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Synthesis and Optical Characteristics of CdSe/ZnS core/shell Nanocrystals

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ABSTRACT: The CdSe/ZnS core-shell nanocrystals (NCs) are synthesized by a simple and low cost chemical route. The optical properties of the prepared samples are characterized by UV–Vis absorption spectroscopy, fluorescence spectroscopy, quantum yields (QYs) and Transmission electron microscopy (TEM). The studies show that CdSe/ZnS nanocrystals sizes at the first excitonic absorption peak increase with increasing time and temperatures. The spectroscopic study of the prepared CdSe/ZnS core-shell nanoparticles shows that the crystal size of the nanoparticles are in the range of 4.47-5.41nm. TEM results reveal that CdSe nanoparticles are well-ordered crystallized with average particle sizes 4.5-5.5 nm. Fluorescence analysis of the synthesized CdSe/ZnS NCs samples reveals that CdSe/ZnS NCs of the crystal size range 5.25-5.74 nm exhibit luminescence output peak around 550-570 nm. The homogenous formation of CdSe/ZnS NCs core-shell are confirmed by the maintained full-width at half maximum (FWHM) of fluorescence emission spectra for the samples prepared under different time. At the room temperature fluorescence QYs of CdSe/ZnS NCs are 27%-45%.

KEYWORDS: Quantum dots, Quantum yield, TEM, Absorbance and Fluorescence emission spectra.

1 INTRODUCTION

Semiconductor quantum dots are tiny clusters of semiconductor material, fabricated length scales between nanometers and a few microns. Quantum dots (QDs) are important because of their applications in solar cells, light-emitting diodes (LEDs), fluorescent biosensors etc [1-4]. A semiconductor quantum dot (also known as 'nanocrystal'or 'quantum box' and abbreviated as 'QD' or 'NC' or 'QB') is a three dimensional (also known as 'zero dimensional') confined structure of semiconductor compounds whose dimensions lie in the range 1nm-20nm. Nanocrystals of one material can be embedded in a shell of another material, and in some cases epitaxial growth is even possible. For example, the growth of epitaxial shells of ZnS around spherical and core CdSe nanoparticles are well established. The UV-Vis absorption spectroscopy (UV-Vis analysis) and fluorescence spectroscopy (FL analysis) reveals the energy state in CdSe/ZnS NCs that causes luminescence [1-2]. The proper passivation of the nanocrystal surfaces is necessary to achieve a high quantum yield (QY). The inorganic passivation of nanocrystal with higher band gap materials, resulting in core/shell structure nanocrystals such as CdSe/ZnS and CdSe/CdS, showed high quantum efficiency up to 50% because of the robust passivation of the surface defects and also the quantum confinement effect which enhances exciton recombination in the core [5-10]. In the present investigation, we address the fluorescence QYs in CdSe/ZnS NCs by determining the ratio of the number of photons emitted to the number of photons absorbed in a given sample. We used UV–Vis absorption and fluorescence spectra for optical properties and TEM for morphological and structural studies.

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2 SYNTHESIS OF CDSE/ZNS NANOCRYSTALS

The CdSe nanocrystals were synthesized by using modifications of R. He and H. Gu's method [11]. 0.69g cadmium acetate and 2.5 mL oleic acid were dissolved with 10 mL phenyl ether in three neck flask. The reaction mixture was heated 140^0C under stirring and continuous nitrogen flow, and then the mixture was cooled. 3 mL 1M TOPSe was added to mixture, rapidly, heated to 160^0-170^0C and 1-20 min. The ZnS nanocrystals have been synthesized by using modifications of Chang-Qing Zhu et. al [6]. Typically, the resulting core solution (reaction for 1-20 min), $Zn(OAc)_2 \cdot 2H_2O$ (0.085 mmol) and S powder (0.085 mmol) were mixed together in the reaction vessel. The reaction volume was adjusted to 15 mL by adding paraffin liquid. Next, with stirring, the mixture was degassed at 80 °C for 20 min. Afterward, temperature was set to 160 °C to 170 °C for the shell growth under N_2 atmosphere. The reaction mixture was cooled to room temperature after 50 min. To grow shell ZnS with different thicknesses around a CdSe core, a seeding-growth technique [7] was applied. After samples cooling to room temperature, the purposed method has been done 1 mL aliquot crude solution has washed with methanol and isolated by centrifugation to remove excess insoluble organics and salts that may have formed during the reaction. After fine isolation of growth CdSe/ZnS, the precipitation has been dissolved with different volume of hexane.

3 CHARACTERIZATION

The reaction process was monitored by UV-Vis absorption spectra with aliquots taken from different time and temperature. In addition to characterize quantum dots, the absorption spectra were used to estimate the size. The fluorescence emission spectra were measured at room temperature using by a fluorescence spectrophotometer. We intend to find the wavelength at which the prepared samples show fluorescence peaks. With excitation wavelength, FL spectra are taken at room temperature. The QYs of NCs were calculated by following the procedure which was used previously [12-14] by comparing with Rhodamine-101 in ethanol, with an assumption of its QYs as 95%, and using data estimated from the fluorescence and the absorption spectra.

$$\phi_x = \phi_s \left(\frac{I_x}{I_s} \right) \left(\frac{A_s}{A_x} \right) \left(\frac{n_x^2}{n_s^2} \right)$$

In this equation, Where

I_x (sample) and I_s (standard) are the integrated emission peak areas;

A_x (sample) and A_s (standard) are the absorption;

n_x (sample) and n_s (standard) are the refractive indices of the solvents;

and Φ_x and Φ_s are the fluorescence QYs for the sample and the standard, respectively.

4 RESULTS AND DISCUSSIONS

Record the absorbance spectra of different CdSe/ZnS nanocrystals. Determine the wavelength (λ_{max}) of the absorbance peaks. The absorbance peaks are identified in the CdSe/ZnS nanocrystals optical spectra shown below in fig 1.

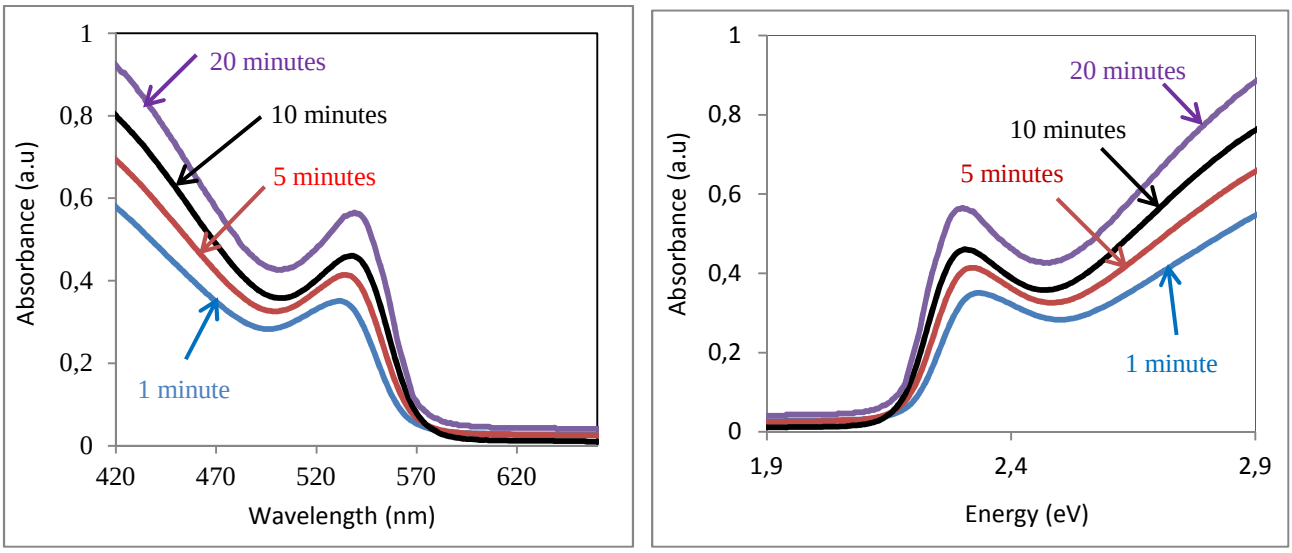

Fig. 1. Absorbace spectra vs (a) wavelength and (b) energy of CdSe/ZnS Nanocrystals at 160^0 C for different times.

In addition temperature effect, we explained time effect of the growth of quantum dots during the reaction process. For this purposed, different reaction times were used to synthesize to CdSe/ZnS NCs. UV-vis absorption spectra explained the formation of the different size according to variation of the reaction time. Fig.1 showed that size of the CdSe/ZnS NCs responded the reaction temperature. At higher reaction temperature larger particles were obtained. Synthesis at high temperatures results in high rate attaching and larger particle size and quick growth of the nanoparticle which are included in Table 1.

Table 1: Values of Particle size and number of CdSe/ZnS NCs for various time and temperatures.

Reaction Temp. (^{o}C)	Reaction Time (Min)	Peak Absorbance Wavelength (nm)	Exciton Energy, (eV)	Quantum Dots Size (nm)	Particle Number
160	1	532	2.33	4.4701	6194
	5	535	2.32	4.9364	6412
	10	538	2.31	4.9842	6640
	20	539	2.30	5.0038	6718
170	1	549	2.26	5.2307	7674
	5	552	2.25	5.2965	7967
	10	555	2.23	5.3643	8278
	20	557	2.22	5.4106	8493

It is seen that from the table the exciton energy at first peak absorption of CdSe/ZnS NCs decreased with increasing time and temperatures whereas the values particle size and particle number increased with increasing time and temperatures as shown in fig 2.

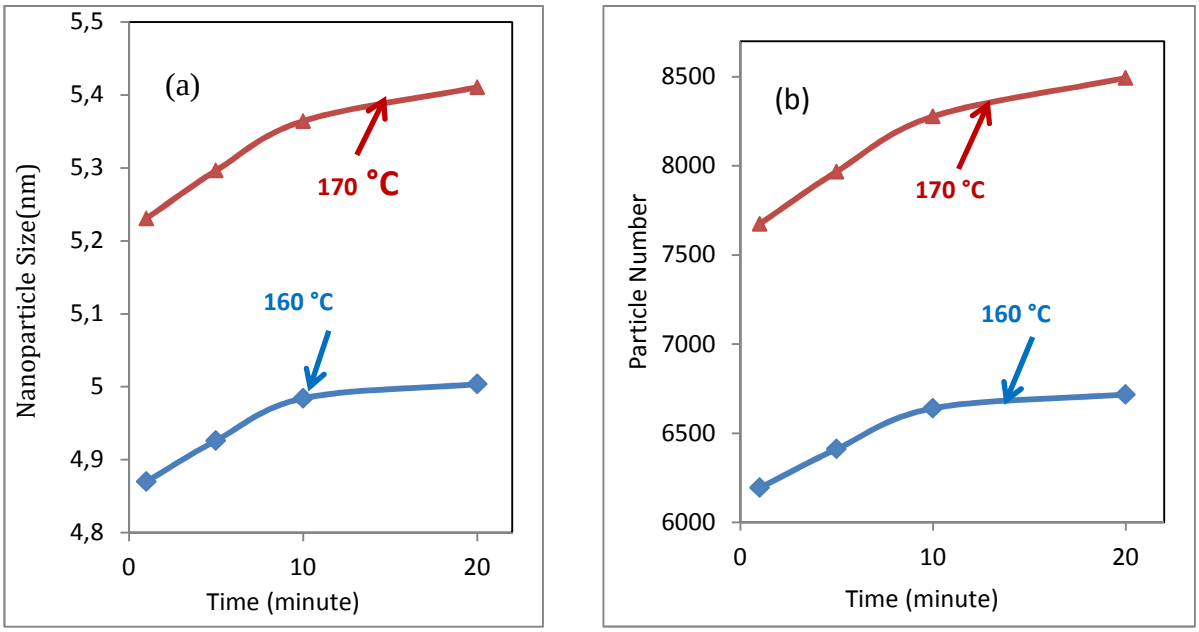

Fig. 2. (a) Nanoparticle size and (b) Particle number at the first peak absorption of CdSe/ZnS Nanocrystals for different times.

The shape and size of CdSe NCs were also observed by TEM as shown in fig.3. TEM Average size sizes of NCs were found to be 4.5-5.5 nm, which accords well with UV-Vis spectrum results [15,16].

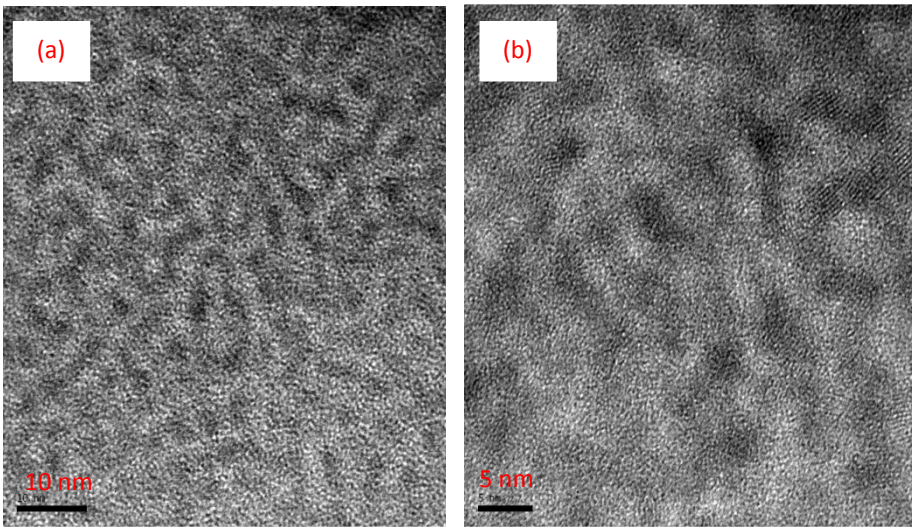

Fig. 3. TEM images of CdSe/ZnS nanocrystals at 20 minutes for (a) 160^{0}C at 10 nm scale bar and (b) 170^{0}C at 5 nm scale bar.

Fluorescence (FL) emission spectra of all the samples are shown in Fig. 3(a). From these spectra, it can be observed that the FL output wavelengths corresponding to the peaks are 560 to 570 nm for the samples of CdSe/ZnS NCs at 170^0 C for 1-20 min.

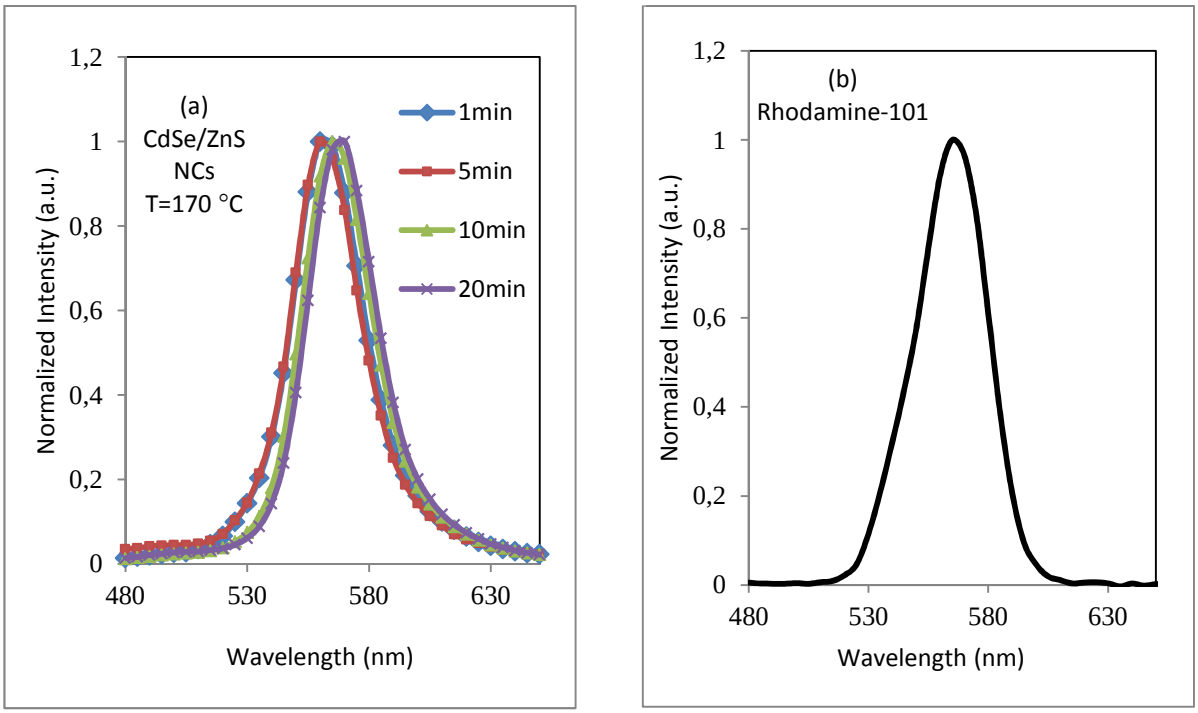

Fig. 4. Normalized fluorescence emission spectra vs wavelength of (a) CdSe/ZnS Nanocrystals at 170^0 C for different times and (b) Rhodamine-101

The overall values of those samples the fluorescence intensity and the emission peaks increase with increasing time and temperatures to the particle size. The band-edge emission of CdSe/ZnS NCs is 560 nm and the corresponding full width at half-maximum (FWHM) of the band-edge luminescence is around 32 nm. The emission peaks of CdSe/ZnS NCs range from 560 to 570 nm, and the corresponding full width at half-maximum (FWHM) of the band-edge luminescence was maintained between 32- 36 nm. The reason for the fluorescence of CdSe/ZnS NCs is the recombination of electrons and holes due to surface-trapped electrons and holes by quantum confinement.

Fig. 4 shows the emission spectra (normalized to the first emission maximum) of CdSe NCs taken at different time intervals and Rhodamine-101. This experiment used the change in fluorescence quantum yield (QY) due to coating CdSe NCs with ZnS as comparison with Rhodamine-101 in ethanol. The room temperature QY of CdSe/ZnS NCs are 27%-45%. The Values of Peak intensity, FWHM and quantum yield (QY) of CdSe/ZnS NCs for various time and temperatures obtained from the plots of Fig. 4 are included in Table 2.

Table 2: Values of Peak intensity, FWHM and quantum yield (QY) of CdSe/ZnS NCs for various time and temperatures.

Reaction Temp. (^{o}C)	Reaction Time (Min)	Peak Intensity Wavelength (nm)	Quantum Dots Size (nm)	FWHM (nm)	QY (%)
160	1	550	5.25	32	27
	5	553	5.32	33	41
	10	554	5.34	32	45
	20	556	5.39	36	36
170	1	560	5.48	35	28
	5	563	5.56	34	40
	10	565	5.61	33	44
	20	570	5.74	33	42

5 CONCLUSION

In conclusion, with increasing time and temperatures the nanoparticles become slowly disordered hence the exciton energy decreases whereas the nanoparticle size increases slowly. It is due to size effect which depends on the

thermodynamic properties of nanoparticles. From UV-Vis absorption spectra the diameters of resulting CdSe/ZnS NCs are about 4.47 - 5.41 nm with narrow size distribution. TEM images show that the nanoparticles are close to spherical and the size of nanoparticles measured from the image in good agreement with the calculation of UV-Vis absorption spectrum of our study. The fluorescence emission peak increases with increasing times and temperatures due to the particle size. Results show that nearly monodispersed and different size nanocrystals are obtained efficiently. FWHM of the fluorescence spectrum does not change more than ±2 nm (34±2 nm), indicating that a narrow, symmetric emission spectrum and small size dispersion can be maintained. The high fluorescence quantum yield is achieved for size of CdSe/ZnS NCs. The synthesized CdSe/ZnS NCs core-shell with high QYs will find potential applications.

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