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Surfactant assisted surface studies of zinc sulfide nanoparticles

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ABSTRACT

We report a simple soft chemical method for the synthesis of ZnS nanoparticles using varying concentration of cationic surfactant CTAB and examine its surface properties. Powder X-ray diffraction, UV–vis spectroscopy, photoluminescence spectroscopy, selective area electron diffraction, and transmission electron microscopy are used to characterize the as prepared ZnS nanoparticles. XRD and TEM measurements show the size of polydispersed ZnS nanoparticles is in the range of 2–5 nm with cubic phase structure. The photoluminescence spectrum of ZnS nanoparticles exhibits four fluorescence emission peaks centered at 387 nm, 412 nm, 489 nm and 528 nm showing the application potential for the optical devices. In Raman spectra of ZnS nanoparticles, the modes around 320, 615 and 700 cm^{-1} are observed.

1. Introduction

Recently a huge amount of the research activities has emerged in the synthesis and characterization of semiconductor nanoparticles for size, shape and composition dependent physical and chemical properties [1,2]. The physical properties of semiconductor nanocrystallites are dominated by the spatial three dimensional confinement of electrons and holes in a small volume called quantum confinement [3,4] in semiconductors; the band gap increases as the particle size decreases when the dimension of nanocrystallites approach to exciton Bohar radius, a blue shift in energy is observed due to quantum confinement phenomenon. The effective mass model [5] is commonly used to study the size dependent of optical properties of Quantum dots (Qds) system. Synthesis of ZnS nanoparticles is, however difficult, since the Bohar exciton radius [6] is ~2.5 nm with dielectric constant $D = 8.76$ [7], which is a consequence of large effective mass of ZnS.

The fact that due to large surface to volume ratio, the atoms situated near the surface regions play a major role in electronic, optical and thermodynamic properties [8–10]. Surface atoms are bounded by weaker forces because of the missing neighbors, which lead to high surface reactivity [11,12]. Due to high surface reactivity, without protection or passivation of their surfaces most nanostructures undergo aggregation and agglomeration.

For nanocrystals prepared by solution based chemical methods, a capping agent which adsorbs to the nanocrystals surface generally added both to control the size of nanocrystals and to prevent agglomeration of synthesized nanocrystals.

Among all II–VI compounds, ZnS is a rather interesting material. ZnS is a direct wideband gap (for bulk cubic and hexagonal phases of ZnS, $E_g = 3.68$ eV and 3.80 eV, respectively) semiconductor has also been widely used as a phosphor in luminescent devices due to its emission in near ultraviolet and visible range [13,14]. ZnS crystal usually exhibits a polymorphism of two phases with different stacking sequences of closed pack planes to each other, one is the cubic phase with a zinc blend structure and other is a hexagonal phase with a wurtzite structure [15,16].

To date there are many methodologies available for synthesizing ZnS nanocrystals such as pulse laser ablation, electrochemical fabrication, solvothermal and sol–gel method [17–23]. However the sol–gel technique is one of the most common methods for preparing semiconductor nanoparticles due to its several advantages, for instance soft chemistry, demanding no extreme pressure or temperature control, easy to handle and requiring no special or expensive equipment.

There are only few reports on systematic investigation of ZnS nanoparticles using CTAB as cationic capping agent that provides detailed understanding of its surface properties. Since rate of adsorption of cationic capping agent is higher than the non-ionic or anionic capping agent, the size, shape and other properties of ZnS nanocrystals must differ from those in non-ionic or anionic surfactant. Keeping above points in view, we report synthesis of ZnS nanoparticles by chemical precipitation method with varying concentration of CTAB as surfactant.

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2. Experimental

All chemicals are of analytical grade and used without further purification. Experiments are done in air atmosphere. Doubled distilled water is used as a solvent and N-cetyl-N, N, trimethyl ammonium bromide (CTAB) (Loba Chem 99%) is used as a cationic surfactant. ZnS nanoparticles are prepared by using simple precipitation method. In the typical procedure CTAB miceller solution contain $ZnSO_4{\cdot}7H_2O$ (Qualigens 50% assay) and is added drop wise to another containing Na_2S (Qualigens 50% assay) with constant magnetic stirring. To study the effect of surfactant three samples S2, S3 and S4 are prepared in 1 mM, 2 mM and 5 mM CTAB solutions respectively and one sample S1 is prepared without CTAB solutions. In each synthesis process, the required amount of CTAB is mixed with $ZnSO_4{\cdot}7H_2O$ solution and the volume is adjusted up to 80 ml, using double distilled water and stirred. After that, 40 ml aqueous solution of Na_2S (0.1 M) is added drop wise into the $ZnSO_4{\cdot}7H_2O$ (0.1 M) with vigorous magnetic stirring. The ZnS formed in the miceller medium of CTAB are white in color. The precipitate are centrifuged and washed several times, with doubled distilled water and ethanol, to remove unreacted reactants and impurities. The precipitate collected from centrifuged are dried at 55 °C for some hours to get dried powders which are used to record XRD pattern, Raman and PL spectra. These powders are uniformly dispersed in ethanol by ultrasonification for recording UV–vis spectra and TEM image.

3. Characterization details

XRD patterns and TEM are used to identify the crystal structure and average particle size of prepared samples. XRD pattern of samples are record on a Rigaku make X-ray model with Cu Kα source (λ = 1.54178) operating at 40 KV, 30 mA. All the samples are recorded in the 2θ regions of 20–70(2θ) at a scan rate of 0.02° per second. TEM and HRTEM analysis are performed using model FEI Tecni G2F30STWIN and JEM 200 CX respectively. For TEM, sample is prepared by dispersing the ZnS on a carbon coated copper grids support. Raman spectra of as synthesized colloidal ZnS nanoparticles are recorded using 514.5 nm line of Ar^+ ion laser as an excitation source and action 0.5 M triple grating monochromator with PMT detector for recording scattered light. Solution is placed in a quartz cell and excited by vertically downward light. Scattered light is collected on the slit of monochromator in the right angle geometry from direction of excitation. UV–vis absorption spectra of as synthesized colloidal solution are recorded with PerkinElmer lambda 35 spectrophotometer. Luminescent characterization is being done using a PerkinElmer Luminescent Spectrometer (Model No. LS-55).

4. Results and discussion

4.1. X-ray diffraction

Fig. 1 shows the XRD patterns of all the ZnS samples. The spectra show three peaks at 2θ values of 28.6, 48.1, and 56.6 corresponds to the crystal planes of (1 1 1), (2 2 0) and (3 1 1) of cubic phase ZnS respectively; which is consistent with the reported data (JCPDS card file No. 05-0566). The broadening of peaks in all XRD spectrums indicates very small size of ZnS nanocrystals. It is also found that the changes in concentration of cationic surfactant do not have any effect in the crystal structure of as synthesized nanocrystals.

The distance between successive lattice planes are determined from Wulf–Bragg relation:

$$d_{nkl} = \frac{n\lambda}{2\sin\theta}$$

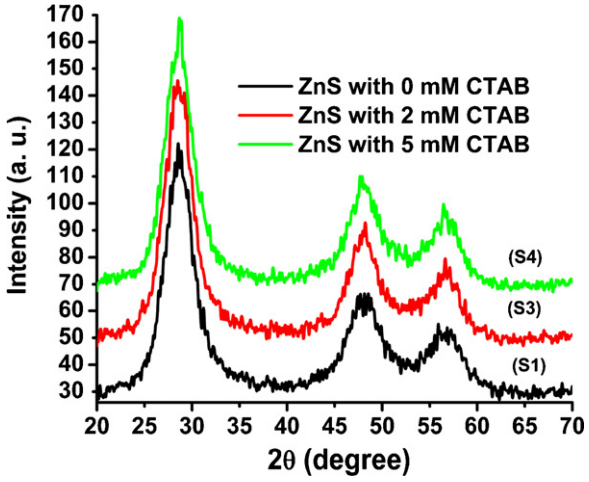

Fig. 1. XRD patterns of ZnS nanocrystals: S1 (without CTAB), S3 (2 mM CTAB) and S4 (5 mM CTAB).

where λ is the wavelength of X-ray diffraction, θ is the diffraction angle and integer n is known as the order of corresponding reflection. By using above equation the lattice constant of ZnS nanocrystallites is derived from XRD patterns using the following formula

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The lattice constants calculated from our XRD spectra are shown in Table 1 and these values are slightly lesser than that of standard ZnS phase (a = 5.398 Å). It indicates the lattice contraction i.e. a small contraction of Zn–S distance for samples are given in the table. These results exhibit the high surface to volume ratio of nanocrystals.

To determine the value of D using Scherer's formula [24] with minimum error, all values are calculated using (1 1 1) peak reflection of XRD patterns.

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where D is the mean diameter of crystallites and β is the full width at half maximum The value of D are found to be in the range of 2.93–3.19 nm, shown in Table 1.

4.2. UV–vis spectroscopy

The UV–vis absorption spectra for different samples are shown in Fig. 2(a).

In amorphous and crystalline material, the optical absorption coefficient (α) at the absorption edge is expressed by the following relationship $\alpha = \frac{\beta}{h\nu(h\nu - E_g)^n}$ where β is the energy independent constant dependent on the nature of optical transition, E_g is the optical band gap of nanocrystallite and exponent n may have the values 1/2 or 2 depending on whether the transition is indirect or direct respectively. The blue shift of the absorption band compared to bulk ZnS causes the band gap widening implying the quantum confinement effects in the nanoparticles i.e. when the electron hole pair squeezed below the dimensions approaching exciton Bohar radius. The UV–vis spectra for all the samples exhibit excitonic peak in the range of 311–316 nm. For $n = 1/2$, E_g in above equation is direct allowed band gap. The average band gap is estimated from the linear portion of $(\alpha h\nu)^2$ vs. $h\nu$ plots, Fig. 2(b). The band gap is found to be 3.96 eV, for 5 mM CTAB which is higher than the value of Bulk ZnS (3.68 eV) due to quantum confinement of ZnS nanoparticles.