CHARACTERIZATION OF CdSe CORE AND CdSe/ZnS CORE/SHELL QUANTUM DOTS SYNTHESIZED USING A MODIFIED METHOD

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In this work we have performed a modified organometallic method for synthesis of CdSe core and CdSe/ZnS core/shell quantum dots of different sizes at room temperature. In this organometallic scheme, one-pot synthesis of core/shell nanocrystalls in HDA-TOPO-TOP mixture is used. The structural features were determined with x-ray powder diffraction and all direction peaks are consistent with the wurtzite structure. The results of x-ray diffraction and high-resolution transmission electron microscopy (HR-TEM) revealed that the prepared CdSe/ZnS quantum dots QDs had a core/shell structure with high crystallinity. The estimated average of the particle size was found to be ~3.10 nm for core and 4.25 nm for core/shell by a TEM image. The average sizes of QDs were also estimated by using various ways such as the Sherrer's formula and the Yu et al theoretical expression. The obtained CdSe and CdSe/ZnS nanocrystals were characterized by using UV-vis spectroscopy which confirmed that a series of CdSe/ZnS particles with diameter of 3.52 - 4.25 nm, corresponding to the first peak of absorption spectra in 570- 592 nm range, were successfully achieved. Shell formation was confirmed by observation of red shift in the UV-vis absorption spectra. The optical band gap of CdSe/ZnS nanoparticles decreased from 2.70 to 2.10 eV with an increasing in the particle size due to change of shell thickness. The narrow photoluminescence from these composite dots spanned most the visible spectrum from blue through red with quantum yields of 30-40 % at room temperature. All the prepared samples have semiconducting behavior and can be used in the field of solar cell and light emitting diodes.

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1. Introduction

Quantum dots (QDs) are semiconducting nanocrystals (NCs) that are found in numerous areas such as sensors [1, 2], laser [3,4], light emitting diodes [5-7] and medicine [8,9]. In the bulk, the dimensions of the semiconducting materials are much larger than the Bohr band gap leading to a radius, and the energy levels are continuous. Excitons have a natural physical separation distance that varies from material to material, and this average separation distance is known as Bohr exciton radius [10]. In semiconductors, when a weak columbic force of attraction exists between the hole and electron pair, an exciton is created. When the size decreases, the energies are discrete that results in a larger effective band gap, leading to a blue shift in the optical transition compared to that of bulk materials. Core-shell type composite quantum dots exhibit novel properties making them attractive from both an experimental and a practical point of view[11-18]. Overcoating nanocrystallites with higher band gap inorganic materials have been shown to improve the photoluminescence quantum yields by passivating the surface of nonradioactive recombination sites. Some examples of core-shell quantum dot structures reported earlier include CdS on CdSe and CdSe on CdS [11], ZnS grown on CdS [12], ZnS on CdSe and

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the inverse structure [13], CdS/ HgS / CdS quantum dot quantum wells [14], ZnSe overcoated CdSe [15], and SiO2 on Si [16,17]. Hines and Guyot-Sionnest reported making (CdSe) ZnS nanocrystallites whose room temperature fluorescence quantum yield was50% [18]. An effective surface passivity of the QDs was achieved by over coating them with a higher band gap material such as ZnS, and potentially more useful for optoelectronic device structures [19].

This study describes the synthesis and characterization of a series of core CdSe core and CdSe/ZnS core/shell nanocrystallites at room- temperature. Synthesis is performed by using a modified organometallic method. ZnS overcoated dots are characterized spectroscopy and structurally using a variety of techniques. The optical absorption and photoluminescence PL spectra of the composite dots are measured. High-resolution transmission electron microscopy (HR-TEM) measurements help to determine the size, shape, and size distribution of the composite dots. Finally, the internal structure of the composite quantum dots and the lattice parameters of the core and shell are determined by using wide-angle X-ray scattering; Philips PW 1710 monochromatic Cu-K α radiation with ($\lambda = 1.54056$ A°)

2. Experimental procedures

2.1. Chemicals

Cadmium oxide (CdO 98.9%) was obtained from Fluka. Zinc oxide (ZnO 99.5%), Selenium powder (Se 99%), Sulfur powder (S 99.5%), Hexadecylamine (HDA 97%), Trioctylphosphine (TOP 90%), Trioctylphosphine oxide (TOPO 97%) were purchased from Aldrich. Oleic acid (OA) 98%, Stearic acid 98%, Acetone 98%, Toluene 99%, Methanol 99% were from united chemical Lab. All chemicals and solvents were used as received without additional purification. The synthesis of CdSe, ZnS and CdSe/ZnS was carried out by a modified organometallic method [20]. In the experiments, TOP was used as the ligand of the Se precursor, and OA was as the ligand of Cd precursor.

2.2. Synthesis of CdSe (core) nanoparticles

Briefly, CdO (0.3g) and oleic acid (3ml) were heated up to 170° C under vigorous stirring to obtain a clear solution of cadmium oleate, TOPO (2g) and HDA (2g) as passivating medium were added to the above Cd oleate solution then heated up to 220° C. TOP-Se (0.3 g Se in 4ml TOP) was fast injected to that mixture. Four samples were collected at different intervals (from 5 to 30 min) and labeled (A₁-A₄) respectively. These aliquots were cooled dawn by dissolving them in toluene. After that, they were kept at room temperature for 3 hours until the orange precipitate was formed. The samples were centrifuged at (4000 rpm, 15 min) and the obtained precipitates were washed three times by adding equal ratio of acetone and methanol.

2.3. Synthesis of CdSe/ZnS core/shell nanoparticles

In three neck flask, the orange precipitate containing CdSe QDs core was reprepared as described in section 2.2. A small sample was taken during the process and characterized by XRD; it was corresponding to the smaller collected sample A_1 . In clean vessel, 0.3g of element S dissolved in 4ml of TOP to achieve TOP-.S solution. This solution (TOP-S) and the mixture of Zn stearate (ZnO + stearic acid) +TOPO + HDA were injected slowly to that previous CdSe in the three neck flask from both sides. In order to demonstrate the possibility to control the final particle size, samples were collected in varying time. Six aliquot samples of CdSe/ZnS were withdrawn at different time ranging from (5-35 min) and labeled (S₁-S₆) respectively. These aliquots were immediately cooled by toluene to monitor UV-vis absorbance and fluorescence spectra. The samples were centrifuged at (4000 rpm, 15 min) and the obtained precipitates were washed three times by adding equal ratio of acetone and methanol. Sample S₂ was characterized by XRD to confirm the crystalline phase and size.

2.4. Synthesis of ZnS nanoparticles

ZnO (0.3g) was added to Oleic acid (3 ml) to get Zn Oleate, and then heated up to 170 $^{\circ}$ C. TOPO and HDA were added to the reaction mixture; then temperature was increased up to 220 $^{\circ}$ C.

When the solution became transparent, the temperature was decreased to 190 °C. At this temperature, TOP-S solution was injected in to the hot flask forming ZnS nanoparticles. The reaction mixture was cooled down by dissolving it in toluene. After that, it was kept at room temperature for 3 hours until precipitate was formed. The samples were centrifuged at (4000 rpm, 15 min) and the obtained precipitate was washed three times by acetone and methanol. The obtained ZnS powder was characterized by XRD to confirm the crystalline phase and size.

3. Result and discussion

3.1 Structural and Morphology Properties

A typical XRD pattern from the prepared CdSe, CdSe/ZnS and ZnS nanoparticles and positions of the x-ray peaks are shown in Fig. 1 Three peaks including (002), (110) and (112) can be clearly seen from these nanoparticles quantum dots.



Fig.1 X-ray powder pattern diffraction collected on three different samples: CdSe (sample A₁), CdSe/ZnS (sample S₂) and ZnS nanoparticles. The solid vertical lines represent peak positions for pure CdSe nanoparticle

All these diffraction peaks are consistent with the wurtzite structure with measured lattice constants. The CdSe/ZnS core/ shell peak position is shifted to a higher reflection angle (towered the ZnS peak). The average crystallite size of the CdSe, CdSe/ZnS and ZnS QDs was calculated from the peak width at half-maximum of the (002) plane of the higher intensities in all patterns, using the Sherrer equation [21].

$$D = K\lambda/\beta Cos\theta \tag{1}$$

where β the broadening at half band width, λ the wavelength, θ is the angle of diffraction obtained from 2 θ value corresponding to maximum intensity peak pattern, and K is a dimensionless shape factor, with a value close to unity. The peak position and resolution were determined by using Gaussian peak fitting method. The calculated values 'd' spacing, lattice constant 'a' and particle size (D) were on the basis of changes in the main peak as is shown in Table 1. The average crystallite sizes were approximately equal to 2.70 nm, 3.87 nm, and 2.21 nm for CdSe, CdSe/ZnS and ZnS respectively.

 2θ °of the FWHM (hkl) d-spacing a (A°) c (A°) XRD Sample Size(nm) intense peak (degree) (A°) (002)3.16 ZnS 28.24 4.23 3.83 6.38 2.21 CdSe/ZnS 25.28 2.19 3.87 (002)3.52 4.31 7.09 25.14 3.21 (002)3.53 4.24 6.90 2.70 CdSe

Table 1. The X-ray diffraction results of CdSe, CdSe/ZnS, and ZnS nanoparticles.



Fig. 2 EDS spectrum of (a) CdSe, (b) CdSe/ZnS and (c) ZnS

Fig. 2 EDS spectra of CdSe, CdSe/ZnS and ZnS nanoparticles indicates chemical purity and stoichiometry of the samples which were investigated by EDS (JEOL JSX 3222 element analyzer). The strong peaks related to Cd, Se and Zn are found in the spectrum. Fig. 2a confirms the presence of CdSe, Cd (48.31%), Se (48.73%) and potassium element K is detected which is attributed to glass substrate. The elemental atomic percentage of CdSe/ZnS is Cd (30.7%), Se (15.7%), Zn (30. 10%) and S (23.5 %) Fig.2b. Fig. 2c reveals the presence of Zn (72.79%) and S (27.21%), confirming the formation of ZnS.



Fig.3 HR-TEM images and size distribution histogram of CdSe and CdSe/ZnS nanocrystalline

Fig. 3 shows the HR-TEM images and size distribution diagram of CdSe and CdSe/ZnS composite nanoparticles synthesized by organometalic method using (JEM-2100 of 200KV). The shape of CdSe NPs is nearly spherical crystalline particles Fig. 3a. The HR-TEM CdSe display as dark core surrounded by gray shell indicating the structure of CdSe cores covered by the ZnS shells Fig. 3c. The particle size distribution histograms and corresponding Gaussian curves fitting, for samples (A₁ (core) and S₂ (core/shell)) are shown in Fig. 3 b,d. The size of the histogram for prepared nanoparticles is 3.10 ± 0.5 nm and 4.25 ± 0.25 nm for CdSe and CdSe/ZnS core/shell particle size is larger than that of the CdSe core. The particle size measured by TEM micrograph is larger than that value calculated by XRD. This might be explained by the fact that, X-ray diffraction results based on the mean size of the sample obtained from XRD pattern which is smaller than that obtained from all the structural layers of sample when using TEM. The size determined by diffraction cannot simply be compared to the sizes determined by other methods [22, 23]. Also in XRD method; system standard errors were not eliminated.



Fig.4 High Resolution transmission electron micrographs of (a) CdSe core, and (b) CdSe/ZnS core/shell

Fig. 4 shows two dots from the prepared samples CdSe core and CdSe/ZnS core/shell. The core/shell nanocrystals are nearly larger than the cores. Images featured in Fig. 4a show nearly spherical crystalline CdSe particles with lattice plane distances identical to hexagonal bulk CdSe. The lattice fringes were observed in the core & core/shells and persisted throughout the entire nanocrystal, indicating epitaxial growth; with a measured lattice spacing in the dots equaled 0.25 nm which correspond to (102) plane for CdSe and 0.17 nm, corresponding to (103) plane for ZnS shell.

3.2. Optical Properties

The absorbance spectra as a function of reaction of CdSe precursor mixture are depicted in Fig. 5. The absorption peaks appear on each curve, indicating that a series of CdSe QDs was formed in the solvent. The reaction time increases from 5 min to 30 min and the absorption peak red-shift from 537 nm up to 586 nm, sequentially.



Fig.5. UV-vis spectra of the prepared CdSe core nanoparticles for different sizes



Fig.6. Absorption peaks vs size relationship (sizing curve) for the prepared CdSe nanocrystals calculated according toYu et al.

As the reaction time increased, the ions that dissolved from the smaller-sized CdSe QDs grew onto other CdSe QDs to form larger size. This clearly indicates an increase in the overall nanoparticle size diameters, with increasing in the growth time. The diameter of the CdSe QDs for each growth time is estimated using the wavelength of the first excitonic absorption peak. From the peak position, one can roughly estimate the average size of CdSe QDs from the following Yu et al formula [24]

$$D\left(\frac{diameter}{nm}\right) = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-4})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + +41.57$$
(2)

where D (nm) is the size of a given nanocrystal sample and λ (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample. The obtained diameters of CdSe range from 2.80 to 4.02 nm, corresponding to the peak position of 537 – 586 nm, as shown in Table 2. The deviation in the peaks of absorption spectra is about 49 nm, which may be due to the difference of the surface states of these QDs. It is also thought that the strong intensity from the CdSe QDs can be attributed to their high crystallinty. The proportional relationship between absorption of nanocrystals and the size is illustrated in Fig. 6.



Fig.7. Plot of $(\alpha hv)^2$ versus hv of prepared CdSe nanoparticles at different sizes

Optical band gap is the lowest excitation energy of the quantum dots and was estimated from absorption coefficient data as a function of wavelength using the Tauc relation [25].

$$(\alpha h v) = B(h v - E_q)^r \tag{3}$$

Where α is the absorption coefficient, hv is the photon energy, B is the band tailing parameter, and E_g is the optical band gap of the nanoparticle, and r = 1/2 for direct band gap, as CdSe is a directband-gap semiconductor. The plot showing the variation of $(\alpha hv)^2$ versus hv is shown in Fig. 7. From the profile, the value of E_g is evaluated by the extrapolation of the linear part of the variation of $(\alpha hv)^2$ along Y axis. It is observed that the band gap values E_g were shifted to higher energy with a decrease in CdSe QDs particle size. The band gap determined for sample A₁ at the present investigation is found to be 2.42 eV. Comparing this with the band gap of the bulk²⁶ CdSe 1.74 eV reveals an enhancement of optical band gap around 0.68 eV, which clearly indicates the nanophase and quantized nature of the prepared CdSe sample. This is due to the strong quantum confinement. The band gap energies gradually decrease from 2.42 eV to 1.98 eV as the particle size increases. When ZnS could be formed on the surface of the core; the total size is larger than that of the core. This allows a further delocalization of electrons wave function and creates redshifts of the band edge transition (size-effect).

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Fig. 8. (a) Absorption spectra vs wavelength of CdSe/ZnS nanoparticles for different reaction time during the shell growth on CdSe core of diameter 2.80 nm (b) Plot of the outerdiameters of CdSe/ZnS samples vs shell thickness

Fig. 8 displays the optical responses of a series of ZnS overcoated samples grown on 2.70 nm core CdSe (sample A₁) TOPO capped having the following ZnS shell. The peak positions of core/shell spectra are red-shifted compared to their corresponding core CdSe nanoparticles. This clearly indicates an increase in the overall nanoparticle size as a result of growth of the ZnS shell around the CdSe core particles. Calculated particle size of the prepared CdSe/ZnS nanocrystals samples from the first excitonic absorption band using Yu's et al [24] equation corresponding to the λ_{max} are shown in Table 2.



Fig.9. Plot of $(\alpha hv)^2$ versus hv, illustrates the crystal size dependent properties of the energy band gaps of the prepared CdSe/ZnS nanoparticles

The optical band gap energy (E_g) of nanocrystalline CdSe/ZnS was calculated by the UV – vis spectrum using the Tauc equation [25]. The energy intercept of a plot $(\alpha hv)^2$ vs hv yields E_g (see Fig. 9). It is shown that the optical band gap decreases from 2.70 to 2.10 eV with an increasing in the particle size due to change of shell thickness. The values of direct band gap energy of the prepared samples were summarized in Table 2. It noticed that the band gap around 0.6 eV for present investigation of CdSe/ZnS nanocrystals.

CdSe (Core)						CdSe/ZnS core/ shell						
Samp.	Reaction	Abs.	Particle	Exciton	Emission	Samp.	Reaction	Abs.	Particle	Exciton	Emission	Stoke
No.	time	λWL	size nm	Energy	$\lambda_{max} nm$	No.	time	λWL	size nm	Energy	$\lambda_{max} nm$	shift
	(min)	nm	by Yu	(eV)			(min)	nm	by Yu	(eV)		nm
			Eq.						Eq.			
A ₁	5	537	2.80	2.42	521	S_1	5	570	3.52	2.70	597	27
A_2	15	558	3.21	2.15	549	S_2	15	586	4.02	2.50	598	13
A ₃	20	566	3.41	1.98	-	S ₃	20	588	4.10	2.30	601	-
A_4	30	586	4.02	-	-	S_4	25	589	4.14	2.25	602	-
						S ₅	30	590	4.17	2.15	602	12
						S ₆	35	592	4.25	2.10	602	-

Table 2. Spectroscopy parameters of CdSe & CdSe/ZnS Nanoparticles



Fig.10 Nanoparticle size at the first absorption peak of CdSe/ZnS nanocrystals for different times

The increases in particle size values for prepared CdSe//ZnS nanoparticles with increasing times are illustrated in Fig. 10.

The particle size measured from TEM micrographs is larger than that size value calculated by XRD data, and that size crossponding to λ_{max} of absorption spectra, Table 3.

Sample No.	Sample type	x-ray size (nm)	Abs.part. size by Yu. Equ. (nm)	TEM size (nm)
A ₁	CdSe (core)	2.70	2.80	3.10 ±0.5
S_2	CdSe/ZnS(core/shell)	3.87	4.02	4.25±0.25

Table 3. Values of particle size of prepared nanocrystals by different means



ig.11. Absorption spectra for CdSe dots (dashed line) and ZnS overcoted CdSe dots (solid line) at various diameters

Fig. 11 shows that the absorption spectra for the CdSe/ZnS dots are broader and slightly red-shifted than their respective core dot spectra.



Fig.12. Photoluminescence intensity of CdSe/ZnS QDs samples at various collected time with a series of shell thickness. The inset "g" shows the normalized PL spectra

Fig. 12 shows the photoluminescence spectra (excitation at 520 nm) of the synthesized CdSe/ZnS nanocrystals at room temperature using JASCO-FP-6300 fluorescence spectrometer. This spectra for a series of ZnS overcoated dots with 2.70 nm diameter CdSe cores and its emission results were presented in Table 2. It is indicates a red shift occurs compared to the maximum emission peaks. The time evolution of the emission intensity for CdSe/ZnS QDs demonstrates that the growth of ZnS shell nanoparticles increases as the reaction time increased and the spectrum broadness increased with increasing ZnS coverage. The reason for the florescence of CdSe/ZnS is the recombination of electrons and holes due to the surface-trapped electrons and holes by quantum confinement. These results are in consistent with previous work on CdSe/ZnS QDs [26-28]. The inset 'g' shows the emission spectra (normalized to the first emission maximum) of CdSe/ZnS NCs taken at different intervals. The emission peaks of CdSe/ZnS NCs range from 597 to 602 nm, and the corresponding full width of half-maximum (FWHM) of the band-edge luminescence was maintained between ~ 23 - 29 nm.



Fig.13 PL spectra of CdSe and CdSe/ZnS core/shell nanocrystals

Fig.13 shows the room-temperature photoluminescence spectra PL of CdSe core (solid line) and the core after overcoat with ZnS (dashed line). The PL spectra are shifted to the higher wavelength (red-shift) with addition of ZnS shell. The emission spectra of CdSe and CdSe/ZnS nanoparticles are most marked by different intensity, due to the growth of ZnS shell to that of the CdSe core. The PL intensity of CdSe QDs increases ~4 times when the CdSe core are capped inside a shell of high band gap material like ZnS to form a CdSe/ZnS core/shell structure. The lattice mismatch is small enough to allow epitaxial growth while still preventing alloying, and the

difference in band gaps is large enough for shell growth to increase the quantum yield and stability of the core. Quantum yields were assessed by comparing the intensity of a given emission band with that due to Rhodamine -101. The PL quantum yield of pure CdSe nanoparticles is calculated and found to be 30% and increased with addition of ZnS, approaching a value of 40% depending on particle size. These results are in agreement with previous finding reported recently by Hines et al. [18].



Fig.14 Absorption and photoluminescence spectra of core / shell CdSe/ZnS QDs obtained at room temperature at excitation wavelength of 520 nm. prepared by means of organometallic method.

Fig. 14 demonstrates absorption (dashed curve) and photoluminescence PL (solid curve) spectra of the CdSe/ZnS core/shell nanocrystals for various samples, controllable optical properties as a function of their size. The absorption and Emission peaks are arranged between 537 and 602 nm for samples S_1 , S_2 and S_5 . The PL spectra of these CdS/ZnS core/shell QDs are shown together with that of their absorption for comparison. An increase is noted in PL intensity as compared to their absorption. This PL enhancement seems to depend on the increase in ZnS shell growth. The values of stoke shift for CdSe/ZnS core/shell samples S_1 , S_2 & S_5 are 27 nm, 13 nm and 12 nm respectively. A red shift of ~ 5 nm, in band edge PL was observed with respect to the QDs. It is observed that the Stock shift values increased as the shell thickness decrease. Table 2 shows the resultant Stock shift for CdSe/ZnS core/shell samples.

4. Conclusion

The CdSe core and CdSe/ZnS core/shell quantum dots were synthesized by using a modified organometallic procedure. These samples are analyzed structurally and optically through using different techniques. Chemical passivation of CdSe by ZnS layers was essential to improve the PL emission of the nanostructures. The change of particle size with reaction time was obtained from UV-spectra measurements. Nanoparticle diameter and shell thickness were estimated independently on x-ray diffraction pattern and transmission electron microscopy (TEM) results. The effect of particle sizes on the optical properties was confirmed from UV-vis and photoluminescence spectroscopic data. UV-vis absorption spectroscopy is used to calculate the exciton energy of CdSe/ZnS nanoparticles and blue shift in absorption peak indicates quantum size confinement. It is observed that there is an increased absorption in the ultraviolet with increasing ZnS coverage as a result of absorption into the higher band gap ZnS shell. The mean size of CdSe/ZnS QDs calculated from x-ray data (~3.87nm) is smaller than that determined by HRTEM images (~ 4.25 nm). The core/shell quantum dots exhibit tunable emission by controlling the thickness of the ZnS shell. The PL quantum yield of CdSe/ZnS nanoparticles is approaching a value of 40% which is in agreement with the previous reported finding.

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