Nanoshell particles: synthesis, properties and applications

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Nanoshells, which are thin coatings deposited on core particles of different material have gained considerable attention. These materials show novel properties which are different from their single-component counterpart. By simply tuning the core to shell ratio, the properties can be altered. With emerging new techniques it is now possible to synthesize these nanostructures in desired shape, size and morphology. Various synthesis routes have been developed over the past few years to prepare these nanostructures. They can be prepared with customized properties such as increased stability, surface area, magnetic, optical and catalytic properties. A review of their synthesis techniques, properties and applications is given here.

Keywords: Core-shell particles, metal nanoparticles, nanoshell particles, semiconductor nanoparticles, surface plasmon resonance.

MONODISPERSED colloids have attracted a lot of attention since a long time because of their novel properties and potential applications[1–5]. Efforts had been limited earlier to produce them in uniform sizes. Now, with the emerging new synthesis techniques, it is possible to synthesize them not only in uniform sizes but also in desired shapes such as rods, tubes, cubes, prisms, etc.[5]. Advances in synthesis techniques have allowed creation of other novel structures such as nanoshell or core shell particles, hollow particles, colloidal crystals, etc.

Nanoshell particles constitute a special class of nanocomposite materials. They consist of concentric particles, in which particles of one material are coated with a thin layer of another material using specialized procedures[6–10]. Nanoshell particles are highly functional materials with tailored properties, which are quite different than either of the core or of the shell material. Indeed, they show modified and improved properties than their single-component counterparts or nanoparticles of the same size. Therefore, nanoshell particles are preferred over nanoparticles. Their properties can be modified by changing either the constituting materials or core-to-shell ratio[11]. The term nanoshell is used specifically because thickness of the shell is ca 1–20 nm. Properties of shell materials (metal or

semiconductor) having thickness in nanometres, become important when they are coated on dielectric cores to achieve higher surface area. Sometimes they are referred as core shell or core@shell particles also. Thicker shells can also be prepared, but their synthesis is restricted mainly to achieve some specific goal, such as providing thermal stability to core particles. Synthesis of nanoshells can be useful for creating novel materials with different morphologies, as it is not possible to synthesize all the materials in desired morphologies. Core particles of different morphologies such as rods, wires, tubes, rings, cubes, etc. can be coated with thin shell to get desired morphology in core shell structures[12]. These materials can be of economic interest also, as precious materials can be deposited on inexpensive cores. By doing so, expensive material is required in lesser amount than usual. These particles are synthesized for a variety of purposes like providing chemical stability to colloids[6,13], enhancing luminescence properties[14], engineering band structures[15], biosensors[16,17], drug delivery[18], etc.

Nanoshell materials can be synthesized practically using any material, like semiconductors, metals and insulators. Usually dielectric materials such as silica and polystyrene are commonly used as core because they are highly stable. They are chemically inert and water-soluble; therefore they can be useful in biological applications. Nanoshell particles can be synthesized in a variety of combinations such as (core-shell) dielectric–metal[11,19–29], dielectric–semiconductor[30–33], dielectric-dielectric[34–39], semiconductor–metal[40], metal–metal[41], semiconductor–semiconductor[13,42–44], semiconductor–dielectric[12,45–48], metal–dielectric[49–57], dye–dielectric[58–61], etc. Core shell particles can be assembled and further utilized for creation of another class of novel materials like colloidal crystal or quantum bubbles. It is indeed possible to create unique core shell structures having multishells[62,63]. Multishell particles can be visualized as core particles having a number of shells around them. Core particles can be coated with a shell to obtain a single nanoshell. Further, these combinations of core and shell can be repeated again to get multishells. These structures show tunable optical properties from the visible to infrared region of the electromagnetic spectrum by choosing different combinations of core and shell.

This review includes synthesis aspects of nanoshells, their properties and applications.

A schematic diagram showing a variety of core shell particles is depicted in Figure 1. Surface of the core particle can be modified using bifunctional molecules and then small particles can be anchored on it (Figure 1 *a*). Nanoparticles grow around the core particle and form a complete shell (Figure 1 *b*)[30]. In some cases, a smooth layer of shell material can be deposited directly on the core by co-precipitation method (Figure 1 *c*). Small core particles such as gold or silver (10–50 nm) can be uniformly encapsulated with silica (Figure 1 *d*). Also a number of colloidal particles can be encapsulated inside a single particle (Figure 1 *e*). Core particles can be removed either by calcination or by dissolving them in a proper solvent. This gives rise to hollow particles also known as quantum bubbles (Figure 1 *f*). Concentric shells also can be grown on core particles to form a novel structure known as multishell or nanomatryushka (named after the Russian doll; Figure 1 *g*).

Synthesis of nanoshell particles

Numerous techniques[6–10] have been developed to synthesize nanoshell particles. Preparation of nanoshell particles involves multistep synthesis procedure. It requires highly controlled and sensitive synthesis protocols to ensure complete coverage of core particles with the shell material. There are various methods to fabricate core shell structures[10], e.g. precipitation[25,64], grafted polymerization[65], micro emulsion, reverse micelle[66–69], sol–gel condensation[70], layer-by-layer adsorption technique[37,71], etc. Although several methods have been established, it is still difficult to control the thickness and homogeneity of the coating. If the reaction is not controlled properly, it eventually leads to aggregation of core particles, formation of separate particles of shell material or incomplete coverage. How

ever, with the new emerging techniques it is now possible to deposit homogeneous coatings. One such method[57] is to coat the surface of colloids with appropriate primer (coupling agent) to enhance coupling of the shell material with the core. Also, the surface of the core material can be charged, and shell material can be adsorbed on its surface by electrostatic attraction[72].

Synthesis procedures for preparation of core particles of dielectric, metal and semiconductor materials and various ways of incorporating them to form core shell particles are discussed in the next section.

Synthesis of dielectric cores

Silica (SiO_2) (dielectric constant ~4.5)[73] is a popular material to form core shell particles because of its extraordinary stability against coagulation. Its non-coagulating nature is due to very low value of Hamaker constant, which defines the Van der Waal forces of attraction among the particles and the medium[6]. It is also chemically inert, optically transparent and does not affect redox reactions at core surfaces[57]. 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 with narrow size distribution can be synthesized following the procedure developed by Stöber *et al.*[74]. This method involves hydrolysis and successive condensation of TEOS (tetraethylorthosilicate $Si(C_2H_5O)_4$) in alcoholic medium in the presence of ammonium hydroxide (NH_4OH) as catalyst. The reaction mechanism is explained in eq. (1). The first step is hydrolysis, in which ethoxy groups are replaced by OH groups. In the second step, silicon hydroxides undergo polycondensation process to form SiO_2.
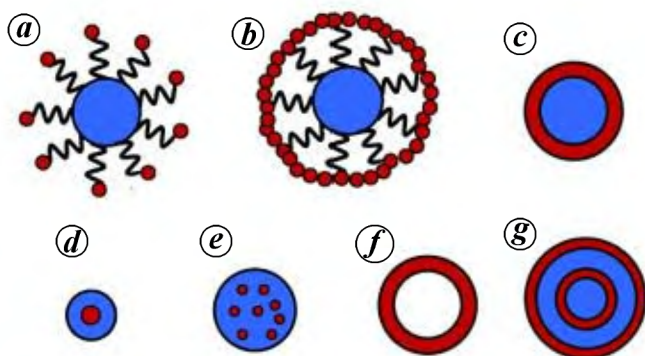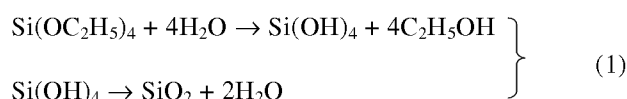
$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$

$$(1)$$

By varying relative ratio of TEOS to solvent (dilution) and amount of catalyst, one can synthesize these particles in various sizes ranging from ~ 50 nm to 1 μm. Reduction in TEOS concentration leads to the formation of smaller particles. Silica particles synthesized by this procedure are amorphous and porous. Variation of NH_4OH (catalyst) concentration changes the size, porosity as well as morphology of these particles[2]. Figure 2 *a* shows SEM image of silica particles prepared by the synthesis procedure described above. It can be seen that particles are quite uniform in size (~ 420 nm). They are noncrystalline, but produce a single broad diffraction peak in powder diffraction (Figure 2 *b*).

The other important core material is polystyrene (PS). PS particles along with high stability offer one added

Figure 1. Variety of core shell particles. *a*, Surface-modified core particles anchored with shell particles. *b*, More shell particles reduced onto core to form a complete shell. *c*, Smooth coating of dielectric core with shell. *d*, Encapsulation of very small particles with dielectric material. *e*, Embedding number of small particles inside a single dielectric particle. *f* Quantum bubble. *g*, Multishell particle.
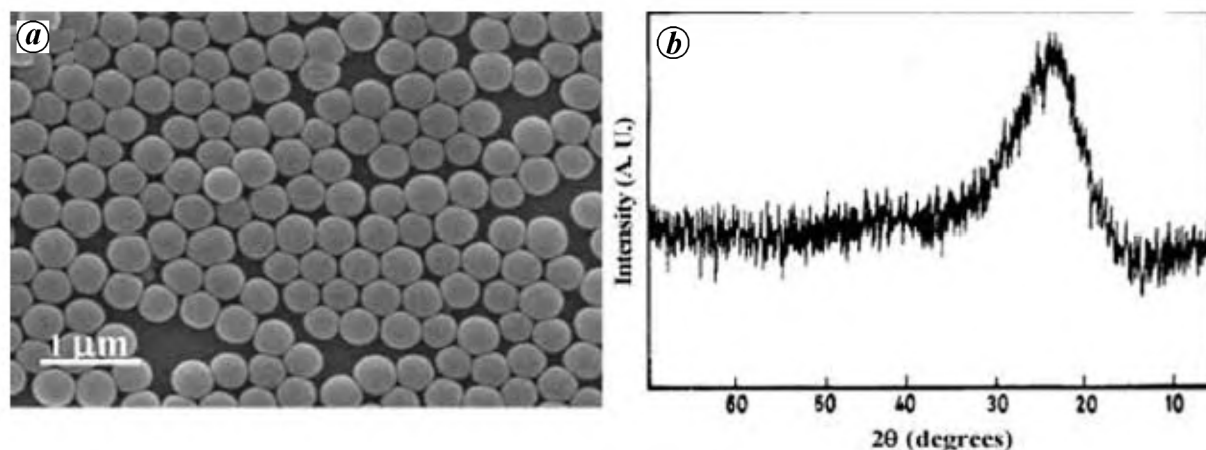
Figure 2. *a*, SEM image of colloidal particles of silica. *b*, XRD pattern of the same.

advantage. They decompose at relatively lower temperature, i.e. 450°C and are soluble in commonly available solvent such as toluene. Therefore, they are frequently used for the preparation of hollow structures (also known as quantum bubbles). Nanoshells can be synthesized on PS core and the core can be removed easily either by calcinations or by dissolution. Use of other cores requires strong acids (HF or HNO₃) or harsh conditions, which may affect the shell material. PS can be prepared by seed-mediated emulsion polymerization method[75,76]. There are several other methods like batch, semicontinuous and dispersion emulsion polymerization methods. However, the main disadvantage of these techniques is the lack of control over the size of the particles[75]. A broad or many times bimodal size distribution is obtained. Seed-mediated methods offer good control over the size of the particles. Preparation of PS spheres using seed mediated method involves dissolution of a monomer in suitable medium, in the presence of emulsifier and initiator. Polymerization of monomer starts when the initiator decomposes to form nuclei. The nuclei grow to form polymer spheres. PS spheres are synthesized using the procedures described above, in which styrene is used as a monomer, sodium styrene sulphonate as an emulsifier and potassium persulphate as initiator. Sodium bisulphite and sodium bicarbonate act as buffer and reaction is carried out in inert atmosphere[75]. Using this method, monodispersed spherical particles of size from 1 to 5 μm can be prepared. Preparation of small PS spheres (~ 20 nm) is also possible[76]. In this procedure, small amount of PMMA (poly(methyl methacrylate)) is used as a seed. Sodium dodecyl sulphate is used as a surfactant and ammonium persulphate acts as an initiator.

Synthesis of metal nanoparticles

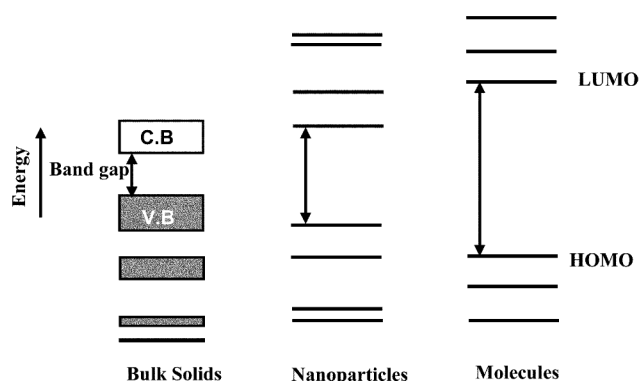Various reviews have appeared on metal nanoparticles, owing to their fascinating optical properties[77–80]. Gold and silver nanoparticles can be easily prepared by reducing their salts (such as chloroauric acid and silver nitrate respectively) in aqueous solutions. Usually tri sodium citrate[81] and sodium borohydride[82] have been used as reducing agents. Sodium borohydride is a strong reducing agent. The reaction takes place almost instantly and small particles are generated (size ~ 10 nm). Reduction using sodium borohydride is done at room temperature, while tri sodium citrate needs higher temperature (around 80°C). Other reducing agents such as ascorbic acid, alcohols, hydrazine and ethylene glycol also have been used. Although aqueous synthesis is well established, it is also possible to synthesize metal nanoparticles in other solvents such as alcohol[83], THF (tetrahydrofuran)[84] and DMF[85], ethylene glycol[86], etc. Alcohols and ethylene glycol play a dual role in the reactions. They act as reducing agents as well as solvents. A comparison[87] of various reducing agents is given in Table 1.

Synthesis of semiconductor nanoparticles

Semiconductor nanoparticles having sizes in the range of 1–10 nm display novel optical, electronic and physical properties. In these materials, when the size of the nanoparticle becomes less or comparable to the Bohr diameter of the exciton, various size-quantization effects such as widening of band gap and formation of discrete orbitals come into the picture[88–90]. In a semiconductor, when an electron is excited from the valence band to the conduction band, a hole is left behind in valence band. The electron and hole can form a bound state which is known as exciton. When the dimension of the nanoparticle approaches the Bohr diameter of the exciton, the electron and hole pair is localized inside the nanoparticle. Bulk semiconductor band gap opens up in the nanoparticle, like HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) gap for molecules (Figure 3). Reduction in the size of nanoparticles leads to widening

Table 1. Comparison of various reducing agents along with reaction conditions for synthesis of metal nanoparticles[87]

Metal species	Redox potential (V)	Reducing agent	Condition	Rate
Cu^{2+}, Ru^{3+}, Re^{3+}	< 0.7 and ≥ 0	$NaBH_4$,	Ambient	Fast
		Hydrazine, hydrogen	< 70°C	Moderate
		Aldehydes, sugars	70–100°C	Slow
		Polyols	> 120°C	Slow
Rh^{3+}, Pd^{2+}, Ag^+, Ir^{3+}, $Pt^{4+,2+}$,	≥ 0.7	Hydrazine, H_2SO_3, H_3PO_2, $NaBH_4$, boranes, hydrated e^-	Ambient	Very fast
$Au^{3+,+}$, Hg^{2+}		Aldehydes, sugars	Ambient	Fast
		Polyols	< 50°C	Moderate
		Organic acids, alcohols	≥ 70°C	Slow
Cr^{3+}, Mn^{2+}, V^{2+}, Ta^{5+}	< − 0.6	Hydrated e^-, radicals	Ambient	Fast
		$NaBH_4$, boranes	Temperature and Pressure > Ambient	Slow
Fe^{2+}, Co^{2+}, Ni^{2+}, Mo^{3+},	< 0	Hydrated e–, radicals	Ambient	Very fast
Cd^{2+}, In^{3+}, Sn^{2+}, W^{6+}	and	$NaBH_4$, boranes	Ambient	Fast
	≥ − 0.5	Hydrazine, hydroxylamine	70–100°C	Slow
		Polyols	>180°C	Slow

Figure 3. Comparison of energy levels in bulk material, nanoparticles and molecules.

of the band gap. This widening can be witnessed by optical absorption spectroscopy, in which a blue shift is observed with reduction in particle size. Brus[91] has developed a theory to explain the observed spectral shifts known as effective mass approximation (EMA), according to which size-dependent band gap of nanoparticles is given as

$$E' = E_g + \Delta E, \tag{2}$$

$$E' = E_g + \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon_2 R} + \text{polarization term}, \tag{3}$$

where, E_g is the bulk semiconductor band gap; ε_2 the dielectric constant of the semiconductor; R the radius of the particle and m_e and m_h are the effective masses of the electron and hole respectively.

Although EMA was useful to understand variation of band gap with size, it quantitatively failed to explain the results for very small particles (<5 nm). This is because the values for effective mass of electrons and holes are those of the bulk material. Therefore, other approaches like tight-binding approximation[92], empirical pseudo-potential method[93] and effective bond orbital method have been developed[94].

Nanoparticles have high free energy because of their large surface area. In order to minimize it, they agglomerate to form bigger particles. They are stabilized by various procedures. Reviews are available on synthesis of these particles[95–97]. They have been synthesized by methods such as arrested precipitation in aqueous as well as nonaqueous solutions[98], reverse micelle[99], using organomettalic precursors[88] and by chemical capping[100–102].

Preparation of core shell assemblies

Nanoshells can be prepared by a variety of approaches as explained earlier. One approach involves synthesis of core and shell particles separately. Later shell particles can be anchored on cores by specialized procedures. In the first method, the surface of the core particles is often modified with bifunctional molecules to enhance coverage of shell material on their surfaces[21,103,104]. Surface of core particles such as silica can be modified using bifunctional organic molecules such as APS (3-aminopropyltriethoxy-silane). The APS molecule has an ethoxy group at one end, and NH group at the other end. APS forms a covalent bond with silica particles through the OH group and their surface becomes NH-terminated (Figure 4).

Now metal and semiconductor nanoparticles can be attached through the NH group on the silica core. There are several other modifiers such as APTMS (3-amino-

propyltrimethoxysilane) and AEAPTMS (*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane) which produce surface terminated with amine group, MPTMS (3-mercapto-propyltrimethoxysilane) which makes surface terminated with thiols, DPPETES (2-(diphenylphosphino)ethyltriethoxy-silane) leaves the surface terminated by diphenylphosphine group and PTMS (propyltrimethoxysilane) giving surface terminated with methyl group[21]. Thus using a variety of linker molecules with different functional groups, a number of materials can be anchored on dielectric cores. Linkage can be verified using techniques like FTIR[30].

Graf *et al.*[105] have demonstrated a general method to coat various colloidal particles (gold colloids, silver colloids, boehmite rods, gibbsite platelets positively or negatively charged polystyrene, etc.) with silica. They have functionalized the surface of colloids using PVP (polyvinylpyrrolidone), which is an amphiphilic nonionic polymer. This method can be used for a variety of colloids, it is fast and does not require the use of silane coupling agents or precoating step with sodium silicate. Using this polymer it is possible to alter the interaction potential on the surface of the colloids. Hence it is possible to disperse them in a wide range of solvents.

It is also possible to make certain nanoshell particles without functionalizing core particles. In this case opposite charges can be developed on the core and shell materials to couple them together by electrostatic attraction[72].

In the second approach, known as controlled precipitation, synthesis of shell particles can be carried out in the presence of cores. The core particles act as nuclei and hydrolysed shell material gets condensed on these cores forming nanoshells[64]. Reactant concentrations and the amount of added core particles play an important role in deciding the shell thickness. Figure 5 illustrates images of titania-coated silica particles prepared using this technique. Silica particles (Figure 5 *a*) have been coated with a thin layer of titania (Figure 5 *b*).

Silica particles do not show any absorption peak in the range 300–800 nm. When these particles are coated with a thin layer (~ 23 nm) of titania, an absorption band at 320 nm is observed (Figure 5 *c*). Hence UV absorption can be an indirect technique to know the presence of coating on dielectric cores[106].

Metallic nanoshells such as gold and silver are usually synthesized by functionalizing the core particle with a linking molecule. It is also possible to deposit metal nanoparticles on the dielectric core using controlled precipitation. Reduction of metallic species can be carried out by commonly used reducing agents such as tri sodium citrate or sodium borohydride. Reduction of metal ions on the core, using tri sodium citrate is found to be more favourable than reduction using sodium borohydride. Coverage may not be complete in one coating step, but the procedure can be repeated several times till a homogeneous shell layer is obtained. Using similar techniques other nanoshells such as silica core silver shell can also be synthesized. The TEM image (Figure 6) shows a particle after a single coating step. Optical absorption spectra for the same are also shown. For silver nanoshells a broad band at 446 nm is observed, while silver nanoparticles show absorption at 431 nm.

In another technique, known as layer-by-layer technique, alternating layers of anionic particles and cationic polymer are deposited on surface-modified template molecule by heterocoagulation[39]. Both these methods lead to the formation of homogeneous and dense coatings. 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[25,36].

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

Surface plasmon resonance of metal nanoparticles and metallic nanoshells

Colloidal dispersions of metal nanoparticles having a size much smaller than the wavelength of visible radiation exhibit intense colours. The art of making coloured glass is
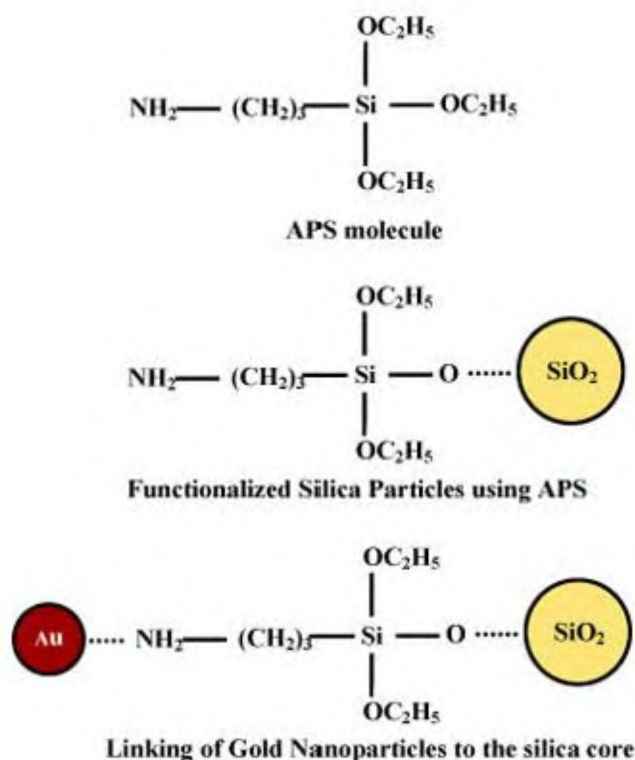

Figure 4. Linking of bifunctional molecule (APS) to core and shell particles to form nanoshells.
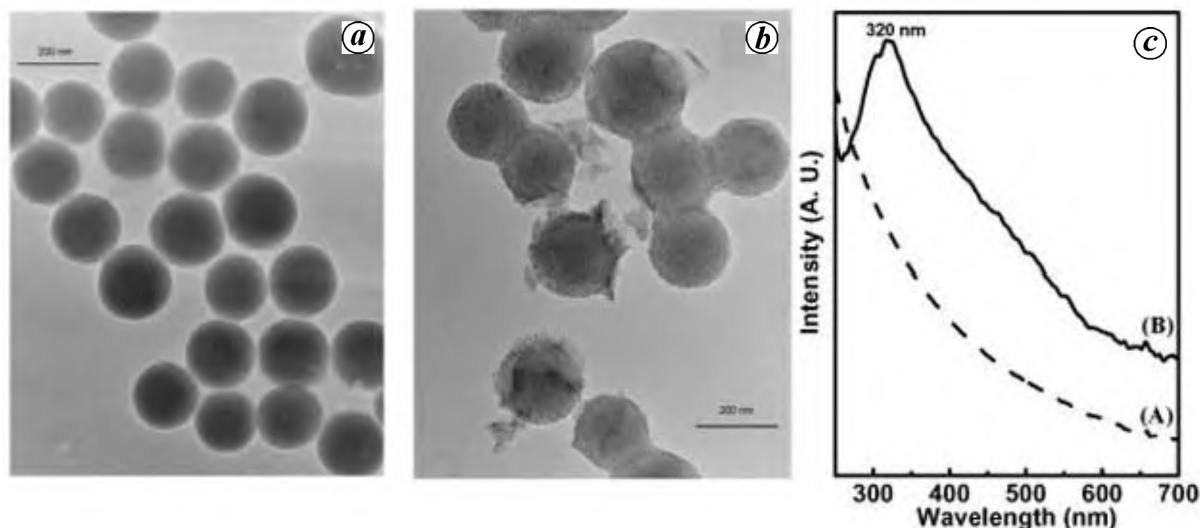
Figure 5. TEM image of (*a*) silica particles (size 170 nm) and (*b*) silica core (170 nm) titania shell (23 nm) particles (Reprinted with permission from ref. 106). (*c*) UV-Vis absorption spectra of (A) silica particles and (B) titania-coated silica particles.
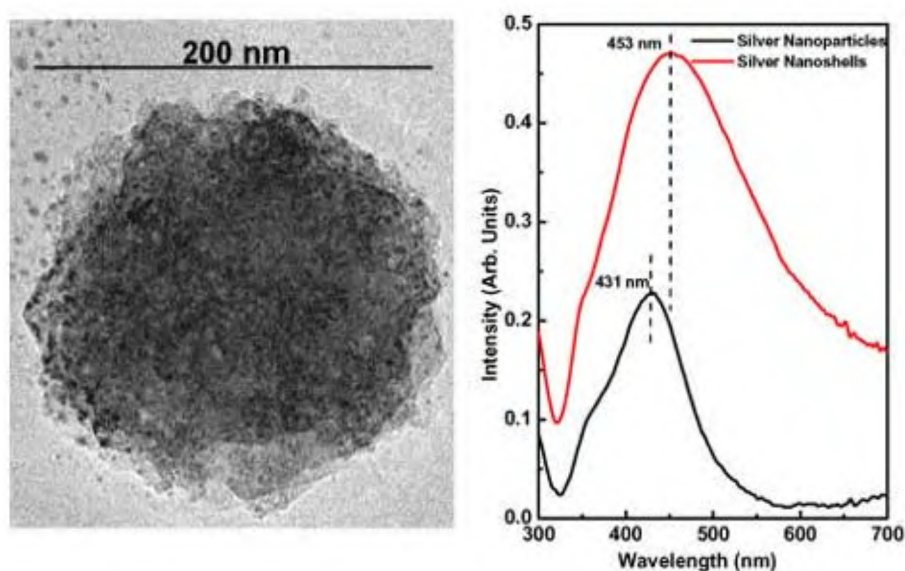

Figure 6. TEM image of silica silver core shell particle and corresponding UV-Vis absorption spectrum.

known over thousand of years. Windows of churches, palaces, etc. are often decorated with such glasses. Small amount of metal nanoparticles such as gold, silver, copper, etc. doped in glass gives rise to beautiful colours. Although the technique of making coloured glass had been known since a long time, it was not known that this is because of presence of metal nanoparticles in glass, until in 1857, Michael Faraday synthesized gold nanoparticles by reducing chloroauric acid. He obtained ruby-red and pink colour dispersion of gold particles. These were probably the first colloidal particles reported in the literature. The nanoparticles synthesized by Faraday are still stable and can be viewed on visiting the website of the London mu-

seum. Thus attempts were made to explain the observed intense colour using classical electromagnetic theory. In 1908, Mie[107] explained this phenomenon using Maxwell's equations, which is qualitatively explained as follows.

Metals can be considered as confined plasma of positive ions (consisting of nuclei and core electrons which are fixed) and conduction electrons (free and mobile). In neutral case, the positive charge cloud of ions and negative charge cloud of electrons overlap with each other. By some external disturbance, i.e. irradiation by electrons or electromagnetic radiation, the charge cloud is disturbed and electrons are moved away from the equilibrium position. If the density of electrons in one region increases,

they repel each other and tend to return to their original equilibrium position. As electrons move towards their original positions, they pick up kinetic energy and instead of coming to rest in equilibrium configuration, they overshoot. They oscillate back and forth. The collective oscillations of conduction electrons in metals upon excitation with electromagnetic radiation are known as plasmons. These oscillations give rise to a strong absorption band in the visible range of the electromagnetic spectra. In short, the origin of this band (known as plasmon resonance band) is attributed to resonance between the collective oscillations of the conduction electrons and the incident electromagnetic radiation[77]. For bulk metals, the plasmon frequency (ω_p) can be shown to be

$$\omega_p = \sqrt{\frac{4\pi n e^2}{m}} . \tag{4}$$

Plasmon energy for bulk gold is 9.0 eV and for silver it is 8.9 eV, and it lies in the UV range. However, for nanoparticles the plasmon energy is small and lies in the UV-Vis range.

The electromagnetic wave striking the metal surface has smaller penetration depth. Hence the electrons on the surface are most significant and their collective oscillations are known as surface plasmons. The extinction cross-section C_{ext}, which is composed of absorption and scattering, is given by

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon''}{(\varepsilon' + 2\varepsilon_m)^2 + \varepsilon''^2}, \tag{5}$$

where R is the radius of the particle, λ the wavelength of the incident electromagnetic radiation, ε' and ε'' are the real and imaginary parts of the dielectric constant of the particles respectively, and ε_m is the dielectric constant of the embedding medium.

Extinction would be maximum when $\varepsilon_1 + 2\varepsilon_m = 0$, which gives rise to a surface plasmon resonance (SPR) band. The position of the SPR band is dependent on the size and shape of the particle and dielectric constant of the medium in which the particles are dispersed[108]. Silver nanoparticles of size around 10 nm show an intense SPR band at 420 nm. Figure 7 shows the absorption spectra of silver nanoparticles of various sizes. The inset shows these silver nanoparticles dispersed in water. Synthesis was carried out at room temperature using sodium borohydride as a reducing agent and tri sodium citrate as a capping agent.

Similar to metal nanoparticles, metallic nanoshells also show the SPR band. Intensity of this SPR is higher than metal nanoparticles of the same size. It is possible to tune the position of the SPR band from visible to IR range of the electromagnetic spectrum by changing the core-to-shell ratio[11]. Several models and theories have been put

forward for calculating the SPR arising from the nanoshell assemblies[77,109]. The Mie theory[107] has been extended for nanoshell particles by considering them as concentric spheres of different materials[77,109]. Recently, Prodan et al.[62] have put forward another model, known as the hybridization model, to explain plasmon response from nanoshells. This model is in good agreement with the Mie theory within dipole limits. Plasmon excitation from nanoshell particles can be viewed as an interaction between plasmon response from a nanosphere and a nanocavity[19,62] as shown in Figure 8.

Electromagnetic excitations in the nanosphere and nanocavity induce charges on the inner and outer interfaces of the metal shell. Strength of interaction between the nanosphere and nanocavity plasmons depends on the thickness of the shell layer. Interaction is weak in the case of a thick layer, while it is strong when the layer is thin. Because of the interaction between two plasmon resonances, hybridization of plasmon resonance band occurs analogous to the interaction between two atoms. They hybridize into lower energy symmetric or bonding plasmon resonance and higher energy antisymmetric or antibonding plasmon resonance. The frequencies of these modes (bonding and antibonding) can be expressed as

$$\omega_{n\pm}^2 = \frac{\omega_B^2}{2} \left[1 \pm \frac{1}{2n+1} \sqrt{1 + 4n(n+1) \left(\frac{r_1}{r_2} \right)^{2n+1}} \right], \tag{6}$$

where, r_1 is the inner radius of the shell, r_2 the outer radius of the shell, n the order of spherical harmonics, ω_B the bulk plasmon frequency, ω_{n+} the antisymmetric plasmon and ω_{n-} the symmetric plasmon.

This model is in full agreement with the Mie theory, expecting a blue shift in energy as the shell thickness is reduced. Plasmon hybridization model suggests that reduction in the shell layer thickness results in increased interaction between the two plasmon resonances. This causes higher hybridization between the two and a blue shift in energy is observed.

Properties of nanoshell particles

Coating of colloidal particles with shells offers the most simple and versatile way of modifying their surface chemical[110], reactive[111], optical[11], magnetic[112,113] and catalytic properties[114]. Silica particles coated with gold shell have been studied for fascinating optical properties[19]. CdSe nanoparticles coated with CdS or ZnTe and CdTe nanoparticles coated with CdSe have been studied for enhancement in their luminescent properties[15]. Similarly, semiconductor particles such as ZnS doped with Mn can be embedded inside a single silica particle[14]. Such doped semiconductor nanoparticles are known to be highly efficient fluorescent materials. Coating of dielectric materials such as silica on

them can enhance the luminescence properties. Magnetic particles of iron oxide have been coated with dye-incorporated silica shell. Such particles show magnetic properties arising from the core as well as luminescent optical properties arising from the shell[63]. Thus functional materials with novel properties can be synthesized using various combinations of core shell materials[115] and by varying shell thickness[51]. Here is a brief review of properties of these materials.

Optical properties

Metal nanoparticles show optical absorption in the visible range of the electromagnetic spectrum. Position of absorption band shows small variations with particle size. Oldenburg et al.[11] have done pioneering work on optical properties
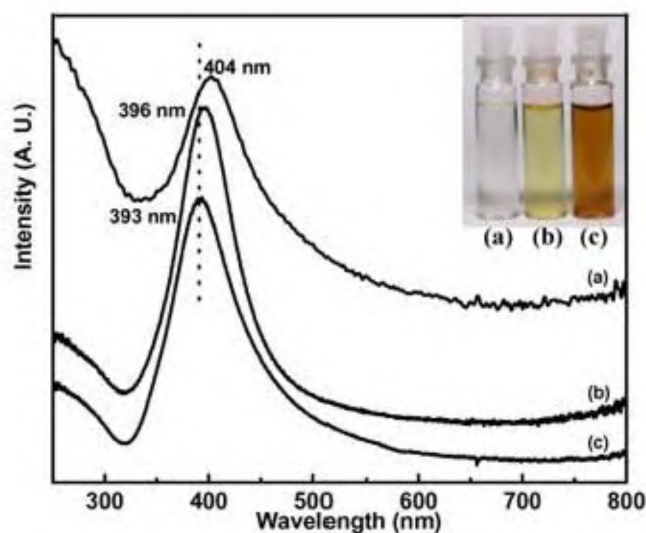
of gold nanoshells. Coating of metallic shells on silica allows one to tune the absorption band from visible to infrared region. Relative thickness of core-to-shell layer is sensitive towards the position of the SPR band[11]. Thus by changing the shell thickness, one can tune the SPR band position in the desired wavelength range (as shown in Figure 9). Metal nanoshells having plasmon resonance in the infrared region are well suited for biological applications, as this range of the electromagnetic spectrum is transparent for biological tissues[19].

Interaction between nanoparticles depends upon the separation between neighbouring particles[53]. Thick coating leads to larger separation of the metal particles, whereas thin coating leads to lesser separation. Dipole–dipole coupling between the particles is responsible for red shift of the plasmon band. If the particles are well separated (thick coating), the dipole–dipole coupling is fully suppressed and the plasmon band is located nearly at the same position as the individual metal particle. By varying the thickness of the shell by a small value, the colour of the core shell particles can be tuned from red, pink, purple to blue and at the same time changes can be monitored spectroscopically by monitoring the SPR bands.

Figure 7. UV-Vis absorption spectra of nanosized silver particles. (Inset) Different colours arising from different sizes.
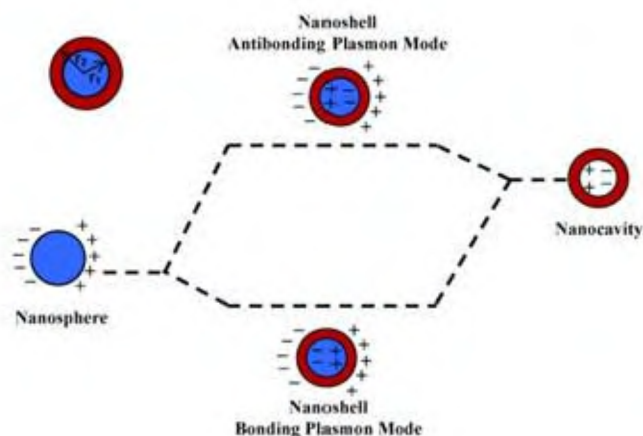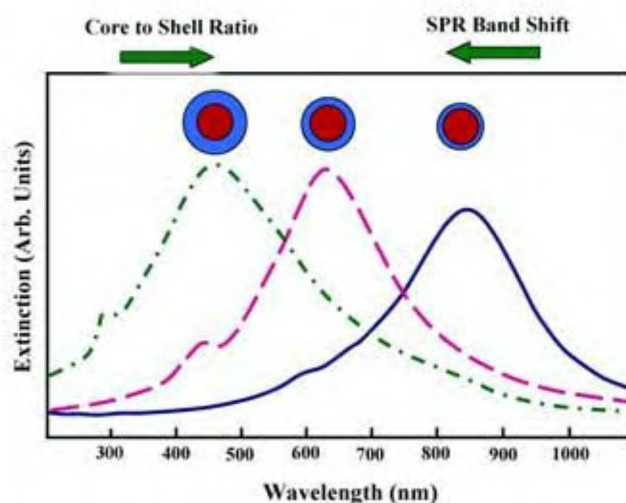

Figure 9. Variation in SPR band with shell thickness.

Figure 8. Hybridization model describing interaction between sphere and cavity plasmons to give rise to nanoshell plasmon.
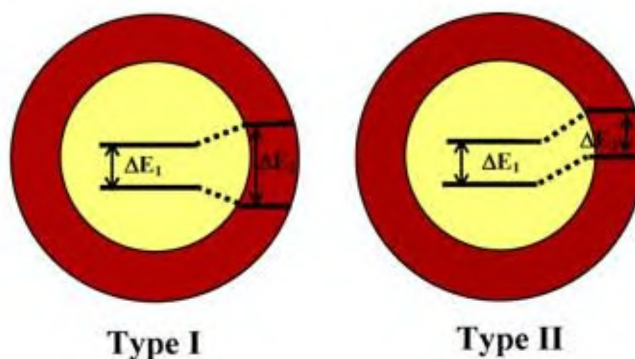

Figure 10. Type-I and type-II semiconductor core shell structures.

Enhancement of luminescence

Semiconductor nanoparticles are well-known fluorescent materials. Coating of silica is often done on them to reduce photobleaching[14]. Semiconductor nanoparticles coated with another layer of semiconductor have proved to be of great importance to enhance the luminescence from these core shell assemblies[15]. The choice of shell material is important for localization of the electron–hole pair. There are type-I nanostructures such as CdSe@CdS or CdSe@ZnS in which the conduction band of the shell material (which is a higher band-gap material) is at higher energy than the core and valence band of the shell is at lower energy than that of the core (as shown in Figure 10). In these materials, electrons and holes are confined in the core.

In type-II nanostructures such as (CdSe@ZnTe or CdTe@CdSe), both valence and conduction bands of the core material are at higher (or lower) energy than in the shell (Figure 10). In this case one carrier is confined in the core and the other in the shell. Type-I and type-II nanostrustures have properties different from each other because of the spatial separation of carriers. It has been noticed that lifetime decay of exciton and quantum yield of core shell nanoparticles is much higher than individual semiconductor nanoparticles[15].

Similar to semiconductor nanoparticles, organic dyes are also well-known phosphor materials. They are used as fluorescent biological labels. These dyes are however, not photostable and bleach out quite fast. Some of the dyes cannot be dispersed homogeneously in water. When these dye molecules were entrapped in silica shell, enhancement of luminescence was observed[58]. Silica coating on these dye molecules makes them disperse uniformly in water.

Enhancement of thermal stability

Depression of melting point in nanoparticles compared to bulk is observed[116]. This has been attributed to large surface tension in the case of nanoparticles. In order to release this tension, they melt fast compared to bulk. Encapsulation of silica on these nanoparticles greatly improves the thermal stability of these particles[115]. By changing the thickness of the shell, variation in melting point is observed[117].

In some nanoshell assemblies (metallic shells on dielectric cores) thermal instabilities are observed. Complete distortion of the shell was observed when silica gold nanoshell particles were heated at 325°C. Bulk gold has a melting temperature of ~ 1064°C. Melting of nanoshells was observed at significantly lower temperature. Due to higher surface area of core shell particle, more number of particles are exposed to the surface and are affected by faster melting. When these particles were encapsulated with silica (to form a multishell having silica–gold–silica layers),

enhancement in thermal stability was observed[117]. It has been observed that 60–70 nm thick coating of silica greatly improves (about 300° higher) the thermal stability of gold nanoshells[117]. Coating of silica on such shells is a way of preserving the identity of individual core particles because of high temperature stability of silica.

Surface chemical and catalytic properties

Core shell particles offer high surface area and can be used as efficient catalysts. Titania is an important photocatalytic material. It has been found that nanoshells and nanoparticles show different catalytic behaviour from bulk titania. It is thermally unstable and loses its surface area readily[114]. Coating a thin layer of some other stable oxide (such as silica) on titania can greatly improve its catalytic activity.

Magnetic properties

Stability of magnetic materials is important when studying their magnetic properties. To improve the surface characteristics and protect them from reacting with various species (to form oxides, e.g. all the oxides of iron are not magnetic), they are coated with inert materials. Silica is a better choice for such a purpose, because it forms stable dispersions. It is also non-magnetic and therefore does not interfere with the magnetic properties of the core particles. Magnetic materials are often susceptible to agglomeration and show anisotropic interactions. Their stable dispersion can be prepared by inducing surface charges on them or adsorbing some organic molecules on their surfaces. Since organic molecules do not form any strong chemical bond (such as covalent bond) with magnetic particles, they can be also desorbed. A thin coating of silica is the best way to protect them from agglomeration. When magnetic particles coated with silica are suspended in the medium, isotropic interactions are observed[112]. Two magnetic materials can be used as core and shell. Magnetic transitions of such materials can be studied. It was found that magnetic properties of such assemblies can be tailored by varying core to shell dimensions[118].

Applications of nanoshell particles

Nanoshell materials have received considerable attention in recent years because of potential applications associated with them. These materials have been synthesized for a variety of applications like fluorescent diagnostic labels[60], catalysis[114], avoiding photo degradation[58], enhancing photoluminescence[14], creating photonic crystals[119–121], preparation of bio conjugates[16,17], chemical and colloidal stability[6,13], etc. A few applications are discussed here in detail.

Colloidal stability

Nanoparticles are susceptible to coalescence and oxidation. Their surface is unstable because of the presence of dangling bonds, surface strains, etc. Often their surface is passivated by coating another stable material on them[6]. Although stable nanoparticles can be synthesized by capping with organic molecules[100–102], these capping agents decompose at elevated temperature (300°C), resulting in agglomeration of nanoparticles. Stability of colloids is greatly enhanced by coating them with stable material. Silica, because of its unusual stability, is a popular choice for shell material[57] as has been discussed earlier.

Photonic band gap materials

Photonic band gap materials are optical equivalents of semiconductors. Behaviour of photons in such materials can be analogically correlated to behaviour of electrons in semiconductors. Colloidal particles can self-assemble to form a three-dimensional crystal having long-range periodicity. Air gaps between the particles form a region of low refractive index, while the particles form a region of high refractive index. When photons are incident on these materials, they pass through regions of the high and low refractive indices. For photons, this contrast in refractive index is similar to the periodic potential that an electron experiences while passing through a semiconductor. If the contrast in refractive index is large, then the photons are either totally reflected or confined inside the dielectric material. The colloidal crystal blocks wavelengths in the photonic band gap, while allowing other wavelengths to pass through. The photonic band gap can be tuned by changing the size of the particles. Similar material can be prepared using core shell particles[120]. Core shell particles are better suited for this application, as relative refractive index contrast in core and shell particles is more. Band gap can be tuned from visible to IR range by changing index contrast[121].

Chemical libraries

Chemical library has applications in drug delivery, gene screening, barcoding and biological imaging[122]. Semiconductor nanoparticles are photostable and have continuous excitation spectra above the threshold of absorption. They have narrow emission spectra, the position of which is dependent on the size of the particles. These particles are therefore well suited for the preparation of chemical libraries[123]. However, dye molecules also have been used for this purpose[122]. Synthesis of chemical library mainly involves combinations of several functional molecules on a single template. Various fluorescent particles (dye or semiconductor nanoparticles) having emission at different energies can be immobilized on a single particle. Excitation of this particle with a single narrow band source produces emission at different wavelengths. Nanoshells which comprise of template particles (core) and immobilized fluorescent particles (shell) can be used as bar codes. The bar code generated on template particles can be easily decoded by fluorescence microscopy. Similar libraries can be synthesized using encapsulation of nanoparticles inside silica or polymer spheres.

Colorimetry and biosensing

Colorimetric sensing is monitoring changes in the colour of the nanoparticles which act as sensors. Usually gold nanoparticles are used for this purpose and polynucleotides[124], oligonucleotides[125] and DNA[126] have been detected successfully. Mirkin et al.[127] have used gold nanoparticles for detection of DNA. Single strand of DNA was immobilized on gold nanoparticles and used for detection of complementary DNA strand. It is shown that an intense ruby red-colour changes to blue upon agglomeration when complementary DNA was added.

Core shell particles can be a better choice for this purpose because of enhanced sensitivity. Core shell particles with highly controlled optical properties are used in several biotechnological applications[18,128]. It is possible to modify these particles to enhance their integration with biomolecules. This can be achieved by modifying their surface layer for enhanced aqueous solubility, biocompatibility and biorecognition. For such applications, mostly silica core and gold or silver shells have been used because they offer highly favourable optical and chemical properties for biomedical imaging and therapeutic applications[129–131]. It is possible to attach biomolecules to these core shell assembly and form an immunoassay to detect analytes[129], cancer cells[130], tumours[132], antibodies[16] and microorganisms[17]. These particles offer a sensitive, reliable and rapid detection of biomolecules.

For such kind of detection, it is necessary that nanoshells have an affinity towards the specific analyte which is to be detected. This can be achieved by immobilizing specific antibodies onto the nanoshells. Antibodies can be conjugated on nanoshells via the amino group present in them. Since these antibodies are raised against a particular analyte, they have an affinity for it and bind to it. It is like a lock and key arrangement, which fits perfectly. The detection is carried out by monitoring changes in the UV-Vis extinction spectra. Nanoshells show extinction maxima at a particular wavelength, which can be taken as reference. When analytes are added to it, because of agglomeration or charge transfer interactions or changes in refractive index (or all), shifts are produced in the spectra. These changes to the nanoshell spectra are an indication of the presence of certain biomolecules. A simple detection test has been developed for checking the potability of

water[17]. Silver nanoshells can also be used for detection of toxic ions such as Cd, Hg and Pb present in water. The extinction spectrum of silver nanoshells changes when it is mixed with a solution containing these ions. Figure 11 a shows the absorption spectra of silver nanoshells with different amount of Hg ions. This test is sensitive and can detect even small quantities of Hg ions. However, this test lacks specificity. Figure 11 b shows variation of intensity with the amount of added Hg ions.

Therapeutic applications and drug delivery

Nanoshells have gained considerable attention in clinical and therapeutic applications[129,130]. By carefully choosing the core-to-shell ratio, it is possible to design novel nanoshell structures, which either absorb light or scatter it effectively[130]. Strong absorbers can be used in photothermal therapy, while efficient scatterers can be used in imaging applications (Figure 12).
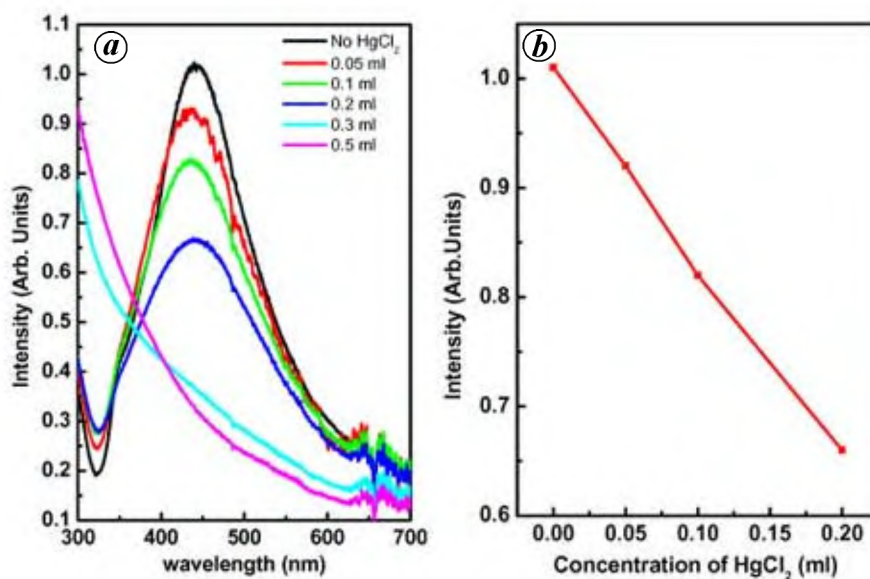

Figure 11 a, Effect of addition of HgCl₂ on SPR of silica silver core shell particles; **b,** Plot of intensity of SPR band as a function of amount of HgCl₂.
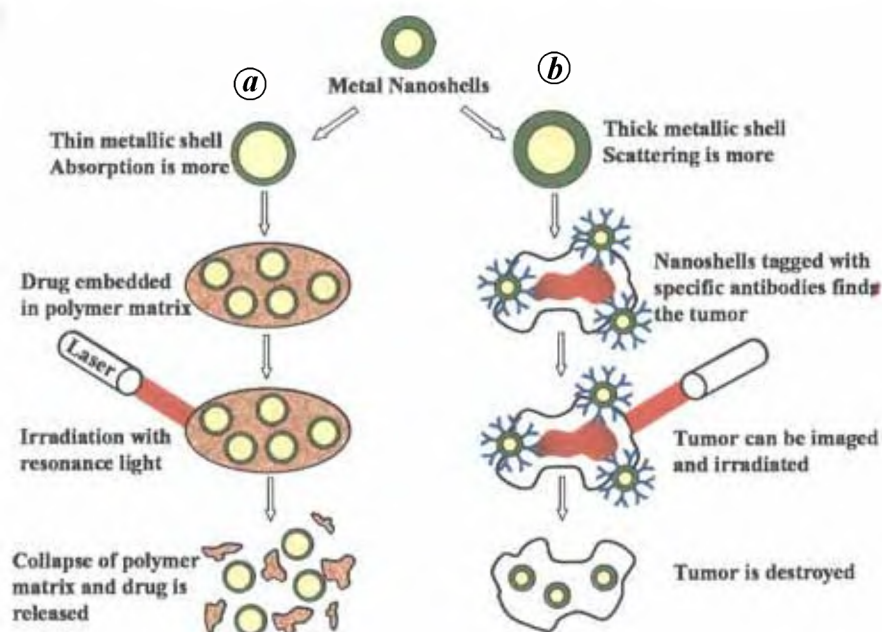

Figure 12 a, b. Drug delivery and imaging system based on nanoshells.

Core shell (mostly gold nanoshells) particles conjugated with enzymes and antibodies can be embedded in a matrix of the polymer[128]. These polymers, such as Nisopropylacrylamide (NIPAAm), and acrylamide (AAm), have a melting temperature which is slightly above body temperature. When such a nanoshell and polymer matrix is illuminated with resonant wavelength, nanoshells absorb heat and transfer to the local environment. This causes collapse of the network and release of the drug, as shown in Figure 12 *a*. In core shell particles-based drug delivery systems either the drug can be encapsulated or adsorbed onto the shell surface[133]. The shell interacts with the drug via a specific functional group or by electrostatic stabilization method. When it comes in contact with the biological system, it directs the drug.

In imaging applications, nanoshells can be tagged with specific antibodies for diseased tissues or tumours. When these nanoshells are inserted in the body, they get attached to diseased cells and can be imaged (Figure 12 *b*). Once the tumour has been located, it is irradiated with resonance wavelength of the nanoshells. This leads to localized heating of the tumour and it is destroyed. The power required for destroying diseased cells is almost half that required to kill healthy cells. The usual methods of tumour treatment, such as chemotherapy or radiotherapy have various side effects like substantial loss of hair, lack of appetite, diarrhoea, etc. The process of attacking the tumour, also leads to the loss of many healthy cells. Nanoshells offer an effective and relatively safer strategy to cure these ailments.

Conclusion

Various methods of synthesis of core shell particles are reported in the literature. Also there are new techniques emerging with which one can ensure complete coverage of core particle and homogeneous coating. However, synthesis of core shell particles is a big challenge. It needs skillful monitoring and highly controlled reaction parameters to produces functional materials. With variations in core and shell materials, one can tune their properties, which make them highly commendable. Nanoshells have a plethora of applications associated with them. These particles are used in imaging cancer cells and other therapeutic applications. Although such applications make them highly fascinating materials, one has to look at the ill-effect of these particles as well. The effect of these particles when inserted inside a human body is not known. For using these particles, intelligent and meticulous studies are needed.

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