Introduction to Nanomaterials
&
Nanotechnology

Dr. Pallab Ghosh
Associate Professor
Department of Chemical Engineering
IIT Guwahati, Guwahati–781039
India

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9.1.1 Introduction

- The term *nano* originated from the Greek *nanos* which means ‘dwarf’. It is one billionth of a meter. Therefore, whenever we think about nanoscience or nanotechnology, very small objects come to the mind. Indeed, this branch of science and technology deals with materials having at least one spatial dimension in the size range of 1 to 100 nm.
- Richard P. Feynman (Nobel Laureate in Physics, 1965) is often credited for introducing the concept of nanotechnology about 50 years ago. In the annual meeting of the American Physical Society at California Institute of Technology on 26 December 1959, he delivered a famous lecture entitled “There’s Plenty of Room at the Bottom”. In this lecture, he talked about writing twenty four volumes of the Encyclopaedia Britannica on the head of a pin, and miniaturizing the computer (see Feynman, 1992). He also suggested that it would be possible to arrange the atoms the way we want. Therefore, a physicist should be able to synthesize any chemical substance by putting the atoms down where the chemist says.
- The lecture of Feynman had inspired many scientists in various ways. For example, K. Eric Drexler wrote a book (in 1986) entitled “Engines of Creation: The Coming Era of Nanotechnology”. Drexler envisioned a world completely transformed by nano-scale robot assemblers. These assemblers would manipulate and build things atom-by-atom working furiously running a nanofactory. They would be able to build anything with absolute precision and no pollution.
- Nanomaterials are expected to have a wide range of applications in various fields such as electronics, optical communications and biological systems. These applications are based on factors such as their physical properties, huge surface area and small size which offers possibilities for manipulation and room for accommodating multiple functionalities.
- In recent years, major progress has been achieved in molecular electronics. As the physical limits of the conventional silicon chips are being approached, researchers are seeking the next small thing in electronics through chemistry. By making devices from small groups of molecules, researchers may be able to pack

computer chips with billions of transistors, more than 10 times as many as the current technology can achieve (see Fig. 9.1.1).

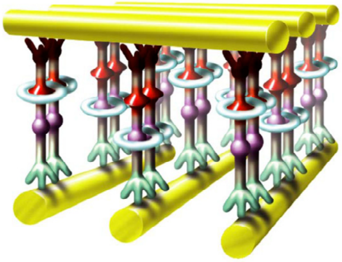

Fig. 9.1.1 Sandwitch structure of nanowires and organic molecules for electronic circuit (Service, 2001) (reproduced by permission from The American Association for the Advancement of Science, © 2001).

- Researchers in molecular-electronics think that it is possible to make complex circuitry by utilizing DNA's ability to recognize molecules and self-assemble. They hope to use DNA as a template for crafting metallic wiring, or even to wire circuits with strands of DNA itself. Makers of computer chips are concerned with the wavelength-limits of light. As the wavelength of the light is reduced, smaller features can be printed on the chip. As a general rule of thumb, a given wavelength can make features about half its length. Typically, light of 248 nm wavelength was used in the past in optical lithography devices, and the smallest features that could be made by these devices were about 120 nm. Chipmakers are trying to build devices which use much shorter wavelengths (e.g., 157 nm). Features as small as 80 nm have already been created on silicon wafers. Researchers expect that the technology will be able to turn out features as small as 10 nm (Service, 2001). This is illustrated in Fig. 9.1.2.
- A very promising and rapidly-growing field of application of nanotechnology is in medicine. One interesting application involves the use of nano-scale devices which may serve as vehicles for delivery of therapeutic agents and act as detectors or guardians against early disease. They would possibly repair the metabolic and genetic defects. They would seek out a target within the body such as a cancer cell and perform some functions to fix it. The fixing can be achieved

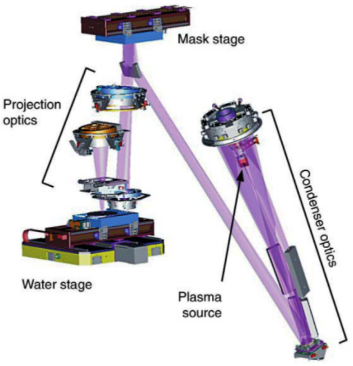

Fig. 9.1.2 Extreme ultraviolet lithography (EUV) employing complex arrangement of reflective optics to pattern chips (Service, 2001) (reproduced by permission from The American Association for the Advancement of Science, © 2001).

by releasing a drug in the localized area. The potential side effects of general drug therapy can be reduced significantly in this manner. As nanotechnology becomes more sophisticated, gene replacement, tissue regeneration or nanosurgeries are the promising future developments (see Fig. 9.1.3).

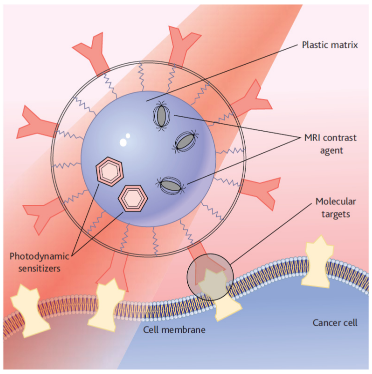

Fig. 9.1.3 Multifunctional nanoparticles can combine tumor-seeking sensors, imaging agents, and toxins that kill cancer cells (Service, 2005) (reproduced by permission from The American Association for the Advancement of Science, © 2005).

- The possible benefits that can be obtained from nanoscience and technology seem to be almost endless. Many of these dreams may be realized in the near future. In this module, various types of nanomaterials, their structures and methods to prepare them will be discussed. The potential applications of these materials will also be explained.

9.1.2 Bottom-up and top-down methods of synthesis

- There are two approaches to the synthesis of nanomaterials: *bottom-up* and *top-down*. In the bottom-up approach, molecular components arrange themselves into more complex assemblies atom-by-atom, molecule-by-molecule, cluster-by-cluster from the bottom (e.g., growth of a crystal).
- In the top-down approach, nanoscale devices are created by using larger, externally-controlled devices to direct their assembly. The top-down approach often uses the traditional workshop or microfabrication methods in which externally-controlled tools are used to cut, mill and shape materials into the desired shape and order. Attrition and milling for making nanoparticles are typical top-down processes.
- Bottom-up approaches, in contrast, arrange molecular components themselves into some useful conformation using the concept of molecular self-assembly. Synthesis of nanoparticles by colloid dispersions is an example of the bottom-up approach.
- An approach where both these techniques are employed is known as a *hybrid approach*. Lithography is an example in which the growth of thin film is a bottom-up method whereas itching is a top-down method.
- The bottom-up approach has been well-known to the chemists for a long time. This approach plays a very important role in preparing nanomaterials having very small size where the top-down process cannot deal with the very tiny objects.
- The bottom-up approach generally produces nanostructures with fewer defects as compared to the nanostructures produced by the top-down approach. The main driving force behind the bottom-up approach is the reduction in Gibbs free energy. Therefore, the materials produced are close to their equilibrium state.
- In top-down techniques such as lithography, significant crystallographic defects can be introduced to the processed patterns. For example, nanowires made by lithography are not smooth and can contain a lot of impurities and structural defects on its surface. Since the surface area per unit volume is very large for the nanomaterials, these defects can affect the surface properties, e.g., surface

imperfections may cause reduced conductivity and excessive generation of heat would result.

- In spite of the defects, the top-down approach plays an important role in the synthesis and fabrication of nanomaterials. The present state of nanoscience can be viewed as an amalgamation of bottom-up chemistry and top-down engineering techniques.

9.1.3 Self-assembly

- Self-assembly is the autonomous organization of components into patterns or structures without human intervention. Self-assembling processes are common throughout nature and technology. They involve components from the molecular (e.g., crystals) to planetary (e.g., weather systems) scale and many different types of interactions.
- Self-assembly is a fundamental principle which creates structural organization from the disordered components in a system. The principles of self-assembly was conceptualized long time ago (*circa* 400 BC). The ancient Greek philosopher Democritus expounded the idea that atoms and voids organized in different arrangements constitute all matter. He explained the growth of the universe from the minutest atomistic building blocks to the stars and galaxies. This is perhaps the oldest recorded vision of matter undergoing self-assembly over all scales.
- The basic principle of nanochemistry lies in the self-assembly of a target structure from the spontaneous organization of building blocks. The building blocks can be molecules or nano-scale clusters, as shown in Fig. 9.1.4.
- There are five important factors that need to be taken into consideration for self-assembly: (i) building blocks, scale, shape and surface structure, (ii) attractive and repulsive interactions between the building blocks, (iii) association, dissociation and adaptable motion of the building blocks in the assembly to attain the lowest energy structure, (iv) interactions of the building blocks with the solvents, interfaces and templates, and (v) the dynamics of the building blocks and mass transport.

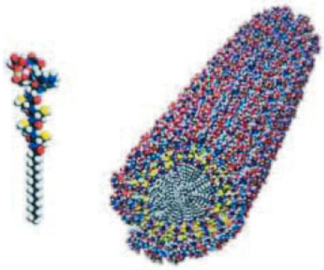

Fig. 9.1.4 Self-assembled peptideamphiphile nanofibers (Hartgerink et al., 2001) (reproduced by permission from The American Association for the Advancement of Science, © 2001).

- The building blocks are usually not monodisperse (unless they are single atoms or molecules). The polydispersity present in the building blocks in terms of size and shape dictates the achievable degree of structural perfection of the assembly, and the defects in the assembled system.
- The making of building blocks with a particular surface structure, charge and functionality is a challenging task. The surface properties control the interactions between the building blocks and their interactions with the environment as well. This determines the geometry and the equilibrium separation between the building blocks in a self-assembled system. The aggregation and de-aggregation processes, and the corrective movements of the self-assembled structure allow it to attain the most stable form.
- The driving forces for molecular organization can be as varied as ionic, covalent, hydrogen bonding or metal–ligand bonding interactions. The chemistry of self-assembly of materials transcends the chemistry of molecular assembly. It is distinct solid state materials chemistry where the building blocks and their assemblages are unconstrained by scale, and they are not restricted to just chemical bonding forces.
- At length scales higher than molecular length scales, other forces such as capillary, colloidal, elastic, electric, magnetic and shear forces can all influence the self-assembly of materials.
- An important feature of self-assembly is hierarchy, i.e., the primary building blocks associate into more complex secondary structures, which are integrated

into the next size level in the hierarchy. This organizational scheme continues until the highest level in the hierarchy is attained (see Fig. 9.1.5).

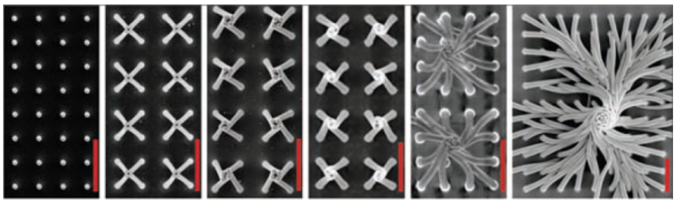

Fig. 9.1.5 Scanning electron microscopy (SEM) images showing the morphogenesis of helical patterns, from the first-order unclustered synthetic polymeric nanobristle to the fourth-order coiled bundle (from the left to the right). Scale bars, 4 µm. Note the hierarchical nature of the assembly reflected in the presence of the lower-order braids in the large clusters braided in a unique structure reminiscent of modern dreadlocks or mythical Medusa (Pokroy et al., 2009) (reproduced by permission from The American Association for the Advancement of Science, © 2009).

- The self-assembly of molecules and materials can be directed by templates. The template can be constituted of molecules, molecular assemblies or additive materials which serve to fill space, balance charge and direct the formation of a specific structure. For example, mesoporous zeolites are templated by block co-polymers or lyotropic liquid crystals. A template patterned at the nanoscale can direct the assembly process. The structure-directing templates which can make, organize and interconnect the building blocks can be porous hosts, lithographic patterns, and channels in polymer, alumina and silicon membranes. Some of these templates are widely used to make nanowires, nanorods and nanotubes.
- A well-known templating method is the use of surfactant micelles and liquid crystals. Many microporous and mesoporous inorganic solids have been prepared by this templating mechanism. The preparation of MCM-41 molecular sieve is schematically shown in Fig. 9.1.6. In this illustration, the silicate material occupies the spaces between the hexagonal arrays of cylindrical micelles. When calcined, the organic material burns-off and the hollow cylinders of silicate remain.

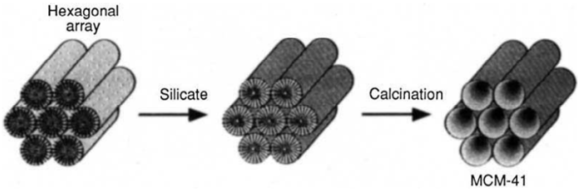

Fig. 9.1.6 Schematic drawing of the liquid-crystal templating mechanism. Hexagonal arrays of cylindrical micelles form with the polar groups of the surfactants (light grey) to the outside. Silicate species (dark grey) then occupy the spaces between the cylinders. The calcination step burns off the original organic material, leaving hollow cylinders of inorganic material (Kresge et al., 1992) (reproduced by permission from Macmillan Publishers Ltd., © 1992).

- We have discussed the hierarchy of the self-assembly process. In fact, it is a well-known characteristic of many self-assembling biological structures. Many biominerals are organized from nanoscale to the macroscopic scale to give hierarchical materials that have complex forms such as spirals, spheroids and skeletons with apparent disregard for the rigid geometric symmetry of their inorganic constituents (Fig. 9.1.7).

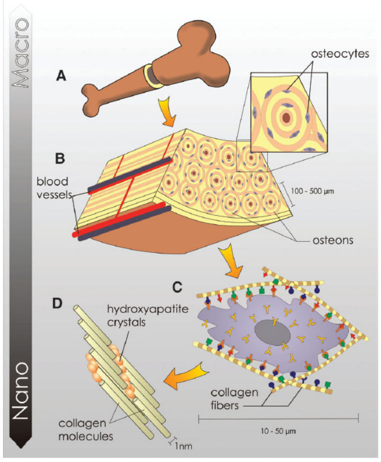

Fig. 9.1.7 Hierarchical organization of bone over different length scales. Bone has a strong calcified outer compact layer (A), which comprises many cylindrical Haversian systems, or osteons (B). The resident cells are coated in a forest of cell membrane receptors that respond to specific binding sites (C) and the well-defined nanoarchitecture of the surrounding extracellular matrix (D) (Stevens and George, 2005) (reproduced by permission from The American Association for the Advancement of Science, © 2005).

- At each level of the hierarchy, distinctive building rules can be observed. The characteristics of self-assembly in biological materials are manifested in a variety of curved shapes, surface patterns and hierarchical order (e.g., the sea-shell shown in Fig. 9.1.8).

Fig. 9.1.8 Pattern formation in Nature.

9.1.4 Structure of nanomaterials

- The structure of the nanomaterials can be classified by their dimensions. The zero-dimensional nanostructures are nanoparticles. The one-dimensional nanostructures are whiskers, fibers (or fibrils), nanowires and nanorods. In many cases, nanocables and nanotubes are also considered one-dimensional structures. Thin films are considered as two-dimensional nanostructures. Colloids bearing complex shapes have three-dimensional nanostructures.

9.1.5 Synthesis of nanoparticles

- The methods of synthesis of nanoparticles are well known for a long time as compared to the other nanomaterials. For the synthesis of nanoparticles, the processing conditions need to be controlled in such a manner that the resulting nanoparticles have the following characteristics: (i) identical size of all particles, (ii) identical shape, (iii) identical chemical composition and crystal structure, and (iii) individually dispersed with no agglomeration.
- Nanoparticles can be synthesized by both top-down or bottom-up approaches. Two well-known top-down approaches are milling (or attrition) and thermal cycling. Attrition produces nanoparticles of a wide range of diameter ranging from 20 nm to several hundred nanometers.

- The shape of the particles varies as well. They may contain impurities from the milling medium. The nanoparticles made by this process are usually used in the fabrication of nanocomposites and bulk materials having nano grains where perfections in size and shape, and presence of impurities do not matter significantly.
- Moreover, some of the defects can get annealed during the sintering process. A bulk material having very small thermal conductivity but a large coefficient of thermal expansion may be subjected to repeated thermal cycling to produce very fine particles. However, this technique is difficult to design and the control of particle size and shape is difficult.
- The bottom-up methods are more popular than the top-down methods. There are several bottom-up methods such as homogeneous and heterogeneous nucleation processes, microemulsion based synthesis, aerosol synthesis, spray pyrolysis and template-based synthesis. In this lecture, some of these techniques will be discussed.

9.1.5.1 Homogeneous nucleation

- In the homogeneous nucleation process, a supersaturation of the growth species is created. The supersaturation can be achieved by a reduction in temperature of a saturated solution or by a chemical reaction *in situ*.
- A solution that is in equilibrium with the solid phase is called *saturated* with respect to that solid. However, it is easy to prepare a solution containing more dissolved solid than that represented by the saturation condition. Such a solution is known as *supersaturated* with respect to the dissolved solid.
- The state of supersaturation is a prerequisite for all crystallization processes. If c is the solute concentration in the solution and c^* is the solubility of the solute at the given temperature, the *supersaturation ratio*, S, is defined as,

$$S = \frac{c}{c^*} \tag{9.1.1}$$

- The *relative supersaturation* (σ) is defined as,

$$\sigma = \frac{c - c^*}{c^*} = S - 1 \tag{9.1.2}$$

- A supersaturated solution, therefore, possesses a high Gibbs free energy and the overall energy of the system would be reduced by segregating the solute from the solution. The reduction in the Gibbs free energy is the driving force for nucleation as well as growth of the crystals. The change in Gibbs free energy per unit volume of the solid phase can be expressed as,

$$\Delta\overline{G} = -\frac{kT}{\overline{v}}\ln\left(\frac{c}{c^*}\right) = -\frac{kT}{\overline{v}}\ln\left(S\right) = -\frac{kT}{\overline{v}}\ln\left(1+\sigma\right) \tag{9.1.3}$$

  where k is Boltzmann's constant, T is temperature and $\overline{v}$ is molecular volume. If $\sigma = 0$, i.e., there is no supersaturation, $\Delta\overline{G}$ is zero and nucleation would not occur. When $\sigma > 0$, $\Delta\overline{G}$ is negative and nucleation occurs spontaneously.

- Let us consider a spherical nucleus with radius r. The change in Gibbs free energy is given by,

$$\Delta G_v = \frac{4}{3}\pi r^3 \Delta\overline{G} \tag{9.1.4}$$

- However, when a new phase is formed, the increase in surface energy is given by,

$$\Delta G_s = 4\pi r^2 \gamma \tag{9.1.5}$$

  where γ is the surface energy per unit area. Therefore, the net change of Gibbs free energy for the formation of the nucleus is given by,

$$\Delta G = \Delta G_v + \Delta G_s = \frac{4}{3}\pi r^3 \Delta\overline{G} + 4\pi r^2 \gamma \tag{9.1.6}$$

- The supersaturated state of the solution is a prerequisite but not a sufficient cause for a system to begin to crystallize. A free energy barrier must be overcome for the generation of a new crystalline phase from the solution. A newly-formed nucleus is stable only when its radius exceeds a critical value. A small nucleus dissolves in the solution to reduce the overall free energy.

- However, when the radius is larger than a critical value, r_c, it becomes stable and continues to grow. At the critical size $r = r_c$, $d\Delta G/dr = 0$. Therefore,

$$r_c = -\frac{2\gamma}{\Delta\bar{G}} \tag{9.1.7}$$

- The free energy barrier can be calculated by substituting r_c from Eq. (9.1.7) and $\Delta\bar{G}$ from Eq. (9.1.3) into Eq. (9.1.6) which gives,

$$\Delta G_c = \frac{16\pi\gamma^3}{3\left(\Delta\bar{G}\right)^2} = \frac{16\pi\gamma^3\bar{v}^2}{3k^2T^2\left(\ln S\right)^2} \tag{9.1.8}$$

- Because r_c represents the minimum size of a stable spherical nucleus, it sets the limit on how small nanoparticles may be synthesized. The value of critical radius can be reduced by reducing γ, and increasing $\Delta\bar{G}$ by increasing S.
- A few other factors such as solvent and additives in solution are important factors for the nucleation process. The rate of nucleation by primary homogeneous nucleation mechanism is given by,

$$J = A\exp\left(-\frac{\Delta G_c}{kT}\right) = A\exp\left[-\frac{16\pi\gamma^3\bar{v}^2}{3k^3T^3\left(\ln S\right)^2}\right] \tag{9.1.9}$$

where A is the pre-exponential factor. Equation (9.1.9) predicts that nucleation would occur only at some high values of supersaturation. The range of values of supersaturation ratio, S, in which the rate of nucleation increases very rapidly is known as the *metastable zone for homogeneous nucleation*.

Example 9.1.1: The interfacial energy for barium sulfate crystals in saturated aqueous solution is 120 mJ/m^2. If the critical radius is 1 nm, calculate the value of the Gibbs free energy barrier.

Solution: From Eq. (9.1.7) we get,

$$\Delta\bar{G} = -\frac{2\gamma}{r_c} = -\frac{2\times 0.12}{1\times 10^{-9}} = -2.4\times 10^{8}\ \text{J/m}^3$$

Therefore, from Eq. (9.1.8) we get,

$$\Delta G_c = \frac{16\pi\gamma^3}{3\left(\Delta\bar{G}\right)^2} = \frac{16\pi\times\left(0.12\right)^3}{3\times\left(-2.4\times 10^{8}\right)^2} = 5.02\times 10^{-19}\ \text{J}$$

- Nanoparticles with uniform size distribution can be synthesized if all nuclei are formed at the same time. In this procedure, all the nuclei are likely to have similar size initially. If their subsequent growth is similar, monodisperse particles will be obtained. Therefore, it is highly desirable if the nucleation occurs in a very short period of time.
- To achieve a sharp nucleation, the concentration of the solute is increased abruptly to a very high supersaturation and then quickly brought below the minimum concentration for nucleation. No more new nuclei form below this concentration whereas the existing nuclei continue to grow until the concentration of the growth species reduces to the equilibrium value. The size distribution of the nanoparticles can be altered in the subsequent growth process also, depending on the kinetics of the growth process.
- The growth of the nuclei depends upon several steps such as, (i) generation of the growth species, (ii) diffusion of the growth species from the bulk to the growth surface, (iii) adsorption of the growth species on the growth surface, and (iv) surface-growth through the irreversible incorporation of the growth species on the growth surface.
- Let us consider the growth of a spherical nucleus. If the growth process is controlled by the diffusion of the growth species from the bulk solution to the particle surface, the rate of growth is given by,

  $$\frac{dr}{dt} = D\left(c_b - c_s\right)\frac{\overline{v}_n}{r} \qquad (9.1.10)$$

  where r is the radius of the nucleus, t is time, D is the diffusion coefficient of the growth species, c_b is the bulk concentration, c_s is the concentration on the surface of the solid particles and $\overline{v}_n$ is the molar volume of the nuclei.
- If the initial radius of nucleus is r_0 and if the concentration in the bulk does not change appreciably with time, we can integrate Eq. (9.1.10) to obtain the following equation.

  $$r^2 = r_0^2 + 2D\left(c_b - c_s\right)\overline{v}_n t = r_0^2 + k_d t \qquad (9.1.11)$$

- It can be shown that for two particles with different initial radius, the difference in radius decreases as the time increases and the particles grow in size. Therefore, uniformly sized particles are formed by the diffusion-controlled growth.
- If the diffusion process is rapid, $c_s \approx c_b$, and the growth rate is controlled by the surface process. There are two mechanisms for the surface incorporation: mononuclear growth and polynuclear growth. In the mononuclear growth, the growth proceeds layer by layer. The growth species are incorporated into one layer and proceeds to another layer after the growth of the previous layer is complete.
- The growth rate for mononuclear growth is proportional to the surface area, i.e.,

$$\frac{dr}{dt} = k_m r^2 \tag{9.1.12}$$

where k_m is a proportionality constant. The variation of radius with time is given by,

$$\frac{1}{r} = \frac{1}{r_0} - k_m t \tag{9.1.13}$$

- It can be shown that the difference in radius between two particles increases with time in this mechanism. Therefore, this mechanism of growth does not favor the synthesis of nanoparticles of similar size.
- On the other hand, for polynuclear growth, the second layer begins to grow even before the growth of the first layer is complete. It is typically observed when the surface concentration is high.
- In polynuclear growth mechanism, the rate of growth of particle is independent of particle size or time, i.e.,

$$\frac{dr}{dt} = k_p \tag{9.1.14}$$

- The radius of the particles varies linearly with time.

$$r = r_0 + k_p t \tag{9.1.15}$$

- Therefore, in this mechanism, the difference in radius between two particles remains constant regardless of the growth time.

- Among the three mechanisms described in this section (i.e., the diffusion-controlled growth, mononuclear surface incorporation and polynuclear surface incorporation), it is evident that the diffusion-controlled growth would favor uniformly sized nanoparticles.
- However, it is likely that the growth of nanoparticles involves all three mechanisms. When the nuclei are small, the mononuclear growth mechanism may dominate. As the nuclei become bigger, the polynuclear mechanism may dominate, and for relatively larger particles, the growth is diffusion controlled. The growth conditions are very important to decide which mechanism would control. For example, if the supply of the growth species is very slow (e.g., due to a slow chemical reaction), the diffusion-controlled mechanism would control the process.

Exercise

Exercise 9.1.1: The growth of gold nanoparticles with time has been measured by the increase in mean radius of the particles. These data are given below.

t (ks)	1.0	1.5	2.5	3.0	4.5	5.5	7.0
r (nm)	6.5	7.5	8.3	9.5	10.8	12.0	13.5

Verify whether the growth is diffusion controlled or not. Determine the initial size of the nucleus.

Exercise 9.1.2: Determine whether the energy barrier to the nucleation process is greater for a cube or a sphere?

Exercise 9.1.3: Answer the following questions clearly.

1) Explain five major areas of technology where nanotechnology can play important roles.
2) Explain with examples the bottom-up and top-down techniques. What are their merits and demerits?
3) What is self-assembly? What are the important parameters behind self-assembly?
4) What is template-directed self-assembly?
5) Explain how mesoporous materials can be synthesized by surfactant-based templates.
6) What is hierarchy in self-assembled nanostructures?
7) Give one example each of zero-, one- and two-dimensional nanomaterials?
8) Describe five methods of synthesis of nanoparticles.
9) What is supersaturation?
10) What is critical radius of nucleus?
11) Explain how the growth of a crystal nucleus takes place.
12) What type of growth-conditions favor uniform-sized nanoparticles?

Suggested reading

Textbooks

- P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 11.

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