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Synthesis and Photoluminescence studies of starch capped ZnSe nanocrystals

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Abstract

Present paper reports synthesis and photoluminescence (PL) of ZnSe nanoparticles prepared by chemical route using starch as capping agent. The absorption studies of the samples show blue shift in absorption peak indicating increased effective band gap and hence formation of nanocrystals. The PL spectra give single peak near 450 nm which shifts towards lower wavelength by increasing capping agent concentration during synthesis. The analysis indicates that the Stoke shifted PL involves surface states within the bandgap of ZnSe. By increasing capping agent smaller particles are prepared which have larger density of surface states giving rise to higher intensity. Slight shift in PL peak indicates slight change in position of surface states or valance band edges.

Keywords: Photoluminescence, ZnSe, Absorption spectra, Starch capped nanoparticles

1. *INTRODUCTION*

Nanoparticles are distinguished from bulk due to their high surface to volume ratio and quantum size effect. Due to finite size of the nanocrystals the continuous energy band of the bulk crystal transforms into a series of discrete states resulting in widening of the effective band gap. Blue shift in the optical absorption spectra, size dependent luminescence, enhanced oscillator strength and nonlinear optical effect are some of the interesting properties exhibited by these nanocrystals. The size may be controlled by using capping agent during synthesis. Wide band gap II-VI nanostructure semiconductors are promising materials for the fabrication of light emitting devices. A number of research groups worldwide are focusing on the development of II-VI semiconductor based optoelectronic devices [1, 2]. Luminescent ZnSe nanocrystals have been produced using various methods. By a sol–gel method, ZnSe ranging in diameter of 3–10 nm is prepared in glass [3]. The photoluminescence (PL) was heavily red-shifted to 600 nm, which is attributed to the presence of Se vacancies. A melt quenched method prepares ZnSe particles of 4–6 nm in diameter dispersed in a glass matrix [4]. A simple aqueous colloidal method produces ZnSe nanocrystals 3 nm in diameter with a broad emission peaking at 455 nm [5]. A reverse micelle method is also used to prepare 3–4 nm particles showing an emission peak at 355 nm [6]. In present paper we have reported environment friendly chemical method for synthesis of ZnSe using starch as a chapping agent. Five different samples were prepared by using different concentrations of capping agent.

2. *EXPERIMENTAL*

2.1 Synthesis

For preparation of ZnSe by chemical synthesis route, we needed selenium and zink sources. Selenium source was prepared by dissolving selenium powder and sodium borohydried in distilled water in two necked flask. The mixture was then stirrer for 3 hours at room temperature under magnetic stirring. The starch solution was prepared by dissolving appropriate amount of soluble starch in 20 ml distilled water in beaker under magnetic stirring at room temperature. The amount of soluble starch was varied from 20 mg to 100mg for preparing different samples S_1 to S_5. 0.32 mmol of $ZnCl_2$ was carefully added to the starch solution. The pH of the solution was adjusted between 9-10 using ammonia solutions. After that 1 ml of selenium source was added drop wise in this solution and the solution was left for 18 hours, while particles settle down in the bottom of the beaker. The samples were prepared with various concentration of starch which gave ZnSe nanoparticles of different sizes.

2.2 Absorption Spectra

The UV/VIS absorption spectra were used to characterize the structure size and band gap variation in the samples. Optical absorption studies were performed by Perkin Elemer λ-12 UV-Visible spectrometer in the range 200nm to 800nm.

2.3 Photoluminescence Studies

The photoluminescence studies were carried out by Cary Eclipse fluorescence spectrophotometer which is controlled by Cary Eclipse software.

3. RESULTS AND DISCUSSIONS

Figure1 shows absorption spectra of starch capped ZnSe nanoparticles prepared with different capping agent concentration.

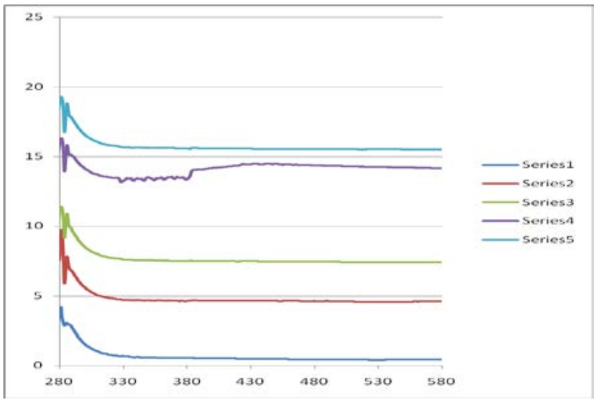

Figure1. Absorption spectra of starch capped ZnSe nanoparticles

It can be seen from the absorption spectra that there is practically uniform absorption in the visible range (800nm-350 nm). Absorption increases in the UV region and a peak is obtained below 315nm giving effective band gap around 4 eV.

From effective mass approximation model (EMA) the effective band gap E_g nanocrystals is given by

$$E_g^{I} = E_g + \frac{\hbar^2\pi^2}{2r^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right]$$

Where E_g^I is band gap of nanocrystals, Eg is the band gap of bulk material, r is the radius of cluster. m_e^* and m_h^* are the effective mass of electron and hole respectively The above equation indicate the increase in band gap with decreasing size of the nanocrystals.

The peak shifts toward lower wavelength side with increasing capping agent concentration, which further indicates that the higher the capping agent concentration, the smaller the size of ZnSe nanoparticles obtained.

Photoluminescence studies provide information of different energy states available between valence and conduction bands responsible for radiative recombination. Fig.2 shows the PL spectra of ZnSe nanocystallites for various concentration of capping agent (starch). It can be seen from the PL spectra that a single peak is obtained. PL emission peaks are shown in table I, for all samples.

Table I Photoluminescence Peaks with varying capping agent

Samples	Starch Concentration	PL peak	
		Wavelength (in nm)	Intensity (in a.u.)
S_1	20 mg	450	119
S_2	40 mg	440	135
S_3	60 mg	430	144
S_4	80 mg	420	195

This stoke shifted PL may involve trapping states/surface states within the band gap. By decreasing particle size, surface increases and hence increased surface states give increased surface states related PL. The emission wavelength shifts towards blue side with increasing the capping agent concentration due to upward shift in surface states or downward shift in of valance band edge. .

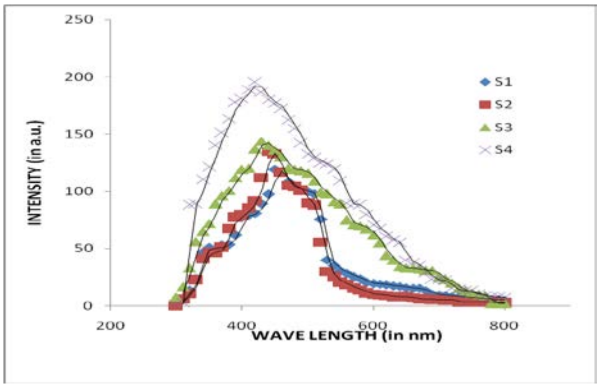

Figure 2. Photoluminescence spectra of ZnSe nanocrystals

4. CONCLUSION

The studies have shown that smaller ZnSe nanocrystals can be prepared by increasing capping agent concentration. Blue Shift in absorption edge indicates increase in effective band gap. The effective band gap energy has been determined from the absorption spectra and particle size is computed from the effective mass approximation (EMA) model. Photoluminescence of ZnSe with different capping agent concentration shows Stoke shifted single peak. The peak shifts towards blue and intensity increases by increasing capping agent concentration. This indicates that PL is due to surface states which increases in number and shifts slightly by reducing the size.

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