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Characterization of CdS nanoparticles Prepared by Liquid – Liquid Interface Reaction

Salma M. Shaban*, Khalad T. Mahdi, Ahmed S. Ahmed

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Abstract

Liquid – liquid interface reaction is one of the method to prepare nanoparticles, the preparation of nanoparticles depends on the super saturation of ions which can satisfy by layered two immiscible liquid (toluene and deionized (DI) water). The XRD-diffraction analysis give a mix structure from hexagonal and cubic and the average grain size is 7.73 nm using Sherrer relation and 9.54 nm using Williamson – Hall method. Transmission electron microscopy (TEM) Showed that the size of particles around 3 nm which is comparable with Bohr radius of CdS.

From UV-Visible spectrum analysis which use two model to estimate the radius of particles , the first one is effective mass approximate (EMA) model and the second one is tight binding model , from the first model the estimated that the radius is 2.069 nm and from the second model. The estimated radius is 1.95 nm which is very comparable with Bohr radius of CdS and this give a strong quantum conferment that distinguish the proper of nano than a bulk.

Keywords: Liquid-Liquid Interface reaction, nanoparticles CdS

خصائص الجسيمات النانوية لكبريتيد الكادميوم المحضرة بتفاعل السطح الداخلي لتماس سائل-سائل

سلمى مهدي شعبان*, خالد طه مهدي، احمد صالح احمد

قسم الفيزياء، كلية العلوم، جامعه بغداد، بغداد، العراق

الخلاصه

تفاعل السطح الداخلي لتماس سائل – سائل هي احدى طرق تحضير الجسيمات النانوية ، تحضير الجسيمات النانوية يعتمد على حالة مافوق الاشباع للايونات والتي يمكن تحقيقها من خلال وضع سائلين غير قابلين للامتزاج احدهما فوق الاخر (التالوين والماء اللابلوني). تحليل حيود الاشعة السينية اعطى مزيج من تركيب المكعب والثماني ومعدل حجم الحبيبة هو 7.73 نانومتر باستخدام علاقة شيرر و 9.54 نانومتر باستخدام طريقة ويلامسون – هول . اما المجهر الالكتروني النافذ (TEM) فقد شخص حجم الجسيمات بحدود 3 نانومتر وهذا الحجم متوافق مع نصف قطر بور لكبريتيد الكادميوم . ولتحليل طيف الامتصاصية ضمن المدى الفوق بنفسجي – مرئي استخدم نموذجين لتقدير نصف قطر الجسيمة النموذج الاول هو تقريب الكتلة الفعالة (EMA) والثاني هو نموذج الحزم المترابطة (Tight binding)، فمن النموذج الاول وباستخدام معادلة بروس تم تقدير نصف القطر بانه يساوي 2.56 نانومترومن النموذج الثاني وباستخدام العلاقة التي اشتقت من قبل سارما وجماعته قدرنا نصف القطر بانه يساوي 1.95 نانومتر وهو جدا متوافق مع نصف قطر بور لكبريتيد الكادميوم وهذا يعطي لنا تقييد كمي قوي الذي هو الصفة المميزة للجسام النانوية عن الاجسام السميكة .

*Email: selmamehdi0@gmail.com

1. Introduction

Nanoparticle is one of the classification of nanomaterial which can be define as three dimensional confinement and its radius is near to the Bohr radius which for CdS is equal to $a_B \approx 3\text{nm}$ [1]. CdS one of the II-IV semiconductors which have a main interest in fabrication of nanoscale device through its potential application which is an important part to build an optoelectronic device such as light-emitting diodes and solar cells [2]. The preparation of nanoparticles needs to prevent the particles to accumulation and aggregation and this can be satisfied through two methods, the chemical and physical method. The chemical method needs to use a capping agent but this may create some difficulties when need to study the behavior of particle with other material such as when inject the nanoparticle in tissue for medical application, the second method is physical method which needs to treat the surface that the particle will react with it and this step needs a high technique equipment. One of the chemical methods that produce nanoparticles without surface surrounding material and without high technique equipment is liquid-liquid interface reaction which depends on the supersaturating principle [3]. There are many factors that can be used to effect on the properties of material, such as the doping and method of preparation, actually in nanoscale, the size plays a main role on the electrical and optical properties which may change dramatically with the reduce of the size, this reducing in size can be controlled through the condition of preparation, the amount of reducing of the size effects on the degree of quantum confinement which is a distinguish properties of nanoparticles. Several workers studied CdS such as L.Hongnan et al. [4] which prepared its films as buffer layer by chemical vapor deposition on SnS and studied the properties of the junction. Moussa and Haider [5] prepared nano CdS by chemical bath deposition and studied the properties of its junction on Si wafers. So in this work report the synthesis of nanoparticle CdS by using the liquid-liquid interface reaction and estimate the size through the analysis of X-ray powder diffraction (XRD), Transmission electron microscopy (TEM) and UV-Visible spectrum.

2. Experimental part

2.1 Method of Preparation

The method used to prepare nanoparticles CdS is liquid-liquid interface reaction need to complete two main steps, the first step is to prepare the precursor which acts as the source of the Cadmium ion and the second step is the reaction at the interface between two immiscible liquid to produce a nanoparticle CdS. the first step need to produce the precursor Cadmium diethyldithiocarbamate, for this aim, the procedure that describe by O'Brien and R.Nomura [6] was applied. This procedure need to finish the following steps:

1. (436 mg) from Sodium hydroxide (NaOH) dissolve in 50 ml methanol (CH_3OH) using a magnetic stirrer.
2. (1.128 ml) diethylamine HN ($(\text{CH}_3\text{CH}_2)_2$) and (0.65 ml) carbon disulfide (CS_2), were added to the solution Produce from step 1. (Note that the solution has a pale yellow).
3. The solution produce from step 2 coole to 4C° , using the refigure for eight hour.
4. Dissolve 1 g of cadmium chloride (CdCl_2) in 50 ml of Methanol (CH_3OH).
5. Add by dropping wisely the solution produce from step 4 to the solution produce from step 3.
6. Put under stirrer for one hour. And then note that there is a yellow solid which represent to produce the precursor.
7. Filtered the solution, then the final output washed by methanol (CH_3OH) then deionized (DI) water and at the last by methanol (CH_3OH).
8. Dry it by oven in the temperature ($65\text{-}70\text{C}^\circ$) for 12 hour

In the Second step, work to prepare the nanoparticles CdS by apply the following steps:

- a. (11.46 mg) of Na_2S dissolve in 50 ml deionized water which consider as the source of sulfide.
- b. (30 mg) of cadmium diethyldithiocarbamate $\text{Cd}(\text{S}_2\text{CN}(\text{CH}_3\text{CH}_2)_2)_2$ dissolved in toluene which act as the source of Cadmium.
- c. Added the toluene to deionize water.
Now one can noticed that two immiscible liquid one above each other and separated by interface layer as shown in the Figure-1.
- d. Put a beaker into an oven held at 65°C and left undisturbed for 24 hour.
At end of this time, a yellow thin film was found adhered to the interface of the two liquids.

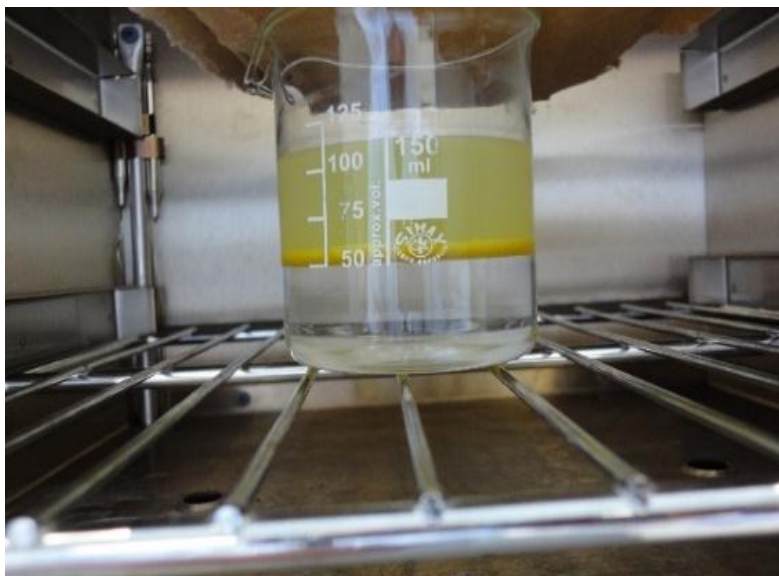
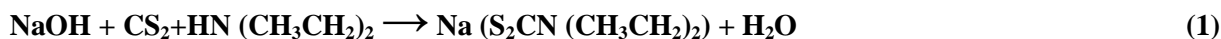


Figure 1 - Two immiscible liquids to get the interface reaction to produce nanoparticles CdS

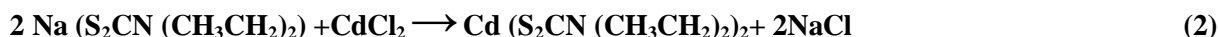
2.2 Procedure of Preparation

The procedure of the previous step can be explained in the following equation:

At the first Sodium hydroxide (NaOH) react with diethylamine ($C_4H_{11}N$) and Carbon disulfide (CS_2) as shown in the following equation:



After cooling Cadmium Chloride was added, then the following reaction was happened:



In this step get the precursor $Cd(S_2CN(CH_3CH_2)_2)_2$ which can be used in the following step to produce nanoparticle CdS as shown in the following equation:

At the first we dissolved Na_2S in deionized water as shown in the following equation:



Then H_2S dissociated according to the following equation:



And at last HS dissociated as in the equation:



All these done in aqueous solution for Na_2S , so the last result is the H^+ and S^{2-}

So when layering toluene above the aqueous solution which contain the $Cd(S_2CN(CH_3CH_2)_2)_2$

The following reaction act in the interfacial layer



3. Results and Discussion

3.1 Analysis of X-ray diffraction pattern

For characterize the structural properties, by using X-ray diffraction pattern a Philips Xpert diffractometer utilizing monochromatic $CuK\alpha$ radiation ($\lambda=0.15406$ nm). From the X-ray diffraction pattern which obtain in Figure-2, can notice that there is a peaks appear at the angles of diffraction as shown in the table .1 equal to ($2\theta = 23.1^\circ, 24.5^\circ, 26.04^\circ$ and 43.8°) attributed to (100), (002), (101) and (103) respectively for hexagonal structure and ($2\theta = 26.6^\circ, 43.95^\circ$ and 52.13°) attributed to (111), (220) and (311) respectively for cubic structure. So can consider that the structure consists of both the cubic and hexagonal form, such mixed phases have been previously reported in chemically deposited CdS nanostructures [7-11]. And the product is free from crystalline impurities

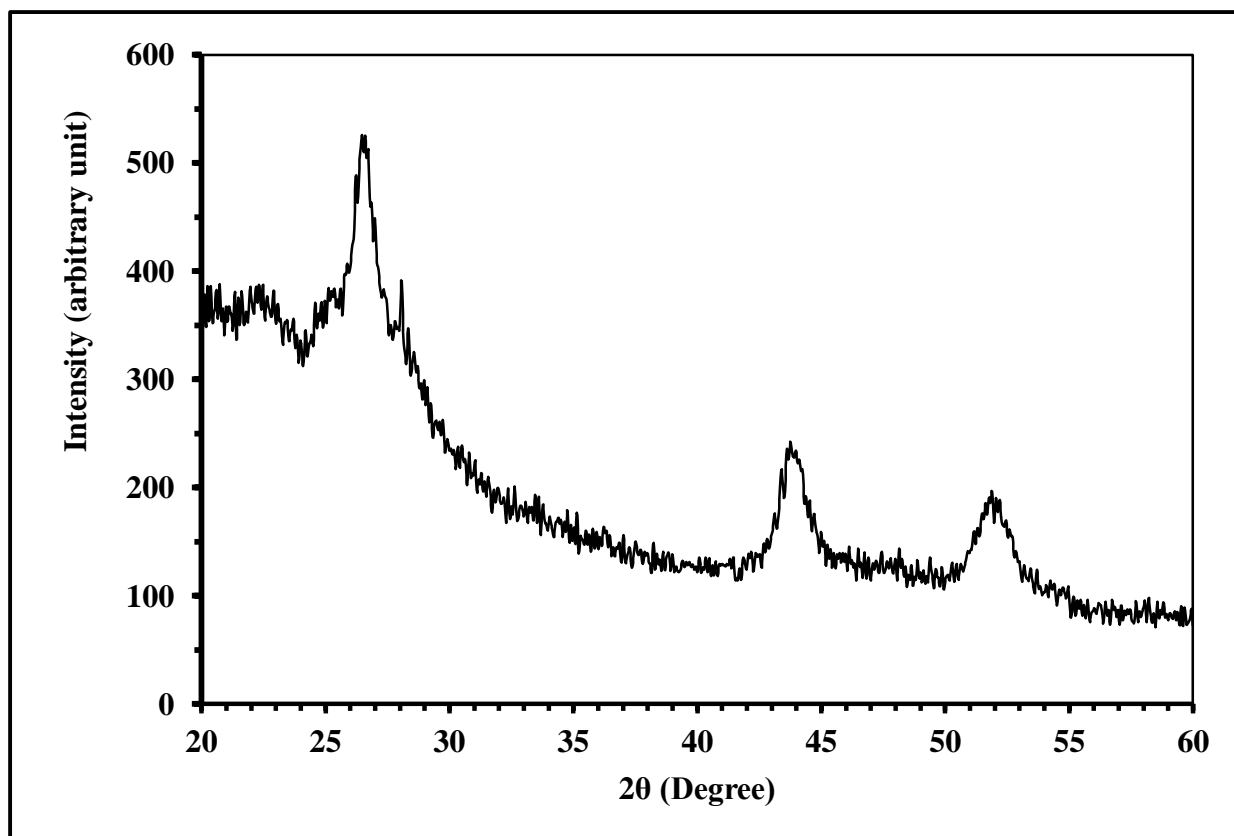


Figure 2 - X-ray diffraction patterns of nanoparticles CdS prepared by liquid – liquid interface reaction

Table 1 - Phase structure of nanoparticles CdS prepared by liquid-liquid interface reaction

$2\theta^\circ$	hkl	Structure phase	JCPDS no
23.1	100	Hexa	04-002-3090
24.5	002	Hexa	04-002-3090
26.04	101	Hexa	04-002-3090
43.81	103	Hexa	04-002-3090
26.6	111	cubic	04-002-3090
43.96	220	cubic	04-002-3090
52.13	311	cubic	04-002-3090

The broadening of the peaks indicates that the size is in the range of a nanosize. The grain size of the particulates can be estimated using Scherer equation:

$$D = 0.9 \lambda / \beta \cos \theta \quad (8)$$

where β is the full width at half maximum in radians, λ is the wavelength of X-ray used and θ the angle of diffraction. And when apply this relation for the diffraction angle that it is clear in Figure-2, the average size of grains was equal to 7.73 nm and this when compare with Bohr radius can note that it is in the range of nanoparticle (two or three multiple of Bohr radius or in the range 2-10 nm).as shown in table.

Table 2 - Grain size from XRD spectrum using Scherer equation

2θ (degree)	FWHM (deg.)	Grain size (nm)
26.6	1.1949	7.9
43.96	1.0584	9.2
52.13	1.6482	6.1

The Scherer's equation may produce results that are different from actual size [12], the broadening of the peaks may be caused by residual stresses that may be present in the grains. There is shifting in the peaks due to the stresses within the crystal causes corresponding strains, which result in a planar spacing. A combination of compressive and tensile strains often results from the residual stresses. In

order to calculate the average crystallite size including strain, adopted the Williamson –Hall method [13], where the strain (ϵ) and crystallite size (D) are related to the measured β , following the equation:

$$\beta \cos \theta / \lambda = K/D + 4\epsilon \sin \theta / \lambda \quad (9)$$

Where β , λ and θ , are the full-width at half maximum (FWHM) of the diffraction peaks, wavelength of the X-ray source and Bragg's angle, respectively, $K=0.9$.

The most prominent peaks as shown in the Figure-2 were analyzed, from the Table-3 and after plot of $(\beta \cos \theta / \lambda)$ versus $(\sin \theta / \lambda)$ can get a straight line as shown in figure.3, The slope of the plot gives the amount of residual strain and equal to 4.7×10^{-3} , whereas reciprocal of intercept on the y-axis give the average particle size equal to 9.54 nm.

Table 3 - The values to apply Williamson –Hall equation

θ	β (rad)	λ (nm)	$\sin \theta / \lambda$	$\beta \cos \theta / \lambda$
13.3	0.0208	0.15406	1.493	0.1314
21.98	0.0185	0.15406	2.429	0.1114
26.07	0.0288	0.15406	2.852	0.1679

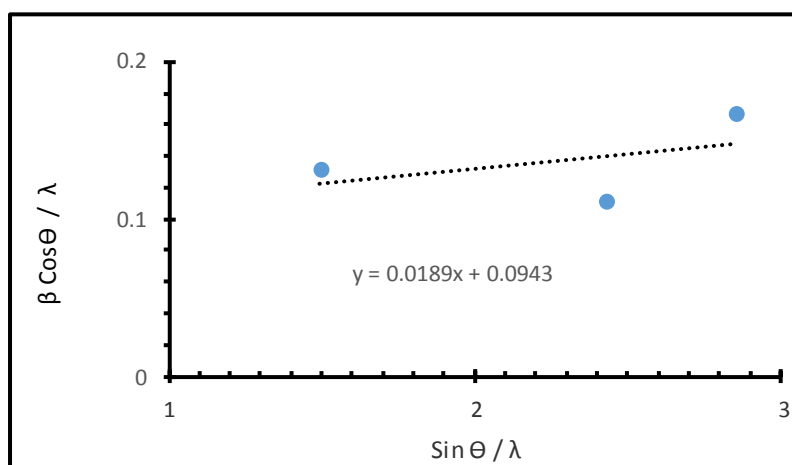


Figure 3 - Williamson –Hall plot to determine the particle size and strain of nanoparticles CdS

3.2 Transmission electron microscopy

Transmission electron microscopy image gives us more details about the structure. From the picture in Figure-4, can consider that the average size of the grain is around 3 nm which gives a strong comparable with Bohr radius of CdS.

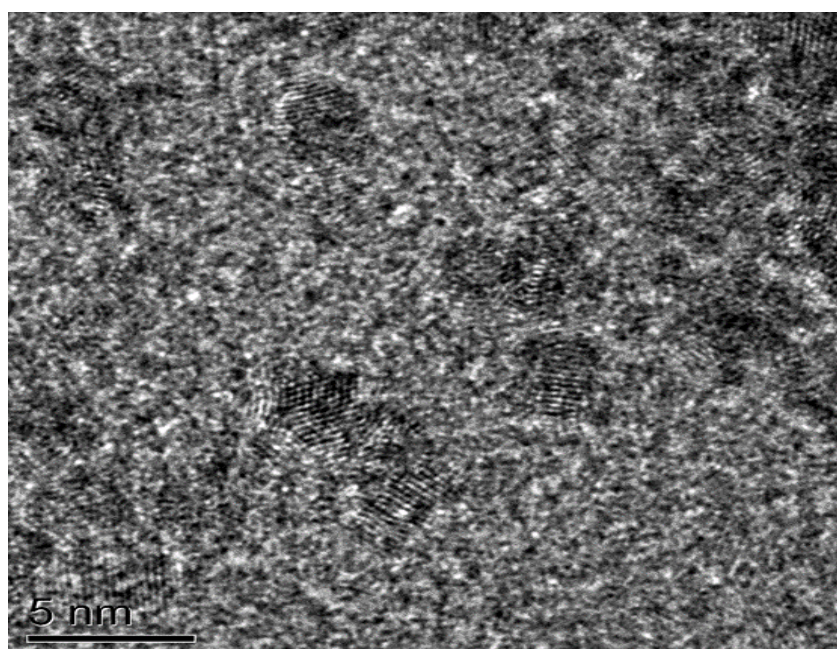


Figure 4 - Transmission electron microscopic images of nanoparticles of CdS

3.3 Optical Energy Gap and Nanoparticles Size

From Tauc relation which obtained in equation 10, can determine the optical band gap as:

$$\alpha h\nu = A (h\nu - E_g)^n \quad (10)$$

Where A is constant, E_g is the band gap and $n=0.5$ for direct band transition. The energy gap E_g are determined from plotting of $(\alpha h\nu)^2$ vs $h\nu$ as shown in Figure-5. The energy gap from Figure-5 is equal to 3 eV, the blue shift in band gap (2.42 eV for bulk) represents to reducing in the size which led to the quantum confinement. From effective mass approximate (EMA), can estimate the nanoparticles size by using the following equation:

$$\Delta E_g = E_{g(np)} - E_g = \frac{\hbar^2 \pi^2}{2R^2 \mu} \quad (11)$$

Where $\hbar = h/2\pi$, h = plank constant, R =radius of the nanoparticle μ is the reduce mass, $1/\mu = 1/m_1 + 1/m_2$, $m_1 = m_e^*$ effective mass of electron, $m_2 = m_h^*$ effective mass of hole $m_e^* = 0.21 m_e$, $m_h^* = 0.8 m_e$ for CdS, and m_e is the rest mass for electron.

For E_g (nanoparticle) = 3 eV that is $\Delta E_g = E_{g(np)} - E_g(\text{bulk}) = 3 - 2.42 = 0.58$ eV, get that $R = 2.069$ nm that is diameter = 4.138 nm.

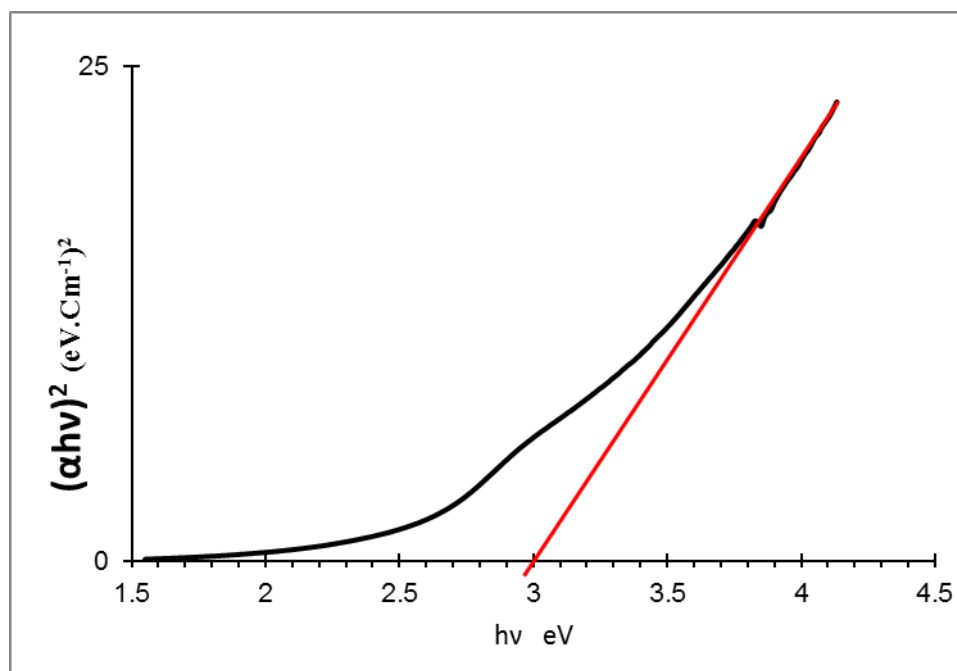


Figure 5 - $(\alpha h\nu)^2$ as a function for $(h\nu)$ for nanoparticles CdS prepared by liquid – liquid interface reaction

Another model to estimate the size is the UV – Visible spectrum. This model which is proposed by Viswanatha and Sarma [14-17] was followed in order to estimate the mean diameters of the nanocrystals using the absorption spectra. The UV absorption spectrum for CdS is shown in Figure-6a. Differentiation of this absorption spectrum yields the curve shown in Figure-6b. In order to obtain the position of absorption maxima, Gaussian function fitting of absorption spectra was performed, as shown in Figure-6b. To apply this method, the position of the peak energy E_0 is obtained using the first derivation of the curve. The E_0 is translated as d (average) [18] by the use of the formula

$$\Delta E_g = 1/ad^2 + bd + c \quad (12)$$

where a, b and c are constants that depend on the identity of the semiconductor, for CdS their values are 0.1278, 0.1018 and 0.1821 respectively. Here, ΔE_g is the observed shift in the band gap (E_g) given by $E_0 - E_g$. E_1 and E_2 can be translated to sizes (d_1 , d_2). Which, E_1 is $(E_0 - \text{FWHM}/2)$ and E_2 is $(E_0 + \text{FWHM}/2)$. The main diameter (d), is obtained by solving equations. Then can define the apparent and real relative percentage distribution according to these equations:

$$\Delta D_{\text{app}} \% = (d_1 - d_2)/d_{\text{av}} \times 100 \quad (13)$$

$$\Delta D_{\text{real}} \% = A \times (\Delta D_{\text{app}})^2 + B \times \Delta D_{\text{app}} + C \quad (14)$$

Where: $A = -0.0025$, $B = 0.524$, and $C = -1.41$.

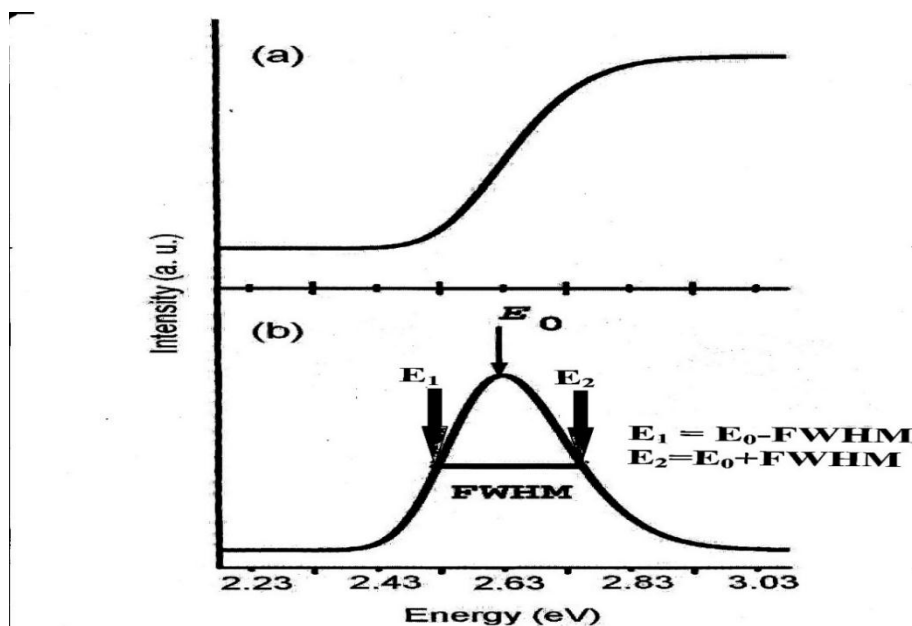


Figure 6 - Exhibits (a) Electronic absorption spectrum of CdS nanocrystalline, (b) The inset Gaussian fitting of the spectra of the CdS nanocrystalline [18]

Figure-7, shows that $E_0 = 2.8$ eV, $E_1 = 2.6$ eV, $E_2 = 3$ eV, then we can get $d_0 = 3.9$ nm, $d_1 = 5.7$ nm, $d_2 = 3$ nm. From ($E_0 = 2.8$, $d_0 = 3.9$ nm), one can note a strong comparable with Bohr radius and this gives a strong quantum confinement. As know that the size increases with temperature and with time, so can say that the sharper in the peaks led to the better in the size distribution, so from the value of $\Delta D_{app}\% = 69.2$ and $\Delta D_{real}\% = 49.66$ note that have a high percentage of appear and real distribution and this refer that have a good distribution, and this can clearly understood from Equation 13 that when the result of $(d_1 - d_2)$ is close to it then can have large value of ΔD_{app} and $\Delta D_{real}\%$ and so can say that the liquid – liquid interface reaction is a suitable successful method to give a nanoparticles with little amount in distribution of the size and this one of the problem when need to synthesis of nanoparticles.

$$\Delta D_{app}\% = (d_1 - d_2)/d_{av} \times 100$$

$$\Delta D_{app}\% = (5.7 - 3)/3.9 \times 100 = 69.2$$

$$\Delta D_{real}\% = A \times (\Delta D_{app})^2 + B \times \Delta D_{app} + C$$

$$\Delta D_{real}\% = (-0.0025) \times (69.2)^2 + (0.524 \times 69.2) + (-1.41) = 49.66$$

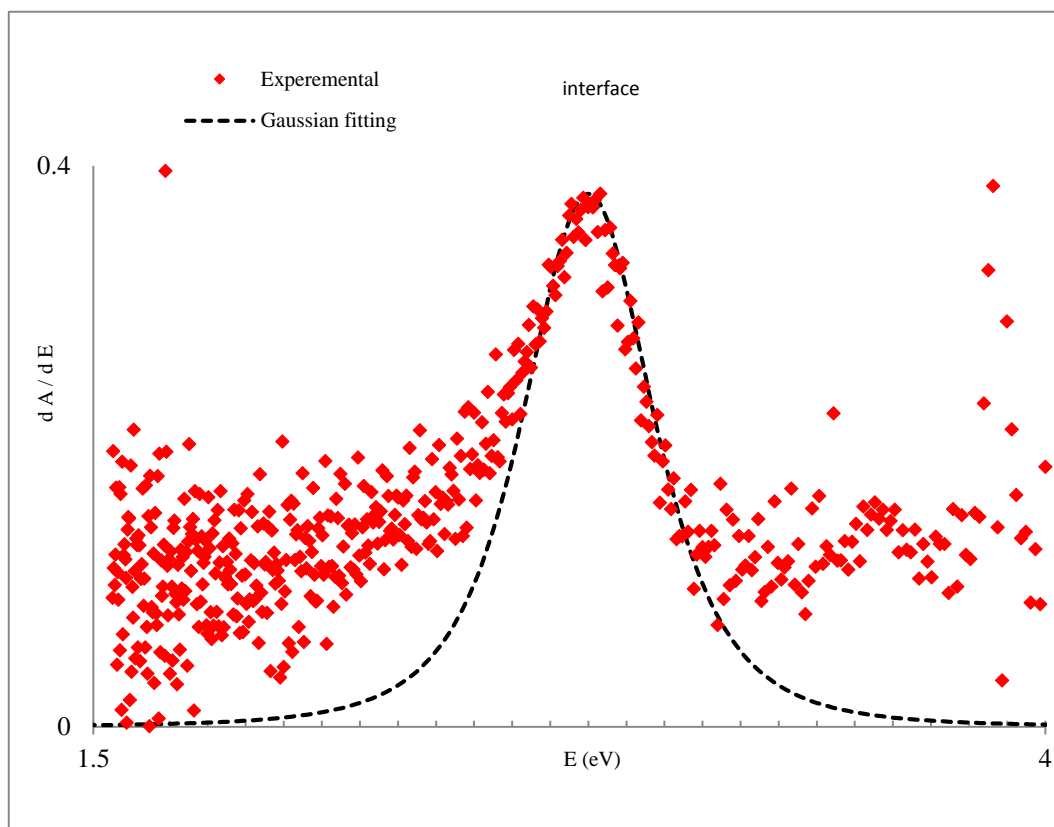


Figure 7 - Derivative of absorbance with respect to energy as function of energy

Now can put the table for the radius value that estimate from different type of analysis as shown in Table-3, and from this Table can note that the result that get from tight binding model has a less deviation from the result that get from TEM measurement, so can consider this result is an accurate result, behind the accurate that came from the theoretical calculate of the model

Table 4 - Estimate the radius of particles using different method

	Technique for estimate	Model or equation to estimate	d nm
NP'S CdS	XRD	Sherrer	7.73
NP'S CdS	XRD	Williamson –Hall	9.54
NP'S CdS	TEM	Scale of image	5
NP'S CdS	UV	EMA	4.138
NP'S CdS	UV	TB	3.9

4. Conclusions

Liquid - liquid interface reaction is a method to prepare nanoparticles with less amount of impurity and good distribution of size. Can estimated the radius of particle from XRD pattern, TEM measurement and UV-Visible spectrum. From XRD pattern was estimate the radius of particle using tow equation the first one is Sherrer equation and the second is Hall-williasmon equation which take car off in the strain effect on the size .The TEM gives an actual size of particles without using mathematical model. From UV-Visible spectrum two model have been used one depend on effective mass approximate and the second depend on tight binding energy model and from this two model get a radius that is very comparable with Bohr radius.And when compared the radius from all method of calculation reach that all value is in the range of nanosize and comparable with Bohr radius of nanoparticles of CdS

References

1. Zou, Y., Li, D. and Yang, D. **2010**. noninjection synthesis of Cd and alloyed CdS_xSe_{1-x} nanocrystals without nucleation initiators, *Nanoscale Res Lett.*,5(6), pp:966-971.
2. Dongre, J., Nogriyas, V., Ramrakhiani. M. **2009** Structural, optical and photo electrochemical characterization of CdS nanowire synthesized by chemical bath deposition and wet chemical etching., *Applied Surface Science*, 255(12), pp:6115-6120.
3. Albrasi, E., Thomas, J. p .O'Brien. **2012**. Deposition of nanostructured films of CdSe and CdS Using Three Layered water–oil–amphiphile/salt system, *J.Mater.Chem.C* , 1(4),pp:671-676.
4. Hongnan, Li., Cheng,S., Zhang, J., Huang, W., Zhou, H. , Jia, H. **2015**. Fabrication of CdS/SnS Heterojunction For Photovoltaic Application, *World Journal of Condensed Matter Physics*,5, pp:10-17.
5. Mousa, A. and Haider, A. **2011**. Performance of a Nano CdS/Si Hetrojunction Deposited by CBD, *Journal of Materials Science and Engineering*,A. 1, pp:111-115.
6. P.O'Brien and Nomura.**1995**. Single-molecule precursor chemistry for the deposition of chalcogenide (S or Se)- containing compound semiconductors by MOCVD and related methods. , *J.Mater.Chem.* 5, p: 1761.
7. Kim, D.J., Yu,Y., Lee,J. and Ghoi,Y. **2008**. Investigation of energy gap and optical properties of Cubic CdS epilayers., *Appl. Surf. Sci.*, 254(22), pp: 7522-7526.
8. Ramaiah, K. , Pilkington, K. Hill, A. Tomlinson A. R. and A.Bhatnagar, A.**2001**. Structural and Optical Investigations on CdS thin films grown by chemical bath technique. *J. Mater. Chem.Phys.* 68(1), pp: 22- 30.
9. Mahanty, S. Basak, D. Rueda, F. and leon, M. **1999**. Optical properties of chemical bath deposited CdS Thin films. , *J.Electron.Matter*, 28(5), pp: 559 -562.
10. Lo, Y., Choubey R., Yu, W., Hsu W. and Lan, C. **2011**. Shallow bath chemical deposition of CdS thin Films, *Thin Solid Film.S*, 520(1), pp: 217 – 223.
11. Cao G. **2004**. *Nanostructure and Nanomaterials*, First Edition, Imperial College Press, London.
12. Williamson,G.K., Hall, W.H.**1953**. X-ray line broadening from filed aluminium and wolfram L'elargissement desraies de rayons x obtenues deslmailles d'aluminium et de tungstene Die verbreiterung der roent geninterferenzlinien von aluminium- und wolframspaenen, *Acta Metal*, 1., pp:122-131.
13. Viswanatha, R. Sapra, S. Satpati, B., Satyam, P., Dev, B. and Sarma, D. **2004**. Understanding the quntum Size effect in ZnO nanocrystals, *J. Mater. Chem.* ,14(4), pp: 661-668.
14. Sapra, S., and Sarma, D.D. **2004**. Evolution of the electronic structure with size in II- VI semiconductore nanocrystals. , *Phys. Rev. B*, 69(12), p: 125304.
15. Viswanatha,R. Sapra,S. Saha-Dasgupta,T. and Sarma,D.D. **2005**.Electronic structure of and quantum size effect in III-V and II-VI semiconducting nanocrystals using a realistic tight binding approach, *Phys. Rev. B*, 72(4):045333.
16. Viswanatha, R., Sapra,S. , Gupta,S. Satpati,B., Satyam,P., Dev,B., and Sarma, D. **2004**. Synthesis and characterization of Mn doped ZnO Nanocrystals., *The Journal of Physical Chemistry B*, 108(20), pp: 6303-6310.
17. Sapra, S.,Shanthi,N., and Sarma, D. **2002**.Realistic tight-binding model for the Electronic structure of II- VI semiconductors. *Physical Review B*, 66(20), p: 205202.
18. ALBrasi, E. **2012**. The growth and characterization of films of noble metal nanocrystals and inorganic semiconductors at the interface of two immiscible liquids, Ph.D. Thesis, School of Chemistry, Faculty of Engineering, University of Manchester, Manchester, United Kingdom.