CHAPTER 1 INTRODUCTION TO NANOSTRUCTURES

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1.1 ORIGIN OF NANOTECHNOLOGY

The prefix "nano," derived from the Greek "nanos" meaning "dwarf," has gained a position of prominence in scientific literature. Many novel terms have been introduced in recent publications, such as in the jounals Science and Nature, which include nanoantennas, nanoarrays, nanocavities, nanocrystals, nanoelectronics, nanoencapsulation, nanofibers, nanolithography, nanomagnets, nanopatterning, nanoporous, nanoscaffolds, nanovalves, and so on. The concept behind nanoscience and nanotechnology was initiated by a talk entitled "There's Plenty of Room at the Bottom" by the eminent physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists can manipulate and control individual atoms and molecules in a nanostructure. Over a decade later, Professor Norio Taniguchi introduced the term nanotechnology in the explorations of ultraprecision machining. It was only with the development of the scanning tunneling microscope in 1981, which provided the ability to "see" individual atoms, that modern nanotechnology began. These interesting facts about nanotechnology have been addressed by Bayda *et al.* (2020).

In general, nanoscience is referred to as the study of the relations between physical properties and material dimensions on the nanometer scale. Nanotechnology can be defined as equipment for the design, fabrication, and application of nanostructures and nanomaterials. Nanoscience and nanotechnology include the idea to observe and control individual atoms and molecules. The age of nanotechnology has evolved with the development of precise tools such as the scanning tunneling microscope and the atomic force microscope.

Nano Scaled Structural Problems: Static and Dynamic Behaviors, Snehashish Chakraverty

As reported by Jeevanandam *et al.* (2018), materials have been in use for several centuries before the proposal of the modern nanoscience and nanotechnology fields. To illustrate this fact, the Chinese are believed to have applied Au nanoparticles (inorganic dye) to introduce a red color into their ceramic porcelains more than 1000 years ago. An exhaustive study on the preparation and properties of colloidal gold was first published in the middle of the 19th century, but the application of colloidal gold has a long and rich history. The colloidal dispersion of gold developed by Faraday in 1857, before being destroyed during World War II, was stable for almost a century. In medical application, colloidal gold has been used for the treatment of arthritis and is even done so currently. A number of diseases have also been diagnosed by the interaction of colloidal gold with spinal fluid obtained from the patient.

1.2 SIGNIFICANCE OF NANOSTRUCTURES

In recent years, nanosized structures have attracted much attention from the research community owing to their extraordinary physical, chemical, mechanical, and electrical properties (Pradhan and Phadikar, 2009). One can easily find the following uses for nanostructures, which have helped to advance nanotechnology.

- In nanoelectronics, silicon may soon be replaced by carbon nanotubes to develop lighter yet efficient microchips and devices.
- With growing energy demands, solar panels and hydrogen fuel cells can be developed using nanostructural components to increase their efficiency. Additionally, the use of such renewable resources will be environmentally friendly and can help to limit CO_2 emissions which has indeed become a major concern these days.
- In the field of nanomedicine, biocompatible tunneling nanotubes can help to deliver drugs to precise targets and monitor health conditions. Creating functional organic or synthetic nanostructural components for medical implanted devices is certainly challenging, yet breakthroughs are being made in developing artificial joints, larynxes, bone prostheses, pacemakers, and so on.
- To improve air quality, catalysts made from nanoparticles are used to transform hazardous gases released from industries and automobiles into harmless gases.
- Nanoscale structures (nanoscale rods, rings, beams, plates, and shells) have been implemented in fundamental structural parts of various nanoelectromechanical systems (NEMS). NEMS-based devices include nanomechanical resonators, nanoscale mass sensors, electromechanical nanoactuators, and nanoenergy harvesters, which are just a few devices with promising scope in different areas of nanotechnology, such as nanoelectronics, nanomachines, and nanomedicine.
- It is worth investigating the dynamic characteristics of such nanostructures when subjected to external mechanical loads, pressures, or even stresses (Farajpour *et al.*, 2018). Performing precise experiments on such a scale is not only challenging, but also cumbersome and expensive (Phadikar and Pradhan, 2010). Therefore, the continuum-based modeling and simulations related to molecular dynamics have attracted different researchers throughout the globe to deal with such complicated problems, and these will be covered in the subsequent chapters.

1.3 NANOPARTICLES AND NANODEVICES

Even to date, scientists have not precisely defined nanomaterials, but they may be partially characterized by their extremely tiny size (measured in nanometers). A nanometer is one millionth of a millimeter, which is approximately 10^4 times smaller than the diameter of a human hair. Nanosized particles do exist in nature (blood-borne proteins, blood cells, etc.) and can be developed from a variety of products (carbon or minerals like silver), but nanomaterials must have at least one dimension less than approximately 100 nanometers. Materials engineered to such a small scale are often referred to as engineered nanomaterials (ENMs), which can have very unique optical, magnetic, electrical, and other properties. It has clearly been mentioned by Jeevanandam *et al.* (2018) that nanodevices are nanoparticles that are created to interact with cells and tissues and are able to perform very specific tasks. The recent progress made in integrated nanodevices has led to technological advancements in microfabrication and microelectronics applications.

1.4 NANOMATERIALS

Nanostructured materials are those with at least one dimension on the nanometer scale, which include nanoparticles (quantum dots, when exhibiting quantum effects), nanorods and nanowires, thin films, and bulk materials. Based on their origin, as suggested by Jeevanandam *et al.* (2018), they can be classified into natural and synthetic.

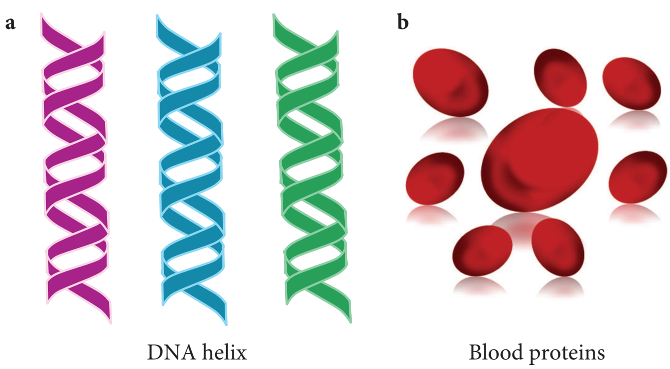


FIG. 1.1
Nanostructural components in living beings.

i. **Natural nanomaterials**
   - These materials are produced in nature either by biological species or through anthropogenic activities, which enables the classification of naturally occurring nanomaterials as organic and inorganic.
   - Organic nanomaterials can occur naturally, such as wax crystals covering a lotus, butterfly wing scales, blood-borne proteins essential for life, and lipids found in the blood and body fat. Two such nanostructural components in living beings are shown in Fig. 1.1.
   - A few other examples are interplanetary dust falling to Earth at the rate of thousands of tons per year, atmospheric dust particles, and undoubtedly viruses, which all have diameters in

the nanometer range. Another example is the SARS-Co-V-2 virus that has resulted in the current COVID-19 pandemic, which has created major havoc worldwide in different sectors (uncountable casualties, economic recession, tourism disruption, unemployment, etc.).

ii. **Synthetic (engineered) nanomaterials**
- These are produced by mechanical grinding, engine exhaust and smoke, or synthesized by physical, chemical, biological, or hybrid methods. However, scientists are particularly interested in ENMs, which are designed for commercial use.
- Thousands of widely used products including sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, and electronics are manufactured using ENMs. There is wide implementation of such nanomaterials in medical diagnosis, imaging and drug delivery, and in environmental remediation to name a few.
- The following discussion will provide the gradual development of synthetic nanomaterials starting with fullerene (discovered by Buckminster Fuller) up to graphene-based nanomaterials. The evolution of synthetic (or engineered) nanomaterials is depicted in Fig. 1.2 and details regarding these materials are described in the subsequent discussion.

C_{60} Buckminsterfullerene ⟹ **Nanotubes** ⟹ **Graphene based nanomaterials**

C_{60} Buckminsterfullerene

1. Discovered by Harry Kroto, Richard Smalley, and Robert Curl in 1985, who together won Nobel Prize in Chemistry in 1996.

2. A soccer ball-like molecule made of pure carbon atoms, which is a polygon with 60 vertices and 32 faces.

Nanotubes

1. Carbon Nanotubes (CNTs): Discovered by Sumio Ijima in 1991 as Multi-Walled carbon shoot by arc discharge method and later on he found single walled Nanotubes (SWNTs) in 1993.

2. Boron Carbon Nitride Nanotube (BNNT): Similar tubular nanostructure as carbon nanotube (CNT) in which boron and nitrogen atoms arranged in a hexagonal network.

3. DNA Nanotube: Developed as self-assembled DNA nanotube by base pairing and stacking allow the design of DNA complexes.

Graphene based nanomaterials

1. Graphene Nanoribbons: Graphene cut into narrow strips by electronic confinement and are classified as armchair-edged GNRs (AGNRs) and zigzag-edged GNRs (ZGNRs).

2. Nanographene: These are commonly Polycyclic Aromatic Hydrocarbon (PAH), which are referred as graphene quantum dots (fluorophores).

FIG. 1.2
Gradual development of engineered nanomaterials.

1.4.1 C_{60}: Buckminsterfullerene

The evolution of nanoscale materials begins with the discovery of a phenomenal structure, the so-called Buckminsterfullerene (or fullerene) which has the soccer ball shape that is well known in architecture, by Buckminster Fuller who was one of the great philosopher-scientists of the past century. In 1985, a new form of carbon (C_{60}: buckminsterfullerene) was discovered while doing experiments aimed at understanding the mechanisms of long-chain carbon molecules, where a remarkably stable cluster consisting of 60 carbon atoms was produced (Kroto *et al.*, 1985). C_{60} is a soccer ball-like molecule made of pure carbon atoms, which is a polygon with 60 vertices and 32 faces (12 of which are pentagonal and 20 hexagonal).

1.4.2 Nanotubes

In addition to the fullerenes, namely, diamond, graphite, and C_{60}, the multiwalled carbon nanotubes (MWNTs; quasi-one-dimensional carbon nanotubes) were discovered as carbon-soot made by an arc-discharge method (Ijima, 1991). Single-walled nanotubes (SWNTs) were also developed two years later (Ijima and Ichihashi, 1993). Since then, nanotubes have gained considerable attention among researchers worldwide. A nanotube is a nanometer-scale hollow cylindrical tube-like structure with diameters of 1 to 100 nm. Nanotubes have promising scope in a wide variety of sectors. So different nanotubes have been developed as per convenience and a few of these are listed in the following.

i. **Carbon nanotubes**
   Ijima (1991) discovered a breakthrough material referred to as carbon nanotubes (CNTs), which helped to create a new branch of science and technology known as nanoscience. Since then, intense research and development has been carried out to reveal the unique structural, electrical, mechanical, electromechanical, and chemical properties of such materials. Carbon nanotubes usually behave like rolled up cylinders of graphene sheets with diameters as small as one nanometer (Dai, 2002). CNTs are efficient and more robust than steel on the molecular level. The commercialization of these nanotubes can be found in various fields, namely, polymers, displays, engineering plastics, thin films, coatings, anticorrosion paints, transparent and non-transparent conductive electrodes, antistatic packaging, and hydrophobic coatings.
ii. **Gallium nitride nanotubes**
   As stated by Goldberger *et al.* (2003), P. Yang and his colleagues must be credited for the synthesis of single-crystal gallium nitride nanotubes (GaNNTs) with inner diameters of 30 to 200 nm and wall thicknesses of 5 to 50 nm, which were successfully obtained by means of epitaxial casting. In this process, zinc oxide (ZnO) nanowires on a sapphire wafer are used as templates inside a reaction tube for chemical vapor deposition of GaN. These nanotubes have high mechanical strength, and superior electrical and optical properties. This process of "epitaxial casting" opens the door to discover other inorganic solids with non-layered crystal structures.

iii. **Silicon nanotubes**
It is interesting to note that silicon (Si) nanotubes have impressive characteristics, such as very high reversible charge capacity and superior retention capacity compared with commercially available graphite. These are prepared in the form of carbon-coated Si nanotubes within alumina membrane templates by means of chemical vapor deposition and then the removal of the alumina template by treatment with NaOH, which has been reported by Park *et al.* (2009).

iv. **DNA nanotubes**
Nucleic acids have been used in the self-assembly of functional nanomaterials because they are more readily available through synthetic chemical means and are more convenient to handle than proteins (Feldkamp and Neimeyer, 2006). DNA is a potential candidate to serve as a construction material in nanoscience and nanotechnology. The properties of base pairing and stacking allow the design of DNA complexes analogous to the abstract tiles of mathematical tilings, also known as Wang tiles. Such DNA tiles can be programmed to self-assemble into a variety of 2D arrays (Rothemund *et al.*, 2004). In this regard, the design of self-assembled DNA nanotubes shows great promise in a wide variety of sectors ranging from nanofabrication to biophysical studies like sensing, imaging, and therapeutic systems.

v. **Boron carbon nitride nanotubes**
Boron nitride nanotubes (BNNTs) have a similar tubular nanostructure as CNTs, but where boron and nitrogen atoms are arranged in a hexagonal network (Kim *et al.*, 2018). New material forms such as diamond (C), cubic-boron nitride (c-BN), and boron carbide (B_4C) have created great interest for many years and now, owing to their covalent bonding, short bond lengths, and low atomic mass, which give the material a low dielectric constant along with excellent thermal and mechanical strength (Nehate *et al.*, 2020). Boron carbon nitride (BCN) compounds exhibit the unique characteristics of B_4C and BN and are adjustable based on the composition and structure.

Apart from these nanotubes, researchers in recent years have made considerable effort in finding other different forms of nanotubes (inorganic nanotubes, tunneling nanotubes, titania nanotubes, etc.) with immense applications in nanoscience and nanotechnology.

1.4.3 Graphene-based nanomaterials

As mentioned by Novoselov *et al.* (2004), a micromechanical cleavage method has been performed for the exfoliation of graphite, based on repeated peeling of highly oriented pyrolyzed graphite. Geim and Novoselov (2007) defined that graphene is the name given to a flat monolayer of carbon atoms tightly packed into a 2D honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. Graphene is the basic structural element of several carbon allotropes, which can be wrapped up into 0D fullerenes, rolled into 1D nanotubes, or stacked into 3D graphite. For their pioneering work revealing the exceptional physical properties of graphene, they were awarded the 2010 Nobel Prize in Physics (Müllen and Feng, 2017). The extraordinary electronic, thermal, and

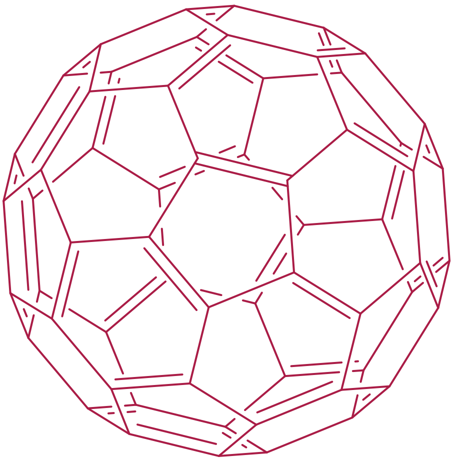
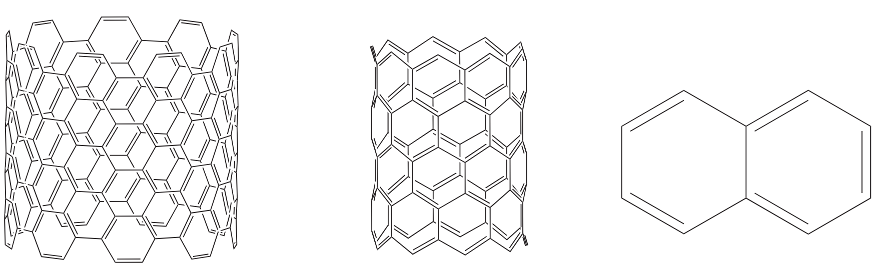


FIG. 1.3
Polygonal structure of fullerene.

mechanical properties of graphene make it a promising candidate for various future applications in electronics, sensing, catalysis, energy storage, and conversion, as well as biological labeling. A few of these graphene-based nanomaterials are presented in Fig. 1.4.

i. **Graphene nanoribbons**
In general, graphene is semimetallic in nature with zero band gap. To achieve a band gap, graphene is cut into narrow strips by means of electronic confinement to generate graphene nanoribbons (GNRs), which makes them useful in digital electronics (Müllen and Feng, 2017). GNRs can be classified into two types known as armchair-edged GNRs (AGNRs) and zigzag-edged GNRs (ZGNRs) based on their edge structures (Nakada *et al.*, 1996). Zigzag ribbons have a honeycomb network oriented in such a way that the edge consists of the triangular edges of the hexagons. Armchair ribbons are oriented at 30 °C (or equivalently at 90 °C) from the zigzag orientation, where the edges consist of the hexagonal sides (Ceils *et al.*, 2016).

ii. **Nanographene**
A polycyclic aromatic hydrocarbon (PAH) is a hydrocarbon (a chemical compound containing only carbon and hydrogen) that is composed of multiple aromatic rings. The simplest of these aromatic hydrocarbons are naphthalene, which has two aromatic rings, and the three-ring compounds anthracene and phenanthrene. Nanographenes are classified as large PAHs, which can be regarded as atomically precise graphene quantum dots, and are a new class of fluorophores for



(9, 9) Armchair

(9, 0) Zigzag

Napthalene: $C_{10}H_8$

FIG. 1.4
Different types of graphene-based materials in brief.

super-resolution fluorescence microscopy. Nanographenes have attracted much interest because of their outstanding photophysical properties: intrinsic blinking even in air, excellent fluorescence recovery, and stability over several months. Graphene quantum dots (GQDs) are nanoscale graphene fragments with well-defined, quantized energy levels and have recently been proposed as being a more favorable option over carbon dots (CDs) and quantum dots (QDs) for microscopy imaging owing to their small size (typically less than 10 nm) and low toxicity (Liu *et al.*, 2019).

1.5 NANOCOMPOSITES

The desire for multifunctionality, enhancement of properties, and improvement of characteristics of materials has given rise to multiphase nanomaterials (nanocomposites), where at least one of their dimensions must be less than 100 nm. However, such an idea is not so recent, as it can be dated back to the ancient material arts (referred to as synthetic nanocomposites) of the Mayan civilization in Mesoamerica. These paintings generally hold a matrix of clay mixed with organic colorant (indigo) molecules. Naturally occurring structures, such as bone, are hierarchical nanocomposites that are built from ceramic tablets and organic binders. Mimicking nature and based on the demands of building new materials that can serve several functions at the same time, scientists have been devising synthetic strategies to produce different nanocomposites such as metal and ceramics nanocomposites, polymer-based nanocomposites, and biologically inspired nanocomposites. Applications of a few of these kinds of materials are reported as follows.

- Ceramic nanocomposites are used in various industrial applications owing to their remarkable properties such as resistant to corrosion, high temperature oxidation, and better wear resistance than that of metals in high-temperature environments.
- As a nanopolymer, silicon nanospheres are considered as biologically compatible and nontoxic. In addition, they are much harder than silicon and their hardness interestingly lies between that of sapphire and diamond.
- The bio-hybrid nanocomposites play a major role in wide variety of sectors, namely, tissue engineering, drug delivery from compartmented nanotubes, chromatography, optical information technology, and sensorics.

1.6 CONCLUDING REMARKS

An exhaustive account on the origin of nanotechnology along with the concepts of different nanostructural elements have been discussed in this chapter. A summary of this chapter is as follows.

i. The chapter begins with the origin of nanotechnology followed by the significance of nanostructural components in nanoelectronics, nanomedicine, and nanoelectromechanical systems (NEMS) owing to their excellent mechanical and electrical properties.

ii. The facts about naturally occurring and synthetic (engineered) nanomaterials are presented thereafter. A comprehensive report on the different ENMs is then provided, which begins with the discovery of the Buckminsterfullerene followed by that of organic (or inorganic) nanotubes and graphene-based nanomaterials. Credit for these remarkable developments on ENMs goes to Professor Kroto and his colleagues for finding fullerene in 1985 and Professor Ijima for obtaining carbon nanotubes in 1991. These were the triggers for ENMs to gain significant attention among researchers worldwide.

iii. Finally, a short review on nanocomposites is given, where the nanocomposites are referred to as multiphase nanomaterials that are meant to enhance the properties of the constituents to serve various functions simultaneously.

iv. The subsequent chapters of this book will review with the extensive studies on static and dynamic problems associated with nanostructural elements. The use of continuum-based modeling and molecular dynamics in dealing with such problems is highly encouraged, because conducting precise experiments at such a scale can not only be challenging but also cumbersome.

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