Narendra Kumar
Sunita Kumbhat

Essentials in Nanoscience & Nanotechnology

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ESSENTIALS IN NANOSCIENCE AND NANOTECHNOLOGY

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PREFACE

The turn of twenty-firs century has witnessed the emergence of three cutting-edge technologies, namely, Information and Communication Technology (ICT), Biotechnology, and Nanotechnology. In 2005, the United Nations Task Force on the Millennium Development Goals touted Nanotechnology as one of three platform technologies that can reduce hunger, promote health, improve water sanitation, develop renewable resources, and improve the environment, and recommended that developing countries should initiate nanotechnology programs at a national level. Inspired by such forecasts, by 2014, over 60 countries followed the United States and established the National Nanotechnology Initiative. These countries range from advanced industrial countries in Europe and Japan to the emerging markets of Russia, China, Brazil, and India.

Physicist Richard Feynman, in his famous speech of 1959, forecasted the development of nanoscience and the punch line “plenty of room at the bottom” became reality by the 1980s when scientists developed techniques and tools to explore and manipulate matter at the atomic scale. The term “nanoscale” define a size range from 1 to 100 nm, although a scientificall based range goes from the atomic scale (0.2 nm) to 100 nm. The focus on the nanoregime relates to the convenience of some standard definitio that can be used to both categorize nanotechnology, nanoscience, and nanoproducts and act as a bridge between quantum mechanical effects and surface area effects.

Nanoscience is not merely about size; it is about the unique physical, chemical, biological, and optical properties that emerge naturally at the nanoscale, whereas nanotechnology is related to the ability to manipulate and engineer such effects. It is a broad new area of science that demolishes boundaries among physics, chemistry, biology, cognitive science, materials science, and engineering at the nanoscale. New technologies, however, are likely to revolutionize the economy and the society only if there is a broader strong National base consisting of trained manpower and infrastructure that allows a new technology to spread and transform to its exciting niche applications, whether civilian or military. To do so, the most important thing is to educate and train the budding manpower at the school and university levels. For that, availability of standard books is necessary, and this book is designed keeping in mind these essential requirements.

Furthermore, keeping in view the unprecedented research and development in the area of nanoscience and nanotechnology and to make the students aware about the latest developments in the field we have attempted to write this book in a manner as simple as possible while including the latest development in the field The subject matter of the book, ranging from fundamentals to the latest developments and technological applications, is presented in 10 chapters. The first chapter on introduction gives a historical prospective, provides living examples of nanoscience in nature and artificia nanomaterials, and brings out the likely impact of nanotechnology on human civilization. Chapter 2 describes general synthetic approaches and strategies, while Chapter 3 deals with the characterization of nanomaterials using modern tools and techniques to provide the basic understanding to students who are interested in learning this emerging area. Chapters 4–7 deal with different kinds of nanomaterials such as inorganic, carbon-based nanocomposites, and self-assembled/supramolecular nanostructures, respectively, in terms of their varieties, synthesis, and properties. Following this, Chapters 8 and 9 are devoted to the unique properties and applications of nanotechnology in various disciplines such as information technology, pollution, environment, energy, healthcare, consumer goods, and so on. Finally, the last chapter deals with the toxicological and ethical issues associated with nanotechnology.

We believe this book will generate and promote the basic understanding on the complex and revolutionary disciplines of nanoscience and nanotechnology, which is offered now as a core subject in most of the academic institutions across the globe.

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Dr. Narendra Kumar, DRDO fellow, graduated and did his PhD degree in "Organometallic Chemistry" in 1976 from Delhi University. From 1976 to 1981, he served at the National Physical Laboratory, New Delhi, and worked toward the development and application of materials including organometallics, liquid crystals, electrochromics, and electrode materials. He served as a postdoctoral research fellow at Windsor University, Canada, during 1981–1983 and worked in the fiel of electrochemical synthesis of metallic and organometallic complexes of transition and actinide elements. In 1984, he joined as Scientist at the Defence Laboratory, Jodhpur, and retired from there as its Director in 2012, where he carried out pioneering research work in the development of conducting polymers, liquid loam, nanomaterials, and products based on them for various defence applications. Dr. Kumar has published more than 100 research and review articles in international journals in the areas of Nanoscience, Organometallics, Conducting Polymers, and Electrochemical Synthesis, and also a chapter entitled "Nanotechnology for Sensor and Display Applications" in the *Encyclopedia of Nanoscience and Technology* published by American Scientifi Publication, USA. He has 12 patents to his credit and authored one book entitled *Nanotechnology and Nanomaterials in the Treatment of Life Threatening Diseases* published by Elsevier (USA) in 2013. He also served as a visiting Research Associate of CSIR, New Delhi, during 1992–1995 and is a recognized supervisor of J. N. V. University, Jodhpur, for PhD and has guided 6 students for their PhD degrees in the area of nanoscience. He has delivered several invited talks on Conducting Polymers and Nanomaterials in several International and national conferences/seminars, as well as at universities in India, Japan, and the United States.

He received the DRDO Technology Cash Award in 1996 for his pioneering research work on conducting polymers, and DRDO Scientist of the Year award in 2005 from the Prime Minister of India for products based on conducting polymers and nanomaterials for defense applications. He is a recipient of the National MRSI-ICSC Super Conductivity and Materials Science Annual Award for the year 2010 by Materials Research Society of India. Dr. Kumar is a member of various scientifi societies including the prestigious American Chemical Society.

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Dr. Sunita Kumbhat, Professor and Chemistry Department at J.N.V. University, Jodhpur, has graduated in Chemistry and obtained her PhD degree in the fiel of Electrochemistry in 1985 from J.N.V. University, Jodhpur. She did postdoctoral research in the field of Photoelectrochemistry and Sonovoltammetry with Prof. R.G. Compton at Oxford University, UK. Dr. Kumbhat joined the Department of Chemistry, J.N.V. University, as permanent faculty member in 1986, and has been serving as a Professor since 2001 where she has been involved in teaching graduate and postgraduate courses on Analytical Chemistry, Electrochemistry, Sensors, and Nanoscience and supervising PhD students. Her areas of interest are Electrochemistry and Biosensors for Biomedical and Environmental Analysis. She has more than 50 research papers in international journals, three educational films and one patent to her credit. She has supervised 14 research students for their PhD degrees. Her awards and recognition include Commonwealth Academic Staff Fellowship (1994–1995) at Oxford, UK, National Associate (1997) at BARC, Mumbai, and the INSA–JSPS Visiting Fellowship (2005) at Kyushu University, Fukuoka, Japan. Dr. Kumbhat is associated with various Indian and International scientifi societies and is also an assessing member of the National Assessment and Accreditation Council, Bangalore, India.

1

INTRODUCTION

1.1 DEFINITIONS OF NANOSCIENCE AND NANOTECHNOLOGIES

Nanoscience is a new discipline concerned with the unique properties associated with nanomaterials, which are assemblies of atoms or molecules on a nanoscale. Nanoscience is actually the study of objects/particles and its phenomena at a very small scale, ranging roughly from 1 to 100 nm. "Nano" refers to a scale of size in the metric system. It is used in scientifi units to denote one-billionth of the base unit, approximately 100,000 times smaller than the diameter of a human hair. A nanometer is 10^{-9} m (1 nm = 10^{-9} m), a dimension in the world of atoms and molecules (the size of H atom is 0.24 nm and, for instance, 10 hydrogen atoms lined up measure about 1 nm). Nanoparticles are those particles that contain from 100 to 10,000 atoms. Thus, the particles in size roughly ranging from 1 to 100 nm are the building block of nanomaterials.

Nanomaterials: These materials are created from blocks of nanoparticles, and thus they can be define as a set of substances where at least one dimension is approximately less than 100 nm. However, organizations in some areas such as environment, health, and consumer protection favor a larger size range from 0.3 to 300 nm to defin nanomaterials. This larger size range allows more research and a better understanding of all nanomaterials and also allows to know whether any particular nanomaterial shows concerns for human health or not and in what

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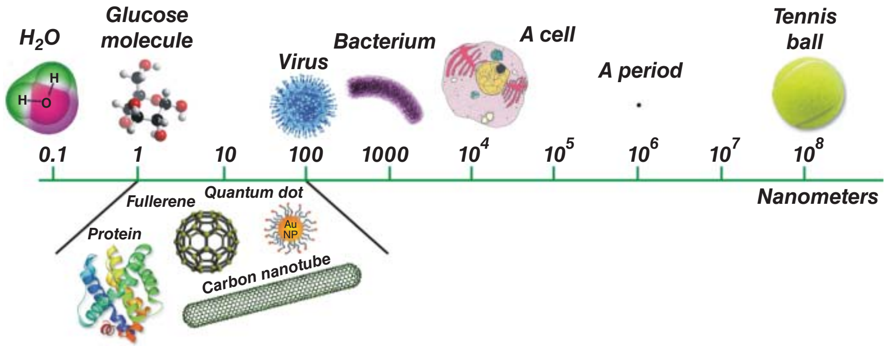

Figure 1.1 Size comparisons of objects, nanomaterials, and biomolecules.

size range. Nanocarbons such as fullerenes, carbon nanotubes, and graphene are excellent examples of nanomaterials. A comparison of the size of nanomaterials with some natural and biological species is illustrated in Figure 1.1.

Nano-object: Material confine in one, two, or three dimensions at the nanoscale. This includes nanoparticles (all three dimensions in the nanoscale), nanofiber (two dimensions in the nanoscale), and nanoplates (one dimension in the nanoscale). Nanofiber are further divided into nanotubes (hollow nanofiber) nanorods (solid nanofiber) and nanowire (electrically conducting or semiconducting nanofiber) However, the term nano-object is not very popular.

Particle: It is a minute piece of matter with define physical boundaries. A particle can move as a unit. This general particle definitio applies to nano-objects.

Nanoparticle: It is a nano-object with all three external dimensions in the nanoscale. Nanoparticles can have amorphous or crystalline form and their surfaces can act as carriers for liquid droplets or gases.

Nanoparticulate matter: It refers to a collection of nanoparticles, emphasizing their collective behavior.

Agglomerate: It is a group of particles held together by weak forces such as van der Waals forces, some electrostatic forces, and surface tension. It should be noted that agglomerate will usually retain a high surface-to-volume ratio.

Aggregate: It is a group of particles held together by strong forces such as those associated with covalent or metallic bonds. It should be noted that an aggregate may retain a high surface-to-volume ratio.

Nanotechnology is the construction and use of functional structures designed from atomic or molecular scale with at least one characteristic dimension measured in nanometers. Their size allows them to exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes because of their size. Thus, nanotechnology can be define as research and development that involves measuring and manipulating matter at the atomic, molecular, and supramolecular levels at scales measured in approximately 1–100 nm in at least one dimension.

When characteristic structural features are intermediate between isolated atoms and bulk materials in the range of approximately 1–100 nm, the objects often display physical attributes substantially different from those displayed by either atoms or bulk materials. The term “nanotechnology” is by and large used as a reference for both nanoscience and nanotechnology especially in the public domain. We should distinguish between nanoscience and nanotechnology. Nanoscience is a convergence of physics, chemistry, materials science, and biology, which deals with the manipulation and characterization of matter on length scales between the molecular and the micron size. Nanotechnology is an emerging engineering discipline that applies methods from nanoscience to create products.

1.2 UNIQUENESS OF THE NANOSCALE

At nanoscale, the laws of physics operate in an unfamiliar way because of two important reasons: high surface-to-volume ratio and quantum effect. The key reason for nano-sized regime being special is the dramatic increase in the surface-to-volume ratio. When the size of building blocks gets smaller, the surface area of the material increases by six orders of magnitude, as illustrated in Figure 1.2, while the volume remaining the same. For example, dissecting a 1 m^3 of any material into 1 nm particles increases the total combined surface area from 6 to 60,000,000 m^2, approximately 10 million times larger [1]. Nanomaterials have a wider range of applications such as catalysts, cleanup, and capture of pollution and any other application where chemical reactivity is important such as medicine. This effect occurs at all length scales, but what makes it unique at the nanoscale is that the properties of the material become strongly dependent on the surface of the material since the amount of surface is now at the same level as the amount of bulk. In fact, in some cases such as fullerenes or single-walled nanotubes, the material is entirely the surface.

Another important attribute of nanoscale materials is the fact that it is possible for the quantum mechanical properties of matter to dominate over bulk properties. One

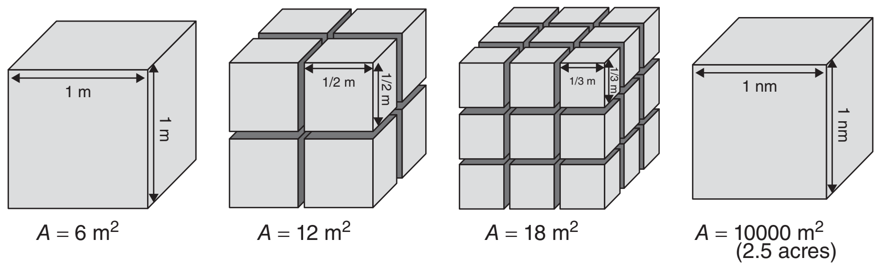

Figure 1.2 Exponential increases in surface area for cubes ranging from meter to nanosize.

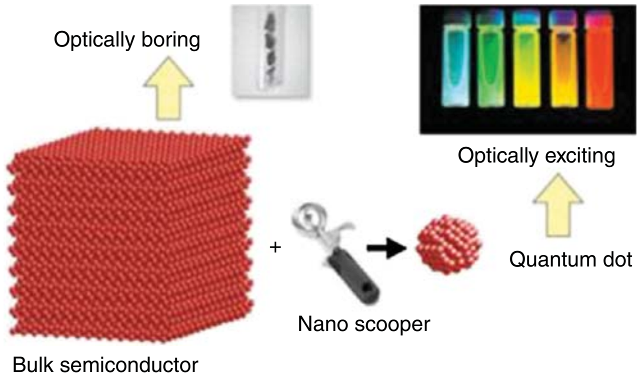

Figure 1.3 Change in optical properties of a semiconductor ranging from bulk to nanosize. Courtesy of Grossman, MIT, USA. (*See color plate section for the color representation of this figure.*)

example of this is in the change in the optical properties, for example, in the photoemission, of many semiconductor materials as they "go nano." Figure 1.3 illustrates how, a material whose optical properties may be considered uninteresting, simply by changing its size to the nanoscale one can control the color of the material [2]. This effect is due to quantum confinement

Important consequence of each of these properties is that they offer completely new methods of tuning the properties of materials and devices. Nanotechnology can provide unprecedented understanding about materials and devices and is likely to impact many fields By using structure at nanoscale as a tunable physical variable, we can greatly expand the range of performance of existing chemicals and materials. Nanoscience and nanotechnology are broad and interdisciplinary areas of research and development activity that have been growing explosively worldwide in the past two decades. Nanoscience has the potential for revolutionizing the methods in which materials and products are created and the range and nature of functionalities that can be accessed; nanotechnology already has a significan commercial impact that will increase exponentially in future.

1.3 NANOSCIENCE IN NATURE

Nanostructures are plentiful in nature. In the universe, nanoparticles are distributed widely and are considered to be the building blocks in planet formation processes. Indeed, several natural structures including proteins and the DNA diameter of around 2.5 nm, viruses (10–60 nm), and bacteria (30 nm to 10 μm) fi the above definitio of nonmaterial, while others are of mineral or environmental origin. For example, these include the fin fraction of desert sand, oil fumes, smog, fumes originating from volcanic activity or from forest fires and certain atmospheric dusts. Biological systems have built up inorganic–organic nanocomposite structures to improve the mechanical properties or to improve the optical, magnetic, and chemical sensing in living species. As an example, nacre (mother-of-pearl) from the mollusk shell is a biologically formed lamellar ceramic, which exhibits structural robustness despite the brittle nature of its constituents. These systems have evolved and been optimized by evolution over millions of years into sophisticated and complex structures. In natural systems, the bottom-up approach starting from molecules and involving self-organization concepts has been highly successful in building larger structural and functional components. Functional systems are characterized by complex sensing, self-repair, information transmission and storage, and other functions all based on molecular building blocks. Examples of these complex structures for structural purposes are teeth, such as shark teeth, which consist of a composite of biomineralized fluorapatit and organic compounds. These structures result in the unique combination of hardness, fracture toughness, and sharpness. The evolution has worked on much smaller scales too, producing finel honed nanostructures, parts less than a millionth of a meter across, or smaller than 1/20th of the width of a human hair help animals climb, slither, camouflage, flirt, and thrive. Figure 1.4a shows an electron microscopic image of a sensory patch in amphibian ears, which consists of a single bundle of stereo cilia projecting from the epithelium of the papilla, and acts as a nanomechanical cantilevers that measure deflection as small as 3 nm because of sound waves. Many of the shimmering colors in butterfly s wings are produced not with pigments but with nanostructures. The scales on their wings are patterned with nanoscale channels, ridges, and cavities made of chitin, a protein. Unlike pigments, which create color by absorbing some wavelengths of light and reflectin the rest, the nanostructures are shaped so that they physically bend and scatter light in different directions, sending particular colors back to our eyes. This scattering can also make them iridescent (i.e., the color changes with the angle one sees it from. When infrared radiation hits the chitin nanostructures, their shape changes because of expansion, thus changing the colors they display. Figure 1.4b shows glittering colors of peacock feather where barbs project directly from the main feather stem,

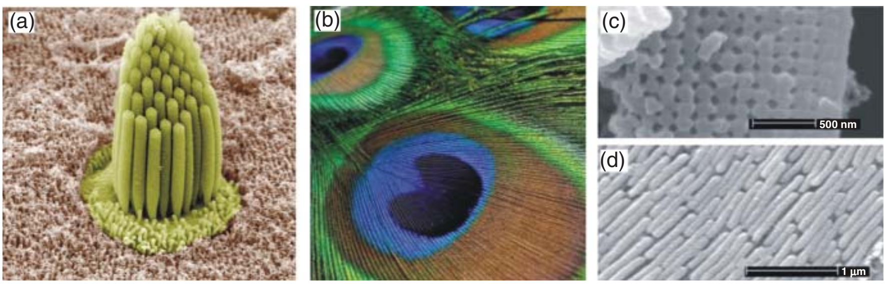

Figure 1.4 Nanotechnology in nature: (a) electron microscopic image of a sensory patch in amphibian ears. http://scinerds.tumblr.com/post/35542105310/stereocilia-stairsteps; (b) peacock feather showing barbules, representing a photonic lattice; (c and d) electron microscopy image of transverse and longitudinal sections of barbules. Zi et al. [2a] © 2003. With permission of National Academy of Sciences, USA. (*See color plate section for the color representation of this figure.*)

and barbules (~0.5 mm long) attached to each side of the barb generate the typical "shimmer" of iridescence. Electron microscopy (Figure 1.4c and d) of barbules reveals a highly ordered structure of melanin rods of high refractive index embedded in keratin of lower refractive index with air tube between each square of melanin rods. The whole array of melanin rods, keratin matrix, and air holes comprises a 2D photonic crystal. There is much interest on mimicking these natural wonders with potential applications in optical engineering and communications. Less seriously, photonic crystal pigment-free paints would not fade, fabrics might be more vibrant.

The compound eye of arthropods uses nanoscale features to enhance their visual sensitivity. An insect's compound eye has about 50–10,000 individual facets, which are studded with an array of nanoscale protuberances called "corneal nipples" (Figure 1.5a and b), each with its own set of optical machinery. These tiny structures of size ranging from 50 to 300 nm cut down the glare that reflect off the insect eye. The nanoscale nipple pattern on moth eyes has inspired new antireflect ve coatings (Figure 1.5c) for solar cells. The male silk moth can detect, with single-molecule precision, the pheromones of a female moth emitted up to 2 miles away. Spider silks are some of the toughest materials known to man, stronger than steel, and their webs can withstand gusts of wind. The spider's silks get their strength from just nanometers of thin crystal proteins, which are stacked with hydrogen bonds, allowing the silk to stretch and fl x under pressure.

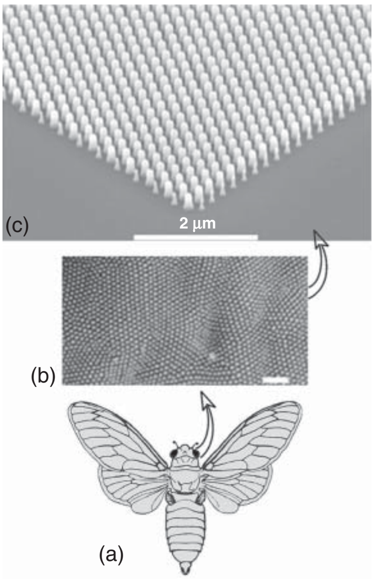

Figure 1.5 Natural and fabricated antireflect ve surfaces: (a) schematic of a moth; (b) scanning electron micrograph of antireflect ve surface of a moth's eye (scale bar = 1 µm); (c) biomimetic replica of a moth eye fabricated with ion- beam etching. Parker & Townley [2c] © 2007. With permission of Nature Publishing Group.

These are only a few of the countless examples of how nature employs nanotechnology in different methods, of course, with the most important technology to us being the human body itself, which contains billions of nanoscale machines! It is both fascinating and humbling to observe that despite all of the phenomenal technological advances in nanoscale synthesis and characterization, in most cases we are still unable to build nanotechnology-based devices that even come close to nature.

1.3.1 Naturally Occurring Nanomaterials

Naturally occurring nanomaterials may originate from one of the following sources:

(i) **Natural erosion and volcanic activity**
Nanoparticles are part of mineral world since they are naturally produced from erosion and volcanic explosions.

(ii) **Clays**
Minerals such as clays are a type of layered nanostructured silicate materials that are characterized by a fin 2D crystal structure. Mica, one among them, is the most studied [3]. In mica, a large number of silicate sheets are held together by relatively strong bonds. On the other hand, montmorillonite, a smectic type of clay, has relatively weak bonds between layers. Each layer consists of two sheets of silica held together by cations such as Li^+, Na^+, K^+, and Ca^{2+}. The presence of the cations is necessary for compensating the overall negative charge of the single layers. The layers are 20–200 nm in diameter laterally and come into aggregates called tactoids, which can be about 1 nm or more thick. The fin nanostructure of clays determines their properties. As an example, the nanostructured clay swells to several times of the original volume, when water is added to it, due the opening of the layered structure by the water molecules that replaces the cations. Clay swelling is a significan factor in soil stability and is taken into account in constructing roads.

(iii) **Natural colloids**
Naturally occurring liquid colloids, such as milk, blood, aerosols (e.g., fog), are some of the examples of natural colloids. In these materials, nanoparticles are dispersed in the medium (liquid or gas) but do not form a solution, rather they form a colloid. All these materials have the characteristic of scattering light and often their color (such as in the case of milk and blood) are due to the scattering of light by the nanoparticles that makes them up.

(iv) **Mineralized natural materials**
Many of the natural materials such as shells, corals, and bones are formed by the self-assembly of calcium carbonate crystals with other natural materials, such as polymers, to form fascinating three-dimensional (3D) architectures. For instance, a shell is grown layer-by-layer coating of protein supported by chitin, a polysaccharide polymer. The proteins act as a nanoassembly mechanism to control the growth of calcium carbonate crystals. Around each crystal remains a honeycomb-like matrix of protein and chitin. This relatively "fl xible envelop" is fundamental for the mechanical properties of the shell and

mitigate cracking. The size of each crystal is around 100 nm. As a result, the mollusk shell has extraordinary physical properties, namely, strength and resistance to compression.

1.3.2 Nanoscience in Action in Biological World

Two most significan examples of active nanoscience in biological world include the following:

(i) **Lotus effect**

Although the water repellency of lotus had long been recognized, its scientifi basis was understood only in 1997 when two botanists Wilhelm Berthelot and Christophe Neinhuis, at the University of Bonn in Germany, examined leaf surfaces of lotus using a scanning electron microscope that resolves structures as small as 1–20 nm [4]. Figure 1.6a shows a nonwettable lotus plant leaf. The self-cleaning property is due to the "**Super hydrophobicity**" of the convex papillae on the surface of leaves, which is coated with wax crystals of nanoscopic dimension of approximately 10–100 nm (Figure 1.6b). Water drop picks up the dirt particles as it rolls off the leaf's surface, showing self-cleaning process (Figure 1.6c). Several other plants such as Nasturtium and cabbages also show lotus effect.

The papilla greatly reduces the contact area of water droplets with it. Every epidermal cell forms a micrometer-scale papilla and has a dense layer of epicuticular waxes superimposed on it. Each of the papillae consists of branch-like nanostructures on the surface, for example, of the lotus leaves, the almost spherical water droplets will not come to rest and simply roll off if the surface is tilted even slightly, which is now usually referred to as the "**Lotus effect**." The self-cleaning effects of the surfaces of the lotus fl wer have been attributed to the combined micro- and nanostructure, which in combination with hydrophobic groups give the surface a water and dirt-repellent behavior. In the past few years, numerous companies have realized products resembling the surface morphology and chemistry of the lotus flower such as paint, glass surface, and ceramic tiles with dirt-repellent properties.

(a) (b) (c)

Figure 1.6 (a) Lotus (*Nelumbo nucifera*) plant; (b) spherical water droplet on a nonwettable lotus plant leaf. Blossey [6] © 2003. With permission of Nature Publishing Group. ; (c) self-cleaning: a drop picks up the dirt particles as it rolls off the leaf's surface.

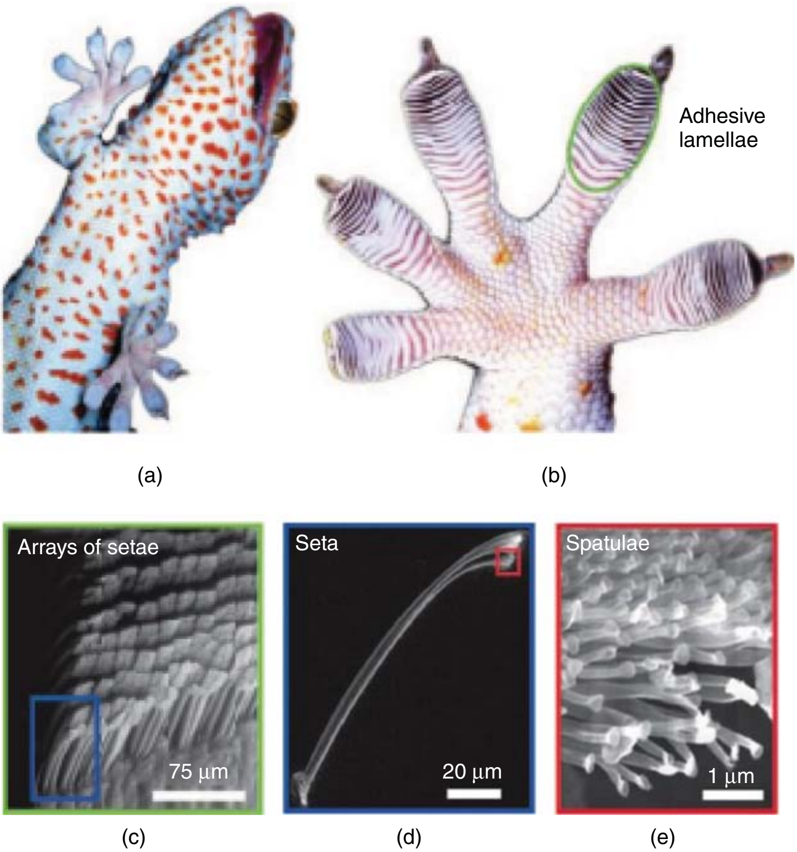

Figure 1.7 Gecko's adhesive system structure: (a) ventral view of a tokay gecko (*Gekko gecko*); (b) sole of the foot showing adhesive lamellae; (c) microstructure: part of a single lamella showing arrays of setae; (d and e) nanostructure: single seta with branched structure at the upper right area, terminating in hundreds of spatular tips. Hansen and Autumn [6], © 2005. With permission of National Academy of Sciences, USA. (*See color plate section for the color representation of this figure.*)

(ii) **Geckos Technology**

Geckos are one of the few species in the animal kingdom that are known for sticky toes that allow them to climb up walls, even hang upside down on ceiling and at the same time can walk on a leaf; they owe this ability to nanoscale attachment elements. As illustrated in Figure 1.7a–e, on the sole of a gecko's toes there are about a billion tiny adhesive hairs, ~200 nm in both width and length. These hairs put the gecko in direct physical contact with the surface. Spatula-shaped ends on the hairs provide strong adhesion. Industry is researching the evolution of these properties in order to develop artificia dry adhesive systems. Potential applications include reusable adhesive fixture with the strength of duct tape, which can be removed as easily as a sticky note.

TABLE 1.1 Bio-Inspired Unique Properties

Natural System/Materials	Bio-Inspired Properties
Substructure of nacre	Low-density, high-strength composites
Spider silk	High-tensile strength fiber
Wood, ligaments, and bone	High-strength structural material
Eels and nervous system	Electrical conduction
Deep-sea fis and glow worms	Photoemission
Butterfl and bird wings	Photonic crystals
Moth eye	Antireflect ve
Lotus leaf, human skin, fis scales	Hydrophobic surfaces, self-cleaning
Shark skin	Drag reducing
Gecko's feet	Adhesion
Human brain	Artificia intelligence and computing

Some more examples of naturally occurring materials such as cotton, spider's silk, and opals are also worth mentioning for their nano features and unique properties. Cotton has nanoscale arrangement of cellulose fiber showing high strength, durability, and absorbance. Spider silk showing five time higher strength than that of steel has natural supramolecular organization of fibroi at nanoscale. Precious stone opal consists of spheres of silicon dioxide (150–300 nm diameter) in a hexagonal or cubic close-packed lattice. These ordered silica spheres produce the internal colors by causing the interference and diffraction of light passing through the microstructure of the opal. The realization that nature can provide the model for improved engineering has created a research fiel called "biomimicking" or bio-inspired material science. It has been possible to process several types of nanostructures inspired from biological nanomaterials, represented in Table 1.1, which provide new technological opportunities and potential for applications.

1.4 HISTORICAL PERSPECTIVE

Thousands of years bc, people used natural fabrics such as fl x, cotton, wool, and silk and processed them into products. What makes these fabrics so special that they developed a network of pores of size 1–20 nm for typical nanoporous materials? Owing to their nanoporous structure, natural fabric possesses high utilitarian properties of absorbing sweat, quickly swelling, and getting dried soon. Since ancient times, people mastered the art of making bread, wine, beer, cheese, and other foodstuffs where fermentation processes at the nanolevel are critical. Romans in the pre-Christian era introduced metals with nanometric dimensions in glass-making: a cup describing the death of King Lycurgus (ca 800 bc) contains nanoparticles of silver and gold [7]; when a light source is placed inside the cup, its color changes from green to red (Figure 1.8a). It was found that it was due to the presence of nano-sized

Figure 1.8 (a) Lycurgus cups. Courtesy of Trustees of the British Museum. © The Trustees of the British Museum; (b) ancient Maya fresco painting. Reproduced from Sanchez et al. [8] © 2005. With permission of The Royal Society of Chemistry. (*See color plate section for the color representation of this figure.*)

particles of silver (66.2%), gold (31.2%), and copper (2.6%) embedded in the glass. Light absorption and scattering by these nanoparticles determine the different colors. The stained-glass windows of the great medieval cathedrals also contain metallic nanoparticles.

The colors of certain Mayan paintings (Figure 1.8b) also stem from the presence of metallic nanoparticles [8]. Mayan artisans concocting in the eighth century the unique pigment we now know as Maya Blue have endured their lively blue tones for more than 12 centuries of harsh jungle environment. Maya Blue is not an ordinary organic dye nor is it any simple mineral; it is a hybrid organic–inorganic nanocomposite in which the organic dye molecules are protected within palygorskite, a complex natural clay. Art history of India and China is also filled with examples of nanotechnology. Photography, which was developed in the 18th and 19th centuries, provides a more recent example of the use of silver nanoparticles. Nanostructured catalysts have also been investigated for over 70 years. In the early 1940s, precipitated and fumed silica nanoparticles were being manufactured and sold in the United States and Germany as substitutes for ultrafin carbon black for rubber reinforcements. Nano-sized amorphous silica particles have found large-scale applications in many everyday consumer products, ranging from nondiary coffee creamer to automobile tires, optical fibers and catalyst supports. In addition, the definitio of nanoparticles based on size allows us to include colloids and soils that have been used for over a hundred years.

In 1857, Faraday had described the use of colloidal gold in his experiments. In his lecture at Royal Society, Faraday presented a purple color slide, stating that it contained "gold reduced in exceedingly fin particles, which becoming diffused, produced a ruby red fluid The various preparations of gold, whether ruby, green, violet or blue etc. consist of that substance in a metallic divided state." Faraday postulated correctly about the physical state of colloids; he also described how a gold colloid would change color (turning blue) on adding salt. Since then, colloidal science has evolved a lot. In the early twentieth century Gustav Mie presented the Mie theory,

Figure 1.9 Richard Feynman. https://commons.wikimedia.org/wiki/Category:Richard_Feynman.

which is a mathematical treatment of light scattering that describes the relationship between metal colloid size and optical properties of solutions containing them. The Nobel Prize winner for Quantum Electrodynamics, Richard Feynman (Figure 1.9), said, "**Nature has been working at the level of atoms and molecules for millions of years, so why do we not?**" Since his call in a lecture in 1959, nanotechnology has made tremendous progress not only in technical disciplines but also in medicine and pharmaceutics [9]. World began speculating on the possibilities and potential of nanometric materials and on the fact that the manipulation of individual atoms could allow us to create very small structures whose properties would be very different from larger structures with the same composition. Moreover, in an even more radical proposition, he thought that, in principle, it was possible to create "nanoscale" machines through a cascade of billions of factories. According to him, these factories would be progressively smaller scaled versions of machine, hands, and tools. In these speculations, he also suggested that there are various factors that uniquely affect the nanoscale level. Specificall , he suggested that as the scale got smaller and smaller, gravity would become more negligible, while van der Waals attraction and surface tension would become very important. Feynman's talk has been viewed as the first academic talk that dealt with a main tenet of nanotechnology, the direct manipulation of individual atoms (molecular manufacturing). Richard Feynman is considered as the "Father of Nanotechnology," although he never explicitly mentioned the term "Nanotechnology."

The evolution of integrated chips may also be considered as the part of history of nanotechnology. The firs transistor invented in 1947 was a bulk macro-object. To keep with the demand for miniaturization, the dimensions of the transistor have been reduced considerably in the last 30 years. In the year 2002, the nanosize was reached with the achieved size of a single transistor as 90 nm [10]. As on today, a single transistor in an Intel Core 2 Quad Processor is 45 nm. In order to keep pace with Moore's law, transistor would be as small as 9 nm by 2016. However, this dimension is below the fabrication capabilities of last-generation tools used in the microelectronic industry. Numerous novel approaches such as quantum computing and molecular engineering are under investigation to achieve the workable transistor of this size. Material science/engineering is also full with examples of nanomaterials! Often these were produced inadvertently and were not characterized at the nanoscale since the analytic tools were not available. For instance, the process of anodizing was first patented in early 1930s. This represents one of the most important processes used in industry to protect aluminum from corrosion. It consists of depositing a thin protective oxide layer on the aluminum surface. The inventors were not, however, aware that the protective layer is actually a nanomaterial; the anodic layer is composed of hexagonally close-packed channels with diameter ranging from 10 to 250 nm or greater. The first use of the term "nanotechnology" was by Norio Taniguchi in 1974 at the International Conference on Precision Engineering (ICPE). His definitio referred to "production technology to get extra high accuracy and ultra-fin dimensions, that is, the preciseness and finenes on the order of 1 nm (nanometer), 10^{-9} m, in length." The development of nanotechnology has been enabled by the invention of two analytical tools that have revolutionized the imaging (and manipulation) of surfaces at the nanoscale. These are the scanning tunneling microscope (STM) and the atomic force microscope (AFM). The AFM and STM are capable of imaging surfaces at an atomic resolution. Both the instruments were invented by Binning and his coworkers at IBM Zurich. Invention of these versatile tools practically opened the doors of nanoworld to the scientists. With the advent of the STM, scientists were given the tool not only to image surfaces with atomic resolution but also to move individual atoms. The STM is the first step in realizing Feynman's vision of atom-by-atom fabrication. In the 1980s, the basic idea of this definitio was explored in much more depth by Eric Drexler, who promoted the technological significanc of nanoscale phenomena and devices through speeches and the books, *Engines of Creation: The Coming Era of Nanotechnology* and *Nanosystem: Molecular Machinery, Manufacturing, and Computation* [11] and so the term acquired its current sense. Birth of "Cluster Science" in the late 1980s gave further momentum to the development of nanoscience and nanotechnology. In another development, the studies on the synthesis and properties of metallic and semiconductor nanocrystals led to a fast increasing number of metal and metal oxide nanoparticles and quantum dots. In 2000, the United States National Nanotechnology Initiative (NNI) was founded to coordinate Federal Nanotechnology research and development. In short, the milestones related to the evolution of nanoscience and nanotechnology, from prehistoric to modern era, are given in Table 1.2.

1.5 NANOMATERIALS

Materials are what the world is made of. They are hugely important and hugely interesting. They are also intrinsically complicated. Materials, in general, are comprised of a large number of atoms and molecules and have properties determined by complex, heterogeneous structures. Historically, the heterogeneity of materials plays crucial roles in determining properties that have been determined largely empirically and manipulated through choice of the compositions of starting materials and the conditions of processing.

TABLE 1.2 Milestones Associated with the Evolution of Nanoscience and Nanotechnology

Year	Milestone
Since origin of life	Cell: a magnificen nanomachine
400 bc	Democritus of Abdera gave reasoning about atoms and matter
500 ad	Glazes artisan in Mesopotamia, Mayan paintings
1857	M. Faraday prepared colloidal dispersion of gold that is stable for almost a century before being destroyed during World War II
1931	Electron microscope by Max Knoll and E. Ruska
1959	R. Feynman during an after-dinner talk “There’s Plenty of Room at the Bottom” described molecular machines’ building with atomic precision
1974	N. Taniguchi used the term "nanotechnology" for fabrication methods below 1 μm
1977	E. Drexler gave, for the firs time, the concept of molecular nanotechnology at MIT, USA
1981	G. Binnig and H. Rohrer (IBM) invented scanning tunneling microscope and received Nobel Prize of Physics in **1986**
1985	Fullerene was discovered by R. F. Curl Jr., H. W. Kroto, and R. E. Smelly won Nobel prize of Chemistry in **1996**
1986	(i) Invention of atomic force microscopy by G. Binning, C. F. Quate, and Ch Gerber (IBM) (ii) ii. Eric Drexler, *Engines of Creation: The Coming Era of Nanotechnology*, the firs book on nanotechnology
1991	Discovery of carbon nanotube (CNT) by S. Iijima
1998	Carbon nanotube transistor by C. Dekkar and coworkers
2000	Discovery of stimulated emission depletion (STED) by S. Hell
2001	Moor’s law surpassed by producing world’s fastest silicon transistor at Intel Corporation, which switches on and off 1.5 trillion times per second
2004	Discovery of graphene by A. Giem and K. Novoselov and they won Nobel Prize in 2010
2004	Intel launches the Pentium 4 “PRESCOFT” Processor based on 90 nm technology
2006	Discovery of single-molecule microscopy (SMM) by E. Betzig and W. Moerner led to the discovery of nanomicroscopy, surpassing the limits of optical microscopy Based on STED and SMM techniques, super-resolved fluorescenc microscopy has emerged to study synapses in Alzheimer’s and Huntington’s disease, and to gain a better understanding of protein development in embryos, which led to winning the Nobel Prize of Chemistry in **2014** jointly by E. Betzig, S, W. Hell, and W. E. Moerner

Nanomaterial means a material that meets at least one of the following criteria:

- Consists of particles with one or more external dimensions in the size range of 1–100 nm for more than 1% of their number.
- Internal/surface structures in one or more dimensions in the size range of 1–100 nm.
- Specifi surface-to-volume ratio >60 m^2/cm^3, excluding materials consisting of particles with a size less than 1 nm.

Nanomaterials can be nanoscale in one dimension (e.g., surface films) two dimensions (e.g., strands or fibers) or three dimensions (e.g., precipitates, colloids). They can exist in single, fused, aggregated, or agglomerated forms with spherical, tubular, and irregular shapes.

Nanostructures are the ordered system of one, two, or three dimensions of nanomaterials, assembled with nanometer scale in certain pattern that includes nanosphere, nanotubes, nanorod, nanowire, and nanobelt [12]. Nanostructured materials are classifie as zero-, one-, two-, and three-dimensional nanostructures, showing typical examples with varied dimensionality in nanomaterials as in Figure 1.10a–i.

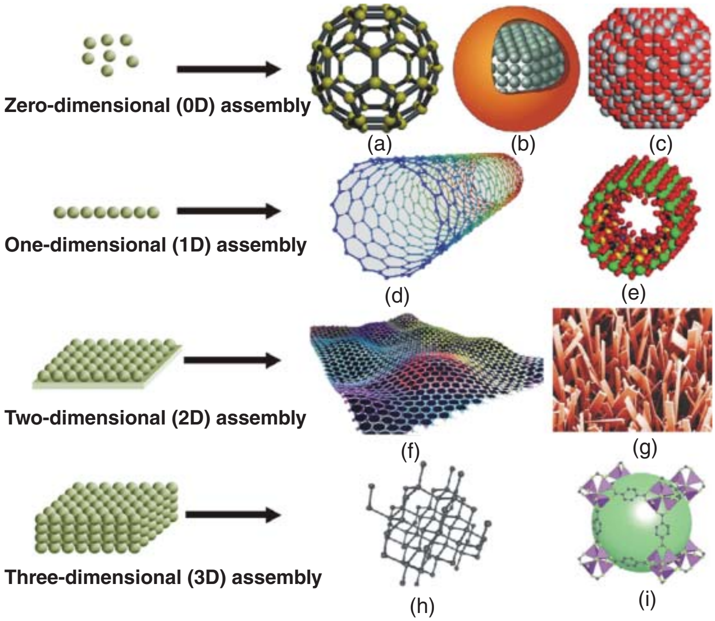

Figure 1.10 Typical examples showing varied dimensionality in nanomaterials: (a) fullerene; (b) quantum dot; (c) metal cluster; (d) carbon nanotube; (e) metal oxide nanotube; (f) graphene; (g) metal oxide nanobelts; (h) nanodiamond; (i) metal organic frameworks (MOFs).

A **nanocrystallite** is generally understood to possess crystalline order in addition to nanoscale size. If one dimension of the 3D nanostructure is at nanoscale, then it is called a **Quantum Well**. If two dimensions of the 3D nanostructure are at nanoscale, then it is called a **Quantum Wire**. If all the three dimensions of the nanostructure are at nanoscale, then it is called a **Quantum Dot**. Nanocrystallites are also called quantum dot. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields Nanocarbons such as fullerenes, carbon nanotubes, and graphene are excellent examples of nanomaterials. Nanomaterials are cornerstones of nanoscience and nanotechnology. The creation of functional materials, devices, and systems through control of matter on the nanometer length scale (1–100 nm) is the exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale. The phrase "nanostructured materials" implies two important ideas: (1) at least some of the property determining heterogeneity in materials occurs in the size range of nanostructures (1–100 nm) and (2) these nanostructures might be synthesized and distributed (or organized), at least in part, by design. The idea of "nanostructured materials" thus focuses on four key questions:

(i) Why nanostructures are interesting?
(ii) How can they be synthesized?
(iii) How can they be introduced into materials?
(iv) How can the relationships between compositions and structures, and matrices and interfaces control the properties of the resultant materials?

"Materials by design," pertaining to the last question, have been a goal of material science since its inception. It remains, however, a difficul task because majority of research is still focused to answer the firs three questions. All conventional materials such as metals, semiconductors, glass, ceramics, or polymers can in principle be obtained with a nanoscale dimension. The spectrum of nanomaterials ranges from inorganic to organic and from crystalline to amorphous particles, which can be found as single particles, aggregates, powders, or dispersed in a matrix, over colloids, suspensions and emulsion, nanolayers, and nanofilms Supramolecular structures, such as dendrimers, micelles, or liposomes also belong to the class of nanomaterials.

1.5.1 Nanoparticles

Nanoparticles are solid particles at the intermediate state, that is, between atoms/molecules and macroscopic objects. Nanoparticles constitute of several tens or hundreds of atoms or molecules and can have a variety of sizes and morphologies (amorphous, crystalline, spherical, needles, etc.). The study of nanoparticles relates various scientifi fields for example, chemistry, physics, optics, electronics, magnetism, and mechanism of materials. Some nanoparticles have already reached practical stage. Owning to their small size effect, large surface effect, and quantum tunnel effect, the nanoparticles demonstrate special physical properties and can be widely used in a variety of applications. Some kinds of nanoparticles are available commercially in the form of dry powders or liquid dispersions. The latter is obtained by combining nanoparticles with an aqueous or organic liquid to form a suspension or paste. It may be necessary to use chemical additives (surfactants, dispersants) to obtain a uniform and stable dispersion of particles. With further processing steps, nanostructured powders and dispersions can be used to fabricate coatings, components, or devices that may or may not retain the nanostructure of the particulate raw materials. Industrial scale production of nanoparticulate materials such as carbon black, polymer dispersions, or micronized drugs has been established for a long time. Another important class of nanoparticulate materials is metal oxide nanopowder that includes silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), or iron oxide (Fe_3O_4, Fe_2O_3); compound semiconductors (e.g., cadmium telluride, CdTe or gallium arsenide, GaAs), metals (especially precious metals such as Ag, Au), and alloys are also included in this category that are being commercialized.

1.5.2 Nanowires and Nanotubes

Linear nanostructures such as nanowires, nanotubes, or nanorods can be generated from different material classes, for example, metals, semiconductors, or carbon, by means of several production techniques. Carbon nanotubes are one of the most promising linear nanostructures that can occur in a variety of modification (e.g., single-, or multiwalled, filled or surface modified) At present, carbon nanotubes can be produced by CVD methods on a several tons per year scale.

1.5.3 Nanolayers/Nanocoatings

Nanolayers are one of the most important topics within the range of nanotechnology. Through nanoscale engineering of surfaces and layers, a vast range of functionalities and new physical effects (e.g., magnetoelectronic or optical) can be achieved. Furthermore, a nanoscale design of surfaces and layers is often necessary to optimize the interfaces between different material classes (e.g., semiconductor compound on silicon wafers) and to obtain the desired special properties.

1.5.4 Nanoporous Materials

Materials with define pore sizes in the nanometer range are of special interest for a broad range of commercial applications because of their outstanding properties with regard to thermal insulation, controllable material separation and release, and their applicability as templates or fillers for chemistry and catalysis. One example of nanoporous material is aerogel, which is produced by sol–gel chemistry. A broad range of potential applications of these materials include catalysis, thermal insulation, electrode materials, environmental filters and membranes as well as controlled release of drug carriers.

1.6 STRATEGIES FOR SYNTHESIS OF NANOMATERIALS

Preparation of nanoparticles is an important branch of the materials science and engineering. Nanoparticles can be produced by a whole series of chemical, physical, or biological processes, some of which are totally new and innovative, while others have existed for a very long time. Four major processes are employed in synthesizing the new nanoparticles: gaseous phase, vapor deposition, wet chemistry, and grinding. Several of the processes for producing nanoparticles are similar to the existing chemical production processes.

(i) The gas phase method includes gas-phase evaporation method (resistance heating, high-frequency induction heating, plasma heating, electron beam heating, laser heating, electric heating evaporation method, vacuum deposition on the surface of fl wing oil, and exploding wire method), chemical vapor reaction (heating heat pipe gas reaction, laser-induced chemical vapor reaction, plasma-enhanced chemical vapor reaction), chemical vapor condensation, and sputtering method.

(ii) Liquid phase method for synthesizing nanoparticles mainly includes precipitation, hydrolysis, spray, solvent thermal method (high temperature and high pressure), solvent evaporation pyrolysis, oxidation–reduction (room temperature and atmospheric pressure), emulsion, radiation-assisted chemical synthesis, and sol–gel processes.

(iii) Solid phase method includes thermal decomposition, solid-state reaction, spark discharge, stripping, and milling method. Most of these methods result in very fin particles that are more or less agglomerated. The powders are amorphous or crystalline and show a metastable or an unexpected phase, the reasons for which are far from being clear.

Owing to the small sizes, any surface coating of the nanoparticles strongly influ ences the properties of the particles as a whole. Studies have shown that the crystallization behavior of nanoscale silicon particles is quite different from micron-sized powders or thin films. It was observed that tiny polycrystallites are formed in every nanoparticle, even at moderately high temperatures.

1.7 PROPERTIES OF NANOMATERIALS

The interest in nanostructured materials arises from the fact that because of the small size of the building blocks and the high density of interfaces (surfaces, grain, and phase boundaries) and other defects such as pores, new physical and chemical effects are expected or known properties can be improved substantially. The physical and chemical properties of nanostructured materials (such as optical absorption and flu orescence, melting point, catalytic activity, magnetism, electric and thermal conductivity, etc.) differ significantl from the corresponding coarser bulk material. Roughly two types of nanostructure-induced effects can be distinguished:

- The size effect, in particular the quantum size effects, where the normal bulk electronic structure is replaced by a series of discrete electronic levels.
- The surface- or interface-induced effect, which is important because of the enormously increased specifi surface in particle systems.

Although the size effect is mainly considered to describe physical properties, the surface- or interface-induced effect plays an eminent role for chemical processing, in particular in connection with heterogeneous catalysis. Experimental evidence of the quantum size effect in small particles has been provided by different methods, while the surface-induced effect could be evidenced by the measurement of thermodynamic properties such as vapor pressure, specifi heat, thermal conductivity, and melting point of small metallic particles. Both types of size effects have also been clearly separated in the optical properties of metal cluster composites. Very small semiconductor (<10 nm), or metal particles in glass composites, and semiconductor/polymer composites show interesting quantum effects and nonlinear electrical and optical properties.

These special properties of nanomaterials are mainly due to quantum size confine ment in nanoclusters and an extremely large surface-to-volume ratio relative to bulk materials, thus leading to the presence of a high percentage of atoms/molecules lying at reactive boundary surfaces. For example, in a particle with 10 nm diameter only around 20% of all atoms are forming the surface, whereas in a particle of 1 nm diameter this figur can reach more than 90%. The increase in the surface-to-volume ratio results in an increase in the surface energy of the particle, which leads to, for example, a decrease in melting point or an increase in sintering activity. Furthermore, large surface area of particles may significantl raise the level of otherwise kinetically and thermodynamically unfavorable reactions. For instance, even gold, which is a very stable material, becomes reactive when the particle size is small enough. Fundamentally, there are seven key characteristics that contribute to the uniqueness of nanomaterials [13], and these are summarized in Table 1.3. In general, the unique properties of nanomaterials are an outcome of three effects: reduced size, high surface-to-volume ratio, and supramolecular structure arising because of the self-assembly of molecules that are summarized in Table 1.4.

1.8 SIGNIFICANCE OF NANOSCIENCE

According to much of the information one reads in printed news articles, on websites, and even in many science journals, nanotechnology is projected to hold the key to meet the global energy needs with clean solutions, providing abundant clean water globally, increasing the health and longevity of human life, maximizing the productivity of agriculture, making powerful information technology available everywhere, and even enabling the development of space. Nanotechnology represents an entire scientifi and engineering field and not just a single product or even group of products. As a consequence, there are several areas of nanotechnology with many associated applications. With the increasing understanding on relationship between shape, size,

TABLE 1.3 Characteristics of Nanomaterial and Their Importance

Characteristic	Importance
Size	Key definin criteria for a nanomaterial
Shape	Carbon nanosheets with a flat geodesic (hexagonal) structure show improved performance in epoxy composites versus carbon fiber
Surface charge	Surface charge is as important as size or shape. Can impact adhesion to surfaces and agglomeration characteristics. Nanoparticles are often coated or "capped" with agents such as polymers (PEG) or surfactants to manage the surface charge issues
Surface area	This is a critical parameter as the surface-to-weight ratio for nanomaterials is huge. For example, 1 g of an 8-nm-diameter nanoparticle has a surface area of 32 m^2
	Nanoparticles may have occlusions and cavities on the surface
Surface porosity	Many nanomaterials are characterized with zeolite-type porous surfaces. These engineered surfaces are designed for maximum absorption of a specifi coating or to accommodate other molecules with a specifi size
Composition	The chemical composition of nanomaterials is critical to ensure the correct stoichiometry being achieved. The purity of nanomaterials, impact of different catalysts used in the synthesis, and presence of possible contaminants need to be assessed along with possible coatings that may have been applied
Structure	Knowledge of the structure at the nanolevel is important. Many nanomaterials are heterogeneous, and information concerning crystal structure and grain boundaries is required

Source: Courtesy of PerkinElmer, Inc.

and their physiochemical and biological properties, nanomaterials are considered to be futuristic material for diverse technologies. Current and potential areas of application include transport, manufacturing, biomedicine, sensors, environmental management, information and communications technology, materials, textiles, equipment, cosmetics, skin care, and defense. Although the list is by no means exhaustive, however, emerging application areas are discussed in the following section.

1.9 COMMERCIAL APPLICATIONS

Many nanotech-based products have already been developed and are commercially available. The nanotech industry is poised for rapid growth with many additional nanotech-based products presently in their developmental stage and expected to be commercialized in the near future. The most common commercially exploited nanoparticles in various areas are those of silver, gold, iron metals, oxides of silicon, aluminum, titanium, iron, zinc, and carbon nanomaterials such as carbon nanotubes (CNT) and graphene. These materials are used for their specifi and unique chemical, physical, and biological properties together with established technology for their

TABLE 1.4 Size and Shape-Related Attributes and Properties of nanomaterials

Physical Entity	Functionality
A. Size confinement/ educed size (Quantum dots, wires, rods, wells, fibers) **Attributes:** • Comparable size of nanoparticles with correlation scale of some physical phenomenon • Characteristic length of some transport process • Abnormal phase state	• Electronic: quantum confinement molecular electronics • Electrical: tunable dielectric, ferroelectric, dc conductivity, electrical rheology • Optical: nonlinear, luminescence, transmission, selective absorption/reflection scattering • Magnetic: new magnetic orders such as supermagnetism, paramagnetism, ferromagnetism; GMR, mechanical force transfer (MRF), magnetocaloric effects
B. High surface area (Powders, films structural elements) **Attributes:** • Predominance of interfacial phenomenon because of the presence of free bonds, free bonding orbital with affinit for electrons, and occupied bonding orbital with low ionization potential	• Adsorption • Molecular recognition (chemical, biological) • Gas sensing, separation • Mechanical: superplasticity, higher structural strength and toughness, improved elasticity • Electrochemical process • Thermal insulation
C. Supramolecular and self-assembled structure (Nanotubes, fibers rods, cables, films **Attributes:** • Noncovalent and coordination bond • No exchange of electrons between molecules	• Adaptation, evolution, molecular forces holding • nanostructure electronics • Molecular recognition, directed chemical synthesis • Nonlinear optical phenomenon • Thermo-, opto- and electromechanical actuations • High-density ultrafast information processing • Ionic and molecular transport

Source: Patra et al. [15] © 2011. With permission of American Scientifi Publisher.

scaled production now. It is also important to note that products are rarely 100% nanotechnology based; nanotechnology will be added to a product and form a part of it. Some of important sectors where nanotechnology-based products are available commercially [15] are given in following sections.

1.9.1 Food Industry

Silver is currently the most common nanoparticle that is used in the food industry. Silver has long been known as an effective antimicrobial agent and in its nanoform can now be easily impregnated invisibly into almost any product to aid in the destruction of bacteria and viruses. This has important applications in the food industry in terms of manufacturing, preserving, and storage. Although the use of nanotechnology directly in food products is limited, however, several food supplements are available that contain nanoparticles as the main active ingredient. The most common nanoparticles used in these supplements comprise silver, gold, copper, or calcium. It is unknown what effect these metals may have on cells and the body as a whole. Refrigerators and food containers are also now available with a silver nanoparticle lining to deter the growth of bacteria and mold. It is not known whether silver nanoparticles can be absorbed by the food while it is being stored and later ingested.

1.9.2 Cosmetics

The fascinating group of nanoparticles known as fullerenes, the C_{60} form, which resemble small "Footballs" of carbon atoms, are being used in cosmetics in the form of face creams to remove other unwanted particles, such as free radicals, which are believed to cause damage to the body and skin. Sun creams are now available with titanium dioxide nanoparticles. The micron-sized particles are used as sunblock, but are white in color and are not used in sun creams that need to be invisible when applied. The nanoparticle form is colorless as the particles are too small to reflec visible light, but still retain their ultraviolet sun-blocking properties that are highly desirable for a sun cream.

1.9.3 Textile

Textile industry is making increasing use of nanomaterials to make them more functional and smart. For example, nanosilver is playing a lead role because of its antimicrobial properties. Clothes can also be treated with nanofilm to make them stain, water and static resistant. These films, which are only a few atoms thick, could be in contact with skin over prolonged periods. Very little information is available what the long-term effect could be, although in the short term most products appear safe as nanotechnology has been used in clothes for several years now.

1.9.4 Medicine

The use of silver nanoparticles for use in medical devices is a hot topic. Nanosilver kills a broad range of harmful microbes and has been shown to be effective against the Methicillin-resistant Staphylococcus aureus (MRSA) superbug and the HIV virus. This could prove beneficia in terms of providing sterile equipment, beds, and wound dressings that limit the spread of harmful bacteria. Nanomedicine is not limited to simple single-element nanoparticles such as silver. More complicated nanoparticles can perform certain tasks such as homing in on cancer cells to destroy them or drug delivery that can send drugs directly into cells. Nanotechnology could also be used to produce new sensors that can detect whether a person has certain types of cancer using only a few drops of blood.

1.9.5 Electrical and Electronic Goods

For the majority of electrical goods, nanotechnology has come from a natural evolution of microtechnology. In order to fi more components into an electronic chip to make it more powerful, the components are made to be smaller. Over the period of time, components that used to be several hundred micrometers are now several hundred nanometers. In this aspect, nanotechnology only represents an arbitrary milestone, as a micron-sized transistor works in the same manner as a nano-sized transistor. Virtually all forms of nanotechnology used in electronics are embedded and are believed to pose a low human health risk and no additional risk to the environment over microtechnology. However, there are many areas that are having a greater impact including quantum computing, nanoelectrical mechanical systems (NEMS), and new display technologies.

Quantum computing uses the quantum mechanical effects available at the nanoscale that gives new methods of performing computational operations. Essentially, some computing tasks that have to be performed sequentially with a standard computer can be performed all at once using a quantum computer. This could dramatically increase the speed of databases, which underpin businesses, and, increasingly, the Internet. NEMS are effectively nano-sized machines that currently perform simple tasks. This type of nanotechnology is currently one of the closest analogies to nano-sized robots, the other type being biological nanomachines that are made from biological molecules. These can produce nano-sized motors and sensors. Applications for NEMS could be very broad, for example, monitoring the environment or even medical nanorobots for targeting cancers or repairing tissues. These examples are still very much in the preliminary or theoretical stage, but once developed could have a huge impact.

Recent display technologies use carbon nanotubes or nano-sized structures to effi ciently emit electrons to be used to excite a phosphor display. This type of technology should have the advantage of being lightweight and efficient Another new display technology is the organic semiconductor film The term organic is used because the semiconductor material is made of organic or carbon-based polymers. These films may one day be printed off as plastic to provide cheap fl xible displays. The nanotechnology element, which lies in the structure of the semiconductor, is not thought to pose any particular new risk over conventional plastics. Some of the commercialized nano-based products and their specifi applications are listed in Table 1.5.

TABLE 1.5 Summary of Some Commercialized Nano-Based Products and Their Specifi Applications

Broad Area	Type of Nanomaterials	Specifi Application
Environmental protection	Nano zerovalent iron (nZVI)	Remediation of ground and surface waters exposed to chlorinated hydrocarbons
	Nano ZnO, TiO_2, CeO_2	Protection from UV radiations to preserve wood, concrete, and metal surfaces
Food technology	Nano clay	Packaging material to enhance shelf life of food
Energy: conversion, storage, and distribution	Pd- and V-doped carbon nanotubes	More efficien fuel cells by increasing storage capacities and faster hydrogen absorption kinetics
Healthcare	NPs of gold, silver, magnetic oxides, polymers	To achieve better resolution and contrast in MRI and CT-based imaging for diagnosis, therapy and targeted drug delivery
Textiles	Silver nanoparticles	Integrated in dressing and clothing to prevent microbial growth and odor
	Nano TiO_2	Self-cleaning and wrinkle-free clothing
Cosmetics	Nano TiO_2 and nano ZnO	Soaps, sun screen lotion, moisturizers
Defense	CNTs, graphene, metal nano-oxides, nanocomposites	Ballistic protection, kinetic energy penetration, stealth technology
Aerospace	Clay nanoparticles	Fire retardant aircraft interiors
Automotive	CeO_2 NPs	As catalyst to enhance combustion in diesel fuel
Sports equipments	CNTs, carbon nanofibe , nanocomposites	Stronger and fl xible golf shafts, tennis racket, racing bicycle components

1.10 POTENTIAL HEALTH HAZARDS AND ENVIRONMENTAL RISKS

It is unclear whether nanoparticles can cause chronic health effects. There are several methods that nanoparticles can enter the body, these include the following: inhalation, ingestion, absorption through the skin, and direct injection for medicinal purposes [16]. The skin is surprisingly permeable to nanomaterials. Carbon nanotubes are strong and can have a similar shape to asbestos fibers several studies suggest that carbon nanotubes are potentially toxic to humans. Given that nano-sized objects tend to be more toxic than their large-scale form, it would be unwise to allow the unnecessary buildup of nanoparticles within the body until the toxicological effects of that nanoparticle are known however, such studies are still speculative. Concerns are, therefore, being expressed about potential risks to workers, public health, and the environment through manufacture, use, and disposition of these newly developed materials with unique and perhaps unknown properties. Because the scope of the nanotechnology industry is broad and involves many different industrial sectors, an understanding of the associated materials, processes, and applications is critical to ensure responsible industry development in a way that both encourages economic growth and protects public health and the environment. Removing nanoparticles from the environment may also present a significan problem because of their small size. If absorbed, the particles may travel up the food chain to larger animals in a similar process to DDT although there is no evidence either way that this is a valid mechanism. There is still too little research into the potential negative impacts of this technology on the environment. However, some nanoparticles such as copper and silver have been shown to be harmful to aquatic life.

1.11 FUTURISTIC OUTLOOK

Nanoscale materials have been used for decades in applications ranging from window glass and sunglasses to car bumpers and paints. Now, however, the convergence of scientifi disciplines (chemistry, biology, electronics, physics, engineering, etc.) is leading to a multiplication of applications in materials manufacturing, computer chips, medical diagnosis and healthcare, energy, biotechnology, space exploration, security, and so on. It is this convergence of science, on the one hand, and growing diversity of applications, on the other hand, that is driving the potential of nanotechnologies. Hence, nanotechnology is expected to have a significan impact on our economy and society within the next 10–15 years, growing its importance over the longer term as further scientifi and technology breakthroughs are achieved. In many cases, nanotechnology might only be a minor – but sometimes decisive contribution to the fina product. It is believed that by the turn of this decade, the commercial value of products "incorporating nanotechnology" or "manufactured using nanotechnology" may exceed several trillion dollars. Nanomaterials in structures have the potential to significantl reduce production costs and the time of parts assembly, for example, in the automotive, consumer appliance, tooling, and container industries. The potential of significan reductions in weight due to these new materials as they are applied in the transportation industries will have great impact on energy consumption and the environment. Understanding nanoparticle formation is paying dividends in dealing with environmental issues such as atmospheric particulate formation as well. Many fundamental phenomena in energy science, such as electron transfer and exciton diffusion, occur on the nanometer length scale. Thus, the ability to arrange matter, that is, to inexpensive pattern and to develop effective nanostructuring processes, is going to be a vital asset in designing next-generation electronic devices, photovoltaic, and batteries. Size and cost reduction due to advances in the design and manufacture of healthcare-related diagnostic systems have the potential to empower individuals to diagnose and treat diseases in their own homes, decentralizing the healthcare system. Sensors based on nanotechnology are expected to revolutionize healthcare (e.g., via remote patient monitoring); climate control; detection of toxic substances (for environment, defense, and healthcare applications); and energy consumption in homes, consumer appliances, and power tools.

Nanotechnology and synthesis of nanomaterials are going to open new frontiers in the design of catalysts and catalyst technology for the petroleum, chemical, automotive, pharmaceutical, and food industries. The design of catalyst supports commensurating with biological structures can be an important bridge between conventional and enzymatic catalyses. In fact, oxidation catalysis can be performed today more effi ciently in a zeolite, "ship-in-a-bottle" catalytic complex than with natural enzymes. This is just one example of an entire array of anticipated future developments.

New discoveries are expected and needed in studies of single objects with nanodimensions ranging in size from single molecules, clusters, and particles to organelles and cells. There is a great scope to learn more about the opportunities for and limits on the synthesis of large, precisely structured objects and clusters. Controlling purity and scale-up of products emanating from such precision syntheses is a major challenge that must and will be tackled in the near future. Many of the important properties of nanostructures depend on obtaining precise building blocks; means of creating and analyzing purity and homogeneity in such products are vitally needed. Furthermore, if production of these materials cannot be done at a sufficientl large scale, this will eventually limit utility in some applications.

Although current microfluidi approaches may be effective for manipulating single objects on the scale of 1 μm or more, new techniques need to be developed for single-object manipulation at smaller scale as well as to do nanomanipulation in three dimensions to guide nanoassemblies in bulk as well as on surfaces. Increasing interactions between nanoscale scientists and system designers are in vogue. An important element of this interaction is toward prototyping methods, an intermediate level of implementation between lab-scale demonstration and mass production. The new nanomaterials are likely to impact not only the performance of the most advanced computational and electronic devices but also objects of daily use familiar to every consumer, such as cars, appliances, films, containers, and cosmetics. The ability to assemble and interconnect nanoparticles and molecules at nanometer dimensions has the potential to develop new types of nanoelectronics circuitry and nanomachinery.

REVIEW QUESTIONS

Q1. Defin nanoscience and nanotechnology.

Q2. What is so unique about materials at nanoscale?

Q3. Justify that living cell is a nanomachine.

Q4. Give few examples of nano biomaterial that have inspired biomimicking.

Q5. What do you understand by mineralization of natural materials? Illustrate with some examples.

Q6. Give name of scientists whom you think have contributed most in development of nanoscience and nanotechnology.

Q7. Name certain nanomaterials found in nature and outline their specifi function.

Q8. Name analytic tools that are considered to have accelerated the growth of nanoscience and nanotechnology.

Q9. Classify the nanomaterials on the basis of their dimension. Give some examples.

Q10. What are nanostructure-induced effects? How do they influenc the properties of materials at nanoscale?

Q11. Write a short note on the following characteristics of nanomaterial and their impact on properties: surface charge, surface area, and surface porosity.

Q12. Mention the change in optical, electrical, magnetic, and biological properties when material is brought down to nanoscale.

Q13. Discuss the commercial applications of following nanomaterials: (1) nanoclay; (2) CNTs; (3) silver nanoparticles; and (4) gold nanoparticles.

Q14. What is the commercial market value of nano-based products in 2013 and expected by the year 2025?

Q15. What are the parameters deciding the role of nanomaterials in (1) quantum computing; (2) self-cleaning; (3) antimicrobial action; and (4) nanoelectrical mechanical systems?

Q16. Discuss the properties of TiO_2 NPs to make it suitable for multiple applications.

Q17. What are the deciding factors for applications of nanostructured materials in the automobile industry?

Q18. Which are the sectors likely to be benefitte in future from the advancements in nanotechnology?

Q19. What is the health-risk factors associated with the increasing use of nanoparticles?

Q20. In what way nanotechnology will help in remote health monitoring?

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2

NANOMATERIALS: GENERAL SYNTHETIC APPROACHES

2.1 INTRODUCTION

Nanotechnology has experienced a rapid growth in the past decade, largely owing to the rapid advances in nanosynthesis and nanofabrication techniques employed to synthesize nanoscale material and fabricate nanodevices. Different approaches used in the synthesis of nanomaterials and nanodevices can accommodate solid, liquid, and/or gaseous precursor materials. In general, most of these techniques can be classifie as bottom-up and top-down approaches (Figure 2.1) and strategies that have elements of both. **The top-down** approaches start with a bulk material and then break it into smaller pieces using mechanical, chemical, or any other form of energy. The **bottom-up** approach, on the other hand, is to synthesize the nanomaterials from atomic or molecular species via chemical reactions or self-assembly, allowing for the precursor particles to grow in size or gradually assembling the atomic or molecular precursors until desired structure is achieved [1].

Both approaches can be performed in the gas or liquid phases, supercritical fluids the solid state, or under vacuum. The most important aspect of any method lies in its ability to control the particle size, particle shape, size distribution, particle composition, and the degree of particle agglomeration. In both approaches of nanomaterial fabrication, two fundamental requisites are control of fabrication conditions (e.g., energy of electron beam) and control of environmental conditions (e.g., dust, contaminations). Nanotechnologies use highly sophisticated fabrication tools that are mostly operated in a vacuum in clean room laboratories. Liquid- and gas-phase

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Figure 2.1 "Top-down" and "bottom-up" approaches for the synthesis of nanomaterials.

processes are based on the assembly of nanoparticles from single atoms or molecules and, thus, allow good control of particle size, morphology, and sometimes size distribution. Green routes involving plant saps/microbes and biomimetic processes of self-organization and self-assembly have also been suggested for nanosynthesis. Innovations and modification of fabrication/synthesis procedure are a continuous process that results in innumerable recipes and techniques. Table 2.1 encompasses some of the noted variations of important synthetic procedures although nanomaterial synthesis is maturing with new postulates and procedures that are being introduced on a daily basis.

2.2 TOP-DOWN APPROACH

Methods to produce nanoparticles from bulk materials include high-energy ball milling, mechanochemical processing (MCP), electro-explosion, sputtering, and laser ablation. These processes are done in an inert atmosphere or in vacuum. Immediately after processing, nanoparticles are very reactive and can easily form agglomerates. If a reactive gas is present, some additional reactions may occur. This can be used to coat nanoparticles with a material that would prevent further interaction with other particles or the environment. Nanolithography, thin-fil deposition, and etching techniques involving progressive removal of material until desired nanomaterial is obtained also belong to top-down category. In the following sections, a more detailed description of the manufacturing techniques from bulk to nano size of the basic nanomaterials is presented.

TABLE 2.1 Common Techniques for Synthesis of Nanomaterials

Top-Down	Bottom-Up
I. Solid-phase techniques	**III. Vapor-phase techniques**
Milling	**Deposition techniques**
Mechanical	Thermal chemical vapor deposition
Mechanochemical	Plasma-enhanced chemical vapor deposition
Etching	Plasma arching
Wet chemical etching	**Chemical vapor condensation**
Dry etching	Molecular beam epitaxy
Reactive ion etching	Sputtered plasma processing
Plasma etching	**Solution-phase techniques (wet chemical)**
Electro-explosion	Chemical reduction
Sputtering	Precipitation (exchange reaction)
Laser ablation	Sol–gel
Lithography	Solvothermal synthesis
Photolithography	Sonochemical synthesis
Soft lithography	**Self-assembly techniques**
Scanning lithography	Use of templates
Electron-beam lithography	Electrostatic self-assembly
Focused ion-beam lithography	Self-assembled monolayers (SAMs)
Next-generation lithography	Langmuir–Blodgett (LB) formation
Nanoimprint lithography	
Nanosphere lithography	
Colloidal lithography	
Scanning probe lithography	
Dip-pen lithography	
Nanocontact printing	
Writing atom-by-atom	
Aerosol-based techniques:	
Electrospraying	
Flame pyrolysis	
II. Liquid-phase techniques	
Electrospinning	

2.2.1 Mechanical Milling

Mechanical milling is a process that is routinely used in powder metallurgy and mineral processing industries. In this process, mixtures of elemental or prealloyed powders are subjected to grinding under protective atmosphere in an equipment that is capable of high-energy compressive impact forces such as attrition or shaker mills. Figure 2.2a shows a commercial ball milling apparatus and Figure 2.2b reveals different forms of possible impact in mechanical ball milling process. A variety of ball mills have been developed for different purposes including tumbler mills, shaker mills, vibratory mills, and planetary mills. Powders with typical particle diameters of about 50 μm are placed together with a number of hardened steel or tungsten carbide (WC)-coated balls in a sealed container that is shaken or violently agitated.