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Optical properties ofcolloidal CdSe/CdS/Zns/PVPQDs core/ shellsembedded in fatty acid medium

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ABSTRACT

Colloidal solutions of CdSewere prepared in fatty acidat room temperature. The prepared samples were coated with CdS, ZnS semiconductors shells. Absorption and fluorescencespectrum were measured. From absorption spectra the diameter of CdSe QDs and energy bandgap were calculated using hyperbolic approximation and some empirical equations. The diameter ofQDs were less than (2)nm and increase with ageing time reaching to 5 nm. CdSe QDs coated with moresemiconductors 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 fluorescenceintensitywith more diluted by fatty acid. Finally, quantum confinement increase when the number of semiconductor shells increase.

INTRODUCTION

Cadmium selenide (CdSe) is solid hexagonal or cubic crystal. It belong 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/molWhere 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 idealsemiconductors in many applications because its ability to control the diameters and itsenergybandgapin 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 differenceproperties 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 groupsof semiconductor; CdSe belongs toII-VI group. The most common methods of CdSeQDs.preparation are chemical method[4]. Many studies have focused on quantum yield,energy bandgap and diversity ofopto-electronic properties compared withCdSebulk materials[5].

In this study, high quality CdSeQDs 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 CDSEDIAMETER'S

Tocalculate QDs diameter's some empirical equations were used. The first one was found by[6],Itis a simple empirical relation between the CdSenanoparticle diameter and wavelength of exciton peak λ(nm) as follow:

$$\mathbf{D(2r) = 0.33\exp(\frac{\lambda - 252}{129.3})} \qquad (1)$$

The second empirical formula proposed by[7], whichdescribe relationship between diameter (d= 2r, nm) of the CdSe particles and the first excitonicabsorption peak wavelength (λ, nm), which given in fallowing expression:

$$D=(1.6122\times10^{-9}).\lambda^{4}-(2.6575\times10^{-6})\lambda^{3}+(1.6242\times10^{-3}).\lambda^{2}-(4.277\times10^{-1}).\lambda+41.57 \qquad (2)$$

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 CdSeQDs can be also determined from absorption wavelength of the UV-VIS spectra by using hyperbolic band model approximation as follow[8].

$$R=\sqrt{\frac{2\pi^{2}.h^{2}.E_{Bulk}}{m^{*}.[E_{QD}^{2}-E_{bulk}^{2}]}} \qquad (3)$$

Where, R = QD radius (2R=D is the diameter and hence, indicates particle size). E_{bulk} isbulk energy band gap (1.74 ev for CdSe). E_{QD} isQD energy band gap (calculated from the absorption peak),h isplanck'sconstant. M* is effective mass of specimen (1.18 x 10-31 kg for CdSe).

MATERIALS

Metallic selenium powder, sodium sulfite (Na_2SO_3),soulfic acid (98%), isopropanol, oleic acid,paraffin oil,Ethelenglycol,N_2H_2 Hydrazine Hydrate NaOH, PvP(ployvinlpyrroidonek30, m =40000gr/mol),. Spectrophotometer type V-630 JASCO and fluoro- spectrophotometerHitachi F-2500.

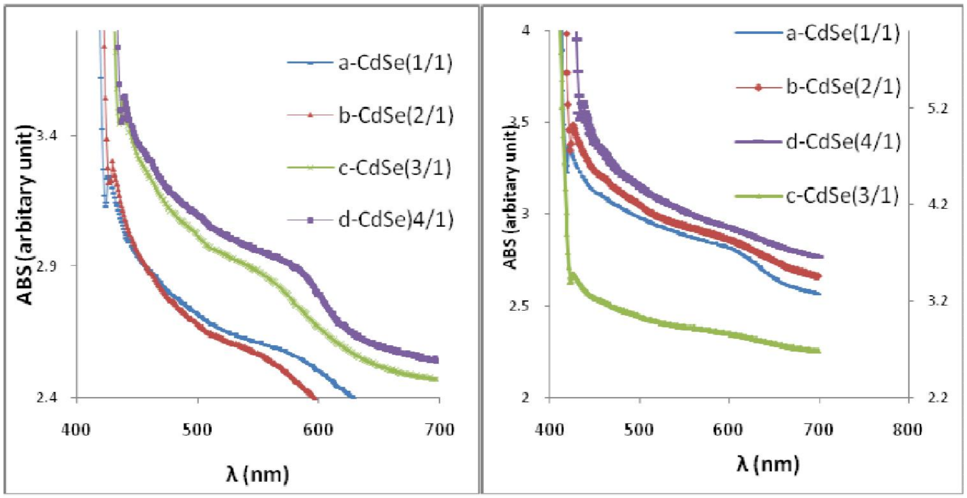
PREPARATION COLLOIDAL SOLUTIONS OF CDSE IN FATTY ACID (OLEIC ACID AND PARAFFIN OIL)

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

UV-VISabsorption ofCdSecolloidal solutions in fatty acid

The absorption spectrum of fourCdSesamples prepared in fatty acid was measured using jasco-v 630 in range(400 – 800 nm). More thanabsorption peakwas foundfor 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 reign) in average 10 nm Figure (1,b). TABLE 1 shows the change



(a) (b)

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 oliec 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 getH_2S gas which by wayinjected through the glass tube to CdSe solution,bubbles gas were formed inside the solution and the color of solution waschangedfrom light red to orange-red.

UV-VIS absorption solutions for CdSe/CdS core shell

Figure 2 shows absorption spectrum of CdSesample after cappedwith CdSinfatty acid solution as it was shown in Figure 2. The absorption band edge has shown a shift toward theredcolor and this is due to the restriction of the quantum electronic levels with the increasing growth of the CdS shell.

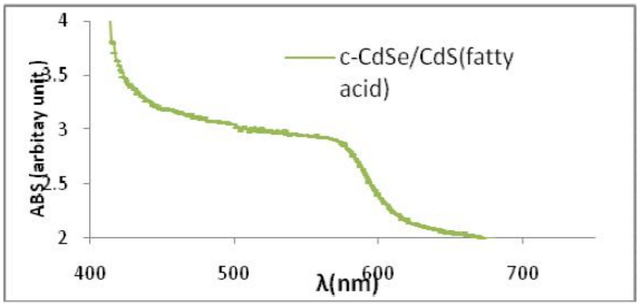


Figure 2 : (a)shows shift in absorption wavelength of CdSe in fatty acid from (495 to 569 nm) due to CdS shell

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

The quantumconfinement weakness raises in the system core-shell CdSe /CdS,which reflects the properties of absorption and fluore scence spectros copy. As it shows the absorption spectrum of core surrounded withCdStend 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 confinement within the coreCdSe despite the presence of shellCdS therefore absorption and fluorescence peaksbe a result of a portion of the electrons transmitted back to CdS shell. The shellCdS has effective in uprooting part of these electrons outside the coreCdSe 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
$\varepsilon(cm^{-1} \cdot M^{-1})$	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

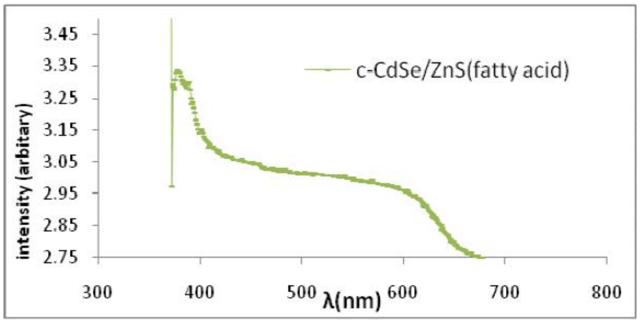


Figure 3 : Absorption spectrum of CdSe / ZnS core shell in fatty acid solutions

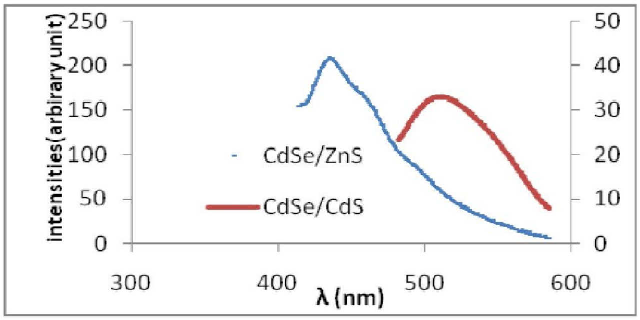


Figure 4 : Fluorescence CdSe/CdS and CdSe/ZnS in fatty acid

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 growthCdSecore.

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 fluorescence spectrum ofCdSe/CdS andCdSe/ZnS in fatty acid. Since observedhigh intensity of fluorescence when capped withZnS comparison with these capped with CdS at the same excitation wavelength $\lambda_{ex} = 370nm$. Fluorescence peak CdSe/ZnS was more sharp and intense thanCdSe/CdS (Fluorescence intensitywas (38) when cappedwithCdS compared with high intensity (208) when capped with ZnS) and that reflect the strength confinement and the QDs size was smaller. Fluorescence peak CdSe/ZnScorresponding 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 acidsolution, 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/ZnSwithdrawal 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 samplehave 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 (oliec)	525	2.36	1.53	2.62	2.72

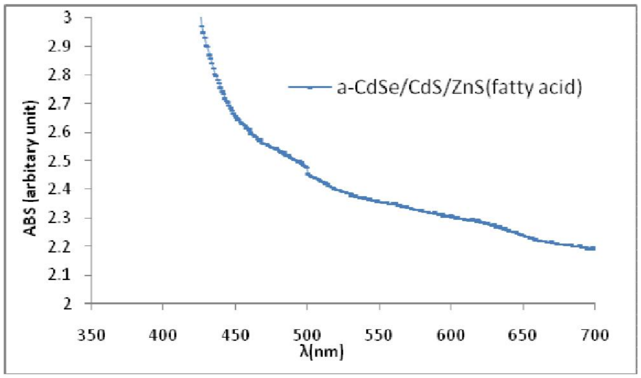


Figure 5 : Absorption spectrum of CdSe / CdS / ZnS in fatty acid solutions

oneis 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 infatty 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 energybandgapbetween CdSe(1.74ev)and CdS (2.42ev).

When CdSe capped with CdS some defects surfaceremain on QDs. surface and this reflect weakness of the intensity in fluorescencespectrum. While in case of coating withZnS (3.4ev) the difference in energybandgap between CdSe and ZnS is the biggest and quality of coating will be better due to absence surface defects of QDs, this interpreted highfluorescenceintensity of CdSe / ZnS core shell. The decreasing in intensity of fluorescence of CdSe/ CdSdue to sulfur layer which cause decline in fluorescence 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 coatedwithZnS and this increasedue to removal of surface defects of QDs. The increasing inintensity of fluorescencespectrum ofCdSe/CdS/ZnSdue to success of coating and possibility of tunneling of the CdSeelectron 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 ofCdS shell around the core which invert the type of core shell from type one to type two.

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

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

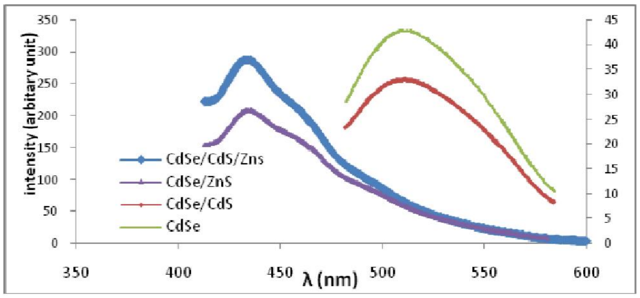


Figure 6 : Fluorescence spectra of the samples CdSe, CdSe / CdS, CdSe / ZnS, CdSe / CdS / ZnS in fatty acid

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

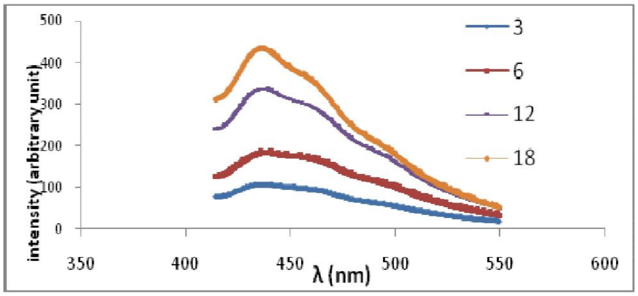


Figure 7 : Fluorescence spectrum of CdSe after coating with PVP in oleic acid solution with extension

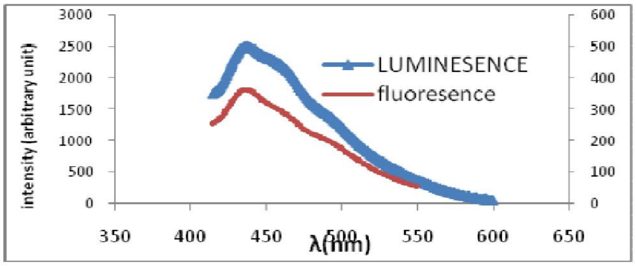


Figure 8 : A comparison between the fluorescence and luminesce spectrum in fat acid solution at excitation wavelength nm 400.

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 fluore scence 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 understandas cases of traps whichdue to defects in the structure of synthetic samples, spaces between closebinding. Raised electron or hole can restrict by minimal energyof trap to behas less possibility to radiant recombination[3]. By increasing dilute, intensity of fluorescence was the best since increasing intensity when the dilutee of about 103 when adding 3ml of oleic to 180 when added6ml and this cause displacement ofpeakfluorescence2.5 nm towards the red color and lead to increase in FHWM(38.45 to 43.49)nm.

Fluorescence and luminescence spectrum of colloidal solution CdSe / CdS / ZnS / PVPcore 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 sameexcitation wavelength $\lambda_{ex} = 400nm$. Spectrum show that the luminescence intensity almost equal to sixtimes of intensity of fluorescence of the same sample at the same wavelength excitation.

When the intensityfluorescence samplequickly, 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 ofQDs synthesized ranged between 2-5nm which increase with ageing time. The sizeof 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 efûciencies related to the ratio of Cd^{+2} /Se^{-2}. Itwas found that the concentration of polymer precursor has playeda major role on determining the stability of the Nano crystals ascolloidal solutions associated with the overall system stabilization through surface interactions at the semiconductor-polymerinterfaces.

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