



Optical properties of colloidal CdSe/CdS/ZnS/PVP QDs core/shell embedded in fatty acid medium

M.A. Batal, Kaesar Al-yamani*

Department of Physics, College of Science, Aleppo University, (SYRIA)

ABSTRACT

Colloidal solutions of CdSe were prepared in fatty acid at room temperature. The prepared samples were coated with CdS, ZnS semiconductor shells. Absorption and fluorescence spectrum were measured. From absorption spectra the diameter of CdSe QDs and energy bandgap were calculated using hyperbolic approximation and some empirical equations. The diameter of QDs were less than (2) nm and increase with ageing time reaching to 5 nm. CdSe QDs coated with more semiconductor shells (CdSe/CdS, CdSe/ZnS, CdSe/CdS/ZnS) were prepared too. Also the system CdSe / CdS / ZnS / PVP [Core / shell / shell / shell] were prepared, that increase fluorescence intensity with more diluted by fatty acid. Finally, quantum confinement increase when the number of semiconductor shells increase. © 2015 Trade Science Inc. - INDIA

INTRODUCTION

Cadmium selenide (CdSe) is solid hexagonal or cubic crystal. It belongs to II-IV semiconductors and has direct band gap n-type semiconducting material with a band gap of 1.74 eV at 300K. Its molecular weight is 191.37 g/mol where Cd is 58.74% and Se is 41.26%. Its appearance is dark red color^[1]. The optical and electronic properties of CdSe QDs make it ideal semiconductors in many applications because its ability to control the diameters and its energy band gap in order to absorb and emit radiation of light. The most important applications of QDs are using in laser technology, Optical, electronics and medical treatment^[2]. The difference properties of QDs. depend on the method of preparation. The strong quantum restriction of holes and electron raised optical and electronic properties, from those of bulk material^[3]. Many studies have focused on the study III-V and II-VI groups of semiconductor; CdSe belongs to II-VI group. The most common meth-

ods of CdSe QDs preparation are chemical method^[4]. Many studies have focused on quantum yield, energy band gap and diversity of opto-electronic properties compared with CdSe bulk materials^[5].

In this study, high quality CdSe QDs was synthesized in fatty acid solutions. UV-VIS absorption, photoluminescence and fluorescence were carried out to characterize the optical properties of these QDs and to put in evidence the effect of organic and inorganic shell material quantum confinement.

CALCULATION OF QDS CDSE DIAMETER'S

To calculate QDs diameter's some empirical equations were used. The first one was found by^[6], it is a simple empirical relation between the CdSe nanoparticle diameter and wavelength of exciton peak λ (nm) as follows:

$$D(2r) = 0.33 \exp\left(\frac{\lambda - 252}{129.3}\right) \quad (1)$$

The second empirical formula proposed by^[7], which describe relationship between diameter ($d=2r$, nm) of the CdSe particles and the first excitonic absorption peak wavelength (λ , nm), which given in following expression:

$$D = (1.6122 \times 10^{-9}) \cdot \lambda^4 - (2.6575 \times 10^{-6}) \lambda^3 + (1.6242 \times 10^{-3}) \cdot \lambda^2 - (4.277 \times 10^{-1}) \cdot \lambda + 41.57 \quad (2)$$

D (nm) is diameter of the CdSe QD, and λ (nm) is the wavelength of the first optical absorption peak. The particle size of the CdSe QDs can be also determined from absorption wavelength of the UV-VIS spectra by using hyperbolic band model approximation as follow^[8].

$$R = \sqrt{\frac{2\pi^2 \cdot h^2 \cdot E_{\text{bulk}}}{m^* \cdot [E_{\text{QD}}^2 - E_{\text{bulk}}^2]}} \quad (3)$$

Where, R = QD radius ($2R=D$ is the diameter and hence, indicates particle size). E_{bulk} is bulk energy band gap (1.74 eV for CdSe). E_{QD} is QD energy band gap (calculated from the absorption peak), h is planck's constant. m^* is effective mass of specimen (1.18×10^{-31} kg for CdSe).

MATERIALS

Metallic selenium powder, sodium sulfite (Na_2SO_3), sulfuric acid (98%), isopropanol, oleic acid, paraffin oil, Ethelenglycol, N_2H_2 Hydrazine

Hydrate NaOH, PVP (polyvinylpyrrolidone 30, $m=40000$ gr/mol), Spectrophotometer type V-630 JASCO and ultraviolet spectrophotometer Hitachi F-2500.

PREPARATION COLLOIDAL SOLUTIONS OF CDSE IN FATTY ACID (OLEIC ACID AND PARAFFIN OIL)

CdSe was prepared using 10 gr of $\text{Cd}(\text{OH})_2$ powder solved in 100 ml of deionized water, paraffin oil (50 ml) added to solution then heated to 220°C with constant stirring for (12) min. 1 ml, 2 ml, 3 ml, 4 ml separately of previous solution, add to them (10 ml) of Oleic acid, then 1 ml of (Na_2SeSO_3) added to each them. To eliminate quenching effect previous solutions were diluted with oleic acid and paraffin oil.

UV-VIS Absorption of CdSe colloidal solutions in fatty acid

The absorption spectrum of four CdSe samples prepared in fatty acid was measured using JASCO-V-630 in range (400 – 800 nm). More than absorption peak was found for these samples that corresponding wavelength between (570-590) nm for first absorption peak after preparation Figure (1,a).

In second day the absorption spectrum of these samples become more intense and sharp with shifted toward to shorter wavelengths (blue region) in average 10 nm Figure (1,b). TABLE 1 shows the change

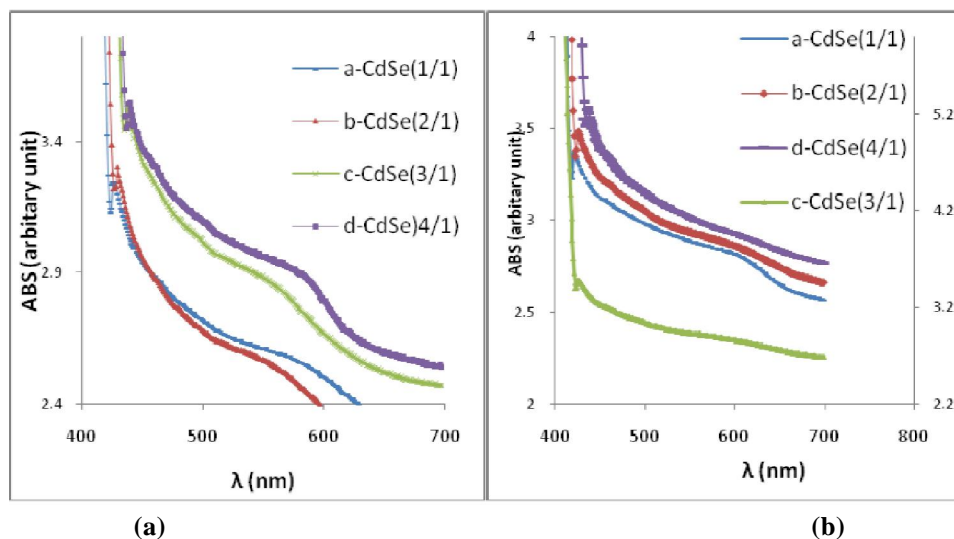


Figure 1 : Absorption spectrum of CdSe in fatty acid with different ratio of Cd/Se (a) immediately (b) after 48 hours

TABLE 1

0.1mol/l oleic acid	λ_{abs} (nm)	E_g (ev)	D(nm) EQ(1)	D(nm) EQ(2)	D(nm) EQ(3)
Cd /se(1:1)	433	2.868	1.338	1.824	1.388
Cd/se(2:1)	435	2.855	1.358	1.839	1.395
Cd /se(3:1)	444	2.797	1.456	1.907	1.427
Cd /se(4:1)	446	2.785	1.479	1.921	1.434
Cd /se(5:1)	451	2.754	1.537	1.958	1.453
0.1mol/l oleic acid 2days	λ_{abs} (nm)	E_g (ev)	D(nm) EQ(2)	D(nm) EQ(3)	D(nm) EQ(4)
Cd 1:1 se	427	2.909	1.277	1.778	1.367
Cd 2: 1 se	429	2.895	1.297	1.793	1.374
Cd 3: 1 se	437	2.842	1.380	1.854	1.402
Cd 4: 1se	441	2.816	1.423	1.884	1.416
Cd 5: 1 se	434	2.862	1.348	1.832	1.391

in absorption wavelength with increase fatty acid concentration depending on ratio Cd/Se and ageing time, the QDs diameters calculated were close to each other.

PREPARATION COLLOIDAL SOLUTIONS OF CDSE / CDS CORE SHELL

Sulfuric acid (4 gr) added to 4 gr of Na_2S to get H_2S gas which by way injected through the glass tube to CdSe solution, bubbles gas were formed inside the solution and the color of solution was changed from light red to orange-red.

UV-VIS absorption solutions for CdSe/CdS core shell

Figure 2 shows absorption spectrum of CdSe sample after capped with CdS in fatty acid solution as it was shown in Figure 2. The absorption band edge has shown a shift toward the red color and this is due to the restriction of the quantum electronic levels with the increasing growth of the CdS

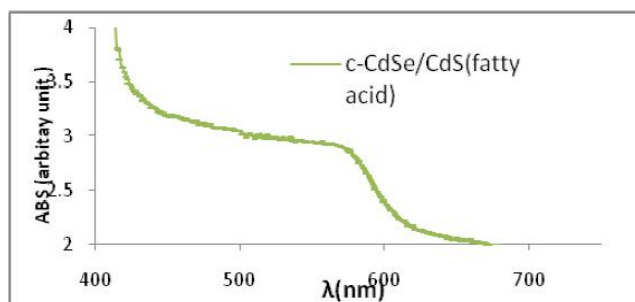


Figure 2 : (a) shows shift in absorption wavelength of CdSe in fatty acid from (495 to 569 nm) due to CdS shell

shell.

The optical intensity is given by Beer Lambert law: $A = \epsilon \cdot C \cdot L$. Where A is the optical intensity, L length of the sample, C concentration of the sample. The extinction factor is given for CdSe^[9]: $\epsilon = 5857 D^{2.65}$. Where D is the diameter of core QDs.

The quantum confinement weakness raises in the system core-shell CdSe /CdS, which reflects the properties of absorption and fluorescence spectroscopy. As it shows the absorption spectrum of core surrounded with CdS tend to shift towards the red wavelength and this will be more pronounced when increasing the thickness of the layer of shell around the core. Since the energy equilibrium for both particles (core and shell) in valence band was large and effective, which is that the holes will be confined within the core CdSe despite the presence of shell CdS therefore absorption and fluorescence peaks be a result of a portion of the electrons transmitted back to CdS shell. The shell CdS has effective in uprooting part of these electrons outside the core CdSe and can abandon. The shell CdS was grown around the CdSe dots to form a core/shell structure to enhance the photoluminescence of CdSe QDs since the higher band gap material will remove the surface defects of CdSe dots and help to confine pairs (electron-hole) more in the CdSe core region.

TABLE 2 : Extinction factor in three solutions

Solution	Fatty acid
$\epsilon (cm^{-1} \cdot M^{-1})$	28716.29

TABLE 3 : Change of diameter of CdSe QD in previous solution

Cd/ se (4:1)	λ_{abs} (nm)	E_g (ev)	D(nm) EQ(1)	D(nm) EQ(2)	D(nm) EQ(3)
Oleic acid	530	2.343	2.83	2.69	1.57

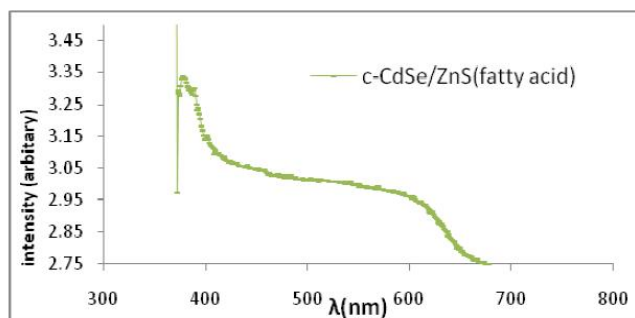


Figure 3 : Absorption spectrum of CdSe / ZnS core shell in fatty acid solutions

PREPARATION COLLOIDAL SOLUTIONS OF CDSE / ZNS CORE SHELL

Zinc chloride (2.33 gr) was solved in 100 ml of distilled water, 4 ml of zinc chloride was added to previous solutions of CdSe. Na_2S (1.94 gr) solved in distilled water and then added to 2.42 gr of sulfuric acid within the trap gas H_2S which collected until the end of interaction and injected into flask container to mix forming shell ZnS surrounds the core of CdSe, isopropanol (1 ml) added to previous solutions for pulling the excess quantity of H_2S .

UV-VIS absorption spectrum of CdSe / ZnS core shell

The Figure 3 shows the absorption spectrum of the sample CdSe/ZnS. Since the absorption peaks of samples in the three previous solutions shifted toward blue color due to quantum adherence and stop growth CdSe core.

TABLE 4 shows Change absorption wavelength, energy bandgap and compare calculated diameters from hyperbolic approximation (Exp.(3)) and empirical relationship (Exp.(2))

FLUORESCENCE SPECTRA OF CDSE/CDS-CDSE/ZNS COLLOIDAL SOLUTIONS IN FATTY ACID SOLUTION

Figure 4 shows comparison between fluores-

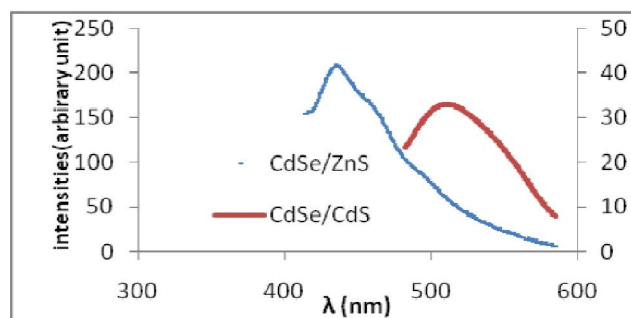


Figure 4 : Fluorescence CdSe/CdS and CdSe/ZnS in fatty acid

cence spectrum of CdSe/CdS and CdSe/ZnS in fatty acid. Since observed high intensity of fluorescence when capped with ZnS compared with these capped with CdS at the same excitation wavelength $\lambda_{ex} = 370\text{nm}$. Fluorescence peak CdSe/ZnS was more sharp and intense than CdSe/CdS (Fluorescence intensity was 38) when capped with CdS compared with high intensity (208) when capped with ZnS) and that reflect the strength confinement and the QDs size was smaller. Fluorescence peak CdSe/ZnS corresponding 445nm other side peaks appear due to quantum transitions between levels of quantum energy.

PREPARATION OF COLLOIDAL SOLUTIONS OF CDSE / CDS / ZNS CORE SHELLS

Zinc chloride solution (7ml) Added to 10 ml of CdSe / CdS in fatty acid solution, Na_2S (4 gr) was solved in distilled water and added to 6 gr of sulfuric acid within the gas trap H_2S which collected until end of interaction and injected into flask container to mix and formed shell of ZnS surrounds core CdSe/CdS, (1ml) of isopropanol was added to CdSe/CdS/ZnS withdrawal of excess quantity of H_2S .

UV-VIS absorption spectrum of CdSe / CdS / ZnS core shells

Figure shows (5) absorption spectrum of CdSe / CdS / ZnS in fatty acid solutions. Figure 5 show the sample have more weak absorption peaks, the first

TABLE 4

Sample	λ (nm)	E_g (ev)	D(nm)EQ(3)	D(nm)EQ(2)	D(nm)EQ(1)
CdSe/ZnS (oleic)	525	2.36	1.53	2.62	2.72

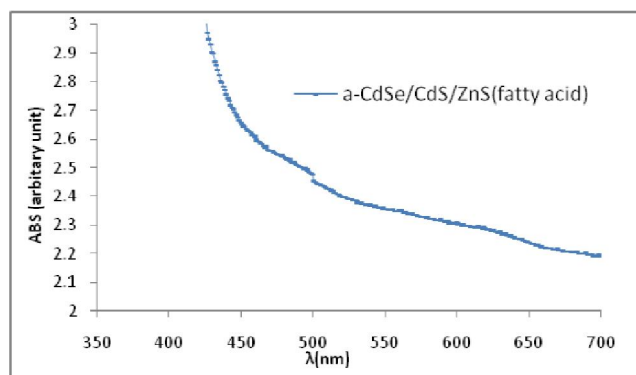


Figure 5 : Absorption spectrum of CdSe / CdS / ZnS in fatty acid solutions

one is at (468 nm), the second peak is at (478 nm), the third peak at (506 nm), and the last one at (626 nm). TABLE (5) shows shift in the absorption peaks, change in energy band gap and compared between calculated diameter of QD from hyperbolic approximation EQ(3) and empirical EQ(1) for CdSe / CdS / ZnS in fatty acid solution

Fluorescence spectrum of CdSe/CdS/ZnS in fatty acid

Figure 6 shows fluorescence spectrum of CdSe after coated with CdS and ZnS in fatty acid solution using 400nm wavelength excitation which shows the emission spectrum peaks shifted 85 nm toward shorter wavelengths. That due to the difference in energy band gap between CdSe (1.74eV) and CdS (2.42eV).

When CdSe capped with CdS some defects surface remain on QDs. surface and this reflect weakness of the intensity in fluorescence spectrum. While in case of coating with ZnS (3.4eV) the difference in energy band gap between CdSe and ZnS is the biggest and quality of coating will be better due to absence surface defects of QDs, this interpreted high fluorescence intensity of CdSe / ZnS core shell. The decreasing in intensity of fluorescence of CdSe / CdS due to sulfur layer which cause decline in fluo-

rescence intensity due to uncompleted bonding of sulfur (the survival of surface defects). Compared these spectrums with fluorescence spectrum of sample without coating, fluorescence intensity of coated material have much sensitive, since intensity of fluorescence improved from 42 to 208 when coated with ZnS and this increase due to removal of surface defects of QDs. The increasing in intensity of fluorescence spectrum of CdSe/CdS/ZnS due to success of coating and possibility of tunneling of the CdSe electron wave function into the CdS shell material and as result the system is less confined, hence the PL behaves as if the core particle were larger. when adding zinc chloride to fatty acid solution an increase in number of saturated binding sulfur atoms surrounding nucleus of CdS, which provides greater stability of the compound. The width of PL of CdSe/CdS due the thickness of CdS shell around the core which invert the type of core shell from type one to type two.

FLUORESCENCE SPECTRA COLLOIDAL SOLUTIONS CDSE / CDS / ZNS / PVP CORE SHELLS IN FATTY ACID SOLUTIONS

Figure 7 shows fluorescence spectra of CdSe / CdS / ZnS sample after embedded its in PVP solution (0.1 mol/L) with diluted the solution more than one. The increase in fluorescence intensity with more di-

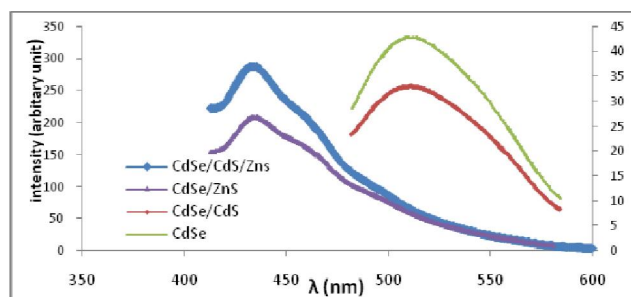


Figure 6 : Fluorescence spectra of the samples CdSe, CdSe / CdS, CdSe / ZnS, CdSe / CdS / ZnS in fatty acid

TABLE 5

Sample	λ (nm)	E_g (ev)	D(nm)EXP.(1)	D(nm)EXP.(2)	D(nm)EXP.(3)
CdSe/CdS/ZnS(olic)0.1mol/L	506	2.45	2.35	2.4	1.424

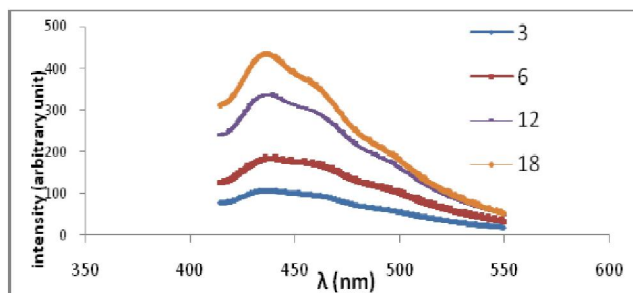


Figure 7 : Fluorescence spectrum of CdSe after coating with PVP in oleic acid solution with extension

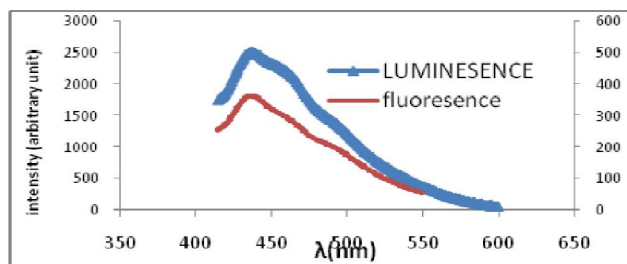


Figure 8 : A comparison between the fluorescence and luminescence spectrum in fat acid solution at excitation wavelength nm 400.

TABLE 6

Diluted rate(ml)	Main sample	3	6	12	18
Intensity (arbitrary unit)	769.1	106.6	182.8	338	434.2
FHWM(nm)	33.95	38.48	43.49	40.17	32.86
Wavelength of Emission peak(nm)	436.5	437	438.5	437.5	436.5

TABLE 7

	Emission peak(nm)	FWHM(nm)	Intensity
Luminescence	437	41.36	2499
Fluorescence	437	31.15	362.4

lution is due to disappear surface defect of previous samples.

From TABLE 6 Intensity of fluorescence decreased with diluted from 769.1 To 106.6 after dilute solution with 3ml of fatty acid, increase intensity with increase the ratio of dilution until reach a ratio of extension 18ml

The surfactants effect on fluorescence spectrum can be understand as cases of traps which due to defects in the structure of synthetic samples, spaces between close binding. Raised electron or hole can restrict by minimal energy of trap to behave less possibility to radiant recombination^[3]. By increasing dilute, intensity of fluorescence was the best since increasing intensity when the dilute of about 103 when adding 3ml of oleic to 180 when added 6ml and this cause displacement of peak fluorescence 2.5 nm towards the red color and lead to increase in FWHM(38.45 to 43.49)nm.

Fluorescence and luminescence spectrum of colloidal solution CdSe / CdS / ZnS / PVP core shells in fat acid solution:

The Figure shows (8) a comparison between spectral of fluorescence and luminescence of sample CdSe / CdS / ZnS / PVP core shells in fatty acid at

the same excitation wavelength $\lambda_{ex} = 400nm$. Spectrum show that the luminescence intensity almost equal to six times of intensity of fluorescence of the same sample at the same wavelength excitation.

When the intensity of fluorescence sample quickly, FWHM tend to be smaller and tend to be more width. Since the wavelength of the is directly connected to size, also imposes adherence to the quantum, the show will be distributed in between the larger particles. TABLE (7) shows that the spectrum band tends to be narrower compared with band width of fluorescence.

CONCLUSION

Cadmium selenide QDs with less than 2nm in average were synthesized using simple method at room temperature. The diameter of QDs synthesized ranged between 2-5nm which increase with ageing time. The size of the quantum dots synthesized was observed to increase when the supersaturation of the solution, optical band gap increases as the QDs size decreases. Thickness of CdS of a drastic difference in the photoluminescence efficiencies related to the ratio of Cd^{+2} / Se^{-2} . It was found that the concentra-

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tion of polymer precursor has played a major role on determining the stability of the Nano crystals as colloidal solutions associated with the overall system stabilization through surface interactions at the semiconductor-polymer interfaces.

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