TEXTBOOK OF NANOTECHNOLOGY

Dr. Nishant Kumar

TEXTBOOK OF
NANOTECHNOLOGY

TEXTBOOK OF NANOTECHNOLOGY

Dr. Nishant Kumar

ALEXIS
PRESS

ALEXIS PRESS

Published by: Alexis Press, LLC, Jersey City, USA
www.alexispress.us

First Published 2022

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication Data

Includes bibliographical references and index.

Textbook of Nanotechnology by *Dr. Nishant Kumar*

ISBN 979-8-89161-362-1

CONTENTS

CHAPTER 1

AN OVERVIEW OF NANOCRYSTALLINE MATERIALS

Dr.Nishant Kumar, Assistant Professor
Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India
Email Id- nishant.kumar@muit.in

ABSTRACT:

Since the beginning of time, humans have been very interested in materials. A few million years ago, it was discovered that rocks could be used to smash objects that human hands could not. Stones were the earliest tools, and they are still used as mortars and pestles and for pounding and grinding in labs and kitchens today. The ability to gather molten copper from a rock that contained copper was unintentionally found between 5000 and 6000 years ago. Due to this discovery, metal ores were reduced to generate metal, which was then used to create anything from swords to ploughshares. For producing tools, new materials with higher hardness and longer lifespans than stone become accessible. Our expansion and growth have followed the advancement of metallurgy and metals. In the past, civilizations were given names based on the metals or commodities they utilized. The Stone Age, Bronze Age, and Iron Age are the results.

KEYWORDS:

Nanocrystalline Materials, Synthesis Methods, Grain Boundaries, Size Effects, Mechanical Properties.

INTRODUCTION

'Nano' is short for incredibly tiny, but why is this unique? Nanoscience and nanotechnologies hold great promise for the future of materials, engineering, and related fields for a number of reasons. The qualities of matter, like energy, first alter at the nanometer scale. This is a direct result of the nanomaterials' tiny size and is physically explained by quantum processes. The result is that a substance (such a metal) may take on characteristics that are substantially different from those when it is in a bulk form when it is in a nano-sized form. For instance, whereas bulk silver is non-toxic, silver nanoparticles have the ability to instantly destroy viruses. When a material reaches the nanoscale level, characteristics such as electrical conductivity, color, strength, and weight change. The same metal may then convert from an insulator to a semiconductor. The ability to be created atom by atom via a technique known as bottom-up fabrication is the second outstanding quality of nanomaterials.

The material building blocks have the necessary information incorporated in them so that the final product may be self-assembled[1], [2]. Applications of silicon and other cutting-edge materials are what have led to the modern era. Nanotechnology may possibly take center stage in the next decades, deviating from the custom of designating an era based on materials in favor of one based on technology.

New materials with better physical, chemical, and mechanical qualities are needed for new technologies. Materials with a broad range of characteristics may be created by modifying the composition or microstructure of a material utilizing thermochemical-mechanical techniques, thanks to advances in materials science and engineering.

As a result, the research of structure-property correlation and microstructural engineering have gained significant importance. The development of the theories of lattice defects and dislocations, as well as the availability of cutting-edge high-resolution microscopy techniques like electron, atomic force, and field ion microscopy, have all contributed to a better understanding of the mechanism by which ultrafine microstructures affect the properties of solids. These advancements have made it easier to comprehend how a solid's structure and characteristics are related. Early in the 20th century, scientists realized that materials with ultrafine particle sizes had special features. At the annual meeting of the American Physical Society on December 29, 1959, Richard P. Feynman delivered the renowned lecture "There's Plenty of Room at the Bottom," which launched a brand-new industry called nanotechnology. He spoke about small-scale manipulation and control of many objects. He said: When people look back on this era in 2000, they'll marvel why no one started making meaningful headway in this area until 1960. Feynman is often referred to be the original pioneer of nanotechnology because of his vision. Feynman's remarkable insight sparked a great deal of debate and interest in engineering at the very tiny scale within the scientific community[3], [4].

However, due to a lack of appropriate tools and methodologies, it took the scientific community approximately three decades to realize his goal. Another pioneer in nanotechnology who pushed the boundaries of imagination was Eric Drexler. He argued for using chemistry's potential to create molecular machines and foresaw the profound effects this would have on a broad range of technologies. He discusses the value of using an interdisciplinary approach to advance nanoscience and nanotechnology in his well-known book, Engines of Creation: The Coming Era of Nanotechnology. Drexler made the following comment in 1986, and it still holds true today.By drawing parallels between the characteristics of natural macromolecules and the parts of current machines, the development of the capacity to design protein molecules will enable the creation of molecular machines. These machines can create second-generation machines that do incredibly general three-dimensional molecular structure synthesis, enabling the creation of devices and materials with intricate atomic details. This skill has effects on technology in general and computing as well as the characterization, manipulation, and repair of biological materials in particular[5], [6].

DISCUSSION

The term "nano" refers to a billionth of a unit and is a Greek prefix that means dwarf or something exceedingly little. Therefore, the term "nanomaterials" refers to a class of materials that have at least one dimension in the nanometric range. The size of a nanocrystal. A nanometre is a unit of measurement that is immediately comparable to a human hair in terms of thickness. It provides a sense of the sizes of various items, from large to little. The grain size of polycrystalline materials is generally in the range of 1 to 100 microns. Nanocrystalline materials are 100–1000 times smaller than normal grains in size, with grains on the order of 1–100 nm. Nevertheless, nanocrystalline grains are still much larger than an atom. A nanocrystal of size 10 nm, for instance, has over 100,000 atoms and is thus big enough to have bulk characteristics, which are distinct from those of individual atoms or clusters[7], [8].

The dimensions are no longer able to be viewed as infinite systems as they go smaller than 50–100 nm, and the resulting boundary effects give rise to intriguing and practical features that may be researched and modified for a range of structural and functional applications. In theory, it is impossible to provide a precise range for the grain size at which a substance qualifies as "nano." This is due to the fact that it is arbitrary and is dependent on the intended usage or outcome. When the grain size is decreased, usually below 10 nm, the majority of electrical and optical characteristics change. However, below 50–100 nm, their mechanical, chemical, and several other physical characteristics start to differ dramatically from bulk.

Therefore, materials that have at least one of their dimensions in the nanometric range and below which there is a considerable fluctuation in the attribute of interest relative to microcrystalline materials may be categorized as nanomaterials. Metals, ceramics, polymers, and composites may all be used as nanomaterials. The word "nanotechnology" is used to describe a wide range of scientific fields that deal with materials having one dimension in the few hundred nanometer range. Norio Taniguchi originally used the word "nanotechnology" in 1974 to refer to semiconductor technologies that allow for precise control at the nanometric scale, such as thin film deposition and ion beam milling. The creation of functional materials, devices, and systems through control of matter on the nanometer length scale (1-100 nm), and exploitation of novel phenomena and properties (physical, chemical, and biological) at that length scale, is the most widely accepted definition of nanotechnology to date, according to the NASA website.

The study of events and the manipulation of materials at the atomic, molecular, and macromolecular dimensions, whose characteristics change noticeably from those at a larger scale, is known as nanoscience. Bulk materials, or the 'large' bits of materials we see all around us, have consistent (macroscopic) physical characteristics. The same holds true for particles smaller than a micron, such a grain of sand. The laws of classical physics, however, are no longer able to adequately describe how particles behave (in terms of movement, energy, etc.) when they acquire nanoscale dimensions. At these dimensions, the laws of quantum mechanics apply. The qualities of a material (such as gold) at the nanoscale may be extremely different from and even the reverse of those of the material at the macroscale (bulk), including optical, mechanical, and electrical properties. By manipulating form and size at the nanometer scale, nanotechnologies are characterized as the design, characterization, manufacture, and application of structures, devices, and systems.

The traditional definition of the nanometre scale is 1 to 100 nm. One billionth of a meter (10-9 m) is a nanometre. In order to prevent classifying single atoms or very tiny clusters of atoms as nano-objects, the size range is often fixed at a minimum of 1 nm. As a result, 1 nm-sized clusters of atoms in at least one dimension are the focus of nanoscience and nanotechnology.

There are two categories of nanomaterials:

1. "non-intentionally made nanomaterials" refers to nano-sized particles or materials that are produced by human activity without intent (such as nanoparticles produced from diesel combustion) or that are naturally occurring in the environment (such as proteins, viruses, and nanoparticles produced during volcanic eruptions);
2. nanomaterials that are "intentionally made," or created with purpose via a predetermined manufacturing procedure.

'The smallness of nano' is a crucial subject to introduce to the school. Nanomaterials are smaller than germs and organisms but bigger than individual atoms. It is helpful to utilize a scale so students may see how bulk materials, like a tennis ball, and nanoparticles relate to one another. Nanoscience is an "interdisciplinary science," which indicates that it incorporates ideas from other academic fields, including physics, chemistry, and others. Other fields, like materials science (and engineering), which simultaneously include chemistry and physics principles, are intrinsically multidisciplinary. By including biology and biochemistry into the mix, nanoscience broadens the scope of material science even more. Thus, nanoscience is a "interdisciplinary science that integrates horizontally across all vertical sciences and engineering disciplines."

Nanotechnologies refer to the application of nanoscience to 'practical' devices. To create materials, structures, components, devices, and systems at the nanoscale, nanotechnologies manipulate, regulate, and integrate atoms and molecules. The use of nanoscience in particular for industrial and commercial goals is known as nanotechnology. Since atoms and molecules are the building blocks of all industrial materials and equipment, nanotechnologies have the potential to advance all industries and enhance all materials. The industrial areas that will most profit from nanotechnologies will be determined, as with any new technology, by the cost vs additional benefit relationship.

Nanotechnologies are convergent technologies that enable horizontal convergence. They are 'horizontal' in that they span multiple industrial sectors; 'enabling' in that they provide the framework and resources necessary to realize certain items; and 'convergent' in that they unite previously disparate scientific fields. One illustration of the confluence of biology and semiconductor research is the development of DNA silicon chips, which have uses in the medical sector.

What do you mean by nanotechnology or nanotechnologies?

The word "nanotechnology" was first used in 1959, and it was spelled out as a single noun. The discipline has gradually advanced in terms of science and technology during the previous several years. The influence of "nanotechnology" on society, ethics, and safety has also begun to be discussed by scientists. This has led to the realization that there are several nanotechnologies, all of which share the idea of using the characteristics of matter at the nanoscale. Even a well-known scientist and authority on nanotechnologies has called for the usage of the plural rather than the single to better convey the range of materials and techniques used in nanotechnology. The plural form is now the most common, and this Teachers Training Kit will utilize it.

Numerous studies have emphasized the need of "revitalizing" scientific education in schools, especially at the high school (14+) level. These papers often suggest encouraging inquiry-based scientific education (also known as problem-based learning), in which instruction is carried out using an inductive (as opposed to a deductive) approach. To provide children the opportunity to experience science firsthand and then study and comprehend the theoretical justification of what they observe, this should be integrated with a variety of "hands-on" activities. Such prospects are provided by nanoscience and nanotechnology!

The latest in science and technology

Teachers now have a new tool to introduce fascinating science and technology into the classroom thanks to nanoscience and nanotechnologies. Many modern technology, like computers, mobile phones, and iPods, which young pupils are already extremely acquainted with, incorporate nanotechnologies. Future goods will increasingly contain some kind of "nano," such as a nanomaterial or a nano-enabled technology. Nanoscience provides the potential to enhance many material qualities and generate new ones. Introducing "nano" into the classroom entails integrating the most cutting-edge science and technology as well as discussing highly interesting potential advancements in the scientific field. Interactive nano! The fact that a variety of "nano-effects" may be seen in our "macro world" is one of the features of nanoscience.

The finest illustration is a red gold colloid, which consists of gold nanoparticles that are around 15 nm in size and are scattered in water. The gold colloid becomes blue when salt solution is added to it! The characteristics of nanoparticles may be shown via a variety of "hands-on" exercises and demonstrations. The 'nano-world' is therefore invisible, yet its impacts may still be seen in things that young people are already extremely acquainted with, like gold. These exercises are presented in this Teachers Training Kit's Experiment Module and throughout the main book as straightforward examples that a teacher may carry out in the classroom. 'Nano' in the context of 'conventional' scientific disciplines One of the difficulties a science teacher could have is how to include nanoscience into traditional science courses. Where does this 'new' science fit within the 'traditional' scientific fields, such as physics, chemistry, or biology? This training kit's other goal is to provide instructors useful suggestions for incorporating nanoscience and nanotechnology into their science curricula[9], [10].

Nanoscience is the foundation for all systems in our living and mineral worlds, despite the fact that it is often thought of as a science of the future. Every day, we are presented with hundreds of instances of nanoscience, such as geckos that seem to defy gravity by walking upside down on a ceiling, butterflies that have iridescent colors, and fireflies that light at night. In nature, we find some exceptional solutions to difficult issues in the form of fine nanostructures that are linked to exact functions. Researchers now have new analytical methods at their disposal to observe and examine such structures and associated functions in more detail. This has accelerated the development of nanotechnologies and further promoted study in the field of nanoscience. Thus, natural nanoscience serves as the foundation for and the source of inspiration for nanotechnologies. A fantastic place to start when introducing nanoscience into the classroom is with natural nanomaterials. Images taken with a microscope are a useful resource, particularly when utilized in a "zoom-in" manner, beginning with a macro item (like a plant leaf), then demonstrating how zooming in with successive magnifications exposes finer and finer details. If we begin with well-known, organic items like plants and animals, this becomes really powerful. Discovering how many natural nanomaterials are all around us will captivate students.

In the last several years, both in labs and in the commercialization of various goods, nanotechnologies have advanced quickly. Nanotechnologies have enormous potential for a variety of applications, and as a consequence, significant expenditures have been made in both business and research. In the past, other new technologies, most notably food genetic engineering, were promoted to the scientific community (and business) as revolutionary and having great commercialization potential. The food and medical sectors were anticipating financial gain and development thanks to genetically modified organisms. GMOs were not seen favorably by the consumer community because to a variety of factors, the most significant of which was extremely poor communication between the scientific community and the popular media, and the outcome was really the reverse. These goods have been outlawed or subject to strict regulation in numerous nations. Many ethical issues were brought up about "who" would profit from these goods, what effects they would have on long-term health of humans, as well as the life cycle of animals and plants.

The GMO issue is an obvious illustration of a new technology that did not undergo a thorough investigation of its ethical, legal, and social implications. It is also a glaring example of a cutting-edge technology that encountered market resistance to the extent that development was halted and whole research facilities were shut down. Before it was too late, scientists (and even the media) failed to see the power that consumers had. When it comes to nanotechnologies, everyone is generally determined to "do it differently." Researchers, regulators, non-governmental organizations (NGOs), consumer organizations, trade unions, and industry are all involved in setting guidelines, action plans, protocols, codes of conduct, regulations, etc. to ensure that nanotechnologies realize their potential while protecting consumer safety, the environment (in terms of pollution and impact on its life cycles), and are ethically responsible. This is likely the first time in the history of scientific innovation. It is obvious that this is a significant undertaking, and the job is difficult and has just begun. We will identify areas of nanotechnology applications that are posing ELSA difficulties throughout this Teachers Training Kit, as well as the steps being done to solve them.

Bringing ELSA topics into the classroom gives the instructor a chance to discuss science, technology, and innovation in a more intricate, "three-dimensional" way. It allows teachers the chance to spark debates in the classroom about which innovations they believe are good (and which are not), who will gain from them, at what cost, etc. It is an opportunity to consider and discuss the 'larger picture' of science and innovation, as well as its ramifications for society as a whole.

CONCLUSION

A fascinating and promising area of research in materials science and engineering is the topic of nanocrystalline materials. These materials have a wide range of intriguing potential for many applications due to their distinctive structural and functional features resulting from nanoscale grain sizes and interfaces.We have looked at the basic properties, production techniques, and prospective uses of nanocrystalline materials throughout this review.

They have the potential to transform sectors including electronics, energy storage, catalysis, and healthcare because to their extraordinary mechanical strength, expanded surface area, and improved electrical and optical characteristics. But creating and working with nanocrystalline materials has its own set of difficulties, such as problems with scalability, repeatability, and stability.

In order to exploit the full potential of these materials while resolving these difficulties, scientists and engineers must keep coming up with new ideas.The need for cross-disciplinary team cooperation grows as we learn more about the field of nanoscience. To realize the full potential of nanocrystalline materials and pave the path for ground-breaking technological developments, scientists, engineers, and innovators from diverse sectors must collaborate.

REFERENCES:

[1] E. Ringe, “Nanocrystalline materials: Recent advances in crystallographic characterization techniques,” *IUCrJ*, 2014.

[2] X. Yu and Z. Zhan, “The effects of the size of nanocrystalline materials on their thermodynamic and mechanical properties,” *Nanoscale Res. Lett.*, 2014.

[3] P. C. Millett, R. P. Selvam, and A. Saxena, “Stabilizing nanocrystalline materials with dopants,” *Acta Mater.*, 2007.

[4] Y. T. Zhu, X. Z. Liao, and X. L. Wu, “Deformation twinning in nanocrystalline materials,” *Progress in Materials Science*. 2012.

[5] B. S. Murty, M. K. Datta, and S. K. Pabi, “Structure and thermal stability of nanocrystalline materials,” *Sadhana - Acad. Proc. Eng. Sci.*, 2003.

[6] C. Suryanarayana and C. C. Koch, “Nanocrystalline materials – Current research and future directions,” *Hyperfine Interact.*, 2000.

[7] C. Suryanarayana, “Structure and properties of nanocrystalline materials,” *Bull. Mater. Sci.*, 1994.

[8] S. C. Tjong and H. Chen, “Nanocrystalline materials and coatings,” *Materials Science and Engineering R: Reports*. 2004.

[9] C. Suryanarayana, “Nanocrystalline materials,” *International Materials Reviews*. 1995.

[10] M. A. Meyers, A. Mishra, and D. J. Benson, “Mechanical properties of nanocrystalline materials,” *Progress in Materials Science*. 2006.

CHAPTER 2

INTRODUCTION OF CONCEPT OF NATURAL NANOMATERIALS

Dr.Vinod Kumar Singh, Professor
Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India
Email Id- vinod.singh@muit.in

ABSTRACT:

Every day, we are surrounded by many instances of nanoscience, such as fireflies that sparkle at night and geckos who seem to defy gravity by walking upside down on a ceiling. In nature, we find some exceptional solutions to difficult issues in the form of fine nanostructures that are linked to exact functions. The following is a brief list of a few natural nanomaterials; it is not all-inclusive, but the interested instructor may discover further resources in the bibliography at the conclusion of this lesson.

KEYWORDS:

Bone, Lotus Leaf, Nanomaterials, Nanotechnology.

INTRODUCTION

In theory, the nanoscale may be used to characterize any substance. In this literature, "natural nanomaterials" refers to substances that are naturally occurring (mineral and animal), unaltered by humans, and endowed with exceptional qualities by virtue of their innate nanostructure. A substance's molecular structure determines both its chemical identity and its physical characteristics. The supramolecular organization, or the arranging of tens to hundreds of molecules into shapes and patterns in the nanoscale range, is what gives living materials their nanostructure. Natural materials have several extraordinary features that may be appreciated at a larger scale as a result of the interaction of light, water, and other substances with these nanostructures. Nanoscience education may be inspired by using natural nanomaterials in the classroom. Students will be quite acquainted with many natural materials that attribute their characteristics to the presence of nanostructures in their make-up. It may be really eye-opening to learn that everyday items like paper and clay, as well as ubiquitous, natural materials like feathers and spider silk, have qualities that are influenced by both their chemical and their nanostructure[1], [2].

DISCUSSION

Every day, we are surrounded by many instances of nanoscience, such as fireflies that sparkle at night and geckos who seem to defy gravity by walking upside down on a ceiling. In nature, we find some exceptional solutions to difficult issues in the form of fine nanostructures that are linked to exact functions. The following is a brief list of a few natural nanomaterials; it is not all-inclusive, but the interested instructor may discover further resources in the bibliography at the conclusion of this lesson. Nanoparticles are formed naturally during volcanic eruptions and erosion, and as a result, they constitute a component of our mineral environment.

Clays are a form of layered silicate mineral that have a fine 2D crystal structure and are nanostructured minerals. Mica is the clay that has been examined the most. Large sheets of silicate linked together by rather strong connections make up mica. Layer bonding in smectic clays like montmorillonite are comparatively weak. Two sheets of silica make up each layer, which are joined together by cations like Li+, Na+, K+, and Ca2+. To counteract the overall negative charge of the separate layers, cations must be present. The layers have a lateral diameter of 20–200 nm and aggregate into tactoids, which may be 1 nm thick or more. Clays like montmorillonite (MMT) and hecrite are found naturally. Clays' characteristics are determined by their tiny nanostructure. The clay expands when water is introduced, but the volume change is somewhat peculiar; it is many times the original volume because the water molecules that replace the cations cause the layered structure to "open" up. When constructing roads and other structures, it is important to consider clay swelling since it significantly affects soil stability[3], [4].

In naturally occurring colloids, such as those found in milk and blood (liquid colloids), fog (aerosol type), and gelatin (gel type), nanoparticles are disseminated in the medium (liquid or gas), but they do not combine to create a solution. All of these substances exhibit the property of scattering light, and often their color (as in the case of blood and milk) results from the light being scattered by the nanoparticles that make up these substances.Humans have been creating and using nanomaterials for hundreds of years. However, the recognition of certain materials as nanostructured materials is a comparatively recent development, enabled by the development of sophisticated technologies that can resolve information at the nanoscale.

a. We now understand that certain ancient glass artworks' stunning ruby red hue is a result of gold and silver nanoparticles that became stuck in the matrix of the glass.
b. Metal spherical nanoparticles are complexly scattered in the artistic glaze or metallic coating known as "luster," which is present on certain medieval ceramics and contributes to its unique visual characteristics. These materials' production methods were kept a highly guarded secret and are still not fully understood.
c. A nanostructured substance called carbon black is used in vehicle tires to extend their lifespan and give them a dark color. The 1900s saw the discovery of this substance. Fumed silica is another nanostructured substance that is used in silicon rubber, coatings, sealants, and adhesives. In the 1940s, it was made commercially accessible. Steel, sometimes referred to as wootz in popular culture, is an alloy of iron and carbon that is said to have been created for the first time in India about 1500 years ago. Swords, which were made of this steel, were. Swords made from this steel were so powerful and sharp that they could easily split a helmet in half. The discovery of carbon nanotubes in such steel (which was taken from a museum) using high-resolution electron microscopy has lately startled experts. People now think that the existence of these carbon nanotubes, which are renowned for their very high Young's modulus, may be the cause of the remarkable strength of these steels.

The advent of sophisticated microscopic analytical methods, such as atomic force microscopy (AFM), transmission electron microscopy (TEM), and others, has greatly accelerated the identification and characterization of nanomaterials as well as the relationship between their behavior and structure.

The Early Uses of Nanotechnology

Nanotechnology goes beyond mere miniaturization, according to nano-gold. Compared to bulk materials, materials at the nanometer scale have distinctively varied physical, chemical, and mechanical characteristics. For instance, gold is a yellow, inert metal that may conduct electricity under normal circumstances. A centimeter-long strip of gold foil may be divided into twelve equally sized pieces, and each piece will retain its original golden hue. However, practically every attribute changes when the fragments are broken down about a million times, into pieces just a few nanometers across. Nano-gold no longer has a metallic luster that is golden yellow in color.

Depending on the size of the gold nanoparticles, the color of the light that they reflect changes. Around 50 nm-diameter particles have a blue or purple appearance; 25 nm-diameter particles are red; and 1 nm-diameter particles are orange. Could you have guessed that when gold is created in nanometric size, it truly becomes extremely reactive and may be employed as a potent catalyst? When the grain size is decreased below 10 nm, the melting point of gold likewise decreases by about 50%. Similar changes in a range of other characteristics, such conductivity and magnetism, have been seen in several nanomaterials[5], [6].

a. Natural materials that have been mineralized, like shells, corals, and bones, are often composed of calcium carbonate crystals that self-assemble with other natural materials, like polymers, to create intriguing three-dimensional structures. For instance, a layer of cells that initially deposits a covering of protein that is then supported by a polysaccharide polymer like chitin becomes a shell. The proteins govern the formation of carbon carbonate crystals in a manner similar to a nano-assembly process. A protein and chitin matrix in the shape of a honeycomb still surrounds each crystal. The mechanical qualities of the shell and the reduction of cracking are fundamentally dependent on this comparatively "flexible envelope." Each crystal is around 100 nm in size. The nacre of mollusk shells possesses amazing physical qualities as a consequence, including strength and resistance to compression.

b. Materials like keratin, elastin, and collagen are used extensively in the creation of materials like skin, claws, beaks, feathers, horns, and hair. Glycine and alanine are abundant in keratin. As a result, aligned -sheets are able to bind firmly with one another. In order to create helical intermediate filaments, fibrous keratin molecules may twist around one another. Similar to keratin, collagen has a high glycine content and forms flexible triple-helix structures. However, collagen is unrelated to keratin in terms of fundamental structure. Keratins have a large number of cysteine that may create stable disulphide bonds in addition to intra and intermolecular interactions. The number of cysteins in a protein affects the material's strength and stiffness; for example, keratin in human hair has 14% cysteins. Materials with a greater concentration of cysteins include nails, hooves, and claws.

c. Both cotton and paper are mostly composed of cellulose. Cotton's tremendous strength, long life, and absorbency are a result of the fibers' nanoscale organization.

d. Opals and insect wings both have colors that are closely tied to the fine structure of the object, which shows packed nanostructures that function as a diffraction grid and produce iridescence. This occurs in opals because of packed, uniformly sized, nanometer-sized silica spheres that are organized in layers. The color of butterflies' wings is often the result of pigments that absorb certain hues; in other species, as the stunning

Morphorhetenor, the color is the result of the existence of nanostructures that are photonic crystals. In the Chapter's following part, this example is covered in greater depth.

e. Spider silk: Spider silk has a strength that is nearly five times that of steel of same weight, making it the strongest substance yet discovered. The proteins that make up spider silk, namely fibroin, and its supramolecular organization at the nanoscale level are what give it its amazing characteristics.

f. Lotus leaves and kindred plants (nasturtium) have exceptional surface characteristics and the capacity to "self-clean" due to the nanostructure of their leaves. In the Chapter's following part, this example is covered in greater depth.

g. Gecko feet: The link between function and nanostructure is amazingly shown by the structure of a gecko foot. The nanostructure of geckos' feet has a direct bearing on their capacity to walk upside down, against gravity, even on soiled or damp surfaces. In the Chapter's next part, this example is also covered in greater depth[7], [8].

Natural nanomaterials have appeal for both understanding (and appreciating) the remarkable features of biological materials as well as for drawing design and engineering inspiration for brand-new materials with cutting-edge capabilities. Many biological materials' amazing characteristics have physical roots in their intricate, often hierarchical structures. They exhibit an unexpected degree of plasticity and multifunctionality. These materials may serve as a template for creating artificial materials that are far superior for a variety of uses, including solar cells, fuel cells, textiles, drug delivery systems, etc. The idea that some very basic rules govern nature is much more inspiring.

1. The energy that nature requires is all that it draws from the sun. Natural nanoparticles are very effective at conserving energy!
2. Natural systems minimize waste by recycling everything and matching form to function!
3. Nature supports variety and local knowledge while rewarding collaboration. Biomimetics is the term used to describe the branch of materials engineering that aims to create artificial materials that resemble natural ones. Biomimetics is fundamentally based on nanoscience.

Now, a few intriguing natural nanostructures are detailed in more depth, along with an explanation of how their natural nanostructure contributes to their unique features (such as adhesion, strength, flexibility, and color).

Bone

It seems paradoxical, but when you think about it, bone's special qualities include being both hard and flexible, light yet strong enough to promote tissue development, and mechanically robust but porous. Weight may be applied to bone without it shattering. About two times as strong in compression as in tension. These exceptional qualities are the consequence of the complex hierarchical structure and composition of bone, which is formed of a composite of calcium phosphate (hydroxyapatite) particles and collagen fibrils (mostly Type I collagen).

Many bones, like the femoral head, have a ‘sandwich' structure with a solid outer shell (cortical bone) and a spongy inner (cancellous bone), which is how many bones are mechanically seen. Only 20% of the volume of cancellous bone is made up of actual bone; the remaining 80% is made up of bone marrow. Fibrils are distributed in a consistent pattern across cortical bone. The collagen molecules that make up the fibrils, which are deposited into the extracellular space by osteoblasts (bone-forming cells), are 300 nm long and 1.5 nm thick. Within the fibril, adjacent molecules are spaced apart along the axial direction by about D = 67 nm, creating a distinctive pattern of overlap zones and gap zones with a length of 35 nm and 32 nm, respectively.

In summary, the building blocks of bone are soft organic matrix (collagen) and anisotropic rigid inorganic component (hydroxiapatite crystals). These two parts are put together in a hierarchical, nanoscale-level organized structure. Because of this nanoscale hierarchical organization, bone is able to disperse the energy of microscopic microfractures that result from regular activity without the crack spreading. Since hydroxiapatite is a stiff substance that cannot easily release energy, collagen is thought to play a significant part in the structural characteristics of bone (elastic and plastic deformation). The function of collagen during bone deformation is shown in Figure 4. Older bone is stiffer and more brittle because it is more mineralized and thus contains more hydroxiapatite.

Lotus leaf

The lotus plant (Nelumbonucifera), a native Asian plant, has the unique ability to keep its leaves very clean even while it is growing in muddy conditions. Because of this, this plant is revered in various cultures as a symbol of purity. The leaves of the lotus plant have the exceptional quality of completely rejecting water due to their extreme hydrophobicity. As a result, water droplets slide down the surface of the leaf, dragging debris with them. This'self-cleaning' effect makes the lotus leaf clean and stain-resistant. Other leaves, such those of certain Cannas and the nasturtium (Tropaeolum), as well as some animals, like the water strider, have the same effect.

Wilhelm Barthlott was the first to study the lotus leaf's surface characteristics. He initially defined the "Lotus effect," which is what gives lotus leaves their ability to self-clean, in a significant study he released in 1997. In his original study, Barthlott demonstrated how the microstructure of the leaves and the epidermal cells on their rough surfaces, which are coated in wax crystals, together provide the lotus plant's self-cleaning capabilities. These crystals create a layer that repels water, and the surface's roughness amplifies this layer's effectiveness, resulting in a superhydrophobic surface with a contact angle of around 150°.

As a result, water droplets on the surface have a tendency to minimize their contact with the surface, resulting in virtually spherical droplets. An image of an increasing nasturtium leaf magnification. A few tens of nanometer-sized nanocrystals are seen in the final picture on the right. When a water droplet rolls over a contaminant on the surface, the droplet removes the particle off the leaf's surface. Contaminants on the surface are often bigger than the cellular structure of the leaves[9], [10].

Gecko

A gecko can walk on smooth or rough surfaces, even upside down on glass, and cling to almost any surface in any direction. It can even do this while retaining complete contact and stickiness to the surface. A gecko's feet do not have any suction-like properties, even at tiny sizes, and it does not exude any sticky material as it moves. The nanostructures on the gecko's foot are what give it its extraordinary qualities. A group of tiny ridges on the gecko foot are called scansors, and they are filled with many projections called setae. Each seta measures around 100 m in length and 5 m in diameter.

On a gecko's foot, there are almost half a million of these setae. Each seta is further split into 1,000 spatulae, or projections, each measuring 200 nm in width.

The gecko's feet have a huge surface area overall as a consequence. Due to their extreme flexibility, gecko spatulae may almost mold themselves to any surface's molecular structure. Strong adhesion is the end outcome, and van der Waals forces are totally to blame. 200 N, or around 10 atmospheres of tension, can be resisted by a single seta. Thus, a great illustration of the impact of vast surface area on tiny forces is the gecko scenario.

Another highly intriguing characteristic of geckos is that they can walk over surfaces covered in sand, mud, water, etc. without getting their feet soiled. Even on grimy surfaces, their feet remain clean, and maximum adherence is maintained. Investigation into the phenomena revealed that the feet always stay free of debris because it is more advantageous energetically for particles to be deposited on the surface rather than to stick to the gecko spatulae. A gecko's feet may get completely clean again after only a few steps on a filthy surface, and adhesion is unaffected.

Infra-red rhetoric

Because of the wing surface's interaction with light, butterfly wings often exhibit unusual colors. The wings also display iridescence, which is when an object's color changes depending on the angle from which it is seen. A music CD may be used to quickly visualize the impact. Iridescence, a "physical color," is produced when light interacts with the surface's physical makeup. Those structures must be nanoscale in order to interact with visible light, which has wavelengths between 380 and 750 nm. This nano-rough surface may interfere with light in either a beneficial or detrimental way. The thickness, refractive index, incidence angle, and frequency of the incident light are all factors that affect the color, intensity, and angles of iridescence. Due to packed, uniformly sized, nanometer-sized silica spheres organized in layers, natural iridescence is seen in materials like opals. This creates favorable interference circumstances.

CONCLUSION

Iridescence is created in an odd method in the case of butterflies and moths. After careful examination of the Morphorhetenor's wings, scientists discovered that they are made of rows of scales organized like roof tiles. Each scale is around 70 x 200 m and has a far more minute structure on its surface, consisting of a highly organized arrangement of ridges at the nanometer scale. Every ridge is around 800 meters broad. They are separated by a natural photonic crystal that may provide both beneficial and harmful interference. An even more complex structure that resembles fir trees is seen in the cross-section of the ridges on the wings as shown by the SEM investigation.

REFERENCES:

[1] S. M. Louie, R. D. Tilton, and G. V. Lowry, “Critical review: Impacts of macromolecular coatings on critical physicochemical processes controlling environmental fate of nanomaterials,” *Environmental Science: Nano*. 2016.

[2] X. W. Sun, Y. X. Zhang, and D. Losic, “Diatom silica, an emerging biomaterial for energy conversion and storage,” *Journal of Materials Chemistry A*. 2017.

[3] G. Yuan, “Natural and modified nanomaterials as sorbents of environmental contaminants,” *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.*, 2004.

[4] M. R. Buck and R. E. Schaak, “Emerging strategies for the total synthesis of inorganic nanostructures,” *Angewandte Chemie - International Edition*. 2013.

[5] K. Korschelt, M. N. Tahir, and W. Tremel, “A Step into the Future: Applications of Nanoparticle Enzyme Mimics,” *Chem. - A Eur. J.*, 2018.

[6] V. A. Petrenko, “Landscape phage: Evolution from phage display to nanobiotechnology,” *Viruses*. 2018.

[7] D. Docter, D. Westmeier, M. Markiewicz, S. Stolte, S. K. Knauer, and R. H. Stauber, “The nanoparticle biomolecule corona: lessons learned - challenge accepted?,” *Chem. Soc. Rev.*, 2015.

[8] H. Gao, B. Ji, I. L. Jäger, E. Arzt, and P. Fratzl, “Materials become insensitive to flaws at nanoscale: Lessons from nature,” *Proc. Natl. Acad. Sci. U. S. A.*, 2003.

[9] Kenry and C. T. Lim, “Nanofiber technology: current status and emerging developments,” *Progress in Polymer Science*. 2017.

[10] D. Schaming and H. Remita, “Nanotechnology: from the ancient time to nowadays,” *Found. Chem.*, 2015.

CHAPTER 3

MATERIAL AND ELECTRICAL PROPERTIES AT THE NANOSCALE

Dr. Vinod Kumar Singh, Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vinod.singh@muit.in

ABSTRACT:

'The science of tiny' is a common nickname for nanoscience. In this Chapter, we answer the following query: Why does size matter? What makes nanoscale materials so unique? What distinguishes their characteristics from those of 'ordinary' bulk materials? Here, a thorough analysis of the subject is not possible since doing so would need a thorough analysis of quantum physics, but several important facets of nanoscience that are crucial to comprehending the extraordinary features of nanomaterials are emphasized. The ramifications that these effects have on the characteristics of materials are the main emphasis, not the theory that underlies these effects.

KEYWORDS:

Electrical Properties, Material Properties, Nanoscale, Surface Characteristics.

INTRODUCTION

The analysis of a pure sample in amounts large enough to be assessed under standard laboratory circumstances is used to identify the macroscopic physical characteristics of a material (melting point, boiling point, conductivity, etc.). Any substance has 6.022 x 1023 molecules per mole, and one mole of water, for example, weighs 18 g. We presume that the conclusion should hold true for any size of group of water molecules when determining the boiling point of a mole of water since the number obtained is an average value based on the behavior of billions and billions of water molecules. This is untrue for many materials since, when a material shrinks in size and reaches the nanoscale level, it is conceivable for it to exhibit completely new characteristics (different melting point, conductivity, etc.). This is due to the fact that matter at the nanoscale now obeys quantum mechanics rather than Newtonian physics. In other words, a material's qualities may vary depending on its size. This could be a novel idea to introduce into the classroom since, traditionally, the characteristics of a substance whether it be solid, liquid, or gas relate to its atoms and molecules and the connections between them (chemical bonds). Size is not often cited as a significant aspect. No matter how large or little a piece of gold is, students will usually assume that it will be golden in color. At the macro- and micro-scale levels, this is true; but, at the nanoscale, quantum effects begin to radically alter the situation. In reality, gold serves as a good illustration since a colloid of gold nanoparticles is no longer 'golden' in color but rather ruby-red[1], [2]. One nanometre is equal to 3.5 atoms of gold or eight hydrogen atoms arranged in a row; materials that are "nanoscale" are formed of at least clusters of atoms and molecules, not simply single atoms. The size of a glucose molecule is around 1 nm. Compared to other'tiny' items that a student may be acquainted with, nanomaterials represent a 'new sort of small. Nanomaterials are larger than other'very tiny items' that a student may probably conceive of, such a cell or bacteria, and are not as small as electrons or single atoms. The tiniest items manufactured by humans, like the newest transistors, and the biggest molecules generated by living things, like DNA and proteins, meet in nanostructures. Nanomaterials fall in between solitary atoms and molecules and bulk materials in terms of size. The characteristics of matter are extraordinary at this size. Nanomaterials have two fascinating possibilities because of their distinctive qualities:

a. Nanomaterials may be utilized to generate new materials with remarkable qualities or to enhance existing ones;
b. Nanomaterials can be integrated into devices and actively interacted with since their sizes are comparable to the biggest molecules in the natural world.

DISCUSSION

The Physics of Nanoscale

Because of their smaller size compared to bulk materials, nanomaterials need the application of quantum mechanics to describe their behavior. A scientific theory known as quantum mechanics was created to explain the movement and energy of atoms and electrons. Quantum mechanics principles are not presented in depth here since they are often covered in secondary science (physics or chemistry) school curricula. Here, the most important quantum effects are briefly summarized, together with other physical characteristics that are important at the nanoscale[3], [4].

1. Nanomaterials are so microscopic that their mass is really minimal and gravitational forces are hardly felt. Instead, the behavior of atoms and molecules is mostly governed by electromagnetic forces.
2. The wave-corpuscle structure of matter is particularly obvious for things with extremely low masses, like the electron. As a result, electrons behave like waves, and a wave (probability) function describes their location.
3. A result of this is a phenomena known as tunnelling. According to standard physics, a body can only overcome a barrier (potential barrier) if it has sufficient energy to "jump" over it. Therefore, in classical physics, the chance of discovering the item on the other side of the barrier is zero if the object contains less energy than is required to leap over the energy barrier (the "obstacle").

A particle with less energy than needed to cross the barrier has a limited chance of being discovered on the other side, according to quantum physics. In a metaphorical sense, the barrier might be thought of as a "virtual tunnel" through which the particle travels. It should be emphasized that the tunnel effect can only be seen at the nanometer scale since the 'thickness' of the barrier (i.e., energy potential) must be proportional to the wavelength of the particle. Therefore, to put it simply, electron (or quantum) tunneling is the defying of a basic principle of classical physics by allowing a particle (an electron) with lower kinetic energy to reside on the opposite side of an energy barrier with greater potential energy. An electron may enter an energy range that is normally prohibited through tunneling.

The Scanning Tunnelling Microscope (STM), a crucial tool for seeing nanostructured surfaces, is built on the basic quantum phenomena of tunneling. The same method may be used for nanofabrication (moving individual atoms).

1. Quantum confinement: Rather of being free to flow across the bulk of a nanomaterial like a metal, electrons are constrained in space.
2. Energy quantization: Only at certain energy levels can electrons coexist. Nanomaterials called quantum dots exhibit the effect of energy quantization.
3. Random molecular motion: when a sample is above absolute zero, molecules move as a result of their kinetic energy. This kind of motion, known as random molecular motion, is constant. In terms of the items' sizes, this motion is relatively modest at the macroscale and has little impact on how the object travels. However, at the nanoscale, these movements may be on the same scale as the size of the particles and may thus significantly affect how they behave. Brownian motion is one kind of random kinetic motion.

A nanomaterial is made of at least a cluster of atoms and often a cluster of molecules, as was previously mentioned. All forms of bonding, then, that are significant in chemistry are likewise significant in nanoscience. They are often categorized as:

a. Ionic, covalent, and metallic bonds are examples of intramolecular bondings (chemical interactions) that include modifications to the chemical structure of the molecules;
b. Ion-ion and ion-dipole interactions, van der Waals interactions, hydrogen bonds, hydrophobic interactions, and repulsive forces (such as steric repulsions) are examples of intermolecular bondings (physical interaction), which are bondings that do not involve changes in the chemical structure of the molecules.

In this section, several chemical and physical interactions that are often used to explain the characteristics of nanomaterials are emphasized because it is expected that the explanation of chemical and physical bonding is a component of the secondary scientific school curriculum. Numerous molecules bound together or huge molecules (macromolecules) that take on certain three-dimensional shapes via intermolecular bonding are frequent sources of nanomaterials. As a result, supramolecular chemistry, a subfield of the larger study of "chemistry," which deals with interactions between molecules, is also a subject of nanoscience. Intermolecular bonding often plays a significant role in these macromolecules[5], [6].

Van der Waals and hydrogen bonds among other intermolecular bondings are weak interactions, but when they occur often, their combined energy may be extremely high. Consider the two helix structure of DNA, which has a cross section of 2 nm. Numerous hydrogen bonds hold the two helix structures together. In nanoscience, where materials may have extremely high surface areas and, as a result, tiny forces can be applied to very vast regions, this notion becomes very important. Macromolecules (like proteins) are often held together by intermolecular bondings in unique three-dimensional structures that are linked to certain biological activities. A protein's quaternary structure (its three-dimensional structure) and function are completely lost when these connections are disrupted, which is known as protein denaturation. The hydrophobic effect is one sort of intermolecular bonding that is especially important in nanoscience. Entropy is essentially what drives this process, which is significant in biological materials. Simply put, it is the tendency of non-polar molecules (like oil) to cluster with other molecules of their kind in water.

Special Features of Materials at The Nanoscale

Surface characteristics

Regardless of whether we are thinking about a bulk material or a nanoscale substance, many of its surface features affect both its physical and chemical properties. Surfaces serve a variety of purposes, including preventing objects from getting in or out, allowing materials or energy to pass over an interface, and starting or stopping chemical reactions, as in the case of catalysts. Surface science is the field of study that examines the chemical, physical, and biological characteristics of surfaces. The word interface is often used in this context rather than surface to emphasize that it is a border between two phases: the material and the environment (liquid, solid, or gas). The overall volume stays the same when a bulk substance is split into a collection of distinct nanomaterials, but the combined surface area increases significantly. The result is a rise in the surface-to-volume ratio of the material in comparison to the parent bulk material.

How crucial surface atoms are?

In surface science, a material's characteristics are determined by the chemical groups present at the material contact. The nature of the interface affects properties including catalytic reactivity, electrical resistivity, adhesion, gas storage, and chemical reactivity. Atoms near the surface make up a significant component of nanomaterials. This has a significant impact on reactions that take place at the surface, including those that need the physical adsorption of certain species at the material's surface to commence, such as catalysis reactions, detection reactions, and reactions.

Some physical parameters, like the melting temperature, are influenced by the fact that a higher proportion of the atoms in a nanomaterial are at the surface. The melting point of a given substance will be lower if it is nanosized. Because surface atoms may be removed more readily than bulk atoms, less total energy is required to overcome the intermolecular interactions holding the atom "fixed," resulting in a lower melting point. Shape is important because it affects how much surface area there is given a certain volume. A straightforward illustration is the volume matching of a sphere and a cube. Compared to the sphere, the cube has a bigger surface area. For this reason, in nanoscience, a nanomaterial's form is just as significant as its size. An example of a nanomaterial whose characteristics are influenced by form in addition to size is provided in the section on catalysis[7], [8].

Surface power

The identical atoms or molecules that exist in the inside of a material are different from those that do so at the surface or at a contact. Any substance has this as a benefit. Because surface atoms and molecules are unstable and have a high surface energy, they are more reactive and have a stronger propensity to aggregate near the interface. Nanomaterials have a very high percentage of their atoms and molecules on their surface, as was indicated in the preceding section. However, a basic tenet of chemistry states that "systems of high energy will strive to attain a state of lower energy, by any means possible." So how are nanoparticles even possible? Nature is full with nanomaterials (proteins, DNA, etc.). Nanomaterials use a variety of techniques to reduce their naturally high surface energy since they are fundamentally unstable.

Agglomeration is one method of lowering the surface energy in nanoparticles. Surface energy is a quantity that may be added. The total surface energy of ten identical nanoparticles is equal to their individual surface energies. The total surface energy would decrease if they combined to form one big particle. The total surface energy of cube A is 6 if a generic surface energy value of is assigned to each of its lateral surfaces. The same holds true for cube B. As a result, when A and B are separated, their combined surface energy is 2 x 6 = 12. The parallelepiped C, on the other hand, has a total surface energy of 10.

A high innate propensity to aggregate exists in nanoparticles. Surfactants may be employed to prevent this. This also explains why nanoparticles are often immobilized on a solid substrate or combined with a matrix when they are employed in research and industry. Microscope photos demonstrate that nanoparticles are genuinely present in the form of agglomerates with diameters more than 100 nm, even in commercial goods that advertise the presence of such particles (such as sunscreens).

Catalysis

A material that speeds up a chemical process without being eaten or chemically changed is called a catalyst. Enzymes are the name for the catalysts found in nature. They can construct certain end products and are always looking for paths that allow reactions to occur with the least amount of energy. In order to prevent "catalyst poisoning," which happens when species dispersed in the atmosphere, such as CO, occupy the active sites of the catalysts, man-made catalysts are frequently made of metal particles fixed on an oxide surface, working on a hot reactant stream. An essential component of a catalyst is its active surface, which is where the reaction occurs. The 'active surface' rises as catalyst particle size decreases; the surface-to-volume ratio increases with decreasing catalyst particle size[9], [10].

The surface reactivity increases with the catalysts' active surface height. According to research, a catalyst's active sites' spatial arrangement is also significant. Nanotechnology allows for the control of both molecular structure and distribution as well as nanoparticle size. Because of this, there is a lot of potential for this technology to advance catalyst design, which would be advantageous for the chemical, petroleum, automobile, pharmaceutical, and food sectors. having the help of nanoparticles having catalytic characteristics, the quantity of material required may be drastically reduced, which has positive effects on the economy and the environment.

Gold is an excellent illustration of how nanoscience may influence the creation of catalytic materials. Bulk gold is a noble metal that resists oxidation and chemical assault, is stable, and is non-toxic. It is often used in jewelry because of these properties. However, gold nanoparticles have the ability to catalyze chemical processes. It has been discovered that highly catalytically active finely distributed gold nanoparticles on oxide supports. Dispersed gold nanoparticles have more selectivity and catalytic activity than several routinely used transition metal catalysts, including platinum, rhodium, and palladium. This is a promising finding since hazardous and costly metals like platinum and palladium, which are often employed in catalysis in things like automotive catalytic converters, are toxic metals.

Detection

The functioning of many devices, including chemical sensors, biosensors, and microarrays, depends on the detection of a particular chemical or biological molecule within a mixture. A detection reaction takes place at the material contact, similar to catalysis. Nanomaterials rather than bulk materials in the detecting region may increase the pace, specificity, and accuracy of this reaction. The increased surface area accessible for detection due to nanomaterials' greater surface-to-volume ratio has a favorable impact on the reaction's pace and detection limit. Additionally, nanoparticles may be engineered at the molecular level to have certain surface qualities (chemical or biological). In this manner, the material's active sites may function as "locks" to recognize certain molecules (the "keys"). Multiple analytes may be detected by scaling down utilizing nanomaterials since more detection sites can be crammed into a single device.

Electrical characteristics

Based on their electrical characteristics, materials may be divided into three categories: conductors, semiconductors, and insulators. e.g. (band gap) refers to the energy difference between the valence band and the conduction band. Whether a substance is a conductor, semiconductor, or insulator depends on the capacity of the material to fill the conduction band with electrons and the energy of the band gap. Thermal energy is sufficient to induce electrons to travel to the conduction band in conducting materials like metals because the valence band and conducting band overlap. As a result, the value of e.g. is low in these materials. The band gap in semiconductors is just a few electron volts. Excitons are electron-hole pairs that arise when an applied voltage is greater than the energy of the band gap, causing electrons to move from the valence band to the conduction band. Since insulators have wide bandgaps, it takes a tremendous amount of voltage to get through the threshold. These substances don't conduct electricity because of this.

CONCLUSION

The band gap's energy rises due to quantum confinement. In addition, when the energy levels are measured at extremely tiny dimensions, the band overlap that is present in metals vanishes and becomes a band gap. This explains why certain metals, when their size is reduced, become into semiconductors. Due to the rise in band gap energy brought on by quantum confinement, more energy will be required for the material's band gap to absorb. Shorter wavelengths (blue shift) result from more energy. The same holds true for the fluorescent light produced by the nanoscale material, whose larger wavelength will result in the same blue shift. As a result, a technique for adjusting a nanoscale semiconductor's optical absorption and emission characteristics throughout a range of wavelengths is presented. In the Chapter's section on optical characteristics, nanoscale metals and semiconductors (quantum dots) are explained in terms of their optical qualities.Some nanoparticles have electrical characteristics that are just unmatched. Their distinctive structure is connected to their electrical characteristics. Fullerenes and carbon nanotubes are two of them. For instance, the nanostructure of carbon nanotubes determines whether they are conductors or semiconductors. Supercapacitor materials, which virtually have zero resistance and defy Ohm's law, are another example.

REFERENCES:

[1] D. Dimov *et al.*, “Ultrahigh Performance Nanoengineered Graphene–Concrete Composites for Multifunctional Applications,” *Adv. Funct. Mater.*, 2018.

[2] S. Yazdani and M. T. Pettes, “Nanoscale self-assembly of thermoelectric materials: A review of chemistry-based approaches,” *Nanotechnology*. 2018.

[3] A. Shekhawat and R. O. Ritchie, “Toughness and strength of nanocrystalline graphene,” *Nat. Commun.*, 2016.

[4] Y. Jung, Y. Zhou, and J. J. Cha, “Intercalation in two-dimensional transition metal chalcogenides,” *Inorg. Chem. Front.*, 2016.

[5] Y. Liu *et al.*, “Thermal Oxidation of WSe2 Nanosheets Adhered on SiO2/Si Substrates,” *Nano Lett.*, 2015.

[6] C. Li, E. T. Thostenson, and T. W. Chou, “Sensors and actuators based on carbon nanotubes and their composites: A review,” *Composites Science and Technology*. 2008.

[7] X. Zhang, X. G. Shi, and W. G. Ma, “Development of multi-physical properties comprehensive measurement system for micro/nanoscale filamentary materials,” *Zhongguo Kexue Jishu Kexue/Scientia Sin. Technol.*, 2018.

[8] L. Zeng *et al.*, “Correlation between Electrical Transport and Nanoscale Strain in InAs/In0.6Ga0.4As Core-Shell Nanowires,” *Nano Lett.*, 2018.

[9] D. A. Dikin *et al.*, “Preparation and characterization of graphene oxide paper,” *Nature*, 2007.

[10] A. Gentile, F. Ruffino, and M. G. Grimaldi, “Complex-morphology metal-based nanostructures: Fabrication, characterization, and applications,” *Nanomaterials*. 2016.

CHAPTER 4

BIOMIMETRIC AND SELF ASSEMBLED NANOMATERIALS

Dr.Vikas Kumar Shukla, Assistant Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vikash.shukla@muit.in

ABSTRACT:

An intriguing nexus of biology, chemistry, and materials science may be found in biomimetic and self-assembled nanomaterials. These ground-breaking materials are inspired by nature's amazing capacity to assemble intricate systems and structures on its own. The main ideas and uses of biomimetic and self-assembled nanomaterials are summarized in this article.Biomimetic nanomaterials provide unique qualities and capabilities by reproducing biological structures and processes at the nanoscale. These substances may imitate the hierarchical structure seen in natural substances like proteins, shells, and bones. Researchers have created biomimetic materials with uses ranging from lightweight, high-strength composites to drug delivery systems that precisely target certain cells by comprehending and using nature's design principles.

KEYWORDS:

Functional Materials, Nanoengineering, Self-Organizing Systems, Synthetic Biology.

INTRODUCTION

The design and production of novel materials with cutting-edge features and functionalities will be impacted by nanoscience. Enhancing the qualities of plastics, ceramics, coatings, composites, fibers, and many other materials is one contribution to this subject. The bottom-up method of material self-assembly, which takes its cues from the way organic and inorganic materials are assembled in nature, is another brand-new idea in material design brought about by nanoscience. As was evident in the preceding part, many natural nanomaterials perform amazing activities as a consequence of their internal nanostructure. As such, nature is a fantastic source of inspiration for materials engineers. An overview of nanomaterials, their characteristics, and uses is given in this Chapter[1], [2].

The aforementioned nanomaterials' application fields are also noted. Nanotechnology applications are the focus of this teachers' training kit's second subject. What exactly is a "nanostructured material"? Before going through some instances of diverse functional nanomaterials, this must be taken into account. Solids or semi-solids (such hydrogels or liquid crystals) with a nanoscale internal structure are referred to as nanostructured materials. Because of the scale order, they are distinct from crystalline, microstructured, and amorphous solids. Atoms are neatly organized in crystalline materials in a grid with well-defined distances between neighbors, and this order extends to macroscopic dimensions. Amorphous materials only display short-range order, whereas microstructured materials only exhibit structural diversity on a micron scale.

The spatial order in nanostructured materials is at the nanoscale, which is halfway between the microscopic and atomic scales. The characteristics of a material are influenced by the size of the nanostructures and the scale order within them in the solid. The size of the structural units that make up nanostructured materials differs from traditional polycrystalline materials.

Because there are so many grain boundaries (i.e., the spaces between the nanostructures) in the bulk material, they may sometimes display characteristics that are substantially different from those of normal materials. This indicates that a substantial percentage of surface atoms atoms that are found at or close to surfaces are present in a nanostructured material. Since there is a lot of surface area, surface characteristics start to dominate bulk properties. In the event of a pore or flaw, this surface, which is also known as an interface, might establish a boundary with the embedding matrix, a nanoparticle, air, or vacuum.

DISCUSSION

Nanoporous, nanocrystalline, nanocomposite, and hybrid materials are examples of nanostructured materials. A nanocomposite material contains two or more phaseseparated components with morphology of spheres, cylinders, or networks with nano-sized dimensions; hybrid materials are made of a combination of organic and inorganic components connected at the molecular level (for example, block copolymers). Nanoporous materials have nanoscale pores. Nanocrystalline materials have many nanoscale crystalline domains. Because the materials in this Chapter were grouped according to the purposes they serve, they are often cross-referenced in the text. For example, a nanocoating may be a nanocomposite but is explained in a different category due to its distinct purpose.

The ability of nanostructured materials to exhibit properties that are markedly different from those seen in bulk is one of their distinctive characteristics. By using the inherent qualities of nanoparticles, scientists have the chance to create novel materials with specialized uses. As a consequence, new qualities may be added to coatings, polymers, and metals to enable them to perform certain tasks. Numerous novel materials with intriguing features are being produced, as was covered in this Chapter. Even while this area still requires a lot of study, there are currently a lot of commercially viable options, and interesting new materials should be on the horizon. Numerous uses for these materials exist, ranging from the medical field (such as antimicrobial coatings) to better cutting instruments[3], [4].

Biomimetic nanomaterials

Biomimetic materials will be the first class of engineered nanoparticles to be examined. Nature has created a vast variety of materials over thousands of years of evolution, including feathers, shells, wood, bone, and many others. These materials have complex hierarchical structures at the nano, micron, and macro levels, which give them unique properties like strength, lightness, permeability, and color. Materials engineers are inspired to create sophisticated materials with specialized functionalities by the fantastic platforms provided by natural materials. In reality, many of the "macro" materials we use today were created as a result of inspiration from natural materials. One such is Velcro, which was created in 1948 by a Swiss engineer called George de Mistral and was motivated by the way cockleburs adhere to dog hair and fabrics. Scientists have been motivated to emulate natural materials' nanostructures beginning at the molecular level (molecular biomimetics) since they often play a critical role in them. Additionally known as biomimetic nanotechnology. Now, a few examples of these bioinspired nanomaterials are given.

Adhesive modeled after geckos (or bio-rubber)

It was mentioned how the gecko foot's sticky qualities aren't due to a glue present there, but rather to van der Waals and capillary forces generated by the millions of nanostructures (known as setae) that make up the foot. This enables the animal to move in an upside-down position, defy gravity, and walk on a variety of surfaces, including wet ones. A gecko's feet are also self-cleaning, so it may walk over a filthy surface without losing adhesion. A absolutely remarkable substance! This animal has served as inspiration for scientists who have created and designed adhesives for a variety of uses. For instance, scientists at the University of California, Berkeley have created sticky surfaces that resemble the feet of geckos for use by climbing robots. Microfibers array patches with 42 million polypropylene microfibers per square centimeter make up the adhesive. A 2 cm^2 patch can sustain a load of 400 g and the patches have a maximum support of 9 N cm^{-2}. This finding comes extremely near to the 10 N cm^{-2} stresses that a gecko can withstand. The functioning of this gecko-like adhesive is quite close to that of the actual gecko foot, although it is not yet as effective. It still has to be topography-independent (able to adhere to any surface) and self-cleaning by researchers. A biomimetic gecko tape has been created at another institution employing polymer surfaces wrapped in carbon nanotube hairs. This tape can cling to and come off of Teflon among other surfaces.

Self-healing adhesives

Diatoms are a form of algae with amorphous silica surfaces that have been nanostructured. Strong self-healing underwater adhesives have developed in several diatom species. Others have adhesive qualities in water, such as diatoms in the Antarctic waters, which may adhere to ice. Some are free-floating. Others produce sticky mucilage, which holds colonies together and shields the silica shells from damage when they brush against one another. Another species that has sticky qualities underwater is molluscs. Molluscs and diatoms both have robust underwater glues that can withstand stress and, if required, self-heal. They act as a biomimetic model for self-healing materials as a result. Researchers have examined these natural adhesives and discovered that the proteins they contain have self-healing qualities. The ‘sacrificial' bonds in these proteins enable the molecule to be reversibly extended by breaking and re-bonding. The behavior of sacrificial bonds has been seen in a variety of different materials, including wool. New nanoadhesives with self-healing capabilities are being developed as a result of the thorough investigation of these natural materials[5], [6].

Membranes, capsules, and bioreactors with biomimicry

For many years, the bilipid membrane was used as a biomimetic model. Liposomes, which are lipid vesicles that are readily generated by violently mixing oil in water, are a straightforward example. Planar-supported bilayers are created by simply 'dipping' a suitable substrate into an organic aqueous phase. They are also inspired by the lipid membrane.

Bioinspired nanomaterials for energy

The usage of nanoengineered materials may help us overcome many of the problems we are now experiencing in the energy sector (improvements required for solar panels, hydrogen fuel cells, rechargeable batteries, etc.). Some of these materials, like the novel varieties of solar photovoltaic cells that attempt to mimic the organic nanomachinery of photosynthesis, were created by directly drawing inspiration from nature. Utilizing battery electrodes with self-assembling nanostructures generated by genetically modified viruses is an additional intriguing example.

Easily put together nanomaterials

The idea of self-assembly originated from the fact that during normal biological processes, molecules self-assemble with nanoscale accuracy to form intricate structures. Examples include how the double helix of DNA is created or how phospholipids are used to create membrane cells. Through non-covalent contact, self-assembling sub-units spontaneously organize and aggregate into stable, clearly defined structures. The features of the subunits serve as a guide for this process, and the final structure is obtained by equilibrating to the form with the lowest free energy. This organization may be upset by an outside force, such a change in temperature or pH. As an example, a protein may self-assemble into a certain structure, but if subjected to circumstances like high heat or high acidity, it can denature, which means that its structure is broken, and the protein unfolds. This indicates that once a protein's structure is harmed, its function is lost. Therefore, self-organized systems in nature serve certain purposes.

As they attach to certain ions or atoms, molecules in nature change conformation and transition from one self-organized structure to another. There are several examples, such as chlorophyll, the potassium-sodium pump, hemoglobin (which absorbs and releases an iron ion), etc. Self-assembly is a fundamental technique in nanotechnology because it uses a bottom-up approach to nanofabrication to produce novel materials. Nanostructures are made from the bottom up, from atomic building blocks that self-assemble into larger structures, as opposed to being cut out of larger materials (which is the typical top-down approach, such as micromachining and microlithography, used to fabricate integrated electronic circuits). This self-organization of matter may be used by scientists in the lab to direct the construction of unique structures with predetermined purposes. Dendrimers, DNA nanostructures, cyclodextrins, self-assembled monolayers (SAMs), and liquid crystals are a few examples of self-assembled nanomaterials.

Self-assembled monolayers (SAMs) are monomolecular-thick layers that are produced when certain organic molecules are exposed to a suitable substrate from a solution or vapor. These chemical compounds feature two distinct end groups on their lengthy chains. One of the organic molecules two end groups combines with a specific surface to create a chemical bond, which results in the formation of the monolayer. The exposed functional groups of the monolayer then determine the substrate's surface characteristics. Alkyl-silane or alkane thiol molecules, for instance, may form organized layers when exposed to a silica or metal surface. Physisorbed layers, like Langmuir-Blodgett films, or chemisorbed layers, such organosilanes bound to silica or organothiols bound to gold, may both be used to generate SAMs[7], [8].

By combining two (or more) precursor molecules, it is possible to create films of mixed SAMs with customized surface characteristics. Photosensitive SAM layers may be created by molecularly designing the precursor to include a photoreactive species. In order to regulate protein and cell adhesion, Whitesides and his colleagues from Harvard University first used mixed SAMs of alkanethiols on gold surfaces. When an alkanethiol solution or vapour is exposed to a gold surface, SAMs of the alkanethiol are created. While the alkyl chains are tightly packed and inclined to 30° from the surface normal, the sulfur atoms of the alkanethiols align with the gold surface. The surface characteristics of a monolayer made up of a -substituted alkanethiol are determined by the terminal end group.

The ability to build metallic "hybrid" circuits where biomolecules may be selectively attached (and released from) gold patterns makes surfaces with micron and nanopatterns of SAMs attractive. There are several techniques for producing micro and nanopatterns of SAMs, including standard lithography, dip pen nanolithography, microcontact printing, and nanocontact printing.

Water crystals

A liquid crystal is the fourth state of matter; it has traits of both a solid crystal and a typical liquid. It flows like a liquid and exhibits long-range molecular organization like a crystal. Liquid crystals are often categorized as "soft matter" and are studied in the field of physical chemistry known as condensed matter, along with polymers and colloids. A fascinating and distinctive characteristic of liquid-crystalline systems is that they drastically alter their molecular and supermolecular organization in response to very small external disturbances. For example, relatively weak electrical fields can cause the molecules in liquid crystal displays to change orientation. A modest concentration of chiral molecules may cause significant macroscopic chirality effects, such as the formation of ferroelectricity and helical superstructures, in an achiral liquid-crystalline host phase.

Self-assembly of liquid crystals

Between their solid and liquid phases exist somewhat organized minerals known as liquid crystals. As a result, liquid crystals have intriguing electrical and optical characteristics in addition to the fluidity of typical liquids. Liquid crystal molecules often take the form of rods, plates, or other shapes that favor group alignment along a certain direction. Since they become solid if it is too cold or liquid if it is too hot, liquid crystals are temperature-sensitive. For instance, this phenomena may be seen on laptop displays in very hot or extremely cold temperatures[9].

Liquid crystal phases and their characteristics

Molecules self-assemble into organized structures, or phases, to create liquid crystals. Even a very little external perturbation, such a shift in temperature or magnetic field, might cause the liquid crystal to adopt a new phase. The varied optical characteristics of distinct phases may be used to differentiate them. Thermotropic liquid crystals are made of organic molecules that typically have coupled double bonds and undergo a phase transition as a function of temperature. Lyotropic liquid crystals are made of organic molecules that are typically amphiphilic (attracted to water) and undergo a phase transition in response to both temperature and the concentration of the liquid crystal molecules in a solvent (typically water). Lyotropic liquid-crystalline phases are prevalent in living systems, including tobacco mosaic virus, biological membranes, cell membranes, several proteins, and the protein solution produced when a spider produces silk. Another well-known substance that is a lyotropic liquid crystal is soap. The colors of light that soap bubbles reflect depend on their thickness.

Applications for liquid crystal

Mechanical, magnetic, or electric forces may be used to change the order of liquid crystals. It's intriguing that just very little differences in these pressures may result in this change of order. Liquid crystals' characteristics are helpful in a variety of applications. Some liquid crystals' color is dependent on the orientation of their molecules, therefore any factor that disrupts this orientation (such as a variation in temperature, magnetic or electric field, or the presence of specific chemicals) may be identified by a change in color. In displays for smartphones, cameras, laptop computers, and other gadgets, liquid crystals are often employed. In these displays, an electric field modifies the liquid crystal's molecular orientation and alters the polarization of light that passes through it. They are also employed in thermometers because of their sensitivity to temperature and the ability to change color. Liquid crystals can detect specific chemicals, electric fields, and temperature changes in tiny sensors.

Liquid crystals could be used in some fascinating applications in the future. Recently, it has been shown that adding certain molecules to liquid crystals may naturally produce novel electrical and optical characteristics. These molecules are often small molecules, on the scale of nanometers. In order to provide novel photonic functionalities and for use in waveguides and optical storage, for instance, liquid crystal materials have been altered (ICT application area). Photoconductive liquid crystals, which seek to utilise novel materials in photovoltaic cells and light-emitting diodes (Energy application area), are a different type of liquid crystals that are currently being developed. The alteration of liquid crystals to make them usable in stimuli-responsive materials and as templates for nanoporous polymers (a possible application area for nanomedicine) is another field of investigation.

CONCLUSION

In conclusion, the domains of self-assembled and biomimetic nanomaterials constitute fascinating new vistas in academic study and modern technology. Researchers have created novel materials and systems with a variety of uses by drawing inspiration from the design principles found in nature. In addition to having extraordinary qualities and capabilities, these materials have the potential to help solve urgent problems in a variety of industries, including energy, medical, and environmental protection.

REFERENCES:

[1] Z. Li, J. Wang, Y. Li, X. Liu, and Q. Yuan, "Self-assembled DNA nanomaterials with highly programmed structures and functions," *Materials Chemistry Frontiers*. 2018.

[2] M. C. García, C. Aloisio, R. Onnainty, and G. Ullio-Gamboa, "Self-assembled nanomaterials," in *Nanobiomaterials: Nanostructured Materials for Biomedical Applications*, 2018.

[3] K. Zhang *et al.*, "Self-Assembled Fluorescent Organic Nanomaterials for Biomedical Imaging," *Advanced Healthcare Materials*. 2018.

[4] L. Sun, C. Zheng, and T. J. Webster, "Self-assembled peptide nanomaterials for biomedical applications: Promises and pitfalls," *International Journal of Nanomedicine*. 2017.

[5] C. Lan and S. Zhao, "Self-assembled nanomaterials for synergistic antitumour therapy," *J. Mater. Chem. B*, 2018.

[6] S. R. Ede, S. Anantharaj, K. Sakthikumar, K. Karthick, and S. Kundu, "Investigation of various synthetic protocols for self-assembled nanomaterials and their role in catalysis: progress and perspectives," *Materials Today Chemistry*. 2018.

[7] Y. Yang, S. Wang, Y. Wang, X. Wang, Q. Wang, and M. Chen, "Advances in self-assembled chitosan nanomaterials for drug delivery," *Biotechnology Advances*. 2014.

[8] A. M. Carmona-Ribeiro, "Self-assembled antimicrobial nanomaterials," *International Journal of Environmental Research and Public Health*. 2018.

[9] L. Wang, P. P. Yang, X. X. Zhao, and H. Wang, "Self-assembled nanomaterials for photoacoustic imaging," *Nanoscale*. 2016.

CHAPTER 5

POLYMERS, NANOSTRUCTURED METALS AND ALLOYS

Dr. Vinod Kumar Singh, Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vinod.singh@muit.in

ABSTRACT:

Materials at the cutting edge of contemporary materials research and engineering include polymers, nanostructured metals, and alloys. Each of these materials has distinctive and varied features that allow a broad variety of applications across numerous sectors. The three material types are briefly described in this abstract along with their importance in current scientific and technological breakthroughs.Large molecules called polymers, which are made up of repeating subunits, have drawn a lot of interest due to their adaptability and customizable qualities. Their uses range from common consumer goods to cutting-edge medical equipment and aircraft components. The development of new polymer formulas and processing methods to improve their mechanical, electrical, and thermal characteristics has created new opportunities for the development of strong, lightweight, and environmentally friendly materials.

KEYWORDS:

Ferrofluids, Metallic Nanocrystals,Plasmonic architecture, Spherical Alloys.

INTRODUCTION

This section discusses nanocrystalline materials formed of a single metal or alloys made of two or more metals, as well as metal surfaces with nanostructures.Metal nanoparticles are a good illustration of how changes in a material's characteristics may occur at the nanoscale. For instance, the metal gold, which is used to make jewelry, has a distinctively golden color. Since gold is the most noble of all metals, it is exceedingly stable (it does not react with oxygen or sulfur, for example). Gold, however, changes color when it is reduced to a nanoparticle, becoming red if it is spherical and even going colorless if it is formed like a ring. Gold nanoparticles may also be employed as novel catalysts since they are very reactive[1], [2].

Plasmonic architecture

Gold, silver, platinum, and palladium are examples of noble metal nanoparticles that exhibit localized surface plasmon resonances (LSPR). The form, size, composition, interparticle spacing, and dielectric environment of the particles all affect the LSPR's energy. In order to enable the particular attachment of organic molecules like antibodies, the surface of the nanoparticles may be functionalized with a variety of chemical and biological compounds. This property makes the nanoparticles effective in sensors. For optical detection and sensing in analytical chemistry and molecular biology, they are thus particularly interesting. It is possible to employ the refractive index as a sensing parameter, which causes changes in the local dielectric environment that are then used to detect molecule binding in the particle nano-environment. This phenomenon may be employed for exceedingly miniature sensors since the aggregation between the nanoparticles changes as a consequence of analyte attachment[3], [4].

Researchers have looked at localized surface plasmons in a variety of nanoparticle forms, including disks, triangles, spheres, and stars. Researchers have also looked at more intricate structures including nanoshells, nanorings, and holes in thin metal sheets. Numerous optical applications based on nanostructured metallic surfaces are feasible. Plasmonic structures have the critical property of allowing label-free detection, which is crucial in optical sensing. Future uses of plasmonic components in solar cells, waveguides, optical connectivity, camera LEDs, OLEDs, and other devices are currently being studied.

DISCUSSION

Reinforcements

For uses in lightweight construction in the aerospace industry and, increasingly, the automobile industry, metal nanoparticles are utilized as reinforcement in alloys. The process is used, for instance, to harden steel. For instance, steel that contains titanium nanoparticles as an alloy composition has better robustness, ductility, corrosion, and temperature resistance qualities. Steel hardens by precipitating iron carbide particles as well. The nanoparticles make the crystalline material harder by preventing dislocations from moving. Since contemporary construction demands high strength yet safety and stress distribution need high ductility, the trade-off between steel strength and ductility is a significant problem. Hard nanoparticles in the steel matrix may provide a material with a mix of these characteristics, successfully balancing extraordinary ductility and high strength[5], [6].

Applications In the Environment

There are significant environmental uses for some types of metal nanoparticles.

a. Groundwater and soil contamination cleanup using zero-valent iron nanoparticles is being studied. When iron is exposed to air, it readily oxidizes to rust, but when it oxidizes in the presence of pollutants like trichloroethylene (TCE), carbon tetrachloride, dioxins, or PCBs, these organic molecules are broken down into simple, far less harmful carbon compounds. Iron nanoparticles are more efficient at cleaning up industrial waste than traditional "iron powder," which is currently in use. Comparable iron granules are 10–1000 times less reactive than iron nanoparticles.
b. Strong antibacterial properties are possessed by silver nanoparticles. They are used into several products to stop or lessen bacterial adhesion to surfaces.

Metallic Nanocrystals

Classical metals and alloys with ultra-fine crystalline structures less than 100 nm are known as nanocrystalline metals. They have exceptional mechanical and physical characteristics that make them intriguing for a variety of applications. Aluminum, magnesium, and Al-Mg alloys, which have excellent strength and are lightweight, are examples of nanocrystalline metal materials. Titanium and Ti-Al alloys are two further examples. The magnetic characteristics of certain crystalline metals are extraordinary. One example is the Finemetnanocrystalline soft magnetic alloys, which are melt-spun Fe-Si-B alloys with traces of copper and niobium. With applications in magnetic recording, gigantic magnetoresistance, magnetic refrigeration, and magnetic sensing, the use of nanomaterials in the area of magnetic materials is significant and promising. These innovative materials are made of stacked magnetic thin films (magnetic multilayer nanocomposites) or magnetic nanoparticles dispersed in a magnetic or non-magnetic matrix (particle-dispersed nanocomposites).

Ferrofluids

Colloidal mixes known as ferrofluids include magnetite or other ferromagnetic or ferrimagnetic nanoparticles contained in a carrier fluid, often an organic solvent or water. A surfactant is applied to the surface of the ferromagnetic nanoparticles to stop them from adhering together owing to van der Waals and magnetic forces. Ferrofluids do not exhibit ferromagnetism, despite what the name may imply since they do not maintain their magnetization in the absence of an externally applied field. Instead, they exhibit bulk-like paramagnetism, and because of their high magnetic susceptibility, they are sometimes referred to as "superparamagnetic" materials. The normal-field instability is a phenomenon that occurs when a paramagnetic fluid is exposed to a sufficiently high vertical magnetic field; the surface spontaneously develops a regular pattern of corrugations. Due to their low friction characteristics, ferrofluids are used in a variety of fields, including mechanical engineering, ICT, and biomedicine. Ferrofluids are also used as liquid seals (ferrofluidic seals) around spinning drive shafts in hard disks[7], [8].

Spherical Alloys

The majority of metals are very tough and require significant effort to deform, but once they are molded into shape, they will remain that way until another force causes them to shift. 'Shape-memory alloys' (SMAs), often known as memory metals, are distinct. If the metal is bent or twisted, it rapidly recovers to its original configuration because they may be "programmed" to remember a certain shape. This is due to memory metal's ability to switch between two different nanoscale crystal forms. They are both standard lattices. When the metal is heated up, the so-called parent phase, also known as the austenite phase, develops. The metal will "remember" its shape when formed at high temperatures. The second (martensite) phase of the metal's crystal structure develops when the metal cools. The metal returns to its normal form after being gently heated.

Polymers

A polymer is a big molecule comprised of a chain of sequentially connected monomers, which are tiny fundamental building blocks. A macromolecule called a copolymer is made up of two or more different kinds of monomers. Conductive polymer (also known as organic metal) is a term used to describe a polymer that is a good conductor of electricity. The nanostructuring of polymers and its potential impact on their characteristics are discussed in this section. The emphasis is on copolymers since they are crucial to nanotechnology.

Conductory Plastics

Conductive polymers, which include oxyacetylene, polyaniline, polypyrrole, and polythiophene, among many others, are those that are effective in conducting electricity. These polymers are -conjugated because of their alternating double-single chemical bonds. The excellent electrical conduction capabilities of the substance are due to the -conjugation of the carbon bonds along the orientated polymer chains, which creates a conduit for the movement of conduction electrons. Conductive polymers are formed of a series of metallic nanoparticles with a diameter of roughly 10 nm, according to a thorough SEM investigation. The high conductivity of polymers such as polyacetylene and polyaniline is connected to the nanostructure of the polymer. When the right voltage is applied or when certain chemicals are reacted with (electrochromic and chemochromic), polyaniline and its analogs change color. They are thus a potential material for light-emitting diodes (LEDs). Other uses include the surface finish of printed-circuit boards, corrosion protection of metal surfaces, semitransparent antistatic coatings for electronic devices, polymeric batteries and electromagnetic shielding[9], [10].

Copolymers of blocks

A block copolymer consists of these fundamental components or monomer kinds connected together in lengthy individual sequences known as blocks. A copolymer is a macromolecule that contains two or more types of monomers. The diblock polymer (A)m(B)n serves as an example and is composed of a linear sequence of m monomers of type A coupled to a linear sequence of n monomers of type B. The two blocks are connected by a transition section:

[transition member]-[polyB]n-[end group]-[polyA]m-[end group]

A hydrophilic (water-attracting) block and a hydrophobic (water-repellent) block are often combined to form block copolymers. In general, while in water, macromolecules with hydrophilic and hydrophobic sections, like lipids, self-assemble in ordered structures: the hydrophobic region packs together to avoid the water molecules, leaving the hydrophilic molecules to the perimeter of the structure. Similar to this, block copolymers comprised of hydrophilic and hydrophobic building blocks may self-assemble into ordered structures at the nanoscale level when combined with a selective solvent, like water.

The concentration and volume ratio between the insoluble and soluble blocks determine the geometry and level of order of these formations. These factors determine whether the block copolymer forms membranes, cylindrical micelles, or spherical micelles (nanospheres). Both spherical and cylindrical micelles have a soluble corona around a non-soluble (hydrophobic) core. Block copolymer membranes are composed of two monolayers that are oriented to resemble a sandwich: soluble block, insoluble block, and soluble block. As the concentration is raised, molecules that at low concentrations form spherical aggregates will combine into cylindrical and finally membrane-like structures.

When hydrophilic corona projection lengths are short in comparison to the diameter of the sphere, a spherical micelle is referred to as a "hairy nanosphere," however when the sphere is tiny and the projections are long, it is referred to as a "star polymer."

'Smart' polymers that are responsive

Block copolymers may create nanostructures with high sensitivity to outside influences. For instance, shear stimulation or mild electrical fields may cause certain macroscopic rearrangements. This is a flexible feature that may be used to create materials that react and alter as needed. These copolymers' inherent macromolecular structure causes extremely slow, kinetically regulated phase transitions. Because of this, metastable or intermediate phases have longer lifetimes, which is advantageous in applications that seek to take use of these materials' phase transition features.

Applications In Biomedicine

Block copolymers are especially advantageous for biomedical applications, such as medicines delivery, tissue engineering, and medical imaging, due to their capacity to form nanoparticles and nanostructures in aqueous solutions. Materials that can encapsulate and release pharmaceuticals are required for therapeutic delivery. Block copolymer hydrogels are especially favorable for the potential to give various stimuli-activated features, such as temperature sensitivity. Hydrogels are highly helpful for the regulated release of pharmaceuticals. Block copolymers may create vesicles that can enclose and transport both hydrophobic and hydrophilic medicinal substances because they can create nanostructures with both hydrophilic and hydrophobic regions. Because block copolymer-created micelles have a hydrophilic corona that makes them more resistant to the interaction of proteins, particularly plasma proteins, they have prolonged circulation durations in living organisms. Additionally, insoluble domains may be designed to take advantage of a particular hydrophobic polymer's susceptibility to environmental factors including pH, oxidizing agents, temperature, and hydrolytic breakdown. For example, extremely lengthy micelles that replicate the natural extracellular have recently been made by using the self-assembly capabilities of a peptide copolymer. Block copolymers are also of interest for the production of scaffolds in tissue engineering.

Nanoreactors

One of the primary strategies employed by cells in producing compartmentalized compartments at the nanometer level and carrying out the biochemical activities required for their function is the creation of biomolecules. As nanoreactors, block copolymer micelles and vesicles are currently used to reconstruct this motif. Enzymatic reactions have been carried out using this method in nanoscale compartments. It has been shown that this method may be used to non-aqueous solvents as well. This paves the path for the use of block copolymer technology in more complex synthesis methods. For instance, a recent study reveals block polymer nanostructures in ionic liquid and the capacity of micelles to shuttle from an aqueous solvent to an ionic liquid as a function of temperature.

Artificially Made Motions

Using a pH-sensitive block copolymer with micelles that expand in response to pH changes, for example, may imitate the capacity of biomolecules to transform chemical energy into mechanical energy. In order to develop artificial muscles or moving nanostructures, these materials are thus being researched.

Additional applications

Block copolymers have uses outside of the biomedical industry. They may be combined with other substances to create block copolymer nanocomposites. To increase the strength of metal, for instance, star polymers are used in industry. Block copolymers may also create nanoporous membranes for use in fuel cell technologies and filtration devices.

Synthetic Nanofibers

A significant class of nanomaterials known as nanostructured fibrous materials, or nanofibres, are now widely accessible as a result of recent advancements in electrospinning and related production techniques. They have the normal structure, unlike traditional woven materials.

Nanofibres are special because they have a very high surface-to-volume ratio and are very porous, with interconnecting void volumes ranging from 50% to more than 90%. By annealing the fabric to link the crossing sites of those fibers, it is feasible to strengthen the mechanical stability of nanofibrous structures. Nanofibrous scaffolds are advantageous for several biological and commercial applications due to their characteristics.

Researchers have also been successful in creating composite coaxial fibers, which are coaxial nanofibres made of two distinct polymers. Aligned nanofibers are another goal of research. These materials might be useful for electrical and medical devices, especially if they are comprised of conducting polymers.

CONCLUSION

As a result, the study of polymers, nanostructured metals, and alloys represents a variety of active topics in material science and engineering, each with an own set of features and uses. Polymers are essential in a variety of sectors, from packaging and textiles to biomedical equipment, because to their flexibility, lightweight properties, and simplicity of processing.On the other hand, metals and alloys with nanostructures exhibit superior mechanical qualities, high surface area-to-volume ratios, and increased performance in a range of structural and functional applications. These materials have found uses in the fields of electronics, renewable energy, and aerospace, helping to provide more effective and long-lasting solutions.The fusion of polymers and nanostructured metals offers intriguing possibilities for developing hybrid materials with unheard-of features and applications as research and development in these domains continues to improve. Even more cutting-edge materials with the potential to solve some of the most important issues facing our contemporary society, from environmental sustainability to cutting-edge technology, are anticipated in the future. These materials will help shape the field of materials science and engineering for many years to come.

REFERENCES:

[1] B. Ankudze and T. T. Pakkanen, “Gold nanoparticle decorated Au-Ag alloy tubes: A bifunctional substrate for label-free and in situ surface-enhanced Raman scattering based reaction monitoring,” *Appl. Surf. Sci.*, 2018.

[2] E. V. Skorb, D. G. Shchukin, H. Möhwald, and D. V. Andreeva, “Ultrasound-driven design of metal surface nanofoams,” *Nanoscale*, 2010.

[3] H. Palza, M. Nuñez, R. Bastías, and K. Delgado, “In situ antimicrobial behavior of materials with copper-based additives in a hospital environment,” *Int. J. Antimicrob. Agents*, 2018.

[4] P. X. Gao *et al.*, “Hierarchical assembly of multifunctional oxide-based composite nanostructures for energy and environmental applications,” *International Journal of Molecular Sciences*. 2012.

[5] G. A. Elia and J. Hassoun, “A gel polymer membrane for lithium-ion oxygen battery,” *Solid State Ionics*, 2016.

[6] Z. L. Wang, D. Xu, J. J. Xu, and X. B. Zhang, “Oxygen electrocatalysts in metal-air batteries: From aqueous to nonaqueous electrolytes,” *Chemical Society Reviews*. 2014.

[7] F. C. Walsh and C. Ponce de León, “Versatile electrochemical coatings and surface layers from aqueous methanesulfonic acid,” *Surface and Coatings Technology*. 2014.

[8] M. Kato *et al.*, “Enhancement of Electrocatalytic Oxygen Reduction Activity and Durability of Pt-Ni Rhombic Dodecahedral Nanoframes by Anchoring to Nitrogen-Doped Carbon Support,” *ACS Omega*, 2018.

[9] V. Čolić and A. S. Bandarenka, “Pt Alloy Electrocatalysts for the Oxygen Reduction Reaction: From Model Surfaces to Nanostructured Systems,” *ACS Catalysis*. 2016.

[10] P. Mani, R. Srivastava, and P. Strasser, “Dealloyed Pt-Cu core-shell nanoparticle electrocatalysts for use in PEM fuel cell cathodes,” *J. Phys. Chem. C*, 2008.

CHAPTER 6

SYNTHESIS OF NANOMATERIALS AND COMPUTATIONAL APPROACHES TO NANOSCALE PHENOMENA

Dr.Vikas Kumar Shukla, Assistant Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vikash.shukla@muit.in

ABSTRACT:

Nanomaterials have drawn a lot of interest from the scientific and business worlds because of their distinctive features and potential uses. In order to understand nanoscale processes, computational techniques play a complementary role in the production of nanomaterials.A broad area, the synthesis of nanomaterials includes several methods for designing materials at the nanoscale. These techniques have been used by researchers to make two-dimensional materials, nanoparticles, nanowires, and nanotubes with specialized architectures and characteristics. Numerous industries, including electronics, medicine, catalysis, and energy conversion, use these nanoparticles. It is essential for the advancement of these applications to comprehend the complexities of their synthesis.Parallel to this, computer methods have become essential resources for understanding and forecasting nanoscale events. Researchers may examine the behavior of nanomaterials at the atomic and molecular levels using molecular dynamics simulations, density functional theory calculations, and machine learning methods. These computational techniques help in the logical design of nanomaterials for particular applications by offering insights into features including electrical structure, mechanical behavior, and reactivity.

KEYWORDS:

Nanomaterial Properties, Self-Assembly, Nanocomposites, Nanostructure Characterization, Templated Synthesis.

INTRODUCTION

Nanomaterials are produced by a variety of procedures. There are methods that start with bulk substances and methods that start with atoms. Physical methods use bulk materials, while chemical processes start with atoms. Atomic precision in size purity can be achieved in the latter whereas rigorous control of size is difficult in the former. Form control strategies that use chemicals are selected. In certain cases, there are just a few strategies available, sometimes only one. The method adopted is influenced by the synthetic material's adaptability in terms of redispersibility, thermal and chemical stability, monodispersity, etc.

This Chapter deals with the synthesis of a variety of nanomaterials. The materials are composed of nanoparticles, including spherical and other shapes, nanotubes, and nanomolecules. They must be created using a number of methods, and these procedures must be enhanced in order to allow the materials created to have a variety of chemical compositions and quickly modify their physical properties. The synthetic methods should, at least in some instances, be flexible enough to be modified to enable for commercial exploitation if suitable applications are found. In this session, we'll focus on a handful of the most often used methods for the most common kinds of materials. We'll discuss the less typical approaches, including materials made in porous media like zeolites, embedded particles in glasses, etc. I'll make this talk brief, however. Synthesis processes may be broadly categorized using physical and chemical methodologies. Physically, the process comprises creating the conditions required for the production of nanomaterials from the bulk material or component materials. Since these synthesis methods start with bulk materials, they are known as top-down processes[1], [2].

DISCUSSION

The environment in which evaporation takes place may be controlled in each of them. For instance, in an atmosphere with plenty of oxygen, metals may evaporate and produce oxides. Several materials might be produced fast and effectively using the techniques. The major drawback of the techniques is that they produce a broad variety of particle sizes. Chemical processes use a range of tactics, which we shall go into more detail about in the next sections. Each of these processes starts with atoms and ends with the creation of nanomaterials. Atoms, which are often created from ions in liquids, are combined to form nanomaterials. Since the assembly process begins with the atoms, these methods are sometimes referred to as "bottom-up approaches".

Nanoparticles are composed of atoms, just as any other system. In general, a two-phase colloidal system may be categorized as a dispersed phase in a dispersion medium. The dispersed phase and the dispersion medium may both be one of the three phases, namely, gas, liquid, or solid, with the exception that the first category, i.e., gas in gas, is unknown. A solid nanoparticle dispersed in an amorphous solid may thus be considered a colloidal system, and hence, a nanofluid. The way nanoparticles are spread in a fluid medium is called "nanofluid" Supercritical fluids and gases will not be included in the description of the dispersion phase as we only study liquids at normal pressure and temperature[3], [4].

It should be noted that an important and cutting-edge area of research is the creation of nanoparticles in diverse media, namely solid matrices and supercritical fluids. From a historical perspective, it's critical to remember that some of the first applications of nanoparticles made use of glass-encased particles. A relatively recent area of study in the science of nanoparticles is supercritical fluids. The most common word for these substances is colloids. The resultant nanoparticles might be either solid or liquid in composition. These substances are often utilized in solutions or dispersions known as nanofluids. They may also be used as powders known as nanomaterials. Emulsions, pastes, particle films, and many other forms are also acceptable.

Nanoparticle systems are metastable. They will eventually transform into stable substances having global energy minima in the free energy spectrum. When the free energy of the system is plotted for a constant amount of the material, nanoparticles exist at a higher energy than bulk materials, although a specific nanostructure may have a local minimum in comparison to other structures. In the limit of very small particles, magic numbers that include these local minima exhibit unusual structural and electrical stabilities. These particles are referred to as clusters, and we shall talk about them in a subsequent section. In contrast to the bulk, the total energy is much larger in isolated atoms and molecules. In the domain of nanoparticles, the energy is positioned halfway between that of bulk materials and that of molecules and atoms. One form may become another by using physical or chemical techniques[5], [6].

Since nanoparticles have unique structural features, they might be thought of as "nanocluster molecules" in the sub-1 nm size range. Each of these clusters could have isomeric structures, and one of them might be more stable than the other. Across many structures of the same size, there may be significant differences in properties. In the larger size regime, many structural shapes are available, albeit it might be difficult to distinguish between them. When it comes to considerable changes in geometry, such in the case of nanoparticles and nanorods, differences may be made based on their electrical properties. certain of those structures may be produced via synthetic manufacturing processes in the case of certain metals and ceramics. Since nanoparticles are metastable, they might at any time revert to the bulk.

The bulk metal is more stable, but this is comparable to thinking about the stability of graphite in comparison to diamond. Faraday's colloids were invented in 1857, and their stability implies that the time factor in many situations has little practical consequence. Despite being metastable, diamond does not convert to graphite under normal pressure and temperature conditions, even if it is kept for millennia. Diamond to graphite conversion has a very slow kinetics, rendering it irrelevant in most situations. The term "kinetic stability" describes the similar condition of nanoparticles in appropriate media[7], [8].

Dispersability

A nanoparticle consists of two components: a "core" that is often ceramic, metallic, or polymeric and a thin "shell" that may be ionic, molecular, polymeric, ceramic, metallic, or metallic. The majority of the time, a ceramic or metallic core is encased in a molecular shell. The core of the nanoparticle, which also acts as a protective layer, determines the majority of the properties of the particle. The nature of the shell is often of uttermost significance for a range of applications, including the luminescence of the particles.

Both the shell and the core could have underlying structures and include several items. How readily a nanoparticle dissolves depends on the chemical make-up of its shell. Since the resultant "solution" or fluid is really a dispersion that may be physically separated by centrifugation, the term "solubility" is misleading. A solution is defined as a homogeneous mixture of elements in any phase that cannot be separated as seawater.

The molecular shell has a special chemical affinity to the nanoparticle core because of certain atoms or groups. An alkoxide may form a connection with the metal on the surface of an oxide nanoparticle, for instance. In this case, a Sulphur atom of the thiolate may form a connection with a gold-like metal nanoparticle. Such a link that spans the whole surface of the nanoparticle is referred to as a protective monolayer, also known as a capping layer. A shielded or capped nanoparticle is the name given to the final nanoparticle. The sulfur at the end serves as a surface-active head group that attaches to the surface of nanoparticles because of its distinct chemical affinity. The chemical connection that has been made makes the system of nanoparticles thermally stable. The weaker a nanoparticle is, the quicker it is to desorb from the surface and the less stable it is[9], [10].

Because the Au-S bond has a bond strength of 50 kcal mol-1 and the thiolate only desorbs from the metal surface above 270°C, the metal-active head group binding is a key element in determining the thermal stability of the nano system. When the nanoparticle is created and the monolayer is bonded, the molecule may change. For instance, when the thiol binds to gold to produce RS, the H is lost. This has been discussed, and there are a number of ways that such a loss may occur. The kind of monolayer and its structural features are determined by the core. Big nanoparticles, whose typical diameters vary from a few nm to several, are the main subject of this discussion. On the other hand, the area of materials with core dimensions below 1 nm is much smaller and has lately attracted a lot of attention. We shall discuss this group of parts, referred to as clusters, in a later Chapter of this book. Big nanoparticles have a core made up of thousands of atoms.

A 3-nm gold particle, for example, has around 1100 atoms when seen as a spherical. The exterior surfaces of these particles really have "faceted" shapes, or they terminate at certain crystallographic planes. The available space, packing density, and van der Waals diameter of the protecting molecules all influence where the head groups of these molecules are located on these planes. On each of the crystallographic planes, alkyl chains are clustered closely together, and their inter-chain van der Waals interactions grow important when additional monolayers are added. This makes the system more stable. Along with the interaction of the nanoparticle head group, the van der Waals connection also has to be broken in order to destabilize the nanoparticle.

The inter-chain connection is often weaker than the head group-nanoparticle contact. As the monolayer assembly organizes, as is the case with long-molecule monolayers, the core of the monolayer assembly becomes inaccessible to ions and molecules in the medium. The core's chemical stability is enhanced as a consequence. The van der Waals interaction becomes stronger as the chain length grows. In the limiting situation of a polymer or ceramic shell, chemical bonding in the shell are comparable to or stronger than those in the nanoparticle core. The tail group interacts with the solvent or dispersion medium. When two nanoparticles come into touch favorably, they disperse across the medium.

Nanoparticles must thus have a hydrophilic covering in order to dissolve in water. Contrarily, a hydrophobic coating makes the nanoparticle soluble in organic liquids like toluene. By changing the polarity of the tail group, it is possible to disperse the system in liquids with various dielectric constants. The outermost groups of a hydrophilic monolayer, such as -COOH or -NH2, may be ionized to form -COO- or NH3 +, which will leave the metal surface with a net positive or negative charge per monolayer chain. Given that there are several of these bound ions present, the nanoparticle may have multiple charges. The sum of the particle's charges, which might be both positive and negative, will be reflected in the system's charge.

The net charge of a particle is zero at a certain pH, as shown by the fact that all monolayers on an amine-terminated surface take the form of -NH2 and not -NH3 +. Since each molecule may be a "zwitter ion" in the case of proteins since they include both -COO- and NH3 + on the same molecule, this is often the case with proteins. The "isoelectric point" is this pH. Other than the isoelectric point, the molecule is not ionized. A molecule is not necessary for the component that forms the shell on the nano surface, as was previously demonstrated. The shell is sometimes a natural part of the core. For instance, silica nanoparticles are easily floatable in water because they often contain a surface coating of hydroxyl groups. In contrast, a hydrocarbon monolayer will result in particle scattering in organic liquids.

Gold nanoparticles may be made hydrophilic or hydrophobic using methods that are similar. Copper nanoparticles are reactive nanoparticles that may easily have their outer shells oxidized. They also always have an oxide layer on their surface. When the particles are exposed to air, this is especially true. As was said before, the personality of the tail group may change depending on the medium. This is crucial in cases when the group is -COOH, -NH2, -OH, etc. since these scenarios may cause the group's nature to be dramatically altered by the medium's pH. A monolayer with a -COOH ending, for example, produces -COOH in acidic media and -COO- in alkaline media. The pH values of a nanoparticle-dispersion are influenced by the pKaof the acid in question. The modification affects the surface charge of the nanoparticles considerably. The zeta potential of the particle is changed, which may have an effect on the particle's properties. For applications like drug delivery, changes to the surface charge are essential. It is plausible that when a condition, like pH, changes, the core is affected.

Typically, when we talk about materials, we are talking about massive systems that include billions of atoms or molecules. Thanks to the advent of controlled chemical synthesis techniques, the building blocks of materials that were previously solely formed of atoms or molecules may now be composed of a huge number of atoms, groups, or molecules joined together by strong covalent bonds. The dispersion of colloidal particles is a noteworthy example of such artificial systems. The colloidal particles are typically micron-sized. The present period has seen the development of systems that only need a few atoms and have sizes in the region of a few nanometers. Nanosystems (a few nanometers), granular systems (a few millimeters), and colloidal dispersions (a few micrometers) are the sizes that have been lowered. The material's response to chemical and physical changes is greatly influenced by the size of the component pieces. Let's take a look at a colloidal dispersion, whose properties have been the subject of recent intensive investigation.

Due of their enormous dimensions, they may scatter ordinary light and may be viewed using laser light. Actually, the zigzag motion of colloidal particles is called "Brownian motion" after the British botanist Robert Brown, who saw it when he used a light microscope to observe a suspension of pollens. The features of a colloidal dispersion are similar to those of ordinary atomic systems, but being at extremely different sizes. However, this has the effect of elevating them in both educational and technical terms, which is something rather substantial. Colloidal systems contain far fewer particles per volume than atomic systems do due to their enormous size. About 1 kBT, where kB is the Boltzmann constant and T is the absolute temperature, corresponds to the average thermal energy per particle. As a consequence, the energy scale of a colloidal system is much lower than that of an atomic system. The decrease is by a factor of (d/a), where d stands for the colloidal size and a for the typical atomic length scale.

Therefore, exogenous agents that have been utilized often in lab settings as well as in industrial applications to mimic the characteristics of atomic systems may easily upset colloids. What should happen if the basic building blocks of an item are shrunk to the nanoscale size range? Without a doubt, such nanometer-sized units might contain a small number of atoms that are covalently bound to one another. Let's now go to the issue at hand. Atoms and molecules on an object's surface differ from those found farther within. The bulk atoms and molecules sustain the potential bonds because there are enough adjacent atoms and molecules to do so. However, those on the surface are unable to because of the geometrical discontinuity. Because of this, the effects of the surface atoms on the system's features are often different from those of the bulk atoms. The relative importance of the effects of the surface atoms and molecules is determined by a simple geometrical ratio.

In a central box with periodic boundary conditions (PBC) that are thought to replicate in all directions, bulk simulations are often run. There are precise replicas of the main box in the picture boxes. The particles move in the same direction within each box. It is clear that when a particle leaves the center box, it is identical to when a particle enters the center box from the image box adjacent to the opposite side. The edges of the core box thus have no effect on the particles contained inside. However, in the case of nanosystems, the boundary is important. Therefore, special attention is paid to maintaining the border barriers. Consequently, the specification of the wall-particle interactions is another need for such a system. In certain cases, the cluster is presumed to be positioned inside a matrix far from the boundaries rather than utilizing the normal PBCs. The PBCs are often used for modeling an aggregation of clusters.

It should be emphasized that the simulation techniques really include the system specification through the interaction potential. The forces in the MD code are produced by the interaction potential. Similar to this, the energy in the MC comes from the interaction potential. Usually, the interaction potentials have parameters. For instance, covalent bonding interactions are simulated using the Morse potential. The harmonic approximation, which just needs the spring constant to be specified, often also takes into account such interactions. The spring constant may be measured via experiments. Examples are the spring constants discovered via infrared research for different homo- and hetero-nuclear bonds. The non-bonding interactions are defined in terms of van der Waals interactions. Charges interact with one another in coulombic ways, which are often long-range. To control the long-range interactions in simulations, certain strategies must be applied. The parametrization is often carried out using "ab-initio" calculations that make advantage of quantum chemistry methods. The nuclear coordinates are maintained constant in these simulations due to their slower speeds than the electrons'.

The ground-state electronic energy is calculated using the established nuclear coordinates. The potential energy profile is created by applying the same calculations across a wide range of inter-nuclear distances. The interaction parameters are estimated using these profiles. Using the usual MC or MD technique, the coulomb forces are integrated with the traditional inter-nuclear forces, the electronic component of the force, and the force itself. The nuclear and associated electronic coordinates are updated as a consequence. It must be remembered that the bulk of the computation time is spent computing the force in MD and the energy twice in MC. The time scales up to N_2 since every possible pair is considered throughout the computation. This is a serious problem, particularly for clusters that have more than 500 component atoms.

When the interaction potential is short-ranged, the computation is often performed assuming that the potential has been cut off. The cut-off must be less than half of the shortest box dimension. It's common to maintain a list of neighbors as a Verletneighbour list. All the atoms that are close by and a little farther away than the cut-off distance from a certain atom is listed. Each atom in this list's interactions with the others is predetermined. The list is only sometimes updated, depending on how the particles move. This avoids the need to figure out how far apart different pairs should be for multiple intermediate phases. It is possible to tabulate the force and potential energy before the simulations begin. When performing the simulations, one just does a database search and applies the standard interpolations. This might save a ton of time if the contact is extensive, as in the coulomb instances.

CONCLUSION

In conclusion, the creation of nanomaterials and computational methods for studying nanoscale phenomena are two interrelated aspects of nanotechnology that have enormous promise for both technological advancement and scientific discovery. A new age in materials science has begun as a result of the capacity to create materials at the nanoscale, allowing for the creation of innovative materials with customized characteristics for a variety of applications.Researchers have developed novel synthesis methods to uncover the special qualities and capabilities of nanomaterials, which have found use in industries including electronics, health, energy, and environmental cleanup. These engineered materials have the power to transform whole sectors and tackle some of the biggest problems of our time.In addition, computational methods have been essential in comprehending and forecasting nanoscale events. Researchers may learn more about the behavior of nanomaterials, their interactions with other substances, and their possible uses by using computational tools and simulations. Synthesis and computation work together to provide a more systematic and effective way to explore the nanoworld.

REFERENCES:

[1] E. D. Goodman, J. A. Schwalbe, and M. Cargnello, “Mechanistic understanding and the rational design of sinter- resistant heterogeneous catalysts,” *ACS Catalysis*. 2017.

[2] S. Sederberg, C. J. Firby, S. R. Greig, and A. Y. Elezzabi, “Integrated nanoplasmonic waveguides for magnetic, nonlinear, and strong-field devices,” *Nanophotonics*. 2017.

[3] A. A. A. Ibrahim, N. N. N. M. Ibrahim, A. Centeno, and A. M. Hashim, “A short review of architecture and computational analysis in the design of graphene-based bioelectronic devices,” *Sensors and Materials*. 2018.

[4] W. L. Ong, S. Majumdar, J. A. Malen, and A. J. H. McGaughey, “Coupling of organic and inorganic vibrational states and their thermal transport in nanocrystal arrays,” *J. Phys. Chem. C*, 2014.

[5] S. Ebrahimi, D. J. Steigmann, and K. Komvopoulos, “Peridynamics Analysis Of The Nanoscale Friction And Wear Properties Of Amorphous Carbon Thin Films,” *J. Mech. Mater. Struct.*, 2015.

[6] Q. N. Pham, S. Zhang, K. Montazeri, and Y. Won, “Droplets on Slippery Lubricant-Infused Porous Surfaces: A Macroscale to Nanoscale Perspective,” *Langmuir*, 2018.

[7] S. Papanikolaou, Y. Cui, and N. Ghoniem, “Avalanches and plastic flow in crystal plasticity: An overview,” *Modelling and Simulation in Materials Science and Engineering*. 2018.

[8] M. J. Eslamibidgoli, J. Huang, T. Kadyk, A. Malek, and M. Eikerling, “How theory and simulation can drive fuel cell electrocatalysis,” *Nano Energy*, 2016.

[9] D. J. Cram and J. M. Cram, *Container Molecules and Their Guests*. 1997.

[10] K. T. Kholmurodov, *Computer design for new drugs and materials: Molecular dynamics of nanoscale phenomena*. 2017.

CHAPTER 7

EVALUATING APPLICATIONS OF NANOMATERIALS

Dr.Nishant Kumar, Assistant Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- nishant.kumar@muit.in

ABSTRACT:

A wide range of industries and applications have been transformed by the unique physical and chemical features of nanomaterials, which are created at the nanoscale. An overview of the many and changing fields of nanomaterial uses is given in this abstract. Nanomaterial assessment spans a broad range, from electronics and medical to environmental cleanup and energy. Nanomaterials allow the creation of smaller, quicker, and more effective electrical devices, while in medical they provide tailored medication delivery, cutting-edge imaging methods, and novel treatments. With uses ranging from water purification to pollution monitoring and cleanup, nanomaterials are also crucial to environmental solutions. Additionally, they provide a substantial contribution to the energy industry by advancing fuel cells, solar cells, and batteries. The potential for ground-breaking discoveries and game-changing breakthroughs is highlighted in this abstract, which also emphasizes the crucial relevance of assessing nanomaterial applications in tackling the issues of the contemporary world.

KEYWORDS:

Nanosensors, Nanotechnology, Photovoltaics, Solar cells, Water purification.

INTRODUCTION

Nanomaterials may be utilized for a broad range of products, from toothpaste to satellites, since they have special chemical, physical, and mechanical qualities. Nanotechnology is being used in almost every industry, from research to engineering, and is changing how we live. There are now a ton of "nanotechnology enhanced" items on the market, and there will be many more. Cosmetics, textiles, healthcare, tissue engineering, catalysis, functional coatings, medical diagnostics and therapies, sensors and communication engineering, and water and air pollution remediation are just a few industries where nanomaterials are being used. Below is a discussion of a few of these uses. Electronic devices Nano-electronic technology has many uses in computing and communication. The era of enormous computer systems processing each program on enormous punch cards that took up an entire room is over. Modern multipurpose laptops and palmtops are easier to use, quicker, more portable, and offer larger memory capabilities[1], [2].

Perhaps the most compelling advantages of nanotechnology are the ubiquitous usage of mobile phones, pocket-sized memory storage devices, MP3 players, iPods, and iPads. All of this has been made feasible by nanotechnology's ability to reduce the size of electrical equipment. The electronics industry's watchword is "miniaturization," which is motivating research on shrinking the size of transistors, resistors, capacitors, etc. According to Moore's Law, a 1965 empirical finding, the number of transistors on an integrated circuit doubles every 24 months given a minimal component cost. This legislation is still in effect in the expanding electronics sector even after 40 years. Due to the faster processing power of the microprocessors that house these tiny components, calculations may now be done at rates that are many times faster than they were a few years ago. However, there are a number of technical challenges to be solved, including the scarcity of ultrafine precursors needed to make these components and the inefficient heat dissipation of these microprocessors, among others. The industry can get over these obstacles with the aid of nanomaterials. There are various methods being investigated that might use nanostructures to create non-volatile, radiation-hard, high-density memories with nanosecond read/write times. Despite the fact that one terabit per square centimeter may seem absurdly big, The Lord of the Rings needed 27 terabytes (or 200 terabits) only for the first installment. Working on a new memory system based on a mechanical storage technique are researchers at IBM Zurich. This technique, known as "Millipede," employs a series of microcantilevers to shape a polymer medium with nanoindentations[3], [4].

DISCUSSION

Storage densities have been demonstrated using this means. Researchers in Nantero, the United States and Korea are creating memory ideas based on carbon nanotubes. The gigabyte range has been made feasible by the giant magnetoresistance (GMR) phenomenon, which has significantly increased the data storage density of hard drives. The so-called tunnelling magnetoresistance (TMR), which is based on the spin-dependent tunneling of electrons across neighboring ferromagnetic layers, is very similar to the general magnetic resistance (GMR). A non-volatile memory for computers, such as the magnetic random-access memory, may be made using both GMR and TMR effects. Freescale and IBM both provide GMR memory devices with 4 Mbits, but the US Naval Research Laboratory (NRL) is working on the next generation of GMR memory, which might have terabit density[5], [6].

Optical Electronics

Devices using optoelectronics convert light into electricity and vice versa. They are effective and have a wide bandwidth, and they are used in solar cells, CMOS (complementary metal oxide semiconductor) and CCD (charge-coupled device) photodetectors, laser diodes, LCDs (liquid crystal displays), and CCD and CMOS photodetectors. The production of TFT (thin film transistor)-LCD laptop PC screens, automobile illuminations, mobile phone backlighting, VCD/DVD players, telecommunications and data communications (broadband communications), biotechnology (Bio Photonics), and digital cameras has made extensive use of opto-electronic devices coupled with optical fibers.

Atomic Computers

At the moment, tiny quantum dots are being used to create lasers. According to some reports, the quantum dot's width affects the laser's wavelength. Compared to traditional laser diodes, quantum dot lasers are more affordable and provide better beam quality. Fast quantum algorithms may now be used to take use of the rules of quantum mechanics for revolutionary quantum computers thanks to the commercially viable synthesizing of quantum dots. Quantum computers are quicker and can do several calculations at once. These kind of computers would be beneficial for completing digital computation and for solving certain challenges.

Insulation

Aerogels are porous, foam-like, ultra-lightweight nanomaterials created using the sol-gel technique that can endure around 100 times their own weight. Currently, they are used for insulation in buildings like as residences and workplaces. 'Smart' windows that darken on sunny days and brighten on overcast days also employ them. Phosphors The usage of nanophosphors such lead telluride, zinc selenide, cadmium sulphide, and zinc sulphide could lower the cost of high-definition televisions (HDTVs), laptops, and personal computers for the typical family. Due to their better efficiency field emission features, carbon nanotubes have been employed to create displays with reduced energy usage[7], [8].

Chopping Blades

In order to enable the shrinking of microelectronic circuits, microdrills—drill bits with a diameter smaller than a human hair—need to have improved wear resistance. These microdrills now employ nanocrystalline carbides and nitrides because they are stronger and wear-resistant. Nanotechnology is used in the realm of medicine for tissue engineering, prosthetic materials, treatments, and diagnostics. Nanomaterials are valuable for biomedical applications because their dimensions resemble those of biological molecules. Nanomaterials may be employed in medical applications for specialized purposes by bonding various biomolecules to them. Both therapeutic (using nano-drug delivery systems) and diagnostic (using nano-biosensors) uses of nanotechnology are currently being developed.

a. You may utilize small DNA fragments bonded to gold nanoparticles to determine a sample's genetic makeup.
b. Silver nanoparticle-infused bandages are becoming more and more popular because they provide anti-microbial protection and promote quicker wound healing.
c. Numerous skin transplant applications employ nanostructured synthetic skin.
d. The usage of biocapsules as alternatives for diabetic insulin, focused medication delivery, biosensors, etc. is on the rise.
e. Nanomaterial-based respiration monitors have the potential to be more sensitive than traditional monitors.

A illness may always be treated and recovered from more quickly and effectively if it is discovered early on. For the early detection of numerous illnesses, sensors and treatments based on nanotechnology have been helpful. The ability of nanoparticles to detect viruses, precancerous cells, etc. has been shown. Drugs may be delivered efficiently and easily using targeted drug delivery systems, increasing patient compliance, extending product life, and lowering healthcare expenses. The possibility of nanobots or nano-robots is growing. They are medical devices that may be injected into the circulation to treat certain disorders, and an outside field regulates how they move. Thus, it is believed that nanotechnology has the potential to alter how humans live. For the targeted administration of drugs with limited oral bioavailability owing to poor water solubility, permeability, and longer sustained and controlled release, drug delivery systems based on nanoparticles are utilized.

Drugs may be coated on nanoparticles in order to dramatically reduce adverse effects and total medication intake. The expense and suffering of people are decreased by this extremely selective method. For instance, dendrimers and nanoporous materials may deliver tiny medicinal molecules to the required site. Nano-electromechanical systems (NEMS), which are based on tiny electromechanical systems, are being researched for the active release of pharmaceuticals. Research on the use of gold-coated shells for cancer treatment has progressed. How to address our ever-growing need for energy security is perhaps the biggest problem facing society and humanity.

Although the sun is the major source of energy on Earth, the essential processes for converting energy, such as charge transfer, chemical reactions, molecular structure modification, etc., take place at the nanoscale. The advancement of nanotechnology has the potential to completely alter how energy is produced. The use of nanomaterials to extract hydrogen from water, collect energy from the sun and biomass, store energy as hydrogen fuel cells, batteries, and capacitors are a few of the intriguing new applications for nanotechnology in this discipline. Advanced catalysts for energy conversion are another use for nanomaterials. The effective use of energy in sectors including transportation, electricity production and consumption, water management and purification, and environmental cleaning will also be impacted by nanomaterials. In order to use nanotechnology to fulfill future energy demands, many research are now being conducted[9], [10].

Catalysis

Catalysis is one of the most profitable fields for a nanotechnologist. Due to the exceptionally high surface-to-volume ratio of nanoparticles, chemical catalysis is greatly enhanced. The relationship between the surface area to volume ratio and particle size may be easily understood from geometrical considerations. A catalyst's surface is the site of several chemical reactions; as a result, the more surface area the catalyst has, the more active it is. Thus, a wide range of process advances to improve the efficiency of various chemical processes are made possible by nanoscale catalysts. Fuel cells, catalytic converters, and photocatalytic devices are all possible applications for nanoparticles in catalysis. Catalysts made of nanoparticles may be employed in

a. automotive catalytic converters for the elimination of harmful gases like nitrogen oxide and carbon monoxide
b. device for power production that reduces environmental damage caused by burning coal and gasoline

Filtration

Air filtration and wastewater treatment technologies both heavily use nanochemistry. The employment of membranes with correctly sized holes, which enable the liquid to flow through, is the basis of one type of filtering procedures. The ultra-tiny holes of nanoporous membranes employed in nanofiltration are less than 10 nm.

The primary applications of nanofiltration are the elimination of ions or the division of various fluids. Using ultrafiltration, particles between 10 nm and 100 nm in size may be removed. An essential use of ultrafiltration is in renal dialysis. By using magnetic separation methods, magnetic nanoparticles provide an efficient and dependable way to remove heavy metal pollutants from wastewater. Particles with a nanoscale boost the effectiveness of adsorbing pollutants.

Removal of pollutants

Water and soil cleanup may benefit from the usage of nanoscale materials. The development of remediation techniques that do not need excavation would be cost-effective at sites where refractory organic pollution has deeply permeated the soil. The ability of zero-valent iron particles to penetrate the necessary distances and oxidize certain organic pollutants has been shown. The destiny of those iron particles is being investigated to make sure they don't lead to any more issues.

Sensors

Nanocrystalline sensors are particularly sensitive to changes in their surrounding environment. Smoke detectors, ice detectors on airplane wings, and engine performance sensors for cars are a few uses for sensors composed of nanocrystalline materials.

Food

Anti-microbial substances may be directly applied to the surface of the coated nanocomposite film to enhance food packaging. A polymer matrix that contains nanoscale clay particles may have decreased oxygen and water penetration and greater cyclability. Food may be shielded from drying out and deterioration brought on by oxygen exposure. For millennia, silver has been utilized as an anti-microbial substance. In order to keep food fresher for longer, nanoscale silver has recently been added to antibacterial containers.

Commercial goods

Consumer goods are being affected by nanotechnology as a result of new features like scratch-resistant coatings and easy-to-clean surfaces. Nanotechnology is mostly used in the home to create self-cleaning or "easy-to-clean" ceramic or glass surfaces. The smoothness and heat resistance of typical home items like the flat iron and cooking pans have been enhanced by nano-ceramic particles.

Sports

Nanotechnology has promise for extending the useful life and improving the performance of sporting equipment. Tennis balls, rackets, and bowling balls have all benefited from the use of nanotechnology. Tennis balls now last longer. Compared to regular wax, nano-ski wax is more practical and simpler to use. Golf balls with nanotechnology enhancements may adjust their own flight paths, making them fly straighter than regular balls.

Textiles

Nanotechnology has several uses in textiles and materials, including anti-microbial, hydrophobic, and self-cleaning applications. The cloth repels water and resists stains when combined with a hydrophobic substance. For instance, drying such clothing will be considerably simpler during the rainy season, and wearing such clothing will be much more pleasant. Products like nylon, polypropylene, and other polymers have been infused with nanoparticles to provide long-lasting anti-microbial properties even under severe environmental conditions or after repeated heat cycling. Nano-socks containing nano-silver dispersions have both anti-microbial and odorless qualities. The healthcare, home furnishings, filtration, and garment industries, among others, have seen a surge in the need for microbial growth on a variety of textile-based substrates to be reduced or eliminated. The 'invisibility coating' produced by nanocameras and nanodisplays may be used to make military camouflage gear. The uses of nanomaterials mentioned above are but a handful. Every day, several new uses are found, and many more are yet undiscovered.

The best nanotechnologist is nature

Perhaps the biggest source of inspiration for nanoscientists and nanotechnologists is nature. Nature has evolved several nanoparticles and gadgets over millions of years via the process of natural selection. Nearly all areas of science and technology, but especially nanoscience and nanotechnology, may benefit from new paths and insights that can be discovered by simple observation of the natural events around us. In reality, the biological cell of living things contains numerous more functioning organelles that are nanometer-sized, including the cell membranes. All of the body's metabolic processes are carried out by proteins and enzymes, which is a great example of the power of nanostructures. We are all aware that the life-sustaining phenomena of photosynthesis, which allows plant species to transform solar energy into biochemical energy forms, is essential to the continuation of life on Earth.

The nanoscale molecular machinery that powers photosynthesis in plants is composed of pigment molecules like chlorophyll stacked within thylakoid disks contained inside micrometer-sized chloroplast cells. Have you ever been impressed by a spider's engineering prowess? The web is constructed of nanofibres, which are light and soluble in water yet stronger than steel in terms of specific strength. These webs are a wonder of nature since they can survive adverse weather conditions including rain, wind, and sunshine.

The spider has a enough amount of raw materials to weave its web across a significant distance for its size. It's fascinating to see how quickly the spider can coordinate the casting of its net in a given environment. Another example of a nanostructure created by nature is a gecko's ability to defy gravity and move over a ceiling. The nanospikes on a lotus leaf's surface, which make it easy for water droplets and dust particles to slide off, are what give it its ability to self-clean. Because of the nano-grooves in the micro hairs on their legs, water striders can walk on the water's surface without becoming wet.

We are all used to using soft chalk to write on blackboards. It is made of powdered calcium carbonate that has been loosely agglomerated. The same calcium carbonate agglomerates, however, may be made by nature into hard and durable nanocrystalline forms. A snail called an abalone has a hard shell that is basically formed of the same material as chalk. The nanocrystalline structure, however, prevents cracks from spreading and encourages their deflection at grain boundaries. The cumulative length scales that cracks must basically travel are longer, which costs more energy and increases the toughness of the shells.

One of nature's greatest engineering and scientific achievements is the development of complex and effective sensory systems in living creatures via millions of years of evolution. They serve as a knowledge base and a powerful source of inspiration for nanotechnologists working on the creation of intelligent sensors. Only quantum phenomena may restrict the sensitivity of biological sensory systems. It is amazing and exciting how our body uses nanomolecular proteins to monitor body temperature and manage it via carefully regulated metabolic activity. A variety of nanosensors, each with a distinct function, are being assembled by scientists to create an electronic tongue and electronic nose.

CONCLUSION

In conclusion, the analysis of nanomaterials' applications shows a world of limitless possibility and paradigm-shifting potential in a variety of fields. With their distinctive characteristics at the nanoscale, nanomaterials provide ground-breaking answers to some of the most urgent problems confronting science, technology, and society.Nanomaterials have shown promise in the fields of tissue engineering, medication transport, and diagnostics in the healthcare industry. They have the potential to completely alter how illnesses are treated, making treatments more efficient and less intrusive.

REFERENCES:

[1] K. Ghosal and K. Sarkar, “Biomedical Applications of Graphene Nanomaterials and beyond,” *ACS Biomaterials Science and Engineering*. 2018.

[2] M. Chen, X. Qin, and G. Zeng, “Biodiversity change behind wide applications of nanomaterials?,” *Nano Today*, 2017.

[3] R. J. B. Peters *et al.*, “Nanomaterials for products and application in agriculture, feed and food,” *Trends in Food Science and Technology*. 2016.

[4] H. S. Nalwa, “A special issue on reviews in biomedical applications of nanomaterials, tissue engineering, stem cells, bioimaging, and toxicity,” *Journal of Biomedical Nanotechnology*. 2014.

[5] G. Shan, S. Yan, R. D. Tyagi, R. Y. Surampalli, and T. C. Zhang, “Applications of nanomaterials in environmental science and engineering: Review,” *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*. 2009.

[6] X. Zhu, J. Li, H. He, M. Huang, X. Zhang, and S. Wang, “Application of nanomaterials in the bioanalytical detection of disease-related genes,” *Biosensors and Bioelectronics*. 2015.

[7] S. Lara and A. Perez-Potti, “Applications of nanomaterials for immunosensing,” *Biosensors*. 2018.

[8] J. Gao and B. Xu, “Applications of nanomaterials inside cells,” *Nano Today*. 2009.

[9] T. Yin and W. Qin, “Applications of nanomaterials in potentiometric sensors,” *TrAC - Trends in Analytical Chemistry*. 2013.

[10] E. L. Bradley, L. Castle, and Q. Chaudhry, “Applications of nanomaterials in food packaging with a consideration of opportunities for developing countries,” *Trends Food Sci. Technol.*, 2011.

CHAPTER 8

EXPLORING TOOLS TO CHARACTERIZE NANOMATERIALS

Dr.Vikas Kumar Shukla, Assistant Professor
Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India
Email Id- vikash.shukla@muit.in

ABSTRACT:

A thorough knowledge of the characteristics and behavior of nanomaterials is necessary given their fast growth and incorporation into a variety of sectors. Characterization tools are essential for revealing the fine features of these materials and assisting in their development, manufacture, and use. This abstract gives a general overview of the many approaches used to describe nanomaterials while highlighting their importance for the advancement of nanoscience and nanotechnology.The investigation starts with microscope methods including transmission electron microscopy (TEM) and scanning electron microscopy (SEM), which can do elemental analysis and high-resolution imaging, respectively. The ability of atomic force microscopy (AFM) to offer topographical and mechanical information at the nanoscale is emphasized. It is highlighted how spectroscopic techniques, such X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, may shed light on the chemical make-up and molecular interactions of nanomaterials.

KEYWORDS:

Nanotechnology, Particle Size Analysis, Raman Spectroscopy, Scanning Electron Microscopy (SEM).

INTRODUCTION

In order to characterize tiny materials or structures at the nanometric scale, specialized characterisation methods are often required. The development of some crucial advancements in traditional characterisation techniques created for bulk materials has been the foundation for the majority of the characterization of nanomaterials and nanostructures. For instance, X-ray diffraction (XRD) has been extensively employed to ascertain the crystal structure, crystallite size, lattice constants, and crystalline nature of nanoparticles, nanowires, and thin films. To determine the size, shape, and presence of flaws in these materials, characterisation of nanoparticles has often employed scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron diffraction. Quantum dots in semiconductors may be measured in terms of size using optical spectroscopy. A relatively recent characterisation method that is widely used in nanotechnology is scanning probe microscopy (SPM). Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are the two subfields of SPM[1], [2].

Despite the fact that STM and AFM are both true surface imaging methods capable of creating topographic images of a surface with atomic resolution in all three dimensions, when used with the right attachments, STM and AFM have a much wider range of uses, including nanoindentation, nano-lithography, and patterned self-assembly. STM/AFM can study almost all solid surfaces, whether they are soft or hard, electrically conductive or not. Surfaces may be investigated in a liquid or a gaseous media, such as air or vacuum. These characterisation methods and their uses in nanotechnology will be briefly covered in this Chapter. It takes atomic-level resolution in addition to great sensitivity and precision to characterize and manipulate individual nanostructures. Consequently, it gives rise to a number of microscopy methods that are crucial for the characterisation and measurement of nanostructured materials and nanostructures. The difficulty of instrument miniaturization is certainly not the only one. At the nanometric scale, the novel phenomena' physical characteristics and short-range forces, which are not very important in macroscopic-level characterisation, may have a big influence[3], [4].

DISCUSSION

Diffraction is the term for the bending of radiation in the direction of the geometric shadow of an object. The diffracted beams in the shadow region may generate either bright or dark fringes, depending on how the scattered waves are distributed. This behavior may be explained by the Huygens wave radiation theory. The diffraction gratings show these effects in the visible region of the electromagnetic spectrum. Max von Laue first demonstrated this phenomenon using X-rays after it was discovered seventeen years earlier. Because the crystal lattice is made up of parallel rows of atoms equivalent to the parallel lines of the diffraction grating, the inter-planar spacing may be correctly determined from the separations of dazzling fringes of the diffraction pattern. The conventional Bragg's law of diffraction states that the chance of constructive interference is linked to the inter-planar separations. A fundamental theorem in the physics of the scattering wave by an extended object relates the r-space density distribution of the scattering object to the Q-space scattered intensity distribution in terms of a Fourier transform. According to this theorem, the characteristic size in r-space, R, and the characteristic breadth of the intensity distribution in Q-space are inversely related. Therefore, to describe the size R, a scattering experiment with Q fluctuating in a range around the value of $Q = 2/R$ is needed. Later, X-ray diffraction was transformed into a unique tool for solids research thanks to successful efforts to develop theory and experimental methods. The scattering factor of an atom is often represented as the scattering power of an electron[5], [6].

Radiation Diffraction

Numerous analytical issues in the area of materials science center on the chemical composition and crystalline structure of materials. X-ray diffraction (XRD) is the only laboratory technique that accurately and non-destructively collects information on chemical composition, crystal structure, crystallite size, lattice strain, preferred orientation, and layer thickness. In order to analyze a range of materials, including powders, solids, thin films, and nanomaterials, materials scientists utilize XRD. X-ray diffraction (XRD), a versatile non-destructive analytical technique, is used to investigate the physical properties of powder, solid, and liquid materials, including their phase composition, crystal structure, and orientation. Numerous different materials are composed of tiny crystallites. Phase describes the chemical composition and structural type of these crystals. Materials may be single phases or multiphase mixtures, and they can include crystalline and noncrystalline components. In an X-ray diffractometer, different crystalline phases result in different diffraction patterns. Phase identification may be done by comparing X-ray diffraction patterns from unknown materials to patterns from reference databases. At a crime scene, this process is similar to comparing fingerprints. The most comprehensive compound database is maintained by the International Center of Diffraction Data (ICDD). A reference database may also be built using patterns from the scientific literature, patterns from your own observations, or patterns from pure-phase diffraction patterns that have been seen. The relative strengths of the patterns from the different phases in a multiphase mixture are used to determine the sample's overall composition[7], [8].

The Principles of X-ray Diffraction

X-ray diffraction is brought on by constructive interference of X-rays with a crystalline material. The wavelength of the used X-rays is comparable to the distance between atoms in a crystalline lattice. A diffraction pattern is produced as a consequence of this, and it may be analyzed in a number of ways. The most popular method is to utilize the well-known Bragg's Law (n=2d sin), which is used to calculate the size of crystals and their phases.

The sample is illuminated by the X-rays from the source. After being diffracted by the sample phase, it eventually arrives to the detector. By adjusting the diffraction angle (2, the angle between the incident and diffracted beams), which determines the intensity, the tube or sample and detector are moved. Depending on the diffractometer's geometry and the kind of sample, the angle between the incident beam and the sample may be either constant or variable and is often connected to the diffracted beam angle.

X-ray diffraction (XRD) is a technique used by many academics and business researchers to develop new materials or improve production efficiency. Research on innovative materials closely follows developments in X-ray diffraction, such as in semiconductor technology or medical investigations. Industrial research focuses on increasing the speed and effectiveness of production operations. Fully automated X-ray diffraction analyses result in more affordable production control systems for mining and the manufacture of building materials.

The main uses of X-ray diffraction are qualitative and quantitative phase investigations of pure substances and mixtures. The most used phase analysis method is known as "X-ray powder diffraction" (XRPD).

1. 1.Analysis of phase shifts in non-ambient research under extra special variables, such as temperature, humidity, and applied pressure.
2. Investigating the "microstructure" of polycrystalline materials, which is the result of combining physical traits such crystallite size (diameter), crystal orientation, and residual stress.
3. Many of these methods may also be used to polycrystalline layered materials, such as coatings and thin films, using a method known as grazing incidence XRD (GIXRD). Microdiffraction is a method for studying small samples of polycrystalline materials.

There are a number of X-ray diffraction techniques for materials that are not polycrystalline, such as single crystal semiconductor wafers or epitaxial layers. One of these techniques is high-resolution analysis of heteroepitaxial layers (HR-XRD), which analyzes materials using both Bragg's Law and dynamical diffraction theory.

Dispersion of X-rays

Additional methods used to investigate a material's non-crystalline components include grazing incidence small-angle X-ray scattering (GISAXS), small-angle X-ray scattering (SAXS), total scattering (also known as pair distribution function (PDF) analysis), and X-ray reflectometry (XRR). A distinct data processing method for each approach is based on the fundamental scattering theory. Immediately after an X-ray scattering or diffraction pattern has been measured. It needs to be examined. Analyzing the results of X-ray diffraction and scattering tests may be challenging. For the user's convenience, there are multiple XRD software packages available to handle all the different measurement types.

The most accurate and reliable method for clearly identifying unidentified materials is often XRD. Additionally, it is rather rapid (typically takes 20 minutes). This technique is popular because it involves minimum sample preparation and may be utilized for both industrial process applications and materials research. With the right analytical tools, data analysis may be quite straightforward, and for industrial processes, it may even be automated such that the operator in QC applications does not need to be an expert in XRD.

The first powder diffraction pattern was found more than a century ago. The sample of a typical powder diffraction experiment consists of a large number of randomly oriented crystallites. When all of these crystallites simultaneously refract the incoming beam in all directions, diffraction cones are created. The intensity and distribution of the cones are then determined along the two axes of the powder pattern. The collapse of three-dimensional reciprocal space into one-dimensional data sets causes a considerable loss of information because of an unintended and purposeful peak overlap. This is the significant "powder problem". During the first 50 years, the use of powder diffraction to the structural analysis of materials was fairly limited. In 1969, Hugo Rietveld published a groundbreaking research on the process that would later become known as the Rietveld refining method. Because of this, powder diffraction has seen a real revolution in its application to crystallographic research during the last 50 years. In honor of this 50-year anniversary, we published a virtual special issue highlighting the Rietveld method's applications in modern chemistry, materials science, and structural sciences[9], [10].

Peak overlap may be gracefully avoided using this method. The basic idea is based on numerically replicating a powder neutron diffraction pattern that is determined by a set of parameters. These characteristics include a wide range of contributions to the pattern, including the background, crystal lattice and symmetry, crystal structure, crystal microstructure, instrumental factors, and others. The process becomes modular when users of modern software may add, delete, modify, or enhance any parameter. Until the calculated pattern matches the data collected via testing, each of these parameters may be fine-tuned simultaneously using the least-squares method. After a successful match, the crystal structure is considered as polished.

Hugo M. Rietveld studied physics at the University of Western Australia in Perth. In Australia in 1960, he and Ted Maslen carried out the first single-crystal neutron diffraction studies on the chemical compound p-diphenyl benzene. Early in his research career, he had to manually draw Fourier maps, there was limited automation in data collection, and processing data was time-consuming. During this time, he gained knowledge of the Fortran II-based IBM 1620 computer's usage of punched cards for input and output. This motivated him to look into the prospects for automation created by the advent of computers. Rietveld's doctoral defense was held in 1964, and Dorothy Hodgkin served as the examiner. After completing his PhD, he joined the neutron diffraction team at the Reactor Centrum Nederland. He joined the group there that comprised Bert Loopstra and Bob van Laar, two of the founders of profile refinement methods.

In the 1960s, it was very challenging to deal with imperfect symmetry and complex crystal forms because of the considerable overlap of diffraction peaks. To solve this puzzle, data that contained both a single Bragg reflection intensity and a group of overlapping diffraction intensities were used to create the crystal structure. The overlapping peaks were manually fitted using least-squares methods to Gaussian profiles in an attempt to separate them, but with limited success—complicated patterns required fitting of multiple parameters. After seeing the potential of computers in this field, Rietveld developed the first technique for handling enormous amounts of data. When used with an Electrologica X1 computer, this approach allows for the simultaneous refining of up to 33 parameters. Although this was a positive development, additional computing power was still required. When the Electrologica X8 was released, the software was completely redesigned. The updated version has enhanced profile settings and structure. This led to the pioneering publication of "A Profile Refinement Method for Nuclear and Magnetic Structures" in 1969.

The method was shown using neutron powder diffraction data, but it was also suggested that it may be applied to data from X-ray powder diffraction. This program was sent to research institutes all across the globe in 27 copies. What follows is history. More than 18,000 sources have cited this significant work thus far. Rietveld first gave the method the name "Profile Refinement Method" in honor of the significant contributions made before his work. However, many authors started using fresh terminology into their work.

At the Neutron conference in Cracow, Ray Young and Terry Sabine proposed the word "Rietveld Method" to prevent further naming uncertainty. Later, the term was authorized by the Commission on Neutron Diffraction. In less than 8 years, neutron powder diffraction data were used to enhance 172 structures. These days, there are many. In this virtual special issue, we provide a collection of 17 papers made possible by the "Rietveld refinement method".

Until recently, the powder diffraction method could only be used to fine-tune the crystal structures of inorganic salts and minute organic molecules. To show how far we've gone, we open our fake special issue with the astounding intricacy of protein crystal structures. Margiolaki et al. provided an overview of the history, progress, and potential applications of the Rietveld refinement process in macromolecular powder diffraction. Such massive structural refinement efforts would not be feasible without significant improvements and integrations of diffraction line profiles in the Rietveld method, as described by Scardi.

The Rietveld technique is only one of several strategies that must be used to resolve and enhance challenging and complicated crystal structures. In this issue, Kaduk et al. performed a thorough analysis of the crystal structure of linagliptin hemihydrate hemiethanolate using Rietveld refinement, 3D electron diffraction, and density functional theory optimization. Harris et al. have shown how employing powder diffraction data, one may improve the structure identification and refinement of multicomponent organic crystalline phases by using complementary experimental and computational methodologies. The Rietveld approach may be used in combination with spectroscopic investigations such -Raman, XPS, and Mössbauer spectroscopies, as shown by Ramos-Guivar et al.

Despite the fact that mechanochemical reactions often result in powders, they may occasionally yield crystalline materials that are hard to make using traditional solvatothermal methods. as shown by Runevski et al. The Rietveld refinement method is the sole alternative remaining to explain the crystal structure of such materials. Nature's idealistic crystal lattice is embellished by flaws and disorder; actual crystals are theoretical.

The good presentation by Chan et al. utilizing defective samples of $Yb0._{5}Co_{3}Ge_{3}$ suggests that Rietveld refinement may help in comprehending these deviations from the ideal order. Rotational disorder is present in scheelite-type solids, as shown by Rabuffetti et al. The Rietveld technique has been very helpful in the investigation of porous crystalline materials. In this issue, Bon and Kaskel et al. investigated the structural evolution of a highly porous responsive metal-organic framework using time-resolved powder X-ray diffraction. The existence of organic structure-directing substances was investigated in the pores of zeolites, according to Paillaud et al.

CONCLUSION

In conclusion, the development of nanoscience and nanotechnology depends critically on the investigation of methods to characterize nanomaterials. Accurate and thorough analysis of nanomaterials' characteristics is crucial as their use in a variety of fields, including electronics, medicine, and environmental research, grows.A broad variety of characterisation approaches are required due to the diversity of nanomaterials, which includes nanoparticles, nanotubes, and nanocomposites. These methods, which include diffraction, thermal analysis, microscopy, and spectroscopy, provide crucial information on the structural, chemical, electrical, and mechanical properties of nanomaterials.

REFERENCES:

[1] J. Abraham, A. P. Mohammed, M. P. A. Kumar, S. C. George, and S. Thomas, "Thermoanalytical techniques of nanomaterials," in *Characterization of Nanomaterials: Advances and Key Technologies*, 2018.

[2] T. C. Chiu, "Recent advances in bacteria identification by matrix-assisted laser desorption/ionization mass spectrometry using nanomaterials as affinity probes," *International Journal of Molecular Sciences*. 2014.

[3] J. Njuguna, O. A. Vanli, and R. Liang, "A Review of Spectral Methods for Dispersion Characterization of Carbon Nanotubes in Aqueous Suspensions," *Journal of Spectroscopy*. 2015.

[4] P. Liu, R. Qin, G. Fu, and N. Zheng, "Surface Coordination Chemistry of Metal Nanomaterials," *Journal of the American Chemical Society*. 2017.

[5] E. N. Saw, M. Kratz, and K. Tschulik, "Time-resolved impact electrochemistry for quantitative measurement of single-nanoparticle reaction kinetics," *Nano Res.*, 2017.

[6] A. Kumar, E. Villarreal, X. Zhang, and E. Ringe, "Micro-Extinction Spectroscopy (MExS): a versatile optical characterization technique," *Adv. Struct. Chem. Imaging*, 2018.

[7] G. Ramachandran, *Assessing Nanoparticle Risks to Human Health, Second Edition*. 2016.

[8] Y. Xing *et al.*, "The application of atomic force microscopy in mineral flotation," *Advances in Colloid and Interface Science*. 2018.

[9] T. J. A. Slater, E. A. Lewis, and S. J. Haigh, "Recent progress in scanning transmission electron microscope imaging and analysis: Application to nanoparticles and 2D nanomaterials," *SPR Nanosci.*, 2016.

[10] B. S. Murty, P. Shankar, B. Raj, B. B. Rath, and J. Murday, "Tools to Characterize Nanomaterials," in *Textbook of Nanoscience and Nanotechnology*, 2013.

CHAPTER 9

AN ENQUIRY OF RAMAN SCATTERING EQUIPMENT AND MASS SPECTROMETRY OF SECONDARY IONS

Dr.Vikas Kumar Shukla, Assistant Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vikash.shukla@muit.in

ABSTRACT:

In the fields of analytical chemistry and materials research, spectroscopy methods like Raman scattering and secondary ion mass spectrometry (SIMS) are significant resources. The ideas, methodology, and applications of these two cutting-edge technologies are highlighted in this paper's thorough study.The analysis's first section examines Raman scattering spectroscopy in order to clarify the fundamental physics that control how photons interact with molecular vibrations. We go into the equipment, talking about spectrum analysis, lasers, and detectors. Additionally, we highlight the several uses of Raman spectroscopy, highlighting its great specificity and non-destructive nature, including pharmaceutical quality control and nanomaterial characterisation.

KEYWORDS:

Mass Spectrometry, Raman Scattering Equipment,Secondary Ions,Spectroscopy.

INTRODUCTION

Understanding how light interacts with matter is one of the most important aspects of understanding the world around us. Light in general, and laser light in particular, are powerful tools to extract new information from materials, especially at the nanoscale. Laser Raman scattering, one such interaction between light and matter, may properly reveal intriguing characteristics of objects like molecules and materials. This methodology has evolved over time into one of the most crucial methods for characterizing nanomaterials and has become a crucial instrument for contemporary nanoscience and nanotechnology. The basics of Raman scattering are covered in this Chapter, which also provides a starting point for further in-depth research.

The study of certain natural occurrences has been known to spur the development of new scientific branches over the course of history. One such example is shown below. In 1919, Sir C.V. Raman started studying the effects of liquids on the diffraction and molecular light scattering phenomena. His interest in this topic was aroused by an unusual experiment that included shooting a beam of white light into a tank containing a solution. Then, additional chemicals were added to this solution, gradually transforming it from a clear liquid into a turbid one. This came about as a consequence of particles being created and then remaining suspended in the liquid. The transmitted light's intensity naturally decreased as the turbidity increased until, at one point, the light was all but eliminated[1], [2].

It was curiously found that as more time passed, the transmitted light's intensity increased and that it also changed hue with time, ranging from indigo to blue to blue-green to greenish-yellow to white. What caused this to happen? A defense was necessary. The early decrease in transmitted light power was understandable, but Lord Rayleigh was baffled by the strange hues that appeared later. Raman may be able to explain this. Then he considered how the many diffracted waves combine to provide an overall effect that may be either positive or negative. He first considered how the light wave is diffracted by the individual particles. There was one more intriguing possibility:

What if a molecule, rather than a suspended particle, had generated the diffraction? In 1921, Raman left India for the first time, and he was returning home by ship. He wondered why the sea was blue, entranced by the deep blue of the Mediterranean. According to Lord Rayleigh, who had properly described the blue color of the sky, the much-admired deep blue of the sea has nothing to do with the color of water and is just the blue of the sky seen in reflection. In essence, Lord Rayleigh's response was that the water seems blue because it is only reflecting the color of the sky. Raman was not pleased with this answer, so he launched a detailed inquiry. His research revealed the following:

The same molecular scattering that gives the sky its blue hue also gives the water its blue hue. Just like air molecules, water molecules have the ability to scatter light. Raman said in his landmark essay on the molecule scattering of light that "in this phenomenon, as in the parallel case of the color of the sky, molecular diffraction determines the observed luminosity and in a great deal also its color." Raman was able to show that water molecules deflect light similarly to air molecules, which is why the sea looks blue. This was an important discovery that, in addition to contradicting Lord Rayleigh's hypothesis, has further implications for our understanding of how light interacts with molecules, notably in the context of the Raman effect.

Two basic phenomena that occur when photons interact with matter may provide light on the features and behaviors of small particles. Both of these light scattering mechanisms are elastic. Photons interact with molecules or other particles in a mechanism known as Rayleigh scattering, also known as elastic light scattering, without changing their energy or wavelength. The Earth's atmosphere's molecules are better at dispersing shorter light wavelengths, such as blue and violet, which gives the sky its blue color. Elastic scattering occurs when the incoming photon's energy is conserved, or when the scattered photon has the same energy, frequency, and wavelength as the input photon. Since it is a coherent process, the dispersed photons maintain their phase relationship with the incident photons. Characterization of aerosols, examination of particle size, and development of laser-based diagnostic techniques have all used elastic light scattering[3], [4].

As contrast to elastic scattering, interactions between photons and particles or molecules cause a change in the energy, wavelength, or frequency of the scattered photons. Inelastic light scattering is what is happening here. Raman scattering and Brillouin scattering are the two main types of inelastic light scattering. When there is a difference in energy between the scattered and incident photons as a consequence of the transfer of energy with the material's rotational or vibrational modes, this is known as Raman scattering. This technique is often used in chemical analysis, materials characterization, and molecular structure study. Brillouin scattering, on the other hand, involves the scattering of photons by acoustic phonons in a material, resulting in a change in the frequency of the scattered light that is tied to the mechanical properties of the material, such as sound velocity and elasticity. Numerous fields, including as solid-state physics and material science, utilisebrillouin scattering.Inelastic light scattering is the scattering of photons with interactions that result in an energy, wavelength, or frequency change, while elastic light scattering is the scattering of photons with no change in energy or wavelength. Both elastic and inelastic light scattering techniques have a wide range of applications in science and industry, enabling us to gain valuable insight into the properties and behavior of tiny materials[5], [6].

DISCUSSION

Raman scattering, often known as Raman spectroscopy, is a powerful technique used in analytical chemistry and materials science to examine the vibrational and rotational modes of molecules. It is named after Sir C.V. Raman and occurs when light interacts with materials and experiences an energy change as a consequence of photons being scattered inelastically. Raman spectroscopy is an essential tool in many scientific disciplines since it provides information on molecular structures, chemical compositions, and even crystallography.A fundamental concept underlies how Raman scattering operates. When a monochromatic light source, often a laser, illuminates a sample, the majority of incoming photons are elastically distributed, which means they retain their initial energy and wavelength. A small part of the scattered photons interacts with the vibrational and rotational modes of the sample, altering their energy. Since these energy changes provide information about the molecular structure of the substance, they may be seen and assessed[7], [8].

Raman spectroscopy calculates the energy changes caused by molecular vibrations by using the frequency difference between the entering and scattered light. This change, denoted by the letter "v," is known as the Raman shift. Researchers may identify specific chemical bonds and functional groups, as well as determine the relative quantities of different compounds in a sample, using the Raman spectrum, which is a plot of intensity versus Raman shift. Raman spectroscopy may be utilized on solids, liquids, and gases, making it helpful for a wide range of scientific and industrial applications.

Because it provides a wealth of knowledge on molecular movements and interactions, the Raman effect is very beneficial in the fields of biology, chemistry, materials science, and medicines. Pharmaceutical research use Raman spectroscopy for drug development, quality control, and analysis of drug-protein interactions. In materials science, it aids in describing and understanding the properties of materials such as semiconductors, nanomaterials, and polymers. Biologists employ Raman spectroscopy as a method to evaluate biological molecules and investigate cellular components. To sum up, Raman spectroscopy, sometimes referred to as Raman scattering, is a vital tool in the scientific community that enables researchers to investigate the rotational and vibrational modes of molecules and learn more about their structures. Its flexibility and non-destructive nature make it an essential technology in a range of scientific and industrial applications, advancing many academic subjects[9], [10].

Recent breakthroughs in optical instrumentation technology have led to significant advancements in Raman spectroscopy equipment. The ability to characterize molecules and materials with modern Raman microscopes is excellent. We'll discuss a few important elements of a typical Raman microscopy setup in this section. Before entering the input port of an upright microscope, a band pass filter permits Raman excitation light from a solid-state laser or gas laser to pass through. The sample is targeted by the laser beam using a dichroic mirror. The sample is brought into fine focus using an objective lens with a high numerical aperture. The two functions of an objective lens are to collect backscattered light and incident laser light.

Depending on the kind of sample, different objective lenses are used. For solid, dry materials like single crystals, powders, substrates, etc., a large numerical aperture, dry objective lens works best. In contrast, a water-immersion objective lens works best for watery samples like nanoparticle solutions, biological cells, etc. It should be noted that the kind of objective lens being used has a significant effect on the Raman scattering's ability to gather data. The backscattered light the objective lens has collected is then filtered by an edge filter at the microscope's output port. The purpose of an edge filter is to separate the collected signal from the strong Rayleigh scattered light. While edge filters only allow the Stokes component of the Raman spectrum, a notch filter allows both the Stokes and anti-Stokes components of the scattered light. The focused, filtered light is now focused on an optical fiber (F).

Mass spectrometry is one of the most sensitive analytical techniques for characterizing molecular molecules. The last 20 years or so have seen improvements that have made it possible to apply it to any kind of material, including organic, inorganic, biological, and environmental materials, despite the fact that it has long been an essential method for studying the structures of organic molecules. Today, mass spectrometry is more adaptable than ever before, able to examine anything from simple compounds to complex macromolecules and proteins. All of these options are now possible because to the advent of soft ionization methods, which allow for the desorption and intact ionization of almost any material. Two techniques that are helpful in this regard are matrix assisted laser desorption ionization and electrospray ionization, both of which produce molecular ions from any form of molecule.

Later in this Chapter, we'll talk about these techniques. In the past, to conduct mass spectrometry, gaseous molecules or atoms were injected into a vacuum system and ionized by high energy electrons on the order of 100 eV. This ionization is challenging because it produces ions that are enough energetic inside to split into smaller molecule ions. As a result, it's often difficult to see the complete molecular ion. A key problem with material characterisation is this. Methods of gentle ionization are quite useful in these situations. The ions, which are typically positive in charge, are collected and separated by the mass analyzers, which are often magnetic sectors, quadrupoles, ion traps, or time of flight analysers, before being detected by a conversion dynode-electron multiplier system. This kind of mass spectrometry only works with species that can be evaporated or introduced to a vacuum chamber.

This is not practical for a variety of molecules, including large biomolecules that do not evaporate intact, metal complexes, and organometallic compounds. They often degrade during the evaporation process. There are several such instances when the investigated molecule is present on the surface as a sub-monolayer and is at very low concentrations. Additionally, for nanoscale entities consisting of fragile species, such as biomolecules, soft ionization methods are helpful. A discussion of quantum clusters, a more recent family of comparable materials, will be covered in a later section of the book. These materials are sub-nanometer in size and contain just a few metal atoms, making them too small to be seen using the conventional electron microscopy apparatuses discussed in this book. To understand the chemical composition of the cluster, mass spectrometry is the best method. The analysis of nanomaterials-based catalysis largely uses mass spectrometry, including its most popular hyphenated approach, gas chromatography mass spectrometry.

In addition to being studied in mass spectrometry, high energy ions may be used in a number of other applications. Popular ion-based techniques include secondary ion mass spectrometry and focused ion beam lithography. Today, ion lithography may be used to create structures as small as 10 nm. Secondary ion mass spectrometry in the spatially resolved mode is the only technique that can get chemically precise, isotopically resolved elemental information at a spatial resolution of 50 nm. Since ion ejection is extremely surface-sensitive and surface damage may be minimal, nanometer thin coatings formed on surfaces can be examined with isotopic specificity. This analysis may be quantitatively carried out at trace levels.

The importance of SIMS imaging is shown by these features. The mass spectrometry of initial particles that have been ionized as a result of contact with a surface is of interest when utilizing SIMS. The surface may be liquid or solid, and the fundamental particles may be electrons, ions, neutrals, or photons. The secondary particles that are emitted from a surface include electrons, neutral or ionic atoms or molecules, and neutral or ionic clusters. The primary emphasis in SIMS is primarily on the ions since the neutrals ejected are often post-ionized and subjected to mass analysis, as in sputtered neutral mass spectrometry. The separation of emission and ionization allows for quantitative elemental analysis. The bulk of current applications are in dynamic SNMS, which was made possible by lasers. A secondary particle emission mechanism is sputtering.

Most of them will be neutrals, but some of them will also be ions. Many methods are used to determine the mass of these ions, including magnetic sector-based methods, time of flight methods, and quadrupole methods. Simultaneous Ion Mass Spectrometry (SIMS) was invented by Sir J.J. Thompson in 1910 after he observed the emission of positive ions from the surface of a discharge tube when primary ions impacted with it. A detector, ion optics that send the ions to a mass spectrometer, and an ion cannon that creates ions or atoms with energy between 0.5 and 50 keV make up the instrument's major components at the moment. Magnetic, quadrupole, or time of flight mass spectrometers are all possibilities.

Using the mass spectral intensities that are collected from a surface, SIMS imaging produces images. The size of the sampled area determines the method's spatial resolution. Therefore, either a highly focused collection of ions or a highly concentrated ion beam are needed. A focused ion beam passes over the material, and each spot's spectrum is captured. This method, referred to as microprobe mode, has lateral resolution on the order of sub-micron levels. The direct mode, sometimes referred to as the microscope mode, is the alternative. In this instance, ion lenses simultaneously gather ions from several locations on the sample, which are subsequently detected by a position-sensitive detector and quantified. The primary ion beam has no rostering. For SIMS imaging, two approaches are generally utilized.

SIMS may be used in both dynamic and static modes. In the dynamic mode, where there is a significant primary ion flow and rapid material removal. As a result, the primary beam is continually exposed to a different surface. However, with static SIMS, just a tiny fraction of the surface is sampled. As a consequence, surface damage is hardly noticeable. In static

SIMS, time-of-flight-based techniques are often used as the analyzer since high-quality data collection is necessary. Consequently, TOF SIMS is a different term for static SIMS. The dynamic SIMS uses magnetic sector analyzers and quadrupoles.

Using the latest apparatus developments, imaging SIMS can achieve a lateral resolution of 50 nm. The selective accumulation of ions in catalysis, the incorporation of certain molecules into cell structures, the separation of ions at grain boundaries, etc. are all fascinating areas to look into. Metallurgy, heterogeneous catalysis, biology, and other fields are among the application areas. At sub-100 nm resolution, a large number of the cell organelles are discernible for high-quality chemical imaging.

The energy of the primary projectile is conveyed in a manner analogous to a billiard ball when an ion or atom bombards a surface. The target atoms then clash several times, with some of these collisions ejecting atoms and clusters that get ionized as a result of their return to the surface. The primary concern with SIMS quantification is the simultaneous ionization and sputtering. Calibration is thus an essential part of quantification. Low doses are necessary for good surface characterization because continuous particle bombardment changes the surface.

Another technique for SIMS uses the ^{252}Cf fission particles to produce sputtering, which is analogous to plasma desorption mass spectrometry. These fragments struck the analyte-coated back of a thin foil with a MeV energy, ejecting massive molecular ions as a result. ^{127}I+ high-energy ions from a tandem accelerator have also been used to achieve the same objective. Additionally, high-energy neutral atoms are used for sputtering. This kind of mass spectrometry, also known as fast atom bombardment, is often employed for organic analytes with acceptable matrices. As a result, the analyte species experiences mild ionization. Low internal energy ions develop during soft ionization, which leads to minimal fragmentation.

Soft techniques are essential for cluster research because clusters are more readily fractured following ejection to the gas phase and are constrained by lower energy. Mass spectrometry, a popular technique nowadays, may be used to analyze nanoparticles, however soft ionization methods are essential. Laser desorption is another mild method for desorption ionization. Matrix-aided laser desorption mass spectrometry, which desorbs the analyte using a low power UV laser, is one contemporary approach for doing this. The analyte is mixed with a matrix to produce a low analyte concentration. Since laser pulses may provide a start time for data collection and ions must be captured with high efficiency, the time of flight method is often used for mass analysis.

Time of flight analysis also has the benefit of being excellent for large macromolecules since there is theoretically no mass restriction for the study. This method is useful, particularly for the study of nano-bio conjugates. Think about contrasting the MALDI mass spectra of myoglobin and hemoglobin with the Mb and Hb coated Au nanoparticles as an example. It is shown that the mass spectra of the conjugated nanoparticles and the original proteins are the same. Here, it is shown how well proteins and other biomolecules may be detected on nanoparticle surfaces using MALDI-MS spectra. To better understand the chemistry and biology of proteins on nanoparticle surfaces, mass spectral investigations may also be enhanced.

Electrospray ionization mass spectrometry (ESI MS), which produces ions from a solution by spraying it in the form of small droplets in a high electric field, is the other soft ionization technique. After being electrosprayed, the solution is forced through a fine needle, and the ions that are produced are often multiplely charged. This makes it possible to analyze large molecules in low mass range devices because to their low m/z value. Both of these techniques are very sensitive and enable high-resolution femtomole analysis. Today, ESI MS is a widely used technique for examining sub-nano clusters that are difficult to see in TEM. Electrospray-induced ions are typically collected and ionized in an orthogonal geometry. In other words, the ion collection often happens at a 90° angle to the axis of the spray.

It is now possible to collect ions without requiring a lot of solvent molecules by placing a pump inlet just beneath the spray. This makes solvent collection substantially more efficient at a reduced cost per pumping. Nevertheless, aggregating organisms with enormous molecular masses is unsuccessful with this geometry. As a result, orthogonal mass spectrometers are unable to efficiently collect data from a number of recently discovered gold clusters. Unfortunately, the vast majority of mass spectrometers manufactured nowadays are orthogonal devices. Despite this, a number of clusters have been investigated utilizing business-related technologies. A variety of ESI MS and MALDI MS cluster examples will be shown in the next Chapter. The parts of entire clusters that were generated in solutions with tens to hundreds of atoms have been detected in the author's laboratory.

Electrospray produces multiply charged species; to produce singly charged ions, the spectra must be deconvolved. Different methods are used to produce the singly charged spectra. These all center on a series of peaks at charges n, n+1, n+2, etc. on the mass spectrum. Better algorithms continually take into account the isotopic separations between peaks and the change in peak separation with charge change. This information is used to separate peaks that might be caused by species with numerous charges. Similar to this, other series of peaks from various molecular species are seen. To connect these peaks to specific ions, further research and understanding of the ions' possible chemical structures are required.

CONCLUSION

In conclusion, spectroscopic analysis, particularly the use of Raman scattering tools and secondary ion mass spectrometry, represents a vital and active field of scientific instruments and study. These methods have greatly improved our knowledge of diverse substances, materials, and biological samples. With its non-destructive and molecular fingerprinting characteristics, Raman spectroscopy has found use in a variety of disciplines, from biology and pharmaceuticals to chemistry and material science.

REFERENCES:

[1] J. S. Becker *et al.*, “Bioimaging of metals and biomolecules in mouse heart by laser ablation inductively coupled plasma mass spectrometry and secondary ion mass spectrometry,” *Anal. Chem.*, 2010.

[2] A. Brunelle, D. Touboul, and O. Laprévote, “Biological tissue imaging with time-of-flight secondary ion mass spectrometry and cluster ion sources,” *Journal of Mass Spectrometry*. 2005.

[3] I. C. Vreja *et al.*, “Secondary-ion mass spectrometry of genetically encoded targets,” *Angew. Chemie - Int. Ed.*, 2015.

[4] T. E. Helser, C. R. Kastelle, J. L. McKay, I. J. Orland, R. Kozdon, and J. W. Valley, “Evaluation of micromilling/conventional isotope ratio mass spectrometry and secondary ion mass spectrometry of δ18O values in fish otoliths for sclerochronology,” *Rapid Commun. Mass Spectrom.*, 2018.

[5] C. Zune *et al.*, “Part list,” *Prog. Org. Coatings*, 2005.

[6] C. S. Weinert *et al.*, “Ignacio montorfano navarro,” *Inorg. Chem.*, 2011.

[7] K. Wu, F. Jia, W. Zheng, Q. Luo, Y. Zhao, and F. Wang, “Visualization of metallodrugs in single cells by secondary ion mass spectrometry imaging,” *Journal of Biological Inorganic Chemistry*. 2017.

[8] A. Chander *et al.*, “Subject index,” *Miner. Eng.*, 2015.

[9] R. R. Abbas *et al.*, “Supporting Information,” *Langmuir*, 2013.

[10] K. K. Chawla, *Composite Materials Science and Engineering Second Edition*. 1998.

CHAPTER 10

QUANTUM MECHANICS OF CONFINED NANOCLUSTERS AND OPTICAL PROPERTIES OF BULK SEMICONDUCTORS

Dr.Vikas Kumar Shukla, Assistant Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vikash.shukla@muit.in

ABSTRACT:

The behavior of constrained nanoclusters and the optical properties of bulk semiconductors are the two primary topics of this work, which investigates the fascinating interaction between quantum mechanics and optical properties of materials.In order to understand how quantum confinement effects work at the nanoscale, the inquiry first explores the quantum mechanics regulating confined nanoclusters. The article explains the fundamental concepts of quantum confinement, such as energy level discretization and quantum dot size quantization. This study reveals how the electrical structure and optical characteristics of nanoclusters are significantly influenced by their size and form. There are also insights into quantum dot-based technologies and applications, including the function of quantum dots in optoelectronics and quantum information processing.

KEYWORDS:

Bulk Semiconductors, Confined Nanoclusters, Nanomaterials, Optical Properties, Quantum Mechanics.

INTRODUCTION

When electrons are crammed into small areas, interesting phenomena are created. This is a theoretical justification for these characteristics. Confinement's spectroscopic manifestation is also presented. This serves as the foundation for the traits that are covered in earlier Chapters of the book. The thermodynamic properties of the nanosystems are under the control of large-surface effects, which are useful in a broad variety of technological applications. Furthermore, due to the several processes' small-length scales, the system's exact chemical composition becomes essential. They both make theoretical understanding of nanosystems difficult. We focus on the difficulties caused by large-surface effects in this Chapter. We next provide an illustration of how computer simulations might help make some of these issues more understandable. We discuss Monte-Carlo, stochastic dynamics, and molecular dynamics simulation basic techniques to do this. We also examine a few recently released articles to show how the basic algorithms are really used in research and to highlight the continuing work on the fundamental algorithms that tries to understand more complicated phenomena[1], [2]. The term "quantum dots" itself is seen to be both intriguing and creative by many individuals. It implies both the appearance of quantum phenomena and the very small size. This expression often describes semiconductor material nanostructures, where electrons are confined to properly designed, low-dimensional structures with suitable potential barriers. However, electrons may be partially or completely confined in low-dimensional structures of different dimensions. To fully appreciate the unique physical properties of these materials, it is essential to quickly review the properties of bulk semiconductors[3], [4].

DISCUSSION

Aspects of the Optical Properties of Bulk Semiconductors

The energy levels of the individual atoms tend to combine to form energy bands, which are regions of acceptable electron energy, since solids are collections of basically infinitely many atoms. The valence band and conduction band are the two regions of permissible values in crystals of insulating or semiconducting materials where electrons cannot absorb energy. The energy range between these bands is referred to as the band gap, also known as the forbidden energy gap, which is a characteristic of the material. For semiconductors and insulators, this energy gap generally has magnitudes of a few electron volts and several electron volts, respectively.

Semiconductors are characterized by the energy band gap, a key element that regulates the material's optical and electrical properties. Energy bands and band gaps are created as a result of how quantum physics explains how electrons behave in crystalline materials. Because crystals have long-range periodicity in all three dimensions, a hole or electron in a crystal experiences a Coulomb potential that is quite different from the Coulomb potential that electrons in solitary atoms face. The potential $V(x)$ in this case is periodic due to the translational periodicity of the positive ion arrangement within the crystal. $V(x) = V(x + a)$, where an is the lattice constant of the crystal. The wave function of electrons also exhibits a periodic pattern with the same frequency. The Schrodinger wave equation solution and the concept of energy bands are used to offer a quantum mechanical explanation of electrons in crystalline materials in standard literature on solid state physics[5], [6].

Insulating crystals are transparent because the energy gap is greater than the quantum energy that corresponds to the visible light spectrum. Crystals may absorb incident photons with quantum energies that are equal to or greater than the band gap energy. The excitation of an electron across the band gap, from the valence band to the conduction band, is a consequence of this absorption. As a result, the crystals are transparent to electromagnetic waves with energies below the band gap energy and opaque to those with energies above. Crystals of materials like ZnO (band gap: 3.37 eV) are transparent to the majority of visible and infrared wavelengths, in contrast to PbS (band gap: 0.41 eV) and silicon (band gap: 1.11 eV), which seem black and impervious to light in the visible region. CdS and CdSe are materials exhibiting color and selective color light transmission, respectively (band gap: 2.4 eV and 1.73 eV).

It might be difficult to change the band gap energy of a semiconductor material at a certain temperature and pressure. The optical properties of the sample are described by acquiring an optical absorption spectrum of the sample, where the optical absorption coefficient is shown as a function of the wavelength of the light impinging on the crystal. The optical absorption spectra of semiconductor crystals distinguish between the wavelength regions where the crystal is transparent and opaque. By examining these spectra, one may determine the band gap.

Quantum Mechanical Structures in the Low Dimensions

The vast majority of bulk semiconductor physics is well understood and has been addressed in widely used textbooks. However, the creation of low-dimensional structures makes it possible to confine electrons and holes in a variety of geometries according to quantum mechanics. Electrons, holes, and excitons are free to move in any of the three dimensions in a crystal of a bulk semiconductor. They become less flexible when they are restricted to smaller dimensions, which affects their quantum states, state density, and ultimately modifies their physical properties.

Quantum wells: For instance, a very thin layer of a low-band gap semiconductor material may be sandwiched between two layers of a different semiconductor with a wider energy gap. Since there is a potential barrier in the direction of going away from the plane of the layers, the electrons in the intermediate layer are consequently limited to two dimensions. It is easy to conceive of the intermediate layer in this situation as being practically two-dimensional since its thickness is often much less than either its length or breadth. Such structures are called quantum wells.

The potential that an electron will encounter is shown in the structure at the top as a function of location along the structure's length. By sequentially stacking thin layers of two appropriate semiconductors with different band gaps, such as AlGaAs and GaAs, in an alternate pattern, a multiple quantum well may be made[7], [8].

Research into quantum mechanical confinement in two-dimensional semiconductors led to the development of quantum well designs for device applications. In a quantum well, electrons may only go in two ways and may run into a barrier if they try to move in the third. An example of such a system is simulated using a one-dimensional potential well problem. The electrons are confined in a deep potential well in this issue and are exposed to steep potential barriers, which limits their movement along one of the dimensions, such as the z-axis.Quantum wires:

It is possible to further restrict electrons to quasi-one-dimensional structures, which are known as quantum wires, by fabricating an exceedingly thin metallic or semiconducting wire that is submerged in a dielectric liquid. Quantum wires may also be made from quantum wells using electron beam lithography. The electrons may be constrained to one dimension, such as along the z-axis, and the energy eigenvalues can be calculated using quantum mechanics.

Quantum confinement may be extended even further by using "quantum dots," which are quasi-zero-dimensional nanostructures in the form of tiny islands of the semiconducting material surrounded by an insulating surrounding. These systems, sometimes known as quantum dots, have received far more attention than quantum wells and wires. In all three dimensions, these materials' potential barriers prevent electron movement. the electron (hole) wave function for a quantum dot with the required coordinates and dimensions Lx, Ly, and

Lz. Because of this, the energy bands in a bulk material exhibit some degree of discreteness in the case of a quantum dot, giving rise to the appearance of energy levels. Additionally, the oscillator power is now concentrated on these specific exciton levels instead of being spread out throughout the continuum states in the energy bands for bulk material[9], [10].

Exciton Contained in Quantum Dots

One may understand quantum confinement by looking at the behavior of the exciton in the semiconductor nanocrystal. The exciton is a pair of bound electrons and holes that are coupled quantum mechanically to one another and exist in the lattice. Frenkel excitons have electrons and holes that are physically close to one another in the crystal, while Mott-Wannierexcitonshave electrons and holes that are physically separated by a few lattice spacings.

The Mott-Wannier exciton is a well-known and thoroughly studied phenomena in bulk semiconductors. It is a loosely coupled electron-hole pair created by the semiconductor's interaction with photons. It is a quantum mechanical system similar to the hydrogen atom because the coulomb interaction keeps its positive and negative charges together. It is predicted that the energy levels of the exciton, a quantum mechanical system consisting of an electron and a hole, are scaled down replicas of the energy levels of a hydrogen atom ensconced in a dielectric medium with corresponding Bohr-like orbits. The scaling factor is the lattice constant since the exciton is a component of the semiconductor lattice.

E is the electronic charge when me and mh stand for the effective masses of the electron and hole, respectively, and when is the bulk optical dielectric constant. It is said that the exciton is in the strong quantum confinement regime when the size of the nanocrystal is less than the exciton Bohr diameter of the semiconductor. This size, for CdS and PbS, respectively, is 6 and 9 nm, respectively.

The effects of spatial confinement are especially obvious in the context of strong quantum confinement. According to the uncertainty principle, the average electron speed in the nanocluster must be significantly greater than it is in the bulk. Therefore, the electron may be imagined rotating several times inside the exciton before being destroyed by thermal motion via electron-hole recombination. In contrast to the bulk, the exciton has a longer lifespan in semiconductor nanocrystals, making it feasible to see exciton features in their optical absorption spectra at room temperature. It is also feasible to see exciton fluorescence at normal temperature.

Confined nanocluster quantum mechanics

A fundamental understanding of quantum mechanics is necessary to understand the behavior of particles at the nanoscale, particularly in the context of confined nanoclusters. These nanoclusters, which are composed of a few atoms or molecules often hundreds or even thousands display unique electrical, optical, and chemical characteristics because of their small size and the effects of quantum confinement. One of limited nanoclusters' most striking features is the quantization of energy levels. In bulk materials, electrons are distributed over energy bands, but different energy levels are more apparent in nanoclusters. This quantization results in the emergence of different energy states or energy "shells" within the cluster, much like the electron orbits in an atom. These quantized energy levels result in various electrical and optical properties, such as discrete absorption and emission spectra. With the use of various spectroscopic techniques, these features may be studied by researchers to learn more about the cluster's size, structure, and electrical configuration.

The behavior of electrons in restricted nanoclusters is also governed by the Heisenberg uncertainty principle, which states that it is impossible to precisely predict a particle's position and momentum at the same time. In nanoclusters, where electrons are physically restricted to a small area, their momentum is more unpredictable, leading to a substantial dispersion in energy levels. The "particle-in-a-box" effect widens the energy gaps between quantum states and may result in a variety of odd electrical characteristics, such as quantum size effects and quantum dots.

Additionally, electron activity is probabilistic and behaves like waves in nanoclusters, according to quantum physics. When the probability distributions of electrons intersect, interference patterns are created due to the wave nature of the electrons. Wave interference is the term for this occurrence. These interference effects may affect the optical and electrical properties of nanoclusters, which may also affect luminescence and the tunable properties of nanoparticles used in several applications, such as quantum dots for displays and sensors.

Quantum confinement effects, which are not just restricted to electrons, but impact other quantum particles, such as phonons, which are quantized vibrational modes in materials. Nanoclusters' phonon energies are quantized as a result of their tiny size, altering their mechanical and thermal properties. These quantum mechanical effects on phonons may have an influence on mechanical stability and thermal conductivity, two crucial elements in the design of nanoscale materials.

Finally, we demonstrate how quantum mechanics has a significant impact on the distinctive characteristics of confined nanoclusters. The peculiar electrical, optical, thermal, and mechanical features seen in nanoclusters are all explained by quantum confinement effects, which also produce quantized energy levels, probabilistic electron behavior, and wave-like phenomena. Understanding and using these quantum events is crucial for the production of complex nanomaterials with specific properties for a range of applications, from electronics to catalysis to medicine.

Due to the dramatic variations in their optical properties, quantum dots are exciting potential applications for photonics. The optical characteristics may be examined using optical absorption and fluorescence techniques. The optical absorption spectrum of a perfect crystalline semiconductor exhibits an abrupt cut-off at a particular wavelength matching the band gap energy, particularly in the case of direct band gap semiconductors, like CdS. Due to phonon contributions, the cut-offs in indirect band gap semiconductors like silicon tend to be less sudden.

In essence, the material is opaque to light with wavelengths less than this cut-off wavelength and transparent to light with longer wavelengths. This is true because the cut-off number corresponds to the energy of the band gap. The optical absorption and emission properties of semiconductors are affected by excitons.

The optical absorption spectrum may show signs of excitron-based absorption close to the optical cut-off. The exciton-induced absorption may be described using energy levels that are tightly spaced between the top of the valence band and the bottom of the conduction band. Because of this, the concept of the band itself is altered in the case of semiconductor quantum dots due to exciton confinement.

At its lowest point, the conduction band seems to divide into numerous layers. As a consequence, shoulders begin to show up close to the abrupt cut-off in the optical absorption spectrum of the bulk semiconductor. So, in this case, we can only talk about an effective band gap.

The recombination of the exciton's electron and hole results in the decay of the exciton and the emission of the resulting energy as light. This manifests as a sharp peak at the band edge in the fluorescence spectra. However, these traits are often only discernible at lower ambient temperatures. This prevents the electron and hole from completing even one orbit before the thermal excitations of the lattice force their recombination. The main feature of the fluorescence spectra of semiconductor quantum dots is the sharp exciton peak, which is not far from the absorption edge. There are other peaks as well, which are brought on by flawed states. This results from the dot's relatively high surface area to volume ratio. It is found that the size-dependence of the exciton peak and the absorption edge are extremely similar. This creates some exciting possibilities, including carefully mixing quantum dots with different diameters and the proper materials to produce a solid state white-light emitter.

In a central box with periodic boundary conditions (PBC) that are thought to replicate in all directions, bulk simulations are often run. There are precise replicas of the main box in the picture boxes. The particles move in the same direction within each box. It is clear that when a particle leaves the center box, it is identical to when a particle enters the center box from the image box adjacent to the opposite side. The edges of the core box thus have no effect on the particles contained inside. However, in the case of nanosystems, the boundary is important. Therefore, special attention is paid to maintaining the border barriers. Consequently, the specification of the wall-particle interactions is another need for such a system. In certain cases, the cluster is presumed to be positioned inside a matrix far from the boundaries rather than utilizing the normal PBCs. The PBCs are often used for modeling an aggregation of clusters.

It should be emphasized that the simulation techniques really include the system specification through the interaction potential. The forces in the MD code are produced by the interaction potential. Similar to this, the energy in the MC comes from the interaction potential. Usually, the interaction potentials have parameters. For instance, covalent bonding interactions are simulated using the Morse potential. The harmonic approximation, which just needs the spring constant to be specified, often also takes into account such interactions. The spring constant may be measured via experiments. Examples are the spring constants discovered via infrared research for different homo- and hetero-nuclear bonds. The non-bonding interactions are defined in terms of van der Waals interactions.

Charges interact with one another in coulombic ways, which are often long-range. To control the long-range interactions in simulations, certain strategies must be applied. The parametrization is often carried out using "ab-initio" calculations that make advantage of quantum chemistry methods. The nuclear coordinates are maintained constant in these simulations due to their slower speeds than the electrons'. The ground-state electronic energy is calculated using the established nuclear coordinates. The potential energy profile is created by applying the same calculations across a wide range of inter-nuclear distances. The interaction parameters are estimated using these profiles.

Using the usual MC or MD technique, the coulomb forces are integrated with the traditional inter-nuclear forces, the electronic component of the force, and the force itself. The nuclear and associated electronic coordinates are updated as a consequence. It must be remembered that the bulk of the computation time is spent computing the force in MD and the energy twice in MC. The time scales up to N2 since every possible pair is considered throughout the computation. This is a serious problem, particularly for clusters that have more than 500 component atoms. When the interaction potential is short-ranged, the computation is often performed assuming that the potential has been cut off.

The cut-off must be less than half of the shortest box dimension. It's common to maintain a list of neighbors as a Verletneighbour list. All the atoms that are close by and a little farther away than the cut-off distance from a certain atom is listed. Each atom in this list's interactions with the others is predetermined. The list is only sometimes updated, depending on how the particles move. This avoids the need to figure out how far apart different pairs should be for multiple intermediate phases. It is possible to tabulate the force and potential energy before the simulations begin. When performing the simulations, one just does a database search and applies the standard interpolations. This might save a ton of time if the contact is extensive, as in the coulomb instances.

CONCLUSION

Condensed matter physics encompasses two independent but linked areas: the investigation of the optical characteristics of bulk semiconductors and the study of the quantum mechanics of confined nanoclusters. Our understanding of the complex interaction between size, structure, and electrical behavior in nanoclusters as well as the well-established rules regulating the optical response of bulk semiconductors has improved as a result of our research.The study of enclosed nanoclusters has shed light on the intriguing quantum phenomena that occur when matter is enclosed in nanoscale dimensions. Discrete energy levels and size-dependent electronic bandgaps are two examples of quantum confinement phenomena that have made it possible to modify the characteristics of materials at the nanoscale. These discoveries have sparked continuing research into using these phenomena for cutting-edge technologies and have broad implications for nanotechnology applications, such as quantum dots in displays and sensors.

REFERENCES:

[1] A. Avidan, Z. Deutsch, and D. Oron, “Interactions of bound excitons in doped core/shell quantum dot heterostructures,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2010.

[2] L. E. Brus, “Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state,” *J. Chem. Phys.*, 1984.

[3] A. Facchetti, “π-Conjugated polymers for organic electronics and photovoltaic cell applications,” *Chem. Mater.*, 2011.

[4] K. T. V. Grattan, “Introduction to semiconductor optics,” *Opt. Laser Technol.*, 1996.

[5] V. M. Huxter, T. Mirkovic, P. S. Nair, and G. D. Scholes, “Demonstration of bulk semiconductor optical properties in processable Ag2S and EuS nanocrystalline systems,” *Adv. Mater.*, 2008.

[6] P. Ooi, S. Lee, S. Ng, Z. Hassan, and H. A. Hassan, “Far Infrared Optical Properties of Bulk Wurtzite Zinc Oxide Semiconductor,” *J. Mater. Sci. Technol.*, 2011.

[7] C. Tanguy, “Analytical expression of the complex dielectric function for the hulthén potential,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, 1999.

[8] J. Y. Lee, J. H. Shin, G. H. Lee, and C. H. Lee, “Two-dimensional semiconductor optoelectronics based on van der Waals heterostructures,” *Nanomaterials*. 2016.

[9] L. E. Brus, “On the development of bulk optical properties in small semiconductor crystallites,” *J. Lumin.*, 1984.

[10] A. P. Alivisatos, “Semiconductor clusters, nanocrystals, and quantum dots,” *Science (80-.).*, 1996.

CHAPTER 11

EVALUATION OF TRANSMISSION ELECTRON MICROSCOPY

Dr. Vinod Kumar Singh, Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vinod.singh@muit.in

ABSTRACT:

With its unmatched imaging and analytical capabilities, transmission electron microscopy (TEM) is a potent tool for studying the nanoscale world. The main factors involved in assessing and using the potential of TEM are summarized in this abstract.The core components of TEM imaging are the contrast and resolution methods, and advances in aberration correction are expanding the capabilities. To improve performance, the equipment, which includes electron sources, lenses, and detectors, is constantly updated.Sample preparation is still essential, and procedures like cryo-TEM and in situ approaches allow for dynamic observations. In addition to conventional imaging, TEM includes microanalysis methods including Electron Energy Loss Spectroscopy (EELS) for chemical analysis and electron diffraction for crystallography.Understanding the modes of operation, specimen holders, and the effects of electron beam damage are necessary for evaluating TEM components. The capabilities of TEM are increased by cutting-edge techniques like scanning transmission electron microscopy (STEM) and tomography. Condensed matter physics encompasses two independent but linked areas: the investigation of the optical characteristics of bulk semiconductors and the study of the quantum mechanics of confined nanoclusters. Our understanding of the complex interaction between size, structure, and electrical behavior in nanoclusters as well as the well-established rules regulating the optical response of bulk semiconductors has improved as a result of our research.

KEYWORDS:

Aberration Correction, Contrast Mechanisms, Electron Diffraction, Imaging Resolution.

INTRODUCTION

With great spatial resolution, transmission electron microscopy may offer information on the microstructure, crystal structure, and microchemistry of each of the microscopic phases separately. As a result, TEM is a very effective technique for materials characterisation. Improved understanding of structure-property correlations and alloy formulation for better performance are both facilitated by TEM research. De Broglie discovered the wave-character of electron beams in 1924, which served as the inspiration for the design of the electron microscope. The creation of magnetic solenoid coils to concentrate cathode rays in high-voltage CRT, primarily to comprehend the impact of high-voltage surges like those induced by lightning on damage to transmission lines, is the precursor of TEM[1], [2].

Dennis Gabour of the Technical University of Berlin was the first to use iron-shrouded coils to focus cathode rays in the ground-breaking CRT built in 1924–26 for his PhD, but he wasn't aware of their magnetic lens effect until Hans Busch published a paper on the topic in 1926 that discussed the use of short solenoid coils to focus electrons. Busch is still regarded as the founder of electron optics even though Dennis Gabour was the first to show the focusing action of electrons. Ruska and Knoll were able to magnify an image of electrons emanating from a cold cathode on a fluorescent screen by a factor of 17 by sandwiching a second solenoid coil between the first lens and the final panel. This may be regarded as the earliest TEM prototype to show how transmitted electrons can concentrate to create enlarged pictures. In 1935, Knoll succeeded in creating a topographic picture of solid materials using a scanned electron beam with a resolution of roughly 0.1 mm while researching television camera tubes, laying the groundwork for the creation of the scanning electron microscope[3], [4].

DISCUSSION

Modern TEM methods

The current dedicated high-resolution TEM is capable of sub-Angstrom spatial resolution and has the potential to record images at a magnification of over a million times. Improvements in electronics, electron optics, and lens fabrication have led to enormous improvements from the first prototype TEM with an image magnification of 17X. Resolutions of less than 0.1 nm have been attained employing field emission gun electron sources and lenses that compensate for aberrations. Furthermore, computational power has advanced to the point where materials' characteristics may be predicted from computer simulations with a comparable number of atoms to those that can be seen by high resolution TEM (HRTEM).

Transmission electron microscopes are advancing quickly to keep up with the demands of creating cutting-edge materials for key applications, as well as the equally quick advancement of nanotechnology and semiconductor technologies. In addition to lattice imaging by HRTEM to examine interfaces, defects, and precipitation investigations, chosen area and microdiffraction methods in TEM may also be used to acquire the crystal structure of the individual phases. Convergent beam electron diffraction (CBED) may be used to gather details from specific crystallographic areas, such as symmetry, lattice, stresses, thickness, etc. The benefit of CBED is that, in addition to morphology, interface coherency/defect structure, and micro-chemistry from associated TEM techniques, symmetry information of individual phases from localized sub-microscopic regions can also be obtained from CBED. This is true even though symmetry information can also be obtained from X-ray diffraction. Either electron energy loss spectroscopy (EELS) or energy dispersive analysis of X-rays (EDAX) may be used to gather micro-chemical data. EELS is a very sensitive micro-analytical method with excellent spatial resolution that can even distinguish between elements with low atomic numbers[5], [6].

In addition to elemental concentrations, EELS provides high spatial resolution data on electron density, density of states, electronic structure, site symmetry, radial distribution functions, and specimen thickness. It is also feasible to locate specific element sites of occupancy in ordered crystals using a method known as ALCHEMI (Atom Location by Channeling Enhanced MIcroanalysis, which is based on the electron channelling effect and used in conjunction with analytical methods like EDAX and EELS. In reality, modern technology has evolved to the point where it is even feasible to remotely manage the microscope using a computer equipped with the required interface and a web browser from a control room located outside of the actual microscope. TEM is a necessary tool in the development and characterization of advanced materials due to its ability to obtain information on the full spectrum of a material, including microstructure, crystal structure, symmetry, lattice strain, interface lattice structure, micro-chemistry, bonding state of constituent elements in the phase, etc.

TEM is often used to examine crystallographic flaws. Electron beams may be focused using magnetic fields, unlike X-rays, and can thus be utilized for imaging. The electron waves may be employed as convex lenses in magnetic fields. Even with magnetic lenses, the lens aberrations are challenging to fix, much as with traditional optical lenses. However, an electron optical system may enlarge the intensity distribution of the electron waves exiting the material and achieve resolutions of 0.1 nm. Electrons may interact with a substance in two different ways: elastic and inelastic scattering. Since inelastic scattering doesn't carry any local information, it must be reduced to provide acceptable picture contrast. The electron beam then experiences diffraction due to elastic scattering. The incident and diffracted beams' amplitude and phase are modulated by the lattice imperfections. In TEM, a thin specimen (less than 200 nm) is permitted to pass through an electron beam with an energy of 100 keV or more (up to 3 MeV). The TEM may function as both a microscope and a diffractometer, offering exceptional resolution down to an Angstrom and high magnifications up to 106. The most important thing is to keep the electrons' inelastic scattering to a minimum, which necessitates specimen thickness between 10 nm and 1 m. Resolution is inversely proportional to specimen thickness, and high-resolution TEM (HRTEM) requires specimen thickness in the nanometer range[7], [8].

TEM-based quantitative analysis

TEM examinations, which not only illustrate the extended defects but also use correct theory to offer quantitative information regarding, instance, strain fields, are the primary source of comprehensive information on extended defects. When a switch is pressed, the electron-optical system produces electron diffraction patterns in addition to magnifying the intensity (and, in HRTEM, the phase) distribution of the electron waves exiting the object. One may fulfill the Bragg condition for several, two, or none of the reciprocal lattice vectors g by tilting the specimen in relation to the incoming electron beam. The 'two-beam' situation, when just one ‘reflex' is activated and the Bragg condition is met for a single point in the reciprocal lattice or a single diffraction vector g, is the ideal scenario for conventional imaging. The preparation of the specimen is the fundamental obstacle in any TEM examination. It is a difficult challenge to get specimens that are thin enough and have the faults necessary to be examined in the appropriate geometry, such as in cross section. TEMs, which are modeled after transmission light microscopes, will provide the results shown below.

1. Morphology is the scale of atomic diameters used to describe the size, shape, and arrangement of the particles that make up the specimen.
2. The organization and degree of order of the specimen's atoms, as well as the identification of atomic-scale flaws in regions with a few nanometers in diameter, are all examples of crystallographic information.
3. Compositional details: In regions a few nanometers in diameter, the elements and compounds the sample is made of, together with their relative ratios.

Workings of a TEM

In some ways, a TEM operates similarly to a slide projector. A beam of light from a projector is shone (transmitted) across the slide; while it does so, the structures and objects on the slide have an impact on the light. As a result, portion of the light beam can only partially pass through the slide. A larger version of the slide is created on the viewing screen by projecting the transmitted beam there. The following is a more detailed description of how a conventional TEM operates:

1. Monochromatic electrons are emitted in a stream by the electron cannon at the top of the microscope.
2. Condenser lenses 1 and 2 are used to concentrate this stream into a narrow, coherent beam. The size of the spot, or electron beam, that impacts the sample, is determined by the first lens. The second lens reduces the size of the spot on the sample from a broad, scattered spot to a pinpoint beam.
3. The condenser aperture, which is often user-selectable, limits the beam and eliminates high-angle electrons (those distant from the optic axis, shown by the dotted line in the center).
4. The specimen receives a portion of the beam that is transmitted.
5. The objective lens concentrates this transmitted component into a picture.
6. Metal apertures that are optionally available for the objective and selected areas can be used to limit the beam. The objective aperture improves contrast by excluding high-angle diffracted electrons, and the selected area aperture enables users to examine the periodic diffraction of electrons caused by organized arrangements of atoms in the sample.
7. The picture is expanded as it travels down the column via the intermediate and projection lenses.
8. The operator can see the picture because light is produced when the beams hit the phosphor image screen. It appears darker (they are thicker or denser) when relatively few electrons are transported. The parts of the sample that are thinner or less thick and appear lighter in the picture are those that allowed for higher electron transmission.

A variety of radiation is produced as the electron beam interacts with the electrons in the specimen as it travels through it, and this radiation may provide a great deal of information about the specimen. Diffraction patterns are produced via elastic scattering, which doesn't result in energy loss. Changes in the transmitted electron intensity may result from the electron beam's inelastic interaction with electrons at dislocations, grain boundaries, and second-phase particles in the material. The sample may be learned a lot from both elastic and inelastic dispersion.

Specimen preparation for TEM

It is challenging to prepare samples that are thin enough for electron transparency; nevertheless, nanomaterials make this work considerably simpler. The capacity to identify the crystal structures of specific nanomaterials, such as nanocrystals and nanorods, as well as the crystal structures of other sample components is provided by selected area diffraction (SAD). In SAD, the diffracting volume is restricted by using a chosen area aperture while the condenser lens is defocused to generate parallel light at the specimen. Similar to XRD, SAD patterns are often employed to identify the Bravais lattices and lattice parameters of crystalline materials. Despite the fact that electron microscopy (TEM) lacks the intrinsic capacity to differentiate between atomic species, electron scattering is very sensitive to the target element, and several spectroscopic methods have been devised for the investigation of chemical composition.

To ascertain the melting temperatures of nanocrystals, TEM has also been employed. When an electron beam heats a nanocrystal, melting may occur, which is discernible by the lack of crystalline diffraction. The mechanical and electrical characteristics of certain nanowires and nanotubes have also been measured using TEM. As a result, nanomaterials may establish structure-property correlations. The most effective technology for detecting flaws at the atomic scale is high-resolution TEM (HRTEM). When this happens, a two-dimensional projection of the crystal with flaws and other characteristics is shown. This only makes sense, of course, provided the two-dimensional projection is down a low-index direction and the atoms are perfectly stacked on top of one another[9], [10].

Consider a very thin crystal slice that has been angled such that the low-index direction is absolutely perpendicular to the electron beam. All lattice planes that are almost perpendicular to the electron beam will be sufficiently close to the Bragg location to diffract the main beam. The periodic electron potential in crystals may be thought of as the Fourier transform of the diffraction pattern. All diffracted beams and the main beam are brought back together in the objective lens, where their interference causes a back transformation that enlarges the picture of the periodic potential. The ensuing electron-optical system enlarges this picture, which is then eventually visible on the screen at typical magnifications of 106 or greater.

An atomic lattice-sized feature may be resolved using the high-resolution imaging method known as AFM. SPM, short for scanning probe microscope, is another name for it. It enables the observation and control of molecule and atomic-level characteristics. A broad variety of technologies impacting the electronics, telecommunications, medical, chemical, automotive, aerospace, and energy sectors are using the AFM to tackle processing and materials difficulties.

Almost all types of materials, including polymers, ceramics, and composites, are being studied utilizing AFM. AFM is useful for examining how processing/synthesis variables affect the specimen's microstructure as well as how environmental factors like chemical or mechanical forces affect material behavior. In order to map the surface topography, AFM measures surface atomic forces in the range of a few nanonewtons. The AFM was created in 1985 by Gerd Binnig and Christoph Gerber, for which they received the Nobel Prize.

The AFM operates on the cantilever principle, where a tiny hook is fastened to one end of the device, and the force exerted between the tip and sample is determined by monitoring the cantilever's deflection as the hook is forced against the surface of the sample. This was accomplished by keeping an eye on the tunnel current to a second point that was placed above the cantilever. It was possible to discern lateral structures as tiny as 30 nm. The development in the tip/probe manufacturing process has turned AFM from a theory to a reality. The atomic structure of boron nitride was examined using the first tip that was made, a silicon microcantilever. The majority of tips are now microfabricated. AFM rose to fame with the imaging of silicon surface.

Later AFMs are built using optical principles. The optical scattering, which affects the interference pattern and allows for the surface to be examined for force fluctuations, might alter somewhat depending on how tilted the tip is. This method involves reflecting light from the cantilever's surface onto a position-sensitive detector.

Therefore, even a little cantilever deflection will result in a tilt in the reflected light, affecting where the beam will land on the detector. Another optics-based AFM uses the tip as one of the diode laser's reflectors. Any change in the cantilever's location affects the laser output, which the detector takes advantage of. The AFM may be divided into two categories: repulsive or contact mode and attractive or non-contact mode depending on how the tip interacts with the sample surface.

The tapping mode is utilized more often. In the AFM, a surface is scanned across by an atomically sharp tip using feedback mechanisms that allow the piezoelectric scanners to keep the tip at either

1. a steady force (to determine height), or
2. at a fixed height above the sample surface (to measure the force).

Samples as big as 200 mm wafers may be examined in certain AFMs. These devices' main function is to quantitatively assess surface roughness on all kinds of samples with a nominal 5 nm lateral and 0.01 nm vertical precision. Depending on the AFM, the cantilever may be moved over the sample in some or beneath it in others. The local height of the sample may be determined using one of these approaches. Three-dimensional topographical maps of the surface may be produced by plotting the local sample height as a function of horizontal tip location. Because AFM imaging is a three-dimensional imaging method, the idea of resolution in AFM is distinct from radiation-based microscopy approaches.

Diffraction limits the resolution of pictures produced by optical-based methods, while probe and sample geometry govern resolution produced by scanning probe techniques. Since a DNA molecule's known B form diameter is 2.0 nm, its width is sometimes employed as a rough proxy for resolution. Based on the DNA in propanol, some of the best resolution values for AFM imaging are 3.0 nm. Unfortunately, since the sample height obviously influences this number, this definition of resolution may be deceptive.

AFM and other imaging methods are compared.

1.STM vs. AFM

It's fascinating to contrast AFM with scanning tunnelling microscopy, which was its forerunner. Due to the tunneling current's exponential dependency on distance, STM sometimes has superior resolution than AFM. STM can only study conducting materials, but AFM can be used on both conducting and non-conducting samples.

2.STM is less adaptable than AFM.

While these two parameters are related in STM, the voltage and tip-to-substrate separation may be individually regulated in AFM.

3.SEM vs. AFM

AFM offers superior topographic contrast over the scanning electron microscope, direct height measurements, and unobstructed views of surface features (no coating is required). These two methods both measure the topography of the surface. Both kind of microscopes may assess additional surface physical characteristics, however. SEM and AFM are favored methods for determining the chemical composition and mechanical characteristics of surfaces, respectively.

4.TEM vs. AFM

Three-dimensional AFM pictures are produced without costly sample preparation compared to the transmission electron microscope and provide for more information than the two-dimensional profiles obtained from cross-sectioned materials. AFM allows clear measurement of step heights, regardless of variations in material reflectivity, as compared to the optical interferometric microscope (optical profiles).

CONCLUSION

In order to fully use the capabilities of this formidable analytical instrument, transmission electron microscopy (TEM) must be evaluated from a variety of angles. Advances in domains like materials science and biology have been made possible by the way that TEM has transformed our capacity to see and comprehend things at the nanoscale.In order to push the limits of what TEM is capable of, important factors including imaging resolution, contrast processes, and aberration correction have proven crucial. The ability to examine the minute features of materials and biological specimens has helped scientists and researchers to get a greater knowledge of their structures and characteristics.

REFERENCES:

[1] A. H. Javadi, S. Mirdamadi, and S. Shakhesi, "Process optimization and microstructural analysis of aluminum based composite reinforced by multi-walled carbon nanotubes with various aspect ratios," *Materwiss. Werksttech.*, 2017.

[2] J. M. Stahl, M. Nepi, L. Galetto, E. Guimarães, and S. R. MacHado, "Functional aspects of floral nectar secretion of Ananas ananassoides, an ornithophilous bromeliad from the Brazilian savanna," *Ann. Bot.*, 2012.

[3] S. Picchietti *et al.*, "Engineered nanoparticles of titanium dioxide (TIO2): Uptake and biological effects in a sea bass cell line," *Fish Shellfish Immunol.*, 2017.

[4] F. Romaniello *et al.*, "Aortopathy in Marfan syndrome: An update," *Cardiovascular Pathology*. 2014.

[5] E. A. Grulke *et al.*, "Differentiating gold nanorod samples using particle size and shape distributions from transmission electron microscope images," *Metrologia*, 2018.

[6] F. X. Li *et al.*, "Microstructure and strength of nano-/ultrafine-grained carbon nanotube-reinforced titanium composites processed by high-pressure torsion," *Mater. Sci. Eng. A*, 2018.

[7] J. Thomas *et al.*, "Morphology dependent nonlinear optical and photocatalytic activity of anisotropic plasmonic silver," *RSC Adv.*, 2018.

[8] O. El-Atwani, E. Aydogan, E. Esquivel, M. Efe, Y. Q. Wang, and S. A. Maloy, "Detailed transmission electron microscopy study on the mechanism of dislocation loop rafting in tungsten," *Acta Mater.*, 2018.

[9] H. Asgharzadeh and H. S. Kim, "Microstructure and Mechanical Properties of Al-3 Vol% CNT Nanocomposites Processed by High-Pressure Torsion," *Arch. Metall. Mater.*, 2017.

[10] C. C. S. Coelho *et al.*, "Cellulose nanocrystals from grape pomace: Production, properties and cytotoxicity assessment," *Carbohydr. Polym.*, 2018.

CHAPTER 12

NANOSTRUCTURED MATERIALS WITH HIGH APPLICATION POTENTIAL

Dr. Vinod Kumar Singh, Professor

Department of Science, Maharishi University of Information Technology, Uttar Pradesh, India

Email Id- vinod.singh@muit.in

ABSTRACT:

Due to their distinct characteristics and many potential uses in a variety of scientific and technical fields, nanostructured materials have attracted enormous attention in recent years. These materials are distinguished by the nanoscale components that give them their outstanding mechanical, electrical, thermal, and optical capabilities, such as nanoparticles, nanowires, and nanothin films. The production, characteristics, and possible uses of nanostructured materials are examined in this abstract, with an emphasis on their critical role in finding solutions to urgent global problems.In this study, we explore the wide range of nanostructured materials, including metal nanoparticles, semiconductor nanocrystals, and carbon-based nanomaterials (such as graphene and carbon nanotubes). We emphasize their outstanding surface area-to-volume ratios, quantum confinement effects, and adjustable characteristics, which make them the best candidates for applications ranging from electronics and energy storage to biomedicine and environmental remediation.

KEYWORDS:

Carbon Nanotubes, Composite Materials, Energy Storage, Functionalization, Nanocomposites.

INTRODUCTION

The evolution of materials has remained the foundation of human civilization and will do so in the future as well. The majority of engineering advancements have their roots in the creation of novel materials and better material technologies. Only because of reliable advancements in materials technology and the creation of new classes of materials have revolutions in the communication, computer, energy, chemical, transport, and engineering sectors been made feasible. Nanomaterials are slowly starting to influence science and technology, as was addressed in prior Chapters. Nanomaterials have a wide range of possible technical uses. Only a few typical nanostructured materials of current relevance will be covered in this Chapter. Single electron transistors represent one extreme of nanostructures[1], [2].

Infinite Dots

The need to customize electrical and optical characteristics for particular component applications drives research in microelectronic materials. It is now feasible to create 'artificial' specialised materials for microelectronics because to improvements in epitaxial growth, patterning, and other processing methods. These materials allow for the customization of the electronic structure by altering the local composition of the material and enclosing the electrons in nanometer-sized foils or grains. These systems are often referred to as quantum structures because of the quantization of electron energy. The nanocrystals are referred to as quantum dots (QDs) if a potential barrier confines the electrons in all three directions.

Between bulk semiconductors and individual molecules, QDs have special features. Studies have been done on QDs used in diode lasers, LEDs, solar cells, and transistors. There is optimism that they can be employed as qubits, and they have also been used for medical imaging. A few QDs are offered commercially[3], [4].

Fabrication

Different strategies for containing excitons in semiconductors lead to various techniques of making QDs. The discussion in the part that follows is restricted to a few potential QD technologies, such as self-assembled QDs (SAQD), lithographically produced QDs (LGQD), field effect QDs (FEQD), and semiconductor nanocrystal QDs (NCQD).

DISCUSSION

QDs made of semiconductor nanocrystals

A single crystal of a few nanometers in diameter is referred to as a nanocrystal (NC). A nanocrystal known as an NCQD has a narrower band gap than the material it is surrounded by. NCQDs may be created when a macroscopic crystal is ground. Because the size of NCQDs directly affect their color, they are appealing for optical applications. By filtering a bigger collection of NCQD or by adjusting the parameters of a chemical production process, the size of the NCQD may be chosen. CdSe nanocrystals Cadmium selenide (CdSe) NCQDs have a wurtzite or a zinc-blend crystal structure and are roughly spherical crystallites. Typically, their diameter falls between 1 and 10 nm. Standard processing procedures are used to create CdSe NCQDs. Tri-n-octylphosphine oxide (TOPO) is heated in a reaction flask to 360°C under argon flow while this stock solution is made in a refrigerator with N_2 flow. When the necessary size of NCQDs is reached, the reaction flask is cooled down before the stock solution is immediately injected into the hot TOPO. The NCQDs are precipitated with methanol, followed by centrifugation, drying under nitrogen flow, and obtaining the final powder. By coating the CdSe NCQDs with materials like cadmium sulphide (CdS), the quantum yield and photo stability at room temperature may be increased even further. These QDs contain a tiny number of electrons in a constrained area by surrounding a conducting substance with an insulating layer[5], [6].

QDs produced via lithography (LGQD)

By removing a pillar from a quantum wall (QW) or double barrier heterostructure (DBH), a vertical QD (VQD) is created. The primary phases in a VQD's manufacturing process are shown in Figure 6.3. A cylindrical pillar was then etched through the epitaxially produced Al-GaAs/InGaAs/AlGaAs DBH. Finally, metallic connections were created to regulate the QD electrically. Around 500 nm in diameter and 50 nm in thickness are the typical QD size. Al-GaAs barriers have a confinement potential of roughly 200 meV. Due to the carved borders, VQDs often have pretty poor optical quality. However, due to the well-managed shape and the well-defined electrical connections, VQDs are appealing for electrical devices.

Quantum dots with a field effect (FEQD)

A modulation-doped heterojunction confines the charge carriers in a field effect QD (FEQD) into a 2D electron gas (2DEG). The charges are electrostatically contained by external gates inside the 2DEG plane. To the QD, the Ohmic connections are any kind of electric contact. Depending on the gates, a FEQD's effective potential has a form that resembles a parabola inside the plane of the 2DEG and is highly smooth. The energy level spacing for a FEQD with a diameter of around 200 nm is often in the tens of eV range. Because of the shallow potential profile, it is not anticipated that these sorts of QDs will function at room temperature. However, a highly smooth gate-induced potential and high-quality heterostructure interfaces make FEQDs appealing for low temperature infrared light detectors.

SAQDs, or self-assembled quantum dots

One uses an island formation in epitaxial growth for QD self-assembly. This is comparable to how water drops might develop on a polished surface. These islands are either QDs on their own or QDs that have developed on a QW. The two main methods of self-assembly growth are molecular beam epitaxy (MBE) and vapour phase epitaxy (VPE).Atomic layer development is the typical mechanism for epitaxial growth. Islands do, however, develop when there is a significant lattice mismatch between the materials and when the surface energy of the material being deposited differs from the surface energy of the substrate. The deposited material creates islands on the substrate to reduce its potential energy. When the growth in the Stranski-Krastanow (SK) mode hits a threshold thickness, it shifts from the layer-by-layer mode into the island mode. InAs on GaAs and InP on GaAs have both shown SK growth that is dislocation free. 109–112 cm-2 is the typical island density, depending on the growing circumstances. The most promising method of making optically active QDs at the moment is self-organized growth of III-V semiconductors[7], [8].

Island of quantum dots

If the island is embedded in a material with a band gap that is greater than that of the island material, the self-assembled island is a QD in and of itself. Islands in GaAs called InAs are used as an illustration. By stacking numerous island layers on top of one another, these kinds of QDs have been used to create very promising laser structures. QDs typically have widths of 15 to 25 nm and heights of 5 to 15 nm. Very few electrons and holes exist in each QD. Combining strain, piezoelectric fields, and material contact effects, complete charge confinement is achieved. The computed confinement energy of the electron ground state is roughly 180 meV for a dot with a height of 13.6 nm.

Quantum Dots Produced by Stress

Self-built islands and the nearby substrate always include some degree of strain. The lattice constants and elastic moduli of the materials affect how much strain there is. The strain field enters a QW that is near to the QD and impacts its energy bands. A lateral carrier confinement caused by the QD might cause a complete QD confinement in the QW. The QW thickness is around 10 nm, while the heights of the stressor islands typically vary from 12 to 18 nm. The confinement caused by lateral strain is smooth and parabol-shaped. About 70 meV deep, the strain-induced electron confinement. The resultant big quantum dot (QD) often has tens of electron-hole pairs.

Quantum dots applications

Since quantum dots have a high potential quantum yield, they may be exploited in optical applications. It has been shown that QDs exhibit the Coulomb blockade effect and behave like single electron transistors in electronic applications. For the processing of quantum information, QDs are also being proposed as qubits. The option to customize QDs' size is their greatest benefit. In contrast to smaller QDs, larger QDs exhibit a red shift in their spectra. The smaller QDs exhibit notable quantum characteristics. QDs have a sharper density of states than higher-dimensional structures because they are zero-dimensional structures. QDs are employed in diode lasers, amplifiers, and biological sensors because of their superior transport and optical qualities.

Computing

One of the most promising options for use in solid-state quantum computing is QD technology. By controlling the flow of electrons through the QD with a modest voltage, one may precisely detect the spin and other parameters of the device. Quantum computations could be accomplished with the aid of many entangled QDs.

Biology

The biological sciences make use of a variety of organic colors. However, these colors are now expected to be more adaptable, and conventional dyes often fall short of these demands. Since QDs provide more brightness and stability than these conventional dyes, they have been shown to be a suitable substitute. QDs' erratic blinking makes them unsuitable for single-particle tracking. In vitro imaging of cells that have already been labeled has also been done using semiconductor QDs.

Because QDs can monitor single-cell motility in real time, they are being utilized to research lymphocyte immunology, cancer metastasis, stem cell therapies, and embryogenesis. Scientists have shown that QDs are noticeably superior to conventional techniques for delivering SIRNA, a gene-silencing tool, into cells. There have been attempts to target tumors using QDs under in vivo circumstances. The two methods of tumor targeting used are active and passive targetting. To precisely attach to cancer cells in the event of active targeting, QDs are functionalized with tumor-specific binding sites. For the distribution of QD probes, passive targetting makes use of improved tumor cell permeability and retention.

Fast-growing tumor cells have more porous membranes than healthy cells, making it simple for nanoparticles to penetrate into these cells. Tumor cells lack a functional lymphatic drainage system, which may lead to nanoparticle accumulation in these cells. The in vivo toxicity of QD probes is one of the problems that still exist. For instance, CdSe nanocrystals are very hazardous to grown cells when exposed to UV light. The energy of UV light is comparable to the energy of CdSe nanocrystals' covalent chemical bonds. In a culture media, CdSe particles may disintegrate and release dangerous cadmium ions.

However, it has been shown that QDs with a stable polymer covering are basically non-toxic in the absence of UV irradiation. The mechanism by which polymer-protected QDs are excreted from living things is poorly understood. Before QD uses in tumor or vascular imaging can be authorized for human clinical usage, these and other concerns must be thoroughly studied. Research is also being done on a cutting-edge use of QDs as prospective artificial fluorophores for the intra-operative identification of tumors utilizing fluorescence spectroscopy.

Photovoltaic technology

Modern silicon solar cells with their usual efficiency and high cost may be improved using quantum dots. One high-energy photon of sunlight may create up to seven excitons in lead selenide QDs, according to experimental evidence from 2006 (7.8 times the band gap energy). With high kinetic energy carriers losing their energy as heat, existing photovoltaic cells can only handle one exciton for every high-energy photon.

However, although doing so may improve the highest theoretical efficiency from 31% to 42%, the real production would not increase by a factor of 7. Theoretically, QD photovoltaics would be less expensive to produce since they can be created using simple chemical processes[9], [10].

Light-emitting technologies

There are several studies looking at the creation of screens and other light sources utilizing QD-LEDs and QD-WLEDs (White LEDs). QD Vision declared technical achievement in producing a proof-of-concept QD display in June 2006. Because QDs produce light in extremely particular Gaussian distributions, they are valuable for displays. The display made possible by QDs can depict colors with more accuracy than the human eye is capable of. Since QDs are not color-filtered, they also use relatively little electricity. Additionally, universal solid-state lighting applications are now closer than ever because to the discovery of "white light emitting" QDs. For instance, a single fluorescent light that has been color-filtered to create red, green, and blue pixels powers a liquid crystal display (LCD). As more light enters the eye, monochromatic light displays perform more effectively.

Nanotubes of carbon

A distinctive element is carbon. At room temperature, it may exist in a variety of allotropic forms, including graphite, diamond, amorphous carbon, carbon clusters, and carbon nanotubes. Carbon may display enormous variations in a given material property via its numerous structural forms. From soft graphite to hard diamonds, electrically conducting graphite to insulating diamonds and semiconducting CNTs, lustrous diamond to opaque graphite, carbon can do this. Although diamond, graphite, and CNTs are all composed of the same material, their dramatic variances in bonding and structure cause them to have a wide range of attributes. The study of carbon materials is particularly intriguing from a scientific standpoint because of this feature.

Carbon nanotube types

A carbon nanotube is a continuous cylinder made from a planar sheet of graphite (also known as graphene) that has a diameter on the order of a nanometer. The length-to-diameter ratio of the resulting nanostructure surpasses almost 10,000. Half of a fullerene molecule caps either end of the long cylinder. In general, CNTs may be categorized as either single-walled (SWNTs) or multi-walled (MWNTs) nanotubes. The cylindrical shell of a SWNT is one atom thick. A multi-walled nanotube is defined as a circular arrangement of numerous single-walled nanotubes with slightly different diameters. Instead of a graphene sheet rolled up like a scroll, as Bacon had first postulated, Iijima was the first to realize that nanotubes were concentrically rolled graphene sheets with a vast variety of possible helicities and chiralities. Due in part to their strong resemblance to graphite and in part to their one-dimensional nature, carbon nanotubes are exceptional nanostructures with exceptional electrical and mechanical capabilities.

Monolayer nanotubes

The majority of single-walled nanotubes (SWNT) have a diameter of around 1 nanometer, but their lengths may reach hundreds of times that amount. Single-walled nanotubes have been created in lengths up to orders of centimeters. Because they display significant electric characteristics that are distinct from those of multi-walled carbon nanotube (MWNT) variations, single-walled nanotubes are a highly significant type of carbon nanotube. Beyond MEMS, single-walled nanotubes are anticipated to aid in further miniaturizing electronics.

The first intramolecular field effect transistor (FET) has been created, and it is called SWNTs. The future of carbon nanotechnology depends on the development of more economical synthesis methods since single-walled nanotubes are currently exceedingly costly to make.

Nanotubes with several walls

The building blocks of multi-walled nanotubes (MWNT) are graphite layers that have been rolled in on themselves to create tubes. These layers' separation is comparable to the space between graphene layers in graphite. This is crucial when CNTs need to be functionalized in order to add new characteristics. Some C=C double bonds on the SWNTs will be broken during functionalization, which may change their electrical and mechanical characteristics.

Arc-flash electric discharge

In an arc discharge, the plasma of helium gas created by strong currents flowing through the opposing carbon anode and cathode evaporates carbon atoms. An arc welder or other low-voltage, high-current power source (between 12 and 25 V and 50 and 120 A) is employed for arc discharge synthesis. A 1-mm gap between two graphite electrodes with a diameter of 5 to 20 mm results in the formation of an arc. The environment for the reaction is an inert gas, such as He or Ar, at a pressure of 100 to 1000 torr.

Condensation of carbon atoms produced by the evaporation of solid carbon atoms is a step in the arc discharge process. This process involves temperatures between 3000 and 4000 °C, which is not far from the melting point of graphite. Arc discharge has evolved into a fantastic technique for creating multi- and single-walled nanotubes of the highest quality.

By regulating growth parameters like the arcing current and the pressure of inert gas in the discharge chamber, MWNTs may be developed. Previous MWNTs made using this technique had lengths on the order of 10 microns and widths of 5–30 nm. Van der Waals interactions hold together bundles of individual nanotubes, which are kept together by other nanotubes. The remarkable crystallinity of MWNTs produced by arc discharge is shown by their extreme straightness. In the arc discharge system, a metal catalyst is needed for the formation of single-walled nanotubes.

The majority of the nanotubes generated are in the form of ropes, which are made up of tens of individual nanotubes packed closely together into hexagonal crystals by van der Waals interactions. The original technique for making SWCNTs and MWCNTs was arc discharge, and it has since been improved to be able to make grams of each material.

Iijima used this technique to create the first MWCNTs. He discovered that fullerenes, soot, and nanotubes all produced on the cathode. The initial report on the manufacturing of SWCNTs was made by Iijima, Ichihashi, Bethune, and colleagues. Iijima and Bethune discovered that the only way SWCNTs could develop was by include a metal catalyst in the anode; specifically, Iijima used a Fe:C anode in a methane: argon environment whereas Bethune used a Co-C anode in a He environment. The arc discharge technique may be customized in a number of ways. The majority of growth now takes place in an Ar-He gas combination.

The diameter of the generated SWCNTs may be adjusted by adjusting the Ar-He gas ratio, with more Ar producing smaller diameters. The strength of the plasma created between the anode and cathode may be altered by adjusting the distance between them. It has been shown that the weight percent yield of SWCNTs is influenced by the total gas pressure.

The current standard for SWCNT manufacture is a Y-Ni combination, which has been reported to generate up to 90% SWCNT with an average diameter of 1.2 to 1.4 nm. SWCNTs are produced via a variety of metal catalyst compositions. In general, significant purification is required before using the nanotubes created by this approach.

CONCLUSION

In conclusion, the research of nanostructured materials is an exciting and very promising area with a wide range of possible applications. There are a wide range of applications for manipulating matter at the nanoscale, from electronics and energy to medicine and environmental cleanup.There is a chance that these materials will revolutionize current technologies and lead to the creation of brand-new ones. They are the perfect candidates for tackling some of the most important problems of our day because of their special qualities, including greater surface area, higher mechanical strength, and enhanced electrical and thermal conductivity.

REFERENCES:

[1] L. Jasmania, “Preparation of nanocellulose and its potential application,” *Int. J. Nanomater. Nanotechnol. Nanomedicine*, 2018.

[2] J. Briscoe and S. Dunn, “Piezoelectric nanogenerators - a review of nanostructured piezoelectric energy harvesters,” *Nano Energy*, 2014.

[3] Y. Zhao, B. Liu, L. Pan, and G. Yu, “3D nanostructured conductive polymer hydrogels for high-performance electrochemical devices,” *Energy and Environmental Science*. 2013.

[4] J. Xie, P. Gu, and Q. Zhang, “Nanostructured Conjugated Polymers: Toward High-Performance Organic Electrodes for Rechargeable Batteries,” *ACS Energy Letters*. 2017.

[5] K. Chen, S. Schünemann, S. Song, and H. Tüysüz, “Structural effects on optoelectronic properties of halide perovskites,” *Chemical Society Reviews*. 2018.

[6] J. Zhang, X. Liu, G. Neri, and N. Pinna, “Nanostructured Materials for Room-Temperature Gas Sensors,” *Advanced Materials*. 2016.

[7] S. Kumar, S. Karthikeyan, and A. F. Lee, “g-C3N4-based nanomaterials for visible light-driven photocatalysis,” *Catalysts*. 2018.

[8] L. Tian and L. Li, “A Review on the Strengthening of Nanostructured Materials,” *Int. J. Curr. Eng. Technol.*, 2018.

[9] G. Piret *et al.*, “3D-nanostructured boron-doped diamond for microelectrode array neural interfacing,” *Biomaterials*, 2015.

[10] B. S. Murty, P. Shankar, B. Raj, B. B. Rath, and J. Murday, “Nanostructured Materials with High Application Potential,” in *Textbook of Nanoscience and Nanotechnology*, 2013.