Chapter 11
Some Special Nanomaterials

11.1 Introduction

We discussed in last few chapters synthesis, characterization and properties of nanomaterials in general. Few examples were given from time to time. In this chapter we shall discuss some nanomaterials like fullerenes, graphene, carbon nanotubes, porous silicon, aerogel, zeolites, self assembled materials and core-shell particles, which form a large section of nanomaterials due to their novel properties.

11.2 Carbon Nanomaterials

Carbon is one of the very interesting elements which constitutes a major part of the living as well as non-living world. It also is the backbone of an important branch of chemistry viz. polymer chemistry. It is not surprising that clusters and nanomaterials that we know today provide a rich variety of carbon forms. We can get carbon in various forms as 0-D (small clusters and fullerenes as well as nano diamonds), 1-D (carbon nanotubes), 2-D (graphene and graphane) and 3-D (diamonds) materials. In fact it is often said that half of the community in science is working on carbon based, particularly fullerenes, graphene and carbon nanotubes, indicating the importance of these materials. In this section we shall briefly try to understand these nanomaterials.

11.2.1 Fullerenes

Crystalline carbon can exist in diamond, graphite, fullerene, carbon nanotubes and graphene forms. Out of these allotropes of carbon, fullerene, carbon nanotubes and graphene are relatively new. Fullerene was discovered around 1985. Fullerene

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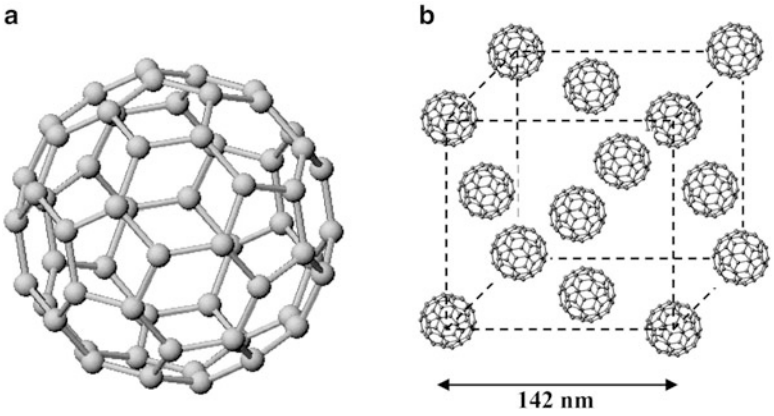

Fig. 11.1 (**a**) Fullerene C_{60} and (**b**) Crystalline form of C_{60}

crystal is a molecular crystal having Face Centered Cubic (FCC) structure as illustrated in Fig. 11.1. At the corners and faces of a cube there are ball shaped carbon molecules which themselves belong to fullerene family. Each fullerene molecule has a cage-like structure. All the carbon atoms are located on the surface of a nearly spherical figure. Fullerenes can have 60, 70, 78 or more (specific or magic) number of carbon atoms on the surface, out of which 60-atom molecule (or cluster) is the most stable and spherical in shape.

11.2.2 Carbon Nanotubes (CNTs)

This 1-D form of carbon was accidentally observed in 1991 by S. Iijima under a transmission electron microscope. He was actually examining some sample of carbon clusters viz. 'fullerens' synthesized using electric arc discharge method. Carbon nanotubes were so less in this sample that Iijima himself said somewhere that it was like observing 'a needle in a hay stack'. However prior to this observation, Smalley, one of the Nobel laureates who made the discovery of Fullerenes had speculated that like fullerenes which were spherical or nearly spherical molecules, even tubes should be possible. This was followed by some elegant theories predicting the nature of electron and phonon spectra of carbon nanotubes. Discovery of nanotubes was a breakthrough in that sense. His experiments suggested that even a simple set up as used in producing fullerenes should produce even nanotubes under certain conditions. It was quite clear as more and more scientists started reporting the nanotubes that the conditions favoured for fullerenes were unsuitable for producing the nanotubes. Novelty and later the potential applications of nanotubes created a wave of excitement amongst the scientists which led to unfolding of many unique properties carbon nanotubes possess. Their potential applications in electronics, optoelectronics and energy saving systems have been well realized. Just in one

decade several groups all over the world have dedicated their research activities to synthesize and analyze the nanotubes. Following the original arc deposition method, it was found that chemical vapour deposition, laser ablation and some other methods could be employed to produce carbon nanotubes. Further it was found that not only carbon but many other materials like ZnO, TiO_2 and MoS_2 can have shape of nanotube (Box 11.1). They have their own applications but carbon nanotubes still remain the most important ones due to their technological potential. A number of excellent reviews and books have been published on carbon nanotubes.

Here we shall briefly discuss some of the unique features of carbon nanotubes, synthesis methods, properties and applications.

Box 11.1: Why the Name Fullerenes?

Why the name fullerene is given to such cage-like carbon clusters has an interesting story. H.N. Kroto of the Sussex University, U.K. and R. Smalley's group in the Rice University, U.S.A. were performing some experiments in the Rice University. Their objective was to simulate some interstellar molecules in the laboratory. They were trying to laser ablate a graphite rod and study its mass spectrum using a mass spectrometer. Evaporation from graphite was carried out in ultra high vacuum chamber in helium atmosphere. To their great surprise they repeatedly got a mass signal due to 60 carbon atom cluster. They tried to model it nearly for a week and suddenly Kroto remembered of an industrial exhibition he had once visited. There he had seen a dome-like steel structure constructed by a very famous architect Buckminster Fuller. This dome had some pentagons and some hexagons distributed on its surface. Kroto, Smalley and Curl succeeded in constructing 60 atoms cluster model with 12 pentagons and 20 hexagons with a restriction that no two pentagons touched each other and each pentagon shared an edge with hexagon. Later it was found that one could also have carbon clusters with more number of atoms having 12 pentagons but more number of hexagons. It was in the honour of Buckminster Fuller that the name Fullerene was given to the family of this newly found cage-like carbon cluster. It is normally written as carbon atom symbol C with suffix to denote the number of atoms present. For example C_{60}, C_{70}, C_{78} etc. are 60 atoms, 70 atoms and 78 atoms carbon fullerenes. Kroto, Smalley and Curl received the Nobel Prize in 1996 for their discovery.

However it was not until 1989 that fullerenes were widely investigated. The original apparatus of Smalley group at Rice University where the discovery of fullerenes was made was quite expensive and not available at many places. Besides one could not get any samples out of this apparatus, it was only detection by a mass spectrometer. Huffman and Krätscmer when they heard of discovery of fullerenes wondered if they too were producing this form

(continued)

Box 11.1 (continued)
of carbon as they had found that they too in their experiments had some strange form of carbon. Their further work showed that indeed they too were producing fullerenes. To their great surprise with a simple set up they were producing large quantities of fullerenes. When their work was published, there started a big activity all over the world to synthesize fullerenes. It was also found that it is possible to trap some ions inside the fullerene cage or attach some functional molecules to fullerene from outside. It was realized that due to small size (diameter of C_{60} fullerene is just 0.7 nm; that is why we can consider fullerenes as 0-D material) of fullerenes, they can be used for even drug delivery. The fullerenes could crystallize in a solid form. Properties of fullerenes and their crystals are well investigated now. Smaller clusters of carbon atoms (<60 atoms) also have been investigated. They are detected in mass spectrometers but are not stable and not possible to collect. But most important is that investigations on fullerenes also led to the discovery of Carbon Nanotubes which are found to have a great technological potential.

11.2.2.1 What Are Carbon Nanotubes?

Carbon nanotubes can be considered as cylinders made of graphite sheets, mostly closed at the ends, with carbon atoms on the apexes of the hexagons, just like on a graphite sheet. Thus, as shown in Fig. 11.2, one can consider carbon nanotube as folding of a graphite sheet (it is only an imaginary sheet, actual growth can be different), just like one rolls a piece of paper into a cylindrical form. The difference however is that, a paper is a two dimensional solid material (area much larger, few cm^2, as compared to thickness of ~few micrometres) and graphite sheet we are talking about has an area of few μm^2 and thickness just the atomic size of

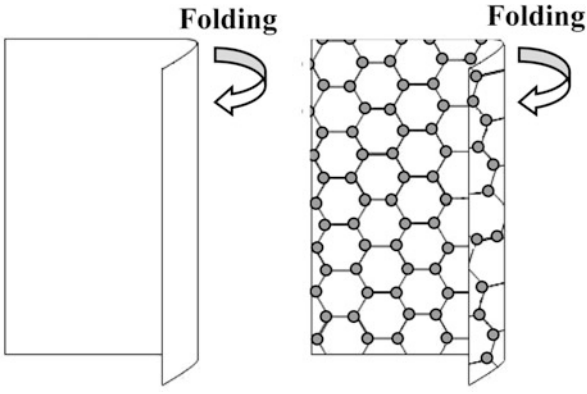

Fig. 11.2 Rolling the carbon sheet to obtain carbon nanotube

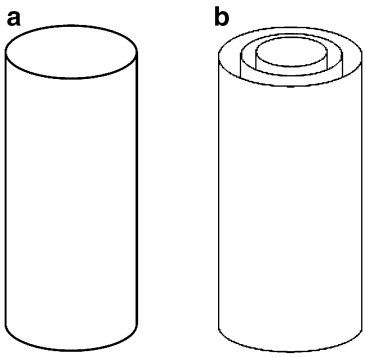

Fig. 11.3 (**a**) SW and (**b**) MW tubes

carbon atom. If we consider the rolling of graphite sheet, we can imagine carbon atoms being spread in hexagonal arrangement with some lattice strain. The lines showed connecting the filled spheres (carbon) are the bonds that exist between the atoms. Besides, during their formation, nanotubes get capped with hemispheres of fullerenes. It is also possible that many concentric cylinders may be formed as a nanotube. Such concentric nanotubes are termed as Multi Wall Carbon Nanotubes (MWCNT). The distance between their walls is 0.334 nm. This is similar to what one gets between two graphite layers in a single crystal. MWCNT are most common and easily formed. However under certain conditions, it is possible to obtain even Single Wall Carbon Nanotubes (SWCNT). Figure 11.3 illustrates the concept of both SWCNT and MWCNT.

MWCNTs can be turned into SWCNTs using some etching methods. SWCNTs have diameters ranging from 1 to 2 nm. MWCNTs have outer diameters ranging from 2 to 25 nm. The concentrically formed MWCNTs are, however, rotationally disordered (turbotactic). Both MWCNTs and SWCNTs have their own range of applications and studied rigorously.

As the carbon nanotubes can be imagined as folding of a graphite sheet, two things are obvious: (1) carbon atoms on nanotubes are sp^2 bonded like in graphite, although some strain would be expected due to curvature and (2) there should be more than one way of folding the graphite sheet.

Indeed three types of carbon nanotubes (we will consider here only the SWCNT for the sake of simplicity) are possible viz. armchair, zigzag and helical, under appropriate conditions of growth. In order to understand the differences in these three types, consider a graphite sheet as shown in Fig. 11.4.

It is indeed possible to uniquely identify each hexagon as (a, b) with $a = 0, 1, 2, 3 \ldots$ and $b = 0, 1, 2, 3, \ldots$ only (b, a) is not allowed. Position of any hexagon would be given by a vector $\mathbf{R}$ as

$$\mathbf{R} = a\boldsymbol{x} + b\mathbf{y} \tag{11.1}$$

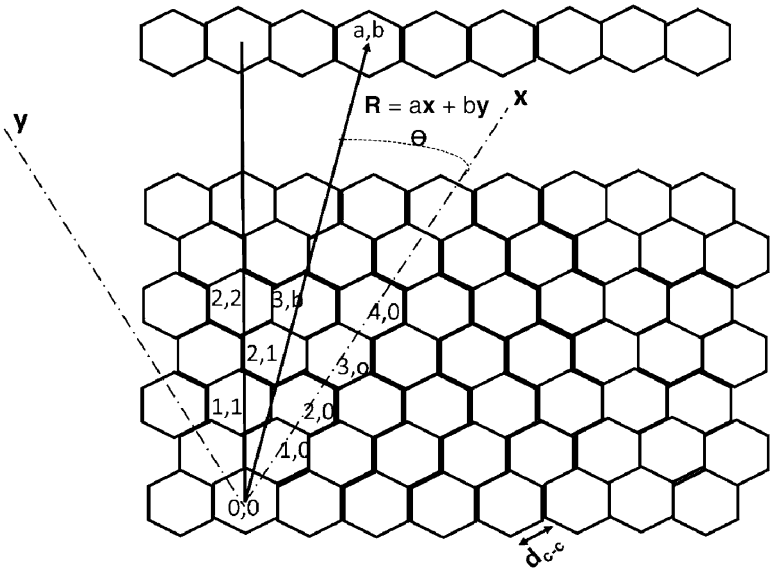

Fig. 11.4 Graphite sheet and generation of tubes

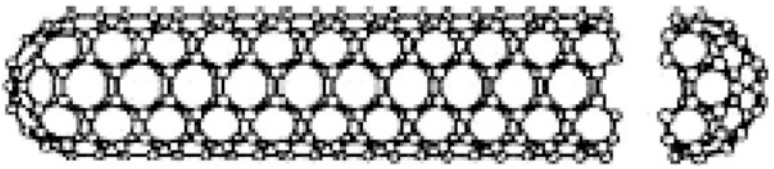

Fig. 11.5 Fullerene with end caps

Consider now the length of primitive vectors **x** and **y**, in terms of distance '*d*' (d_{c-c}) between two nearest carbon atoms. It is clear from the simple geometrical considerations that

$$\mathbf{x} = \sqrt{3}.d \quad \text{and} \quad \mathbf{y} = \sqrt{3}.d \tag{11.2}$$

Vector **R** denoting the position of a hexagon is known as a 'chiral vector'. A tube obtained by folding the sheet along **R** (*a*, *b*) is called a chiral tube (*a*, *b*). An angle between x-axis and vector **R**, θ also can be used to denote the folding. It is observed that all the angles between $0 < \theta < \pi/6$ are sufficient to uniquely define different types of tubes except (*b*, *a*) is not possible. The tubes whose mirror image is identical with its own image is known as 'achiral' tube and 'chiral' otherwise. The tubes are normally terminated with the hemispheres of fullerenes (see Fig. 11.5), as was predicted by Smalley.

These are simply called as 'caps' or 'end caps'. Caps contain six pentagons (half the number in C_{60} fullerene) and different number of hexagons so that they can fit

on the tubes properly. It should be remembered that in the notation used here, for a nanotube we need to have $a > b$. Diameter of the nanotube is obtained as follows

$$D = \frac{\text{circumference of tube}}{\pi} \tag{11.3}$$

$$\begin{aligned}\text{Circumference of tube} &= |\mathbf{R}| \\ &= \sqrt{\text{R.R}} \\ &= \sqrt{(ax + by) \,.\, (ax + by)} \\ &= \sqrt{3}.d_{\text{c-c}}\sqrt{(a^2 + ab + b^2)}\end{aligned} \tag{11.4}$$

as

$$x \cdot x = y \cdot y = 3d_{\text{c-c}}^2 \tag{11.5}$$

$$D = \sqrt{3}.d_{\text{c-c}}\frac{\sqrt{(a^2 + ab + b^2)}}{\pi} \tag{11.6}$$

where D is diameter, $d_{\text{c-c}}$ – distance between two nearest carbon atoms, and a and b are chiral lengths of vector $\mathbf{R}$.

Angle θ in terms of chiral lengths a and b is obtained as

$$\cos\theta = \frac{\mathbf{R} \cdot a\mathbf{x}}{|R| \cdot |a\mathbf{x}|} \tag{11.7}$$

$$= \frac{(a\mathbf{x} + b\mathbf{y}) \cdot a\mathbf{x}}{\sqrt{3.d}_{\text{c-c}}\sqrt{(a^2 + ab + b^2)}\,\sqrt{3d_{\text{c-c}}} \cdot a} \tag{11.8}$$

$$\theta = \cos^{-1}\left\{\frac{2a + b}{2\,(a^2 + ab + b^2)}\right\} \tag{11.9}$$

For the angles $0 < \theta° < \pi/6$.

11.2.3 Types of Carbon Nanotubes

Depending upon their chirality or the way of folding as discussed above for a SWCNT, basically three types arise viz. zigzag, armchair and helical CNT.

Zigzag CNT: These are formed for $\theta = 0$ and chirality $(a, 0)$. i.e. by folding parallel to x-axis. The name zigzag has been given due to zig zag arrangement of carbon atoms that can be seen (Fig. 11.6) if cross section of the tube as shown in the figure is taken. This type of tubes are 'achiral' tubes i.e. their mirror images are similar as the original structure.

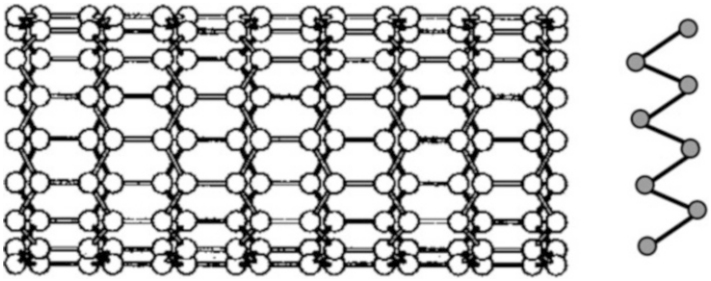

Fig. 11.6 Zigzag CNT

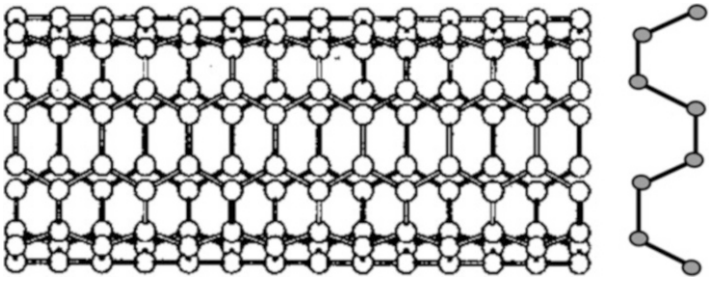

Fig. 11.7 Armchair CNT

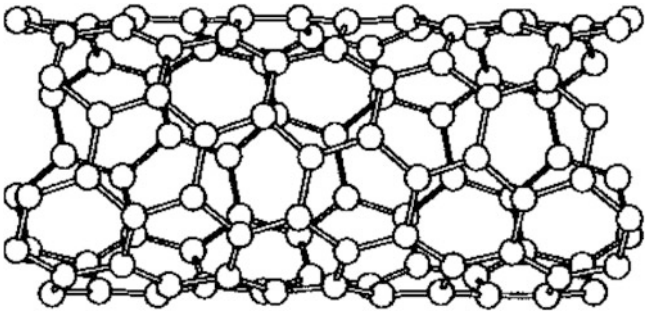

Fig. 11.8 Helical CNT

Armchair CNT: These are formed for the angle $\theta = \pi/6$ and chirality (a, a). These also are 'achiral in nature'.

Armchair structure with arrangement of carbon atoms can be seen in Fig. 11.7.

Helical CNT: These are obtained when angle θ is anywhere between 0 and $\pi/6$ and chirality is (a, b). Helical structure of CNT is shown in Fig. 11.8.

Such tubes are 'chiral' and their mirror images appear to differ from their original structure. Table 11.1 shows the comparison of three types of CNT.

Table 11.1 Comparison between different types of CNTs

Type of CNT	R	θ°	Cross section
Zigzag (achiral)	a, 0	0	Trans
Armchair (achiral)	a, a	30	Cis
Helical (chiral)	a, b	$0 < \theta < 30$	Mixture of trans and cis

Besides these basic types, a variety of shapes like ropes, springs, stripes, bamboo structure, conical shapes etc. are observed to have been formed of CNTs under different experimental conditions.

11.2.4 Synthesis of Carbon Nanotubes

Iijima had detected carbon nanotubes in an electric arc discharge set up for synthesizing fullerenes. His nanotubes were multiwall type. The yield of nanotubes was very low compared to the fullerene content. Due to tremendous interest the scientific community took in CNTs, soon arc discharge and other methods like laser ablation and chemical vapour deposition were optimized to increase the yield and even to get SWCNTs. It is now understood that electric arc discharge mostly can produce MWCNT and laser ablation can be used for SWCNT. There are also some attempts to use ion beams to obtain CNTs. However such methods are uncommon. In the following we briefly discuss the parameters and few points regarding the CNT synthesis using electric arc discharge, chemical vapour deposition and laser ablation techniques. More details about these techniques are discussed in Chap. 3.

11.2.4.1 Electric Arc Discharge

Carbon nanotubes, in an electric arc discharge set up (see Fig. 11.9) between two graphite rods as electrodes, are formed under certain conditions as follows.

Electrodes: Graphite
Diameter of electrodes: 5–20 mm
Gap between the electrodes: ∼1 mm
Helium gas pressure: 100–500 Torr (no CNT formed if $p < 100$ Torr)
Current: 50–120 A
Voltage: 20–25 V
Cooling of the chamber is preferred.
Yield of MWCNT: ∼30–50 %

Nanotubes are found to be deposited in the central region of cathode. For MWCNT it is not necessary to use any catalyst. Central region of cathode reaches a temperature close to 3,000 °C and nanotubes are aligned in the current direction

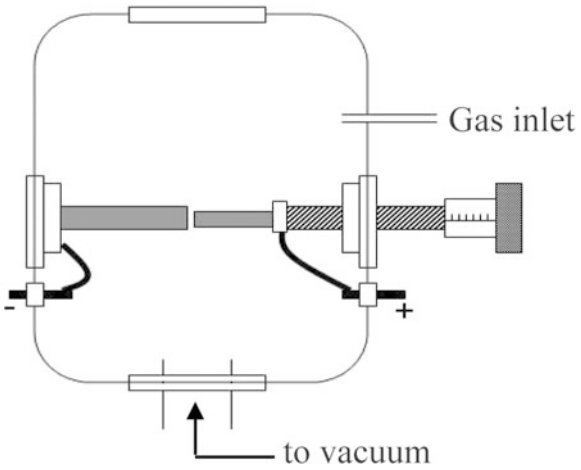

Fig. 11.9 Electric arc discharge set up

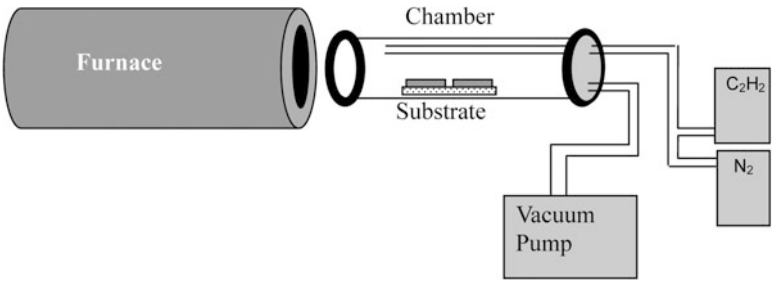

Fig. 11.10 CVD set up (schematic). The chamber and the substrates are shown outside the furnace just for the illustration

between the two electrodes. The central region of cathode is surrounded by a region in which nanoparticles, fullerenes and amorphous carbon are formed. It, therefore, becomes necessary to purify the MWCNTs to get rid of these other particles. No tubes are found to be deposited on the walls of the experimental chamber as is the case with fullerenes.

Diameters of nanotubes are in the range of 0.7–1.5 nm. Incidentally, 0.7 nm is the diameter of C_{60} fullerene. Length of the tubes is typically 1 μm. However lengths in the few mm to mm range also have been possible.

11.2.4.2 Chemical Vapour Deposition (CVD)

For large scale production of the nanotubes, this method is most useful. Here a hydrocarbon gas is cracked under certain conditions. Experimental set up is shown in Fig. 11.10.

As there are no graphitic hexagons present in some of the precursors used to deposit carbon nanotubes, catalysts play a very important role in carbon nanotubes formation. Advantage of this method is that aligned nanotubes can be deposited on some solid substrates so that they can be used for some electronics or other application. Both MWCNT and SWCNT are possible to obtain by this method. No nanoparticles or amorphous carbon formation takes place, making high purity nanotubes.

Gases: CH_4, C_6H_6 etc.
Pressure in the chamber: $\sim 10^4$ Pa
Catalyst: Fe, Co, Ni or Pt
Furnace Temperature: ~1,000 °C

11.2.4.3 Laser Ablation

Schematic sketch of the laser ablation set up for CNT deposition is given in Fig. 11.11. Advantage of using laser in the synthesis of carbon nanotubes is that the nanotubes are invariable SWCNTs. Ropes of 10–20 nm diameter and lengths ~100 μm also are observed. Narrow size distribution of diameters of SWCNTs is an attractive feature of this technique.

11.2.5 Growth Mechanism

One may wonder at this stage as to how do the nanotubes grow at all. At the synthesis temperatures as high as used in CVD (>800 °C) and electric arc deposition (~3,500 °C) or laser ablation, we really don't think that long sheets of graphite are really released and folded. It is probably *atom by atom* or *molecule by molecule addition* that under certain favourable conditions nanotubes are formed. Some scientists think that an initially formed fullerenes with 12 pentagons and hexagons would open up its cage to accommodate a dimer (C_2) and/or a trimer (C_3) as shown in Fig. 11.12.

Pentagons on a fullerene are more strained and can break to accommodate a C_2 dimer or C_3 trimer. This can continue and long nanotubes be formed. Some

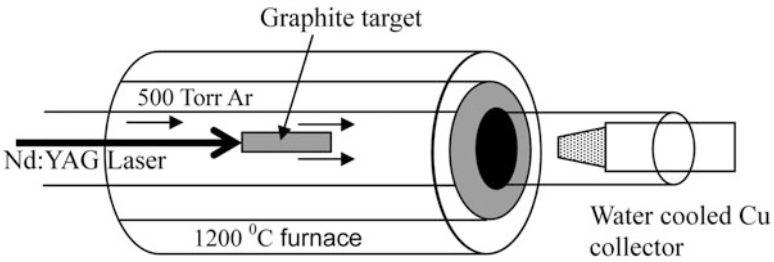

Fig. 11.11 Laser set up (schematic) to deposit CNTs

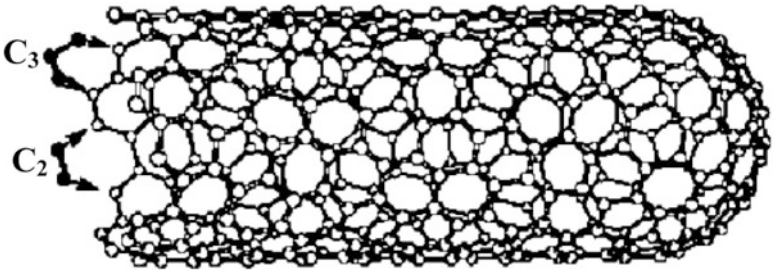

Fig. 11.12 Growth of CNT by absorption of C_2 dimers and C_3 trimers

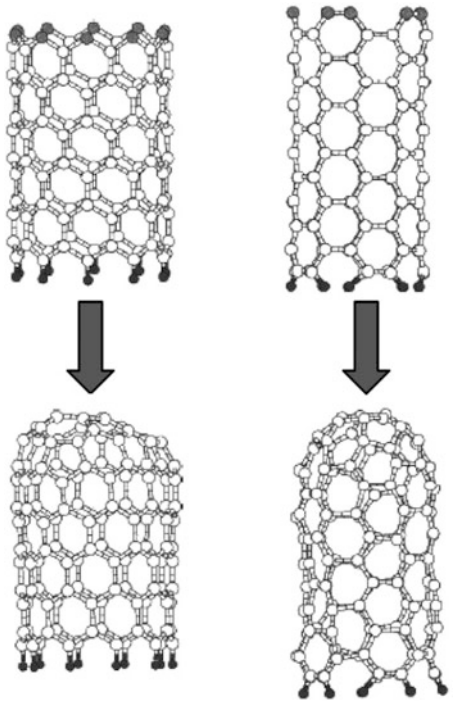

Fig. 11.13 Carbon without end cap, dimer, trimer addition for growth and spontaneous closure

others are of the opinion that during the growth process, nanotubes are not capped but ultimately get end caps (Fig. 11.13). Other structures with concentric tubes and different shapes also have been explained. As there are a variety of methods, temperature, catalysts and pressure which dictate the growth, it is rather impossible that a single mechanism would be responsible for the nanotube growth.

Experiments to determine the conductor type of CNT includes Scanning Tunnelling Spectroscopy, Electron Spin Resonance and ^{13}C nuclear magnetic resonance. Measurements are in agreement with the theoretical prediction that both semiconductor and metallic nanotubes should be formed with above mentioned conditions.

Table 11.2 Carbon polymorphs and their properties

Dimension	3D	2D	1D	0D
Polymorph	Diamond	Graphite/graphene	Nanotube	Fullerene
Bonding type	sp^3	sp^2	sp^2	sp^2
Bond length, Å	1.54	1.42	1.44	1.40
E_g, eV	5.47	0	1–0	1.9
Conductor type	Insulator	Metal/semimetal	Semicond. to metal	Semicond.
Density, gm/cc	3.52	2.26	∼1.2–2.02	1.7 (for C_{60})

Superconducting transition temperature T_C in CNT is as low as $\sim 1.5 \times 10^{-4}$ K. Doping can alter T_C in superconductors as well as affect metallic or semiconductor behaviour (Table 11.2).

11.2.6 Graphene

Graphene is just a single layer of graphite crystal. As was discussed in Chap. 2, a graphite crystal has stacks of carbon layers weakly bonded to each other. That is why these layers can easily slip over each other. Each layer has heaxagonally arranged carbon atoms. Such layers when appear as single, self standing material is graphene, when rolled into a tubular form it becomes carbon nanotube or even becomes something like a fullerene.

Graphene, which is an isolated sheet of carbon atoms, was considered to be difficult to achieve. However, in 2004 it was shown by the scientists from the University of Manchester, U.K. and Institute of Microelectronics Technology, Chernogolovaka, Russia that it is possible to separate single carbon sheets (monolayer thick) by simply peeling them off using a scotch tape. The properties of graphene sheets could be measured which led to lot of interesting work on graphene. It is also possible to produce graphene by other methods like chemical vapour deposition. Electronic structure and transport studies have revealed a great deal of interesting properties of graphene. For example quasiparticles in graphene are found to be massless Dirac fermions and Quantum Hall Effect which is usually observed at very low temperatures is observed at room temperature in graphene. Discussion on these topics is beyond the scope of this book. We just end this topic here by remarking that it is a topic with tremendous scope in electronics, spintronics (spin cherence length as large as 1 μm is observed in graphene at room temperature), sensors as well as quantum computers. The electron mobility of graphene at room temperature is very large and its resistivity is even smaller than silver. Mechanical properties of graphene are superior to steel. It is ∼200 times stronger compared to steel. The work on graphene has been considered to be a breakthrough which led Geim and Novoselov to receive prestigious Nobel Prize in the year 2010.

As there would be dangling bonds on carbon atoms, they can be passivated by hydrogen. This form of carbon is known as ‘graphane’.

11.3 Porous Material

There is a large variety of porous materials with pores of few nanometers to micrometres. Porous materials are classified as microporous, mesoporous and macroporous materials based on the pore sizes. Materials with pore diameters less than about 2 nm are called microporous materials and those with larger than about 50 nm size are known as macroporous. The pores of intermediate sizes i.e. between 2 and 50 nm are referred to as mesoporous materials. There exist some natural porous materials like soil, snow, sandstone, corals, bones, wood and so on. Several examples of manmade porous materials around us are bread, biscuits, sponge, brick, chalk etc.

In this section we shall discuss some of the artificially synthesized porous materials. These materials have emerged over a long period and have considerable applications from drug delivery, energy storage to space science. Due to their porous nature in general, all types of porous materials inherently have lower density and larger surface area (includes surface area of pore walls) than the corresponding bulk materials.

11.3.1 Porous Silicon

Silicon is the most widely used semiconductor material by electronics industry. It is abundant in nature and techniques to purify, grow single crystals economically and on large scale are well developed. The methods of doping and polishing also have been perfected. Oxide of silicon is stable and metal-silicon contacts can be made and understood to good extent. Thus microelectronics industry is well established to use silicon in making various components and systems like diodes, transistors, Field Effect Transistors (FETs), Metal Oxide Semiconductor FETs (MOSFETs), Integrated Circuits (ICs), Very Large Scale Integrated Circuits (VLSIs) and Mechano-Electrical Machines (MEMS). However, there is a basic drawback with silicon viz. unlike some other semiconductors like ZnS, CdS, GaAs, InAs and InP, light emission capability of silicon is extremely poor. Therefore it is not possible to make light emitting diodes (LED) or lasers using silicon wafers that are usually used in electronics. It was thus considered for a long time that silicon cannot be an optoelectronics material.

However in 1990, Canham showed that porous silicon can be very easily and routinely formed on silicon wafers, used by electronics industry, to emit photoluminescence in the visible range at room temperature. He further showed that silicon nanocrystallites formed, as a result of pores formation, were responsible for light emission and as the crystallite size reduced, the emission wavelength also decreased. This triggered the wave of enthusiasm in the scientists and technologists, as it was a major breakthrough for silicon industry to use silicon as an optoelectronic material. As a result, considerable work has been carried out since 1990 to make porous silicon by number of ways, use different substrates, etchants etc. and investigate the various structural, optical and electrical properties and demonstrate new applications. Even other semiconductors like GaAs also have been made porous and inves-

tigated. It should be remembered that scientists were using for quite a long time the procedures, specially the electrochemical polishing, similar to that used in porous silicon formation and some interesting properties were already noticed. However, prior to Canham's publication, emphasis of early work was on studying the properties of thin film observed during etching or electropolishing of silicon. Detailed investigations showed that such films were porous and since 1970 the word 'porous silicon' was being used. Canham showed the nanocrystalline nature of the pore walls and its role in luminescence that became interesting and decisive to consider porous silicon as an optoelectronic nanocrystalline material. Here we will discuss, how porous silicon can be made, its properties and briefly some applications (Box 11.2).

Box 11.2: History of Silicon Etching

- 1956—A. Uhlir at Bell Labs. USA [ref. *Bell Syst. Tech. J.* **35** (1956) 333] observed while polishing silicon by electrochemical method that at high current density polishing occurred but at low current density surface looked as if there was some blackish, brownish or sometimes reddish deposit. He attributed this to the formation of some silicon suboxides.
- 1958—D.R. Turner [ref. *J. Electrochem. Soc.* **105** (1958) 402; Surface Chemistry of Metals & Semiconductors (H.C. Gatos, ed.), Wiley, New York (1960); The Electrochemistry of Semiconductors (P.J. Holmes, ed.) Academic Press, New York, Vol. 155 (1962)] attributed anodic film formation to $(SiF_2)_n$ polymeric network with predominance of silicon. He considered that the formation of anodic regions depends upon whether oxidizing or reducing species attack a certain region. When HNO_3 attacks, it removes an electron from the surface making it a local cathode. The positively charged hole is created as a result of loss of electron. Hole can wander around and towards Si where HF attacks. It is then ready to form an anodic region. Silicon complexed with fluorine, dissolves into the solution forming a pit.
- 1959–1956—Robins and Schwartz used HNO_3 and HF solution for etching silicon. In a series of papers [*J. Electrochem. Soc.* **106** (1959) 505; ibid. **107** (1960) 108; ibid. **108** (1961) 365; ibid **123** (1976) 1903], they discussed that process of etching first involved the formation of silicon oxide and then its removal by HF. They, however, did not mention the formation of any porous film.
- 1960—R.J. Archer [*J. Phys. Chem. Solids* **14** (1960) 104] mentions porous silicon formation and observation of silicon hydride formation.
- 1965—K.H. Beckman [*Surf. Sci*. **3** (1965) 314] studied infra red spectrum of porous silicon and showed that polymeric network of–SiH_2 existed on the etched silicon surface. If electrochemically prepared SiH_2 gets connected through Si-Si bonds and if chemically prepared, the network is connected through Si-O-Si bonds.

(continued)

Box 11.2 (continued)

- 1972—M.J.J. Theunissen [*J. Electrochem. Soc.* **119** (1972) 351] clearly showed for the first time that porous silicon had crystalline nature.
- 1983—G. Bomchil, R. Herino, K. Barla and J.C. Pfister [*J. Electrochem. Soc.* **130** (1983) 1611] measured surface area and sizes of pores in various lightly and heavily doped p and n type silicon samples.
- 1984—C. Pickering, M.I.J. Beale, D.J. Robbinson, P.J. Pearson and R. Greef [*J. Phys.* **C 17** (1984) 6535] carried out optical studies of etched Si. Refractive index of p^+-Si varied from 3.47 towards 1.0 with increasing porosity. They observed the presence of complex amorphous alloy of Si, H and O along with crystalline Si in the porous film. They also mentioned the observation of an intense band gap luminescence at 4.2 K as well as orange red luminescence. They attributed it to amorphous SiHx formation. Further by changing H concentration, room temperature photoluminescence also was observed.
- Rutherford Back Scattering (RBS) and nuclear measurements of porous silicon showed that it was crystalline and surface was covered with 50 % H, 5 % O, 1 % F and 3 % C (mostly as contaminant). SiH formation was concluded.
- 1988—Work on porous silicon was reviewed by G. Bomchil, A. Halimaoui and R. Herino [*Microelectron. Eng.* **8** (1988) 293]. Even some applications of porous silicon for semiconductor on insulator (SOI) appear but optical studies were neglected.
- 1990—Canham [*Appl. Phys. Lett.* **57** (1990) 1046] proposed that quantum confinement took place as a result of nanocrystallites formation in porous silicon. Photoluminescence was observed from porous silicon at room temperature and its wavelength depended upon the size of nanocrystallites produced by etching. This observation of Canham can be considered as the most important step in porous silicon research.

11.3.2 How to Make Silicon Porous?

Surface of solid silicon can be turned into porous layers by a variety of methods like ion irradiation, spark erosion, chemical etching or electrochemical etching. However, many of the investigations show that most effective method of making porous silicon is electrochemical etching. Chemical etching involves dipping the crystalline silicon in some strong etchant solution like HF mixed with HNO_3. The reaction responsible for making pores begins autocatalytically. Reproducible and controlled porosity in relatively short time can be obtained using electrochemical method and is described here.

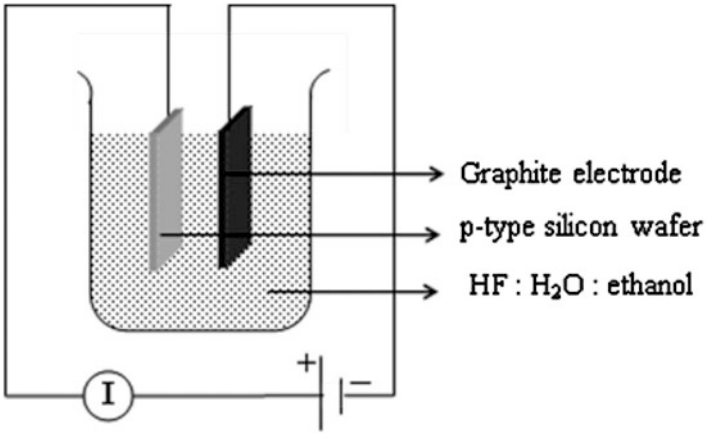

Fig. 11.14 Electrochemical cell

11.3.2.1 Electrochemical Etching

Porous silicon can be easily formed with appropriate conditions at room temperature in a simple electrochemical cell. There are various designs that can be used to obtain anodic etching of silicon but a schematic one is shown in Fig. 11.14. A crystalline piece from a silicon wafer is dipped in an electrolyte, usually a solution of HF, water and ethanol. By making silicon a working anode and a piece of graphite or platinum as cathode a current is passed through the solution. Typical parameters used to etch a *p*-Si are shown in Box 11.3. As HF (hydrofluoric acid) is used as an etchant, precaution has to be taken to use Teflon or polyethylene container as HF severely attacks glass. *It also should be remembered that although the experimental procedure is very simple, HF is extremely dangerous to use. If HF comes in contact with the skin, fluorine makes entry through the skin to the bones affecting the limbs. CaF_2 is formed which mixes with the blood, poisoning it and can turn out to be fatal. Even the waste electrolyte needs to be handled properly, otherwise due to contact with some chemicals it can even explode.*

Box 11.3
Typical parameters in electrochemical reaction used for making porous silicon

Substrate: *p*-Si (111) (B doped)	Voltage: 24 V
Current: 30 mA	Solution: HF + ethanol + water

11.3.3 Mechanism of Pores Formation

Mechanism of pores formation on silicon surface is a complex process. Attempts are made to understand them from the observed species formed on the surface.

For the formation of a porous network on silicon surface, it is necessary that local cathode and anode regions be formed on its surface. When an electron is extracted into the electrolyte from certain region of silicon, usually some sharp point acts like a local cathode. Release of an electron is equivalent to the production of a positively charged hole. The hole can migrate to some other region on the surface, which becomes an anode. If such a region is also attacked by HF present in the electrolyte, following reaction becomes feasible.

$$\begin{gathered} 2h^+ + Si + 2F^- \rightarrow SiF_2 + \left(2h^+ + 2e^-\right) \rightarrow SiF_2 \\ \left(h^+ - \text{hole change},\ e^- - \text{electron charge}\right) \end{gathered} \tag{11.10}$$

$$SiF_2 + 2HF \rightarrow SiF_4 + H_2 \tag{11.11}$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \tag{11.12}$$

H_2SiF_6 dissolves in the electrolyte forming the initiation of pits. It can be seen from above equations that two holes are necessary for the formation of pores. At some low current value and HF concentration such conditions are created.

As the current density is increased beyond a certain value, it is possible to generate more holes at a time and chances of forming surface oxide are increased. If following reaction becomes possible then it is expected that polishing would occur rather than porous structure.

$$4h^+ + Si + 4(OH)^- \rightarrow (SiOH)_4 + \left(4h^+ + 4e^-\right) \tag{11.13}$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \tag{11.14}$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{11.15}$$

H_2SiF_6 and water dissolve in the electrolyte. Obviously the h^+ and e^-, already present in the silicon substrate as a result of doping, would greatly influence the pores formation. Specially, it would matter considerably, whether it is a p-type (excess h^+) or n-type (excess e^-) silicon substrate being used for pores formation. It should not also be surprising if doping level—whether low concentration, moderate concentration or extremely high concentration—would alter the nature of pores formed. Depending upon the concentrations of excess charges, either thermionic or tunnelling of charge carriers would be effective.

High porosity of a material means large area of the exposed material to the ambient. Therefore porous silicon can easily get oxidized. The optical properties of porous silicon are found to be unstable after their formation. However they are reversible too.

11.3.3.1 Factors Affecting the Porous Structure of Porous Silicon

From the vast literature available now on porous silicon, few trends are noticed as follows.

The morphology, optical and structural properties of porous silicon depend upon (1) Substrate type (n or p), (2) Doping level (low or high), (3) Concentration of HF in the electrolyte, (4) Current density used to etch silicon, (5) Effect of light, and (6) Duration of etching (Box 11.4).

Box 11.4: Porous Material

Materials become porous when some solid portion is removed from them leaving voids in them. The volume of the original material does not alter. Therefore density of a porous material is lower than the original material. Materials can be made even 98 % porous. There is a large variety of porous materials, natural (e.g. wood) as well as synthetic (e.g. thermocole). The pores can be of regular, irregular and different sizes and shapes. Pores can be closed, open, penetrating or ink bottle type. Internal area increases with pores (Fig. 11.15).

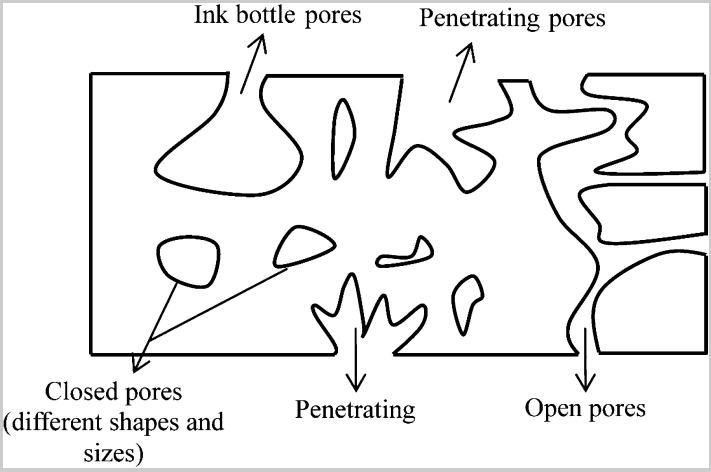

Fig. 11.15 Various types of pores

(continued)

Box 11.4 (continued)

In general, properties of porous materials are quite different than those of corresponding bulk materials. Porous materials are often divided into microscopic (less than 2 nm), mesoscopic (2–50 nm) and macroscopic (larger than 50 nm) depending upon the diameters or size of the pores.

1. **Substrate Type:** Pore structure is normally formed due to holes and silicon atoms interacting together with fluorine. As was discussed in the mechanism of pore formation, it is necessary to consider the substrate type viz. p or n type as they already have excess holes or electrons due to doping. For example it has been found in case of moderately doped n or p type silicon that columnar or sponge-like structure is respectively formed.
2. **Doping Level:** One can identify four types of silicon wafers for forming pores on their surfaces by electrochemical etching. They are: p^+-Si (very high concentration of holes), p-Si (moderate or low concentration), n^+-Si (high concentration of electrons) and n-Si (moderate or low concentration of electrons). It is found that p, p^+ and n^+-Si substrates have similar trends in their pores formation, but n-Si needs large voltage to form pores.
3. **Concentration of HF:** If the current density is held constant, concentration of HF in the electrolyte is an important factor in determining pore formation. Although porosity has been found to increase with decrease of HF concentration, it also is a function of current density. At large current density, usually electropolishing takes place as schematically shown in Fig. 11.16. In the transition region, a rough surface is produced. At lower concentration of HF, the pH of the solution increases, which promotes pore formation.
4. **Current Density:** Figure 11.17 shows three different regions viz. a region of pores formation, an intermediate region and electropolishing region, similar to that in Fig. 11.16.

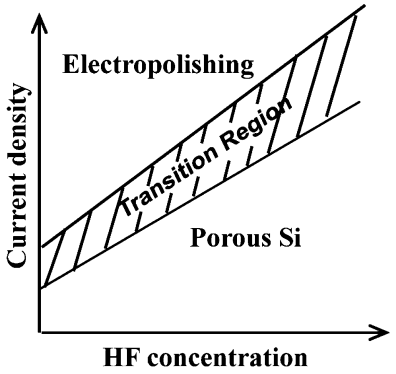

Fig. 11.16 Different regions of silicon surface morphology, which depend upon current and HF concentration in electrochemical etching of Si

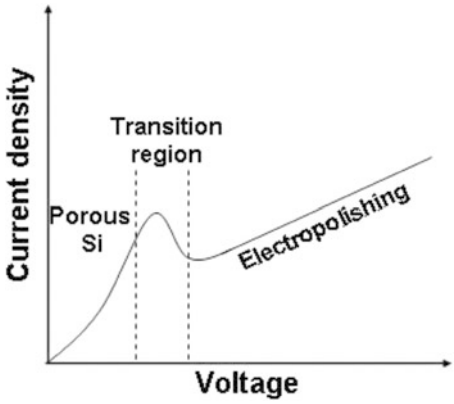

Fig. 11.17 Region of silicon morphology which depends upon current density and the applied voltage in the process of electrochemical etching of silicon

For a given electrolyte, it can be seen that porous structure can be formed only at low voltages and low current densities. The curve may differ for n-Si substrate quite considerably.

5. **Effect of Light:** Chemical reactions can be often controlled using light. When light of appropriate wavelength falls on a semiconductor, it generates electron-hole pairs. If intensity of light is adequate, a large number of charge carriers necessary for the pores formation can be generated using light. Thus the illumination of the silicon anode during electrochemical reaction can affect pores formation. It is found that p-Si can etch out in dark but for n-Si illumination by photons is necessary for pores formation. Sometimes, ambient light can be sufficient.
6. **Duration of Etching:** Etching creates pores which are surrounded by the silicon walls or pillars. These walls contain nanocrystallites of silicon as was first postulated by Canham. Longer the etching time, smaller are these crystallites. The photoluminescence which is observed in porous silicon is due to the formation of these nanocrystals. Therefore properties of the porous silicon are affected by the crystal size and the etching time.

11.3.4 Properties of Porous Silicon Morphology

Depending upon the substrates used for etching, the morphology of porous silicon can change. In general, it is found that 'nanopores' produced with sizes less than ~10 nm (difficult to image) when p-Si with low doping level are used. On the other hand if n-Si substrates are etched using large current, pores even larger than ~1 μm size are easily formed. Medium sized (mesopores) pores ~10–100 nm can be formed in heavily doped p^+ or n^+ type silicon. Porosity, of course, will go on increasing with etching time and typically 50–90 % porosity can be achieved. Shapes of pores also can be altered using different substrates. Often circular, square,

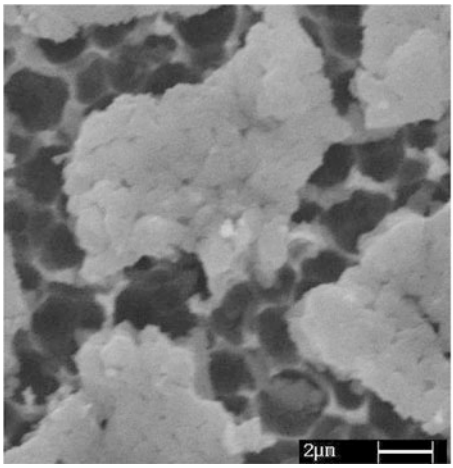

Fig. 11.18 SEM image of porous silicon

triangular, star or random shapes and non-homogeneous are observed. Heavily doped p-Si substrate has columnar structure but lightly doped p-Si has spongy surface structure. Heavily doped n-Si substrate also has columnar porous structure. Figure 11.18 shows an SEM image of porous silicon.

11.3.4.1 Structure

Structure of porous silicon is quite complex. Nanocrystallites of silicon are usually embedded in amorphous silicon. However, in order to produce porous structure, it is necessary to use crystalline silicon. Attempts to use amorphous silicon substrates have failed to produce porous silicon.

11.3.4.2 Chemical Nature

Surface of porous silicon alters chemically during the etching process. It is non-homogeneous on microscopic level and different researchers often obtain conflicting results. This is because of the use of different substrates and variations in electrochemical parameters. In general, along with Si, one finds F, H and O to be present. The relative amounts, however, differ from experiment to experiment. Sometimes carbon also can be detected which arises as a contaminant from the solution or ambient. Samples left in the laboratory environment changes in H or O content with time, also altering the electrical or optical properties. Networks of SiH_2, SiO_2 or complex Si-O-H are often reported.

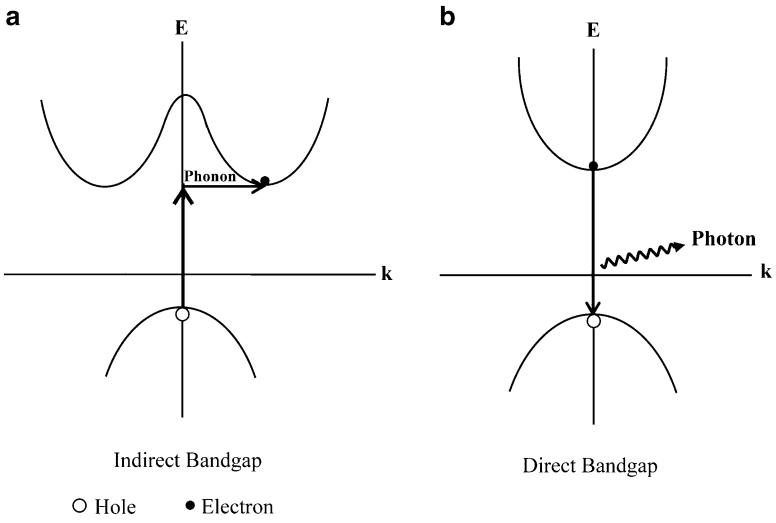

Fig. 11.19 Schematic band diagrams (**a**) silicon bulk and (**b**) Nanocrystalline silicon

11.3.4.3 Electronic Structure

Electronic structure of porous silicon differs considerably from that of the bulk, crystalline silicon. For the bulk silicon crystal the band gap is 1.17 eV at absolute zero and is 1.125 eV at room temperature. This band gap is an indirect band gap as schematically shown in Fig. 11.19.

This is because the maximum in the valence band occurs at $\mathbf{k} = 0$ or Γ (gamma) point in Brillouin zone. The minimum in the band is closer to Brillouin zone boundary. An electron from valence band, even if excited using a photon with sufficient energy, cannot go to conduction band minimum, as both energy and momentum must be conserved in an absorption or emission process. Thus an electron in conduction band minimum at $\mathbf{k} \neq 0$ also cannot make a transition to valence band state at $\mathbf{k} = 0$. This is why Si is not an optoelectronic material. However, as soon as Si nanocrystallites are formed, the electronic structure alters dramatically.

As there is no long range periodic arrangement, the small momentum conservation rule breaks down and transitions become allowed. According to the Effective Mass Approximation (EMA) theory, energy gap increases compared to that in the bulk and depends upon the magnitude of the nanocrystallite size.

11.3.4.4 Photoluminescence

Depending upon the preparation conditions and the nanocrystallite size porous silicon can exhibit photoluminescence over the entire visible range as illustrated in Fig. 11.20.

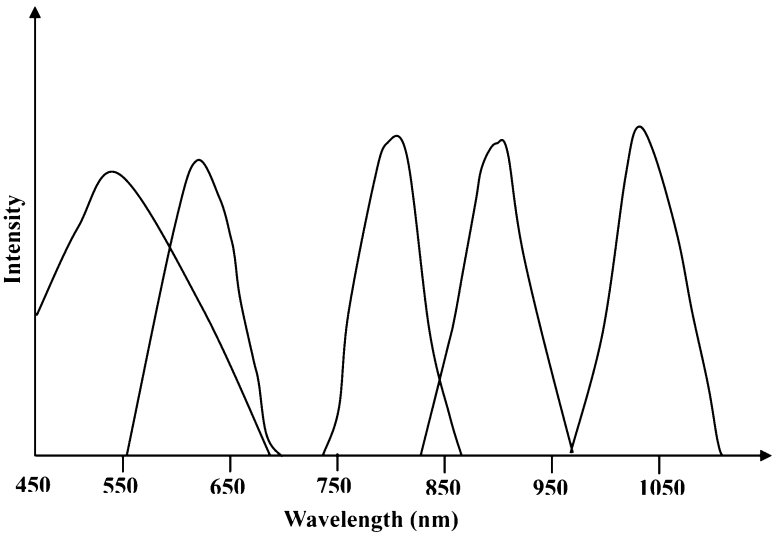

Fig. 11.20 Photoluminescence spectra for different porous silicon samples at room temperature

Due to wide distribution of nanocrystallites, luminescence peak widths can be large.

11.4 Aerogels

Aerogels constitute another class of highly porous materials. These ultra low density, monolithic materials are formed by interconnection of particles of nanometer size, to form a nanoporous solid. The pores themselves are usually nonuniform with sizes from ∼10 to 100 nm. These materials are synthesized by sol-gel method (discussed in Chap. 4) and dried by special procedures to retain their porous structure. Mixture of reactants forming colloidal particles, which are dispersed in liquid, is known as 'sol' (Box 11.5).

Box 11.5: Brief History of Aerogels
Aerogels were first synthesized by an American scientist Samual Kistler in 1930s. He was working in Stanford University on puzzle of cracking of gels while drying. It was found that gels were made up of network of interconnected solids dispersed in some solvent (water). Drying of gels led to evaporation of this solvent and surface tension exerted by evaporating liquid

(continued)

Box 11.5 (continued)
collapsed the solid network. It was realized that while drying gels, they shrink and develop cracks. Kistler developed, therefore, crack-free drying method by removing the solvent above its critical point. Dried materials thus obtained were crack-free and retained their original size and shape. Kistler replaced water in the gel (which has very high critical temperature and pressure) with alcohol and removed it by putting it in an autoclave (a vessel able to withstand high temperature and pressure, just like a pressure cooker, but equipped with temperature, pressure measurement gauges) and raising its temperature and pressure above critical point of the alcohol. Above critical point, alcohol is a gas-like fluid which can be removed from the solid network without any surface tension. He named that transparent, low density solid 'aerogel'. These first aerogels synthesized by Kistler required very long (weeks) time consuming process. In 1970s, S. Teichner at University of Lyon, France, wanted to use these highly porous materials for storing rocket fuel. Looking at lengthy and laborious process he tried to develop a simpler and faster process to synthesize aerogels. He used tetra methylorthosilicate (TMOS) and hydrolyzed it in methanol, in presence of some catalyst. He could get gel in one step and exchange of solvent with alcohol was not required. He could synthesize aerogels in 1 day (Fig. 11.21).

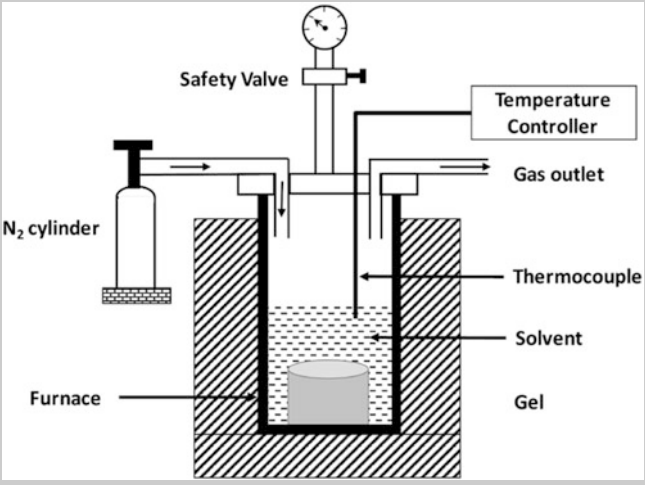

Fig. 11.21 Schematic diagram of an Autoclave (for the photograph, see Fig. 4.32)

These colloidal particles aggregate to form a continuous three dimensional network, which occupies total volume of the solution. The viscous semi-fluidic solid hence formed is known as 'gel'. Formation of gel from solution is dependent

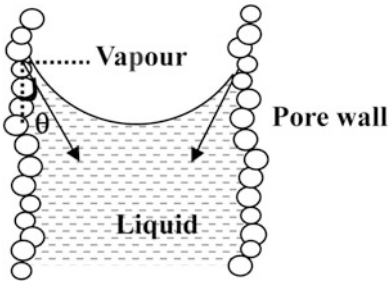

Fig. 11.22 Surface tension at liquid vapour interface

on various parameters such as reactant concentration, temperature, pH value etc. In such gels, liquid is filled in the pores (empty space between the networks of solid particles). In simple evaporation, liquid and vapour coexist within the pore and surface tension of liquid at liquid vapour interface causes collapse of the network (as showed in Fig. 11.22). Magnitude of this interfacial force is given by Eq. (11.16).

$$P_s = \rho g h = \frac{2\sigma \cos \theta}{r} \tag{11.16}$$

where ρ is density of liquid, g – acceleration due to gravity, h – height of the capillary, σ – surface tension of the liquid, r – radius of the pore, θ is contact angle of the liquid with the pore wall.

Hence liquid has to be evaporated in such a fashion that network of particles does not collapse. One way to achieve this is by supercritical drying in which drying of gels is carried out above the critical point of liquid present in pores. Above critical point surface tension is zero. Whole liquid is present in vapour state and can be removed from gels without rupturing the network. In recent years it was realized that it is also possible to dry gels in ambient condition. This method is known as sub-critical drying. A comparison of sub-critical and super-critical drying procedure is shown in Fig. 11.23. In this case to overcome the interfacial pressure (surface tension), various techniques such as strengthening of gel by aging it in suitable solvent or use of some polymers or template to produce uniform size pores (to avoid pressure gradient while drying) etc. are used. Only drawback of this process is that it is time consuming and aerogels obtained by this method have higher density as compared to those dried by supercritical drying. Another way of drying is by freezing the liquid in the pores and sublimating by vacuum pumping. This method is known as freeze drying.

11.4.1 Types of Aerogels

Kistler had successfully demonstrated aerogel formation of various materials such as silica, alumina, nickel tartarate, stannic oxide, tungstic oxide, gelatin agar,

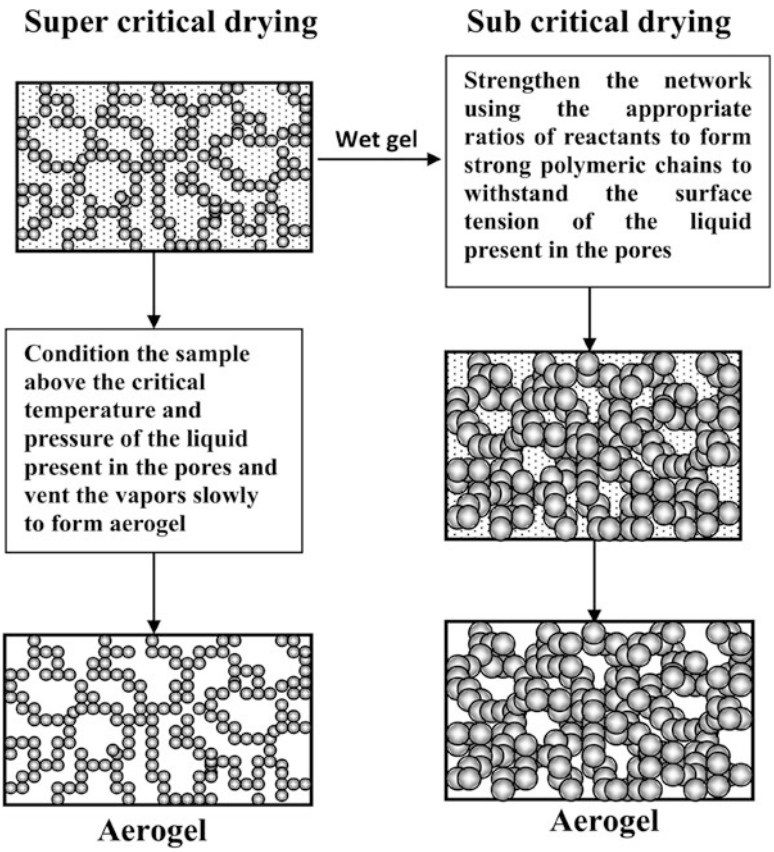

Fig. 11.23 Comparison of supercritical and sub critical drying

cellulose egg albumin etc. Inorganic aerogels such as SiO_2, TiO_2, ZrO_2 and Al_2O_3 have interesting properties and applications. It is also possible to synthesize mixed oxide aerogels such as SiO_2:TiO_2, Al_2O_3:SiO_2, SiO_2-ZrO_2 etc. Fascinating properties and applications of inorganic aerogels motivated also the development of organic aerogels such as RF (Resorcinol Formaldehyde) and MF (Melamin Furfural). They were synthesized by using different organic precursors such as Phenol-Furfural, Polyurethane, cellulose-toluene 2, 4-diisocyanate etc. RF aerogels were first synthesized by R.W. Pekala in United States in 1989. Organic aerogels can be heat treated with some specific heat cycle in inert atmosphere to convert them into carbon aerogels. It is indeed possible to dope aerogels with various metals such as gold, silver, manganese and even organic dyes for variety of applications. Among these materials silica aerogels are very commonly synthesized in many laboratories as well as commercially. Aerogels can be treated by various chemicals to make them hydrophilic or hydrophobic.

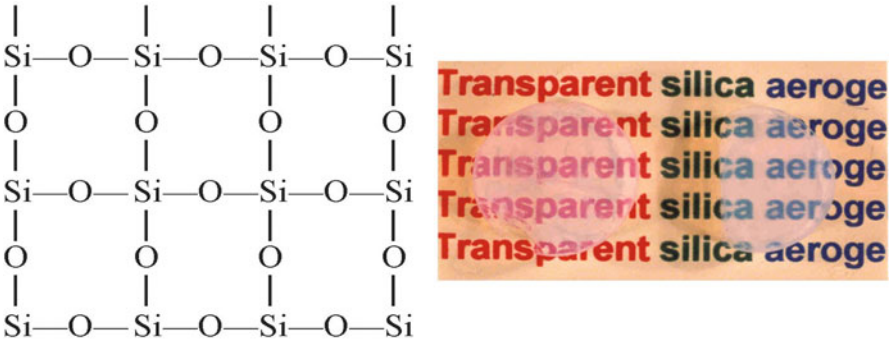

Fig. 11.24 Formation of 3D network of silica aerogel and a photograph showing transparent silica aerogel (diameter 2.5 cm and thickness 1.0 cm)

11.4.1.1 Silica Aerogel

Silica aerogels are historically the first ones that scientists have synthesized. They have been explored a lot due to their immense applications in various fields. Tetraethylorthosilicate (TEOS) or Tetramethylorthosilicate (TMOS) are typically used as primary reactants with ethanol or methanol used as solvents. Acid (HCl, HNO_3, NH_3) or base (NH_4OH, NH_4F) catalyst or combination of both is used for accelerating the reaction. Reaction consists of two steps viz. hydrolysis and polycondensation. For example, TEOS is first hydrolyzed using water. Two hydrolyzed molecules get condensed to form a dimer. The condensation process continues to form polycondensed silica gel, with Si-O-Si linkage as shown in Fig. 11.24. These gels can be further dried using supercritical drying. For carrying out this type of drying, autoclave is used. Ethanol or methanol can be used as solvent. Critical temperature for ethanol is 249°C and critical pressure is 78 bars. Depending upon reaction conditions aerogels can be transparent or opaque and density can typically vary between 0.01 and 0.8 g/cm^3.

$$\mathrm{Si(OR)_4 + H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH} \tag{11.17}$$

$$\equiv \mathrm{Si - OR + HO\text{-}Si} \equiv \rightleftarrows \equiv \mathrm{Si - O - Si} \equiv + \mathrm{ROH} \tag{11.18}$$

$$\equiv \mathrm{Si - OH + HO\text{-}Si} \equiv \rightleftarrows \equiv \mathrm{Si - O - Si} \equiv + \mathrm{HOH} \tag{11.19}$$

11.4.1.2 RF Aerogels and Carbon Aerogels

Inorganic aerogels such as silica have been explored a lot but organic aerogels such as RF (Resorcinol Formaldehyde) have been relatively less investigated. These aerogels are interesting, particularly because of the possibility to convert them

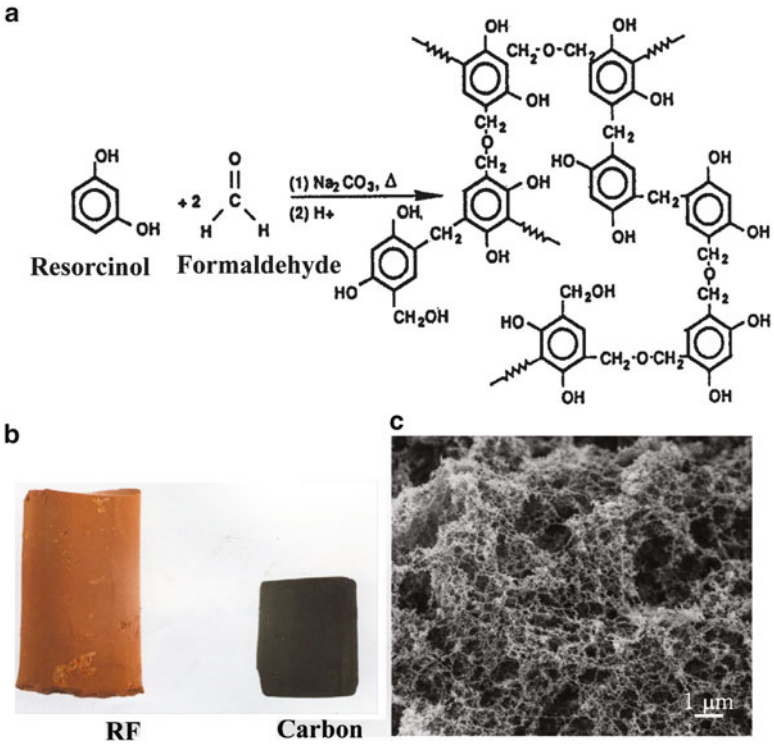

Fig. 11.25 (**a**) Formation of three dimensional network of RF aerogel; (**b**) photograph of RF and carbon aerogel and (**c**) SEM of RF aerogel

into carbon aerogel by pyrolysis (i.e. by heat treatment). Unlike silica aerogels they need high temperature (85°C) for gelation. For synthesis of these aerogels, resorcinol ($C_6H_5(OH)_2$) and formaldehyde (CH_2O) are reacted in presence of sodium carbonate in aqueous medium. The reaction is shown in Fig. 11.25. The chemicals are mixed in a flask and stirred vigorously for 3 h and then left to themselves for 1 day at room temperature. The solution is then kept at 85°C for 6 days to form a gel. This gel can be dried supercritically or subcritically. To convert RF aerogel into carbon aerogel, it is necessary to heat RF aerogel under inert atmosphere at ~1,100°C. A photograph showing RF and carbon aerogels along with SEM image of RF aerogel showing porous structure are as in Fig. 11.25.

Aerogels, however, due to their weak network of nanoparticles (bonded by Van der Waals interaction) have inferior mechanical properties. Therefore they can be easily broken with as small pressure as exerted by fingers. There are now attempts to increase the strength of aerogels by incorporating high strength nanomaterials like graphene or carbon nanotubes during gel formation process as strengths of graphene or carbon nanotubes are even superior than the steel of same dimension.

Table 11.3 Densities in g/cm^3 of some commonly known materials

Iron	Diamond	Glass	Graphite	C_{60}	Paper	Charcoal	Aerogel	Air
7.87	3.5	2.4	2.3	1.7	0.7	0.57	0.003–0.8	0.0013

Fig. 11.26 Photograph of silica aerogel as best thermal insulator

11.4.2 Properties of Aerogels

Aerogels possess many interesting properties because of their highly porous structure. They are the lightest materials (comparison is made with densities of other materials in Table 11.3) man has ever synthesized having pore diameters of few tens of nanometers with 2–5 nm size particles. It is possible to have very high porosity (80–90 %), very low density and high surface area (500–1,500 m^2/g) for these aerogels. They have very low index of refraction (1–1.05) and very low speed of sound through them (∼20 m/s). Young's modulus in these materials is quite low (10^6–10^7 N/m^2). Very low value of thermal conductivity (0.003 W/m.K) which is lower than most commonly used insulators make them best available thermal insulator. See Fig. 11.26.

11.4.3 Applications of Aerogels

For the decades since their first formation it was considered to be quite difficult to use aerogels commercially because of number of reasons like risky supercritical drying process, expensive synthesis procedure and their low fracture toughness etc. With the development of cost effective synthesis routes and technological developments and demands, interest in aerogels is increasing. They are nontoxic and biodegradable making them eco-friendly. Their unique properties such as very low thermal conductivity makes them best thermal insulators for various applications such as insulation of space vehicles, automobile engines etc. Aerogels have been commercially used in jackets and blankets to be used under extreme low temperature conditions. Large windows of aerogels are being used in houses and buildings

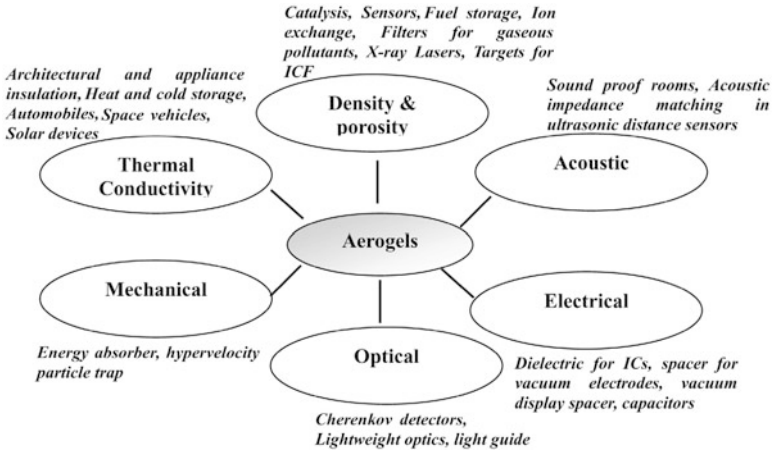

Fig. 11.27 Various applications of aerogels depending upon their properties

in some places to control the temperature in the interior. The transparency and heat insulation properties are used. Indeed it is possible to make aerogel-textile composites so as to make blankets, coats etc. by making them rollable. They can be obtained in the form of thin films, molds and tiny balls. Various applications of aerogels depending on their properties are shown in Fig. 11.27.

11.5 Zeolites

We discussed in the previous two sections two different types of porous materials viz. porous silicon and porous aerogels. Both the materials have disordered pores of irregular shapes and sizes. There is another class of materials known as zeolites, which has pores usually smaller (<2 nm) than aerogels or porous silicon but the pores are highly ordered. The zeolites have not only the pores of uniform size but are periodically arranged to have long range order. The material is crystalline. Some zeolites occur naturally. However due to their technological importance as catalysts and highly sorbent material, they are also synthesized on large scale.

The word ‘zeolites’ origins from ‘zeo’ and ‘lithos’ meaning ‘boil’ and ‘stone’ respectively. Boiling away water from some materials makes them porous zeolites. They have a crystalline structure with translational long range order for their unit cells in three dimensions. Unit cell itself is often the result of some quite complicated subunits. Most common zeolites have the building blocks of tetrahedral units of Si and Al connected together by Si-O-Al types of bonds. There can be Si-O-Si bonds also in zeolites but no Al-O-Al bonds exist. This implies that the number of silicon atoms will be always equal or larger than Al. The network of zeolites can be viewed as shown in Fig. 11.28.

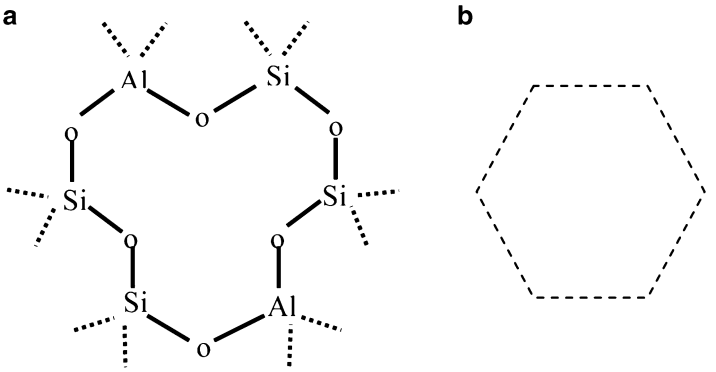

Fig. 11.28 (**a**) Al–Si–O subunit and (**b**) its schematic subunit

However, valence of silicon is 4 and that of aluminum is 3. This would mean that with Al substitution, there would be excess negative charge on the network, which needs to be balanced. This is done by adding some cations or electron acceptors in the material. A general formula of a zeolite can then be written as

$$\left[\mathrm{Al_xSi_yO_{2(x+y)}}\right]\mathrm{M_xzH_2O} \tag{11.20}$$

known as aluminosilicate. Besides this there can be some other tetrahedral units such as (GeO_4), (ZnO_4), (PO_4) etc. which can be used instead or in addition to Al. There are around 40 naturally occurring zeolites and much larger variety can be synthesized.

11.5.1 Synthesis of Zeolites

Synthesis of zeolites, however, is quite a delicate balance of additives as well as processing conditions. Often some organic additives of some ammonium or amines have to be added in some suitable quantities. Both metal cations and organic additives are believed to act as templates for building various structures. Variation of Si/Al, Si/H_2O, cation/Si and organic additives can give rise to numerous zeolites exceeding the number of natural zeolites. Some of the chemical species are responsible for achieving particular structure in zeolites. Such chemical species play the role of so called molecular templates. However particular structure can be obtained using more than one organic molecule and one molecule can create different structures for different precursors forming zeolites. Silicon and aluminium precursor solutions are hydrolyzed and polycondensation takes place similar to that in sol-gel process. Organic and inorganic reactants are added and a gel thus formed is hydrolyzed in an autoclave at high pressure (several tens or hundreds of bars) and temperature (usually 100–350 °C).

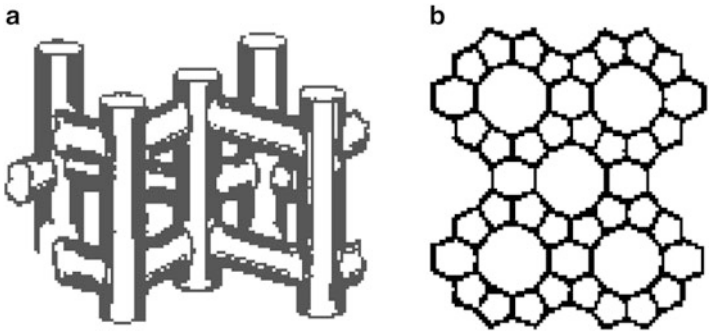

Fig. 11.29 Zeolite ZSM-5 (**a**) side view and (**b**) top view

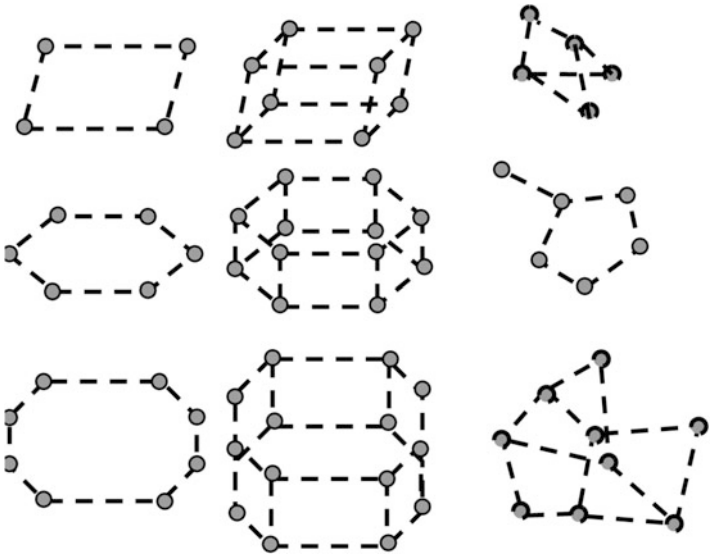

Fig. 11.30 Structural sub units in zeolites

Pore diameters can be controlled with a narrow size distribution in the size range of 0.3–2.0 nm. The pores can be connected in 1-D, 2-D or 3-D. Such porous materials find numerous applications. A widely used ZSM-5 zeolite structure is as shown in Fig. 11.29.

11.5.2 Properties of Zeolites

Zeolites are crystalline, highly ordered porous materials. The pore sizes can be precisely controlled. As illustrated in Fig. 11.30, there can be a large number of subunits forming zeolites of different constituents.

Pores in zeolites are useful to carry out different reactions. Zeolites are useful catalysts or sorption material. By controlling the pore sizes to desired size, it is possible to synthesize and organize nanoparticles inside zeolites.

11.6 Porosity Through Templates

Porosity in nanomaterials can be obtained through various procedures. Here we shall discuss the method in which micelles are used as the templates. Another method involves using core-shell particles in which core is partially or completely removed and the shell becomes porous in the whole process. This part we shall discuss in the core-shell particles.

11.6.1 Micelles as Templates

This also is a good example of self assembled materials. Large (2–10 nm) and ordered pores in three dimensional solids can be obtained using micelles as the templates. However major difference between zeolites and M41S and its family as they are known, is that the pore walls are amorphous in this case. These are only synthetic materials with no naturally occurring material of this type. They were first synthesized in 1992 by some scientists in Mobil company. These are synthesized as 1-D ordered (MCM41), 2-D ordered lamellar (MCM-50) and 3-D ordered (MCM48) arrangement of pores.

11.6.1.1 Synthesis of Ordered Porous Materials Using Micelles

Very interesting, novel route of synthesis has been adopted to synthesize these materials. Amphiphilic organic chain molecules, water, inorganic silica precursor and some catalyst are used in making these materials. Reaction temperature can vary over a wide range from −14 to 180 °C depending upon the materials of interest. However the underlying idea is as follows. As discussed in Chap. 3, when amphiphilic molecules are mixed in water, depending upon the molecules above the critical concentration, one can spontaneously obtain micelles. With increasing concentration, one can even obtain different structures like hexagonal, cubic or lamellar at certain temperature. If silicates are condensed on preformed structures of micelles, it is possible to obtain ordered composites as shown in Fig. 11.31.

Alternatively, the formation of observed periodic pore structure can be viewed as follows. Before the self assembly of micelles takes place forming some ordered structures, each micelle may acquire a silicate shell around it and then form the ordered structure. The assembly always occurs irrespective of the stage at which the silicate precursor is added to the micellar solution. Once the reaction is over, micelles can be removed by plasma etching, calcination or solvent exchange processes.

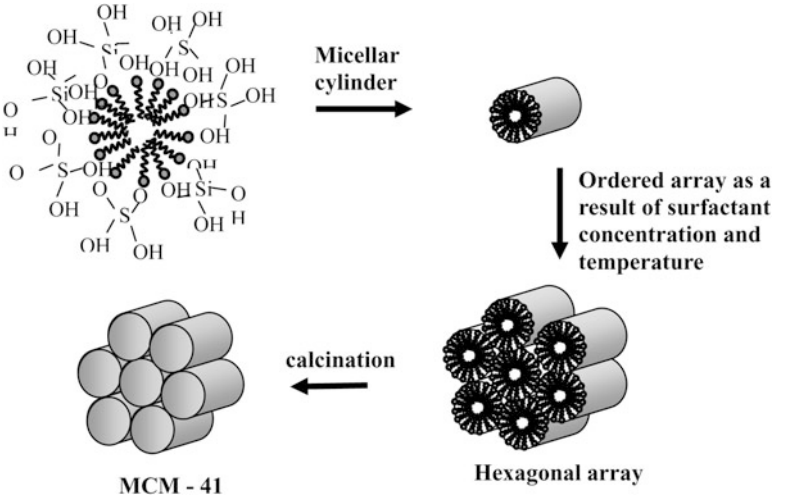

Fig. 11.31 Micelles covered with silica

Such ordered pore structures themselves are nanomaterials and can be also used as templates to synthesize nanoparticles in their cavities.

11.6.2 Metal Organic Frameworks (MOF)

Metal organic frameworks are under intense investigations from the point of view of finding new MOFs and their applications. MOF frameworks are co-ordination polymers in which metal ions make a one-dimensional, two-dimensional or three-dimensional pore network through organic molecules. They resemble zeolites to some extent but they are different from zeolites. Zeolites are mainly alumino silicates. The densities of zeolites are quite high and can be $\sim$50 g/cm^3 as against the densities of MOFs which can be $\sim$0.5 g/cm^3 viz. two orders of magnitude smaller than zeolites. The pore sizes in MOFs can be as low as $\sim$5 nm diameter. This results into extremely large internal surface area ($\sim$6,000 m^2/g). In MOFs this large surface area is the most important parameter as this is important in deciding the choice of a material as the potential candidate for H_2 storage application or drug delivery. Some of the organic molecules which have been used in the synthesis of MOFs are oxalic acid (HOOC–COOH), malonic acid (HOOC–CH_2–COOH), succinic acid (HOOC–$(CH_2)_2$–COOH), gltanic acid (HOOC–$(CH_2)_3$–COOH), pthalic acid ($C_6H_4(COOH)_2$), citric acid (HOOC)$CH_2C(OH)(COOH)$ $CH_2(COOH)$), trimeric acid ($C_9H_6O_6$), 1,2,3 tiazole ($C_2H_3N_3$) and squaric acid ($C_2H_2O_4$). Some of the metal ions used are Mg, Fe, Zn, Mn and Cu.

The synthesis of MOFs is carried out mostly by hydrothermal or solvothermal and mechanochemical techniques. Hydro or solvothermal reaction of precursor

chemicals is carried out in an autoclave at high temperature and high pressure similar to that in the synthesis of zeolites. In mechanochemical synthesis metal acetates are mixed with organic molecules and ground in a ball mill.

The biodegradability of MOFs is excellent. Their functionality makes them useful in H_2 and other gases like CO_2, O_2 storage. Additionally MOFs can be useful in catalysis, drug delivery, data communication and replacement of liquid crystals which are under investigations.

11.7 Core-Shell Particles

Core-shell particles form a novel class of nanocomposite materials in which a thin layer of nanometer size is coated on another material by some specialized procedure. The core can be just a nanoparticle (few nanometers to tens of nanometers) with a nanometer thick coating or it can be a large core (few tens to hundreds of nanometer diameter) with nanometer thick coating as schematically shown in Fig. 11.32. The properties of core-shell particles are different from core or shell material. Their *properties depend usually upon core to shell ratio.* These particles are synthesized for a variety of purposes like providing chemical stability to colloids, enhancing luminescent properties, engineering band structures, sensors, drug delivery etc. These materials can be of economic interest also as precious materials can be

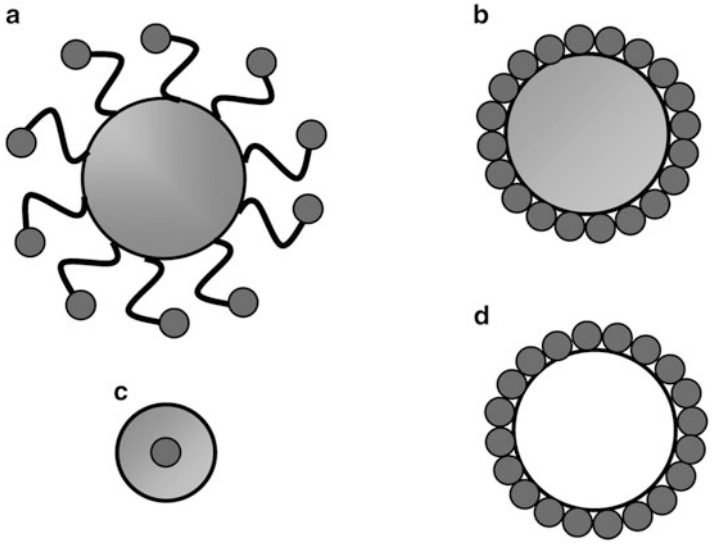

Fig. 11.32 Variety of core-shell particles: (**a**) Surface modified core particles anchored with shell particles, (**b**) Smooth coating of dielectric core with shell, (**c**) Encapsulation of very small particles with dielectric material and (**d**) Quantum bubble

deposited on inexpensive cores. Core particles of different morphologies such as rods, wires, tubes, rings, cubes etc. also can be coated with thin shell to get desired morphology in core shell structures.

Core-shell materials can be synthesized practically with all the materials, like semiconductors, metals and insulators. Dielectric materials such as silica and polystyrene are popular materials to use as core because they are soluble in water and hence can be useful in biological applications. Core-shell particles can be synthesized using variety of combinations such as dielectric-metal, dielectric-semiconductor, dielectric-dielectric, semiconductor-metal, metal-metal, semiconductor-semiconductor, semiconductor-dielectric, metal-dielectric, dye-dielectric, dielectric-biomolecules etc. Although core shell particles have novel properties, these can be further assembled and utilized for creation of another class of novel materials like colloidal crystal or quantum bubbles (i.e. hollow spheres with thin shells). It is indeed possible to create novel core shell structures having multishells and tuning optical properties from visible to infrared region of the electromagnetic spectrum.

Synthesis of core-shell particles requires highly controlled and sensitive synthesis protocols to ensure complete coverage of core particles with shell. There are various methods to fabricate core-shell structures which involve precipitation, polymerization, micro emulsion, reverse micelle sol-gel condensation etc. Although these methods themselves may appear to be simple, it is rather difficult to control the thickness and homogeneity of the coating. If reaction is not controlled properly, eventually it leads to aggregation of core particles, formation of separate particles of shell material or incomplete coverage.

Here we shall discuss some silica based core-shell particles as an example. Preparation of core-shell particles is a multi-step synthesis procedure. One can make coating of silica on nanoparticles or grow silica particles of large size and then anchor nanoparticles or coat thin shell around, of few nm thickness. As mentioned earlier one can use metals, semiconductors or any other dielectric material as shell or core with silica.

11.7.1 Synthesis of Silica Cores

Silica is a very widely used material to form core-shell particles because of its stability against coagulation. It is also chemically inert and optically transparent. For various purposes it is desirable that particles remain well dispersed in the medium which can be achieved by coating silica on them to form an encapsulating shell.

Silica particles having very good monodispersity can be synthesized by what is known as Stöber method. This method involves hydrolysis and successive condensation of TEOS (tetraethylorthosilicate $Si(C_2H_5O)_4$) in alcoholic medium in presence of ammonium hydroxide (NH_4OH) as a catalyst. By varying relative concentration of TEOS to solvent (dilution) and amount of catalyst, one can synthesize these particles in various sizes ranging from 50 nm to 1 μm.

11.7.1.1 Synthesis of Metal, Semiconductor or Insulator Particles (<20 nm)

Synthesis of metal, semiconductor and insulators with very small size (<20 nm) and small size distribution can be performed using some of the chemical techniques described in Chap. 4 (as well as Chap. 14).

11.7.2 Core-Shell Assemblies

Core-shell assembly is a multi-step process in which core and shell particles are separately synthesized and then shell particles are anchored on cores by specialized procedures or shell is directly synthesized on preformed cores.

In the first method, surface of core particles is often modified with a surfactant or bifunctional molecules to enhance the coverage of shell material on its surface. Surface of core particles such as silica can be modified using bifunctional organic molecules such as APS (3-aminopropyltriethoxysilane). APS molecule has an -OH group at one end while -NH group at the other end. APS forms a covalent bond with silica particle through -OH group and -NH group is available for interaction. Some nanoparticles having affinity for nitrogen can be attached with silica particles through NH group. There are several other modifiers such as APTMS (3-aminopropyltrimethoxysilane) and AEAPTMS (N-(2-aminoethyl)-3-aminopropyltrimethoxysilane) which produces surface terminated with amine group, MPTMS (3-mercaptopropyltrimethoxysilane) which produces surface terminated with thiols, DPPETES (2-(Diphenylphosphino)ethyltriethoxysilane) leaves the surface terminated by diphenylphosphine group and PTMS (propyltrimethoxysilane) gives surface terminated with methyl group. It is thus possible to make variety of core-shell materials with dielectric cores such as silica, titania and polystyrene can be anchored with different materials.

In another approach, synthesis of shell particles is carried out in presence of preformed cores (may be single nanoparticles or many nanoparticles). These core particles act as nuclei and shell material hydrolyses and gets condensed on cores forming core-shell particles. Reactant concentrations and amount of added core particles play important role in deciding shell thickness.

In other technique, which is known as layer by layer technique, alternate layers of anionic particles and cationic polymer are deposited on surface-modified template molecule by heterocoagulation.

Successive removal of core material (either by calcination or dissolution in suitable solvents such as toluene or HF) yields hollow particles consisting of shell material, popularly known as quantum bubble. This is known as template based synthesis of porous or hollow particles. For example SiO_2 nanoparticles are coated with SnO_2 thin film and etched mildly in controlled way using HF. Then with repeated deposition of SnO_2 and mild etching, core SiO_2 which mixes with SnO_2

layers is slowly etched out. This leaves SnO_2 particles with hollow core as well as porous SnO_2 shell. The process is known as galvanic replacement (of SiO_2 by SnO_2 in this case).

Selection of suitable pair for core and shell assemblies requires understanding of individual properties of core and shell materials. Core particle should withstand the process used for the coating of shell material. Core and shell particles should not interdiffuse and surface energies of core and shell particles must be similar so that probability of heterogeneous nucleation is more than homogeneous nucleation.

11.7.3 Properties of Core-Shell Particles

Coating of colloidal particles with shell offers most simple and versatile way of modifying its surface chemical, reactive, optical, magnetic and catalytic properties. Silica particles coated with gold shell have been studied, which show changes in the Surface Plasmon Resonance (SPR) position of which depends upon core/shell optical properties. CdSe nanoparticles (<5 nm) coated with ZnO, CdS/ZnTe and CdTe nanoparticles coated with CdSe also have been studied for enhancement in luminescence of core nanoparticle. Use of higher band gap material as a shell for lower band gap material as a core increases the probability of photoexcited electron of core particle being trapped and increases the photoluminescence of core particle. Magnetic particles of iron oxide also have been coated with dye incorporated silica shell. Such particles show magnetic properties arising from core as well as luminescent optical properties arising from shell. Thus functional materials with novel properties can be synthesized by using various combinations of core shell materials.

11.8 Metamaterials

The literary meaning of ‘metamaterials’ is ‘beyond Nature or Supernatural’. These materials have been fabricated artificially as a consequence of advances in the fabrication of nanomaterials in the desired shapes and sizes as well as improved understanding of materials, particularly their interaction with the electromagnetic waves. Metamaterials are also known as ‘negative refractive index materials’ or ‘left handed materials’.

These materials are subwavelength periodic artificial structures capable of producing negative refraction. It has been realized after about year 2000 that having such materials would help making ‘superlenses’, band pass filters, novel photonic devices and even cloaking (invisibility of objects).

The concept of negative refractive index is not really new in physics. Lamb and Schuster had come across it in their theoretical work. However they had dismissed the idea thinking that it would not have any physical meaning or application.

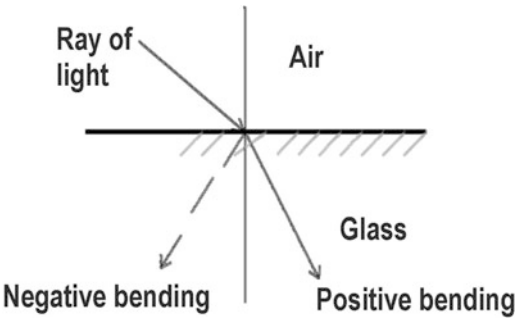

Fig. 11.33 Illustration of usual (positive) refraction of a ray and negative refraction of the ray when ray of light traverses from medium of low density into higher density medium

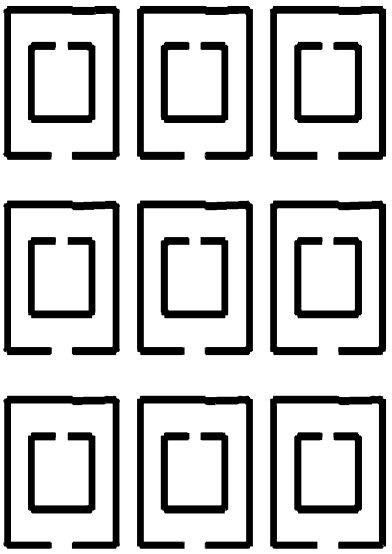

Fig. 11.34 Split resonators. Such structures are obtained in gold and form three dimensional arrays

In 1967, Victor Veselago revisited the concept and showed that negative refractive index was possible provided dielectric constant ε and magnetic permeability μ were simultaneously negative. Dielectric constant ε is frequency dependent and becomes negative at certain frequencies (this was seen in the discussion on plasmonic materials, Sect. 8.4). However, permeability μ can be achieved negative with some artificial structures (usually some resonating circuits are required). Around 2002, several structures were theoretically suggested and experimentalists proved that indeed it is possible to obtain negative refraction, as shown in Fig. 11.33.

One such resonator arrangement section is illustrated in Fig. 11.34. Usually these are lithographically constructed by electron or ion beams in gold as gold does not get easily oxidized and has negative dielectric constant in the large frequency range.

With considerable research progress in this branch, it has been found that negative refractive index materials can be Double Negative (DNG) Refractive Index materials in which both dielectric constant ε and permeability μ are negative or only ε (epsilon) is negative (ENG) or only μ (mu) is negative (MNG).

Superlenses and cloaking also have been demonstrated. In superlenses the focussing can be achieved without the usual distortions due to curvature and other aberrations of the optical lenses. Cloaking has been demonstrated in the microwave region. In object kept inside the 'cloak' is invisible to microwaves as they are completely reflected. Based on this idea even 'plasmonic' cloaking has been proposed which would make the object invisible to particular wavelength but seen at other wavelengths.

11.9 Bioinspired Materials

We had discussed in Chap. 5 that the nature has mostly taken the 'bottom up' approach in building the animal and plant kingdom. Once the nanostructures are formed they may assemble (self assembly) into hierarchical structures to give functionalities. The scientists after getting the powerful microscopes at hand have gone into the details and found that many interesting phenomenon like cleanliness of water leaves, crawling of lizards on walls without falling or beautiful colours of peacock feather or butterflies or fish, birds are the results of 'Nature's Nanotechnology'. In this section we will try to understand some of the effects and the reasons behind them.

11.9.1 Lotus Effect (Self Cleaning)

In recent times there has been new understanding about how the hydrophobic (water hating) and hydrophilic (water loving) surfaces work. This effect has been there for millions of years and is now recognized as the 'lotus effect'. Lotus is a beautiful flower known to all civilizations and is being praised over generations in many cultures, religions and languages. How it appears beautiful and its leaves do not become dirty even by staying in muddy water without letting water stick to it has been a point of wonder. However, it has been investigated and found that this is due to the hierarchical micro-nano structure of the lotus leaf and many other leaves as well as body of animals.

A lotus leaf when observed under the microscope exhibits some bumps of micrometre size. The bumps are decorated with nanometer sized structure. This can help a water drop stay on the lotus leaf without spreading on it. The waxy substance on the lotus leaf also helps the water drop to form the droplet and not spread on the surface. When the water drop rolls on the leaf, it collects the dirt on the surface and makes the surface clean. Lotus effect can be understood from Fig. 11.35.

The phenomenon of wettability in lotus leaf is also common in many other plant leaves, butterfly wings, skin of fish and many others in plant and animal kingdom. It is understood in terms of hydrophobicity/hydrophobicity and the contact angle a water drop makes with the surface. A hydrophilic surface is water loving and

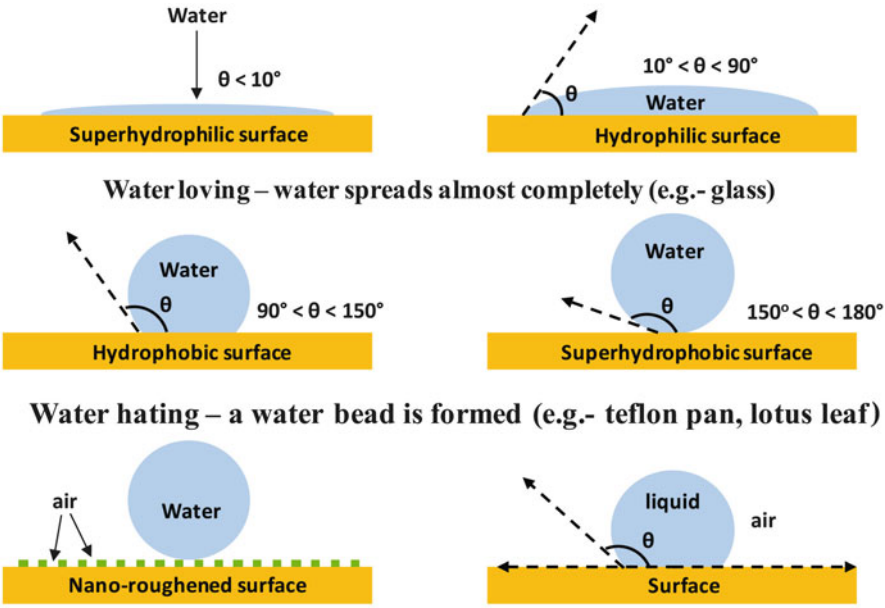

Fig. 11.35 Formation of water drop on the surface

hydrophobic surface repels water. Depending upon the contact angle of water drop, one can quantify the amount of hydrophilicity or hydrophobicity. As illustrated in Fig. 11.35, water contact angle is defined as the angle between solid surface and the liquid-surface. Contact angle depends upon surface roughness, surface condition and surface material. Interaction between liquid and solid surface is very important. When the contact angle is less than 90° the surface is known as the hydrophilic and if more than 90° it would be hydrophobic. If the angle is above ∼150° then it is superhydrophobic and if less than ∼20° then it is superhydrophilic. The angles which distinguish between superhydrophilic and hydrophilic or hydrophobic and superhydrophobic are not very precise and could vary within 5°–10°.

Scientists have tried now to make use of this phenomenon to artificially obtain the hydrophilic/hydrophobic surfaces in various materials of various shapes and sizes. One can even make coatings which would not only make a surface just hydrophobic or hydrophilic but also can change the nature in the controlled way using external stimuli such as application of an electric field or irradiation with UV light or X-rays.

Another interesting and more dramatic natural phenomena, which often goes unnoticed is known as ‘petal effect’. It can be easily seen in common flowers e.g. a rose. If water is sprinkled on flowers, very tiny droplets can be observed. These droplets cling to the petals so strongly that even if the flower is turned upside down, the droplets do not fall under gravity. This effect is due to micropapillae of ∼16 μm diameter and ∼7 μm height with micropapillae folds ∼730 nm size.

11.9.2 Gecko Effect (Adhesive Materials)

Somewhat similar interesting phenomenon observed in nature over centuries and wondered about is so-called 'Geko (family name for lizard) effect' or crawling of a lizard on wall. How does a lizard balance its weight? Does it secrete any fluid to stick or what else? Now the scientists believe that the peculiar construction of the tips of its feet on which millions of nano hair exist which help lizard in crawling. Interestingly the force that each hair strand exerts between wall and itself is just weak Van der Waals force. However, due to millions of hairs total force is sufficient to balance its weight and remove the force in controlled way to crawl. This effect may be useful to make robots which would climb the walls or do some scientific operations without manual aid. Some simple application of geko effect would be a stick tape which can be used number of times without falling like a lizard. One may also be perhaps able to make seals without nuts and bolts.

Basically understanding even natural phenomenon around us can lead to new discoveries and progress in science and technology.

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