

Research Article

Zinc-Blend Cadmium Selenium Colloidal Nanoparticles preparation by Chemical Reaction

Mohammed T.Hussein^A , Thekra K. Abd Al Raheem^{A*} , Omar A. Ebrahim^A , Bushra A.Hassan^A and Hasan B.Jasim^A

^ADepartment of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Accepted 15 Sept 2014, Available online 30 Sept 2014, Vol.4, No.3 (Sept 2014)

Abstract

II-VI Zinc-blend cadmium selenium CdSe nanoparticles were prepared as a collided by chemical reaction of sodium selenosulfide (Na_2SeSO_3) and cadmium chloride CdCl_2 at various concentration of Selenium Se precursor. UV-Visible , X-Ray Diffraction , AFM as well as D.C conductivity are used for characterization studies of the CdSe QDs. The X-R diffraction pattern shows Zinc-blend phase of CdSe QDs. The absorption spectra show a blue shift with decreasing QDs size which is attributed to quantum confinement effect. The results indicate the increasing of Cd and Se molar ratio effect the size and roughness of CdSe QDs as shown in AFM measurements . The results of the energy gap are in comparable with theoretical calculation which has been done by using Density functional theory coupled with large unit cell approximation.

Keywords: Zinc-blend of CdSe nanoparticles, colloidal by chemical reaction

Introduction

Semiconductor nanoparticles are currently being extensively studied in the context of their size dependent photophysical and photochemical properties. The sizes of the nanocrystals in all three dimensions are less than the de broglie wavelength of the electronic system excitations. Therefore, many properties of these materials can be systematically described and understood in term of quantum confinement effects. From the view point of basic science, a nanocrystal is in an intermediate state of matter between molecule-like cluster and bulk crystals, and therefore offers a possibility to trace an evolution of electronic and optical properties of the matter from atomic cluster to bulk solids. In the context of applications, nanocrystals can be efficiently used in novel light emitting devices, optical transformers, photonic switches, nanoelectronic circuitry and other applications (Kapitonov *et al*, 1999).

For II-VI QDs, in particular, the CdSe QDs prepared by chemical methods are by far, the most popular (Y.Donazhi *et al* , 2007 ; X.G.Peng *et al*, 1998 ; D.Zhengtao *et al*, 2005). Recently a new method has been developed for the synthesis of CdSe QDs without the use of trioctylphine (TOP) solvent (G.G.Yordanov *et al*, 2008 ; H.Mao *et al*, 2005 ; T.Aichele *et al*, 2007). The method is inexpensive, safer and produces CdSe QDs of high quality. Furthermore (S.J.Rosenthal *et al*,2007) the process can be operated in open atmosphere. It is noteworthy that non. Top based routs produce colloidal CdSe QDs with high quality zinc-blende structures and have attracted a

great deal of interest due to their size-tunable photoemission characteristics. The photoemission characteristics originated from the quantum confinement effect of both electron and hole in all three dimensions. Leading to an increase in effective energy band gaps of nanocrystals (L.E.Brus,1984 ; C.B.Murray *et al*, 1993 ; A.P.Alivisatos ,1996 ;Y.N.Xu and W.Ching ,1993) . In addition CdSe QDs exhibit almost full-range visible light emission within a reasonable size range. Thus in turn, leads to numerous intensive studies on CdSe QDs for applications such as light – emitting diodes, laser and biological labels (G.W.Huang *et al*,2004 ; V.I.Klimon *et al*, 2000 ; P.Guyot *et al*,1998 ; M.J.Bruchez *et al*, 1998 ; Y.M.Sung *et al*, 2006).

It has shown that at the initial nucleation and growth stage, the size of nanocrystals is primarily determined precursor concentration capping ligand and procures anion types, and temperature (E.M.Wong *et al*, 2001). However after nucleation and growth , ripening dominates between the nanoparticles. The final size of nanocrystals is thus determined by the temperature and the time period of repening, as well as the colour of the emitting light (N.A.Hamizi and M.R.Johan , 2010).

Experimental

Synthesis of colloidal CdSe nanoparticles

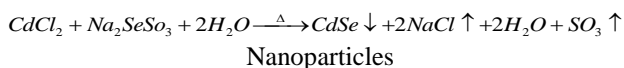
The cadmium selenide CdSe nanoparticles were prepared as a colloidal by chemical reaction of sodium selenosulfide (Na_2SeSO_3) and cadmium chloride CdCl_2 with 0.1gm gelatin of 40mM at different molar ratio (1:1, 1:2, 1:4) and agitated continuously at temperature until the

*Corresponding author: Thekra K. Abd Al Raheem

Table 1: Illustrated the different concentrations of CdSe Miller indices , intensity , 2θ , FWHM , interplaner distance (d), grain size and crystal structure

Cd:Se concentration	Hkl	I/Io	2θ	β(FWHM)	d (nm)	Grain size (G.S) (nm)	Crystal structure
			(degree)				
1:01	111	100	26.3112	1.9	0.33845	5.044703	zinc-blende
1:02	111	100	25.9493	2	0.343088	4.341128	zinc-blende
1:04	111	100	25.8058	2.18	0.344763	3.859279	zinc-blende

CdSe nanoparticles were formed. The resulting solutions were obtained by adding ethanol followed by centrifugation as shown in the following equation:



The Cd²⁺:Se²⁺ ratios indicated are the molar ratios of (CdCl₂) solution to (Na₂SeSO₃) solution. During the experiment the concentration of Cd²⁺ and Se²⁺ ions in the final solution is adjusted by changing the volume of CdCl₂ solution while holding the volume of Na₂SeSO₃ solution is constant.

Preparation solutions

Sodium selenosulfide (Na₂SeSO₃) was chosen as the selenium source. Na₂SeSO₃ solution 20mM was prepared by mixtuing 2mmol selenium powder and 4mmol Na₂SO₃ in 100ml dionized water at 80°C for three hour and final solution was adjusted to 20mM.

Results and discussion

To study the CdSe Nano-particles crystallites structure prepared by chemical reaction method X-Ray diffraction spectrum method was using (XRD-6000 labx, supplied by shimadzu, X-Ray source is CuKα) as X-ray instrument. The x-ray as a widely used method to determine the dimensional parameters for crystals and for the estimation of quantum dot size. For this purpose the following equation, known as the scherrer equation is used:

$$G.S = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

Where G.S is the grain size, λ is the wavelength for X-ray source is CuKα = 1.5406Å , β is the full width at half maximum (FWHM) θ is the diffraction angle

Fig.(1) shows XRD patterns of three CdSe thin films obtained by size selective process. It can be noticed from the x-ray diffraction that all three samples have the same diffraction pattern. These diffraction features appearing at about 26° and 42° correspond to the (111) and (220) planes to the zinc-blende phase CdSe (JCPDS file No.19.0191). The average particle size estimated from the broadening of XRD patterns with scherrer formula (5,4.3 and 3.8)nm with different molar CdSe ratio (1:1, 1:2 and 1:4) respectively.

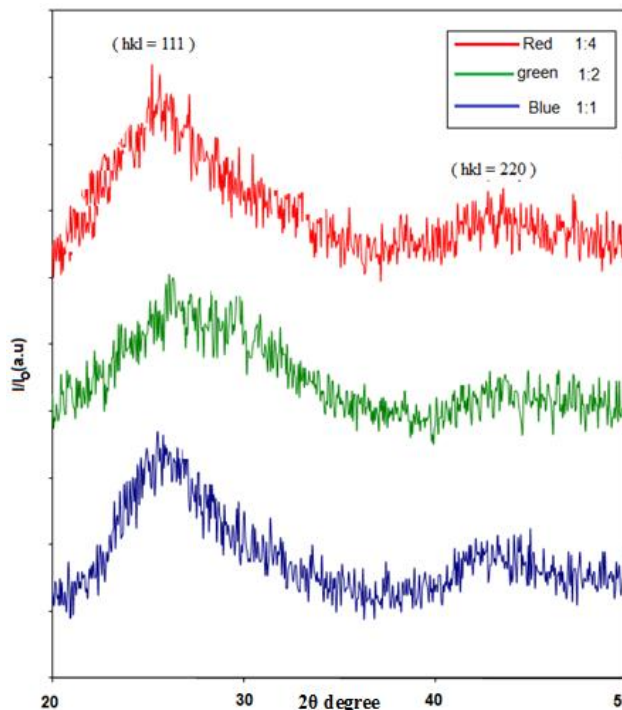


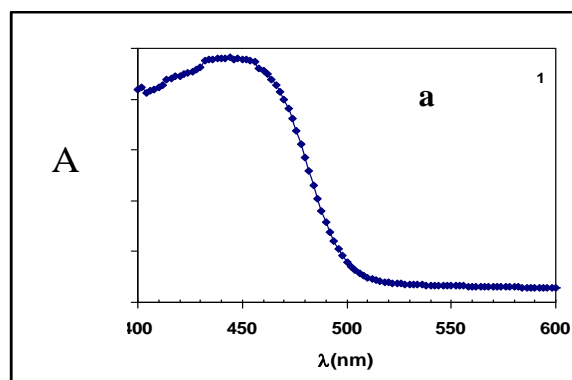
Fig. 1: X-ray diffraction pattern of CdSe nanoparticles at different Se concentrations

The x-ray peaks and their band width are illustrated in table (1). The listed table contains the corresponding grain size of the prepared nanoparticles measured according to the scherrer equation.

The formation structures are in the Nano-dimension this evidence is usually recommended by other authors (G.Preeti and M.Ramrakhiani , 2009).

Optical properties

The optical properties of the prepared CdSe Nanoparticles has been investigated.



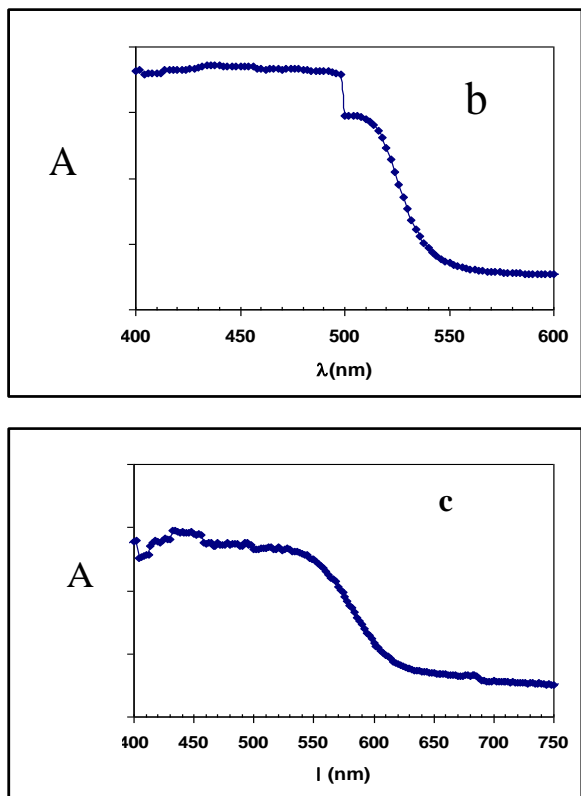


Fig.2: UV-Visible absorption spectrum of CdSe nanoparticles at different Se concentration a)1:1 b)1:2 c)1:4

The properties include the UV –Visible absorption, transmission spectra of the product.

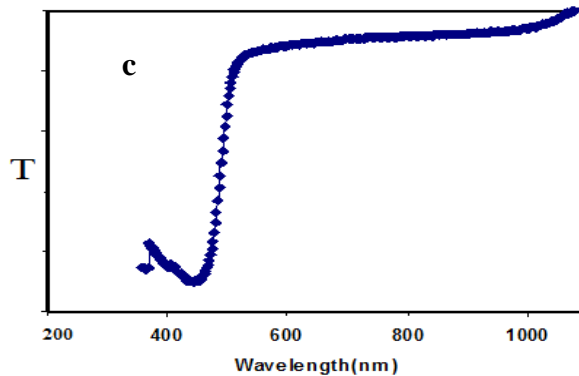
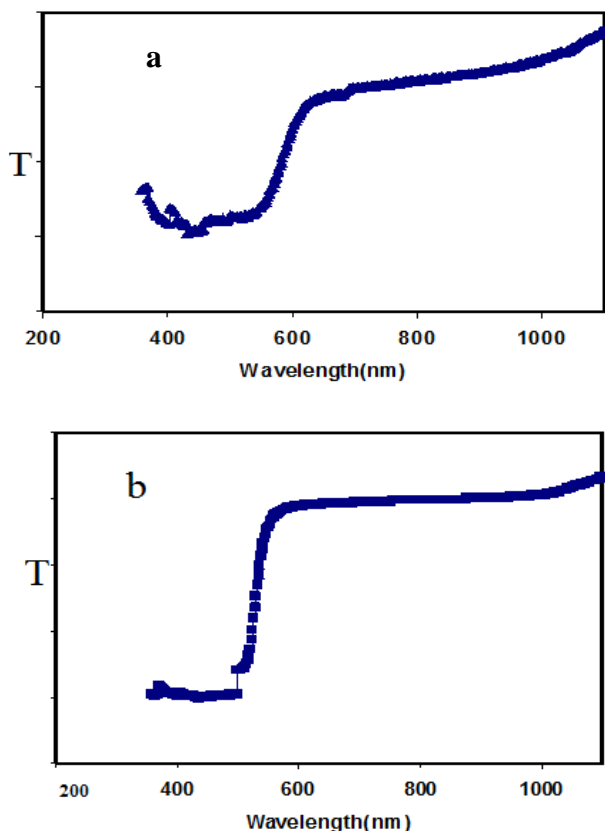


Fig.3: Transmission spectrum of CdSe nanoparticles at different Se concentration a)1:1 b)1:2 c)1:4

The UV –Visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum sized particles. The absorption and transmission spectra of the CdSe Nanoparticles are shown in Fig.(2) and (3) respectively. These figures show that the absorbance will be increase with increase the Se concentration while the transmission will be decrease correspondingly.

The optical energy gap calculation

The UV-visible absorption spectrum of semiconductors is mainly a particle size dependent , which give size to calculate the mean nanoparticles size . The optical energy gap (E_g) of the semiconductor is calculated from Tauc relation can be used to estimate the nanoparticles size as follows

$$\alpha h\nu = \beta(h\nu - E_g)^r \tag{2}$$

Where β is constant , r is a parameter that has different values (1/2, 3/2) for direct transition allowed and forbidden respectively or (2,3) for indirect transition allowed and forbidden respectively .

Then the crystal size or nanoparticle size (diameter) was calculated from energy gap using equation as follow

$$\Delta E(eV) = \frac{\pi^2 \hbar^2}{2m^* r^2} \tag{3}$$

$$\Delta E = E_{q.dot} - E_{g.bulk} \tag{4}$$

Where $E_{q.dot}$ is quantum dot energy band gap, $E_{g.bulk}$ is bulk energy band gap

m^* is effective mass for crystal

r is radius of quantum dot

A plot of $(\alpha h\nu)^2$ versus $h\nu$ shows intermediate linear region , the extrapolation of the linear part can be used to calculate the E_g from intersect with x- axis as shown in Fig.(4) . The resultant values of E_g for CdSe at different ratio molarity of Se concentration is found to be varied from (1.8- 2.5)eV.

The particle size of CdSe quantum dots can be assessed from the absorption wavelength of UV-visible spectra by using Hyperbolic band model (K.Vishwakarma et al, 2010).

Table 2: Optical parameters like absorption coefficient α , extension coefficient k , refractive index n , real and imaginary dielectric constant (ϵ_r, ϵ_i) and energy gap E_g , Absorbance (A), Transmittance (T) and Reflectance (R) at ($\lambda=650\text{nm}$)

Molar ratio of CdSe	$\alpha \times 10^4 \text{ cm}^{-1}$	K	n	ϵ_r	ϵ_i	$E_g(\text{eV})$	Particle size (nm)	A	T	R
1:1	126.96	6.57	7.92	19.5	104.08	1.8	45	0.5	0.244	0.186
1:2	36.54	1.89	3.01	5.5	11.39	2.3	56	0.164	0.785	0.051
1:4	28.277	1.46	2.50	4.13	7.33	2.5	57.8	0.126	0.896	-0.022

$$R_{\text{parical size}} = \sqrt{\frac{2\pi^* h^2 E_{gb}}{m^* (E_{gn}^2 - E_{gb}^2)}} \tag{5}$$

Where R = quantum dots radius (2R is the diameter and hence, indicates particle size)
 E_{gb} =bulk band gap (1.74 eV for CdSe)
 E_{gn} =quantum dots band gap (calculated from the absorption peak).
 h =blank's constant
 m^* = effective mass of specimen (1.18X10⁻³¹ Kg) for CdSe .

The resultant values of E_g and partical size were found to increase with increasing molar ratio of CdSe concentration and others optical parameters as tabulated in table (2). The results of the energy gap are incomparable with the theoretical calculation which has been done by using Density functional theory (M.T.Hussain *et al* , 2013).

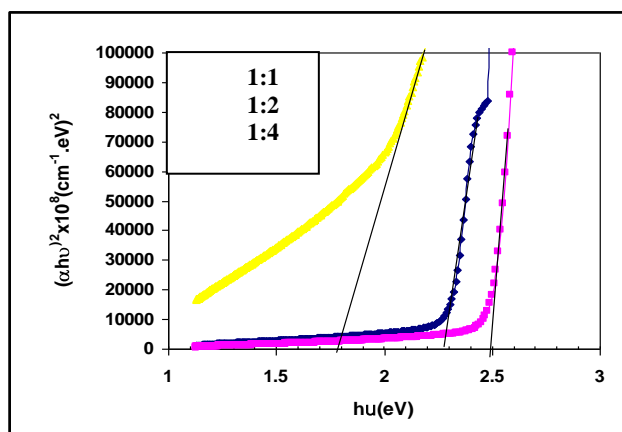


Fig. 4: $(\alpha h\nu)^2$ versus photon energy for CdSe nanoparticles of different Se concentration

Atomic force microscope (AFM)

It is well known that the atomic force microscope (AFM) is one of the effective ways for the surface analysis due to its high resolution and powerful analysis software. The CdSe at different ratio of Se thin films were morphologically characterized using Atomic Force Microscopy (AFM) technique. Figure 5 and Figure 6 shows the two and three-dimensional representation of 1000X1000nm area of the CdSe at different ratio of Se thin films deposited at room temperatures. The grains are made of different sizes varying from 132 to 91 nm. However, the sizes of the grains are noticed to decrease as the Se ratio is increased from 1:1 to 1:4. From AFM

image, the grain density increased indicating the higher grains agglomerate together to form smaller grains of these films.

On the other hand, the surface roughness and Root Mean Square (RMS) of the films were measured using AFM technique. The surface roughness defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness. The surface roughness is unavoidable since the grains are grown with different sizes. It can be seen that the surface roughness and RMS values increase from 0.897 to 1.09nm with increasing Se ratio indicating a decrease in the grain size.

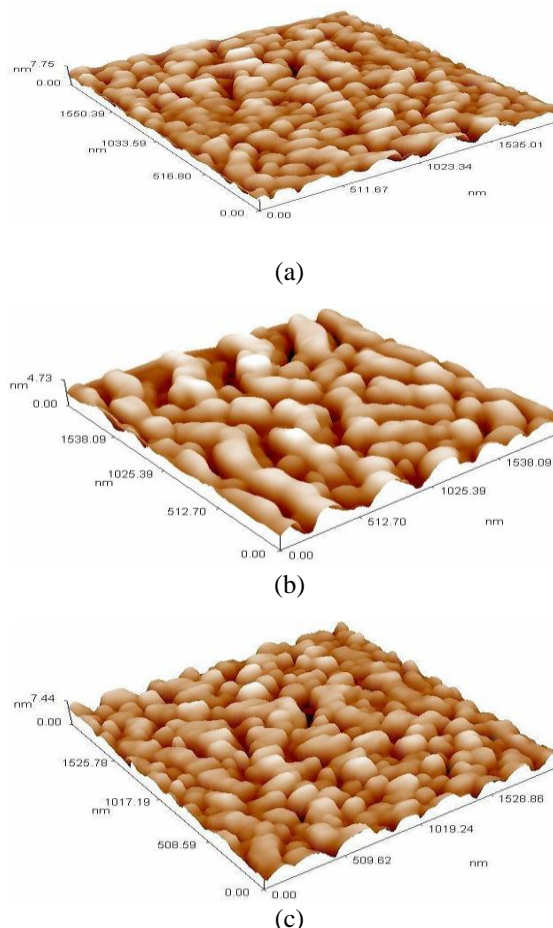
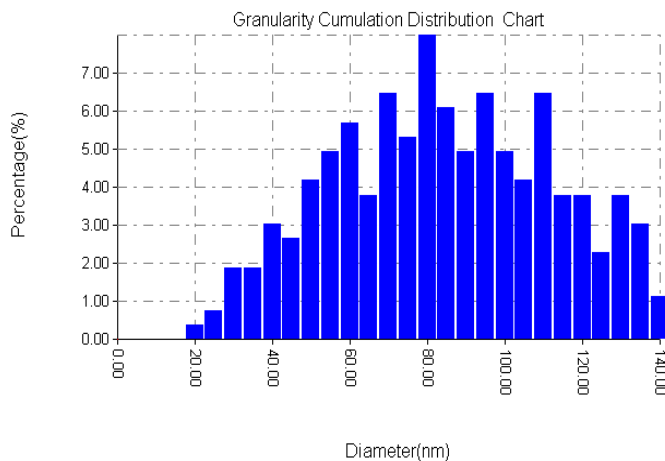
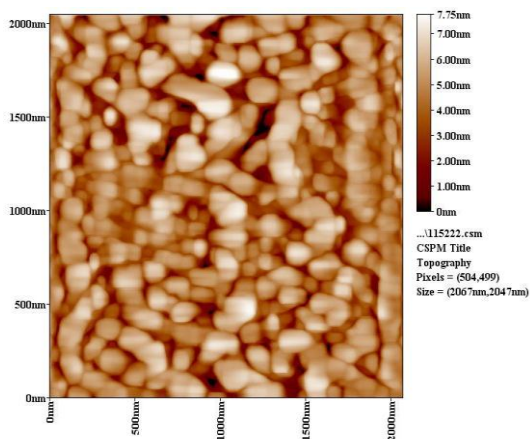
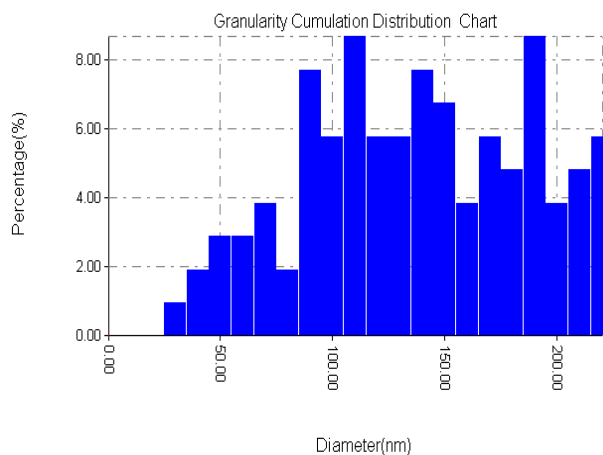
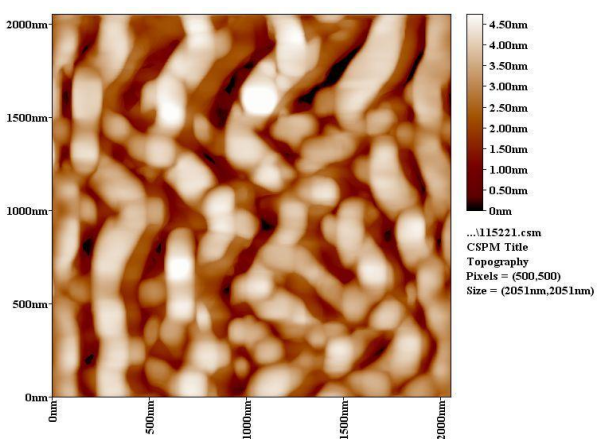


Fig. 5: The AFM image of the surface morphology of the CdSe nanoparticles films at different Se concentration a)1:1 b)1:2 c)1:4

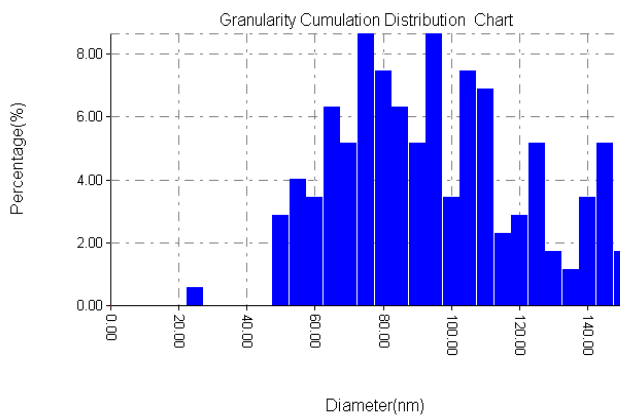
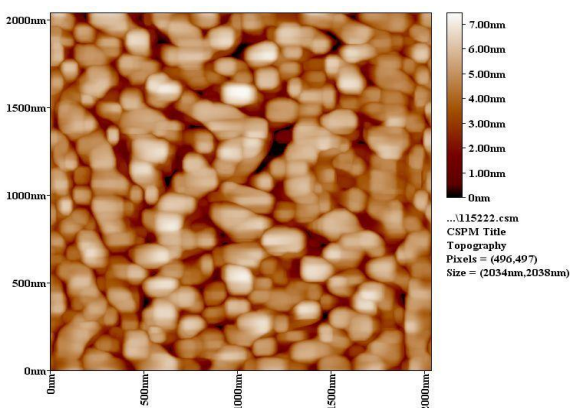
The results are obtained from AFM of CdSe nanoparticles with different Se concentration in 2D and histogram as a function of the grain size as shown in fig.(6) :



(a)



(b)



(c)

Fig.6: AFM of CdSe nanoparticles with different Se concentration in 2D and histogram as a function of the grain size , a)1:1 b)1:2 c)1:4

The AFM measurements indicates that CdSe will be change from spherical forms to a nanotube and come back again to spheres with different Se concentration.

D.C conductivity and Hall effect measurements

In order to study conductivity mechanisms, it is convenient to plot logarithm of the conductivity (ln σ) as a function of 1000/T for CdSe thin films in the range (303 – 453) K at ratio of 1:1 as shown in Fig. (7). It is seen that

resistivity decreases with temperature, indicating semiconducting nature of films.

The thermal activation energy was calculated using the relation

$$\rho = \rho_o \exp(E_a /KT) \tag{5}$$

Where, ρ is resistivity at temperature T, ρ_o is a constant (resisitvity at 0 K), K is Boltzmann constant (8.62 × 10⁻⁵ eV/K) and E_a is the activation energy required for conduction.

Table 3 The Variation of D.C conductivity parameters of CdSe thin films at concentration (1:1)

CdSe	$\sigma_{RT} (\Omega.cm)^{-1}$	$R_H (cm^2/c)$	$n_H (cm)^{-3}$	$\mu (cm^2/V.s)$	Type
1:1	1.15×10^{-5}	-4.66×10^7	1.34×10^{11}	539	n-type

Also it is clear from the figure that there are two transport mechanisms, giving rise to two activation energies E_{a1} and E_{a2} . At higher temperature range (393 – 453) K the value of E_{a1} is 0.699eV, the conduction mechanism is due to carrier excited into the extended states beyond the mobility edge and at lower temperature range (303 – 388) K; the value of E_{a2} is 0.04eV, the conduction mechanism is due to carrier excited into localized states at the edge of the band.

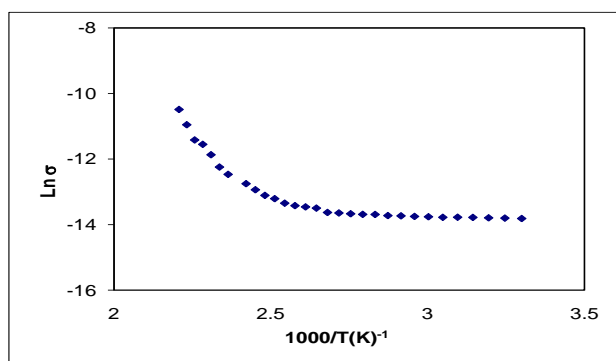


Fig.7: Ln σ versus 1000/T for CdSe thin films at ratio of (1:1)

These observations may be due to size effects that are arising because of quantum confinement of charge carriers within the particles.

Also from Hall measurement, It is observed that the type of concentration is n-types, and the conductivity, Hall coefficient and mobility have been calculated as in table (3).

Conclusions

The following conclusions can be drawn from the results of the studies on the effect of the Se concentration on CdSe nanoparicles prepared by chemical reaction .

- 1- Colloidal II-VI Zinc-blende CdSe nanoparticles can be synthesized by chemical method with narrow size distribution.
- 2- The average particle size is reduced by increasing se ratio.
- 3- In absorption spectrum, peak is obtained in visible region and shift towards lower wavelength by increasing se ratio. This indicates increase in effective band gap.
- 4- For smaller average size, there is larger distribution of nanocrystalline sizes , causing broadening of XRD peak.
- 5- The D.C conductivity and Hall effect measurement indicate that the conductivity of CdSe nancrystals increase with temperature with n-type semiconductor.

Acknowledgment

The authors like to thanks Dr.Eman M.Naser for her helps and discussion at physics department – College of Science, university of Baghdad

References

Kapitonov, A.M.Stupak, A.P.Gaponenko, S.V.Petrov , E.P.Ragach, A.C.Eychmiller,(1999); A Luminescence nproperties of thiol stabilized CdTe nanocrystals, J.Physics. Chem.B,103,10109.

Y.Donazhi, CQifan and X.Shukun, J.Lumin , (2007), 126,853.

X.G.Peng, J.Wickham and A.P.Alivisator, (1998), J. Am.chem. Soc.120, 5343.

D.Zhengtao,C.Li,T.fanggiong and Z.Bingsuo, (2005), Am. Chem. B.109,16671.

G.G.Yordanov, H.Yoshimura and C.D.Dushkin coll. Surf. A. physicochem , (2008) ,Eng. Aspects, 322 ,177.

H.Mao. J.chem, H. Wang, Z.Li, N.Dai and Z. Zhu , (2005), Physics, E. 27,124.

T.Aichele , I.C.robin, C.Bougerol, R.audre, S. Tatarenko and V.G.Tendeloo,(2007), J.Cryst. Growth ,301,281.

S.J.Rosenthal,J.Mcbride, S.J.Pennycook and L.C.Feldman, (2007) sur. Sci. Rep. 62,111.

L.E.Brus, (1984), J.Chem. Phys. 80,4403

C.B.Murray , D.J.Norris and M.G.Bawendi, (1993), J.Am. Soc.115,8706.

A.P.Alivisatos, (1996) , Science, 271 .

Y.N Xu, and W. Ching, (1993), Electronic, optical, and structural properties of some wurtzite crystals , Physical Review B , 48 , 7, pp 4335-4351.

G.W.Huang, C.Y. Chem. , K.C.Wu, M.O.Ahmed and P.T.Chov, (2004) , J.cryst. Growth, 26

V.I.klimon , A.A.Mikhailovsky, S.XU.A.Malko, J.A.Hollingsworth, C.A.Leatherdale, H.J. Eisler and M.G.Bswendi, (2000) , Science , 290, 314.

P.Guyot. sionnest and M.A.Hines, (1998) , Appl. Phys. Lett.72, 686

M.J.Bruchez , M.Moronne , P.Gin, S.Weiss and A.P.Alivisatos, (1998), science , 281, 2013.

Y.M.Sung, Y.J.Lee and K.S. Park , (2006) , J.Am.chem. Soc. 128, 9002

E.M.wong, P.G.Hortez, C.J.Liang, B.M.shi., G.J.Meger and P.C.Searson , (2001) , Langmuir, 17 ,8362

N.A.Hamizi and M.r.Johan, (2010) , J.Mat. Chem. Phys. 124,395.

G.Preeti and M.Ramrakhiani , (2009) , Influence of the particle size on the optical properties of CdSe nanoparticles The open Nanoscience Journal, Vol.3,pp15-

K.Vishwakarma, O.P.Vishwakarma and M.Ramrakhiani , (2010) , Inter. J. Nanotech 4.

M.T.Hussain , B.A.Hassan, T.K.Abd Al-Raheam and H.B.Jasim, (2013), Study the electronic properties of core – oxidization CdSe nanocystals. J. of (JAIEM) , Vol.2 , Issue 9 , pp 70-76.