

Thus the optical and other properties of **gold nanoshells** are similar to those of colloidal gold particles. The optical properties of gold nanoshells change as the relative dimensions of the silica core and gold shell change.

The gold nanoshells find a potential use in the treatment of cancer. The gold nanoshells can be injected into the body. When they are concentrated to the targeted cancer cells, they are illuminated **with a laser beam to produce heat** that can destroy the heat sensitive cancer cells (*cf.* cell-killing effect at a temperature above *ca.* 45°C). The **plasmonic gold nanoshells or gold nanoparticles** resonant with the NIR (near infrared) light (**biologically transparent window**) being irradiated with the NIR light can rapidly convert the absorbed light energy into the localised heat energy to raise the temperature which can destroy the cancer cells (**hyperthermia treatment**).

Here it is worth mentioning that the magnetic nanoparticles can also be used in **hyperthermia treatment** (*i.e.* thermal treatment of cancer) of cancer cells (Sec. 10.3.9). In fact, the **superparamagnetic particles** (*e.g.* iron oxide particles or the magnetite (Fe_3O_4) particles having the diameter about 10 nm) when subjected to an alternating magnetic field (AC - magnetic field) undergo **Brownian relaxation** in which heat is generated by the **rotation of particles** in the suspending viscous medium under the applied field. Thus the Brownian relaxation mechanism actually represents the mechanical friction in the given viscous suspending medium.

2.3 BULK OR 3D-NANOMATERIALS

The bulk nanomaterials **do not have any dimension at the nanoscale but they exhibit the features at nanoscale**. The bulk nanomaterials represent the different types of materials like **nanocrystalline material, nanocomposites, nanoporous materials** (*e.g.* metal organic frameworks, MCM-zeolites) and **inorganic-organic hybrid nanocomposites**. The bulk nanomaterials find versatile types of applications. The properties and characteristics of these materials are separately discussed in Sec. 2.4.

The level of understanding the properties and structures of **bulk nanomaterials** is relatively lower compared to that of **isolated nanoparticles**.

2.4 3D-NANOMATERIALS OR BULK NANOMATERIALS: NANOCRYSTALLINE MATERIALS, NANOCOMPOSITES, NANOPOROUS MATERIALS INCLUDING METAL-ORGANIC FRAMEWORKS, INORGANIC-ORGANIC HYBRID NANOCOMPOSITES

2.4.1 Nanocrystalline Material: Three Dimensional Nanocrystalline Material in Bulk Form

It is a **single or multiphase polycrystalline** solid material having the grain size of a few nanometers (size less than 0.1 μm or 100 nm). Thus bulk or 3D-nanomaterial is composed of multiple arrangement of nanosize crystals (called **crystallites**). It may be noted that a polycrystalline **coarse-grained material** is full dense aggregate of crystals or grains having size in the range 10–100 μm .

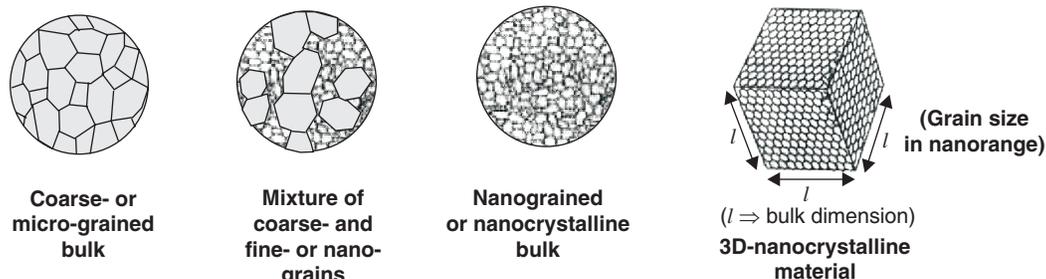


Fig. 2.4.1.1 Comparison of the structural features of coarse-grained and nanograined polycrystalline solids.

(iii) **Classical and historical examples of nanocomposites**

- **Gold-Ruby-Glass:** This ancient material consists of gold nanoparticles dispersed into the glass matrix (*i.e.* inorganic-inorganic nanocomposite) (*cf.* Fig. 1.1.2).
- **Damascus Steel:** This historical material consists of the dispersion of CNTs and iron carbide (Fe_3C) nanowires in high carbon steel. This steel is of unique mechanical properties (*cf.* Fig. 1.1.2).
- **Lycurgus Cup:** This historical object represents the dispersion of Ag- and Au-nanoparticles in glass (*cf.* Fig. 1.1.2).
- **Polymer Nanocomposites (PNCs):** These are industrially very much important because of their exciting mechanical strength and thermal stability. They are now occupying the multibillion dollar market.
- **Polymer-phyllsilicate Nanocomposites** (developed by **Toyota Company** in 1989) **in the Automotive Industry:** Nylon-6 polymer is treated as the matrix forming phase and **montmorillonite** (MMT) (a 3-layered silicate) is used as the nanofillers. Such PNCs with the polymer matrix and defoliated phyllosilicates are so industrially important that now they possess a **multibillion dollar business** only in automotive industry.

(iv) **Material composition:** In terms of chemical composition, the nanocomposite may be the combinations like: *organic with organic*, *organic with inorganic* and *inorganic with inorganic* (*e.g.* dispersion of zirconia nanoparticles within the alumina matrix). In the nanocomposite, the matrix phase may be constituted by *metal*, *ceramic* or *polymer*. Among these, **polymer nanocomposites (PNCs)** consisting of the polymer or copolymer (*e.g.* thermosets, *i.e.* thermosetting plastics, thermoplastics, elastomers) as the matrix having the dispersion of nanomaterials as the nanofillers, have been widely used. The PNCs may have the different structural shapes. In PNCs, the **most commonly used nanofillers** are:

montmorillonite (MMT) clay (layer silicate consisting of 2D-platelets), metal nanoparticles including the plasmonic nanoparticles; CNTs; nanosilica; nanoalumina; nanoceria; nanotitania; nanozirconia; etc.

The **commonly used polymers** as the matrix forming bulk phase are:

nylon; polystyrene; polyolefin; polyurethane; poly methyl methacrylate (PMMA); polyethylene terephthalate (PET), etc.

- **Inorganic-organic nanocomposites:** This synthesized material is a chemically **hybrid material** and they find many important applications in **paint and polymer industries** where the **inorganic nanofillers and nanosized-pigments** are dispersed into the organic material acting as the matrix. The representative examples of organic matrix are organic solvents, polymers, etc.

(v) **Common routes of the synthesis of PNCs:** In the PNC, the polymer matrix can be incorporated as the polymer species itself or the polymer can be generated *in situ* from its precursors (*i.e.* polymerization of its monomer) as in the **TOYOTA PROCESS** of synthesis of **nylon-6-clay** nanocomposite widely used in the automotive industry. The nanofillers may be directly incorporated into matrix or the nanoparticles like metal nanoparticles may be generated *in situ* (*e.g.* reduction of Ag^{I} - or Au^{III} - salts by the suitable reducing agents) for incorporation into the matrix. These common routes of synthesis of PNCs are illustrated in Fig. 2.4.2.2–4.

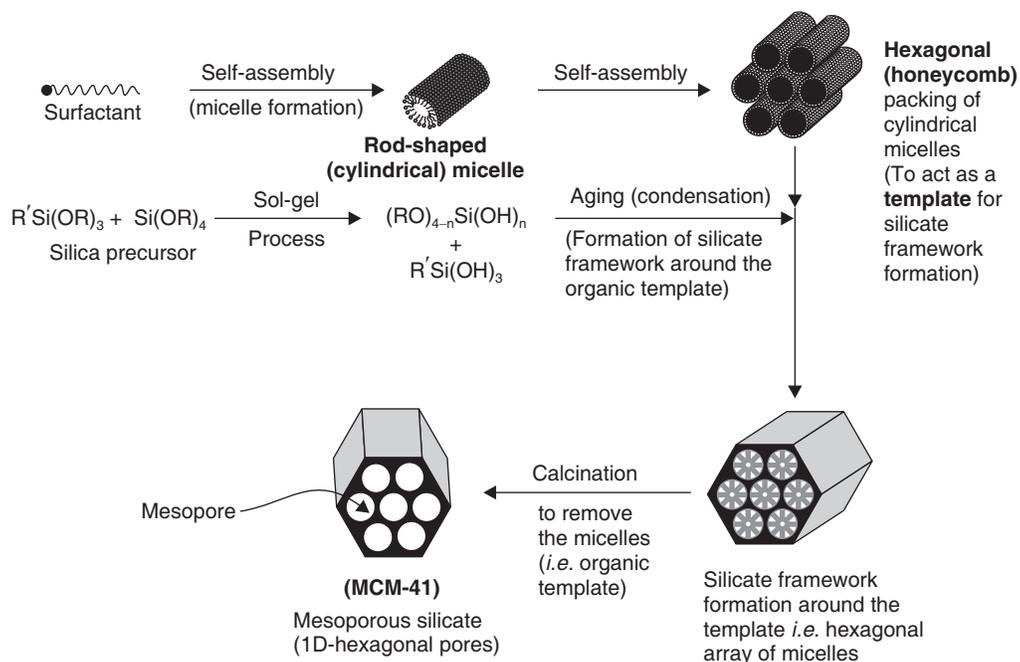


Fig. 2.4.3.1a Schematic representation of the synthesis of mesoporous silicate material (MCM-41) by using the supramolecular framework of micelles as a template. (Refs: A. Mueller *et al.*, *Chem. Rev.*, **102**, 727, 2002; M.E. Davis, *ibid.*, **102**, 3589, 2002; F. Hoffmann, *et al.*, *Angew. Chem. Int. Ed.* **45**, 3216, 2006; **118**, 3290, 2006; A. Corma *et al.*, *New J.Chem.*, **32**, 1338, 2008).

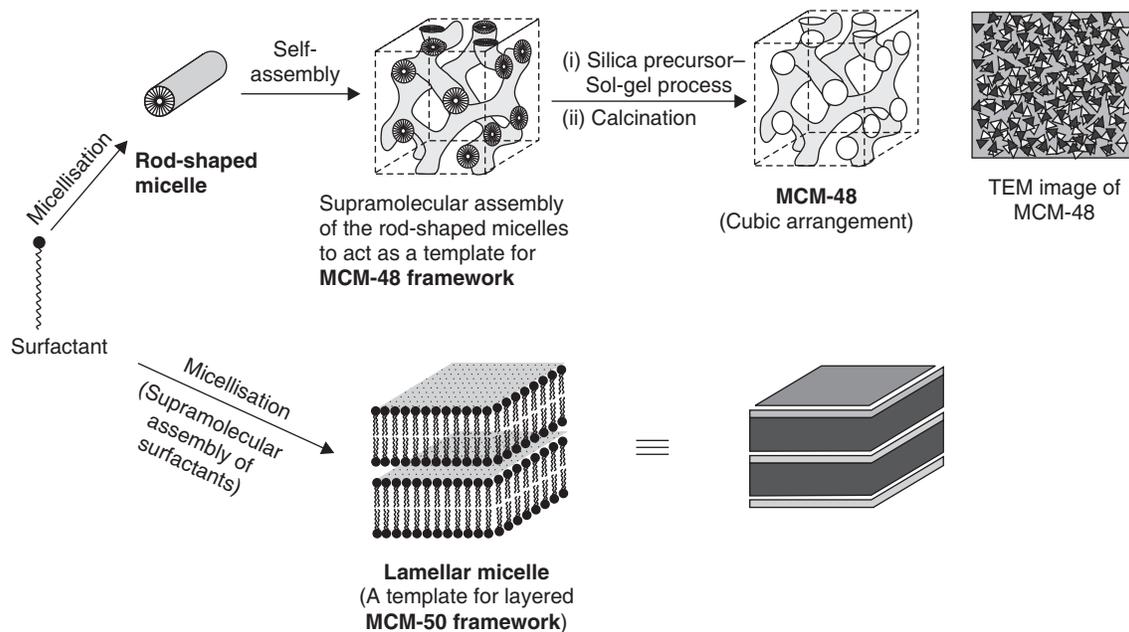
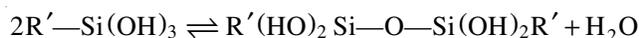
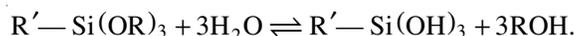
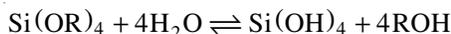


Fig. 2.4.3.1b Schematic representation of the organic templates (supramolecular assemblies of surfactants) for the synthesis of MCM-48 and MCM-50 mesoporous silicates (*cf.* A. Mueller *et al.*, *Chem. Rev.*, **102**, 727, 2002; and other Refs. cited in Fig. 2.4.3.1a).

- **Class-II hybrids** are synthesized through the simultaneous hydrolysis followed by condensation of organic and inorganic precursors. The **inorganic oxide precursors** are $\text{Si}(\text{OR})_4$, $\text{Al}(\text{OR})_3$, $\text{Ti}(\text{OR})_4$, SiCl_4 , etc. while the **organic precursors** are $\text{RAl}(\text{OR})_2$, $\text{R}_2\text{Si}(\text{OR})_2$, $\text{RSi}(\text{OR})_3$, etc. bearing at least one **nonhydrolysable** group (*e.g.* $\text{Al}-\text{R}$, $\text{Si}-\text{R}$). Sometimes, in organic precursors, the nonhydrolysable organic groups may bridge two inorganic centres (*e.g.* $\text{Si}-\text{CH}_2-\text{R}-\text{CH}_2-\text{Si}$). A typical example of synthesis of Class-II hybrid is illustrated here.



($\text{Si}-\text{R}'$ bond is nonhydrolysable; in the polymer, R' provides the organic part)

Commercial importance of inorganic-organic nanocomposites: These hybrid materials find many uses in commercial products because of the improved material property including the material strength, thermal stability, photostability, ultrafast photochromic response, etc. The products now occupy the multibillion dollar business market. Some representative examples of **polymer nanocomposites** (PNC) having the 2D-silicate layers (constituting the ceramic phase) dispersed in the organic polymer matrix have been discussed in (B) of this section. Some other representative examples are:

- (i) inorganic pigments as the nanofillers dispersed in organic matrix including organic solvents and polymers finding applications in **paint and polymer industries**;
- (ii) production of fire-retardant and stain-resistant clothing in **textile industry**;
- (iii) production of sunscreens and cosmetics;
- (iv) nylon-6/montmorillonite PNC in **automotive industry**;
- (v) indigo dyes dispersed in silica/zirconia matrix used in making **TV-screens**.

The **de Broglie wavelength** (λ_{DB}) of the particle for its thermal motion along the x -axis given by:

$$\lambda_{DB} \approx \frac{h}{p_{x(T)}} = \frac{h}{\sqrt{2mE_{x(T)}}} = \frac{h}{\sqrt{mk_B T}} = \sqrt{\frac{h^2}{mk_B T}} = \Delta x$$

Thus the condition of quantum confinement of a particle along a particular direction is:

the dimension of confinement must be of the order the de Broglie wavelength (λ_{DB}) for the thermal motion of the particle in the direction.

The above condition tells us *how small the dimension must be if we want to observe the size-dependent quantum confinement.*

In general, it can be stated that a nanomaterial is in the state of **quantum confinement when its size is in the order of de Broglie wavelength (λ_{DB}) of the charge carrier (i.e. electron or hole).**

In a semiconducting nanoparticle like **quantum dot (QD)**, **its size must be comparable to that of the Bohr radius (r_B) of the exciton** (i.e. bound electron-hole pair produced by the absorption of a photon in a semiconductor). This aspect will be discussed later in detail in Sec. 6.1.2.

Conditions of quantum confinement: Size $\approx \lambda_{DB}$ of electron or hole; size \approx exciton Bohr radius (r_B) in a semiconductor nanoparticle.

3.1.3 2D-Quantum Well: Quantum Confinement along One Direction

Let us consider a 2D-quantum well, where the carrier is allowed to move freely in the xy -plane while its motion is restricted along the z -axis. Then the quantised energy levels of the carrier (say electron) can be obtained by solving the following 1D-form of the time-independent Schrödinger equation.

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V(z) \right] \psi(z) = E\psi(z)$$

$E_n = \frac{n^2 \hbar^2}{8m L^2}$
 $V = 0$

Fig. 3.1.3.1 Particle in a box model to describe the fate of electrons in nanoparticles.

It is a problem similar to ‘**particle in a box**’ (Fig. 3.1.3.1) and $V(z)$ is zero within the box which extends $z = 0$ to $z = L_z$. Solving the Schrödinger equation under the boundary conditions and infinite depth approximation, we get:

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