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PHOTOLUMINESCENCE STUDIES OF STARCH CAPPED CdSe NANOPARTICLES

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Abstract

The capping of nanocrystals with polymer is expected to increase the life of the device and enhance the emission intensity. CdSe nanocrystal capped with starch have been studied. Absorption spectra of specimens have shown blue shift in absorption edge of CdSe. It has been observed that by increasing the concentration of capping agent the photoluminescence intensity increases and the peaks slightly shift towards shorter wavelength.

Keywords: Photoluminescence, CdSe Nanocrystals, Absorption spectra, Starch capped nanoraticles

1. INTRODUCTION

The semiconductors nanocrystals are nanoparticles with a typical size of 2-20 nanometers (nm) consisting of few hundreds to few thousand atoms in each particle. These are new materials which have properties that are intermediate between those of bulk materials and those of isolated or discrete molecules [1,2].

The capping of nanocrystals with polymer is expected to increase the life of the device and enhance the brightness [2,3]. These display unique electronic and optical properties including size tunable light emission.

2. EXPERIMENTAL

2.1 Synthesis

For prepration of CdSe by chemical synthesis route, we needed Selenium and Cadmium sources. Selenium source was prepared by adding 0.32 mmol of selenium powder to 120 ml distilled water in two necked flask then 0.81 mmol of sodium borohydried was carefully added to this mixture, and the flask was immediately purged with nitrogen gas. 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 to 20 ml distilled water in beaker under magnetic stirring at room temperature. The amount of soluble starch was varied from 20 mg to 100 mg for preparing different samples S_1 to S_5. 0.32 mmol of $CdCl_2$ 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 capping agent concentration controls the size. For the present investigation five different samples were prepared by using different concentrations of capping agent varying from 20 mg to 80 mg.

1.2 Absorption Spectra

The UV/VIS absorption spectroscope is used to characterized 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 on a Pentium PC is used.

3. RESULTS AND DISCUSSIONS

Figure 1 shows UV/VIS optical absorption spectra in the range of 600-200 nm for S_1-S_4 samples prepared with different concentration of capping agent. It can be seen from the spectra that there is practically uniform absorption in the visible range (600nm-350 nm). Absorption increases in the UV region and a peak is obtained below 325nm. The peak shift toward lower wavelength side with increasing capping agent concentration. This further indicates that the higher the capping agent concentration, the smaller the size of CdSe nanoparticles obtained. For S_1, sample edge of absorption is obtained at about 293 nm. Similarly the absorption edges for other samples are obtained at 291, 289 and 287 nm for S_2,S_3,S_4 samples, respectively.

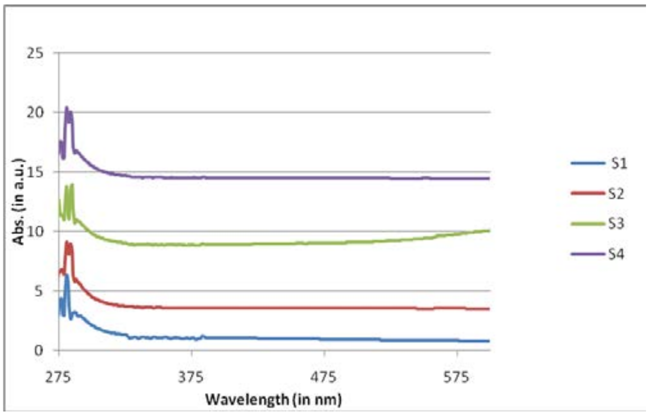

Figure 1. Absorption spectra of starch capped CdSe nanoparticles

The optical band gap of the nano crystalline samples were calculated from the absorption peak using the formula:E_g=hc/λ, Where h is the Planck's constant, c is the velocity of light and λ is the wavelength at which absorption peak occurs. The values of Eg are obtained as 4.23 ,4.26 ,4.29 and 4.31 eV, respectively for the samples S1-S4 corresponding to the absorption peak with increasing the capping agent concentration.The effective band gap is increased as compared to the bulk value 1.74eV and this could be the consequence of a "size quantization effect" in the samples. The changes in absorption spectra of CdSe nanoparticles with changing size illustrate the effect of the size quantization.The increase in the energy difference between valance level and excited levels is a consequence of quantum confinement effect[4]. The confinement of the electron in the nanocrystal causes the quantization of the energy spectrum in conduction band, which gives rise to a blue shift of the threshold of absorption with decreasing crystalline size.

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

$$E^1g = E_g + \frac{\hbar^2\pi^2}{2r^2}\left[\frac{1}{m^*_e} + \frac{1}{m^*_h}\right]$$

where E^1g 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 increase in the effective band gap of nanocrystals as a function of crystalline size is estimated from

$$\Delta E = h^2\pi^2/2r^2[1/ m_e + 1/m_h]$$

The values of effective mass of electrons and holes for the CdSe are m_e*=0.13 me, and M_h*=0.13 m_h.Table1 shows all the values computed from the absorption spectra.

TABLE I Absorption spectra for various concentration of capping agent

Sample	Concentration capping agent (In mmol)	Wavelength at abs. peak (In rim)	Band gap Eg (In eV)	Particle size By E.M.A. (In nm)
S_1	20	293	4.23	2.41
S_2	40	291	4.26	2.40
S_3	60	289	4.29	2.39
S_4	80	287	4.31	2.38

Photoluminescence studies provide information of different energy states available between valence and conduction bands responsible for radiative recombination.

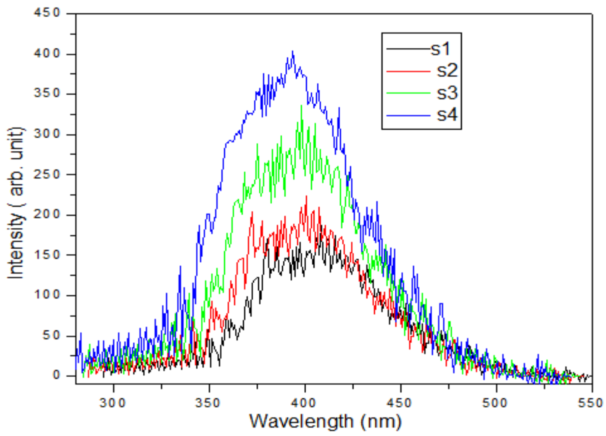

Figure 2. Photoluminescence spectra of ZnSe nanocrystals

Figure 2 shows the PL spectra of CdSe nanocystallites for various concentration of capping agent (starch). It can be seen from the PL spectra that a single peak was obtained. The PL peak is found to shift towards shorter wavelength by increasing the capping agent concentration and it is also observed that the PL intensity increases. PL emission peaks were obtained at 408.5, 405, 401.7 and 390.7nm for sample S_1, S_2, S_3 and S_4 respectively. The wavelength of PL spectra is tabulated in the Table II. It is clear from the table that by increasing concentration of capping agent, PL peaks shift towards lower wavelength.

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 shift towards blue side with increasing the capping agent concentration due to quantum confinement effect PL intensity increases by increasing capping agent concentration, i.e., by decreasing particle size [4].

Table II Photoluminescence Peaks with varing capping agent

Samples	**Concentration**	**PL peak**	
		Wavelength (in nm)	**Intensity (in a.u.)**
S_1	20 mg	408.5	186.6
S_2	40 mg	405.2	220.4
S_3	60 mg	401.7	337.1
S_4	80 mg	390.7	395.7

4. CONCLUSION

The studies have shown that smaller CdSe 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. Surface state related PL has been observed showing a single peak. The peak shifts towards blue and increase in intensity by reducing the particle size. This may be attributed to increased density of surface states and slight shift in their energy position.

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