersing SWNTs in water. Nanotubes have also been solubilized using non-ionic surfactants, such as triton X-100, for various purposes, including the creation of composite materials. They work by combining steric dispersion forces with hydrogen bonding. The nanotubes are trapped in the hydrophobic core of the micelles that are formed when the surfactants are present in high quantities.

Nanotubes' non-covalent functionalization. In the first, relatively tiny molecules with planar groups are used, and these molecules are permanently adsorb to the surfaces of nanotubes due to -stacking pressures. In the second, bigger polymeric molecules are wrapped around the tubes. The first method was invented in 2001 by the team led by Hongjie Dai. The molecule they utilized has a succinimidyl ester group as its "tail" and a planar pyrenyl group to create the van der Waals bonds. It was shown that bonds with this group might immobilize biomolecules on the sidewalls of nanotubes, as covered. After this groundbreaking study, pyrenes have been used rather often to solubilize nanotubes and bind species like magnetic nanoparticles and fullerenes to nanotubes. Porphyrins and phthalocyanines, two heterocyclic polyaromatic compounds, have also been utilized to non-covalently functionalize and solubilize nanotubes. It is thought that the interaction between these compounds and SWNTs is mostly van der Waals in nature, similar to pyrenes. Dirk Guldi, Maurizio Prato, and others have provided a thorough explanation of the interactions between single-walled nanotubes and pyrenes, porphyrins, and other compounds. Helically wrapping the tubes in a polymer is the second method for non-covalently functionalizing SWNTs. Of course, the interaction of nanotubes with polymers in relation to the creation of composite materials has been well explored, and this is discussed. In this case, the usage of polymeric systems to solubilize nanotubes is our main focus.

The Smalley group first disclosed the non-covalent association of linear polymers like polyvinyl pyrrolidone (PVP) and polystyrene sulphonate with SWNTs to solubilize them in 2001. (PSS). It was discovered that the polymers wrapped around the tubes. Many potential wrapping combinations. By altering the solvent solution, the nanotubes might be released. At the same time, studies employing the conjugated polymer poly (m-phenylenevinylene) replaced with octyloxy chains were reported by Fraser Stoddart, James Heath, and his colleagues from the University of California, Los Angeles. They were able to create a stable nanotube suspension by adding SWNTs to a solution of this polymer and sonicating the combination. In subsequent research, they wrapped both individual nanotubes and tiny nanotube bundles using similar polymers. They think that this method may really be utilized to put together nanoscale electrical gadgets. As shown in the molecular model, the UCLA group has also functionalized SWNTs non-covalently using stilbenoid dendrimers. These moderately hard polymers, according to the scientists, could be especially helpful in separating bundles of nanotubes and stabilizing individual tubes because of their well-defined topologies. There have been many more investigations of the non-covalent functionalization of nanotubes employing polymers, including the usage of crosslinked, amphiphilic copolymer micelles, pyrene-containing poly (phenylacetylene) chains, and poly(phenylacetylene) (pheny- leneethynylene).

Chemically functionalized nanotubes: Characterization

Several reaction schemes that demonstrate the creation of covalent and non-covalent bonds with carbon nanotubes are used to explain the previous sections. In reality, it is sometimes challenging to get convincing proof that such ties have developed. There are many causes for this. First off, the majority of samples include non-nanotube carbon, which may also be functionalized. Another issue is that tubes of all shapes and sizes are always present, which makes it more difficult to analyze functionalized materials. The interpretation of spectral characteristics itself is not always straightforward when spectroscopic techniques are used. Transmission electron microscopy (TEM) is beneficial in determining if functionalization has had an impact on the tubes' structure, although direct imaging of functional groups on nanotube sidewalls has not yet been proven. The existence of non-carbon species adhering to tubes may also be verified using energy dispersive X-ray microanalysis in the TEM.

Functionalization of living things

Malcolm Green, Edman Tsang, and his colleagues from Oxford conducted what is likely the first research on the interaction of biological molecules with carbon nanotubes in the middle of the 1990s. While the main goal of this research was to introduce molecules inside tubes, it was discovered that biological molecules, such as enzymes and DNA oligomers, could be immobilized on the surfaces of the tubes. These pairings of biomolecules and conducting nanotubes might be used in nanoscale sensing technology. The study by Lieber and colleagues noted above, in which modified MWNTs were utilized as tips for AFM, was likely the first instance of bio-functionalized nanotubes being employed in practical applications. One of these experiments employed nanotube tips that had been covalently modified with the biotin ligand by the creation of amide bonds to probe immobilized streptavidin molecules adsorbed on mica. Hence, the binding forces between the biotin-streptavidin pairs could be measured. The next sections can only provide a brief overview of this topic since interest in biological functiona- lization has skyrocketed since these groundbreaking investigations. Once again, a lot of outstanding reviews have been released.

Proteins

As the Oxford group has shown, proteins may bind to nanotubes by non-specific adsorption or through more specialized connections that can be covalent or non-covalent. The observed robust protein interaction in the case of non-specific adsorption may be partially due to the carbon nanotubes' affinity for amino acids. A variety of proteins have been bonded covalently or non-covalently using one of the several functionalization techniques covered in the preceding sections.Streptavidin and HupR, a transcriptional regulator from a photosynthetic bacteria, were orderedly adsorbed onto MWNT surfaces in 1999, according to a fascinating investigation of the non-specific adsorption of proteins by French researchers. This adsorption resulted in a helical shape. It was proposed that crystallizing proteins on nanotubes would be advantageous for TEM structural analyses. Studying the relationship between streptavidin and SWNTs was done by Hongjie Dai and colleagues. They discovered that SWNTs, like MWNTs, were easily coated with the protein. A combined US-Italian group demonstrated that single-walled tubes may also be solubilized by sonication in the presence of streptavidin. The nanotube surfaces must be responsive to specific proteins while rejecting others in order to be useful in various applications, such as the creation of particular biosensors. This was made possible, as Dai et al. showed, by coating the tubes with a surfactant that contains poly-(ethylene oxide), followed by the conjugation of certain receptors to the coated tubes. The subsequent electronic detection of the adsorption of certain proteins to the functionalized tubes, as previously covered, is possible. Ferritin strongly adsorbed onto SWNTs in an aqueous environment, according to reports from the Oxford and Clemson groups. According to the Clemson researchers, ferritin adsorption was really so significant that it caused the SWNTs to become soluble in water.As associates have shown that a molecule with a planar pyrenyl group may attach non-covalently to the surfaces of SWNTs. This molecule's "tail" was made up of a succinimidyl ester group. These researchers used a procedure that entailed the nucleophilic replacement of the succinimide by an amine group on the protein, resulting in the creation of an amide bond, to show that proteins could be immobilized on the nanotubes. It was also shown that additional biomolecules, such as ferritin and streptavidin, may be immobilized.Enzyme binding to nanotubes has also received a considerable lot of attention, in part because of potential uses in sensors. It has previously been established that the Oxford Group performed early research on the immobilization of enzymes on both the inner and outer surfaces of MWNTs. In this study, it was shown that when linked to the tubes, the enzymes maintained a reasonable level of bioactivity. Researchers from the Rensselaer Polytechnic Institute in New York examined the functions of two enzymes that were adsorbed onto SWNTs in 2004: R-chymotrypsin (CT) and soybean peroxidase (SBP). In contrast to the adsorbed R-chymotrypsin, the soybean peroxidase preserved just 1% of its original activity after adsorption. Both enzymes exhibited structural modifications during adsorption, according to FT-IR spectroscopy analysis. Researchers from Australia have attached the enzyme glucose oxidase (GOx) to vertically aligned arrays of SWNTs on gold, for potential use as a sensing device, while researchers from Arizona State University demonstrated that enzyme multilayers on MWNTs exhibited remarkably sensitive electrochemical detection of proteins and nucleic acids. Cees Dekker's team immobilized glucose oxidase on semiconducting SWNTs produced on a silicon wafer by using a planar pyrenyl group connecting molecule.

A lot of the research on the bio-functionalization of nanotubes has focused on potential medicinal uses. Finding that functionalized tubes may cross cell membranes has been found to be a highly significant advance in this regard. It seems that a European team headed by Alberto Bianco, Kostas Kostarelos, and Maurizio Prato gave the first demonstration of this in 2004. Here, we go into more detail about this technique, which involves introducing plasmid DNA into mammalian cells. Soon after, Nadine Kam and Hongjie Dai published a study demonstrating the ability of protein-functionalized nanotubes to traverse cell membranes. It was thought that endocytosis, in which cells take in foreign objects by engulfing them with protrusions of their cell membranes, was the mechanism behind this process. In a follow-up investigation, Dai's team demonstrated that cancer cells grown in culture could be targeted with nanotubes and killed using high temperatures. Folic acid was attached to the nanotubes' surface to achieve this. Folic acid interacts with a folic acid receptor protein that is widely distributed on the surfaces of several cancer cell types.

Using antibodies that are specific to antigens on the surfaces of cancer cells would be a more direct method of attacking cancer cells. Nanotubes that have been functionalized with antibodies may be beneficial for biosensors. Several teams have looked at the antibody binding to nanotubes with these types of applications in mind. Using the Langmuir-Blodgett approach, James Ruling of the University of Connecticut created aligned arrays of SWNTs and affixed antibodies to the ends of the tubes. They were subsequently put to use in an electrochemical sensor that could detect up tiny concentrations of secondary antibodies to the prostate specific antigen.

The University of Delaware's Balaji Panchapakesan and his colleagues have shown the potential use of antibody-functionalized nanotubes in photodynamic treatment for breast cancer. Using a succinimidyl ester bond, monoclonal antibodies targeted to breast cancer cells were joined to SWNTs. The complexes were joined to particular employing lasers to stimulate cancer cells using near-infrared light. This caused the cells to be destroyed by heat. Moreover, radioactive therapeutic drugs have been delivered to tumors using nanotubes functionalized with antibodies.

DNA and RNA

Several factors might make the bonding of DNA and other nucleic acids to nanotubes fascinating. Nucleic acid functionalization of nanotubes may provide a practical way to solubilize the tubes at a relatively basic level. It's possible that DNA-guided assembly may be utilized to create networks of nanotubes, and that nucleic acid-modified nanotubes could be helpful in sensors. Maybe most intriguingly, therapeutic DNA might be delivered into cells via nanotubes. The development of DNA-nanotube complexes and their use are now briefly covered.

In the presence of single-stranded DNA, they demonstrated that bundled SWNTs may be disseminated in water by sonication (ssDNA). AFM measurements and optical absorption and fluorescence spectroscopy gave proof that the carbon nanotubes were separately distributed. According to molecular modeling, the ssDNA was wrapped around the tubes in a helical pattern, with the bases on the inside, connected to the surface via -interactions, and the hydrophilic sugar-phosphate backbone on the outside, enabling water solubility. They also showed that using ion-exchange chromatography, carbon nanotubes coated with DNA could be divided into fractions with various electrical configurations. Other teams have also utilized DNA to dissolve nanotubes.

Single-walled tubes coated with DNA have been investigated as potential sensing technologies by Zheng and colleagues. In a preliminary investigation, they demonstrated that

SWNTs could identify minute structural changes in adsorbed DNA brought on by metal ions. They started by wrapping DNA molecules around the tubes, and then they added different ions (such as Ca2+, Hg2+, and Na+), which caused the DNA to alter conformation. This decreased the area of contact between the DNA and the tubes, which perturbed the electrical structure and altered the IR spectra. Zheng's team showed that the device can detect Hg2+ ions in whole blood, ink, and live mammalian cells and tissues, demonstrating that it can function as a sensor. In a later publication, they discussed using a similar technique to identify certain DNA sequences. To do this, single DNA strands were wrapped around the test tubes, and the binding of complementary DNA strands was detected using this method. This kind of sensor may be used to find pathogenic organisms or discover genes linked to cancer.

There has been a lot of research on the covalent attachment of DNA to tubes in addition to investigations of non-specific interactions of DNA with nanotubes. Chris Dwyer and colleagues from the University of North Carolina in Chapel Hill gave one of the first demonstrations. In order to create a solution of open-ended tubes containing terminal carboxyl groups, single-walled nanotubes were first purified in HNO3 and then oxidized in an HNO3/H2SO4 combination. Then, between them, a condensation reaction was carried out.

Amide bonds are created between the DNA and tube ends by carboxyl groups and DNA strands with amino termini. As previously reported, Australian researchers have functionalized MWNTs using azide photolysis, and subsequently attached DNA oligonucleotides to the tubes. By attaching gold nanoparticles modified with complementary sequence DNA to the functionalized tubes, the locations of DNA attachment could be seen.

Carbon nanotubes functionalized with DNA have been shown by many groups to be effective DNA sensors. For instance, Liming Dai and associates covalently bonded certain DNA sequences to nanotubes and used them to detect complementary DNA and DNA chains of particular sequences with excellent sensitivity and selectivity. Nanotube networks have furthermore been constructed using DNA. One of the first instances of this was shown by Israeli researchers who demonstrated in 2003 that the interactions between proteins and DNA could be utilized to assemble nanotubes into a field-effect transistor that worked at ambient temperature. About the same time, Huijun Xin and Adam Woolley from Brigham Young University reported how to place single-walled tubes using aligned DNA molecules on a Si substrate. The chemical PMA was used as a linker between the DNA and the tubes. This molecule's amine group is electrostatically drawn to the DNA's negatively charged phosphate backbone, while its pyrenyl group engages in stacking forces with SWNT surfaces. Almost 60% of all deposited SWNTs on substrates were aligned on DNA segments, according to AFM pictures. The progress of using DNA to create networks of nanotubes and other nanostructures is still in its infancy. The field's potential has been examined.

Another fairly recent field of study is the use of nanotubes to transport DNA into cells for potential gene therapy. The 2004 study by Bianco, Kostarelos, and Prato seems to be the first example of this, as was already noted. In this study, the walls of nanotubes with ammonium functionalization were coupled with plasmid DNA. After that, a culture of mammalian cells was in touch with the functionalized tubes, and the cells' entry into the functionalized tubes was seen. This groundbreaking breakthrough sparked a lot of attention, and many organizations are surely working to employ nanotubes to transport nucleic acids into cells all across the globe. Nevertheless, there have only been a few number of published investigations too far. One example is a 2007 publication by Hongjie Dai's team that outlines a method for using RNA-functionalized nanotubes to prevent HIV infection. Once the short RNA snippets were joined to the SWNT sidewalls by amine groups, human T-cells and primary blood cells were given the nanotube-RNA hybrids. The RNA snippets 'turned off' the genes for HIV-specific receptors on cell surfaces, preventing HIV viruses from attacking. There are broad reviews on DNA and carbon nanotubes in addition to the review article previously mentioned.

Carbon nanotube toxicity

A consensus has not yet been reached in the early stages of research on how carbon nanotubes interact with biological systems and how harmful they are. Nanotubes' security and biocompatibility. So, the purpose of this section is only to present some of the research that has been done in this area without attempting to reach any firm conclusions. It is advisable to start by taking into account several proven types of carbon's biocompatibility. Carbon compounds, such as pyrolytic carbon and diamond-like carbon, are already utilized rather often in medicine, as Darren Martin and colleagues noted in a helpful overview. On the other hand, it has been shown that high-purity carbon black may cause pulmonary tumors in rats and increased oxidative stress in human lung cells when tested in vitro. Significantly, it was shown that smaller carbon black particles were more harmful than bigger ones, which may indicate that extensively scattered carbon compounds need extra caution.

Andrzej Huczko and colleagues from the University of Warsaw made one of the first efforts to evaluate the health risks of carbon nanotubes in 2001. This study examined the impact of soot containing nanotubes on guinea pig lung function and found no indication of any abnormalities. However in later research, the same team claimed that guinea pigs exposed to nanotubes might develop quantifiable lung disease. Several research teams have verified that nanotubes may cause inflammation in mice's lung tissue. In a research that received a lot of attention when it was published in 2004, David Warheit and colleagues discussed the results of injecting rats' lungs with SWNTs. While it was shown that 15% of the rats given the injections died within 24 hours, the cause of death was mechanical obstruction of the major airways by aggregation of tubes rather than actual toxicity. If the nanotubes were intentionally infused rather than breathed in, this type of barrier may not happen. Warheit has consequently advised doing a research on inhalation toxicity using tube aerosols.

The cytotoxicity of carbon nanotubes, or their toxicity to certain cells, has been the subject of several research. The US National Institute for Occupational Safety and Health's Anna Shvedova and colleagues published one of the first studies on nanotube exposure in 2003, demonstrating how exposure to them damaged human keratinocyte (skin) cells. Yet, Irish researchers discovered that SWNTs were hardly harmful to human lung cells. Researchers from Rice University discovered in an intriguing research that sidewall functionalized SWNTs had much lower cytotoxicity than unfunctionalized tubes.

There is still considerable work to be done in demonstrating the toxicity and biocompatibility of carbon nanotubes, Martin and colleagues said in their review from 2006. the issue was stated more bluntly by Vicki Colvin of Rice in November 2007: "The bad news is that we now have far over five distinct viewpoints regarding carbon nanotube toxicity". It is sensible to err on the side of caution while preparing and handling these documents given the ongoing ambiguity in this area. Notwithstanding the fact that nanotubes seem to be less likely than previously believed to get airborne, precautions should be made to prevent inhaling nanotube-containing material. Thus, it is advised to use a face mask. There isn't much precise information available here about skin contact, although using gloves while handling nanotube material would seem like a prudent precaution. For further details on the studies of the interactions of carbon nanotubes with biological systems.

DISCUSSION

In recent years, significant progress has been made in the chemistry and biology of nanotubes. The chemical modification of nanotubes was mostly restricted to the creation of carboxyl and other groups at the tips by acid treatment until about 1999, when the previous edition of this book was released. Further research has shown that reactive substances like halogens, arynes, or carbenes may be used to functionalize the sidewalls of nanotubes. Many compounds, including biomolecules, may be chemically bonded to the sidewalls in this manner. Large strides have also been achieved in the non-covalent functionalization of nanotubes, which involves coiling polymeric molecules around the tubes or -bonding tiny molecules to the walls of the tubes. Non-covalent bonds may also be formed between biomolecules including proteins, nucleic acids, and others and nanotubes.

The whole field of nanotube research is reaping the rewards of these developments. Purification or processing of the nanotubes have been substantially eased by the ability to solubilize and separate the tubes. Functionalization is often utilized in the creation of carbon nanotube composites to strengthen the link between the nanotubes and the matrix material, as will be covered in the next chapter. Moreover, many organizations have shown how functionalization may be utilized to arrange nanotubes into specific arrays or networks. Another fast expanding field is the fabrication of chemical and biological sensors using functionalized nanotubes, and the potential for employing nanotubes in medical applications, such as gene therapy, is generating a lot of interest.

There is still considerable work to be done despite these significant accomplishments. Before considering any medicinal uses, we must have a far greater knowledge of how carbon nanotubes interact with biological systems and their toxicity. It might be claimed that carbon nanotube chemistry won't mature until we have a completely dependable method of creating tubes with a known structure. Then, using spectroscopic and other techniques, chemically modified nanotubes may be thoroughly characterized.

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CHAPTER 13

CARBON NANO COMPOSITES

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The best way to take use of many of the remarkable features of carbon nanotubes and other materials discussed in this book is to incorporate the materials into a matrix. A great deal of interest has been generated in the creation of composite materials including nanotubes for structural purposes, especially because of their outstanding mechanical characteristics. While polymer matrices have been used in many of these composites, other matrix materials including metals and ceramics are also of interest. The propensity of nanotubes to cling together, the difficulty of forging links between tubes and matrix, and issues related to specific nanotube-matrix mixes' physical qualities all make it challenging to manufacture such composites. This chapter's goal is to provide a summary of the enormous amount of research that has been done on carbon nanotube composites and to evaluate how well that research has succeeded in maximizing the potential of nanotubes. The addition of nanotubes to polymer matrices is first taken into account [1], [2].

Making composites out of polymers and carbon nanotubes

Mixing of solutions

The process of mixing nanotube dispersions with solutions of the polymer and then carefully evaporating the solvents is perhaps the easiest technique to create nanotube/polymer composites. Many polymers, such as polyvinyl alcohol, polystyrene, polycarbonate, and polyethylene, have been processed using this technique (methyl methacrylate). Before adding the nanotubes to the polymer solution, they are often functionalized to aid in solubilization and mixing. An early use of this strategy was developed by Windle and colleagues, who utilized acid treatments to disperse catalytically generated MWNTs in water. These dispersions were then combined with an aqueous solution of the polymer to create nanotube/PVA composites, which were subsequently cast as films. The impact of covalent functionalization on the characteristics of composite materials has been studied in the past. The compatibility of functional groups with the polymer matrix may sometimes cause issues. This may be prevented by functionalizing the nanotubes with polymers that are structurally related to or identical to the matrix polymers [3], [4].

The solution technique may be used to generate a polymer composite without always functionalizing the nanotubes or using a surfactant. In order to scatter MWNTs in toluene, Rodney Andrews and colleagues from Kentucky utilized a high-energy ultrasonic probe. They next combined the dispersed suspension with a weak solution of polystyrene in toluene, once again using ultrasonic agitation. The polymer solution's low viscosity made it possible for the nanotubes to travel freely throughout the matrix. To produce MWNT-doped films, the mixture was cast onto glass and the solvent was drained. Drops of the blended solution were applied on Cu TEM grids to create specimens of the composite for TEM. A thin coating of the composite was left hanging over the grid bars after the toluene evaporated. This is a micrograph of one of these films, which shows the superb dispersion that was accomplished.

Notably, nanotube/polystyrene composites have also been made by in situ polymerization, as will be explained below. Inhomogeneous distribution of the nanotubes in the matrix due to agglomeration of the nanotubes during solvent evaporation is a possible issue with solution mixing. Spin-casting, which speeds up evaporation, may help with this.

This entailed adding an excess of non-solvent to the nanotube/PMMA sus- pension (water). The tubes are then trapped by the chains of precipitating polymer, avoiding agglomeration. Nanotube ribbons and fibers may be created using the solution mixing technique. As mentioned, Ray Baughman and colleagues enhanced the mechanical characteristics of MWNT yarns by incorporating PVA into them by soaking them in a solution of the polymer. In 2000, Philippe Poulin of the University of Bordeaux and colleagues reported a process for making SWNT/PVA ribbons constantly. They started out by soaking the tubes in sodium dodecyl sulfate. A stirred PVA solution was then injected with the SWNT dispersion using a syringe needle, where it produced ribbons with widths corresponding to the needle. SEM analysis of the ribbons revealed that, as a result of flow-induced alignment, the SWNT bundles were preferentially orientated along the main axis. Baughman's team improved this procedure by adding a second step that required unwinding the fibers, followed by washing and drying to create composite fibers with theoretically infinite length. The mentioned good mechanical qualities of the fibres, which were around 50 m in diameter and included 60% SWNTs by weight, were evident.

Electro-spinning is another method that has been utilized to create nanotube/polymer fibers. This entails filling a syringe with a polymer solution (or melt) and forcing the liquid toward the needle's tip where it will condense into a droplet. A long-lasting jet results from the introduction of a strong electric field between the needle and a collecting electrode, and the evaporation of solvent causes the creation of fibers. This method has been used to create polymer fibers with multiwalled tubes and single-walled tubes.

Melting procedure

The solution mixing method is only applicable to polymers that readily dissolve in ordinary solvents. Using melt processing methods while using thermoplastic polymers, which soften and melt when heated, provides an option. The drawback is that owing to the high viscosities of the mixes, it is challenging to generate large concentrations of nanotubes and homogenous dispersions of nanotubes in melts as compared to solutions. Nevertheless, shear mixing may be used to enhance nanotube dispersion. Moreover, melt processing is well suited for processes like extrusion and injection molding.

In order to disperse catalytically generated nanotubes in a variety of polymers, including high-impact polystyrene, acrylonitrile-butadiene-styrene, and polypropylene, the Kentucky group employed shear mixing. Nanotube dispersion was calculated as a function of temperature and mixing energy, and the composites were made into thin films and fibers. SWNTs were dispersed in polystyrene, polyethylene and poly (methyl methacrylate) (PMMA) using melt mixing techniques developed by the Pennsylvania group in collaboration with colleagues from NIST. The PE composites were created by melt-spinning in this instance [5]–[7].Fibers with a strong alignment of nanotubes. Other teams have also created composites made of nanotubes and polyethylene and polypropylene using melt processing. The Polymer Research Institute in Dresden's Petra Pötschke and associates created MWNT/PE composites with weight fractions ranging from 0.1 to 10 wt% using a screw extruder. It was discovered that the composites' electrical conductivity was more than 16 orders of magnitude greater than PE's. Excellent mechanical characteristics were also seen, albeit they started to deteriorate over a certain tube loading.

Pötschke and associates have investigated how to disseminate nanotubes in polycarbonate using melt processing methods. First, they prepare a nanotube/polycarbonate "masterbatch" with a high concentration of tubes usually 15% weight percent. Next, in a conical twin screw extruder, this is carefully diluted with various quantities of PC to produce various tube concentrations. This method resulted in good dispersions of MWNTs and SWNTs generated catalytically in PC resin. A fiber-spinning equipment might also be used to create extruded strands of the composite. The polycarbonate/nanotube composites had excellent mechanical characteristics.

In situ polymerization

Using the monomer as a starting material rather than the polymer and then performing in situ polymerization is an alternate technique for creating nanotube/polymer composites. One of the first to use this technique was Wolfgang Maser and colleagues, who created a MWNT/polyaniline composite. They demonstrated how this method might be used to create composites with MWNT load-ings of up to 50%. As detailed later, transport studies on the composite showed significant changes in the electrical behavior, demonstrating the strong interaction between nanotubes and polymer. Following this pioneering study, other additional nanotube/polymer composites, such as MWNT/polystyrene, MWNT/polyurethane, MWNT/polypyrrole, and MWNT/nylon, have been created utilizing in situ polymerization.

A lot of research has been done on creating nanotube/epoxy composites. In order to do this, the nanotubes are normally initially dispersed in the resin before the resin is hardened using a hardener. Most of the time, epoxy is liquid at first, making it easier to combine with nanotubes. Ajayan and colleagues conducted one of the early investigations on an epoxy that contains nanotubes, although not with the intention of creating a composite material. Purified tubes were embedded in epoxy resin with the intention of obtaining cross-sectional pictures of the nanotubes after being thinly sliced with a diamond knife. The nanotubes were discovered to have oriented themselves in the direction of the knife movement, as illustrated, although cross-sections were not seen after this treatment. While in some instances tubes seem to come into direct contact with the knife and are dragged out of the matrix and orientated unidirectionally on the surface, Ajayan et al. claim that the alignment is mostly a result of extensional or shear flow of the matrix created by the cutting. Recent study by Australian scientists shown that entangled MWNTs in an epoxy matrix may be separated and straightened out by continuous shear between steel discs.

There have been several reported novel methods for creating nanotube/epoxy composites. By soaking "buckypaper" in epoxy that has been diluted with acetone, Ben Wang's team at the Florida Advanced Center for Composite Technologies has created SWNT/epoxy composites and reported excellent mechanical characteristics. Using a technique called "bubble-blowing," Charles Lieber's team has created thin films of a nanotube/epoxy hybrid. In this study, MWNTs were suspended in tetrahydrofuran after initially being treated using n-octadecylamine. The nanotube suspension was then physically combined with an epoxy before being let to cure. The mixture was blown into a bubble when it reached a certain viscosity range. It would be possible to transfer the films made in this manner to substrates or open frame architecture. This method of creating large-scale thin films of polymers containing nanotubes seems to be quite promising [7]–[9].

How nanotubes affect the structure of polymers

It is important to quickly address the impact that the addition of nanotubes may have on polymer microstructure before moving on to a detailed discussion of the characteristics of carbon nanotube/polymer composites. While little research has been done on this subject, many groups have shown that even modest amounts of nanotubes may have a significant impact on the polymer's shape and crystallization. Consequently, MWNTs generated by an arc boosted the crystallinity of PVA, according to research by Jonathan Coleman and colleagues. The similar result was seen by Georgia Tech researchers, who captured HRTEM pictures displaying sharp PVA lattice fringes oriented perpendicular to the nanotube axis. Several other polymers have also shown evidence of nanotube-induced crystallization, which may play a significant role in influencing the characteristics of composite materials. It has been discovered that in chiral polymers, the inclusion of nanotubes may enhance stereochemical selectivity. One of the enantiomers was synthesized in large quantities by Wenhui Song and colleagues. The causes of this are not entirely known.

Characteristics of Polymer/Carbon Nanotube Composites

Physical characteristics

To take use of the stiffness and strength of the tubes has been a major motivation for most of the work done on the creation of nanotube/polymer composites. Even in cases where emphasis has been concentrated on other characteristics, nanotubes' capacity to enhance a polymer's mechanical characteristics has often been a significant additional advantage. One of the first to do an in-depth analysis of the mechanical characteristics of nanotube/polymer composites was Shaffer and Windle. They previously detailed their method for creating MWNT/PVA composites. In a dynamic mechanical thermal analyser, the tensile elastic moduli of the composite films were evaluated as a function of nanotube loading and temperature. At room temperature, the composites' rigidity was not very high. The experimental results at room temperature were used to derive a 150 MPa nanotube elastic modulus using the theory created for short-fibre composites. This low value could be caused less by ineffective stress transmission than by the fragility of the nanotubes. The characteristics of the composite were more significantly impacted by the nanotubes above the polymer's glass transition temperature of 85°C.

In 2002, Jonathan Coleman and colleagues used PVA- and MWNT-based composites to get noticeably improved outcomes. Drop casting was used to create the films on the glass substrates after the composites had been created by solution-mixing. The PVA's Young's modulus and hardness were both improved by factors of 1.8 and 1.6, respectively, by the addition of 1 weight percent of nanotubes. This improvement over Shaffer and Windle's first findings is due to both better tube quality and stronger interfacial adhesion. Studies using TEM data supported the latter. The same group reported a 4.5-fold rise in the Young's modulus of a PVA with the inclusion of carbon nanotubes in more recent study. As mentioned above, it was discovered that an increase in polymer crystallinity caused by the presence of nanotubes contributed to the improvement of the Young's modulus [10].

The Kentucky group investigated the mechanical characteristics of nanotube/polystyrene composites. The average length of the two samples of catalytically generated MWNTs was 15 m, whereas the average length of the other sample was 50 m. They increased the elastic stiffness of the polymer by 36% and 42% for short and long tubes, respectively, with the addition of 1% nanotubes by weight (the pristine polymer modulus was 1.2 GPa). A 25% improvement in tensile strength was seen in both situations. The results of theoretical calculations with a 450 GPa nanotube modulus were as follows:

The rigidity of the polymer improves by 48% and 62% for short and long tubes, respectively. As the observed and theoretically anticipated composite moduli were within 10% of each other, it was clear that the external tensile stresses had been successfully transferred to the nanotubes through the tube-polymer interface. The mechanical characteristics of the composites changed more noticeably with greater nanotube concentrations. Young's modulus rose gradually for MWNT/polystyrene composites containing 2.5 to 25 vol% nanotubes from 1.9 to 4.5 GPa, with the biggest increases occurring when the MWNT concentration was at or above around 10 vol%. The relationship between tensile strength and nanotube concentration, however, proved more complicated. Tensile strength fell from the pristine polymer value of around 40 MPa at lower concentrations 10 vol.%, only reaching it when the MWNT level reached over 15 vol.%. In a research on nanotube-reinforced polyethylene by a team from the University of Sydney, it was discovered that when the nanotube loading reached 10 wt%, the Young's modulus and tensile strength increased by 89% and 56%, respectively. State of Pennsylvania

According to group, the addition of 5 wt% SWNT increased the tensile modulus of PE fiber from 0.65 to 1.25 GPa. In their SWNT/nylon composites, the same group also noted remarkable results: the addition of 2 wt% SWNTs resulted in a 214% increase in elastic modulus and a 162% rise in yield strength compared to pure nylon. The usage of functionalized nanotubes, which created a tight link between the nanotube and the polymer, probably contributed to these capabilities. The SWNT/PVA fibers made by Baughman and colleagues may have shown the most amazing mechanical capabilities (9.16). These materials possessed very high toughness, 1.8 GPa tensile strengths, and Young's moduli up to 80 GPa, which suggested uses like bullet-proof vests. SWNT/PVA fibers generated using the coagulation spinning technique possessed outstanding shape-memory properties, as shown by Poulin's group in 2007.

Nanotube/polymer composites' tensile fracture processes have been the subject of much research. The Kentucky employees conducted deformation measurements inside a transmission electron microscope while working on MWNT/PS composites. Above was a description of their sophisticated TEM specimen preparation technique. Localized thermal strains caused by the electron beam's focus on the thin coating caused the composite to shatter. Changing the beam flux onto the sample would allow one to regulate the crack's rate of propagation. Our in-situ TEM investigations revealed that the fractures often originate in low nanotube density locations and spread along porous nanotube/polymer interfaces or places with relatively low nanotube densities. As shown in Fig. 9.4, the nanotubes aligned perpendicular to the fracture path and spanned the crack faces in their wake. The nanotubes started to form when the crack opening displacement was more than 800 nm to separate from the matrix and/or shatter it. There is opportunity for improvement in the bonding between nanotubes and polymers, as shown by the fact that some of the pulled-out tubes do not seem to be covered with polymer.

In contrast to a research conducted by Paul Watts and Wen-Kuang Hsu at the University of Sussex, the work of the Kentucky group is fascinating (9.53). A nanotube/polymer composite's fracture behavior was also investigated by these researchers using TEM. Their composite was made of MPC-DEA, a diblock copolymer, with arc-grown MWNTs embedded inside it. The tubes were combined with the polymer in an acidified aqueous solution, and droplets of this solution were applied to TEM grids, which were subsequently dried in vacuum, to create specimens of the composite for TEM. The method for creating fractures in the material was the same as that employed by the Kentucky group, except that a modest accelerating voltage (75 kV) was utilized to prevent significant damage of the thin composite coating. When the fissures widened, it was found that individual tubes and groups of tubes got strained, and pull-out often occurred. The tubes did not shatter, in contrast to the Kentucky group's work. This was most likely caused by the use of premium arc-grown nanotubes rather than catalytically generated tubes.

Ajayan et al. investigated the fracture behavior of SWNT/polymer composites (9.54). A pressed pellet comprising SWNTs and carbonaceous soot material produced during nanotube synthesis was created, as well as a SWNT/epoxy composite. The SWNTs were utilized in their prepared form, which was often in bundles rather than divided into individual tubes. The fracture surfaces of the composites were meticulously analyzed using SEM after being subjected axially in tension till failure. During the deformation and fracture of the composites, it was discovered that the tube bundles in some instances were pulled out of the matrix, whilst in other situations, the nanotubes were partially pulled out but were stretched between two fracture surfaces. The failure seen at significant fracture distances was not the failure of individual tubes, according to the scientists, but rather the bundles ripping apart when the nanotubes moved axially inside the ropes during pull-out. This theory was confirmed by micro-Raman spectroscopy research. The application of axial stress was found to have no effect on the second order A1g band, indicating that the individual nanotubes were not being considerably stretched. It is obvious that load must be properly transmitted from the matrix to the nanotubes in order to fully benefit from the high Young's modulus of SWNTs in polymer composites. According to Ajayan et al., slicing bundles into individual tube pieces before disseminating them throughout the matrix might enhance load transmission. As an alternative, cross-linking the tubes inside the bundles might strengthen the bundles themselves (e.g. by chemical treatments or irradiation).

Electrical characteristics

In addition to their mechanical characteristics, carbon nanotube/polymer composites have also undergone extensive electrical research. These studies may be divided into many different groups. Utilized as an alternative to presently used fillers like carbon black to improve the conductivity of very cheap non-conducting polymers. Nanotubes have also been incorporated into conducting polymers like polyaniline in other research. In many instances, the addition of nanotubes has resulted in increased mechanical qualities as a beneficial byproduct. We start by thinking about the incorporation of nanotubes to bulk, inexpensive polymers.

Many applications need better electrical conductivity of bulk polymers. For protection against electrostatic discharge and electromagnetic-radio frequency interference, for instance, greater conductivity is needed in several aircraft components. Other uses for static electrical dissipation include computer housings and the outside of automobile components. Shaffer, Windle, and their colleagues looked at the electrical characteristics of nanotube/epoxy composites with these types of applications in mind. At filler volume fractions as low as 0.1 vol.%, matrix resistivities of around 100 m were attained. Using carbon black in the same epoxy matrix, these findings showed an improvement above the best conductivity values previously achieved. In later research, the same group found composites made of aligned, catalytically generated MWNTs in epoxy to have an extremely low electrical percolation threshold. The amount of filler necessary for a polymer to reach its percolation threshold and become electrically conductive is known as the filler content. It is distinguished by a significant increase in conductivity, often by many orders of magnitude. The Cambridge group reported percolation limits for their composites as low as 0.0025 vol.%. Moreover, composites incorporating SWNT have found low conductivity thresholds. The aspect ratios of the tubes in these composites have an impact on the electrical characteristics, as shown by Arjun Yodh and colleagues (9.62). This team created tubes for the SWNT/epoxy composites utilizing the HiPco and laser vaporization techniques. They measured 167 and 516 nm in length, respectively. It was discovered that the percolation threshold was substantially lower in the longer tubes.

These and other research in the literature imply that carbon nanotubes have tremendous potential for lowering the electrostatic charge of bulk polymers that are not conducting. In addition, nanotubes are more readily processed and may be distributed more evenly throughout the matrix than traditional fillers like carbon black and carbon fibers. There is clearly a lot of commercial work being done on the use of nanotubes to lessen the electrostatic charge of plastics in addition to the research that are accessible in the open literature. In reality, commercial items currently employ polymers that include nanotubes. Examples include the gasoline lines in cars, where the nanotubes aid in dissipating any potentially harmful charge that may accumulate. Certain external vehicle components are also made of thermoplastic polymers with nanotubes so they may be grounded during electrostatic painting.

So let's talk about nanotube composites using conducting polymers as the matrix. Polyaniline (PANI), a conducting polymer with several desirable qualities including processability and environmental stability, has been the subject of the majority of investigations in this field. There has been interest in adding nanotubes to this polymer to increase its mechanical characteristics and conductivity. Maser and colleagues created MWNT/polyaniline composites using in situ polymerization, as was previously described. It was discovered that the nanotubes had a significant impact on the transport characteristics of the Polymer. As a result, it was discovered that the composite's resistivity at normal temperature was an order of magnitude lower than that of pure polyaniline, while its resistivity at low temperatures was substantially lower than that of MWNTs or PANI. Moreover, resistivity's temperature dependency was less pronounced than PANI's alone [11]. These results were explained by the hypothesis that charge transfer between PANI and MWNTs is encouraged during in situ polymerization, resulting in a more conductive final product than the initial constituents. Raman investigations revealed that the quinoid ring of the polymer and the MWNTs interacted in a site-specific manner during these charge transfer activities. It has been proven that SWNT/polyaniline composites may be employed as printable conductors for organic electronic devices, and other groups have also shown high conductivity in MWNT/polyaniline. Moreover, conducting polymer polypyrrole was used to create composite materials including nanotubes.

Ceramic/carbon Nanotube Composites

Although having relatively moderate breaking strengths, ceramics offer strong thermal stabilities and stiffnesses. One could anticipate that adding carbon nanotubes to a ceramic matrix will result in a composite material that is both robust and stable at high temperatures. But it is more difficult than inserting tubes into a polymer to get a homogenous dispersion of tubes in an oxide with strong connection between tubes and matrix. The many methods that have been used to incorporate nanotubes into oxides will now be enumerated, starting with efforts to create composites out of nanotubes and alumina.

One of the pioneers in this discipline was Alain Peigney from the University of Toulouse, along with his colleagues. They have created a clever method that uses catalytic metals like Fe to impregnate the ceramic and then use them to grow creating the precursor for a composite made of nanotubes and oxide. The final composite material may then be created by hot pressing the resultant particles. Yet, these composites' mechanical characteristics have often fallen short of expectations. The possibility of the nanotubes being harmed during hot pressing is one issue. As a result, the fracture strengths of composites are typically only slightly greater than those of pure ceramics.

By the process of spark-plasma sintering, nanotube/ceramic composites seem to have been able to obtain somewhat improved mechanical characteristics (SPS). In this procedure, the sample material is held in a graphite die between pressure-applied electrodes made of stainless steel. The die and the sample are then subjected to pulses of current. As a consequence, the sample becomes heated and sparks fly between nearby particles. This procedure encourages the development of necks between the fast sintering, and particle size. SPS has the key benefit of enabling the manufacture of completely dense ceramics or composites with nanocrystalline microstructures in benign circumstances by allowing ceramic powders to be annealed at lower temperatures and for substantially shorter durations than in conventional sintering methods. SPS does not harm the nanotubes, in contrast to some of the other procedures used to create nanotube/oxide composites. Amiya Mukherjee of the University of California, Davis, and colleagues have conducted a thorough investigation of the utilization of spark-plasma sintering to create composites made of ceramic and nanotubes. In 2003, this group generated Al2O3 composites with 10% SWNTs using SPS. Ball-milling was used to combine the powders before sintering, which resulted in a substantially homogenous dispersion while protecting the nanotubes. The resultant composites' extraordinary fracture toughnesses were almost double that of the completely densified but unreinforced Al2O3 matrix.

Contrary to earlier research on nanotube/ceramic composites, it was discovered that the density of the nanotubes increased the fracture toughness. This is attributed to the development of single-walled carbon nanotube entangled networks, which may prevent fracture propagation. The composites of nanotubes and Al2O3 were further studied, and the results revealed that they exhibited good electrical conductivities. Korean researchers have also employed spark-plasma sintering to create Al2O3 reinforced with nanotubes. Using the sol-gel method, the tubes and alumina were combined in this instance. Once again, strong tenacity was shown.

Carbon nanotube/silica composites have been prepared using a variety of processes. Tetraethoxysilane (TEOS) was used to create a composite gel of MWNTs, and Mauricio Terrones and colleagues disclosed a process that entailed sintering the gel at 1150 °C in Ar. This approach has the disadvantage that the partial crystallization of SiO2 caused a highly uneven matrix as a consequence of the sintering process. There is an alternate approach that has been created that eliminates these issues. In order to partially melt the matrix, a TEOS/nanotube combination was heated quickly using a Nd:YAG laser. This resulted in a matrix of amorphous SiO2 that did not crystallize. Nanotube/SiO2 composites have also been created by spark-plasma sintering, turning insulating SiO2 into a metallically conductive composite.

Using oxides besides alumina and silica to create nanotube composites has been the subject of a few research. Sol-gel techniques have been used by many organizations to create nanotube/TiO2 composites. Such composites may be used as optical wave guides, conductive sheets, or sensors. Sakamoto and Dunn also created SWNT/V2O5 composites via the use of sol-gel techniques with the intention of using them as electrodes for secondary lithium batteries. Supercapacitors made of nickel oxide/MWNT composites have been produced. Ian Kinloch and colleagues have investigated the potential use of hydroxyapatite/nanotube composites for biomedical applications such bone transplants. Furthermore, nanotubes have been integrated into ceramics devoid of oxygen, most notably silicon carbide. Chinese researchers created nanotube/SiC composites in an early work by combining SiC nanoparticles with 10 weight percent MWNTs and pressing them hot at 2000 °C. The nanotubes were discovered to be had a function in the composite's strengthening and toughening; compared to monolithic SiC, both bend strength and fracture toughness rose by around 10%. A high-pressure reactive sintering process may produce MWNT/SiC with excellent mechanical characteristics, according to more recent research by Tadeusz Zerda of Texas Christian University and colleagues. SiC has also been enhanced by the use of single-walled nanotubes.

Composites of carbon and carbon nanotubes

The addition of nanotubes to carbon matrices has generated some attention. Single-walled nanotubes were found in the carbon fibers that Rodney Andrews and colleagues made. They were made by mixing SWNTs with petroleum pitch, heating, and then cooling. As compared to pure carbon fibers, the tensile strength, modulus, and electrical conductivity of the composite fibers were found to be much higher. A team from Cambridge has used plasma assisted CVD to produce MWNTs on a carbon fiber fabric, leading to a noticeably higher bulk electrical conductivity.

The performance of Li-ion batteries may be significantly enhanced by adding MWNTs created by catalysis to the synthetic graphite used in the anodes. This was shown by Morinobu Endo and colleagues. It was discovered that nanotubes outperformed the traditional carbon black filler in several ways. The anodes' physical flexibility was improved as well as their conductivity by the tubes. Moreover, the electrolyte penetrated the skin more effectively. Li-ion batteries using nanotubes have finally reached the market.

Composites of metal and carbon nanotubes

In a variety of specialized applications, composite materials with traditional carbon fibers in a metal matrix like aluminum or magnesium are employed. Such composites are particularly appealing to the aircraft sector because they combine high strength and modulus with low density. The incorporation of carbon nanotubes into metal matrices is gaining popularity. In 1998, Toru Kuzumaki and colleagues from the University of Tokyo detailed the creation of a nanotube/aluminum composite, carrying out groundbreaking work (9.94). By combining a nanotube sample with a fine Al powder, putting the combination in a 6 mm silver sheath, then drawing and heating the wire at 700 °C in a vacuum furnace, they were able to get their desired result. The outcome was a composite wire with nanotube alignment in the axial direction to a certain extent. The composite wires' tensile strengths as-prepared were equivalent to those of pure aluminum, but following lengthy annealing at 600 °C, the composite wires maintained their strength whereas the strength of pure aluminum dropped by around 50%. Since these early investigations, quite a bit of research has been done on nanotube/aluminum composites, and in the majority of situations, considerable improvements in the mechanical characteristics over the pure metal have been discovered. Just a little amount of research has been done on adding nanotubes to other metals, such as magnesium and titanium.

As was said at the start of this chapter, adding carbon nanotubes to a matrix material comes with a number of unique difficulties. The main challenges include creating strong bonding between the nanotubes and matrix, as well as homogenous nanotube dispersion throughout the matrix. Although problems still exist, a number of organizations have achieved significant advancements, notably with polymer matrices. The use of surfactants or functionalized nanotubes has been utilized relatively often to increase interfacial bonding and improve dispersion. Dispersing tubes using ultrasonic mixing has also shown to be effective. These developments are helping nanotube/polymer composites reach their full potential. Hence, researchers from the University of Pennsylvania have shown that adding 2 wt% SWNTs to nylon results in an improvement in elastic modulus of 214% and an increase in yield strength of 162% compared to the polymer's pure form. A significant amount of effort has also been done on the creation of polymer fibers that include nanotubes. The Poulin group's groundbreaking work served as the foundation for the Baughman group's creation of SWNT/PVA fibers with exceptional mechanical characteristics. Moreover, adding carbon nanotubes to polymers may provide them advantageous electrical characteristics. For potential uses in the aerospace or automotive industries, there has been a lot of interest in utilizing nanotubes to increase the conductivity of inexpensive bulk polymers. For more specific applications, promising results have also been obtained using nanotube/conducting polymer composites.

Little research has been done on adding nanotubes to other matrices, such ceramics, in comparison to the extensive study of nanotube/polymer composites. Despite more difficulties than with polymers, spark-plasma sintering has enabled advancement in this area. Composites made of carbon nanotubes have only had a small number of commercial uses so far. As was previously indicated, nanotubes have been employed to enhance the anti-static capabilities of automotive body panels and fuel-handling components. The pioneers in this field were Hyperion Catalysis International of Cambridge, Massachusetts. Tennis rackets made with nanotubes have been produced by the French business Nanoledge, and high-performance racing bikes made with the help of the Swiss cycling manufacturer BMC and the American company Easton now have frames made with nanotubes. Yet, the price of these goods puts them well beyond the reach of the typical customer. A wider range of applications won't be possible until nanotube production costs are reduced. In Li-ion batteries, nanotubes do seem to have had a substantial commercial effect. Endo and colleagues have shown that adding MWNTs created by catalysis significantly improves the performance of such batteries.

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CHAPTER 14

FILLED AND HETEROGENEOUS NANOTUBES

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Soon after Iijima's research was published in 1991, attempts to introduce foreign elements into the bare center voids of carbon nanotubes started. The concept to use nanotubes as templates for nanowires inspired some of this work, while the unfilled voids served as perfect "nano-test-tubes" for the investigation of matter in restricted spaces. There was considerable curiosity in the idea of creating new size-selective catalysts by putting catalytic metals within opening tubes. In 1993, the first multiwalled nanotubes were successfully filled using a method that entailed performing arc-evaporation as normal while employing an anode that contained part of the material to be enclosed. This technique only works with materials that can withstand the harsh conditions of the electric arc and typically tends to favor the creation of filled nanoparticles rather than nanotubes [1]–[3]. A short while later, a more widely applicable technique was created, in which the tubes were opened and filled using chemicals. A broad variety of materials, including biological molecules, have now been subjected to this. Since 1997, when single-walled tubes were first opened and filled, intriguing research has been done on how confinement in SWNTs affects the structure of crystalline materials. The idea of adding fullerenes to SWNTs has also generated a lot of attention. The techniques utilized to open and fill carbon nanotubes, as well as the novel science and potential applications that are emerging from this study, will be discussed in the first section of this chapter. A short review of heterogeneous nanotubes, which are nanotubes whose carbon atoms are partly replaced by hetero-atoms, often nitrogen and/or boron, is provided in the second section of this chapter. Pure boron nitride nanotubes are not discussed in this book since it only deals with structures that incorporate carbon [4]–[6].

Arc-evaporation filling

Arc-evaporation was utilized in the first efforts to insert foreign material into nanotubes to evaporate a combination of graphite and lanthanum oxide. As a result, a combination of La2O3 and graphite powder was injected into the anode instead of utilizing electrodes made entirely of graphite. The carbon that had been deposited on the cathode was retrieved after the standard arc discharge procedure. Both Yahachi Saito's group in Japan and Rodney Ruoff's group in the United States independently conducted experiments of this kind in 1993, and both groups came up with the same results: the cathodic soot included a significant amount of filled nanoparticles rather than filled nanotubes.

A French group has examined the manufacture of filled nanotubes using this method, despite the fact that arc-evaporation with modified electrodes often tends to favor the synthesis of filled nanoparticles rather than nanotubes. They have had success producing nanotubes filled with a variety of transition elements, rare earth elements, and non-metals like S, Se, and Ge using arc-evaporation in its entirety. Arc-evaporation filling has also been tested by a few other organizations. Nevertheless, chemical procedures, which are covered in the following section, are considerably more extensively applicable and provide a higher level of control, hence they have not been used as often to fill carbon nanotubes. Yet it should be mentioned that arc-evaporation filling experiments resulted in the finding of single-walled nanotubes. Chemical approaches for opening and filling multiwalled nanotubes [7]–[9].

According to earlier theoretical research, opening nanotubes should function as "nanopipettes," drawing liquid within by capillary action. By heating a sample of tubes with molten lead in the hopes that some of the lead would be pulled into open tubes, Ajayan and Iijima tested this theory. By employing electron-beam evaporation, they were able to deposit lead particles onto the tubes in a vacuum before heating them in air at 400 °C, which was hot enough to melt the lead. They discovered that just a tiny percentage of the nanotubes had obviously been filled when they used TEM to study the final samples. The fillings might travel for up to a few hundred nm before being often obstructed by internal caps. According to estimates, 1% of nanotubes were filled with lead. It is obvious that the lead was not getting into the tubes via holes that already existed since there are only around one in a million open tubes in a new sample. It seems that lead-catalyzed oxidation was what caused the tubes to open. A short while later, research by Edman Tsang, Malcolm Green, and the current author at Oxford and Iijima's group in Japan shown that nanotubes could be opened with a good level of selectivity just by heating in a slightly oxidizing environment without the need for a catalyst.

Nanotube samples were heated for up to 24 hours in CO2 at temperatures ranging from 950 °C. The tube caps had been targeted in a small but significant number of instances, according to the TEM analysis of the oxidized samples, which revealed that they had often been thinned at the extremity and sometimes entirely opened. Similar behavior was seen when the tubes were heated in oxygen by the Japanese team up to 850 °C. Little oxidation was seen below around 700 °C, but at higher temperatures, oxidation happened quickly; at 850 °C, the whole sample was gone within 15 minutes. By briefly heating in oxygen at 700 °C while containing opened tubes, samples including such tubes might be produced (typically 10 minutes). While there were more open nanotubes when oxygen was used as the oxidizing agent as opposed to carbon dioxide, the process was far more damaging and many tubes experienced significant corrosion.

Once both groups were successful in opening the nanotubes, they attempted to fill the tubes with inorganic materials, but this proved to be far more challenging than anticipated. In an effort to dry out the solvent and reduce the salt to leave metal crystallites within the tube, the Oxford Group made an attempt to introduce solutions of metal salts into the tubes using "incipient wetness" procedures similar to those employed in the preparation of supported catalysts. Both of these efforts, as well as those by the Japanese group to fill opening tubes with molten lead, were unsuccessful. It was not immediately evident why the one-step technique employed by Ajayan and Iijima to fill tubes with molten lead worked so effectively whereas the two-step procedure for filling nanotubes failed. One theory is that as soon as tubes are opened, amorphous carbon blocks them, making future filling difficult.

Opening via acid treatment

After encountering problems with the carbon dioxide oxidation technique, Tsang, Green, and their Oxford colleagues sought for alternate strategies for opening nanotubes. A similar procedure was used on nanotubes since earlier research on the treatment of other fullerene-related carbons with nitric acid had shown that this would be a successful method of selectively targeting pentagonal rings. This turned out to be really effective. Nitric acid treatment not only produced a large output of opened tubes, but it also attacked the tube tips with amazing selectivity. This is seen in the micrographs of tubes from a sample that was subjected to 4.5 hours of boiling nitric acid treatment. Attacks on the tube cap have occurred at two sites, X and Y, both of which are where pentagonal rings should have been. While the rest of the tube is still intact, the tube cap has been opened and the internal caps have been strategically removed to provide a path to the center hollow. This shows that only the pentagonal rings have been affected by the acid; even when the margins of the graphite sheets have been exposed, they have not been damaged, and there has been very little weakening or peeling of the outer layers. Tsang and colleagues also demonstrated that, in contrast to nanotubes opened using the less selective gas-phase oxidation techniques, those opened using the nitric acid approach did not seem to be blocked by amorphous material. This method of opening tubes made them much easier to fill.

The reason why the nitric acid procedure is so incredibly selective is a valid issue. Why are the basal planes not quickly destroyed as is the case with gaseous oxidants after the reactive edge has been exposed? The surface carboxyl and other groups that serve as a barrier to further reactions are most likely formed as a consequence of a reaction between the exposed edges and the nitric acid, which is the most likely explanation for the phenomenon. As mentioned below, it would be predicted that these hydrophilic groups will make it easier to fill tubes with aqueous solutions and biological material.

Filling up opening tubes

The Oxford researchers demonstrated that the tubes could be opened and filled in a single step in their original Nature study. As a consequence, tubes containing crystalline nickel oxide were produced when nickel nitrate was introduced to the nitric acid used in the oxidation process. It was shown that chemical processes might occur within the opening tubes by reducing the oxide to nickel metal after further treatment with H_2 at 400 ^oC. A micrograph of a nickel tube with metallic material. Similar to this, closed tubes were treated with $Sm(NO_3)_3/HNO_3$ to produce samarium oxide (Sm_2O_3). An alternative method involves filling opening tubes with the chemical in a second step by either treating them with the substance in solution or molten form. The benefit of using molten materials is that they allow for full tube filling. As the precipitated material will always take up much less space than the solution, deposition from solution can never lead to full filling. After treating a sample of tubes with oxygen or nitric acid and mixing in V_2O_5 powder (m.pt. 690 °C), Ajayan and colleagues heated the sample to a temperature of 750 °C. The Oxford Group demonstrated that heating in H_2 after treating opened nanotubes with molten MoO_3 resulted in tubes that were entirely filled with single-crystal MoO_2.These investigations revealed that certain compounds entered the opening tubes far more easily than others. The amount of energy at the interface between two substances determines whether or not a liquid will reach the central core of a nanotube. Liquid will enter the tube spontaneously if the liquid-solid contact angle is less than 90°, but not if it is larger than 90°. In an effort to identify the "critical" surface tension below which wetting would take place, Dujardin, Ebbesen, and colleagues researched the wetting of nanotubes with a variety of materials. They came to the conclusion that the cutoff surface tension ranges between 100 and 200 N/m 1. Water, which has a surface tension of 72 mN m1, and the majority of organic solvents, which have lower surface energies than water, would thus be anticipated to enter nanotubes naturally. This is in line with the finding that aqueous solutions penetrate tubes that have been opened.Multiwalled nanotubes have also been filled with biological molecules in addition to inorganic components. Bioinorganic chemists from Oxford and Birkbeck College, London, as well as Green and Tsang, demonstrated how tiny enzyme molecules may be placed into opening MWNTs. Simple samples of opening nanotubes were suspended in aqueous protein solutions for 24 hours, with the volatile water subsequently being removed under decreased pressure. They were able to efficiently and in high yield insert the enzymes Zn_2Cd_5-metallothionein, cytochrome c3, and -lactamase I into the center cavities of the nanotubes in this manner. Moreover, the enzyme molecules stuck to the tubes' exteriors. This work possibly marks the first investigation into the relationship between biomolecules and nanotubes, a field that has since expanded quickly.

Catalytically-grown multiwalled nanotube filling

The multiwalled tubes created by arc-evaporation have been used in all of the work that has been discussed up to this point. A significant number of investigations on filling catalytically-grown multiwalled nanotubes have been conducted as of late. In samples of CVD-grown tubes, partially filled nanotubes are often seen, but full filling necessitates the presence of an excess of catalyst. By pyrolyzing precursors that include the catalytic metals and a source of carbon, it has been discovered that this can be accomplished in a one-stage process.

In 1998, C. N. R. Rao and colleagues from Bangalore demonstrated that ferrocene or ferrocene-acetylene combinations heated to a temperature of around 1100 °C generated aligned MWNTs, the majority of which were filled partly or entirely with Fe. About the same time, thin films of C60 and Ni that had been formed on a silica plate were pyrolyzed by Nicole Grobert and colleagues to create MWNTs that were filled with Ni. Since then, it has been routinely utilized to create tubes containing Fe, Ni, and Co as well as their alloys. Micrographs of several typical filled tubes made in this manner by Paul Watts and colleagues at the University of Sussex. These ferromagnetic metals might be used to fill tubes for magnetic storage applications.

A multinational team of researchers lead by Terrones, Ajayan, and Banhart published a remarkable investigation of filled MWNTs made by pyrolysis in 2006. This showed what happened when filled tubes were exposed to an electron beam. Prior research had shown that annealing and irradiating carbon onions simultaneously might create very high internal pressures that led to the production of diamond. Also, it has been shown that subjecting pure MWNTs to electron irradiation might cause the tubes to contract due to atom loss and interstitial diffusion via the inner cavity. In the 2006 study, metallocene-based pyrolytic techniques were used to fill MWNTs with Fe, Fe3C, and Co. The filled tubes were then heated to a temperature of 600 °C in the TEM and exposed to radiation. The tubes shrank as a consequence, applying extreme pressure to the contents, much as with the pure tubes. The tube remodelling may induce such a severe constriction that the crystals within can be forced out and extruded. According to calculations, pressures in the radial direction might exceed 40 GPa. This technique therefore provides a means of researching the impact of high pressures on nanoscale materials.

Multiwalled nanotubes with water

Yury Gogotsi of Drexel University and his colleagues have detailed some amazing experiments of water within multiwalled nanotubes. In the first of these research, tubes were made using a hydrothermal catalytic method, which trapped liquid water and gases (such as CO and CH4) within the center chambers of the tubes. Pictures of the half filled tubes revealed that the carbon had high water wetability, demonstrating that the synthesis of functional groups had made the carbon surface hydrophilic. The interaction of the water with the nanotube walls was further investigated in a subsequent work. There was some hydrated carbon layer breakdown and liquid infiltration between the tube's layers. The tube walls began to dissolve more dramatically when the electron beam was used to locally heat the tubes. Gogotsi and colleagues have not only created water-filled tubes via hydrothermal synthesis, but they have also added water to tubes that had already been created using the catalytic and arc procedures. By subjecting them to high pressure in an autoclave, this was achieved. The flow of water across membranes made of aligned carbon nanotubes was studied by a team at Lawrence Livermore National Laboratory under the direction of Olgica Bakajin. The measured flows exceeded those of commercial polycarbonate membranes by many orders of magnitude. Even if the tube diameters were lower than the pore sizes of the commercial membranes, this was still the case. These results, which are in line with theoretical expectations, imply that nanotube membranes could be effective in processes like salt removal from water.

Single- and double-walled nanotube filling

Single-walled nanotubes are more challenging to fill than multiwalled nanotubes due to their exceedingly tiny diameters. Nevertheless, Jeremy Sloan and colleagues from Oxford revealed in 1998 that SWNTs may be opened and filled using methods similar to those used for MWNTs in a remarkable piece of work. A short while later, Brian Smith, Marc Monthioux, and David Luzzi made the astounding finding that raw SWNT material created by the laser vaporization approach spontaneously developed fullerene-filled SWNTs during the purification and annealing procedures. These investigations sparked a lot of attention, and wonderful work has since been produced on filled SWNTs. We'll talk about filling using inorganic materials first.

Using inorganic materials to fill

In their first investigation, the Oxford Group used a solution approach to insert Ru crystallites and other materials into the tubes. Further research revealed that molten materials might be used to nearly completely fill single-walled tubes. As-made nanotubes would be heated to a temperature 100°C over the melting point of the molten salt or oxide in a standard filling technique. This method was used by Sloan.

Using electron diffraction and HRTEM, the structure of crystals within SWNTs has been investigated, with the Oxford Group once again taking the lead. They addressed some of their work on determining tube structure using HRTEM. They provided details on HRTEM imaging of KI crystals within SWNTs in 2000. Only the highly scattering I atoms and barely detectable amounts of the considerably lighter K atoms significantly contribute to the contrast in this picture. Digitally merging a tilt or focus series of photos might result in photographs of higher quality with certain aberrations corrected. An example of one of these reconstructed images, which depicts a 3 3 KI crystal within a 1.6 nm SWNT. Here, both the K and I atoms' contributions are apparent.

Both 1D crystals were discovered to have significant lattice aberrations in comparison to their bulk structures. A lattice expansion of almost 17% took place throughout the nanotube in the 2 2 case, however a differential expansion was seen in the 3 3 instance, with the columns being more compressed than the K columns. Twisted 1D crystals have sometimes been seen within single-walled tubes. Co2I4 repeating units were used to assess the contrast of the enclosed crystal. The asymmetric Co2I4 subunits in this system have an amazing ability to deform the cross-section of the tube. Sloan and colleagues have added molecular species to SWNTs in addition to inorganic crystals. For instance, individual o-carborane molecules were observed when ortho-carborane was sublimated into SWNTs. Research like these and the work on fullerene-filled tubes detailed below demonstrate that stabilizing molecules within single-walled nanotubes is a great method to use them for HRTEM imaging.

Using fullerenes to fill: "nano-peapods"

Since the first research of Smith, Monthioux, and Luzzi, some extraordinary work has been done on single-walled tubes packed with fullerenes, sometimes known as "peapods." As mentioned earlier, the fullerene-filled tubes were first unintentionally created when SWNT soot was being purified and annealed. Further research showed that, albeit having a poor yield, peapods also spontaneously developed during the synthesis of SWNTs utilizing arc discharge. Recently, more controlled synthesis techniques have been created, in which the tubes are first opened using acids and then vacuum-annealed when fullerenes are present. A typical picture of a peapod is shown. Average C60-C60 separation was measured by Smith et al. and found to be 0.97 nm. The intermolecular separation in FCC crystalline C60 is somewhat larger than this, albeit this might be because the tube was slightly tilted. Measurements of selected-area diffraction led to separations that were quite similar to those in crystalline C60.

While the idea that they could enter via side-wall flaws has also been taken into consideration, it is believed that the fullerenes enter the SWNTs through opening ends. Raman studies by Kataura and colleagues revealed that both C60 and C70 molecules had been encapsulated in significant amounts. Smith and colleagues have also shown that electron irradiating peapods within a microscope causes the encapsulated fullerenes to diffuse and consolidate. Moreover, high-temperature heat treatments of peapods may cause numerous nearby fullerenes to coalesce, creating very tiny inner tubes. In 2004, Andrei Khlobystov of the Materials Department at Oxford and colleagues published a remarkable investigation of fullerenes within both double- and single-walled nanotubes displays one of their photos of a DWNT with a single chain of fullerenes (a). Larger-diameter DWNTs were also filled, and in this instance, various unique packings were seen, such as double-helical phases and zigzag configurations.

Ali Yazdani of the University of Illinois and researchers from Pennsylvania investigated the electrical characteristics of peapods in 2002. They discovered that the C60 molecules caused the local electrical structure of the nanotube to undergo periodic modifications using a low-temperature scanning tunneling microscope. This was explained by a mixing of the C60 orbitals with the electronic states of the nanotubes. While it goes without saying that the level of control necessary to do this is beyond what is now possible, it is feasible that encapsulated molecules may be utilized to purposefully "tune" the electrical characteristics of carbon nanotubes.

Iijima, Suenaga, and colleagues from Japan and France first reported the encapsulation of metallofullerenes in single-walled nanotubes in 2000. This work included heating a combination of tubes and molecules in a sealed ampoule to 500 °C to introduce gadolinium metallofullerenes into SWNTs. According to the metallofullerenes were found to pack densely within the tubes. Surprisingly, on several of the C82 molecules, the individual contained Gd atoms could be seen as black patches. A schematic illustration of the SWNTs incorporating metallofullerene.

In nanotubes, gases

Hydrogen

In a Letter to Nature published in the beginning of 1997, a team led by Michael Heben of the National Renewable Energy Laboratory (NREL) in Golden, Colorado, asserted that single-walled carbon nanotubes could store up to 8% of their weight in hydrogen when kept at room temperature and under moderate pressure. These outstanding findings generated a lot of media attention and launched the most contentious nanotube scientific controversy.

The material contained in the tubes was subjected to H2 at 300 torr, cooled to 90 K, and then the temperature programmed desorption (TPD) spectroscopic technique was employed to investigate the desorption behavior. The desorption behavior of the freshly generated SWNT soot resembled that of an activated carbon sample. However soot heated in vacuum to 970 K revealed an additional desorption peak that seemed to be compatible with H2 adsorption in the tube cavities. The authors proposed that the heat treatment in vacuum had opened the tubes, making the H_2 accessible.

The findings attracted a lot of attention since the high uptakes seen indicated that single-walled tubes would be suitable candidates for H_2-storage materials. Lack of a good way to store H_2 is one of the main barriers inhibiting the adoption of H_2 fuel cells to power cars. The US Department of Energy established a goal capacity of 6.5 wt % for a usable H_2-storage material for use in automobiles, which the NREL group easily surpassed. When the Heben Nature article was published, additional researchers observed significant H_2 uptakes on SWNT-based materials. For instance, a team lead by Mildred Dresselhaus showed that large-diameter SWNTs had a storage capacity of 4.2 wt% at room temperature and at a moderately high pressure.

The National University of Singapore's Jianyi Lin and colleagues reported even more astounding uptakes for MWNTs doped with alkali metals (up to 14 wt% at room temperature). Yet regrettably, many additional organizations were unable to replicate these findings (10.70–10.75). Consequently, at room temperature and ambient pressure, Michael Hirscher from the MPI in Stuttgart and his colleagues discovered uptakes of less than 1 wt% (10.74). These scientists hypothesized that the uptake Heben saw may be brought on by titanium contamination in the nanotube samples. Researchers from the University of Utrecht investigated the H2 adsorption of a variety of carbon adsorbents at 77 K and 1 bar and discovered that the storage capacity relied only on surface area, with carbon nanotubes exhibiting no particular features (10.75). Although physisorption is now largely accepted to be the primary cause of any H_2 absorption by carbon materials, it is only thought to be significant at low temperatures. According to Lin and colleagues' research, the observed mass increase has been linked to the development of hydroxide. The assertions made by Nelly Rodriguez and coworkers at Northeastern University that "graphite nanofibres" could retain H2 at amounts more than 50 wt% at ambient temperature were even more contentious than those made by Heben and colleagues. The findings, which other researchers have not been able to duplicate, were universally regarded as unbelievable.

Is the tale of hydrogen storage in carbon nanotubes an example of "pathological science"? This is a fascinating question to ask. Irving Langmuir first used this phrase to refer to the way that "people are fooled into misleading findings by subjective effects, wishful thinking, or threshold interactions." Several others considered cold fusion, a phenomenon that also utilizes hydrogen, to be an example of pathological science. Yet applying such a moniker to hydrogen storage in nanotubes would probably be inaccurate. The fact that "The impact is of a size that stays near to the limit of detectability, or numerous measurements are required because of the extremely low statistical significance of the data," is one trait of pathological research. The sheer extent of the effects in the trials of Heben, Rodriguez, Lin, and others looked unbelievable. One feature of pathological science, however, does appear to be applicable: "The ratio of supporters to detractors grows and then progressively declines to oblivion.

Several gases

There hasn't been nearly as much research done on incorporating other gases into nanotubes as there has been on storing hydrogen, which has garnered enormous attention. Nonetheless, there have been a few studies recorded. In a study headlined "The World's Smallest Gas Cylinders," Australian researchers detailed the trapping of argon within graphitic tubes in 1997, soon after the Heben experiment on hydrogen the catalytic preparation of these tubes decrease of CO2 and had sizes between 20 and 150 nm, which was substantially greater than ordinary carbon nanotubes. Energy dispersive X-ray spectroscopy was used to identify the argon, which was introduced via hot isostatic pressing (HIP) the carbon material for 48 hours at 650 °C and 170 megapascals. As a consequence of amorphization during the HIPing process, the argon may have been sealed within the tubes after entering via flaws in the rather shoddy construction. It seemed plausible to store gases within these tubes for extended periods of time since the pressure inside the tubes, which was estimated to be 60 megapascals, appeared to fluctuate little over many months at ambient temperature.

In 2004, Mauricio Terrones, Nicole Grobert, and other researchers disclosed the encapsulation of gaseous nitrogen within MWNTs that resembled bamboo. Heat aerosols of ferrocene/benzylamine solutions at 850 °C to create the filled tubes. US employees reported the trapping of SF6 and CO2 in opened SWNT bundles in 2005. Cryogenically adsorbing the gases into the opening SWNTs, they were then sealed within by functionalizing the sample with low-temperature ozone. Hence, an impenetrable barrier was created to close the tube apertures. The samples remained stable in a vacuum for at least 24 hours, and vacuum heating to 430 °C allowed the trapped gases to escape.

The flow of gases through unsealed nanotubes has also been studied in addition to studies of gases enclosed within nanotubes. It was claimed before that employees from Lawrence Livermore Laboratory have seen water flowing quickly through membranes made of aligned nanotubes. The flow of gases across the membranes was also shown to be very high in the same investigation. This concurs with many theoretical research.

Differentiated nanotubes

Boron nitride may be stacked to resemble graphite, and in the 1980s, many groups demonstrated how to create graphite hybrids using C, B, and N. Theoreticians expected that BN and BCN nanotubes should be stable after the discovery of carbon nanotubes. This was subsequently confirmed when both kinds of nanotubes were successfully created utilizing different Krätschmer-Huffman method modifications. A "catalytic" synthesis of BN nanotubes was also reported about the same time, and subsequently, several more techniques for creating BN nanostructures have been devised. Pure boron nitride nanotubes are not discussed since, as was previously stated, we are only interested in carbon-containing structures.

Carbon-nitrogen-boron tubes

Arc-evaporation, laser ablation, and catalytic CVD are the three main methods that have been employed to create nanotubes that include boron, carbon, and nitrogen. Researchers from the French universities of Montpellier and Paris-Sud published the first arc-evaporation synthesis in 1994. Their technique entailed filling a container with a powdered boron and graphite combination. Carrying out the arc-evaporation in a nitrogen environment using a hollowed-out graphite anode. The BCN tubes were discovered within the deposit that had grown on the cathode, much as with pure carbon nanotubes. These were accompanied by BN and BCN sheets, disordered carbon, and pure carbon nanotubes and nanoparticles. Electron energy loss spectroscopy was used to analyze these structures' elements (EELS). There were two different kinds of B- and N-containing nanotubes: longer, narrower tubes up to 100 m in diameter and comparatively big fibers with uneven thickening (100–500 nm).

Since five-membered rings are more difficult to form in BCN networks than in pure carbon networks, the caps of the tubes were found to be poorly formed in both instances compared to the caps of pure carbon nanotubes. It's also likely that the difficulty in producing caps explains why, in certain instances, the BCN tubes developed to significantly longer lengths than typically seen for carbon nanotubes. Shortly after the French study was published, Marvin Cohen's team from the University of California, Berkeley, also documented the synthesis of BCN nanotubes. This time, they used a graphite anode that had been hollowed down to hold a BN rod and arc-evaporated in helium. BCN nanotubes and nanoparticles were created in 1997 by a French team headed by Christian Colliex by arc-evaporating a hafnium diboride rod with graphite in a nitrogen environment.

Iijima and colleagues utilized laser ablation to create BCN nanotubes for the first time in 1997. At 1000 °C under N2, laser ablation of a composite target including BN, C, Ni, and Co-produced multiwalled nanotubes with B, C, and N as well as pure carbon tubes. Mauricio Terrones and colleagues described a catalytic pyrolysis technique in 1996. This process involves heating CH3CN.BCl3 to 900–1000 °C over Co powder, which produced graphitic BCN nanofibres and nanotubes with a variety of topologies. BCN nanotubes were most recently created by Renzhi Ma and Yoshio Bando by pyrolyzing dimethylamine borane ((CH3)2NH BH3) at 1050 °C in the presence of Fe or Ni nanoparticles in N2 atmosphere. Boron, carbon, and nitrogen nanotubes have also been created using chemical vapour deposition processes. Using a gas combination of N2, H2, CH4, and B2H6, Xuedong Bai and colleagues used this technique to create highly aligned BCN tubes on Ni substrates.

The majority of boron-carbon-nitrogen nanotubes exhibit rather shaky bamboo-like structures. The distribution of nitrogen and boron in the carbon lattice is not completely known. Two scenarios have been thought of: first, a random distribution of the three species inside the tube walls; and second, a potential "sandwich" structure within the tubes with distinct C and BN layers. EELS has shown to be the most effective method for figuring out the atomic make-up of BCN nanotubes.

The majority of the tubes created approach exhibited a sandwich shape with carbon layers both in the center and at the edges, separated by a few BN layers, as shown by EELS. The stoichiometry of Terrones and colleagues' pyrolytically generated tubes was discovered to be BC2N in 1999, which is compatible with the sandwich construction. By recording concentration profiles across different tubes, this was supported. Ma and Bando, however, discovered that the B:C:N ratio may change inside a single tube.

Theoretically, BCN nanotubes should be semiconducting in terms of characteristics. In 1988 (10.97), Marvin Cohen and colleagues computed the electrical characteristics of crystalline BC2N and predicted a 2.0 eV band gap. Bando and colleagues' experimental measurements on bundles of BCN tubes produced a result of 1.0 eV.. Promising field emission and photoluminescence behavior with BCN tubes has been observed by Xuedong Bai and colleagues. The discussion that follows only applies to multiwalled BCN nanotubes. Xuedong Bai, Enge Wang, and Dmitri Golberg were part of an international team that published a study on the synthesis of BCN SWNTs in 2006. A Fe-Mo/MgO catalyst, CH4, B2H6, and ethylenediamine vapour were employed as the reactant gases in a CVD technique. The tubes seemed to be of a high caliber and would be anticipated to have special qualities. There have been a number of reviews on boron-carbon-nitrogen nanotubes.

Tubes for carbon-nitrogen

Producing nitrogen-doped carbon nanotubes has attracted attention due to the hypothesis that the carbon-nitrogen compounds CN and C3N4 could constitute a new class of superhard materials (10.104, 10.105). If we start with multiwalled tubes, the majority of preparation efforts have included pyrolytic or catalytic techniques. Japanese researchers developed N-doped MWNTs on a quartz substrate in what was likely the first study of its kind in 1997. Terrones and coworkers came up with comparable

Arrays of CN multiwalled tubes using pyrolyzed melamine and ferrocene mixes. The nitrogen content of the tubes created in this manner was only around 2%. By using aerosol assisted CVD procedures, Marianne Glerup and colleagues were able to integrate larger amounts of nitrogen (up to 20%) into multiwalled nanotubes. Even a 20% concentration, however, is still far below a CN or C3N4 stoichiometry, and it would seem that these levels of nitrogen doping have not yet been reached. Multiwalled CN nanotubes often feature stacked-cone or bamboo morphologies structurally. The interactions between the catalyst particles and the nitrogen have been used to explain this.

Arc-evaporation was used to create the nitrogen doped single-walled tubes in question. In order to make CN SWNTs, a Brazilian research team evaporated a graphite rod that included metal in a N2-He environment in 2002. A somewhat different strategy was utilized by Glerup and colleagues, who combined a nitrogen-rich precursor with graphite and catalysts in the anode rods (10.111). The morphologies of the N-doped SWNTs were comparable to those of their undoped counterparts.

Boron-carbon tubes

Interesting interactions occur between boron and carbon-based compounds. For instance, it is widely known that boron may serve as a "catalyst" for graphitization, and that boron doping can increase the oxidation resistance of carbons. Boron doping in carbon nanotubes has also yielded some interesting outcomes. In an early experiment, a team from Stuttgart created carbon nanotubes that were doped with boron utilizing an arc discharge with a BC4N anode. B doping had the effect of lengthening the tubes to around 100 m and improving graphitization. This is thought to be caused by the B's surfactant-like properties.

avoidance of tube closure A international team under the direction of Xavier Blase provided data in 1999 demonstrating that B doping caused "near zigzag" chiralities in addition to lengthening MWNTs (10.115). Again, arc discharge was used to produce the tubes, this time using anodes filled with B or BN powders. They analyzed the energetics of B-doped zigzag and armchair nanotubes to try to make sense of these findings. The researchers discovered that B atoms were better stable at zigzag edges than at armchair ones, indicating that the atoms would preferentially stay on zigzag edges and serve as surfactants throughout the growth. If true, this is one of the very rare instances in the literature of a technique that may favorably create tubes with a certain structure.

Robert Chang and colleagues have shown that boron may stimulate the formation of MWNTs by high-temperature heat treatment. They discovered that although annealing fullerene soot and other carbons to 2200–2400 °C in a graphite resistance furnace may produce MWNTs, adding boron significantly increased the output. It is unclear whether the tubes made in this manner were B-doped or pure carbon. Many papers describe the CVD production of B-doped multiwalled tubes. It seems that single-walled boron-carbon tubes have not yet been made.

Discussion

Carbon nanotube filling research has not yet produced any significant commercial uses. Yet, introducing material inside nanotubes has made it possible to undertake some fascinating investigations into the behavior of confined matter at the nanoscale. One such is the work of Terrones, Ajayan, Banhart, and others on filled MWNTs made using pyrolysis. These workers made the filled tubes constrict by exposing them to a powerful electron beam, which allowed them to analyze how high pressures affected the material within. Similar to this, Gogotsi and colleagues' investigations on the behavior of water within MWNTs may provide fresh perspectives on how fluids behave at the nanoscale. With their very tiny and well-defined diameters, single-walled nanotubes offer even greater promise for researching confined materials. The Oxford Group has shown that crystals within SWNTs are compelled to adopt a really 1D morphology, often adopting configurations not observed in the bulk. SWNTs that have been filled have shown to be excellent "nano-test-tubes" for HRTEM imaging of encapsulated compounds. The investigations of retinal linked to C60 by Suenaga, Iijima, and their associates are particularly noteworthy in this context. The placement of such molecules within SWNTs makes it possible to capture amazing pictures like those in Fig. 10.13, which would normally be impossible since such molecules are exceedingly unstable under an electron beam.

Heat treatment of multiwalled nanotubes at high temperatures

The creation of nanotubes by the high-temperature heat treatment of disordered carbons has not been the subject of as much research as arc-evaporation. Yet, this strategy could be a viable way to produce high-quality MWNTs on a wide scale. Research on the transformation of disordered carbon into multiwalled nanotubes may potentially provide light on the mechanisms behind nucleation and growth. Full-erene soot was heated in the initial investigations in this field. As was previously stated, fullerene soot is the fine, fluffy carbon that accumulates on the evaporation vessel walls during the fullerene manufacturing process. The C60, C70, and higher fullerenes may be extracted using organic solvents from this soot. Fig. 2.6 shows a typical micrograph of fullerene soot. The extremely disordered soot structure is made up of curved carbon particles with pentagons and heptagons randomly scattered across a hexagonal network, resulting in continuous curvature [10], [11].

Walt De Heer and Daniel Ugarte, the Oxford group, the Oxford group, and the École Polytechnique Fédérale de Lausanne in Switzerland were the first to perform high-temperature heat treatments on fullerene soot. The outcomes varied slightly. As observed in the micrograph the Oxford group discovered that heat treatment created a structure that seemed to be made up of huge holes that were often extended in form and resembled large-diameter single layer nanotubes. The expanded pores showed a range of capping morphologies and, like nanotubes, were virtually always closed. In certain instances, characteristics were seen that are regarded to be a sign of seven-membered carbon rings. While multilayer structures were also observed, single carbon layers often surrounded the expanded pores. While the particular method of the production of nanotube-like structures from fullerene soot is unknown, it may include rearrangements like the Stone-Wales mechanism.

De Heer and Ugarte discovered that fullerene soot often tended to convert into tiny, graphitic nanoparticles rather than nanotubes after high-temperature heat treatments. Nonetheless, the heat-treated soot sometimes included fairly brief multiwalled nanotubes. It provides an example. These findings prompted the current author and his coworkers to suggest the above-discussed solid phase model of MWNT development. In a publication that was published in 2000, Robert Chang and colleagues from Northwestern University revealed more research on the high-temperature heat treatment used to create MWNTs. Beginning with the annealing of fullerene soot produced by the arc evaporation of graphite at 450 torr of He, their research was conducted. The soot was heated to 2200–2400 °C in a graphite resistance furnace after being activated at 850 °C in a CO2 environment to enhance its surface area.

According to research by de Heer et al., this heat treatment mostly caused nanoparticles to develop in the case of pure soot. Nevertheless, heat treatment caused the development of nano-tubes several microns in length when the soot and amorphous boron were combined. Thereafter, similar tests were performed on additional forms of disordered carbon, including carbon black, sucrose carbon, and ball-milled graphit.

Even when doped with boron, heat treatment of ball-milled graphite or carbon black failed to yield any nanotubes. Nevertheless, multiwalled nanotubes were created when sucrose carbon was annealed with boron, although in a low yield. These tests provide further proof that solid-state development of nanotubes occurs. The topic of heterogeneous nanotubes has been briefly covered. Although boron nitride tubes rather than carbon-containing tubes have drawn the majority of attention in this field, a thorough examination of these structures is outside the purview of this work.

Sensors and Probes

Modern research has a strong focus on the creation of novel imaging, measuring, and sensing techniques, and carbon nanotubes have a lot of promise in these fields due to their special features. For instance, the exceptional mechanical characteristics and distinctive shape of nanotubes indicate that they should make the best tips for atomic force microscopy (AFM). Today, silicon or silicon nitride microfabricated pyramids placed on cantilevers make up the majority of AFM tips. These probes are often unable to probe small cracks on the specimen surface because they might be rather "blunt" in comparison to the size of the features that are being photographed. With their long form and small diameter, carbon nanotubes are able to probe even the smallest crevices, which opens up the prospect of considerably better resolution imaging. Nevertheless, preparing nanotube AFM tips is not simple. You have a choice between growing the tubes in situ or affixing already manufactured tubes to the probes. The procedures for creating nanotube AFM tips are outlined in the first section of this chapter. Next, the effectiveness of nanotube AFM tips is addressed.

Another use for carbon nanotubes' characteristics is gas sensing. It was noted that Alex Zettl's team has discovered that the electrical characteristics of carbon nanotubes are very sensitive to the presence of oxygen. While the tremendous sensitivity to oxygen first seemed to be bad news for the use of nanotubes in electrical devices, it was also proposed that they would be extremely helpful in gas sensors. There has been a lot of interest in the gas sensing capabilities of nanotubes since Zettl's study and another one published recently by Hongjie Dai and colleagues. A short overview of this subject is provided, and then a discussion of the use of nanotubes in biosensors another quickly developing field follows. Lastly, various applications for nanotubes as physical sensors are discussed.

Atomic force microscopy nanotube hints

Nanotube preparation advice: mechanical assembly

In the early efforts to employ carbon nanotubes as AFM tips, the points of commercial Si or Si_3N_4 pyramids were attached to ready-made tubes. A 1996 article by Smalley and a technique for gluing multiwalled nanotubes to the tips of commercial silicon pyramids was reported by colleagues. As a result, this was accomplished. Initially, an acrylic glue was applied to the base of a pyramid by lowering it onto a carbon tape that had adhesive on it. Under the direct vision of an optical microscope, this tip was then brought into contact with a bundle of 5–10 MWNTs, and a single tube was then pulled out to serve as the imaging probe. The AFM pictures of a patterned film were then captured using the nanotubes' tips.

Lieber and colleagues have created carbon nanotube AFM probes utilizing mechanical assembly after this groundbreaking work. Using an optical microscope, they adhered open-ended MWNTs on silicon pyramids with acrylic glue. As will be detailed later, the tips were utilized to image biological systems. Lieber's team also created single-walled nanotube AFM tips in addition to multi-walled tubes. On oxidized silicon substrates, the SWNTs were produced using CCVD with an iron catalyst.

Next, using silicon tips in tapping mode, images of the nanotube-covered wafers were captured. In silicon pyramids, isolated, vertically aligned SWNTs were found and 'picked up'. The pyramids were covered with a tiny coating of a UV-cure glue prior to scooping up the nanotubes so that probes could be utilized for imaging underneath fluids. It was also explained how to use voltage pulses to gradually reduce the length of the tube tips. SWNT probes were discovered to require to be extremely short (about 10 nm) in order to be utilized for imaging. Lieber and colleagues have employed gold nanoparticles to characterize the nanotube tips in addition to SEM or TEM examination. As they can be created with very uniform sizes and are practically incompressible, these nanoparticles serve as suitable imaging standards for AFM. The two-sphere model is used to compute the effective tip radius from the particle picture. The diameter of MWNT tips that were manually constructed was found to be as tiny as 12 nm, which is typical for arc-produced MWNT tubes. The observed radii for the mechanically assembled SWNT tips were greater than what could be anticipated if the tips were separate tubes, indicating that the tubes were bundled together.

The University of Warwick's Neil Wilson and Julie Macpherson, together with their collaborators, have also created SWNT tips using the "pick-up" method and employed them for non-contact (tapping) imaging. This allowed for the attachment of both single SWNTs and bundles of SWNTs to metal-coated silicon tips (gold and platinum). Due to the fact that the SWNT bundles adhered to the tips far better than the individual SWNTs, they could be utilized in solutions and for extended periods of time (several months). Moreover, the bundles may be utilized without being shortened; imaging could be done with tips longer than 1 m. Producing electrically conductive nanotube-based probes for electrochemical, conducting AFM, and electrostatic force microscopy applications is of special interest to this group. In this regard, they have proposed a technique for producing metal probes with a diameter of as little as 30 nm by sputter coating SWNT-AFM probes with AuPd or Au.

With a scanning electron microscope, mechanical construction of nanotube AFM probes may also be done in a somewhat more controlled manner. The approach was disclosed by Japanese researchers who initially used an AC electrophoresis technique to align nanotubes on the edge of a razor before moving one of the tubes to a standard Si tip within a SEM with two independent translation phases. The nanotube tips then outperformed conventional tips in terms of resolution when used to scan DNA strands in tapping mode. A team from Korea attached nanotubes to AFM tips using piezoelectric nanomanipulators within a SEM. The electron beam was employed to "weld" the tubes to the tips a similar method was used by Ruoff and colleagues in their work on mechanical properties. University of Nottingham researchers have more recently employed mechanically formed nanotube tips to scan proteins in very high resolution.

Nanotube preparation advice: chemical vapour deposition

Growing carbon nanotubes directly on a cantilever using catalytic chemical vapour deposition is another way to connect them to AFM pyramids (CVD). There are various methods to do this. One method, developed in 1999 by Lieber's group, involves creating a porous surface, depositing catalytic metal particles there, and then subjecting the particles to a high-temperature carbon-containing gas (for example, ethylene at 800 °C). This allows for the formation of aligned nanotubes outside of the pores. By initially establishing a flattened region of 1 to 5 m on Si AFM tips (by "hard scanning" the tips on a diamond surface), Lieber and colleagues were able to construct a porous Si surface. The surface was then anodized in hydrofluoric acid to produce pores with a diameter of 100 nm. Thin, individual multiwalled nanotubes with average sizes of 6 to 10 nm were seen by TEM projecting from the ends of the silicon tips. The same group has then shown the development of tiny SWNT bundles with a diameter of 1-3 nm from holes created at the ends of silicon tips. There is no doubt that the pore-growth technique can produce nanotube AFM probes. There are downsides, though: creating a porous layer might take a while, and the holes could not be oriented correctly to encourage the development of nanotubes in the best direction. Lieber and colleagues have shown that the nanotubes can also be produced on the surface of Si pyramids in addition to in porous Si. In this method, the pyramids are coated with catalytic metal particles, which are subsequently exposed to ethylene under favorable circumstances for the development of nanotubes. It is discovered that surface energy tends to direct the tubes toward the tip as they expand.

AFM tip preparation via direct growth of nanotubes has gained a lot of popularity. This method may theoretically be used to mass-produce nanotube AFM tips. The Stanford group provided the first proof of this in 2002. They began with a wafer that was readily available on the market and had 375 premade Si cantilevers with pyramidal AFM tips on them. The pyramids' tops were left uncovered after spin-coating and baking polymethylmethacrylate onto the wafer. The PMMA layer was removed, and catalyst particles were then placed onto the wafer from a solution. Just the pyramids remained with the catalyst particles after this, which were subsequently utilized to generate nanotubes. Ultimately, voltage pulses were used to shorten the tubes. It's unclear whether these suggestions for imaging were effective.

Using nanotube AFM tips for imaging

Smalley and colleagues captured tapping-mode AFM pictures of a patterned layer on a silicon wafer using their mechanically built SWNT probes. It was discovered that the tips could penetrate deep pits in the film and provide far more realistic pictures than those produced with pyramidal tips. In addition to the above-mentioned investigations using gold nanoparticles, the Lieber group has also investigated isolated proteins employing nanotube probes. Isolated immunoglobulin-G (IgG) and immunoglobulin-M (IgM) antibody proteins were imaged using pore-grown MWNT CCVD tips. The molecular weight of immunoglobulin-G is 180 000, and it has a distinctive Y-shaped structure that is 15 nm in size. The Y-shape was only seen at cryogenic temperatures in earlier AFM tests using conventional tips. Lieber et al. successfully resolved the Y-shaped structure at room temperature using MWNT CCVD tips. Using this kind of probe, the pentameric structure of IgM was also determined. Lieber and colleagues employed the smaller protein GroES as a test specimen to assess the performance of the smaller diameter CCVD SWNT tips. They acquired greater resolution pictures than they did with conventional tips.

The Lieber group is also credited with being the first to employ functionalized carbon nanotube tips to detect certain interactions with functional groups on substrates. The caps were originally removed from the tubes by oxidation, which also caused the production of carboxyl surface groups. Afterwards, surfaces that had been patterned with various compounds were chemically sensitively imaged using the carboxyl-terminated tubes. Similar techniques were used to tubes that ended in amine groups. Lieber and colleagues employed nanotube tips in addition to chemical imaging to study interactions between biological molecules, particularly the ligand-receptor interaction of biotin with streptavidin. The modified nanotube tips were utilized to probe immobilized streptavidin molecules adsorbed on mica after being covalently coupled to biotin ligand by the creation of amide bonds. The binding forces between the biotin-streptavidin pairs might be measured in this manner.

The majority of research using nanotube AFM tips has used biological material. The potential of nanotube tips for high-resolution imaging of non-biological materials has received little research. It has previously been reported that Smalley and his colleagues' early research on photographing a patterned silicon sheet. To resolve substructure inside SWNTs placed on surfaces, the Lieber group employed mechanically assembled SWNT tips. Moreover, researchers from Japan have employed carbon nanotubes as friction force microscopy probes. Periodic hexagonal pictures that matched the mica surface's atomic structure were produced. The usage of carbon nanotubes as AFM tips has been reviewed in a helpful way by NASA's Cattien Nguyen and colleagues.

Gas Sensors

Zettl and colleagues detailed measurements of the DC electrical resistance and thermoelectric power of bundles and thin films of SWNTs in their Science publication that was published in 2000. The samples were set up in a vacuum test chamber that included features for chilling, heating, and introducing various gases. A four-probe contact setup was used to test resistance at ambient temperature. The presence of air was shown to cause a 10-15% decrease in resistance, which could be reversed by re-evacuating the chamber. When pure oxygen was employed, a similar result was seen. Also, measurements of the SWNT samples' thermoelectric power, S, or the voltage produced when their two ends were held at various temperatures, were performed. Although a smaller, negative S occurred in vacuum, which is consistent with n-type behavior, a positive S was seen in the presence of oxygen, suggesting p-type behavior. While the Zettl findings were supported by theoretical work by Marvin Cohen's group, their validity has since been questioned by further experimental and theoretical investigations. In contrast to the chemisorption that the Zettl group had assumed, Tobias Hertel and colleagues' research in 2002 demonstrated that the binding energies for oxygen on SWNTs might be attributable to van der Waals interactions, or physisorption. In a 2003 publication, Goldoni and colleagues hypothesized that contamination may have contributed to the observed oxygen sensitivity. By using photoemission spectroscopy, this group investigated the adsorption of oxygen on carbon in pure "buckypaper." They discovered proof that oxygen had been chemically absorbed onto the nanotubes, which is consistent with the idea that oxygen may have a significant impact on the tubes' electrical characteristics. The photoemission spectra, however, also revealed the existence of a number of impurities in the purportedly cleaned buckypaper. In particular, a significant quantity of Na, likely a byproduct of the purifying procedure, as well as Ni from the catalyst particles and other minor impurities, were present. So, it seems that there may be some uncertainty over the first findings.

The somewhat earlier-published study of Dai and colleagues seems to be less contentious. The results of this investigation demonstrated how delicately nitrogen dioxide and ammonia affected each SWNT's ability to conduct electricity. Each end of a single semiconducting SWNT was linked to gold or titanium pads in a specific configuration. They discovered that exposure to nitrogen dioxide and ammonia quickly affected the conductivity of the SWNT across many orders of magnitude using the pads as electrodes. Consequently, after exposing the tube to 200 ppm NO_2, a rise in conductivity of up to three orders of magnitude was seen within 10 seconds. After two minutes of adding 1% NH_3, the conductivity dropped by two orders of magnitude. The fact that the sensors operated at room temperature was a key component of the effort. Traditional NO_2 and NH_3 sensors need operating temperatures up to 600 °C for high sensitivity, while those based on conducting polymers have limited sensitivity. So, it seems that the SWNT sensors have a lot of potential. At room temperature, they do have a downside in that they take many hours to release the analyte, however heating might hasten this process.

Numerous other teams have investigated the use of SWNTs to detect NH3, often using functionalized tubes. According to research by Robert Haddon and colleagues, functionalized SWNTs are more sensitive as sensors since they vary their resistance significantly more when exposed to NH3 than pure tubes do. This was ascribed to electron transfer between the valence band of the semiconducting SWNTs and the connected molecules. NO_2 sensors have also used functionalized tubes (11.30). Using SWNTs functionalized with poly(ethylene imine), Alexander Star and colleagues from the University of Pittsburgh developed a nitric oxide sensor in 2007. The conductance of the tubes changed when the NO was first oxidized to NO_2, which was then transmitted across a network of SWNTs in a field-effect transistor device. By detecting NO in exhaled air, the gadget, according to the scientists, may aid in the diagnosis of asthma.

Metal-particle-adorned nanotubes have also been used to sensing. Dai and colleagues provided the first example of this in 2001, demonstrating that SWNTs coated with Pd nanoparticles can specifically detect hydrogen in an air flow. In this study, Pd nanoparticles were sputter-coated onto both individual SWNTs and nanotube bundles. After being exposed to a flow of air containing 400 ppm hydrogen, the conductivity of the Pd-coated individual SWNT and nanotube bundles decreased by up to 50% and 33%, respectively. Immediately after the hydrogen flow was stopped, the conductivity quickly returned. The work function for Pd decreases when atomic hydrogen dissolves into Pd, which is thought to be the sensing process. In turn, this results in a reduction in the number of hole-carriers in the p-type nanotube and, as a result, a drop in conductivity due to electron transfer from Pd to the SWNTs. NASA researchers have created SWNT arrays with Pd, Pt, Rh, and Au decorations and used them to detect H_2, CO, CH_4, and H_2S, while the Pittsburgh group has created SWNT arrays with Pd, Pt, Rh, and Au decorations (11.34). Researchers from the USA and Sweden demonstrated in intriguing research that electrical transport in metallic SWNTs was sensitive to collisions with inert gas atoms or tiny molecules, such as He, Ar, Ne, Kr, Xe, and N_2, in Science, 2005. With present technology, it is challenging to detect these gases

Biosensors

There are several ways that carbon nanotubes have been used as biosensors. There has been a lot of interest in replacing or enhancing conventional electrode materials like glassy carbon or precious metals with "bulk" volumes of nanotubes in macroscopic electrodes. On the other end of the spectrum, it has been shown that single-walled tubes can be utilized as sensors. We start by thinking about large-scale nanotube electrode-based electrochemical biosensors.

A reference electrode, an active electrode, and a sink electrode are often included in electrochemical biosensors. A signal is formed when the reference electrode's potential is subtracted from the analyte's reaction with the active electrode surface. The large surface areas and conductivities of carbon nanotubes are only two of the characteristics that point to the possibility that they might create desirable electrode materials. As was previously mentioned in Chapter 8, the use of functionalized nanotubes in electrodes is also interesting. Nanotube-containing electrodes have now been used in several investigations, and in many instances they have shown characteristics that are comparable to or better than those of traditional electrodes. The electrodes have been created using a variety of techniques, such as simply combining the nanotubes with a binder or drop-coating a glassy carbon electrode.

Furthermore, electrodes have been made using aligned nanotubes. They have sometimes been made via direct growth and occasionally by self-assembly.

Now let's talk about nanotube-based biosensing at the nanoscale. A field effect transistor (FET) configuration, such to that seen in several of the chemical sensors mentioned above, has often been employed in this. The creation of protein sensors and the work of Hongjie Dai's team were both acknowledged. This entailed applying a surfactant coating to SWNTs before affixing certain receptors to the coated tubes. These devices' tubes were produced on quartz surfaces in-situ. The source and drain electrodes were then created by metal evaporation via a shadow mask. Monitoring the electrical current flowing through the apparatus while adding proteins served as the method for sensing in solution. Using electron-beam lithography once again, metal electrodes were placed on top of the SWNTs after the tubes were produced in situ on SiO2. The next step included immobilizing glucose oxidase (GOx) on the tubes using a pyrenyl group connecting molecule. In order to show that single nanotubes may function as sensors, it was discovered that the conductivity of the GOx-coated tubes changed with pH and with the presence of glucose. Many top-notch evaluations are accessible if you want more information on the extensive research done on nanotube biosensors.

Physical Sensors

As was mentioned above, carbon nanotubes are used in atomic force microscopy. In this case, we're interested in using nanotubes as "nanobalances" to monitor physical phenomena like pressure and flow rate. Researchers at the Weizmann Institute in Israel, led by Daniel Wagner, have investigated the use of nanotubes as pressure sensors. These researchers demonstrated how the stress or strain placed on the nanotubes has a significant impact on the disorder-induced D* band in the SWNTs' Raman spectra. The strain in composite materials containing nanotubes may be calculated using this phenomena. Yet, interpretation may not be simple if the nanotubes are arranged randomly in the matrix. This is due to the possibility that the nanotubes perpendicular to the load may undergo compression when a uniaxial stress is applied to the material. In order to prevent this, Wagner and colleagues choose the nanotubes that are aligned with the polarization direction using polarized Raman spectroscopy. It is also feasible to map the strain distribution in these materials using Raman microscopy. This method might also have other issues. The Raman frequency changes brought on by strain are rather tiny, and they will become even smaller as the optical signal travels through the surrounding medium. Because of this, the approach could be challenging to use in certain circumstances.

the notion that running a liquid through carbon nanotubes could be able to produce energy. According to their calculations, a polar liquid, like water, should cause an electron flow along the walls of the conducting nanotubes in the same direction as the liquid flow. Ajay Sood of the Indian Institute of Science in Bangalore and colleagues claimed to have experimentally shown this effect at the beginning of 2003. They presented a device that was made up of a bundle of SWNTs that were randomly orientated, packed between two metal electrodes, and hung in a glass tube that was one meter long. The voltage across the nanotubes was measured as water was circulated through the tube. It was discovered that even very slow flow rates generated significant voltages across the nanotube bundle. A voltage of 0.65 mV was therefore produced with a flow rate of 5 m s1. Higher voltages were discovered to be induced by liquids with stronger ions than water, however non-polar liquids like methanol had a considerably lesser impact. When studies using graphite failed to create any detectable signal, it seems that the one-dimensional character of the SWNTs is essential for the production of an electrical signal. While multiwall nanotubes did create a voltage, it was around 10 times lower than that of SWNTs. It's unclear if Sood and colleagues' findings have been replicated by other teams.

The notion of using nanotubes to weigh tiny particles is another intriguing one that does not seem to have gained much traction. By de Heer and colleagues in 1999, this was proved. These scientists made nanotubes within an electron microscope quiver by applying alternating voltages to them. They were able to stimulate the nanotubes resonantly at both their fundamental frequency and higher harmonics by varying the frequency of the applied potential. They could measure the masses of carbon nanoparticles adhering to the tubes as well as the moduli of the tubes using this method. They propose that additional particles with comparable size, such as viruses, may be studied using this "nanobalance" technique.

Smalley and his colleagues were among the first to identify the potential of carbon nanotubes as AFM tips. The Lieber group also performed significant early work in this field. After these ground-breaking investigations, there has been a noticeable advancement in the manufacturing of nanotube AFM tips, and several spectacular pictures have been captured with these probes. Many AFM businesses are currently selling nanotube tips. Today, the cost of these tips is significant (usually \$400 per tip as opposed to \$50 for traditional tips). Whether nanotube tips will ultimately be utilized as often as Si and Si3N4 probes is yet to be determined. Since the Zettl and Dai groups' Science publications were published in 2000, interest in gas sensing using nanotubes has likewise gradually increased. Nanotubes offer a significant surface area advantage over other materials (single-walled nanotubes are practically "all surface"), which results in great sensitivity. Also, by functionalizing them and loading them with catalysts, nanotubes may be made to detect certain gases.

The ability of nanotube-based sensors to function at ambient temperature gives them an additional advantage over traditional solid-state sensors, which normally operate at temperatures exceeding 400 °C. Nonetheless, it seems that there are still problems with the'recovery period' after gas exposure. As much attention as their use in gas detection, nanotubes are also being used in biosensors. Macroscale electrochemical biosensors using nanotube electrodes have been the subject of much research, and it seems that they have considerable benefits over traditional electrodes. There have also been some spectacular demonstrations of the use of individual tubes as biosensors.

Few materials have likely undergone as much research as carbon nanotubes. We now have a plethora of knowledge about these structures' electrical, mechanical, thermal, optical, and other physical characteristics as a consequence of the vast amount of study done on them since 1991. We know how to place items inside tubes and how to connect things to the outside. Nanotubes may be manipulated into specific configurations and integrated into polymer, ceramic, or metal matrices. Yet, there are now still a limited number of nanotube-containing goods available. The few commercial goods that have been developed are in very niche markets, such AFM tips. While these batteries use MWNTs that were catalytically generated, lithium ion batteries have perhaps been the most commercially important use of nanotubes to date. So, it is reasonable to conclude that carbon nanotubes have not yet reached their full potential. This is mostly due to the fact that they are still prohibitively pricey. Single-walled nanotubes are now priced at roughly \$100 per gram, vs about \$30 for gold. It is obvious that there is still more to be done to increase the output and quality of nanotube synthesis. A succinct and personal assessment of some of the highlights of the study on carbon nanotubes is provided in this chapter. The areas where improvement is still required are then discussed.

Research on carbon nanotubes' top achievements

Sumio Iijima's 1991 letter to Nature would undoubtedly have to be at the top of any list of influential works on carbon nanotubes. It should be noted, nevertheless, that Terr) and their colleagues performed significant research on catalytically generated carbon fibers in the 1970s and 1980s. Its importance is not diminished by the fact that this work was not well-known until after the publication of Iijima's article. They were first made using arc-evaporation, a process that is difficult to scale up. Thus, it was crucial to show in 1996 that single-walled tubes could be made catalytically.

This has substantially enhanced the availability of single-walled tubes (although, as noted above, the commercial price remains stubbornly high). It's crucial to remember that the quality of single-walled nanotubes formed using catalytic techniques is comparable to that of materials created through arc or laser vaporization. It is possible to generate carbon nanotubes in certain configurations by catalytically producing them. The formation of vertical arrays of multiwalled tubes on substrates has been the subject of much investigation since Zhifeng Ren and colleagues' ground-breaking work in 1998. While it is unclear if this has resulted in any commercial goods, one of the main objectives of this study has been to develop field emission display devices. The guided development of SWNTs across substrates to create nanoscale circuits has also attracted a lot of attention. The group led by Hongjie Dai demonstrated how to do this using electric fields in 2001. In 2004, the same team used catalytic growth to include nanotube transistors into a silicon circuit. On a far bigger scale, catalytic techniques have been utilized to make aligned MWNT aerogels continuously, which may then be treated to create fibers with exceptional stiffness and strength. Processing pre-made tubes is an alternative to producing nanotubes in specific layouts.

The Ralph Krupke group has produced some remarkable work on the dielectrophoresis-based assembling of single-walled nanotubes into predetermined designs. They assert that this method can be used to build millions of nanotube devices. Ray Baughman and colleagues' work on spinning MWNT yarns from arrays produced catalytically on substrates is equally impressive. The creation of "buckypaper," or thin sheets of pure single-wall tubes, should be included while talking about the processing of nanotubes. The initial account of this came from Andrew Rinzler and his colleagues. Rinzler has been able to create ultra-thin buckypaper films that are both electrically conductive and transparent to visible light by improving his initial procedure. It seemed inevitable that this remarkable substance will be used in significant ways.

Now let's talk about the electrical characteristics of carbon nanotubes, an area where theory predominated over experience. Carter White's team from the Naval Research Laboratory and Mildred Dresselhaus and colleagues from MIT both submitted articles on the electronic characteristics of fullerene tubes before Iijima's study appeared, as was mentioned in the introduction chapter. Soon after, the MIT team and Noriaki Hamada and colleagues from Tsukuba performed band structure simulations that showed how the diameter and tube structure affected electronic characteristics. In other words, depending on their size and structure, nanotubes might either be metallic or semiconducting. The exact placement of nanotubes on surfaces and very sensitive conductivity measurements necessary for the experimental testing of these hypotheses called for great competence. The direct association between electronic characteristics and SWNT structure, discovered by Dekker and coworkers in 1998, and the demonstration of quantum transport in SWNTs and MWNTs a year later were significant milestones in this field.

These were made by Ebbesen and colleagues in 1996. Additional notable accomplishments include the development of a single-electron transistor based on a SWNT bundle and a logic gate based on a single nanotube bundle in 2001. It goes without saying that developing methods for consistently growing or arranging nanotubes in a certain way will also be necessary if we are to successfully translate these laboratory demonstrations into real-world electrical devices. Recently, several researchers have stated that graphene presents a greater possibility for the creation of nanoscale electronics than nanotubes. Graphene is undoubtedly an intriguing and significant material, but nanotubes have significant benefits over graphene in terms of chemical and physical stability, and their employment in nanoelectronics is still in its very early stages. So, switching from nanotube electronics research to graphene research would be premature.

The 1996 work by Michael Treacy and colleagues, who conducted in situ measurements of the inherent thermal vibrations of multiwalled carbon nanotubes in a TEM, provided the first proof that nanotubes have exceptional mechanical capabilities. Due to the lack of accuracy in this method, the Young's modulus values ranged widely, with an average of 1.8 TPa. Later, more precise measurements have consistently yielded values for the modulus that are near to 1 TPa. As a result, carbon nanotubes are the stiffest materials currently used; they are around five times stiffer than steel and much stiffer than the best carbon fibers. Yet, the combination of a high modulus and other unique mechanical qualities of nanotubes is what actually distinguishes them from other materials. For instance, according to Rodney Ruoff's team, their tensile strength may reach 63 GPa, which is around 50 times more than steel. Moreover, nanotubes have the amazing capacity to rebound from deformations that seem to have caused no harm. It's crucial to recognize, nevertheless, that not all nanotubes possess these remarkable qualities. Most multiwalled tubes have substantially lower stiffnesses and strengths when manufactured catalytically.

Due to the exceptional mechanical capabilities of carbon nanotubes, there has been significant study into the creation of composite materials comprising nanotubes, often with a polymer matrix. It has not been simple to properly integrate the tubes into a matrix in a manner that completely uses their characteristics, and some of the early achievements in this field were underwhelming. In recent years, considerable advancements have been achieved in the homogenous dispersion of nanotubes in a range of matrices and the achievement of excellent tube-matrix bonding. As a consequence, several research teams have created nanotube/polymer composites with outstanding mechanical attributes. The SWNT/PVA fibers created by the Baughman group and the SWNTs/nylon composites created by Karen Winey and colleagues are two examples. Also, and for a number of years now in commercial applications, nanotubes have been utilized to increase the conductivity of polymers.

Improvements in nanotube functionalization have made it possible to produce better nanotube-containing composites, and the chemistry of nanotubes has become a thriving area. Work on nanotube functionalization has assisted in the development of methods for solubilizing, purifying, and processing nanotubes in addition to making the creation of composite materials easier. While it is still a young field, the functionalization of nanotubes with proteins is very exciting due in part to the potential medicinal uses. The finding by Bianco, Kostarelos, Prato, and others that functionalized tubes may cross cell membranes is a significant advancement in this regard.

Since the first experiments by Iijima and colleagues and the Oxford Group, research on putting objects inside of nanotubes has also made significant strides, which is maybe why the science of attaching things to the exterior of nanotubes is gaining more and more attention. Jeremy Sloan and others have done remarkable work on the structure of inorganic crystals within single-walled nanotubes, and fullerene-filled SWNTs, also known as "nano-peapods," which were initially created by Smith, Monthioux, and Luzzi, are generating a lot of attention. The Suenaga group has also captured some incredible photos of individual molecules within SWNTs. This kind of study of tiny organic compounds is fairly novel for transmission electron microscopy.

AFM tips and sensors made of nanotubes are a significant emerging field. The Smalley groups' groundbreaking research showed that nanotube AFM probes have a number of benefits over traditional silicon or silicon nitride AFM probes. As the concept of employing nanotubes in this manner has gained some traction, nanotube tips are currently marketed for sale. The use of nanotubes as sensors represents a field with more economic potential. Due to two investigations that were published in 2000, there has been a lot of interest in the use of nanotubes as gas sensors. A significant amount of research is being put into the use of nanotubes in biosensors. This method can be employed with both bulk quantities of nanotubes and individual tubes, and the likelihood of economic exploitation is high.

It's the mechanism, idiot, said Richard Smalley, echoing Bill Clinton, at a conference in 1993 (12.52), when asked what he thought was the most crucial question in nanotube research. Smalley understood that a fully developed nanotube science could only be based on a solid grasp of the growth process at this early point in the field's development. Without such an understanding, there would be little chance of creating methods for bulk synthesis of high-quality nanotubes or for the creation of nanotubes with specified architectures.

The mechanism is still the main issue in nanotube research 16 years later. Despite advancements, there is still debate concerning the growth methods of single- and multi-walled nanotubes. In particular, it is still unclear how exactly multi-walled tubes originate in the arc. This is true even though arc-grown MWNTs have been used to display some of the most amazing nanotube features. Hence, nanotube science has in some ways gotten ahead of itself (12.53). Carbon nanotubes can be used to create single-electron transistors, however we are unsure of how to create nanotubes with a certain structure. Maybe it's time for nanotube research to shift its focus from some of these more spectacular places to the more basic problem of understanding how these incredible structures really form.

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CHAPTER 15

APPLICATION OF CARBON NANOTUBE

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MWNTs' conductivity is a complicated phenomenon. Several metallic "armchair"-structured CNT varieties seem to conduct differently. Additionally, it has been shown that interwall interactions inside MWNTs cause the current to be redistributed throughout individual tubes unevenly. Yet, the current in metallic single-walled CNTs does not vary in various regions. Nevertheless, the behavior of semiconducting SWNT ropes behaves differently because the transport current suddenly changes at different locations on the CNTs. Electrodes were positioned at various CNT locations to test the conductivity and resistivity of ropes made of SWNTs. At 27°C, the SWNT ropes' resistivity was in the range of 10-4 ohm-cm. As a result, SWNT ropes are the known carbon fibers with the highest conductivity. The most stable current density that the SWNT ropes should be able to support is 1013 A/cm2, which is substantially higher than the current density that could be achieved, which was 107 A/cm2. It has been claimed that certain SWNTs have flaws. Luckily, these flaws enable the SWNTs to function as transistors. Similar to that, connecting CNTs may create devices that resemble transistors. A nanotube with a natural junction where a straight metallic segment is connected to a chiral semiconducting section behaves like an individual molecule rectifying diode, or a half-transistor. The ability of SWNTs to transport electrical signals at high speeds (up to 10 GHz) when employed as interconnects on semi-conducting devices has also recently come to light [1]–[3].

Both power and elasticity

Each carbon atom in a single sheet of graphite (graphene) forms a planar honeycomb lattice with three other carbon atoms via a strong chemical connection. The basal-plane elastic modulus of graphite is one of the highest of any known material because of these robust links. CNTs are anticipated to be the ultimate high-strength fibers as a result. SWNTs are far more resistant to physical force damage than steel and are stiffer than steel. A nanotube's tip may be bent by applying pressure on it without harming the tip. The tip reverts to its initial state when the force is released. Because of this characteristic, CNTs are excellent probe tips for very high-resolution scanning probe microscopy.

It has proven difficult to put a precise number on these impacts, and no consensus has been reached. A freestanding nanotube's unanchored ends may be forced out of equilibrium using an atomic force microscope (AFM), and the force needed to do so can be calculated. It has been stated that SWNTs have a Young's modulus as high as 1.8 TeraPascal. Nevertheless, this figure has been challenged. There have also been reported figures that are noticeably higher.

Different experimental measuring methods are likely to blame for the disparities. Others have shown theoretically that the Young's modulus, which ranges from 1.22 Tpa to 1.26 Tpa, depends on the size and chirality of the SWNTs. They arrived at a figure of 1.09 Tpa for a typical nanotube. Others have shown that while dealing with various MWNTs, the modulus measurements of MWNTs utilizing AFM methods do not significantly rely on the diameter.

Conversely, they contend that the degree of disorder in the nanotube walls is correlated with the modulus of the MWNTs. It should come as no surprise that the topmost layers of MWNTs break first.

Thermal Expansion and Conductivity

According to recent studies from the University of Pennsylvania, CNTs may be the best heat-conducting substance ever created. Even below 20oK, it has been shown that ultra-small SWNTs display superconductivity. According to research, these unusual strands, previously praised for their unmatched toughness and exceptional capacity to assume the electrical characteristics of either semiconductors or ideal metals, may one day find use as tiny heat conduits in a variety of materials and systems.

They are very stiff and resistant against axial stresses because of the strong in-plane graphitic C-C bonds. Strong in-plane coupling and excellent flexibility against nonaxial stresses are implied by SWNTs' nearly negligible in-plane thermal expansion but substantial inter-plane thermal expansion. CNTs have a wide range of potential uses, including in functional composite materials, sensing and actuation devices, nanoscale molecular electronics, and reinforcing additive fibers.

There have also been reports of a number of recent studies on CNT-polymer composite production and mechanical characterisation. These tests indicate slight improvements in the strength properties of CNT-embedded polymer matrix systems compared to bare polymer systems. Studies using modeling and preliminary testing on CNTs' thermal characteristics reveal very high thermal conductivity. Hence, it is anticipated that adding nanotube reinforcement to polymeric materials may also greatly enhance the composites' thermal and thermo-mechanical capabilities [4]–[6].

Emission of Electrons

Multi-walled-carbon-nanotubes-field-emitters

Field emitters for multiple-walled carbon nanotubes

Field emission is caused by electrons tunneling into vacuum from a metal tip while being subjected to a high electric field. CNTs' high aspect ratio and tiny diameter make them ideal for field emission. Because of their sharpness, supported CNTs exhibit significant electric fields at their free ends even at modest voltages.

De Heer and colleagues at EPFL noted this in 1995. He also saw right away that these field emitters had to be better than traditional electron sources and could be used in a variety of applications, most notably flat-panel displays. It is amazing that Samsung was able to develop an extremely brilliant color display utilizing this technology in only five years, and it will soon be on sale.

Carbon-nanotubes-field-emission-display

Field Emission Display using Carbon Nanotubes

When researching the MWNTs' field emission characteristics, EPFL researchers Bonard and colleagues found that light is also released along with electrons. As it cannot be observed without an applied voltage, this light is caused by the electron field emission. The visible portion of the spectrum is where this light emission occurs, and it may sometimes be seen with the unaided eye.

Superior Aspect Ratio

For all sorts of polymers, CNTs serve as a very tiny, high aspect ratio conductive addition. In comparison to other conductive additives, CNTs' high aspect ratio indicates that a smaller loading (concentration) is required to produce the same electrical conductivity. This minimal loading maintains other essential performance characteristics of the matrix resin and increases the toughness of the polymer resins, particularly at low temperatures. CNTs have shown to be a great addition for giving polymers electrical conductivity. Compared to common additive materials like carbon black, chopped carbon fiber, or stainless steel fiber, their high aspect ratio (approximately 1000:1) imparts electrical conductivity at lower loadings.

Uses of Carbon Nanotubes

Many potential uses for carbon nanotubes are made possible by their distinctive composition, structure, and characteristics. Cost reduction to economically feasible levels has proved difficult, although scaling up is taking place. Single-wall CNTs are endowed with outstanding material qualities, such as extremely high electrical and thermal conductivity, strength, stiffness, and toughness, thanks to the unique features of carbon and the molecular perfection of these nanotubes.

The carbon-carbon bond is the strongest one that exists between any two elements in the periodic table. The first known molecule with metallic-type electrical conductivity results from the delocalized pi-electron provided by each atom being free to wander throughout the whole structure rather than staying with its donor atom. The inherent heat conductivity of the high-frequency carbon-carbon bond vibrations is greater than that of even diamond.

Yet, in most materials, the development of structural flaws significantly degrades the actual apparent material attributes, such as strength, electrical conductivity, etc. For instance, high-strength steel often breaks at barely 1% of its potential breaking strength. Nonetheless, because to the molecular precision of their structure, CNTs obtain values that are very near to their theoretical limitations.

This feature is a part of what makes CNTs special. True nanotechnology is shown by CNTs, which, while having a diameter of just a few nanometers, are molecules that can be chemically and physically altered in highly beneficial ways. They bring up a wide variety of possibilities in a number of disciplines, including materials science, electronics, chemical processing, energy management, and many more.

Energy Reserves

CNTs possess the inherent qualities sought in a material used as an electrode in batteries and capacitors, two fast expanding fields of technology. The surface area of CNTs is astronomically large (1000 m^2/g), they have strong electrical conductivity, and most significantly, because of their linear design, the electrolyte has a very easy time accessing their surface. According to research [B. Gao, Chem. Phys. Lett. 327, 69 (2000)], CNTs have the largest reversible capacity of any carbon material for use in lithium-ion batteries. Moreover, CNTs are presently being promoted for use as supercapacitor electrodes due to their remarkable performance. Moreover, CNTs are used in a number of fuel cell parts. They are advantageous as electrode catalyst supports in PEM fuel cells because to a variety of characteristics, including large surface area and thermal conductivity. Due to their high electrical conductivity, they may also be used as current collectors and gas diffusion layers.

The high strength and toughness-to-weight properties of CNTs may potentially be useful in composite fuel cell parts used in transportation applications where durability is crucial.

Electro molecular Chemistry

In the last five years, the concept of creating electrical circuits out of the fundamental building blocks of materials molecules has seen a resurgence. This concept is a significant part of nanotechnology. The connections between switches and other active devices play an increasingly significant role in every electronic circuit, but especially so when circuit dimensions approach the nanoscale.

CNTs are the perfect materials for the connections in molecular electronics because of their shape, electrical conductivity, and ability to be precisely generated. They have also been shown to function as switches on their own. CNTs used in thermal materials exhibit exceptional mechanical, electrical, and heat conductivity. They are most likely the best feasible electron field-emitter. These are pure carbon polymers that can be altered and interacted with utilizing the well-known and very complex chemistry of carbon. This offers the chance to change their structure, as well as to improve their solubility and dispersion [7], [8]. Most importantly, CNTs are molecularly flawless, which implies that they often don't have structural faults that would degrade their property. As a result, their material qualities might nearly resemble the very high levels inherent to them. CNTs have promise in a wide range of applications because to their exceptional properties. Many applications that need the transfer of heat from one location to another are being made possible by CNTs' record-breaking anisotropic thermal conductivity. Such a use is common in electronics, especially in high-end computing, where uncooled chips today often reach temperatures of above 100°C. The development of aligned CNT structures and ribbons is a significant step toward the creation of highly effective heat conduits. Moreover, even at extremely low loadings, composites containing CNTs have been demonstrated to significantly improve their bulk heat conductivity.

Building Materials

In addition to their better electrical and thermal conductivities, CNTs also possess superior mechanical qualities including stiffness, hardness, and strength. These characteristics enable a wide range of applications to take use of them, such as advanced composites that need high values of one or more of these characteristics.

Emitters of Electricity

The most well-known field emitters of all materials are CNTs. With their high electrical conductivity and very pointed tip (he lower the radius of curvature, the more concentrated the electric field, resulting in enhanced field emission; this is the same reason lightning rods are sharp, this is reasonable. The fact that they emit at a particularly low voltage due to the sharpness of the tip is crucial for the development of low-power electrical devices that make use of this property. As much as 1013 A/cm2 of current may be carried by CNTs, which is an astoundingly high current density. The current is also quite steady.Field-emission flat-panel displays are one obvious use of this phenomenon that is generating a lot of attention. For each each pixel in CNT-based displays, there is a distinct electron gun (or possibly many of them), as opposed to a single electron gun, as in a conventional cathode ray tube display. CNTs are very desirable field emitters in this application because of their high current density, low turn-on and operating voltages, and consistent, long-lasting behavior. General low-voltage cold-cathode lighting sources, lightning arrestors, and electron microscope sources are a few more uses for CNTs' field-emission properties.

Fibers and Fabrics

Recent research has shown that pure CNTs may be spun into fibersas well as CNT composite fibers, are also developing quickly. Transmission line cables, body and vehicle armor, woven fabrics, and textiles are just a few uses for these very strong fibers. CNTs are also employed to create stain-resistant fabrics.

Activator Supports

In reality, SWNTs' individual atoms are located on both the inside and outside of the nanotube, giving them an extremely large surface area that is inherent to CNTs. This opens up the possibility for special catalyst supports when combined with the functionalization capacity to attach almost any chemical species on their sidewalls. To find novel catalysts and catalytic activity, their electrical conductivity may also be used.

Biomedical

CNT research in biological applications is only getting started, but it has a lot of promise. As carbon makes up a significant portion of the human body, it is often regarded as a material that is particularly biocompatible. CNTs seem to have no harmful impact since it has been shown that cells can grow on them. Also, the cells do not cling to the CNTs, which might lead to applications like coatings for prostheses and anti-fouling coatings for ships. The sidewalls of CNTs may be functionalized chemically, which has implications for biological applications including vascular stents and neuron development and regeneration. Also, it has been shown that a single strand of DNA may effectively bind to a nanotube before being injected into a cell.

Air and water filtration using CNTs

Devices for air and water filtration based on CNTs have already been developed by several academics and businesses. These filters are said to be able to eliminate the majority of germs in addition to blocking even the tiniest particles. CNTs have already achieved commercial success in this field, and there are products available right now.

Plastics that Conduct

The usage of plastics as a substitute for metals has dominated the history of the past 50 years. Plastics have advanced significantly in structural applications, but not in areas where electrical conductivity is necessary since they are excellent electrical insulators. To make up for this shortcoming, conductive additives like carbon black and bigger graphite fibers are added to polymers the ones used to make golf clubs and tennis rackets. Nevertheless, the loading necessary to achieve the needed conductivity with traditional fillers is often substantial, resulting in heavy components and, more significantly, plastic parts with severely compromised structural characteristics. It is generally known that less loading is necessary to attain a given level of conductivity the greater the aspect ratio of the filler particles [9], [10]. As CNTs have the largest aspect ratio of any carbon fiber, they are perfect in this regard. Also, even at very low loadings, their innate propensity to form ropes creates extremely lengthy conductive paths. Applications that take advantage of this behavior of CNTs include radar-absorbing materials for low-observable ("stealth") applications, EMI/RFI shielding composites, coatings for enclosures, gaskets, and other uses, electrostatic dissipation (ESD), and antistatic materials and even transparent conductive coatings.

Adhesives for Conductivity

CNTs are desirable for electronics packaging and connectivity applications such as adhesives, potting compounds, coaxial cables, and other kinds of connections due to the same characteristics that make them desirable as conductive fillers for use in electromagnetic shielding, ESD materials, etc.

CNT Ceramic Products

Materials researchers at UC Davis have created a ceramic material enhanced with carbon nanotubes. Depending on how the nanotubes are oriented, the novel material may function as a thermal barrier and transmit heat as well as being much harder than ordinary ceramics. It also conducts electricity. Ceramic materials are highly brittle but also very durable, heat and chemical resistant, making them excellent for coating turbine blades and other uses. Alumina (aluminum oxide) powder was combined with 5 to 10% carbon nanotubes and an additional 5% of finely ground niobium by the researchers. The combination was subjected to a spark-plasma sintering procedure in which the researchers used an electrical pulse. Compared to other techniques, this one consolidates ceramic particles more rapidly and at a lower temperature. The novel substance possesses up to five times the standard alumina's fracture toughness, or resistance to breaking under force. Seven times more electrical conductivity than earlier ceramics created with nanotubes is shown by the substance. Also, it has intriguing thermal characteristics that make it a desirable material for thermal barrier coatings since it conducts heat in one way along the alignment of the nanotubes but reflects heat in a different direction.

Additional Uses for Carbon Nanotubes

CNTs have a wide range of other potential uses, including solar collecting, nanoporous filters, catalytic supports, and coatings of many kinds. In the years to come, there will very definitely be many unforeseen uses for this extraordinary substance that may turn out to be the most significant and useful ones of all. Numerous scientists are studying conductive and/or water-resistant paper created using CNTs. Also shown to absorb infrared light, CNTs may find use in the I/R optics sector.

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CHAPTER 16

NANOMATERIALS USED IN THE AUTOMOTIVE SECTOR

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Due to the unique physical and chemical characteristics inherent in both the nanomaterial itself and its end product, nanomaterials come into play. Everything whose size is similar in the range of 0.1 to 100 nanometers, as indicated in Fig. 1, is the best approach to characterize nanomaterials. The automobile sector has made extensive use of nanotechnology to innovate its processes and boost vehicle performance. As shown in Fig. 2, the use of nanomaterials in automotive applications may outperform traditional materials in terms of strength and endurance. In order to manage or change the structures and characteristics of the materials to improve performance, nanomaterials may provide new techniques or tools. We are aware that innovation is necessary for the contemporary world, but we also need to think about safety and durability for things like cars, airplanes, and ships. Nanomaterials tend to meet these needs. Without the use of nanotechnologies such lightweight nanomaterials, scratch-resistant coatings, and nanofluids, new smart, high-performance cars are not possible in today's transportation [1]–[3].To improve the performance and longevity of numerous body sections, such as the chassis, tires, windows, and engines, nanotechnologies may be used. Yet, there are also health concerns and environmental problems related to the use of nanotechnology in transportation that need careful consideration. As shown in Figure 1 effect vs. demand graph, the specifics of nanotechnology's transportation applications are described.

Uses for Nanomaterials in the Automotive Industry

Nanomaterials are employed in more than a thousand different applications. This review study focuses only on the uses of nanomaterials in the automotive industry. We only discuss the cases that have the most appeal to scientists, researchers, and the general public. Each example we are using is based on research that they conducted. The first use is Nano Base, a Nano-type structure that strengthens tire caps, enhances their gripping ability and handling characteristics, and also works to lessen tire heat effect and rolling friction. WR A3 tires now utilize it.

The second example is Nano pro-Tech, which is a tyre thread nanocoating that lowers heat production.

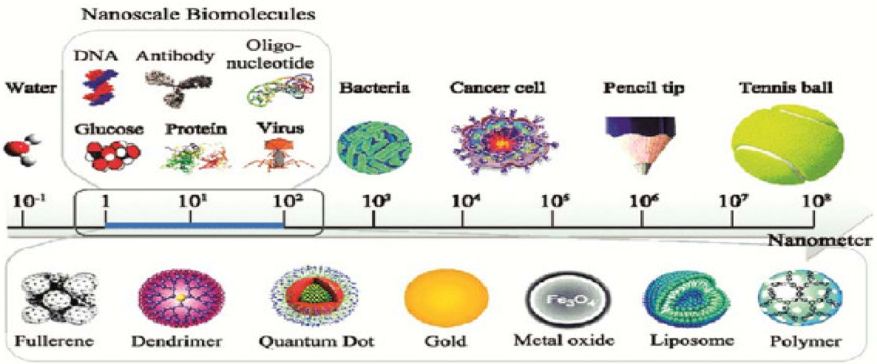

Figure 1: Illustrate the nanostructure.

Vehicle requirement

The most important and difficult need for creating a good material is that it be strong and light. ratio that is optimal for a car that efficiently combines better engine performance with improved fuel efficiency. The crucial elements of an automotive component. High specific strength, Low coefficient thermal expansion and high thermal resistance, strong damping capacity, superior wear resistance, High specific Stiffness, and a satisfactory degree of corrosion resistance are some of the qualities of metal matrix composites (MMCs) [4], [5].

Composites reinforced by nanotechnology

For processing metal matrix composites, some previous processes included polymerizing rigid rod polymer, assembling laminate composites, and polymerizing filled polymers. Nano Reinforced composites serve two main purposes. The first is that it can replace the older, less effective materials, while nano reinforced composites can help push the envelope and be better. The utilization of these Nano reinforced composites in locations where conventional and antiquated materials cannot be used serves another benefit.

Nanocarbon tube

The diameter of the carbon that makes up carbon nanotubes is measured in nanometers. Carbon nanotubes are abbreviated "CNT" in this sentence. When rolled into a tube, a carbon nanotube's properties are identical to 1- or 2-dimensional graphene sheets. As illustrated in Fig. 9, these sheets may have a single wall or several walls (a). Carbon nanotubes have certain unique, exceptional qualities, such as an elastic modulus that is roughly equivalent to 1 TPa, strength that ranges from 30 to 100 GPa, and a low coefficient of thermal expansion.

Also having a high heat conductivity are carbon nanotubes. There are three different varieties of carbon nanotubes: single-walled nanotubes (SWNT), multi-walled nanotubes (MWNT), and double-walled nanotubes (DWNT).The use of carbon nanotubes reduces weight. It may be able to lower the danger of fuel system explosion and electrostatic discharge in the fuel system. Basically, the reason Carbon Nanotubes enter the scene is because they are excellent at creating covalent connections. The automotive sectors provide several opportunities for carbon nanotubes. Because to their extraordinary qualities, they may be used to produce components for automobiles such as engine blocks, head shields, and chassis, as well as for hydrogen fuel cells.

Composites made of aluminum and carbon

Al-CNT composites, commonly known as aluminum carbon nanotube matrix composites, are photo after the identification of carbon nanotubes. In actuality, this is a crude rendition of carbon nanotubes. Al-CNT composite has the capacity to enhance the composites' high-temperature deformation resistance. In Fig. 9, the Al-CNT composite is shown (b). Al-CNT enhances performance at high temperatures as well. Nevertheless, AI-CNT has several restrictions. It is apparent that it is somewhat unstable at lower temperatures and greater strain rates.

Silicon carbide

High performance "ceramics" employ silicon carbide, a silicon infiltrated carboncarbon composite. They can function well in hot environments. As an example, consider brake discs, which are employed in current automobiles like racing cars, motorcycles, etc. Sintered steel for diesel particle filters also contains Si-C.

Si-Al Composites

We continuously seek for new methods to improve the characteristics in order to acquire more and more advantages. The clearest illustration of this is the addition of SiC (silicon carbide) particles to Al-CNT composites, which are highly valued for their better strength, stiffness, wear resistance, and corrosion resistance. The most obvious usage is because it can be found in many automotive-related businesses, including vehicle drive shafts. However we are aware that each item has advantages and disadvantages. As normal, it has certain drawbacks. For example, while producing Al-SiC, Al does not combine with molten SiC composites at 600°C, but molten Al interacts quickly with SiC and produces a new material when the temperature is between 650 and 920 °C.

Graphene Graphene is a single layer of carbon atoms arranged in a two-dimensional hexagonal lattice. Every atom has a pi (π) bond that is orientated out in one plane and three bonds with one sigma with each neighbor make up the quartet. Van Der Wal l forces keep graphene layers in place. Due of its high cost, graphene is not widely used. Yet, it has a few advantages that set it apart from the competition.

Graphene is employed in automobiles, making them lighter and 200 times stronger than steel, carbon fiber, steel, and aluminum components. It creates cutting-edge interiors with self-cleaning and thermally conductive fibers that provide high-end automotive interiors. In the next years, lithium ion batteries may be replaced or improved with the usage of energy-efficient batteries made from graphene. Both carbon nanotubes and graphene are relatively new materials. Both exhibit some notable characteristics in terms of their qualities. Some of their shared qualities and some of their unique ones. The first factor contributing to the two materials' stronger nature is the presence of sp^2 bonds between their carbon atoms. They are made much stronger by the sp^2 connection, which allows them to surpass diamond, the hardest substance as well. Due to their special molecular structure, they have the maximum tensile strength as well as the ability to transmit heat and electricity. The only thing that separates them is that although carbon nanotubes may either function as a semiconductor with a varied band gap or as a metallic material depending entirely on its kind of structure, graphene is a zero gap semiconductor [6]–[8].

We need inventiveness in the automotive sector. And the use of nanotechnology and nanomaterials encourages this sort of improvisation. We might claim that the automobile industry are entering a golden age thanks to nanomaterials. Our objective in the auto motive industries is to improve engine efficiency and extend the lifespan of the vehicle motive components.

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CHAPTER 17

BIOTECHNOLOGY AND MEDICAL USES FOR CARBON NANOTUBES

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Carbon nanotubes are one of the most promising materials for the electronics, computer, and aerospace sectors because of their electrical, chemical, mechanical, and thermal capabilities. Below, we go through their characteristics in light of potential biotechnology and biomedical applications. It is explained how to clean carbon nanotubes and modify them chemically using organic, polymeric, and biological materials. Moreover, we discuss their use in biosensors, the construction of devices and structures, scanning probe microscopy, and as neural development substrates. We point out that further research on the toxicity of carbon nanotubes is required in order to quickly set exposure standards and safety requirements.

Even though man was able to recognize shapes at the nanoscale level long before nanomaterials existed in nature, breakthroughs in synthetic chemistry have been one of the main motivations behind the emergence of a biological nanotechnology. Many biomedical and biotechnological uses of nanomaterials have been developed, such as bone development, enzyme encapsulation, biosensors, and DNA delivery vesicles for living cells. Biotechnology already has incredibly sophisticated tools to precisely place molecules and create hierarchical structures and devices, unlike nanotechnology, which may provide innovative materials that might lead to ground-breaking new structures and technologies. The use of biological principles in nanotechnology offers a useful path for further shrinking and performance enhancement of manufactured products. In several inorganic-organic hybrid systems and devices, the viability of the bottom-up strategy, which is based on the molecular recognition and self-assembly characteristics of proteins, has previously been shown. The ability to examine biochemical processes and influence live cells at the single molecule level is made possible by nanodevices having biorecognition characteristics. Future advancements in tissue engineering, prosthetics, genomics, pharmacogenomics, drug delivery, surgery, and general care are highly anticipated as a result of the synergistic interaction between nano- and biotechnologies [1]–[3].

The peculiar characteristics of carbon have captivated scientists ever since Edison found that it alters its resistance with pressure and glows when an electric current is sent through it. Carbon has reached its apogee in fullerenes and carbon nanotubes (CNTs), possibly the most promising of all nanomaterials, after more than a century of research. CNTs have attracted the interest of physicists, chemists, and materials scientists because to their distinctive quasi one-dimensional structure and intriguing mechanical and electrical capabilities. The use of CNTs in biology and medicine is fast expanding in these fields. The application of biological principles for the manipulation and self-assembly of functional structures and devices based on CNTs, as well as the use of modified CNTs to control and study live cells, are two areas of the connection between biology and CNTs that are highlighted in this article.

TYPES AND STRUCTURES OF CARBON NANOTUBES

With the discovery of carbon nanotubes in 1991, which was the first observation to be reported, the discipline advanced quickly. Two different forms of carbon nanotubes: multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes8 (SWNTs). Many coaxial cylinders constructed of a single graphene sheet enclosing a hollow core make up MWNTs. Electric arc9 and chemical vapor deposition are the most widely used manufacturing processes for them (CVD). A catalyst could be required for MWNTs to grow. MWNTs have an outside diameter that varies from 2 to 100 nm, an interior diameter of 1 to 3 nm, and a length of 1 to several m.

CARBON NANOTUBES ARE MODIFIED BY BIOLOGICAL MOLECULES

The engineering of the interface between biological molecules and SWNTs has been investigated using both non-covalent and covalent methods with the aim of retaining the functional characteristics of the biomolecules. The bi-functional chemical 1-pyrenebutanoic acid succinimidyl ester, which irreversibly adsorbs on the hydrophobic graphene surface of the SWNTs through a -stacking interaction, is used in a non-covalent method that has been devised. 69 This method gives the carbon nanotubes particular biological recognition capabilities and enables subsequent protein attachment through a nucleophilic substitution reaction of succinimidyl by an amine group of the protein [3]–[5].

Carbodiimide chemistry has been used to accomplish the covalent binding of CNTs to proteins and DNA. Shown in Scheme the diimide-activated amidation of carboxylic acid-functionalized carbon nanotubes is often used for the covalent binding of proteins, including enzymes and antibodies. Bovine serum albumin (BSA) was used to functionalize a fiber made of SWNTs, and indirect immunochemistry was used to validate the functionalization. A unique antibody-antigen interaction was produced by incubating the assembled BSA-functionalized SWNT fiber with a BSA-reactive antibody. Following washing, a secondary, fluorescent (FITC)-conjugated antibody was added to the main antibody. This combination made it possible to use fluorescence microscopy to see the fiber. Similar to this, amidation processes may be used to connect amine-terminated DNA to the carboxylic acid functional groups of CNTs. Other methods include cross-linking succinimidyl 4-(N-maleimidomethyl) cyclohexane-1-carboxylate (SMCC) with amine-terminated SWNTs to form maleimide groups, which are then further reacted with thiol-terminated DNA.

DNA-BASED SWNT SEPARATION AND DISPERSION

SWNTs are created using every known synthetic technique and come in a variety of lengths, diameters, and combinations of metals and semiconductors that are typically hexagonally packed in bundles. The biggest barrier to SWNTs' use in electronics, field emission displays, and nanosensors is the difficulty to currently differentiate individual SWNTs by length, diameter, or electrical characteristics. The earlier-discussed chemical alterations may help dissolve and unbundle SWNTs. According to recent research, the dispersion and de-bundling of SWNTs as well as their separation based on electrical structure may be resolved by DNA complication. In the presence of an aqueous solution of single-stranded DNA, sonication of bundled SWNTs produced a stable dispersion. According to research using molecular modeling, the DNA helically surrounds individual SWNTs and successfully competes with their ability to attach to nearby tubes, scattering them. It is suggested that the binding is caused by a -stacking contact between the bases in the DNA and the sidewall of the SWNT. Because of this contact, DNA is wrapped into helices, exposing its hydrophilic sugar-phosphate groups to the solvent. A SWNT-DNA hybrid's phosphate groups create a negative charge density on the surface of the CNT, which causes the individual nanotubes to separate and dissolve in water. Ion-exchange liquid chromatography may be used to fractionally separate DNA-metallic SWNTs from DNA-semiconducting SWNTs thanks to this dissolving process. Hence, this method depends on DNA to spread out distinct SWNTs and enable electrical structure-based discrimination of these macromolecules.

FOR BIOSENSORS: MODIFIED CARBON NANOTUBES

Current biosensing methods are very sensitive and precise, yet they are challenging to miniaturize. SWNT-based biosensors may be made smaller due to the structural characteristics and tiny size of carbon nanotubes. Every carbon atom in SWNTs is located on the surface, resulting in a high area to volume ratio for interactions with relevant molecules. SWNTs may also be employed for the electrical detection of binding events, offering a relatively simple method of biosensing, thanks to their distinct electronic structure and ballistic conductance. SWNTs have previously been used successfully by many organizations as adaptable biosensors. A considerable conductance shift has been seen in SWNTs in response to the presence of proteins and small biomolecules. A SWNT device has been used to in situ detect the adsorption of cytochrome C, a redox catalyst in the respiratory chain of mitochondria. Biotin-streptavidin binding has been electrically detected using 88 biotin-modified SWNTs. It has been shown that the carbon nanotubes' conductance is decreased as a consequence of streptavidin's binding to biotin-functionalized SWNTs. It is still unclear exactly how SWNTs detect chemicals, however it is likely that the resistance changes these devices encounter are caused by the carbon nanotubes being doped as a consequence of charge transfer mechanisms connected to interactions between the SWNTs and the analyte. Nonetheless, since carbon nanotube networks are made up of a mix of bundled semiconducting and metallic SWNTs, it is difficult to understand the electrical responses in thin film devices. In certain instances, the electronic changes that take place at the metal-nanotube contacts during adsorption are the cause of the conductance shift. 89 Amazing developments in electrical biosensing have been reported despite the lack of a clear knowledge of the sensing process. The maximum sensitivity for electrical DNA detection has been achieved (detection limit of 1 pg L1) by covalently attaching the alkaline phosphatase (ALP) enzyme to CNTs. By using particular antibody-antigen recognition, this CNT-ALP-linked test may be customized for antigen detection. As a result, it could provide a quick and easy method for molecular diagnostics in illnesses that include molecular markers like DNA or protein [6]–[9].

Research on the creation of biosensors based on CNTs has been sparked by the need for accurate blood glucose monitoring. Investigations have been made on the voltametric behavior of oxidized SWNTs with physically adsorbed glucose oxidase. In comparison to what was seen with a glassy carbon electrode, the catalytic reaction to the addition of -D-glucose was 10 times more significant. Using individual SWNTs that have had glucose oxidase functionalized in a FET configuration, which enables the measurement of enzyme activity at the level of a single molecule, further increases sensitivity and temporal resolution. If FET devices could be made from thin films of SWNTs, it may be more advantageous for the individual SWNT-FET device, which needs a difficult CVD manufacturing procedure. SWNT-based biological substances and processes may be studied visually in addition to electrically thanks to the creation of optically transparent conductive SWNT films. CNT nanoelectrode assemblies have also proved successful in selectively and sensitively detecting glucose. The precise arrangement of the nanoelectrode assemblies accounts for the biosensor's outstanding performance. The distance between the nanoelectrodes is several times higher than the diameter of the nanotubes, which prevents the diffusion layers between neighboring electrodes from overlapping. As a result, the biosensor responds linearly to glucose concentrations up to 30 mM with a detection limit of 0.08 mM. Furthermore, acetaminophen, uric acid, and ascorbic acid, which often obstruct the detection of glucose, do not affect the electrochemical analysis for glucose.

Many methods for the manufacture of nanoelectrode arrays have been suggested in order to increase the usability of CNT-based devices for biosensing. A spin-on-glass film has been used to mechanically fortify a MWNT array generated by CVD. 98 In order to further functionalize the open ends of the nanotubes with nucleic acids, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and sulfo-N-hydroxysuccinimide are used (NHS; Scheme 1). In a comparable work, aligned MWNTs were encased with SiO2 using a tetraethoxy silane CVD method, followed by chemical polishing and covalent connecting of primary amine ended oligonucleotides99 to create a MWNT nanoelectrode array. The Ru (bpy) 2+3 mediated glucose oxidation technique in conjunction with such electrodes enables the detection of oligonucleotide hybridization at concentrations lower than a few attomoles. When the carbon fibers were enzymatically functionalized, oxidizable secretory products or transmitters, such as dopamine and serotonin, as well as non-oxidizable transmitters, such as glutamate, were detected using carbon fiber microelectrodes and amperometric measurements.

Future avenues for carbon nanotube-based technologies are suggested by such advances. A recently developed nanofabricated carbon-based detector (NACAD) that can measure the secretion from a single secretory vesicle has been created (the spherical structure that stores transmitters). Future uses of this technology might offer comparable measurements of complete cells or particular cell sections, expanding its potential beyond the study of internal organelles. One option would be to construct individually addressable arrays of miniature NACADs, where each detector would be a separate SWNT connected to enable continuous monitoring of each SWNT's electrical condition.

TAILORED TREATMENTS USING CNT

In the medical industry, effective medication administration is a serious challenge. Moreover, poor selectivity and short half-lives might result in multiple doses, which can have side effects and even be lethal. CNT are extensively researched as nanocarriers for medication and gene delivery as well as cancer therapy due to their anticipated biocompatibility and acceptable size.

CNT AS A DRUG AND GENE DELIVERY CARRIER

NT as a Drug and Gene Delivery Carrier Due to CNT's extraordinary capacity for cell transfection, the use of CNT as nanocarriers has attracted increasing interest in recent years. According to research by Liu et al., non-covalent constraints allow pharmaceuticals like doxorubicin (DOX) to be loaded onto the surface of poly(ethylene glycol) (PEG) coupled SWCNT and the increased permeability and retention (EPR) effect allows these medications to penetrate tumorous tissue. Delivery near to the tumor tissues might also be possible if there was a pH-release dependence. To load medicines onto CNT, a mesoporous silica covering. In such cases, DOX was readily released in the acidic surroundings of tumorous tissues but remained bound to CNT at neutral and alkaline pH, limiting toxicity inside the healthy body parts. Moreover, PEG branches improved SWCNT's hydrophilicity and safeguarded the DOX linked to the nanotubes, enhancing the stability and longevity of the compound in blood circulation. 10-hydroxycamptothecin (HCPT), another anticancer agent, was effectively covalently attached to MWCNT and demonstrated the improved efficacy of CNT-conjugated pharmaceuticals as well as the potential to tie imaging to this kind of therapy (theranostic approach). Recently, SWCNT-COOH modified with hydroxypropyl-cyclodextrin (HP-CD) also shown a fairly excellent formononetin entrapment and a gradual and prolonged release that may be helpful for enhancing cancer therapy.

In addition, CNT have the ability to penetrate cells, regardless of the functional groups they may have on their surface, enabling the delivery of genes, proteins, and intracellular medicines. Since short interfering RNA (siRNA) is delivered into the cytoplasm, this is particularly interesting for the development of gene silencing treatment. Without using any functionalization of the nanotubes, Bartholomeusz et al. successfully dispersed SWCNT in siRNA solutions and showed 90% of transfected cells within 6 hours, along with 70-80% HIF-1 silencing, and more importantly, without the drawbacks of viral vectors, such as inflammation or immune response. With a 96% silencing effectiveness, successfully delivered siRNA into cells that were difficult to transfect. For the transport of DNA plasmids, combined functionalization on the surface (polyethyleneimine) and inside (chloroquine). In this study, the DNA plasmid could be delivered to the cytoplasm and then to the cell nucleus because the lysosomotropic chemical chloroquine was only released from the CNT at the low pH within lysosomes. As gene silencing is more effective than direct inhibitor injection, it offers a practical alternative to traditional therapies for disorders, especially those that are localized in sensitive areas like the brain used rhodamine (Rhod) doping and imaging to clarify the cellular absorption mechanism of MWCNT -cyclodextrin nanoplatform with branching poly(ethylenimine) (MWCNT-CD-PEI) loaded with cidofovir (Cid). Small medicines like Cid would escape lysosomes vesicles, but MWCNT-CD-PEI-Rhod were internalized by endocytosis.

In a recent study, Kaboudin et al. showed that nucleic acid transfection may occur by a different method than endocytosis. Nucleic acids bound by -interactions were carried by MWCNT functionalized with pyridine and magnetic particles across the cell membrane and released in the cytoplasm. The nanocarriers were subsequently extracted from the cell using a magnetic field, which reduced their cytotoxicity. additionally took into account magnetically directed nanocarriers by the one-step synthesis of magnetic MWCNT with a paramagnetic surfactant coating. Electrostatic forces condense the DNA, enabling the endocytosis transfection of the nanoplatform. DNA was able to be released into the cytoplasm thanks to salts that protected the connection between the CNT and the payload. NIR light irradiation as an additional tactic to aid DNA transport. SWCNT photothermal activity caused membrane permeabilization in response to laser stimulation of SWCNT coated with poly(ethyleneimine)-cholesterol (PEI-Chol), facilitating cellular uptake and DNA release. As was previously said, further research is still required to identify the paths and destiny of CNTs within tissues based on their composition [10].

Cancer Treatments using CNT The use of NIR laser stimulation in combination with CNT photothermal characteristics was thought to be a sophisticated method of treating cancer. Burke et al. demonstrated that the intra-tumoral injection of MWCNT suspension followed by brief laser stimulation caused tumor ablation in mice and improved survival. Nevertheless, Wang et al. reported that intravenous injection of SWCNT conjugated with anti-CTLA-4 induced immunological response and improved cytotoxic activity in addition to Photothermal Treatment (PTT), which led to the eradication of the residual nodules/metastasis [58]. In order to facilitate treatment of primary tumors and the identification of linked lymph nodes in a single step, the coupling of imaging technologies with PTT was also recommended. Recently, MWCNT/gold nanostar hybrids have significantly improved photothermal conversion, allowing for a reduction in the amount of time that laser stimulation is used during treatment. The application range of this cancer treatment approach is further expanded by Wang et aland .'s Wells et aldescription .'s of the combination of molecules delivery and PTT. Nevertheless, the depth of laser penetration in tissue limits CNT-assisted PTT, and it still has to demonstrate its effectiveness for thicker samples.

Nevertheless, the destiny and potential degradation of such things were not fully investigated. The majority of the research in this part have evaluated the toxicity of CNT on cells throughout their use. When CNTs are used in biomedicine and they are not contained within or on the surface of a device, this debatable problem might be the biggest disadvantage.

NANOTUBES OF CARBON AS MOLECULAR TRANSPORTERS

CNTs are strong candidates to transport medicines, DNA, proteins, and other molecular probes into mammalian cells because of the variety of accessible chemistries and cell-penetrating structures. The carrier's capacity to bind to physiologically significant molecules is one of the requirements for such a mission. Streptavidin molecules self-organized and grew helical crystals on the nanotube surface, according to early experimental research on the interactions between MWNTs and proteins. Similar to MWNTs, tiny protein molecules like cytochrome c and -Lactase I may be introduced within the internal cavity of open carbon nanotubes. Similarly, DNA molecules may be adsorbed on MWNTs. It would be more practical to fill the inside chamber of tubes, whose open ends could be closed to create a nanopill carrying a medicine for delivery to the cell, rather than attaching molecules to the exterior of the CNTs. To that purpose, nano test tubes—nanotubes with one end closed and the other open—have been created using a template approach. Such a strategy may be seen as a first step toward the creation of a nanopill, in which the medication is placed within the nanotube before being sealed at the open end to create a bottle.

The low permeability of the plasma membrane to many medicines is a significant problem in intracellular drug delivery. To make it easier for medications to enter cells, several carriers, such as polyethylene glycol, peptides, and lipids, have been created. SWNTs have recently been shown to be a viable option for intracellular medication delivery. To enable tracking of SWNTs, FITC, a fluorescent probe, was functionalized onto water-soluble SWNTs.The accumulation of the nanotubes within the cells was seen after SWNT-FITC exposure of murine and human fibroblast cell lines. Similar to this, SWNTs that had been covalently functionalized with biotin and had reacted with streptavidin were internalized by human T cells, Chinese hamster ovary (CHO) cells, and 3T3 fibroblast cell lines. These findings indicate the feasibility of CNTs as carriers for delivering relatively big compounds to mammalian cells, even if the mechanism of the CNT cell entrance is yet unknown.

ASSEMBLY OF CARBON NANOTUBES-BASED FUNCTIONAL STRUCTURES AND DEVICES

Using CVD, several structured nanotube topologies have been created. Escherichia coli and nanometer-sized poliovirus have recently been proved to be removed from water using membranes made of freestanding monolithic macroscopic cylinders with radially aligned MWNTs. 114 An alternate method for building CNT-based nanoscale devices is to use biological self-assembly principles. The main challenges to the biological assembly of CNTs are related to the manipulation, dispersion, and separation of these materials. Surfactants, which are now employed extensively for this purpose, have not been shown to be as effective in dispersing CNTs as biomolecules, notably DNA, peptides and phospholipids.

It has been shown that peptides can put together CNT-based structures.

Individual SWNTs are de-bundled and stabilized by amphiphilic -helical 29 residue peptides, and the controlled assembly of the nanotubes into macromolecular structures is made possible by the employment of certain peptide-peptide interactions. It has been discovered that around 25% of the distributed SWNTs may form X, Y, and intraloop junctions. It has been shown that this amphiphilic -helix is capable of self-assembling into more intricate structures. Head-to-tail stacking of the helices via H-bonding causes the SWNTs to be wrapped along their whole length, resulting in the development of a vast network of microfibrils. The environment may influence the size and shape of the fibrils; for example, increasing the concentration of NaCl causes the fibrils to become larger, but dimethylformamide, a solvent, has been discovered to cause ribbon-like formations.

A revolutionary bottom-up method based on individual SWNTs and using homologous genetic recombination and DNA-mediated self-assembly has been devised for the manufacturing of FETs. The RecA protein from Escherichia coli bacteria was used in this method to locate a semiconducting SWNT to a specified address on a DNA scaffold molecule. Wires that are electrically connected to the SWNTs were created as a result of DNA metallization. This strategy might be expanded to create functional circuits on a scaffold DNA network, allowing for the simultaneous localization of several molecular devices at various locations within the network and their interconnection via DNA-templated wires. The development of DNA-assisted SWNT-FET assembly demonstrates the effectiveness of self-assembly methods for the production of CNT-based electronics.

TOXICITY

The toxicity of CNTs used in biology and medicine is a significant issue. CNTs are now mostly being studied in labs, however if they become widely commercialized, the general public cannot be exposed to this substance without sufficient testing. As a result, toxicological research will be required, and a number of studies have shown that CNTs may be harmful to human health. Dermal exposure may result in skin problems since human skin cells in vitro were exposed to SWNTs, which led to oxidative stress and cell viability loss. Given that graphite and carbon compounds have been linked to an increase in dermatitis and keratosis, this is possibly to be anticipated. Further research have examined the lung toxicity of SWNTs, and it has been shown that animals exposed to SWNTs develop granulomas. More research is needed to determine the inhalation toxicity of SWNTs since they were directly injected into the animal's lungs in these tests at extremely high doses. Calculations of the amount of SWNTs that were left on production-related gloves and in the air suggested very little worker exposure (perhaps one million times lower than the concentrations used in the toxicity studies). As comparable tests were made on carbon soot and carbon black-based toners, it is probable that the necessary measurements may be made promptly. It is obvious that further toxicological studies of CNTs should be done to define acceptable exposure levels.

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CHAPTER 18

PROTEIN DETECTION USING FLUORESCENT SINGLE-WALLED CARBON NANOTUBES

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The study of the fundamental mechanisms of biological processes, healthcare, agriculture, food security, and environmental sciences all need the molecular identification of DNA, tiny molecules, proteins, or viruses. Current sensing technologies rely heavily on nanosensors, which let us comprehend biological processes that haven't been thoroughly investigated before. With growing interest in nanomaterials-based biosensors, recent breakthroughs of innovative nanosensors provide potential strategies for better clinical diagnostics and therapies. Target recognition and signal-transduction, which converts recognition into a quantifiable signal, are the two essential functions that a sensor must have. A sensor may include lectins, DNA sequences, molecular imprints, aptamers, antibodies, or synthetic moieties for recognition. For immunohistochemistry and other methods, signal transduction is often accomplished by labeling with fluorescent dyes or gold nanoparticles, which gives a visual indication of target binding. The sensitivity and selectivity of the sensor in biological contexts are influenced by the combination of recognition and signal transduction. Numerous nanoparticles, including metal nanoparticles, quantum dots, nanowires, graphene, graphene quantum dots, and carbon nanotubes, have demonstrated the potential to be highly sensitive and selective in such a way that they can bind and detect biologically relevant concentrations of a target analyte [1]–[3]. The use of carbon nanotubes as sensors for biotechnological and biomedical applications is of particular interest among the many nanosensor platforms because of their electrical and thermal properties, mechanical toughness, and the abundance of possibilities for additional functionalization, doping, and chemical modifications. According to the number of cylindrical graphene layers, carbon nanotubes may be split into two primary categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). MWCNTs are made up of multiple concentric SWCNT layers, whereas SWCNTs are made up of a single, one-atom-thick graphene sheet that is rolled into a cylinder with a diameter ranging from 0.7 to 3 nm. The diameters of MWCNTs can range from 1.5 nm for double-walled carbon nanotubes to 220 nm for tens of layers.

We concentrate on SWCNT nanobiosensors in this study because of their distinctive physical, chemical, and optical characteristics. Then, we introduce various strategies for identifying proteins using their natural substrates, such as protein receptors, protein-binding partners, antibodies, or aptamers, or using a non-biological synthetic substrate bound to the SWCNT surface. We briefly review the properties of SWCNTs and their various biomedical applications. We concentrate on recent examples of using synthetic recognition sites on nanotubes to identify various proteins. The pinned configuration of the synthetic substrate when it is wrapped around the SWCNT scaffold is where the proteins show their affinity, rather than the synthetic substrate itself. In conclusion, we discuss future prospects and compare SWCNT sensors to various sensing systems.

INDIVIDUALLY WALLED CARBON NANOTUBES

SWCNTS PROPERTIES

One atom thick graphene sheets are rolled to make single-walled carbon nanotubes, which have unique chirality and dimensions [6] that govern their physical, chemical, electrical, and optical characteristics. The circumference of the SWCNT and the orientation of the honeycomb lattice of the nanotube are determined by the roll up vector, which joins two lattice sites on the sp2 hybridized graphene sheet. The optical transitions are impacted by the higher persistence length and smaller level spacings in larger diameter nanotubes' electronic densities of states. Chirality-based separation and sorting are made possible by the lattice structure, which also governs the chemical interaction of the SWCNT with adsorbed surfactants or polymers.

SWCNTs are one-dimensional, high-aspect-ratio nanocarbon materials with large surface areas that are easily functionalized. They have a diameter on the order of 1 nm and a length ranging from 100 nm to several micrometers. SWCNTs are hydrophobic and have a significant tendency to bundle when the surface is not functionalized. Individually dispersed SWCNTs are often sonicated non-covalently functionalized with amphiphilic compounds or polymers to create a colloidal suspension. They may be made biocompatible by surface functionalization, making them useful for a variety of biological uses as sensing, drug administration, nanoinjection, phototherapy, imaging, or artificial actuation [4]–[6].

For effective delivery applications, SWCNTs can carry a reasonably substantial cargo weight because to their high surface-to-volume ratio. With circulation periods varying from minutes to hours, SWCNTs, for instance, may serve as an all-purpose drug delivery system (DDS) for small interfering RNA (siRNA) and other oligonucleotides. In numerous cell lines, the administration of siRNA has been shown to affect pharmacokinetics, toxicity, anticancer efficacy, and target protein knockdown. Moreover, SWCNTs have the ability to enter cells and release siRNA into the cytoplasm, which is crucial for applications involving gene silencing. Moreover, recent research has shown that carbon nanotubes may be used to carry plasmid DNA and siRNA unaided into a number of model and non-model plant species.

As compared to organic molecules, semiconductor SWCNTs have a wider absorption spectrum and brilliant fluorescence emission in the near-infrared (nIR) spectral region, primarily between 900 and 1600 nm. They also don't blink or photo-bleach. Due to their relative transparency in this spectral region, photostable nIR fluorescence and robust functionalization enable the sustained detection of SWCNTs through biological materials including tissues, blood, and cells. For instance, the optical transparency window in human blood is just around 3-5 cm wide and extends from 900 to 1400 nm. Few conventional markers exhibit substantial absorption or emission in this area, although several have weak photochemical stability or poor biocompatibility. Together with their optical qualities, SWCNTs' physical dimensions, which range from a few nanometers to several microns, are similar to the usual size of biological molecules, allowing for accurate targeting and observation [6]–[8]. SWCNTs are thus ideal candidates for applications in biological sensing, detection, and imaging .

SWCNTS AS OPTICAL SENSORS

SWCNTs' fluorescence signal is environment-sensitive and may be impacted by local changes in surface functionalization or even single-molecule adsorption, as well as global variations in pH and ionic strength. The corona phase that the surface functionalization creates around the nanotube scaffold facilitates the interaction of the SWCNT with nearby molecular analytes, which in turn controls the fluorescence modulation upon surface contact. Excitons, which have a high binding energy, undergo a radiative recombination that gives rise to the SWCNT fluorescence. Multiple mechanisms, including exciton quenching due to competitive non-radiative decay, a shift in the Fermi level leading to absorption bleaching, and reorientations of the solvent dipole moments in close proximity to the SWCNT due to conformational changes of the corona phase, can all result in the modulation of the emitted light upon target binding.

Due to their great photostability, absence of photobleaching, and physical size that is equivalent to the size of the target biomolecules, SWCNTs may be employed for sensing applications as fluorescence signal transducers. By observing the emission in several wavelength channels, the diverse chiralities may allow multiplexed detection enabling high throughput screening and hyperspectral imaging. Moreover, due to variations in the chemical interactions between the wrapping polymer and the underlying lattice structure of the nanotube, various chiralities within a single SWCNT solution might react to a target analyte differently.

SWCNTs have been used as optical sensors for indicators of human illnesses, including various cancers, blood glucose levels in diabetics, and H2O2 in reactive oxygen signaling pathways This is due to their distinctive optical features. Even in complicated biological contexts, single-walled carbon nanotubes functionalized with nucleic acids or peptides form stable complexes with higher temperature stability up to 200 °C. Furthermore, SWCNTs functionalized with DNA sequences including endonuclease recognition sites have been utilized effectively to track their fluorescence emissions in order to analyze restriction enzyme activity. The DNA-SWCNTs have effectively detected dopamine efflux in neuroprogenitor cell cultures as well as in acute brain slices.

They have also shown enhanced fluorescence intensity in response to neurotransmitters. Moreover, the fact that (GT) 6-SWCNT has effectively identified dopamine and norepinephrine across a wide pH range and salt concentration range suggests that it may be suitable for in-vivo neurophysiological usage. Using SWCNTs coated with a serotonin-aptamer, a recent research showed how to recognize the neurotransmitter serotonin. The ability of this nanosensor to detect serotonin release patterns from the cells in real time was shown when it was mounted on a glass surface on which human blood platelets were being cultivated. Moreover, DNA-wrapped SWCNTs were used for the detection of doxorubicin, a chemotherapeutic agent efficient against proliferating cells owing to its affinity for DNA and of a single-stranded RNA genome of an intact HIV particle. Moreover, DNA-SWCNTs were developed to measure microRNA hybridization by a solvatochromic-like reaction when DNA was displaced from the surface of the nanotubes. Moreover, it has been shown that SWCNTs functionalized with boronic acid-modified dextran, PEG-brush, and rhodamine isothiocyanate functionalized-PEG are each effective selectivity sensors for the small molecules riboflavin, L-thyroxine, and estradiol.

SWCNTS FOR PROTEIN RECOGNITION

Due to the size, complexity, and range of target conformations, as in the case of proteins, the identification of big bio-macromolecules presents a unique difficulty. Nevertheless, by surface functionalizing SWCNTs with either natural or synthetic substrates, protein detection and the research of protein-protein interaction have been effectively accomplished.

NATURAL PROTEIN RECOGNITION

Using the target protein's natural binding partner as a recognition site on the SWCNTs is one method for protein detection. In order to take use of the first protein-protein or protein-DNA interactions for sensing purposes, this may be accomplished, for instance, by utilizing an antibody, an aptamer, or a DNA recognition sequence. Using nanotubes functionalized with chitosan polymer modified with nitrilotriacetic acid (NTA) chelator, a label-free detection was achieved. Due to the availability of functional groups for further modification, chitosan was used. The NTA chelated Ni2+ and functioned as a proximity quencher, adjusting the intensity of the SWCNT fluorescence in relation to distance. Any his-tag (hexahistidine-tagged) capture protein may attach to the NTA-Ni2+ group, which acts as the protein's natural binding site. For instance, human immunoglobulin G (IgG) was captured using a hip-tagged protein. A that was coupled to the NTA-Ni2+ group. In order to research protein-protein interactions, protein glycoprofiles, and protein quantitation, a target protein's binding modifies the fluorescence intensity.

A small molecules library was the focus of the first high-throughput screening of synthetic polymer coronae of SWCNTs. A sensor for the protein fibrinogen was subsequently found thanks to the first protein-targeted corona phase screen. In this study, 20 SWCNT corona phases were tested against a protein library made up of 14 proteins that were either the most abundant or had clinical significance in whole human blood, such as albumin, transferrin, haptoglobin, fibrinogen, 1-antitrypsin, 1-acid-glycoprotein, human chorionic gonadotropin (hCG), 2-macroglobin, immunoglobulin A (IgA), I A particular fibrinogen sensor employing dipalmitoyl-phosphatidylethanolamine (DPPE)-PEG(5kDa) corona was seen on the screen (Figure 3d). One of the most prevalent proteins in plasma is fibrinogen, which has an extended structure with three globular domains joined by coiled-coil helical chains. In competitive tests using albumin, which is often utilized as a nonspecific binding agent or in a serum environment, the detection of fibrinogen was also shown. Nonselective factors like the molecular weight, hydrophobicity, and surface coverage of the polymer did not correlate with the fluorescence response, supporting the idea that the three-dimensional structure of the target protein in conjunction with the conformation of the phospholipid-PEG corona adopted when pinned around the nanotubes is an important component of successful molecular recognition.

A sensor for insulin was discovered by an extended corona phase screen against the same protein panel. A little peptide hormone called insulin is essential for controlling blood sugar levels. The pancreas secretes insulin, which inhibits the formation of ketone bodies and the breakdown of proteins, glycogen, and lipids while stimulating glucose absorption to synthesize lipids. PEGylated-lipids-SWCNTs were used in a high-throughput corona phase screen, and the C16-PEG (2kDa)-ceramide-SWCNT complex displayed a particular and selective quenching response to insulin. Using isothermal titration calorimetry to compare the heat generated while infusing the C16-PEG(2kDa)-ceramide into an insulin solution or phosphate-buffered saline, the corona phase shown no previous affinity for insulin. With the aid of an implantable encapsulant, the novel synthetic nIR fluorescent nanoparticle opens the door to in vivo real-time insulin level measurement. A pharmacokinetic model of insulin, glucose, and glucagon metabolism may be used to infer the insulin levels in the different bodily compartments.

In a recent work, SWCNTs functionalized with polycarbodiimide polymers including phenyl rings were used to create an albumin nanosensor that mimicked fatty acid binding to albumin.

With comparable sensitivity to an antibody-based clinical assay, albumin detection was demonstrated in minimally processed urine samples from microalbuminuria patients under ambient conditions. This suggests that this antibody-free detection can speed up diagnosis in point-of-care and resource-constrained settings. Chio et al. used peptoid-functionalized SWCNTs to show an alternative method for protein recognition. Peptoids can selectively detect enzymes and proteins, are simple to make, and are resistant to the actions of proteases. Wheat germ agglutinin (WGA), a lectin protein, was recognized by Chio et al. in their investigation using an anchor-loop peptoid corona, and it was further shown that the WGA retained its ability to bind to target sugars.

BENEFITS OF SWCNTS

Antibodies are used in conventional recognition techniques to recognize both tiny and large molecular targets. There are several uses for antibody-antigen combinations, including diagnostic and therapeutic purposes as well as scientific and clinical research. A key drawback of antibodies in high-throughput research is the need that the antigen be injected into an animal as the initial stage of synthesis, despite the fact that they benefit from having great selectivity and specificity to the antigens. SWCNT-based protein corona phase molecular recognition provides an alternate strategy for a number of tests when the use of natural recognition components like antibodies is limited by issues including degradation, stability, cost, and production scale. The synthetic polymer utilized in this approach for recognition need not have any preexisting affinity for the target protein; rather, it creates a conformational binding site upon wrapping the nanotube surface. High-throughput screening and quick production procedures may be used to find these nanosensors. This has the potential to produce synthetic, non-biological antibody analogs that can get around some of the drawbacks of conventional ones, such as lengthy development times, high production costs, the requirement for using living organisms for initial production, difficult reproducibility, poor stability due to hydrolysis in ambient temperature, resulting in a limited shelf life, and sensitivity to degradation while circulating in vivo. SWCNTs, on the other hand, were shown to be long-term stable in vivo and to shield DNA or siRNA from cellular nuclease degradation. As a result, SWCNT identification provides a consistent and repeatable architecture that may further field discovery research [9]–[11].

Compared to fluorescent quantum dots and typical organic fluorescent dyes, SWCNTs' fluorescence offers a number of benefits. Organic fluorophores' principal drawback is the inescapable photobleaching, which prevents their use in real-time microscopy operations that run for many hours. Also, when used in conjunction with the crucial stain hematoxylin and eosin (H&E), which is employed to assess histological sections, organic fluorophores are quenched. Due to their photophysical characteristics, such as their photostability and narrow bandwidth fluorescence emission with a broad excitation range, quantum dots are appealing probes for microscopy and imaging. For both in vitro and in vivo applications, they are mostly employed as inert markers and FRET-based sensors. These are highly luminous semiconducting nanoparticles that can withstand photobleaching up to 100 times better than organic fluorophores. Nevertheless, they exhibit fluorescence blinking, complex surface chemistry, and signal attenuation during extended stimulation, which may result in long-term heavy-metal toxicity. Due to their intrinsic non-photobleaching, non-blinking fluorescence, and sp2 hybridized all-carbon structure, which facilitates simple surface functionalization and biocompatibility, single-walled carbon nanotubes are able to circumvent these restrictions. In order to use their nIR fluorescence emission and surface chemistry for target identification and signal transduction, SWCNTs are thus the topic of extensive study in a variety of new optical nanosensor applications.

CONCLUSION

An overview and thorough assessment of the use of SWCNTs for biosensing applications are provided in this paper. SWCNTs are optical sensors because of their non-photobleaching, non-blinking fluorescent emission, which enables in situ, label-free, real-time detection with both spatial and temporal resolution. Recent research has shown that proteins can be detected using a variety of surface functionalization techniques, including natural substrates and synthetic polymers. This technology has the potential to enable long-term continuous monitoring of key biomarkers or to replace expensive and time-consuming laboratory testing. With an emphasis on protein recognition, we have emphasized SWCNTs' benefits for in-vivo and in-vitro biomedical applications such drug delivery, imaging, and sensing. In recent years, their significant potential to expand this field's research and applications has attracted increased attention, creating new opportunities for future discoveries. The development of new SWCNT-based fluorescent sensors will be aided by advances in nanotechnology design, synthesis, characterization, and modeling. In conclusion, the special properties of SWCNTs make them excellent candidates for sensing proteins and bio-macromolecules with optical signal transduction.

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CHAPTER 19

FLUORESCENT CARBON NANOTUBE BIOSENSING

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Upcoming medical concerns include early illness diagnosis, point-of-care diagnostics, and customized therapeutics need for innovative biosensing techniques. Biosensors may also provide light on the intricate dynamics of chemical and biological systems. As a result, they are crucial resources for both basic science and medical. Particularly for contactless real-time readouts needed in biomedical research, industrial healthcare, and agricultural applications, optical sensing techniques hold considerable promise. The development of nanomaterial-based biosensors has advanced significantly during the last ten years. Carbon-based nanomaterials like graphene, graphene quantum dots, and carbon nanotubes are among these materials (CNTs). SWCNTs, or single-walled carbon nanotubes, are of special importance in this context. They are useful for extremely selective biosensing because of their optoelectronic features, which are sensitive to the environment. SWCNTs glow without bleaching in the near-infrared range (NIR, around 870-2400 nm) when distributed in aqueous solutions [1]–[3]. This portion of the electromagnetic spectrum is advantageous for detection and imaging because it has a very low background and a high tissue penetration depth (tissue transparency window). The penetration depth and signal to noise ratios of fluorescence techniques utilizing popular visible fluorophores are often constrained by strong scattering, absorption, and autofluorescence. 1 Excitation of common fluorophores with visible (Vis) or ultraviolet (UV) light also increases phototoxicity. SWCNTs are advantageous because they combine NIR emission with the biocompatibility and photostability needed for optical sensing and imaging. Moreover, SWCNTs' structural variety offers adjustable emission wavelengths. The foundation for molecular identification is the great environmental sensitivity of SWCNTs, which was first shown using optical sensors for DNA polymorphism and glucose detection. Customizing molecular interactions near to the SWCNT surface requires both covalent and noncovalent functionalization techniques. SWCNT-based biosensors for a variety of vital biomolecules have been created employing similar ideas.

More recently, this made it possible to map chemical signaling in an entirely new way. For instance, high spatial and temporal resolution neurotransmitter release patterns from cells provide novel insights into basic biological issues. Moreover, new developments in distant in vivo biosensing applications have been made possible by the multimodal optical detection of several analytes. Analytes may be recognized and discriminated on the basis of their distinctive visual signatures by combining several nanosensor components and merging them into functional arrays. The next generation of quick and accurate in situ diagnostics may be possible with such an array of optical nanosensors. Moreover, these methods open up whole new possibilities for standoff process control, such as antibody production or monitoring in the food and agricultural sectors (smart plant sensors). To provide a summary of this rapidly developing topic, we concentrate on optical biosensing using SWCNTs in this Review. We thoroughly compare the biocompatibility, specificity, sensitivity, and spatial resolution of several SWCNT-based biosensors. This study builds on other assessments by discussing novel chemical tactics developed in recent years. SWCNTs may be used as NIR labels as well. This is not covered here, and instead, we recommend reading other fantastic reviews.

The fundamental structural characteristics, photophysics, and functionalization techniques of SWCNTs are discussed. We touch on the most crucial aspects of SWCNT biocompatibility to wrap off this section. An overview of common chemical identification techniques. We provide a thorough and current overview of all the biomolecular target classes that are now available, including reactive oxygen species (ROS), neurotransmitters, proteins, antibodies, lipids, and sugars. Mechanistic understandings of the operation of various sensors are provided to support this review. We present a viewpoint on the field and talk about potential future directions. This comprises cutting-edge chemical tools (defects), unique screening techniques, multiplexing, and novel biological issues like plants. It also contains ways for better (hyperspectral) imaging [4]–[6].

Ideas of Functionalization

With the publication of their structure, CNTs have generated a great deal of interest both inside and outside of the scientific community. They have opened the door for applications in the domains of innovative materials, microelectronics, biosensing, imaging, drug delivery, and many more because to their exceptional mechanical, electrical, and photophysical capabilities. Here, we'll provide a quick overview of the SWCNTs' structure and photophysics before discussing methods for modifying their surface chemistry and biocompatibility.

STRUCTURE AND PHOTOPHYSICS OF SWCNT

CNTs may be thought of as graphene cylinders that have been rolled up. Both the precise sp2-hybridized carbon lattice and the number of stacked cylinders affect the characteristics of these materials. Single-walled carbon nanotubes (SWCNTs) are CNTs made from a single graphene cylinder, while multiwalled carbon nanotubes are tubes made up of many layers (MWCNTs). The chiral index (n,m), where n and m are integers that characterize the carbon lattice structure, is often used to name 7 SWCNTs. The SWCNT is theoretically rolled up along the vector c=na1+ma2 in this notation (a1 and a2 are the graphene lattice vectors). As a result, the diameter is likewise determined by the roll-up vector. The reported sizes for SWCNTs vary from 0.4 nm to 10 nm.

ACTIVATION OF NONCOVALENT BONDS

By sonicating surfactants that produce micellar structures surrounding the SWCNT or by strong - interactions with the SWCNT surface, noncovalent functionalization in aqueous solution is accomplished. Sodium dodecylsulfonate (SDS), sodium cholate (SC), sodium deoxycholate (DOC), lithium dodecyl sulfate, Triton X-100, and pluronic F127 are prominent examples of surfactants. Functional surfactants, such as those having a perylene core and a hydrophilic dendron, also facilitate energy transfer via adsorbing through "-" stacking. In general, to stabilize dispersed SWCNTs in solution, a surfactant concentration above the critical micelle concentration is needed. However, these methods have limitations when it comes to conducting studies on intricate (biological) systems [7], [8].In contrast, the production of stable conjugates is made possible by functionalization with bigger biopolymers. Here, DNA and ribonucleic acid (RNA) bind to the surface of the SWCNT in strong -stacking contacts, exposing the negatively charged phosphate backbones of the nucleobases and dissolving the SWCNT-nucleic acid complex. Locked nucleic acids have been employed as more stiff synthetic derivatives at higher salt concentrations because the conformation of the SWCNT-nucleic acid complex is altered by changes in the local ion concentration.

Some polycyclic aromatic compounds with hydrophilic functionalities have successfully solubilized SWCNTs as an alternative to nucleic acids. The functionalization of SWCNTs with peptides, proteins, and other polymers has been extensively proven and is analogous to the -stacking of such molecules. By attaching antibodies, their analogs, and peptides to polymers or by coating SWCNTs with boronic acids and aptamers, SWCNT-based biosensors have been rationally constructed. Since sonication might compromise the structural integrity of the (bio-)polymers, the SWCNTs were first suspended in a surfactant and then exchanged with the polymer by dialysis. The screening and search for new organic phases is a different approach from this logical design. Corona-phase molecular recognition is the term given to this idea. Here, a heteropolymer produces a new structure (corona) after adhering to the carbon nanotube surface, acting as a molecular recognition site for interaction with an analyte. The biomolecules used are usually amphiphilic, with hydrophobic domains facilitating SWCNT adsorption and hydrophilic domains entropically stabilizing the SWCNT in suspension and forming a binding site for the analyte. It is crucial to remember that the biomolecules or polymers do not necessarily need to interact with the target analyte in a targeted manner. As a result, it is impossible to anticipate how these recognition sites will emerge; they are usually discovered by screening or high-throughput methods. The discovery of SWCNT-based neurotransmitter sensors and the application of the CoPhMoRe idea to proteins are notable instances of CoPhMoRe screens.

COVALENT FUNCTIONING

The sp2-hybridized SWCNT structure gains new -bonds as a result of covalent functionalization. The conjugates offer greater stability compared to noncovalent functionalization techniques. The inherent NIR fluorescence, however, is diminished and the electrical and optical characteristics are destroyed when covalent sp3 links (defects) are introduced uncontrollably. Preserving the sp2-hybridized structure of SWCNTs during their covalent functionalization is one way to solve this issue. On the other hand, certain sp3 defects result in unique characteristics, such as red-shifted emission features that can emit a single photon. As a result, these flaws are sometimes referred to as quantum flaws or quantum color centers.

At low densities, it has been shown that these sp3 faults cause an increase in SWCNT fluorescence. These flaws capture excitons and provide an alternate decay route (E11*) that results in a novel red-shifted fluorescence characteristic when included at low concentrations. In order to improve the fluorescence characteristics of SWCNTs, a variety of sp3 defects have been added utilizing diazo ether, aryl halide, (bis-)diazonium, Billup-Birch, and alkyl halide reductions. In addition, it has been observed that O-doping techniques utilizing ozone and light, sodium hypochlorite, and polyunsaturated fatty acid hydroperoxides improve the red-shifted emission of SWCNTs at low defect concentrations.

BIOCOMPATIBILITY OF SWCNT

For materials coming into touch with living things, biocompatibility is crucial. The results of the many biocompatibility tests are difficult to compare. The fundamental cause is the comparison of various materials, surface responses, and biological systems, which results in an incoherent viewpoint. Also, the SWCNT field has developed significantly over time, and modern sensors based on well-defined chirality pure SWCNTs are available, while earlier investigations employed less well-defined materials. 49 Also, the viewpoint is decided by the program itself. SWCNTs shouldn't have a biased effect on the biological system when used as a research instrument. The destiny of SWCNTs in biological systems is very crucial to their biocompatibility for long-term in vivo investigations and applications in people. It has been shown that oxidative reactions brought on by neutrophils and macrophages may degrade SWCNTs. Moreover, the functionalization modifies the nanotubes' surface characteristics, which in turn affects how SWCNTs interact with the molecules in a (biological) system.

For instance, studies on endocytosis have shown that the length of the DNA sequence has a significant impact on the endocytosis and retention times of DNA-functionalized SWCNTs in mammalian cells. In addition, investigations have been performed to examine the fate of DNA-functionalized SWCNTs throughout the endosomal process utilizing a combination of NIR fluorescence spectroscopy and resonant Raman scattering. 94 The authors suggest that DNA-SWCNTs enter the cell and are then transported into early endosomes based on the experimental results. A drop in luminal pH marks the beginning of endosome maturation. Then, a series of physicochemical events convert the endosome into a lysosome, where the SWCNTs eventually congregate [9], [10].

Since that effective functionalization has been proven to reduce SWCNTs' pathogenicity, When long-term stability is crucial, one method to protect the design of SWCNT-based sensors in the future is via stable functionalization. It has been shown that SWCNTs with adequate functionalization have outstanding biocompatible qualities. A recent study that evaluated the long-term biodistribution and compatibility of DNA-encapsulated SWCNTs following intravenous injection in mice provides a nice example. 96 During the course of 14 days, the SWCNT fluorescence in the liver quickly declined after initially increasing. The long-term SWCNT biodistribution in several organs exhibits the similar pattern. One month after injection, modest concentrations of SWCNTs were discovered using hyperspectral microscopy in the tissues of mouse hearts, lungs, livers, kidneys, and spleens. No SWCNT fluorescence was seen in the lung tissue or the heart and lung tissues when these tissues were examined after three and five months. 96 Moreover, hematoxylin and eosin (H&E) staining of the chronically exposed tissues revealed no abnormalities at any of the time periods studied, and the analyzed biomarkers revealed insignificant alterations up to four months and slight changes after five months.

The research cited above point to amazing possibilities for SWCNTs in biological applications. Because of how various materials, surface reactions, and biological systems interact, it is clear that biofunctionalized SWCNTs belong to a class of unique materials. The biocompatibility should be assessed for each kind of chirality, purity, functionalization, and delivery route, as it should be for any novel materials. The scientific community is aware of this issue, and it has been noted that the setting of the experiment, the timeframe, and the application of the nanomaterial all affect how these parameters are evaluated in the context of biocompatibility. So, it is very vital to put experimental findings in the appropriate perspective.

An in-depth knowledge of the structure of the protein corona in biological media is a crucial prerequisite for a biocompatible design of SWCNT-based sensors. A recent research described the enrichment of certain proteins in the SWCNT corona in this respect. To protect the advancement of biocompatible sensors, long-term research evaluating the biocompatibility of various SWCNT subclasses (purity, chirality, surface chemistry) would be preferable in the future. The MIRIBEL (Minimum Information Reporting in Bio-Nano Experimental Literature) reporting standard may serve as a basis for the standardization of procedures. The design of robust SWCNT functionalizations must be carefully considered to guarantee long-term usage since the functionalization of the SWCNT is crucial to the biocompatibility of SWCNT-based sensors. Hence, new developments in covalent functionalization techniques may provide intriguing entry sites for future research.

DEVELOPMENT OF CHEMICAL DESIGN METHODS FOR SWCNT-BASED SENSORS

The first SWCNT-based sensor was created when band gap fluorescence from SWCNTs and their structure-dependent NIR emission wavelength were discovered. It was rapidly predicted that SWCNT fluorescence would be sensitive to the chemical environment due to the high surface to volume ratio of SWCNTs. Protons and reactive oxygen/nitrogen species (ROS/RNS) were among the smaller molecules that the initial generation of sensors focused on. In these instances, direct quenching was probably what produced the fluorescence shifts. At the same time, it was shown that various surface reactions with biopolymers result in impressively specific molecular interactions even without the use of a conventional strategy using antibodies. The term "corona-phase molecular recognition" was used to describe this notion (CoPhMoRe). The chemical design of sensors for healthcare and environmental applications has advanced significantly in recent years. We will provide an overview of several sensing techniques in the sections that follow, sorted by the molecular target. Here, the target molecule's sensing has uses in both biomedicine and the environment.

ANALYTES FOR TARGET BIOSENSING

Powerful SWCNT-based biosensors have been developed as a result of continual improvements in recognition strategy development. Combining a recognition unit with the SWCNTs allows for the selective and sensitive detection of a variety of targets. The two basic types of recognition procedures are screening and logical approach. The first method is theoretically accomplished by screening a library of synthetic organic phases (coronas) made up of diverse amphiphilic polymers wrapped around SWCNTs for a specific interaction. The other method involves attaching a known binding partner of the target analyte to the SWCNT surface in order to detect bigger molecules, such as proteins65 or carbohydrates. There are many methods based on the utilization of SWCNTs wrapped in single-stranded DNA (ssDNA), with various lengths of the (GT)x sequence likely being the most popular up to this point.

Divalent ions, genotoxins, NO, 20 H2O2, riboflavin, doxorubicin, -carotene, endolysosomal lipids, arsenite, and neurotransmitters, particularly dopamine, have all been detected using this method, demonstrating its flexibility. The significant developments over the last several years for many types of biomolecules are highlighted in this section. Tables 1 through 9 in the Appendix provide a thorough review of the majority of fluorescent SWCNT-based sensors that are now available, broken down into the target categories.

ROS/RNS

Many species employ ROS/RNS as key signaling molecules, but it may be difficult to detect them because of how quickly they diffuse and how quickly they break down owing to their strong reactivity with O2 and other chemicals. The performance of SWCNT-based ROS sensors has improved since the discovery of the first NO sensor based on SWCNTs, going from the first selective detection of NO and H2O2 at the single molecule level and first in vivo applications to a new method to study NO generation and spatiotemporal imaging of intracellular NO signaling. 128 Recently, a mathematical model was developed to determine the NO concentration from changes in SWCNT fluorescence. Prior until now, this was not conceivable because of the response's nonlinear fluorescence quenching rate. It has become obvious that H2O2 is the main mediator that reacts to various stressors in plants, and ROS perform a mediating function in the cell-to-cell communication of plants to activate defense mechanisms.

Novel SWCNT sensor techniques have been developed as a result to research ROS in plants. Used fluorescent SWCNT-based sensors to show remote H2O2 monitoring of plant health with sensitivity in the plant physiological range. A DNA aptamer that particularly binds to the porphyrin hemin served as the foundation of their logical strategy (HeAptDNA-SWCNT). A Fenton-like reaction between ferric ions and H2O2 results in the production of hydroxyl radicals, which immediately extinguish the SWCNT fluorescence when hemin binds them. SWCNTs were placed in plant leaves for spatiotemporal in vivo monitoring, and the plants were subjected to several stimuli including UV-B, high light intensities, and a pathogen-associated peptide.As insulin regulates blood glucose levels, its detection is crucial for diabetes. The first optical SWCNT-based sensor method for insulin detection was successfully implemented. They used an aptamer that binds to insulin and exhibits a very sensitive and specific drop in fluorescence intensity upon formation of a guanine quadruplex. In addition, they integrated these sensors into a collagen extracellular matrix and showed sensor reversibility by detecting insulin released by pancreatic -cells and by enzymatic proteolysis.

Recently, by screening a library of PEG-conjugated lipids, insulin detection was made possible. In contrast to other pertinent proteins identified in human whole blood, it was discovered that the C16-PEG (2000 Da)-Ceramide-SWCNT complex significantly reduces the fluorescence intensity in the presence of insulin. Moreover, general recognition processes like hydrophobicity and molecular weight were disregarded. For instance, the sensor reaction to smaller insulin fragments was evaluated, but no relationship between the sensor response and the molecular weight was found. Enthalpy studies that revealed no affinity for the PEG-conjugated lipid itself further confirmed the study of insulin fragments and demonstrated that the precise CoPhMoRe phase attached to the SWCNT is what is responsible for the insulin binding. While the sensor affinity was decreased in more complicated settings, such as serum, it was still sensitive enough.It may be difficult to use sensors in intricate biological samples. The real corona structure is altered by the spontaneous adsorption of proteins onto various surfaces, which may have an impact on sensing. A basic comprehension of the interaction between sensors and their biological environment is required to enhance the performance of sensors in such protein-rich settings. Studied the protein corona development on (GT) SWCNTs in cerebrospinal fluid and blood plasma using mass spectroscopy to solve this problem. Their findings demonstrated robust binding to proteins involved in complement activation, lipid transport, and blood clotting, including fibrinogen. In order to limit the creation of the outer corona, electrostatic interactions must be optimized by sensor design and dynamic flow conditions (e.g., using lateral flow assays or microfluidic systems). Entropic calculations, on the other hand, must be taken into account for the inner corona. This work emphasizes the critical necessity to research sensors in physiologically complicated settings in addition to basic buffers. The most recent development of a complementary strategy was made by Ehrlich et al., who used an insulin aptamer (located inside the native insulin gene promoter) functionalized to the SWCNT surface by a (AT) ssDNA anchor sequence. This aptamer has a known affinity to insulin, in contrast to the synthetic PEGylated-lipid, which has no previous affinity to the hormone. The measured sensitivity, nevertheless, was less than the prior method.The majority of the SWCNT-based sensors mentioned up to this point were measured in solutions. For a reliable assay, immobilizing SWCNTs on various porous paper matrices, such as nitrocellulose, provides a number of benefits, as shown in figure 1. Formerly impossible, analyte detection in non-aqueous solvents like edible oil was made achievable through paper-based immobilization. The scientists further developed this device by patterning hydrophobic patches onto the paper using wax to produce a multiplexed one-dimensional sensor barcode made up of several ssDNA-wrapped SWCNTs.

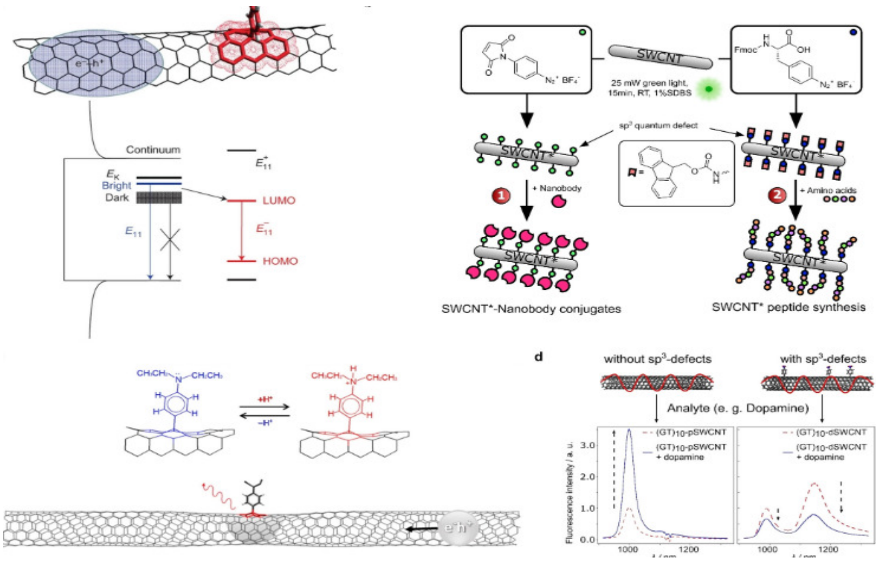

Figure 1: A different decay route is created by the controlled insertion of sp3 defects, which brightens dark excitons without obliterating the typical E11 NIR fluorescence.

Antibodies are a crucial class in biomedical diagnosis. The use of chitosan-wrapped SWCNTs that had been noncovalently modified with immunoglobulin-binding proteins allowed for the detection of immunoglobulin G (IgG) with SWCNTs. In recent years, developed a flexible fiber optic interface attached to nanosensors that could report the relative percentage of monomers and dimer aggregates with diameters of 5.6 and 9.6 nm, allowing them to determine the human IgG's aggregation state. The SWCNT-based sensors were used for this and affixed to the end of a fiber waveguide by embedding them in a hydrogel (HG). Pathogens and subsequently disease indicators include proteins as well. Angiotensin-converting enzyme 2 (ACE2), a host protein with a strong affinity for the SARS-CoV-2 spike protein, is functionalized using a SWCNT-based sensor. created 157 90 minutes following the injection of the isolated spike protein, a two-fold increase in NIR fluorescence was observed. In order to make it possible to detect the spike protein in saliva and viral transport media, passivation using a hydrophilic polymer was utilized.

Nevertheless, not all targets are always compatible with antibodies. In order to overcome the restricted selectivity of current single sensors, new techniques are oriented toward the creation of multiplexed sensor arrays since developing new recognition units may be costly and time-consuming. A SWCNT solution-based sensor device was recently created by Yaari et al. to identify several gynecologic cancer indicators in uterine lavage samples. The optical shift in the intensity and wavelength was recovered for the twelve chiralities present in the sample using an array of eleven separate ssDNA-SWCNT sensors, yielding distinct ssDNA-SWCNT complexes. A classification accuracy (F1 score) of 0.95 was attained using machine learning methods. This sensor technology may be extended beyond the detection of cancer biomarkers with retraining. The wide range of potential SWCNT chiralities and the availability of many SWCNT wrappings provide opportunities to satisfy the growing need for innovative identification techniques.

Sugars have a crucial role as metabolites and building blocks. The blood glucose level should be continuously monitored since glucose in particular is a primary objective. Glucose-specific enzymes proteins, and the first affinity sensor based on the competitive interaction between glucose and its polymer dextran are all examples of SWCNT-based sensing. Notwithstanding advancements, the first methods had issues with limited reversibility and/or physiological detection range. One sensor that satisfies the criteria is built on the functionalization of SWCNTs with the glucose-specific enzyme glucose oxidase (GOX). 161 The amount of fluorescence emission increases with the addition of glucose. The suggested mechanism is based on defect sites on the SWCNT surface that are hole-doped by oxygen adsorption quenching SWCNT fluorescence. The oxidation of the GOX wrapping brought on by the addition of glucose acts as an electron donor and passivates the oxygenated sites of the SWCNT, increasing fluorescence. By eliminating the glucose, this impact may be reversed. The sensor responded to the other five tested saccharides, but glucose elicited the strongest reaction. Phenylboronic acids, which have been employed to functionalize SWCNTs noncovalently for the detection of sugars, are another recognition component for saccharides. Covalent aryl-boronic acid defects have also recently been added to SWCNTs. These sensors' fluorescence intensity reduced and their E11* signal shifted in response to interactions with fructose and glucose, which may be exploited for spectrally encoded sensing.

DNA and RNA

Nucleic acids are one of the most prevalent and significant classes of biomacromolecules, and they process and store genetic information. SWCNTs were recently employed to directly detect microRNA and other oligonucleotide hybridization events in blood, urine, and animals in vivo using a design containing a complementary capture sequence coupled to a (GT)15-sequence acting as an anchor, enabling colloidal stability. When complementary nucleic acids were added, a particular blue-shift for various chiralities during hybridization was seen. The sensors also had a LOD in the picomolar range and the sensor response was reversible by toehold-mediated strand displacement. The first SWCNT-based sensor for the detection of HIV in serum was created via further development of this sensor. Found that serum proteins subjected to SDS denaturation result in an improved optical response of the SWCNTs in response to DNA hybridizations. They proposed that the presence of SDS guaranteed the release of the viral RNA genome as well as the denaturation of the proteins that competed for binding to the liberated sensor surface. The contact causes the SWCNT emission to shift to the blue. In contrast to control R23 DNA, this was initially shown for hybridization with complementary target miR-19 DNA The area of the critical micelle concentration of SDS saw a dose-dependent amplification of the blue-shift; as a result, it is believed that the unfolding of the protein's tertiary structure leads to full denaturation during the denaturation of proteins by SDS.

EXCITATION ALTERNATIVES AND REMOTE IMAGING

Remote imaging, which involves spatially separating molecular sensors and detectors, is especially useful for non-invasively observing biochemical processes, such as in vivo or during biomanufacturing. Remote detection necessitates either strong fluorophores or cameras with a high quantum yield in the spectral window of the fluorophore emission since only a tiny percentage of the emitted light is collected by a camera within a specific distance to the sensors. NIR fluorescent nanosheets, which were remotely detected in a specialized portable setup, are an example of remote imaging. A cheap CMOS camera (Complementary Metal Oxide Semiconductor, Si based), which normally has a poor quantum efficiency of roughly 5% in the NIR region, might be employed here due to the high brightness and emission closer to the visible range (910 nm). An NIR-sensitive InGaAs camera, a white-light LED, and appropriate filters for wavelength-specific excitation and emission detection were also added to this system to make it suitable for SWCNT detection. Till recently, microorganisms have been identified29 and plant health has been monitored using remote imaging of fluorescent SWCNT-based sensors, where resolutions in the (sub-)millimeter range were attained with standoff distances of up to 1 In addition to making use of the Si-detectors' declining NIR sensitivity, simple designs for low-cost NIR fluorimeters have been used to promote NIR-fluorescent transducers.

Single InGaAs diodes were paired with a motorized stage and an open source programming language in place of expensive InGaAs photodiode arrays. Through field-side measurements of soil samples, the reliability of these devices outside of the lab was shown in a high-throughput mode. Future advancements may potentially include remote detection utilizing pure SWCNTs and cameras based on silicon, as well as flexible use of smart surfaces for tracking contamination by diseases like bacteria on medical surfaces or even implants. When measurements are made in living biological tissues, fluorophore brightness is not the sole performance-related element. It is also necessary to take into account the stability of the fluorophores, wavelength-dependent tissue scattering and absorption, as well as background autofluorescence. From this perspective, SWCNTs have superior photophysical characteristics. Nonetheless, achieving a good signal to noise ratio is usually taken into account while imaging at the single molecule level. For SWCNTs in live cells and brain tissue, long-term single SWCNT imaging is already well-established.

Alternative excitation pathways, such as the K-momentum exciton-phonon sideband (KSB) excitation and up-conversion excitatio, have been successfully demonstrated despite the fact that the second-order excitonic transition, E22 (S22), is typically used for excitation. However, excitation efficiency, photostability, as well as the absorption and scattering of molecules in tissue, differ depending on the excitation wavelength. For the best single SWCNT imaging, Danné et al. tested the various excitation settings. Here, it was discovered that E22 excitation of PEG-PL SWCNTs was four times as efficient as KSB excitation and an order of magnitude more efficient than 1064 nm up-conversion excitation, despite the fact that the signal to noise ratio for KSB and up-conversion excitation was more than five times higher. Unfortunately, because to low tissue penetration depth and autofluorescence, the excitation at the E22 transition is not optimal. Moreover, simulations to determine the effect of tissue absorption revealed that a larger tissue temperature increase brought on by up-conversion excitation may be problematic, indicating that KSB excitation is the best option overall. Nonetheless, in the kW cm2 range, it still requires rather strong excitation doses.

In biological imaging applications, multi-color imaging is often limited by large spectral bandwidths, photobleaching interactions and interference from the intrinsic optical properties of tissue. Semiconducting single walled carbon nanotubes (SWCNTs) exhibit intrinsically photostable3 excitonic fluorescence in the near-infrared (nIR) region of the spectrum (800–1700 nm)—a region which facilitates biological imaging due to attenuated tissue absorbance, scattering and autofluorescence. Carbon nanotube fluorescence responds to its environment via changes in intensity, wavelength, or spectral bandwidth. Nanotube-based optical sensors have been developed to detect various analytes including small molecules, oxidative radicals8 and macromolecules. Nanotube emission bands corresponding to each unique (n,m) species (chirality) are narrow (~20 nm)10 compared to organic fluorophores, allowing a larger number of spectrally-separated emitters to be imaged simultaneously. Recently, nanotubes have been fluorescently imaged in brain blood vessels of live mice, used for in vivo long term sensin and deployed as fluorescent markers for surgical tumor resection at depths up to 18 mm. However, these imaging-based applications treated the entire family of emissive nanotubes as a single fluorophore, even though as many as 33 spectrally different fluorescent species exist.

Spectral imaging is a powerful tool for detection, validation, separation and quantification in applications ranging from mineral assessment of geological satellite images to semiconductor material characterization. In contrast to multi-spectral imaging of discrete wavelength bands, hyperspectral imaging produces a continuous emission spectrum at every spatial pixel. A recent approach to spectral imaging, termed global hyperspectral imaging, uses volume Bragg gratings (VBG) to acquire spectrally-defined images from the scanned wavelength space. This method has been applied for the mapping of solar cell saturation currents and in astronomical imaging.

Herein, we developed a wide-field near-infrared hyperspectral microscopy approach to spatially observe the fluorescence and spectral heterogeneity from single nanotubes in complex environments, including live cells and tissues. Exploiting the narrow spectral bandwidth (full width at half maximum, FWHM) of nanotubes, we resolved 17 distinct chiralities of individual nanotubes on a surface using a single excitation laser. In live cells, 12 distinct fluorescent nanotube species were simultaneously detected in a 500 nm imaging window. We used this approach to spectrally image and identify the chiralities of individual nanotubes in mouse tissue ex vivo and within zebrafish embryos in vivo. This approach is the first to spatially identify multiple nanotube photoluminescence emission bands in living systems and the first measurement of single nanotube spectra in biological specimens. The work portends the use of the family of photoluminescent carbon nanotube probes, as well as other nIR fluorescent materials such as quantum dots, for multiplexed biomedical imaging.

The author constructed a near-infrared hyperspectral microscope by incorporating a volume Bragg grating between the emission port of a standard inverted fluorescence microscope and the nIR camera to obtain the spectral properties of the spatially-resolved emitted light. By specifying the angle (θ) of a turret-mounted grating with respect to the collimated emission beam from the sample (λAll), a ray of center wavelength $\lambda B = 2n \Lambda \sin(\theta)$ is reflected by the grating into the detector, where n is the refractive index and Λ is the period of the grating (Fig. 1b). The emission was passed twice through the volume Bragg grating which resulted in a reduced bandwidth. A continuous stack (hyperspectral cube) of 152 images (256 × 320 pixels) with a 3.7 nm bandwidth was obtained between 844 to 1452 nm, collected in 4 nm steps and rectified to create a stack of 126 images between 900 to 1400 nm (described further in the Supplementary Information). The integration time for each of the 152 images generally ranged from 0.05–4 s, dependent upon signal, which resulted in hyperspectral cube acquisition times between 20 s and 10 min.

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CHAPTER 20

THE CREATION OF OPTICAL CARBON NANOTUBE SENSORS FOR THE EARLY DIAGNOSIS OF DISEASE

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The creation of nanoscale sensors to identify cancer in its early stages is one of the key topics of study at the Memorial Sloan Kettering Cancer Center in New York City. By using cutting-edge nanomaterials with distinctive optical characteristics, the research team under the direction of Dr. Daniel Heller is able to more easily identify illness indicators inside the body and so enable identification before symptoms appear [1]–[3]. These nanotechnologies also make it possible to monitor significant chemicals in living cells and tissues, providing new equipment that speeds up scientific research. There are several benefits to working in the near-infrared (NIR) region of the spectrum, including the ability to avoid undesired fluorescence backgrounds and to delve deeper into sample surfaces. The usefulness of different NIR spectroscopic and imaging methods for low-light scientific applications has risen in recent years with the development of deep-cooled cameras using InGaAs focal plane arrays (FPAs).

The molecular cylinders known as carbon nanotubes are made of carbon. The single-walled carbon nanotubes (SWCNTs), which come in both multi- and single-walled forms, have well defined characteristics that change with diameter and chiral angle. SWCNTs may exhibit metallic, semi-metallic, or semiconducting properties and have sizes between 0.5 and 2.5 nm. The basis for optoelectronic applications, particularly in sensing, is provided by this tunability. SWCNT-based electrodes, for instance, have been used to the detection of diverse bio-analytes through a change in electric potential. These devices depend on immobilizing the proteins or enzymes that bind to analytes or catalyze changes in the system. SWCNTs may be utilized as optical sensors in addition to electrical ones. The band gaps of semiconducting SWCNTs are dependent on the chiral angle and nanotube diameter. A dispersion of chirality-dependent excitation and fluorescence emission peaks is produced by this difference in bandgap. The SWCNT functions as an optical modulator due to the fluorescence emissions' sensitivity to the surrounding environment. Analyte binding often depends on protein conjugation to the nanotube surface, much as with electrical sensors [4]–[6].Hence, a crucial element that is present in all sensing setups is protein conjugation. Many methods may be used to conjugate this word. Immobilization by non-covalent interactions such hydrophobic, and van der Waals contacts is the most popular method producing pure nanotubes. While the preparation is rather simple, the resultant conjugates often exhibit heterogeneous structures and unequal protein loading. Purification and separation of these conjugates are still difficult tasks. Further protein orientation control is possible via the application of non-covalent electrochemical coatings and linkers. Some strategies, like non-specific adsorption, depend on non-covalent interactions, which are less reliable than covalent connections. Furthermore, denaturation and degradation are more likely to occur in immobilized proteins. It is possible to utilize enzyme entrapment to fix the protein on the nanotube surface but this often comes at the expense of the enzyme's accessibility to the analyte.

The radiative recombination of the brilliant E11 excitons has been primarily blamed for the fluorescence that is finally released. Its fluorescence changes depending on the chirality of the SWCNTs and the surrounding conditions, such as dielectric and solvent effects that remove electrons. The resultant fluorescence emissions often occur in the near-infrared with bandgaps on the order of 1 eV. (NIR). The fluroescence emissions are little absorbed by biological tissue and clearly opaque fluids at these wavelengths. SWCNTs are used for biological and biomedical imaging because of their low absorption and low-energy light's comparatively deep penetration. These SWCNTs provide an outstanding framework for continuous optical biosensing when taking into account their long-term optical stabilities and sensitivity to their surroundings.

Hence, maintaining these fluorescence characteristics is essential for optical applications. Other covalent techniques may produce sp3-defect sites that are more conducive to radiative recombination than acidification, where the carboxylic groups may act as non-radiative recombination sites for diffusing excitons. For instance, localized lower energy E11 states may be created by covalently altering the sidewalls of SWCNTs. The bottom right-hand corner of the fluorescence peak is red-shifted due to radiation recombination at these spots. To keep SWCNT fluorescence intact, these defect locations could also prevent the non-radiative decay of excitons. In order to brighten SWCNTs, the inclusion of sp3-defects may boost the quantum yield. The sp3 defect reactions often take place under gentler temperatures than acid oxidation, which helps retain the SWCNT length in addition to the benefits in fluorescence. Moreover, as shown, the surface of the nanotube may be exposed to a variety of chemical handles. This variety increases the flexibility of the cross-linking chemistries that may be utilized to immobilize proteins and peptides in the future. These various sp3-defect handles are more fully detailed.

When combined with a new class of dispersive spectrographs that use an inventive Schmidt-Czerny-Turner (SCT) design, this kind of scientific camera may be even more beneficial to researchers. Researchers may use the whole two dimensions of the FPA sensor to capture pictures thanks to the considerably reduced optical aberrations produced by high-precision SCT spectrographs, which also provide clear images with excellent spatial resolution over the entire focus plane. Such light-dispersion and -detection tools have been successfully employed by Dr. Heller's research team in New York to conduct novel experiments examining the properties of photoluminescent (PL) single-walled carbon nanotubes (SWCNTs), which may ultimately lead to the development of new optical probes and sensors for biophysical measurements and biomedical applications. In addition to highlighting the significant contributions made by deep-cooled InGaAs FPA cameras and sophisticated SCT spectrographs, this application note will highlight some of the group's research's high points.

An additional method for controlling, stabilizing, and accessible protein immobilization is covalent conjugation. The covalent disruption of the carbon lattice often causes fluorescence quenching, which restricts the use of the SWCNTs for optical sensing. Until recently, these tactics were mostly restricted to electronic sensors. However current chemical developments enable covalent functionalization of nanotubes in a way that maintains their fluorescence. We sum up various covalent methods for conjugating proteins to fluorescent SWCNTs in this review. We briefly review techniques for adding covalent functional handles that reduce nanotube fluorescence that are based on acid oxidation. After that, we go into covalent strategies that maintain or even improve SWCNT fluorescence, outlining how they might be used for protein and peptide immobilization. The purification and use of these covalent bioconjugates comes last in the review.

Cycloaddition. The unsaturated carbon bonds of SWCNTs may experience reactive cycloaddition, much like the majority of organic molecules. SWCNTs have been used to show a number of cycloadditions, including the cycloaddition (Diels-Alder reaction), cycloaddition, and 1,3 dipolar cycloaddition. A number of these reactions have been carried out under regulated circumstances that keep the NIR fluorescence. The Diels-Alder reaction, the most well-known of these cycloadditions, takes place between a conjugated diene and a dienophile. The conjugated SWCNTs surface serves as a dienophile in this process. One of the first to show a Diels-Alder reaction between various dienes and unmodified SWCNTs was Cécilia Ménard-Moyon et al. Using a cobalt catalyst at high temperatures, the SWCNTs demonstrated variations in reactivity with linear diene (2,3-dimethoxy-1,3-butadiene) and cyclodiene (9,10-dimethylanthracene). These reactions provided as a starting point for modified Diels-Alder reactions using SWCNTs that make use of more intricate structures (polymers containing diene groups), unique catalysts, and unique solvents. Multifunctional SWCNT-polymer composites are presently created using the Diels-Alder chemistry [7]–[9].

SWCNT cycloaddition may also be accomplished using 1,3 dipolar addition in addition to the Diels-Alder process. Vasilios Georgakilas et al., for instance, used azomethine ylides made from aldehyde and glycine derivatives to show the 1,3 dipolar addition of SWCNTs. 56 Transmission electron microscopy, nuclear magnetic resonance (NMR) spectroscopy, and Raman spectroscopy were used to confirm the cycloaddition (TEM). The addition may be utilized to incorporate long-chain polymers and conjugates often needed for biomedical applications, even though the scientists found a drop in NIR emissions after the chemical change.The additions, which were among the first cycloadditions to result in an increase in SWCNT fluorescence, are of special relevance for fluorescent SWCNT conjugation. Cycloaddition process between SWCNTs and electron-deficient aromatic nitrenes derived from azido compounds. These cycloadditions may happen at ambient temperature without the addition of a catalyst, in contrast to the cycloaddition processes discussed above that needed high temperatures and a metal catalyst. In these reactions, the initial step is followed by a phase that rebuilds the conjugation system by opening rings and rehybridizing. These reactions may be extended to include other substrates like spiropyran or thiol-substituted nitrenes. Similar to that, linoleic acid's oxidation products may likewise be used to perform cycloaddition. Under UV or 566 nm irradiation, the enone in linoleic acid may react with a conjugated bond on the surface of a SWCNT in the presence of a photocatalyst. While to a lower degree than with substrates containing enone, reactivity was also seen with substrates having a carbonyl group without a carbon double bond. While there haven't been many research on the effects of cycloaddition on SWCNT fluorescence, the range of substrates made possible by this chemistry has been essential for diversifying sp3-defects.

SWCNT SURFACE CHEMICAL ALTERATION ACID OXIDATION OF SWCNTS

The placement of useful chemical handles on the nanotube surface is necessary for covalent bioconjugation. Using functional handles made of carboxylic acid is the most typical method. In this method, the carbon sp^2 bonds on the SWCNT ends and sidewalls are broken by adding a highly oxidizing acid (HNO_3, H_2SO_4, a combination of HNO_3 and H_2SO_4, or a mixture of $KMnO_4$ and H_2SO_4) to the SWCNTs. This oxidative process adds a number of functional groups, including hydroxyl and acyl groups in addition to carboxylic groups. The key reactive sites for the ensuing immobilization stages are the carboxylic groups. Most often, a condensation process with the carboxylic group that creates an amide bond is used to accomplish the direct amino conjugation to the protein. The loading of the carboxylic groups, while being poorly regulated, is often adequate for protein immobilization since the yield of this step is typically limited by the steric barrier between the amino residues.

While the relatively high oxidative yields and simple process make the acidification functionalization advantageous, its use in optical sensing is constrained by a number of drawbacks. First, SWCNT fragmentation and shortening are influenced by the strong reaction circumstances. This shortening lowers the nanotube quantum yield because the ends serve as exciton quenching sites. In addition to acting as non-radiative recombination sites, the oxidative functional groups themselves act to further dim the SWCNT fluorescence. The consequent reduction in SWCNT fluorescence has long been a dissuader against using this technique for optical applications. Nevertheless, these restrictions may be addressed by designing chemical handles that prevent non-radiative recombination or even encourage radiative recombination, respectively, to maintain or boost SWCNT fluorescence.

SWCNT OPTICAL CHARACTERISTICS MAY BE CHANGED BY SP3 DEFECTS

Understanding the fundamentals of SWCNT exciton dynamics is essential for understanding the processes for fluorescence preservation and amplification. On E22 excitation and relaxation, an E11 exciton is produced. The excitation may also produce dark excitons, which have been demonstrated to eventually restrict the quantum yield of the nanotube, in addition to brilliant excitons. SWCNTs have excitons with high binding energies and extraordinary stabilities, unlike conventional fluorophores. As a result, rather than free electrons, the behavior of the excitons in SWCNT optical transitions is what defines them. Also, before recombination, the resultant excitons may spread a significant distance along the nanotube length. Hence, the presence of defects, such as oxidative groups throughout the nanotube as well as the nanotube ends, may act as exciton quenching sites. Hence, the non-radiative recombination of brilliant excitons that takes place at these places may restrict the fluorescence of nanotubes [10].

The research team of Dr. Heller has recently conducted a number of PL spectroscopy tests on SWCNTs. This note will focus on three of these research. In the first research, which was published in 2014, SWCNTs were coated with a variety of functional polymers, resulting in ordered surface coverage of the carbon nanotubes and the ability to systematically modify the nanotubes' optical characteristics. In the second investigation, the team resolved the relative permeability of two separate multicellular tumor spheroids by optically reconstructing the localisation of carbon nanotubes inside a three-dimensional volume using the intrinsic NIR emission of semiconducting SWCNTs. The third research looked at the SWCNT emission energy response to solution ionic potentials, and it found that the nanotubes react to cell surface electrostatic potentials that are mediated by membrane proteins.

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