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NANOTECHNOLOGY—AN INTRODUCTION

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Learning Objectives

After going through this chapter, the reader will be able to

- trace the origin of nanoscience and technology
- learn about the efforts taken towards miniaturization of devices and systems, particularly in the fields of integrated circuits and computer technology that prepared the ground to embark upon research and development programmes in science and technology of the small world
- have a glimpse of Richard Feynman's 'big vision of the small world'
- learn about the advances in the field of imaging technologies such as optical, electron, and atomic force microscopy, NMR imaging (MRI), and X-ray and electron diffraction methods in determination of the physical and electronic structures of atomic clusters/nanostructures, setting the stage for the arrival of nanotechnology in the 1980s
- understand the important role played by the development of scanning probe microscopes—particularly the use of scanning tunneling microscopes—in providing atom-by-atom handling capability in the assembly of nanostructures and devices
- learn about the position of nanometre scale (nanoscale) in the scheme of different scales and form an idea about the relative size of nanosize objects
- appreciate the multidisciplinary nature of nanotechnology that embraces all the branches of science and technology
- know that the properties of nanoscale particles and structures show dependence on size and dimensions, with high surface-to-volume ratio
- realize that quantum mechanics is the key to understanding the behaviour of nanosize structures, devices, and machines
- learn about the existence of nanostructures in nature, both living and non-living
- know that nanomaterials were already in use for ages
- have a glimpse of the prospects of nanotechnology

1.1 INTRODUCTION

The word 'nano' is derived from the Greek word *nanos* or Latin word *nanus*, meaning 'dwarf'. It qualifies objects of matter having at least one physical dimension in the range 1–100 nanometres, as nanoscale objects. Here, one nanometre, abbreviated as nm, refers to a billionth of a metre, that is, 10^{-9} metre.

Such nanoscale objects of matter [illegible]
as nanoparticles, nanomaterials, or nanostructures.

Norio Taniguchi

• The branch of science dealing with [illegible] study of nature and behaviour of nanomaterials based on experimental observations and formulation of general laws [illegible] their properties is called nanoscience. Norio Taniguchi professor at Tokyo University, coined the term nanotechnology for the first time in 1974 to describe semiconductor processes such as thin-film deposition and ion-beam milling exhibiting characteristic control on the order of a nanometre. Nanotechnology cuts across all disciplines, borrowing liberally from physics, chemistry, material science and biology, and is truly multidisciplinary in nature, as shown in Fig. 1.1. Based on the fundamental research and understanding of nanomaterials, nanotechnology enables development of products with possible practical applications employing nanostructures.

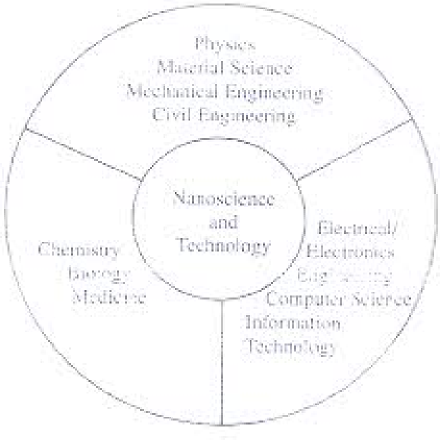

FIG. [illegible] Various disciplines engaged in research and development in nanotechnology

Scientists and technologists have always been fascinated and are working tirelessly to make novel and improved devices as a symbol of the continuous progress of mankind, in terms of their size, performance, and cost. To achieve this goal, they have laid major emphasis on the miniaturization of the devices and implements, which has been particularly useful in the field of electronics. The bulky vacuum tubes were replaced by discrete semiconductor junction transistors, which in turn, gave way to integrated circuits. The bipolar integrated circuits have been substituted by low power, economic, metal-oxide semiconductor (MOS) technology. Then, microelectromechanical systems (MEMS), with devices and machines on the micron to millimetre scale, were developed in the last three decades. In a quick succession to MEMS technology, nanotechnology has opened new avenues for fabrication of devices and systems on the nanoscale with high sensitivity and frequency response in the range of gigahertz and beyond.

1.2 HISTORICAL PERSPECTIVES

The emergence of nanotechnology is based on the fundamentals of quantum

[illegible] tubes. Even today, microwave vacuum tubes form a part of the high frequency communication systems such as mobile phones, Wi-Fi, radar, and satellite transmission. This era has provided sophisticated tools and techniques for investigating the atomic structure of solids such as X-ray, electron, and neutron crystallography and imaging techniques such as scanning probe electron and atomic force microscopes, making it possible to image down to the atomic level. These tools and techniques form the basic necessity for imaging and characterization of nanostructures and devices. They are discussed in the following sections.

1.2.1 Vacuum Electron Tube

Developments in the field of electronics beginning from the late 19th century have played the most dominant role in the rapid progress of science and technology. The invention of the vacuum tube, an active component of electronic circuits, was crucial to the initial growth of electronics and was the first major landmark in the history of electronics. The vacuum tube, consisting of two or more electrodes vacuum-sealed in a thin transparent glass or metal–ceramic container, is essentially based on thermionic emission of electrons, and is used in electronic circuits to control the flow of electrons between electrodes.

The thermionic emission, later used in making vacuum tubes, was first observed by Frederick Guthrie in 1873. He observed that the negatively charged red-hot iron sphere was getting discharged, but the same effect did not happen if the sphere was positively charged. Thomas Edison took the next step in 1883 while developing the incandescent electric bulb. He faced the problem of the glass casing of the electric bulbs becoming blackened, making their lives short. It was known to him that the particles leaving the hot element were negatively charged, which on striking the glass caused blackening. He, therefore, introduced a second element with positive polarity to attract the negative particles to get rid of the problem and observed the flow of current between the hot element and the positive electrode in the circuit. However, on reversing the potentials, he noticed that this did not happen. Though fascinated by the effect, Edison could not make any practical use of the effect and it was later termed as the *Edison effect*. Subsequent to identification of the electron by J.J. Thomson, Owen W. Richardson further studied the phenomenon of electron ejection from red-hot metals, terming it the *thermionic emission*, thus formulating the law of thermionic emission in 1901.

John A. Fleming was the first to transform the observation of the Edison effect into a practical device in 1901. By then it was known that the charged particles emitted by the hot filament were electrons, which were attracted by positive electrodes. Fleming observed that when an alternating current with frequency 80–100 Hz was passed through the bulb, only half cycle was passed, that is, it was rectified producing direct current. He called the device *oscillating valve* in analogy to the valve in a pump that allows water or gas to flow only in one direction. This was the first electronic rectifier diode and was known as *Fleming valve*. The

② Nanomaterial

Engineered. - carbon black (form of paracrystalline carbon that ~~has~~ has a high surface - area - to - vol. ratio

carbon black is widely used as a model compound for diesel soot form ~~titanium dioxide~~ diesel oxidation experiments.

carbon black is mainly used as a reinforcing filler in tires & other rubber products. In plastics, paints and inks, carbon black is used as a color pigment

(carcinogenic - [illegible])

Titanium dioxide - ultrafine (TiO_2) is used in sunscreens due to its ability to block UV radiation while remaining transparent on the skin.

- ultrafine TiO_2 is used in housing & construction as an additive to paints, plastics, cements, windows, tiles.

Incidental - vehicle engine exhausts, welding fumes combustion processes from domestic solid fuel heating & cooking.

ultrafine particles (UFP) - by product printer toner & automobi exhaust

medical & technology fields (Diagnostic imaging & novel drug delivery system

Natural - The structure of foraminifera (mainly chalk viruses (protein, capsid), the wax crystals covering a lotus or nasturtium leaf, spider & spider-mite silk, some butterfly wing scales, natural colloids (milk, blood) horny material (skin, claws, beaks, feathers, horns, hair) pape classical mechanics deals with the motion of objects under forces or their own momentum.

Quantum mechanics deals with the behaviour of objects at the microscopic level where matter & energy start to mathematically coverage because both can be observed to have wave-like behaviours at the level of planck's constant.

(F = ma)
Newton second law

schrodinger eqn
matrix mechanics
Werner Heisenberg
- path integral formula

$$i\hbar \frac{\partial}{\partial t} |\psi(r,t)\rangle = \hat{H} |\psi(r,t)\rangle$$

i = imaginary unit
$\hbar$ = planck constant $= \frac{h}{2\pi}$
ψ = Greek letter psi
r & t = position vector & time
$\hat{H}$ = Hamiltonian operator.

(wavefunct

scale representing them is known as 'nanoscale'. Thus, the lower part of the microscopic/mesoscopic scale below 100 nm is now distinctly designated as the 'nanoscale'. The three sizes of scales, that is, macroscopic scale (down to 10 μm), microscopic scale (10 μm down to 0.1 nm), and nanoscale (100 nm–0.1 nm) are shown in Fig. 1.4.

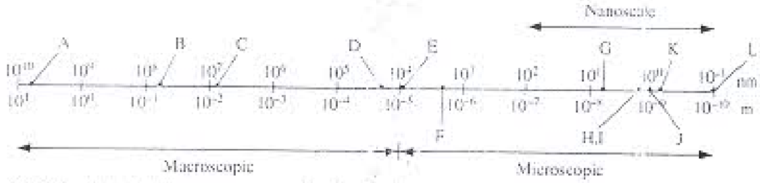

FIG. 1.4 Material objects on macroscopic, microscopic, and nanometre scales, indicated on the line in nanometres (above) and in metres (below). The nanometer scale (0.1–100 nm) is shown forming a part of microscopic scale.

In order to form an idea about the large difference in the sizes of worldly objects involved, they are represented by the dots on the scale for comparison and marked by alphabets A, B, C, D, etc. The relative sizes of these objects with respect to the hydrogen atom (diameter 1 × 10^{-10} m or 0.1 nm) are given in the last column of Table 1.3. A–D and E–L belong to macroscale and microscale, respectively. Objects G–L are common to both microscale and nanoscale. Our sun is nearly a perfect sphere with a diameter of about 1.392 million km, which is *1.392 × ten quintillion* times larger than the hydrogen atom. The figure *quintillion* represents 10^{18}.

Table 1.3 Comparison of the sizes of different objects to that of the hydrogen atom

Serial alphabet	Object	Size		Size relative to hydrogen atom (times)
		metre (m)	m/cm/mm/μm/nm	
A	Height of Indian male	1.66	1.66 m	1.66 × ten billion
B	Cricket ball	7.2 × 10^{-2}	7.2 cm	7.2 × hundred million
C	House fly	8.0 × 10^{-3}	8.0 mm	8.0 × ten million
D	Human hair	2.0 × 10^{-5}	20.0 μm	2.0 × hundred thousand
E	Red blood cell (RBC)	9.0 × 10^{-6}	9.0 μm	9.0 × ten thousand
F	Tuberculoses bacillus length	2.0 × 10^{-6}	2.0 μm	2.0 × ten thousand
G	Quantum dot	5.0 × 10^{-9}	5.0 nm	fifty
H	DNA helix diameter	2.0 × 10^{-9}	2.0 nm	twenty
I	Nanotube diameter	2.0 × 10^{-9}	2.0 nm	twenty
J	Bucky ball	1.0 × 10^{-9}	1.0 nm	ten
K	Amino acid molecule	8.0 × 10^{-10}	0.8 nm	eight
L	**Hydrogen atom**	**1.0 × 10^{-10}**	**0.1 nm**	**one**

cm = 10^{-2} m, mm = 10^{-3} m, μm = 10^{-6} m, and nm = 10^{-9} m

Some of these objects lying on the three different scales are shown in Fig. 1.5. Since only the objects larger than 10 μm are visible to the naked eye, it forms the lower limit of the macroscopic scale. The conventional microscopic scale (10–0.0001 μm) has been split into microscopic scale (10–0.1 μm) and nanoscale (100–0.1 nm) scales, with transition at 0.1 μm (100 nm).

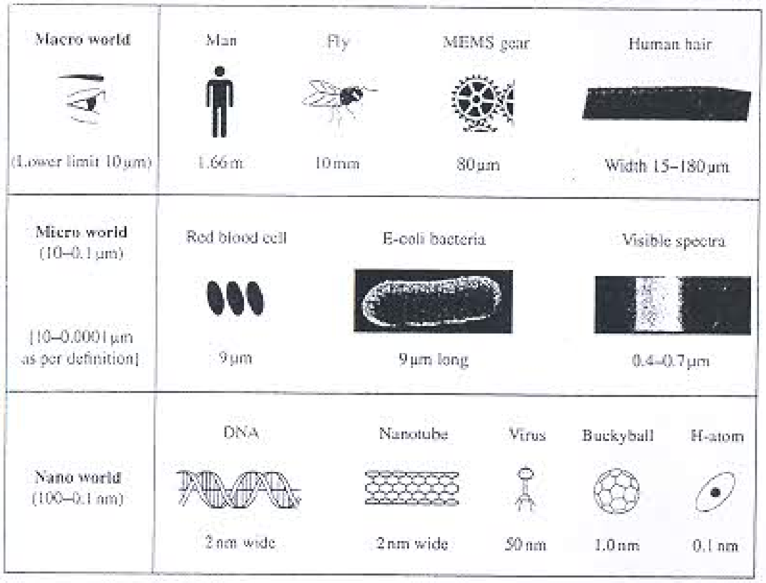

FIG. 1.5 Different material objects on macroscopic, microscopic, and nanometre scales

1.4 BIG VISION FOR THE SMALL WORLD

The recent origin of nanoscience and technology can be traced back to the predictions made by Richard P. Feynman, one of the greatest scientific geniuses of the 20th century. He demonstrated that there is scope to decrease the size of things in a practical way (what is possible according to the laws of physics). He envisioned that small structures could be formed in the future by arranging the atoms one by one, in the way we want. He was very confident and speculated that if we can have some control on the arrangement of things at a small scale, we will get an enormously greater range of i) possible properties that substances can have, and ii) different things that we can do. He thought about building electrical circuits on a small scale (nanoscale) that work at higher frequencies due to reduced transit time of the carriers in smaller components, resulting in very low time constant of the circuit. In addition, he envisioned that as we get to a very, very, small world, for example, a circuit consisting of a few atoms, this group of atoms on a small scale (read: the nanoparticles), forms an entirely new system that obeys the laws of quantum mechanics. By working with different laws, we can do different things involving quantized energy levels, interaction of quantized spins (values in multiples of ½), etc.

Table 1.1 (Contd.)

Discovery/Invention/Contributions	Nobel Prize winner(s)	Year
Discovery of fullerenes	Robert F Curl Jr, Harold W. Kroto, and Richard E. Smalley	1996
Discovery of superfluidity in helium-3	David M. Lee, Douglas D. Osheroff, and Robert C. Richardson	1996
Discovery of a new form of quantum fluid with fractionally charged excitations	R.B. Laughlin, H.L. Störmer, and D.C. Tsui	1998
Developing semiconductor heterostructures used in high-speed- and opto-electronics	Zhores I. Alferov and H. Kroemer	2000
Basic work on information and communication technology inventing of the integrated circuit	Jack S. Kilby	2000
The achievement of Bose–Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates	Eric C. Cornell, Wolfgang Ketterle, and Carl E. Wieman	2001
Pioneering contributions to the theory of superconductors and superfluids	Alexei A. Abrikosov, Vitaly L. Ginzburg, and Anthony J. Leggett	2003
Contribution to the quantum theory of optical coherence	Roy J. Glauber	2005
Discovery of giant magnetoresistance	Albert Fert and Peter Grünberg	2007
Ground-breaking experiments regarding the two-dimensional material grapheme	Andre Geim and Konstantin Novoselov	2010
Ground-breaking experimental methods that enable measuring and manipulation of individual quantum systems	Serge Haroche and David J. Wineland	2012

1.3 PHYSICAL SIZE SCALES ■

Depending upon how many physical dimensions of nanostructures lie within the nanoscale, and consequently, degree(s) of charge carrier confinement, they are further classified into three categories—one-dimensional quantum wells, two-dimensional quantum wires, and three-dimensional quantum dots nanostructures—that will be discussed in detail in Chapter 3. Conversely, the degree(s) of free movement of charge carriers in a nanoparticle will be the same as the number of physical dimensions of size larger than 100 nm. For example, a quantum well has one degree of carrier confinement, and two degrees of free carrier movement, and so on.

In order to visualize the size-scale of nanomaterials with respect to the vast size variation of objects existing in the universe, we should look at the different size-scales in use, prior to the formal arrival of nanomaterials in the late 1980s. In a broader sense, material objects can be represented on two size-scales, leaving aside the astronomical and subatomic scales on the two extremes, namely, *macroscopic* and *microscopic*. The macroscopic scale refers to the large objects visible to the naked eye. The lower size limit of these objects, which are visible to the naked eye is around 10 µm (Symbol µ stands for factor micro = 10^{-6}, m for metre, and µm normally called *micron*, being a millionth of a metre). Thus, all objects larger than ten micron fall within the macroscopic scale, such as the height of a human being, the size of a tennis ball, a house fly, and a human hair. The human hair's thickness lies in the range of 15–180 µm, with the lower side being close to the visibility limit of the unaided eye. All the macroscopic objects obey the laws of classical mechanics characterized with average or bulk properties. Different factors used in scientific notations are given in Table 1.2

Table 1.2 Factors used in scientific notation to express small and large numbers in metric system

Prefix (symbol)	Factor	Name	Prefix (symbol)	Factor	Name
deca (da)	10^1	ten	deci (d)	10^{-1}	Tenth
hecto (h)	10^2	hundred	centi (c)	10^{-2}	hundredth
kilo (k)	10^3	thousand	milli (m)	10^{-3}	thousandth
mega (M)	10^6	million	micro (µ)	10^{-6}	millionth
giga (G)	10^9	billion	nano (n)	10^{-9}	billionth
tera (T)	10^{12}	trillion	pico (p)	10^{-12}	trillionth
peta (P)	10^{15}	quadrillion	femto (f)	10^{-15}	quadrillionth
exa (E)	10^{18}	quintillion	atto (a)	10^{-18}	quintillionth
zetta (Z)	10^{21}	sextillion	zepto (z)	10^{-21}	sextillionth
yotto (Y)	10^{24}	septillion	yocto (y)	10^{-24}	septillionth

The objects that are smaller in size than the eye's visibility limit and that require a microscope to be detected or observed clearly, down to individual atoms, fall within the microscopic scale. Presently, electron microscopes are capable of imaging even the individual atoms. The scanning-probe-type electron microscopes, particularly, the atomic force microscope (AFM) and scanning tunnel microscope (STM), are used in scientific investigations to image objects as small in size as that of an atom. Thus, all objects with size variation between 10 µm and an individual hydrogen atom of 0.1 nm may be considered to lie on the microscopic scale. As the size of objects decreases, they continue to obey the laws of classical mechanics with average/bulk properties, independent of particle size. The number of atoms on the surface of such particles is quite negligible, as compared to the number of atoms lying inside the particle, the bulk properties being dominant. As the particle size approaches a sub-micron limit of about 0.1 µm (100 nm), a transition occurs in material properties, shifting their size-independent classical behaviour to size-dependent quantum-mechanical behaviour. The surface-to-volume ratio of these particles increases with decrease in size, and their surface properties start dominating the bulk properties. This amounts to increase in the number of atoms on the surface as compared to those inside the particle. Obeying quantum mechanical laws would mean that they possess discrete energy states like those of atoms or smaller molecules. These material particles are called 'nanoparticles' and the

Nanoparticles / Nanostructures

particles, objects or devices with size in the range 0.1 - 100 nm are called nanostructures or nanoparticles.

Ex Nano-structure our own body is a perfect example of a nano-structured material.

nanoparticles - Titanium dioxide metal, dielectric & semiconductor

✓ Nanomaterial - CNT, nanoparticles, metal rubber, quantum dots, nanopores

Nanoscale - Scale of length that is used in measurement and characterization of nanoparticles in units of 10^{-9}m or nm spanning the range 0.1 - 100 nm

* Macroscopic scale refers to the Large objects visible to the unaided naked eye. The lower size limit of these objects visible to the naked eye is around 10 micron

without them

* Ex - ht of a human being, the size of a tennis ball, a house fly and a human hair.

* All the macroscopic objects obey the laws of classical Mechanics characterized with avg. or bulk properties. (projectile motion, colors of rainbow

* objects that are smaller in size than the eye's visibility limit and that require a microscope to detect or observe them, down to individual atoms, fall on the microscopic scale which also encompasses the nanoscale.

* Today, electron microscopes are capable of imaging even individual atoms.

- obey the laws of quantum mechanics (jumping from the roof of 1 building onto another)

Nanoscale Properties

Mechanical - Increase in hardness and strength of Metal & alloys, enhanced ductility, toughness and form ability of ceramics, super strength and super plasticity

Electrical - Higher electrical conductivity in ceramics & magnetic nanocomposites, higher resistivity in Metals

optical - Increase in luminescent efficiency of semiconductors, transparency of nanoparticle

Chemical - substantial increase in catalytic properties & reaction rates

Mechanical - vibrational modes
elastic moduli
Yield limits
strength
toughness
Temp. & pr. effects on mechanical properties (Creep)

Electrical

- chemical potential (for electrons, protons)
- band gaps in the bulk & at the surface
- Fermi energy pinning by defects & surfaces
- Electron transfer rates (tunneling through barriers at surfaces)

optical · Density of electronic states

- polariability
- Dielectric constant (frequency dependent)
- optical absorption as function of wavelength
- quantum dots & lines
- Nonlinear optical properties

optical (color, transparency)
Electrical ((onductivity)
~~physical (Hardness, boiling point~~)
chemical (reactivity, reaction rates)