Studies of 2 - mercaptoethanol passivated ZnS core-shell nanoparticles

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We report the synthesis of luminescent nanoparticles of Zinc Sulfide (ZnS) with and without mercaptoethanol as a capping agent. Nanoparticles of ZnS are prepared by a co-precipitation method. These nanoparticles are stabilized using organic polymer 2-mercaptoethanol. The change in optical and morphological properties of ZnS nanoparticles is observed by using organic capping agent. The most probable distribution of nanoparticles in case of mercaptoethanol 2% are of range 13.2–19.8nm in diameter and 6.6-19.8nm in case of mercaptoethanol 4% as seen from TEM. The primary crystallites size is 1.9nm in case of mercaptoethanol capped nanostrucures and 2.2nm for uncapped nanostructures for 111 planes that was estimated from the X-ray diffraction patterns. Band gap measurements are done by UV- visible spectrophotometer. UV visible spectro-fluorometer shows emission and excitation spectra of capped as well as uncapped ZnS nanostructures. It is found that Band gap increases by introducing capping material. Photoluminescence studies show that emission intensity increases for capped sample.

1. Introduction

Size dependent properties are exhibited by semiconductor nanoclusters or quantum dots (QDs)[1-7]. As these nano quantum dots have very high surface to volume ratio so surface defects play an important role in their study. Nanoparticles, in general, are supposed to have nearly half of their atoms contained in top two monolayers, which make optical properties highly sensitive to surface morphology. The chemical synthesis has the advantages of producing size-controlled, un-agglomerated nanoparticles. Chemical precipitation in presence of capping agents, reaction in microemulsions, sol gel reaction and auto combustion are commonly used techniques for synthesis of nanoparticles. Particle size must be less than twice of Bohr radii of exciton as quantum confinement regime is limited to that size. The tunability of the properties of nanoparticles by controlling their size may provide an advantage in formulating new composite materials with optimized properties for various applications. But applications of these materials are restricted due to different non–radiative relaxations pathways [6-8]. One important non-radiative relaxation is surface related defects. Most of the physical or chemical properties exhibited by these nanoparticles are due to their crystallites. Further growth in their size is due to agglomeration of these crystallites to form primary particles. If this growth of particles is not controlled, then due to Ostwald ripening and Vander-Waals interactions between particles, they agglomerate and settle down [5-8]. This agglomeration can be arrested by either stabilizing them electrostatically or by inducing steric hindrance at appropriate stages to achieve size selective synthesis during precipitation reaction. Electrostatic stabilization involves the creation of an electrical double layer arising from ions adsorbed on the surface and associated counter ions that surround the particle in the dispersing media. Thus, if the electric potential associated with the double layer is sufficiently high, columbic repulsion between the particles will prevent their agglomeration. Steric hindrance can be achieved by the adsorption of large molecules such as polymers on the surface of the particles. In order to control the growth one can use different organic and inorganic capping agents to passivate the free QD's. To control the growth of nanoparticles organic stabilizers (polymers) e.g. polyethylene oxide (PEO), poly(N-vinyl-2pyrroledone)(PVP), Polyvinyl carbazole(PVK), mercaptoethanol, thiophenol, thiourea , SHMP, sodium polyphosphate, chitosan etc. can be added during the wet chemical synthesis for capping [11-19, 25]. Such materials have applications in luminescent devices, light emitters, phosphors optical sensors etc. [8-11]. Here in this paper, 2-mercaptoethanol (2%, 4%) capped as well as uncapped ZnS nanoparticles have been synthesized, using chemical precipitation methods. Optical and morphological measurements on ZnS nanoclusters have been carried out to investigate surface effects along with quantum size effects.

2. Experimental

Chemical precipitation method is used to synthesize Zinc Sulphide (ZnS) nanoparticles. Solutions of zinc

acetate and sodium sulphide were prepared in an aqueous media. 0.5 M zinc acetate (Zn ($CH_3COO)_2$. H_2O) solutions and 0.5 M sodium sulfide solution were used for synthesis of ZnS nanoparticles. As a capping agent 2 mercaptoethanol was used. In the first attempt, no surface-capping agent has been used for the stabilization of the nucleated particles; instead, the nanoparticles are allowed to interact freely in the aqueous medium. In the second attempt 2-mercaptoethanol (2 % ,4% at. wt) was added in 0.5 molar zinc acetate and then 0.5 M sodium sulphide was added drop wise. The precipitate appears soon after the addition of sodium sulphide (Na_2S). The stirring was allowed for 15 minutes at room temperature using a magnetic stirrer. Then the particles were centrifuged at 4000 rpm for 5 minutes. The precipitated particles were filtered using Whatman 40 filter paper. To remove the last traces of adhered impurities, the particles were washed several times using double distilled water. The washed particles were dried at 60ºC in air and are ready for characterization.

3. Characterization of nanostructures

The ZnS nanoparticles were characterized by X-ray diffraction (XRD) using Rigaku, model D–maxIIIC diffractometer with Cu Kα radiation. TEM studies were conducted using a Transmission Electron Microscope, Hitachi (H-7500) 120 kV equiped with CCD Camera. This instrument has the resolution of 0.36 nm (point to point) with 40-120 kV operating voltage and can magnify object up to 6 lakh times in high resolution mode. Optical reflectance of the ZnS particles were recorded with an double beam UV-Visible spectrophotometer (Model: Hitachi - 330) in the range 220–800 nm. The instrument has also integrating sphere to analyze the powder samples in the 200 nm to 800 nm range and a specular reflectance accessory to study reflective surfaces. PL studies were done by Fluromax-3 spectrofluorometer.

4. Results and discussion

The XRD pattern of synthesized capped and uncapped powder is shown in Fig. 1. Both shows three broad peaks corresponding to the (111), (220) and (311) planes.

Crystallite size of ZnS nanoparticles was calculated by following Scherrer's equation,

$$D = 0.9\lambda / \beta cos\theta \qquad (1)$$

where D-crystallite size (Å), λ(Å)=1.54 be the wavelength of Cu Kα radiation and β-corrected half width of the diffraction peak. The primary crystallites' size is around 1.9 nm in case of 2-mecaptoethanol capped nanoparticles and 2.2 nm for uncapped nanostructures. Three peaks have been observed in the span ranging from 10º to 80º. Lattice planes corresponding to above mentioned peaks have been identified by applying extinction rules. The ratios correspond to FCC structure. It is to be noted that, the peaks observed in the XRD patterns match well with those

of the β-ZnS (cubic) reported in the JCPDS Powder Diffraction. Intensities of the three most important peaks of ZnS, namely <111>, <220> and <311> reflections corresponding to 27.28º, 47.57º and 55º respectively do not deviate much from the Powder Diffraction File intensities. Broadening of the XRD peaks both in capped and uncapped samples indicates the formation of ZnS nanocrystals. Elongation of the XRD pattern in case of capped nanoparticles shows the surface passivation.
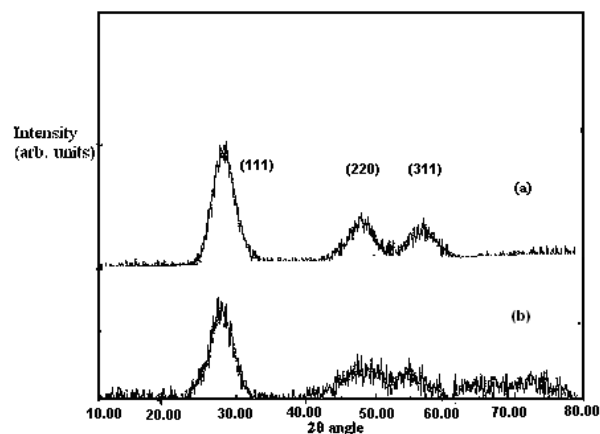

Fig. 1. XRD pattern of uncapped ZnS (a) and 2 mercaptoethanol capped ZnS (b).

From Fig. 2 it is clear that 2 mercaptoethanol capped nanoparticles are un agglomerated and on right side shown are agglomerated ZnS nanoparticles. On left side we can see ZnS nanoparticles which are capped with organic 2-mercaptoethanol layer that hinders agglomeration both sterically and electrostatically. The particle size distribution of nanoparticles in case of 2-mercaptoethanol 2% is 13.2–19.8nm in diameter and 6.6-19.8nm in case of 2-mercaptoethanol 4% as seen from TEM. Inorganic core and organic shell ZnS nanoparticles are better passivated with shell layer that seize nucleation at very early stage and can passivate surface defects or dangling bonds that is further shown by increase in PL intensity with capping in Fig. 5.
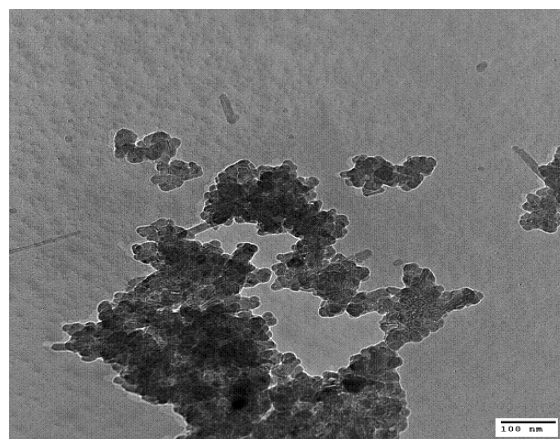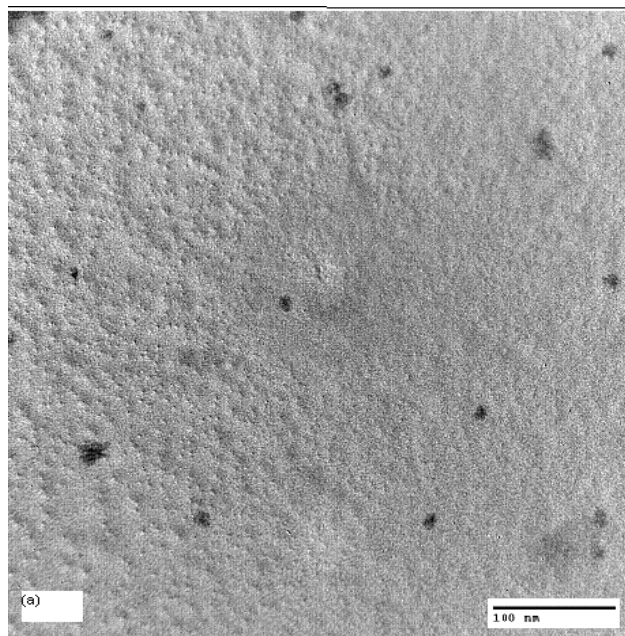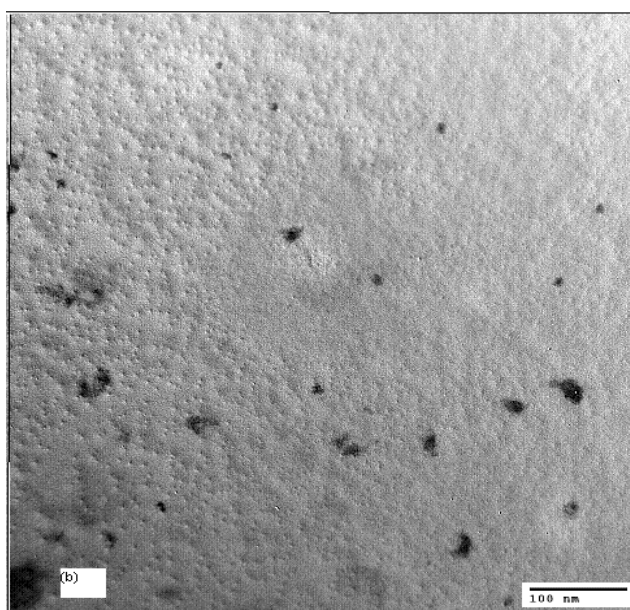

Fig. 2 TEM micrograph of Uncapped ZnS. Length bar is 100 nm.

(a)

(b)

Fig. 3. (a) Showing TEM of ZnS nanoparticles capped with 2 mercaptoethanol 2% and (b) Mercaptoethanol 4%. length bar is 100 nm.

Attempts have been made to identify various features seen in the PL studies on ZnS nanoparticles. Excitation peak (Fig. 5) of uncapped ZnS is at 320 nm showing excitonic absorption at 3.87eV where as for capped ZnS with 2-mercaptoethanol (2%, 4% at. wt.) excitation peak is at 300 nm and 291 nm and there excitonic absorption is 4.13eV and 4.26eV respectively which are more than band gap of bulk ZnS semiconductor which explains quantum size effects with introduction of capping agents with

different concentrations. It has been reported in previous work on colloidal ZnS that vacancy states lie deeper in the gap than states arising from interstitial atoms [15]. The SH group of mercaptoethanol dissociates and the organic group gets attached to Zn ions. Thus the organic groups are responsible in removing Zn dangling orbitals (electron traps) from the band gap. The unsaturated sp^3 hybridized orbitals of surface S atoms dangle out of the crystal surface. Hence the ligand terminated surfaces often show deep hole traps. The appearance of broad, red shifted luminescence and the absence of band edge luminescence is caused by these trap levels [24-25].   Fig. 5 compares emission spectra of 2-mercaptoethanol (2% at. wt. and 4% at. wt.) with uncapped ZnS nanoparticles. From Fig-5 it is clear that emission spectra of capped ZnS is blue shifted in comparison to uncapped ZnS nanoparticles. Emission peak due to uncapped ZnS samples is at 415 nm, whereas for 2 mercaptoethanol 2% it is 390 nm and 2 mercaptoethanol 4 % it is   400 nm. So from this observation, we can conclude that with increase in capping amount there in increase in emission intensity or quantum yield but at the same time it is slightly red shifted also. So it can be concluded that the appropriate amount of capping agent is required to reduce agglomeration and increase emission intensity simultaneously. Beyond that amount, there would be increase in red shift of emission that suggests decrease in band gap, which will resemble again bulk behaviour in comparison to nanoparticles. Yanagida et al. [21] have observed longer wavelength defect luminescence at about 420 nm in addition to the band gap luminescence. The emission spectra shows that the emission intensity of capped ZnS nanoparticles is comparatively high in comparison to uncapped ZnS nanoparticles which shows dangling bonds are better passivated in 2 mercaptoethanol(2%, 4% at. wt.) capped nanoparticles in comparison to uncapped ZnS nanoparticles. This is expected because in the absence of capping agent uncontrolled nucleation and growth of the particles occurred, resulting in the formation of defect states. From Fig. 5 it is clearly shown that there is considerable increase in intensity of emission peaks of capped ZnS nanoparticles as compared to uncapped ZnS nanoparticles. This is attributed due to better passivation of surface defects in capped ZnS nanoparticles as compared to uncapped ZnS nanoparticles. Also enhanced photoluminescence has been observed from the ZnS nanocrystals due to efficient energy transfer from the surface adsorbed 2 mercaptoethanol molecules to interstitial and vacancy centers in nanocrystals. But as undoped ZnS nanoparticles also shows visible emission. It can be concluded that transfer of energy takes place from mercaptoethanol energy levels to sulfur states (native or defect related). G Ghosh et al. [22] also have shown increase in PL intensity of capped ZnS nanoparticles in comparison to uncapped ZnS nanoparticles.
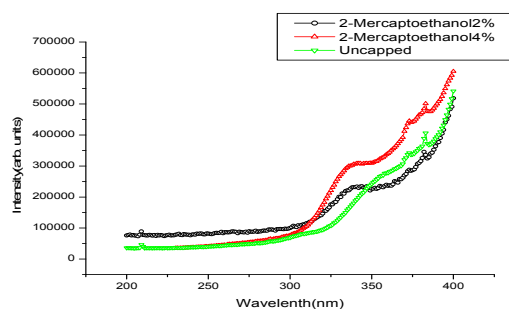
Fig. 4. Comparison of Excitation spectra of ZnS nanoparticles (a)uncapped (b)capped with 2-mercaptoethanol 4% (c) capped with 2-mercaptoethanol 2%.
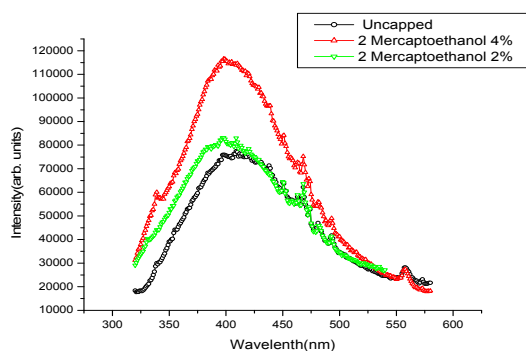

Fig. 5. Comparison of emission spectra of ZnS nanoparticles capped with 2-mercaptoethanol 2%, 2-mercaptoethanol 4% and uncapped ZnS nanoparticles.

Uncapped ZnS nanoparticles have absorption edge (Fig. 6) at 300 nm and 2- mercaptoethanol 2% and 2 mercaptoethanol 4% capped ZnS nanoparticles have absorption edges at 286.6nm and 293.3 nm respectively. So band gap of 2-mercaptoethanol 2% and 2-mercaptoethanol 4% capped ZnS nanoparticles comes out to be 4.32eV and 4.27 eV and for uncapped ZnS nanoparticles it is 4.06eV.
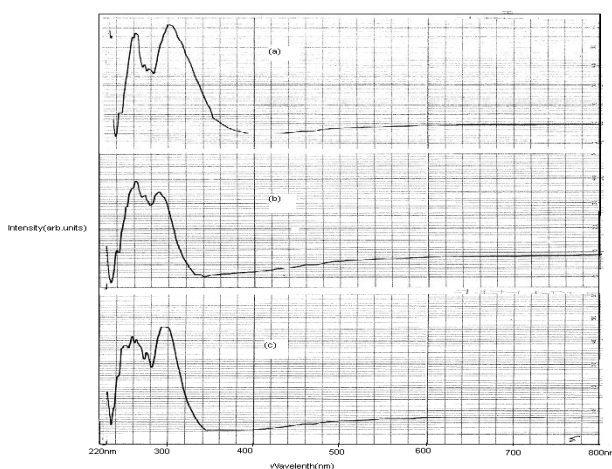

Fig. 6 UV visible Reflectance spectra of ZnS nanoparticles (a) uncapped (b) 2- mercaptoethanol 2 % (c) 2-mercaptoethanol 4%.

From these results we have found 2 mercaptoethanol 2% have maximum band gap (4.27eV) which shows better quantum confinement effect compared to other capped and uncapped samples. From emission spectra of all samples we have also found emission intensity of 2-mercaptoethanol 4% to be maximum and then next to this is 2 mercaptoethanol 2% which is having band gap to be 4.32eV and this emission spectra is blue shifted also. Excitation spectra as shown in Fig-4 were monitored by keeping the detector at the blue emission band located at 420nm. These peaks are slightly red shifted compared to the excitonic absorption peaks. So results from PLE spectra match reasonably well with the optical absorption of ZnS nanoparticles. TEM micrograph and XRD of different capped and uncapped samples also correlates with these results showing uncapped samples are agglomerated in comparison to capped ZnS nanoparticles.

5. Conclusions

Core-Shell ZnS nanocrystals have been synthesized using chemical precipitation method. Optical and morphological measurements on ZnS nanoclusters have been carried out to investigate the effect of capping on ZnS nanoparticles. XRD results show the crystallite size to be from 1.9-2.2 nm depending upon the peaks. TEM results show uncapped agglomerated nanoparticles as well as 2-mercaptoethanol (2% at. wt., 4% at. wt.) capped ZnS particles. It is clear from the TEM that capping forms core-shell nanostructures and they also avoid agglomeration of the particles. Band gap of capped ZnS nanoparticles is found to increase in comparison with uncapped ZnS nanoparticles indicating quantum size effects. The band gap data from UV-visible reflectance and excitation are in correlation with each other. Increase of intensity in case of capped ZnS compared to uncapped ZnS shows better surface passivation. 2-mercaptoethanol 2% capped ZnS nanoparticles shows blue shift in comparison to 2-mercaptoethanol 4% capped ZnS nanoparticles and uncapped samples although emission intensity is more in 4% mercaptoethanol. So we have to add appropriate capping amount in order to control agglomeration but for tunable band gap properties and increased quantum yield we have to optimize best capping input which in our case is 2% mercaptoethanol. Experiments can be conducted with more combinations of same capping material on ZnS nanostructures so to get more precise amount of capping agent. In conclusion capping layer leads to the transfer of energy to the possible transition levels in ZnS. It means we can synthesize highly efficient ZnS nanoparticles using this transfer mechanism.

Physics, Kurukshetra University, for their help in recording the Photoluminescence spectra.

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