

Semiconductor Nanoparticles

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Abstract. Semiconductor nanoparticles exhibit size dependent properties, when their size is comparable to the size of Bohr diameter for exciton. This can be exploited to increase fluorescence efficiency or increase the internal magnetic field strength in doped semiconductors. Nanoparticles are usually unstable and can aggregate. It is therefore necessary to protect them. Surface passivation using capping molecules or by making core-shell particles are some useful ways. Here synthesis and results on doped and un-doped nanoparticles of ZnS, CdS and ZnO will be discussed. We shall present results on core-shell particles using some of these nanoparticles and also discuss briefly the effect of Mn doping on hyperfine interactions in case of CdS nanoparticles.

Key Words: core-shell, doping, ESR, semiconductor nanoparticles, TEM.

1. Introduction

Since last two decades there has been an explosive growth of research in the field of nanomaterials. Several review articles and books have been published on different aspects of nanomaterials. See for example [1–8]. Nanomaterials may be in the range of 1 to 100 nm size and one can reduce the dimension in one, two or all three directions to obtain thin films, wires or dots, respectively. Nanomaterials can be of various shapes too and properties may change according to size and/or shape. These materials may be metals, semiconductors, metal oxides, organic materials or biomaterials. Thus there is a tremendous scope to design new materials with unusual properties.

Amongst the various types of nanomaterials, semiconductor nanoparticles have been widely investigated. This is quite understandable. Semiconductors have been useful in making devices. The drive towards miniaturization of electronic components and integration to accommodate huge number of them in small volume has been there for decades. This has enabled to have very compact digital watches, calculators, computers, laptops etc. In fact Moors' law

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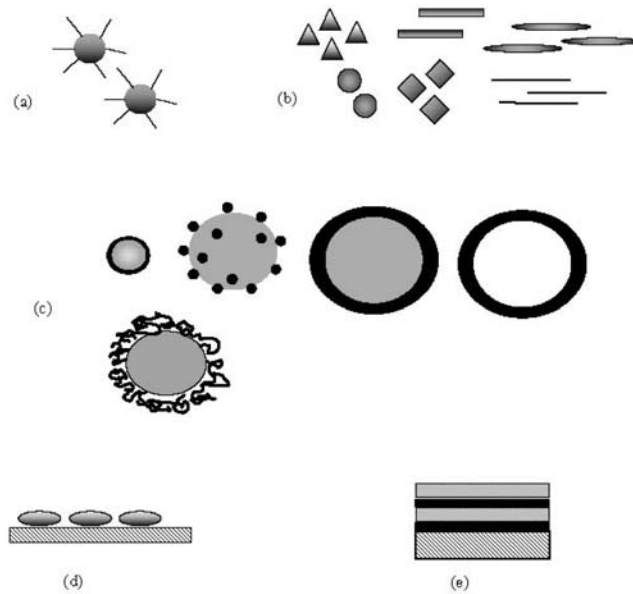


Figure 1. Some possible nanostructures: (a) surface passivated nanoparticles (b) different shapes of nanoparticles (c) core-shell particles (d) self assembly, and (e) multilayers.

predicted in 1960 has now reached its limits in such a way that any further reduction in size changes the materials properties. Dimensions of some of the devices are now in the nanometer range. Electronic structure of nanomaterials may be different compared to corresponding bulk material. This has led to interesting devices like single electron transistors, tunnel junctions, magnetic spin valves etc. which do not have bulk counterparts. Besides this, at nano scale, semiconductor materials like silicon that are not optoelectronic materials due to indirect band gap have showed strong luminescence in visible range [9]. Moreover they exhibit emission which is size dependent luminescence. Some groups have showed [10–13], for II–VI and III–V semiconductors, the change in band gap with particle size.

Materials with zero dimensions i.e. the ones whose all three dimensions are reduced to nanometer regime are known as quantum dots or simply nanoparticles. There is a variety of nanoparticles. A few possibilities are illustrated schematically in Figure 1. We have synthesized a large number of oxides, sulphides, core-shell particles, self-organized islands of Ge/Si, fullerenes, Diluted Magnetic Semiconductor (DMS) nanoparticles like TiO_2 doped with cobalt and metallic multilayers like Fe/Si, Cu/Ni Co/Pt etc. Here we will discuss a variety of semiconductor nanoparticles viz. ZnS, CdS and ZnO, their synthesis and some optical properties. We shall then discuss how nanoparticles can be encapsulated inside some robust shell of silica or how to anchor such particles on silica for exploiting large surface area of silica particles. We also discuss how doping with

manganese can alter the splitting of energy levels in CdS nanoparticles causing changes in the internal magnetic field of the nanoparticles.

2. Experimental

Synthesis of semiconductor nanoparticles was carried out using a chemical route known as chemical capping. In this procedure, some inert organic long chain molecules are used to passivate the surface of the particles so that the particles do not agglomerate or ripen to form larger particles. This ensures that the nanoparticles synthesized using some particular set of parameters yields stable nanoparticles with uniform size distribution. Figure 2 shows the flow chart of synthesis procedure used to synthesize ZnS, CdS and ZnO nanoparticles having <8 nm particle size. Details of synthesis are given below.

2.1. SYNTHESIS OF NANOPARTICLES

2.1.1. ZnS nanoparticles

Zinc sulphide nanoparticles were synthesized using zinc acetate [$\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$], *N, N*-dimethylformamide [$\text{HCON}(\text{CH}_3)_2$], sodium sulphide [Na_2S], thioglycerol [$\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$], sodium hydroxide [NaOH] and ethanol [$\text{C}_2\text{H}_5\text{OH}$]. Synthesis was carried out as follows. Zinc acetate (2.2 mM in 50 ml ethanol) was mixed with thioglycerol (3.5 mM in 50 ml ethanol) in DMF medium and both were stirred together for 30 min. Sodium sulphide (0.55 mM in 8 ml ethanol) was slowly mixed over a period of 4 h. The reaction was carried out at room temperature under nitrogen atmosphere. The solution was constantly stirred using a magnetic stirrer. Sodium hydroxide solution was then added till pH of the solution was 8. The whole solution was then refluxed for 14 h. Nanoparticles of ZnS were then obtained by size selective precipitation method [14] described as follows. The colloidal solution of nanoparticles in ethanol was concentrated using roto-evaporator. To this concentrated solution acetone, a non-solvent, was added slowly till flocculation was obtained which was then allowed to settle down. The supernatant was removed and flocculate was centrifuged to get precipitate enriched with largest crystallites in the sample. Precipitate was washed repeatedly using methanol. Dispersion of precipitate in ethanol and size selective precipitation was repeated till no further sharpening in sample's absorption spectrum had been seen.

2.1.2. CdS nanoparticles

Non-aqueous solutions of cadmium acetate [$\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$], thioglycerol and sodium sulfide prepared in ethanol were used to synthesize CdS nanoparti-

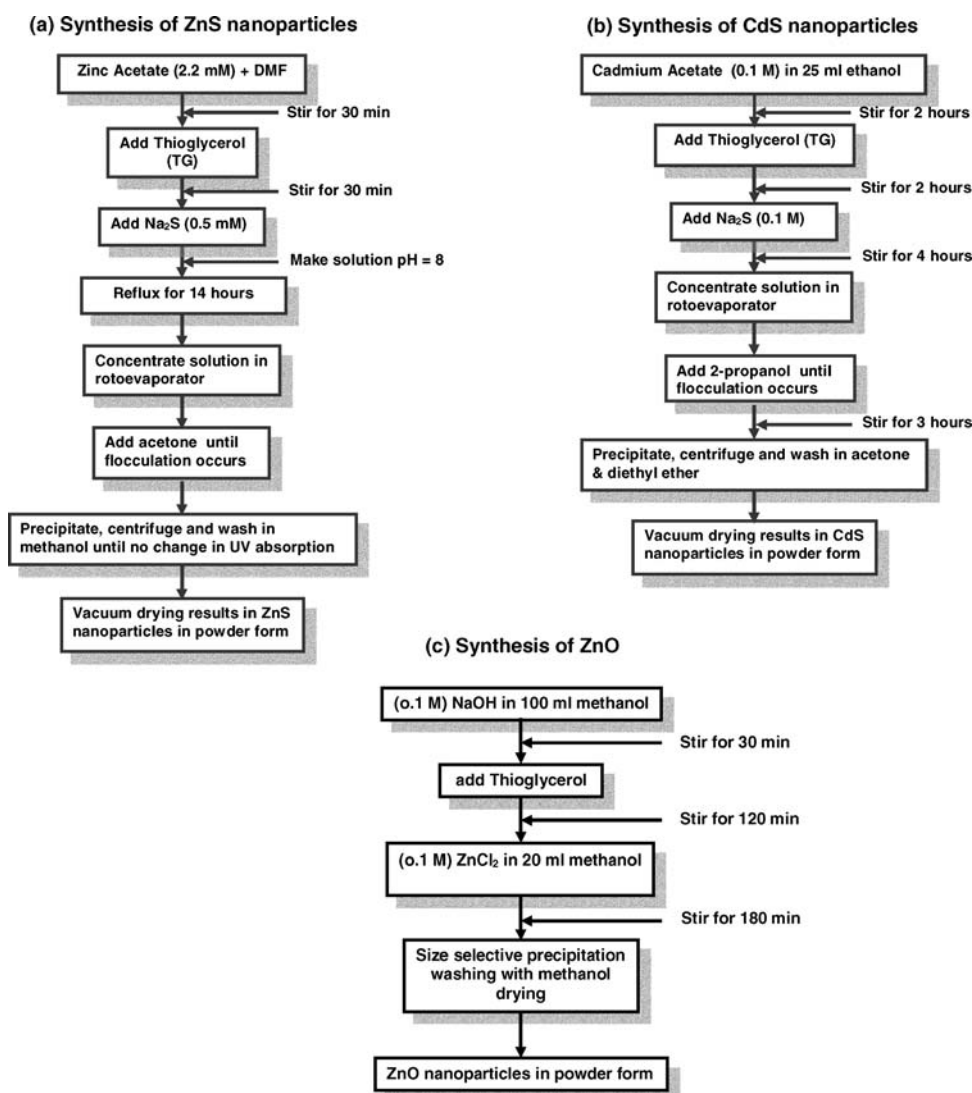


Figure 2. Procedure for synthesis of different nanoparticles (a) ZnS, (b) CdS and (c) ZnO nanoparticles. Variation of thioglycerol gives particles of different sizes.

cles. Thioglycerol was used as a capping agent. Cadmium acetate solution (0.1 M in 25 ml ethanol) was taken in reaction vessel and stirred continuously using magnetic stirrer. After two hours, thioglycerol (0.95 M in 25 ml ethanol) was added dropwise to cadmium acetate solution and stirred for two more hours. Finally sodium sulfide solution (0.1 M in 25 ml ethanol) was added and the solution was stirred continuously for 4 h. The synthesis was carried out at room temperature under nitrogen atmosphere to prevent the oxidation of nanoparticles. Size-selective precipitation method discussed above was used to obtain the

monodispersed particles. Precipitate was separated by centrifugation and washed with acetone and diethyl ether. It was then vacuum dried to get CdS nanoparticles in powder form.

2.1.3. ZnO nanoparticles

Zinc oxide nanoparticles were synthesized using zinc chloride [$\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$], methanol [CH_3OH], sodium hydroxide and thioglycerol. The synthesis was carried out in non-aqueous medium. The solutions were prepared in methanol. Thioglycerol was used as capping agent. Sodium hydroxide (0.1 M in 100 ml methanol) was stirred for 30 min. Thioglycerol (0.1 M in 20 ml methanol) was added drop wise to above solution and stirring was continued further for 60 min. Zinc chloride (0.1 M in 20 ml methanol) solution was then slowly added to this solution. The solution was then stirred for 180 min. The precipitate obtained by size selective procedure was washed with methanol and dried to get ZnO nanoparticles in powder form.

2.1.4. Doping of nanoparticles

For manganese doping both in ZnS and in CdS nanoparticles, manganese salt ($\text{MnCl}_2 \cdot \text{H}_2\text{O}$) was added to the respective metal salts in the solution form and resulting solution was stirred for 2 h before adding capping agent to the solution. After that the same synthesis procedure described above was used to synthesize doped nanoparticles. Doping of other elements can be achieved by using corresponding salts.

2.2. CORE-SHELL PARTICLES

2.2.1. Synthesis of SiO_2 particles

Figure 3 shows the flow chart explaining various steps used in synthesizing silica particles, encapsulation of nanoparticles or coating of nanoparticles in general.

Following the procedure developed by Stöber *et al.* [15], we synthesized SiO_2 particles. Here we use tetraethylorthosilicate, water and ammonia. A solution of ethanol, water and ammonium hydroxide in the molar ratio 49:31:4 was used. The solution was stirred at room temperature for 30 min and TEOS (1M) was added to it. Solution was further stirred for 3 h. Centrifugation and drying in ambient resulted in silica powder. By varying the reaction time, spherical silica particles of different sizes (50 nm–0.1 μm) could be obtained. In most of the cases particles with very narrow size distribution (1–3%) could be obtained.

2.2.2. Encapsulation of nanoparticles inside SiO_2

The synthesis procedure used to obtain silica particles can be further extended to encapsulate the nanoparticles inside silica. Here we have encapsulated man-

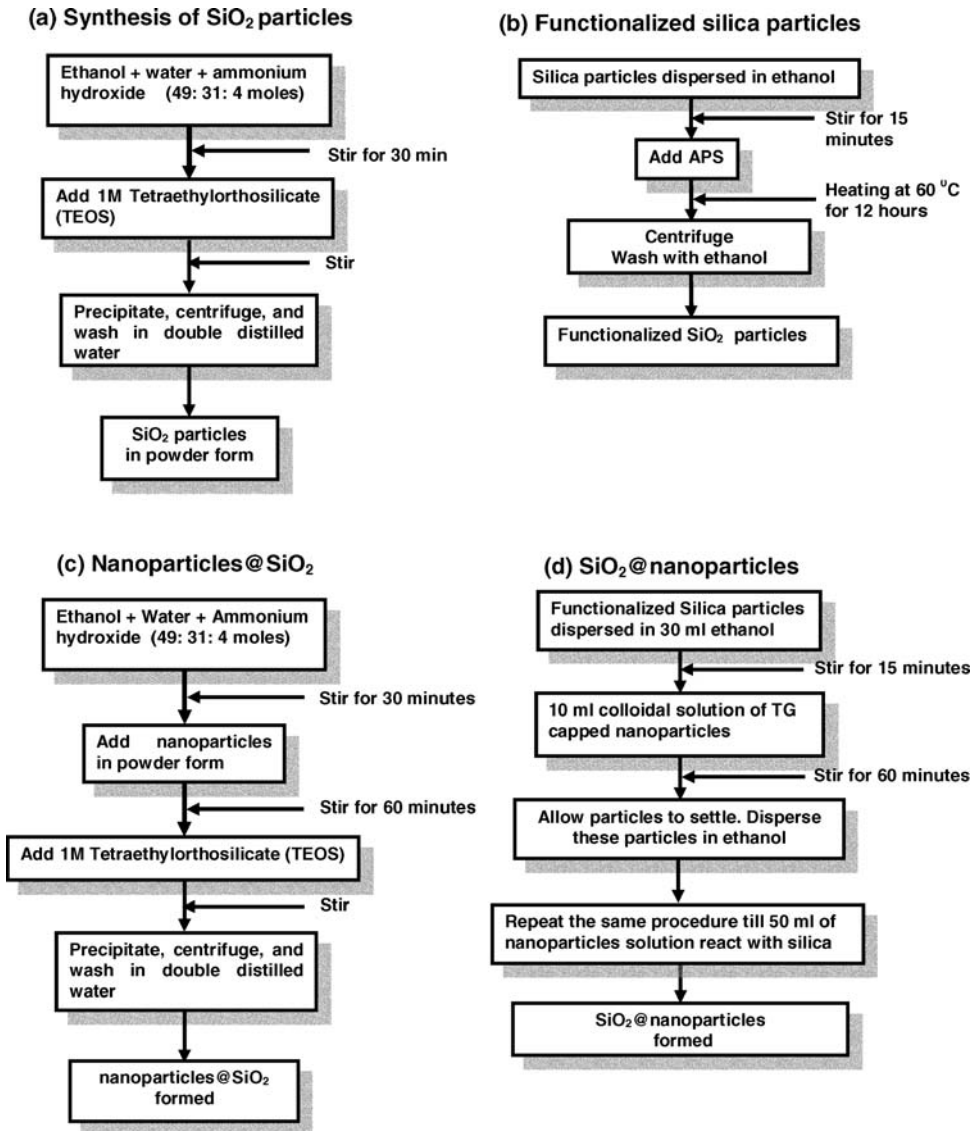


Figure 3. Procedure to synthesize (a) spherical SiO₂ particles, (b) functionalized SiO₂ (c) nanoparticles@SiO₂ core-shell particles and (d) SiO₂@nanoparticles core-shell particles. Variation of stirring period after TEOS addition gives particles of different sizes.

ganese doped zinc sulphide nanoparticles inside spherical silica particles. The synthesis procedure can be briefly outlined as follows. A solution of ethanol, methanol and water is made. It is continuously stirred for 30 min. Thioglycerol capped nanoparticles in the form of powder are added to the solution and further stirred for 60 min. By adding TEOS to this solution silica spheres start forming with nanoparticles trapped inside the core. By removing the solution at

different intervals core-shell particles of different sizes can be obtained. It may be pointed out that in this case many nanoparticles are trapped inside each silica sphere.

2.2.3. Functionalization of SiO_2 particles

Bifunctional molecule 3-aminopropyltrimethoxysilane (APS) has three $[-\text{OCH}_3]$ groups and one $[\text{NH}_2-(\text{CH}_2)_3-]$ group bonding to a silicon atom. Therefore it can link with two different types of molecules or particles. This has been used by various groups to bind nanoparticles to larger particles of silica or polymers and has been reviewed in [16, 17]. Here we use similar approach and attach TG capped ZnS nanoparticles and CdS nanoparticles to SiO_2 particles. One can control the amount of particles added to the shells using the procedure used here.

Silica particles are dispersed in ethanol and stirred for 15 min. To this solution APS (1×10^{-3} M) was added. The solution was then heated to 60°C and stirred continuously at this temperature for 12 h. Solution was allowed to cool to room temperature, and was centrifuged to obtain a precipitate. Precipitate was finally washed in ethanol.

2.2.4. Coating SiO_2 particles with nanoparticles

APS functionalized silica particles were mixed in ethanol along with TG capped nanoparticles, either of CdS or ZnS. Using different concentration of nanoparticles one can get thin or thick coating of nanoparticles on silica. See Figure 3 for flow chart.

2.3. CHARACTERIZATION

Characterization of above mentioned nanoparticles and core-shell particles has been carried out using different techniques like optical absorption, fourier transform infra red spectroscopy, photoluminescence, X-ray diffraction, electron spin resonance and transmission electron microscopy. The description of samples (liquid or powder) and instruments is briefly given below.

2.3.1. Optical absorption

The samples were analyzed using Shimadzu 300 double beam spectrometer by dispersing them in ethanol in case of ZnS, CdS and methanol in case of ZnO. Pure ethanol and methanol were used as reference for ZnS, CdS and ZnO, respectively. Spectra were recorded from 600 to 200 nm.

2.3.2. Fourier transform infra red spectroscopy

Samples for FTIR analysis were prepared in the form of pellets. Powder samples of nanoparticles or core-shell were mixed with KBr powder and pellets were

formed. Shimadzu 8400 spectrometer was used to record the spectra in the 300–4000 cm^{-1} frequency region.

2.3.3. Photoluminescence spectroscopy

Spectra were acquired using Perkin-Elmer LS-50 model. The dry powder samples were held in a powder sample holder. Spectra were recorded from 200 to 350 nm in excitation mode and 350 to 700 nm in emission mode using appropriate filters.

2.3.4. X-ray diffraction

X-ray Diffraction of powder samples was carried out on Philips PW1840 powder diffractometer. Copper radiation ($\text{CuK}\alpha$ 1.54 Å) was used in the analysis with nickel filter.

2.3.5. Electron spin resonance

The powder samples were analyzed using Bruker EMX-X band ESR spectrometer. The microwave source frequency was 9.5 GHz and 100 kHz modulation was used.

2.3.6. Transmission electron microscopy

Philips CM 200 FEG microscope equipped with a field emission gun was used for TEM analysis of the samples. EDAX analysis also could be carried out using this microscope. For the analysis, powder samples were dispersed in ethanol and a drop of solution was placed on ~ 5 nm thick carbon film on copper grid. After air drying, the grid was inserted in the microscope and using 200 KeV energy images were acquired.

3. Results and discussion

Nanoparticles of II–VI semiconductors have been investigated for a long time for their optical properties [18–20]. As the particle size reduces below the Bohr size of exciton, the energy gap increases and can be observed as shift in the absorption edge in UV–VIS absorption spectra. Band gaps for zinc sulphide, zinc oxide and cadmium sulphide bulk materials are 3.68 eV, 3.35 eV and 2.4 eV respectively [21]. The absorption edges are expected at 337 nm for ZnS, 370 nm for ZnO and 517 nm for CdS. As showed in Figure 4, the absorption spectra for ZnS, ZnO and CdS nanoparticles are well shifted from their bulk values. In case of ZnO the binding energy of exciton is 60 meV. This is quite large compared to

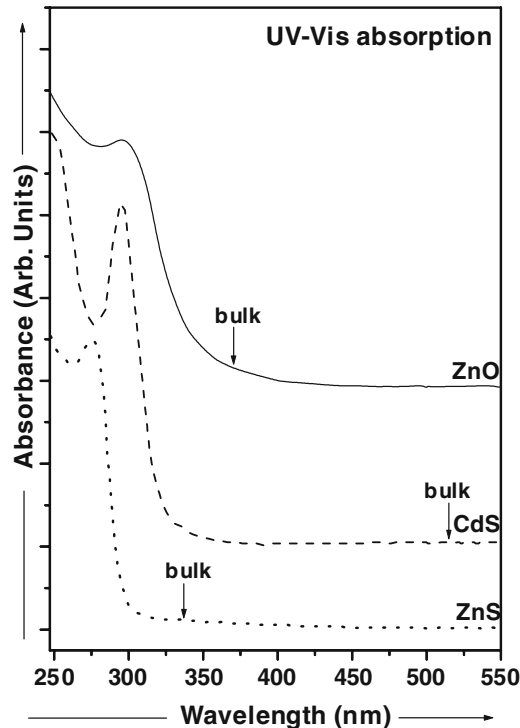


Figure 4. UV-Vis absorption spectra for ZnS (1.1 nm), CdS (3.6 nm) and ZnO (3.1 nm) nanoparticles.

thermal energy available at room temperature (~ 25 meV) to destroy the exciton. Therefore in ZnO, exciton is detectable even at room temperature. However ZnS (29 meV) and CdS (27 meV) excitons with very low binding energies are destroyed and are not detectable for bulk semiconductors of CdS or ZnS. However one can detect well defined excitonic peaks even for ZnS and CdS at room temperature, when CdS and ZnS are in the form of nanoparticles. Average particle sizes can be determined using the widths of X-ray diffraction peaks. In the present case the particle sizes are 1.1 nm for ZnS, 3.1 nm for ZnO and 3.6 nm for CdS particles. The presence of excitonic peak is expected theoretically too [22, 23]. Depending upon the preparation method there are variations in the quality of spectra obtained.

Semiconductor nanoparticles are quite useful as biological labels, barcodes, display screens etc [24–26]. Advantage with semiconductor nanoparticles is that they are photostable i.e., unlike many organic dyes they do not show degradation of luminescence intensity after some time. Besides they can be excited with any of the wavelengths in UV range rather than some fixed wavelength. It has also been showed [2, 7, 28] that efficiency for luminescence is large in case of nanoparticles compared to their bulk materials. Thus it is possible to excite photoluminescence in different nanoparticles using a single wavelength. In

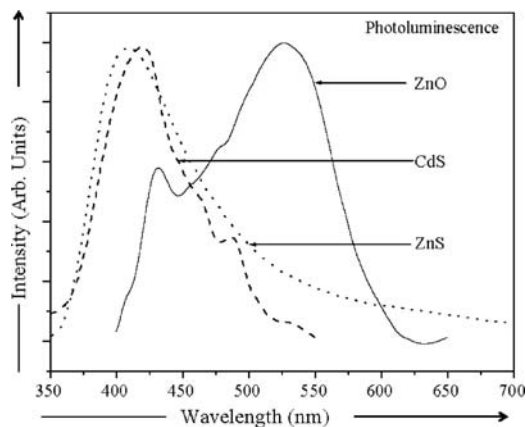


Figure 5. Photoluminescence of different nanoparticles.

Figure 5, photoluminescence for ZnS, ZnO and CdS nanoparticles has been showed. Nanoparticles in general have higher quantum efficiency of luminescence as compared to their bulk counterparts. Mechanism of luminescence of ZnS, CdS and ZnO nanoparticles has been discussed widely in the literature, see e.g. [27, 28].

Interestingly it is possible to coat the chemically capped nanoparticles on SiO_2 particles. SiO_2 particles of 50–500 nm size are well suited to adsorb such 1–5 nm size particles. Figure 6 (a) shows TEM images of SiO_2 particles while Figure 6 (b) and (c) show SiO_2 particles coated with CdS and ZnS respectively. Such coated particles often known as core–shell particles are written as core (material)@shell (material). Thus SiO_2 core and CdS coating is written as SiO_2 @CdS. If CdS would get encapsulated inside SiO_2 then this would be written as CdS@ SiO_2 . The details are reported elsewhere [29, 30]. However it can be mentioned here that there is no significant change in the properties of nanoparticles due to such coating of nanoparticles. FTIR analysis (not shown here) indeed showed the presence of TG molecules as well as APS [29, 30]. This type of core – shell particles would be useful for some applications where large number of well dispersed nanoparticles are required.

In some applications, specially the biological applications, it is necessary to use water soluble materials. SiO_2 particles are water soluble. Therefore fluorescent nanoparticles can be encapsulated inside SiO_2 particles forming core–shell particles. Advantage with this type of coating is that, nanoparticles can be excited with UV radiation as SiO_2 are found to be nearly transparent to UV radiation. We have found [31] that by encapsulating nanoparticles inside silica particles the photoluminescence increases. Increase in luminescence is due to protection provided by silica shell.

Transition metal doping, specially in II–VI semiconductors, is further interesting for the applications in spintronics [32]. Recently there have been reports about observation of giant magnetic field in nanoparticles of CdS doped with Mn

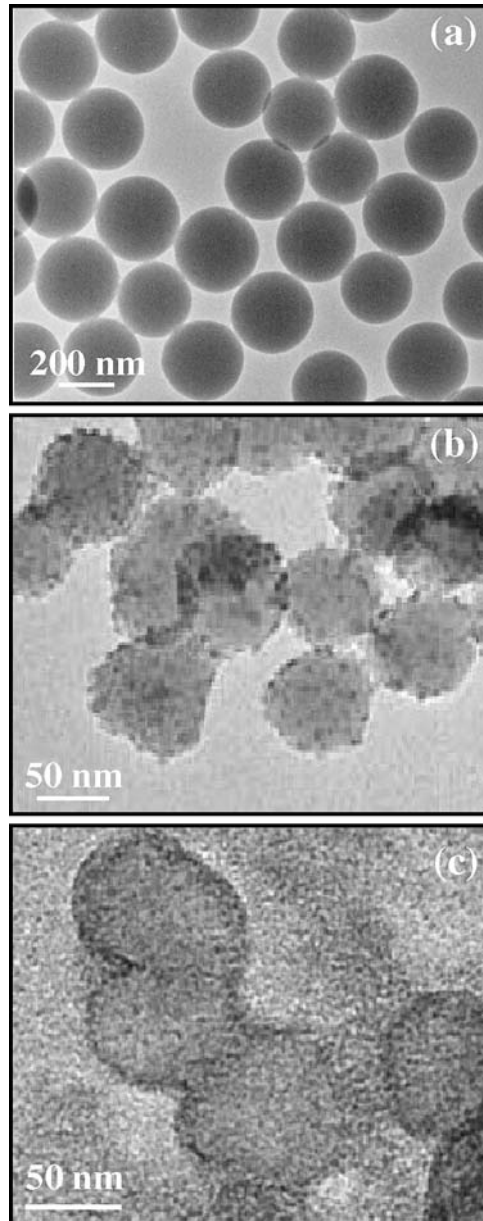


Figure 6. Transmission electron micrographs of (a) silica particles, (b) core-shell particles of SiO₂@CdS and (c) core-shell particles of SiO₂@ZnS.

in absence of zero external magnetic field [33]. This leads to observation of large splitting of exciton sub levels which has been interpreted as due to increase in the electron-hole interaction in nanoparticles. Also it is possible to observe ferromagnetism in nanoparticles as discussed for (GaMn)As system [34]. Pileni group [35] has showed that there are concentration dependent changes in ESR spectra

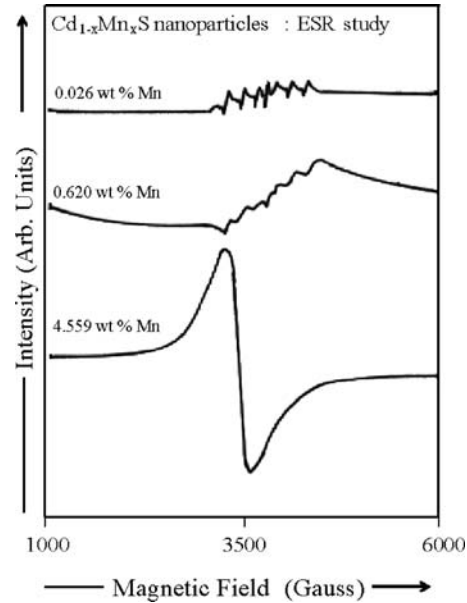


Figure 7. Electron spin resonance study of Mn doped CdS nanoparticles.

for CdS doped with Mn ions, synthesized using inverse micellar route. It is thus interesting to dope II–VI semiconductor nanoparticles to obtain ferromagnetism or even large paramagnetic moment in them. We have therefore initiated the investigations of Mn doped nanoparticles. Figure 7 shows ESR spectra for Mn doped CdS nanoparticles (3.8 ± 0.2 nm). It can be seen that six line pattern characteristic of isolated Mn ion doping, converts to a single line characteristic of strong Mn–Mn ion interaction similar to that discussed earlier [36, 37] for Mn doped in ZnS. Note that in Figure 7 the spectra are for CdS nanoparticles having same size but varying concentration of Mn ions. These results are in qualitative agreement with some earlier work on differently prepared nanoparticles of CdS doped with Mn [33, 35]. In order to assess the utility of doped II–VI semiconductor nanoparticles as spintronics materials, more experiments would however be necessary.

4. Conclusions

Stable semiconductor nanoparticles and core–shell particles can be synthesized using chemical routes. Quality of nanoparticles and core–shell particles is quite good and such particles would be useful for biological labeling, barcodes or fluorescent materials for display screens. Doped nanoparticles may find applications in spintronics too. However more experiments would be necessary in future to evaluate this aspect.

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