تركيب أغشية رقيقة من كبريتيد الكادميوم بلوراتها الجسيمية في حدود النانو بتقنية الحمام الكيميائي ودراسة خواصها التركيبية والضوئية

عبد الله الحسام [1] ، صلاح عبد الجبار جاسم [2]

قسم الكيمياء [1] ، كلية العلوم التطبيقية ، جامعة ذمار، اليمن
قسم الفيزياء [2] ، كلية العلوم التطبيقية ، جامعة ذمار، اليمن

الملخص:

رسبت أغشية رقيقة من كبريتيد الكادميوم بلوراتها الجسيمية في حدود النانو بطريقة الحمام الكيميائي على شرائح زجاجية وكانت درجة حرارة الترسيب $80^{o}C$ وزمن الترسيب $6h$ باستخدام تركيبتين مختلفتين من اليوريا الكبريتية. وقد تم التعرف على جميع متغيرات الحمام الكيميائي والتي أعطت أغشية رقيقة بلوراتها الجسيمية في حدود النانو. أثبتت تحليلات الخواص الضوئية أن فجوة الطاقة للأغشية المحضرة عانت انحراف باتجاه اللون الأزرق كما حسبت البلورات الجسيمية للأغشية المحضرة وتراوحت قيمها بين 3.826 الى 8 نانومتر.

Synthesis, structure, and optical properties of CdS thin films nanoparticles prepared by chemical bath technique

Abdullah M.A. Al-Hussam [a], Salah Abdul-Jabbar Jassim [b],*

[a] *Chemistry Department, Faculty of Applied Science, Thamar University, Thamar, Yemen*
[b] *Physics Department, Faculty of Applied Science, Thamar University, Thamar, Yemen*

Abstract CdS nanocrystalline thin films were deposited onto glass substrates by chemical bath deposition (CBD). The films deposited at 80 °C for 6 h with two different concentrations of thiourea. The deposition parameters were optimized. The obtained films were characterized for structural and optical properties, X-ray diffraction patterns revealed that the films were nanocrystalline in nature with cubic structures. A blue shift in the band gap was observed in the UV–visible absorption spectra indicating the formation of nano particles of sizes between 3.826 and 8 nm.

1. Introduction

Semiconductors nano-particles (also known as quantum dots), belong to state of matter in the transition region between molecules and solids, have attracted a great deal of attention because of their unique electrical and optical properties, compared to bulk materials (Alivisatos, 1996). Their electrical and optical properties are directly associated with the quantum confinement of charge carriers leading to the blue shift of the band gap with the shrinkage of their size (Kotkata et al., 2009). Particularly When the dimension of the semiconductor quantum dots

reduced close to characteristic length known as the exciton Bohr diameter, these characteristic lengths are usually in the range of a few nanometers, there will be large changes in their properties, this effect changes the surface to volume ration and it also shifts electronic energy levels towards higher energy leading to an increase in the band gap (Alivisatos, 1996). CdS as a semiconductor material has received much attention due to its direct band gap resulting in emission in the visible wavelength. CdS nanostructures are being widely investigated for applications in semiconductor laser (Dunan et al., 2003), nonlinear optical devices (Grohs et al., 1994), biological applications (Santos et al., 2008) display devices (Schmitt-Rink et al., 1989) and as window materials for hetero-junction solar cells because it has a high absorption coefficient (Xiaoxia et al., 2010).

In recent years, considerable efforts have been made to synthesize CdS nanostructures by several methods such as, dc- sputtering (Ghosh et al., 2006), solvothermal route (Ujjal et al., 2003), sonochemical (Raghvendra et al., 2010) and chemical bath deposition (Dongre et al., 2009). The chemical bath deposition (CBD) is the deposition technique most widely employed to obtain CdS thin films .The CBD process is a simple and inexpensive technique to obtain homogeneous, hard, adherent, transparent and stoichiometric CdS thin films. Typically, chemically deposited CdS thin films are formed from

* Corresponding author.
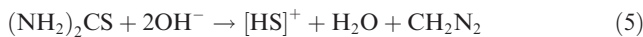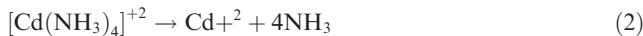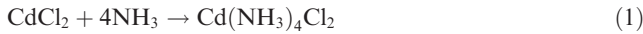E-mail address: salahjassim200@yahoo.com (S.A-J Jassim).

the reaction between a cadmium salt and thiourea in an ammoniacal alkaline solution. The main role of ammonia in the CBD process is as complexing agent for the cadmium ions in the reaction solution. It has been reported that CdS may have either cubic or hexagonal structure depending on the synthesis conditions.

In this work, we report the CBD preparation of nanostructure CdS thin films deposited on the glass substrates using a mixed aqueous solution of cadmium chloride, thiourea and ammonium chloride. Structural and optical properties have been investigated.

2. Experimental detail

CdS thin films are deposited on glass substrates using CBD at various concentrations of thiourea. The substrates used for the deposition of CdS thin films were $(35 \times 25 \times 1)$ mm commercial glass slides. Before the deposition the substrates must be cleaned using nitric acid for 48 h, scoop water followed by distilled water and finally dried in air. Aqueous solutions of 0.02 M cadmium chloride with 0.05 M ammonium chloride NH3Cl in 100 ml distilled water. Then ammonia solution of 0.55 M as a complexing agent in 50 ml distilled water was added to the solution to adjust the PH value of the bath to 9. The solution was continuously stirred. Then add 0.05 M thiourea $(NH_2)_2CS$. Solution was mixed with a magnetic stirrer and after obtaining a clear homogenized bath, the stirrer was turned off and glass slides were placed in the bath vertically. The solution temperature was kept constant at 80 °C for given time of deposition 6 h .After the deposition the samples were pulled out from the bath and washed with distilled water and dried in air. The CdS films were deposited for different concentrations of $(NH_2)_2CS$ as shown in Table 1.

The possible chemical reaction that takes place to produce CdS films may be as follows:

$$CdCl_2 + 4NH_3 \rightarrow Cd(NH_3)_4Cl_2 \tag{1}$$

$$[Cd(NH_3)_4]^{+2} \rightarrow Cd^{+2} + 4NH_3 \tag{2}$$

$$NH_3 + H_2O \rightarrow NH_4^{+2} + OH^- \tag{3}$$

$$Cd^{+2} + 2OH^- \rightarrow Cd(OH)_2 \tag{4}$$

$$(NH_2)_2CS + 2OH^- \rightarrow [HS]^+ + H_2O + CH_2N_2 \tag{5}$$

$$[HS]^+ + OH^- \rightarrow S^{-2} + H_2O \tag{6}$$

$$[Cd(NH_3)_4]^{+2} + S^{-2} \rightarrow CdS + NH_3 \tag{7}$$

The deposited CdS thin films are uniform, light yellow in color, highly adhesive, smooth and reflecting. For thickness measurement, gravimetric weight different method with the

relation $t = m/(\rho \times A)$ where, m is the mass of the film deposited on the substrate in g, A the area of the deposited film in cm^2 and ρ the density of the deposited material (CdS = 4.84 g/cm^3).thickness of the films were 434.7 nm and 453.36 nm for samples (a) and (b) respectively.

Optical properties of chemical bath deposited CdS thin films were measured at room temperature by using UV/VIS spectrophotometer Cary 50 Cm-Exlena in the wavelength range of (300–900 nm). X- ray diffraction pattern of the dry nanopartical powder was obtained using Siemens D5005 X-ray diffract meter with CuKα radiation ($\lambda = 0.1542$ nm).

3. Results and discussion

3.1. Optical studies

The optical studies of the CdS films were performed using the transmission and absorption spectra observed in the wavelength range 300–900 nm.

Fig. 1 shows the transmission spectra of CdS films, it can be seen that the films present high transmission (72–85%) in the visible range which is good for opt-electronic devices, especially for solar cell window layers. and have sharp fall at the band edge, which is an indication of good crystallinity of CdS in the films.

Absorption spectra of the two synthesized CdS films are shown in Fig. 2 it can be seen that the films show peaks at 478,470 for sample (a) and (b) respectively that means the absorption edge shifted toward blue .The blue shift can be attributed to the exitonic absorbance due to the quantum confinement at low dimensions compared to its bulk counterparts. The band-gap value (E_g) of the deposited films were determined by analyzing the optical data with the expression for the optical absorbance α and the photon energy hυ using Taucs formula relation (Tauc and Abeies, 1970).

$$\alpha h\upsilon = C(h\upsilon - E_g)^n \tag{8}$$

where C is a constant and the exponent n depends on type of transition, n may have values 1/2, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. As CdS nanoparticles have direct allowed transitions we choose $n = 1/2$ .The band gap of CdS nanoparticals was determined by extrapolating the straight line portion of the $(\alpha h\upsilon)^2$ vs. (hυ) graphs to the (hυ) axis as shown in the Fig. 3. It can be observed from Fig. 3 that the band gap of CdS nanoparticales is 3.2 eV and 2.6 eV for sample (a) and (b), respectively. These values of the energy gaps reflect a considerable blue-shift relative to the corresponding absorption band edge of bulk CdS, such observed shift reveals quantum size effect in the synthesized CdS thin films. Our present E_g values were in a good agreement with those reported by (Raghvendra et al., 2010; Dongre et al., 2009).

Table 1 The compositions of the sample in the start solution.

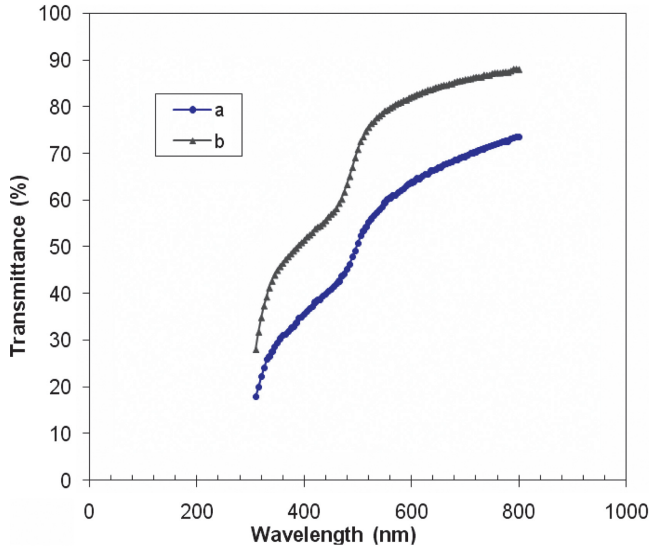| Reaction bath	pH	CdCl$_2$		$(NH_2)_2CS$		NH$_4$Cl		NH$_3$ H$_2$O	
		Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)
Sample-a	9	0.03	50	0.1	50	0.05	50	0.6	50
Sample-b	9	0.03	50	0.05	50	0.05	50	0.6	50

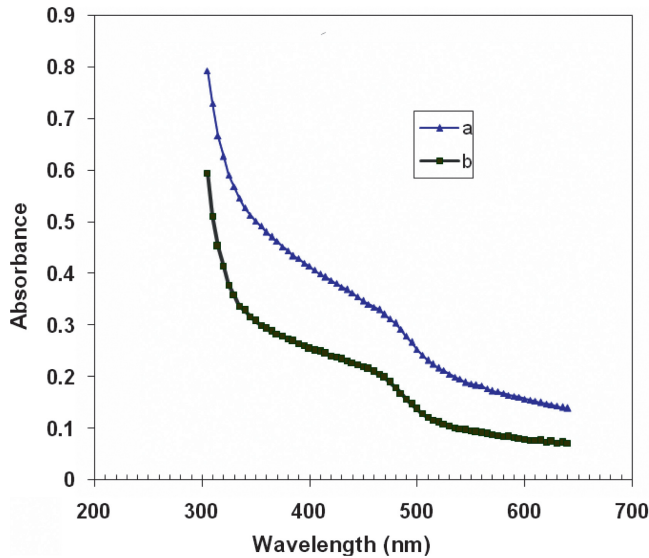**Figure 1**   Plot of transmittance with wavelength for CdS films.

Figure 2   The variation of optical absorbance vs. wavelength for CdS films.

The values of the band-gap were higher than the band gap of bulk CdS (2.42 eV) (Enriques and Mathew, 2003) therefore, the blue shift of band gap edge is 0.78 eV and 0.18 eV for samples (a) and (b) respectively. The increased effective band gap makes nanocrystalline CdS a more effective window material in photovoltaic applications like the CdS/CdTe solar cells.

For CdS nanoparticles (Brus, 1986) proposed the effective mass approximation formal (EMA) to explain the theory of blue shift, which gives energy E_{nd} for lowest 1s states as a function of nanoparticle radius, shows as follows:

$$E_{np} = E_g^{bluk} + E_{comf} + E_{coul} \qquad (9)$$

where E_{np} is the band gap of CdS nanoparticle, E_g is the band gap of the bulk of CdS, E_{comf} is the electron–hole pair confinement kinetic energy and E_{coul} is the coulomb interaction energy between the hole and the electron, which is given by
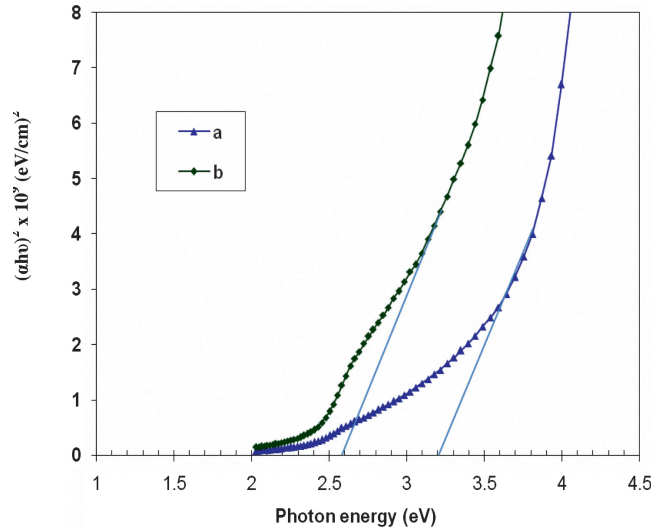

Figure 3   The variation of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ to determine the direct band gap of CdS thin films.

$$E_{coul} = -1.8e^2/\pi\varepsilon_o\varepsilon_\tau R \qquad (10)$$

And $E_{comf} = (\hbar^2\pi^2/2R^2)(1/m_e^* + 1/m_h^*)$ corresponding to the lowest energy transition.

Now the above equation can be written as

$$E_{np} = E_g^{bulk} + (\hbar\pi^2/2R^2)(1/m_e^* + 1/m_h^*)$$
$$- (1.8e^2/4\pi\varepsilon_o\varepsilon_\tau R) \qquad (11)$$

where $\hbar = h/2\pi$, h is plank constant, R is the radius of nanoparticles, m_e^* is the effective mass of electron ($m_e^* = 0.19m_e$), m_h^* is the effective mass of hole ($m_h^* = 0.8m_e$), m_e is the mass of electron, ε_τ is the dielectric constant of material (5.7) and ε_o is the permittivity of free space. In the EMA formula, the coulomb term of electron–hole interaction was small compared to electron - hole confinement kinetic energy, which supported the blue shift result.

Applying Eq. (11), values 4 nm (the diameter is 8 nm) and 1.913 nm (the diameter 3.826 nm) have been estimated for the radius of the two nanoparticales CdS samples (a) and (b) respectively.

It can be seen clearly that the decreasing particle size (as the thiourea concentrations increases) causes increase in the band gap. Similar observation of the decrease in particle size as the thiourea concentrations increased was reported by Yao et al. (2003). The dependence of band gap on particle size in semiconductor nanocrystals has been extensively studied by Brus (1984). Particles whose dimensions become comparable to the bulk excition Bohr radius (a_B), equal to 5.3 nm for CdS, are observed to exhibit strong quantum confinement effect, which result in increase in the band gap with decreasing particle size. So there is a very good agreement with our result. These values are in good agreement with the sizes determined from XRD.

3.2. X-ray diffraction studies

Fig. 4 shows the XRD pattern of CdS powered nanoparticles for sample b. Comparing with the data of the JCPDS file (Powder Diffraction File Card, No. 10-454), it was found that the CdS nanoparticles are identified as β-CdS, which belong to
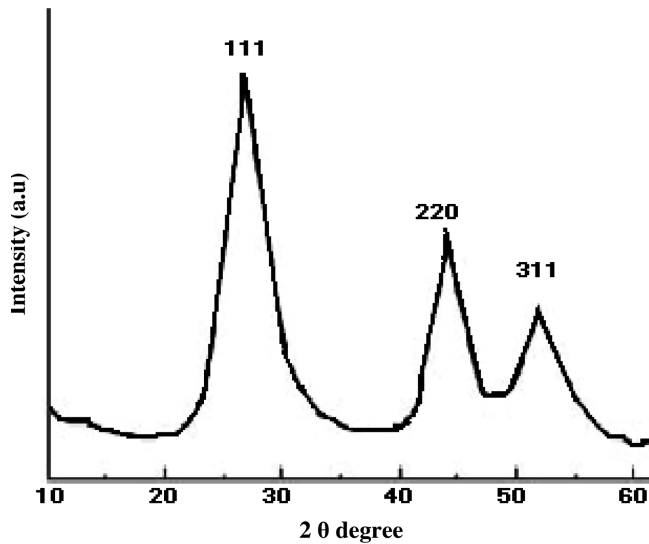
Figure 4 XRD of powder CdS nanoparticales for sample for sample b.

the cubic crystal system. The XRD peaks are found to be broad indicating fine size of the sample grains. The XRD pattern of a typical CdS sample exhibits prominent broad peaks at 2θ values of 26.7°, 44° and 52° which could be indicated as scattering from the (111), (220), and (311) cubic phase CdS plans, respectively, suggesting that the nanoparticles are in cubic (Zinc blend phase) form and are in good agreement with the reported data on CdS (Rodrgues et al., 2008; Wang et al., 2001). No peaks attributable to other phases were observed. The broadening of the diffraction peak provides information about crystallite size. As the width increases, the particle size decreases and vice versa (Banerjee et al., 2000).

From the position of different peaks and by the Bragg condition,

$$n\lambda = 2d\sin\theta \tag{12}$$

where n is the order of diffraction, λ the wavelength of the incident X-rays, d the distance between the plans parallel to the axis of the incident beam and θ is the diffraction angle, d-spacing has been evaluated, the obtained value is (3.139 Å).

Nanoparticle lattice constant is calculated using the following formula (Kittel, 1996).

$$1/d^2 = (h^2 + k^2 + l^2)/a^2 \tag{13}$$

where (a) is the lattice constant, and (h,k,l) miller indices, (a) was calculated to be (0.59 nm) for our sample, which matches with the earlier reported lattice constant for cubical zinc blend structures of CdS nanoparticles (Rodrgues et al., 2008).

The average size of the crystallites (D) has been calculated using Scherer's equation as (Cullity, 1972)

$$D = K\lambda/\beta\cos(\theta) \tag{14}$$

where the constant K is a shape factor usually $= 0.94$, λ is of X-ray wavelength (0.15418 nm), β is the full-width at half-maximum (FWHM) of the peak which has maximum intensity and θ is the Bragg's angle. The estimated X-ray domain size of this sample was 6.27 nm derived from FWHM of peak corresponding to $2\theta \approx 26.7°$ for sample (b).

4. Conclusion

An aqueous solution system for growing CdS thin film nanocrystals network was investigated. The present method is simple, economic and easy .The crystal structure and grain size of the particles was determined using XRD. The radius of the particle was calculated using an effective mass approximation mode. The calculated radius of CdS nanoparticles was found to be similar to that obtained from XRD through Scherer's formula.

UV–VIS spectra of the films showed blue shift in absorption edge compared with bulk CdS. The nanocrystals size was observed in the range of 3.826–8 nm.

References

Alivisatos, A.P., 1996. Perspectives on the physics chemistry of semicoductor nanocrysts. J. Phys. Chem. 100 (31), 13226–13239.

Banerjee, R., Jayakrishnan, R., Ayyub, P., 2000. Effect of the size-induced structural transformation on the band gap in CdS nanoparticles. J. Phys. Condens. Matt. 12, 10647–10654.

Brus, L.E., 1984. Electron-electron and electron-hole interactions in small semiconductor crystallites: the size dependence of the lowest excited electronic state. J. Chem. Phys. 80, 4403–4409.

Brus, L.E., 1986. Time dependent calculation of the absorption spectrum of a photo dissociating system with two interacting excited electronic states. J. Chem. Phys. 90, 2555–2560.

Cullity, B.D., 1972. Elements of X-ray Diffraction. Addison-Wesley, Reading, MA, p. 102.

Dongre, J.K., Vikas, N., Ramrakhiani, M., 2009. Structural, optical and photoelectrochemical characterization of CdS nanowire synthesized by chemical bath deposition and wet chemical etching. Appl. Surf. Sci. 255, 6115–6120.

Dunan, X., Huang, Y., Agarwal, R., Lieber, CM., 2003. Single-nanowire electrically driven lasers. Nature 421, 241–246.

Enriques, J., Mathew, X., 2003. Influence of the thickness on structural, optical and electrical properties of chemical bath deposited CdS thin films. Solar Energy Mater. Solar Cell 76, 313–332.

Ghosh, P.K., Maiti, U.N., Chattopadhyay, 2006. Structural and optical characterization of CdS nano fibers synthesized by Dc-sputtering technique. Mater. Lett. 60, 2881–2885.

Grohs, J., Apanasevich, S., Jung, P.I., 1994. Noise-induced switching and stochastic resonance in optically nonlinear CdS crystals. Phys. Rev. A 49, 2199.

Kittel, C., 1996. Introduction to Solid Stat Physics. Wiley, New York, Chapter 2.

Kotkata, M.F., Masoud, A.E., Mohamamed, M.B., Mahmoud, E.A., 2009. Synthesis and structural characterization of CdS nanoparticles. Physics E 41, 1457–1465.

Raghvendra, S.Y., Priya, M., Rupali, M., Manvendra, K., Avinash, C.P., 2010. Growth mechanism and optical property of CdS nanoparticles synthesized using amino-acid histidine as chelating agent under sonochemical process. Ultrason. Sonochem. 17, 116–122.

Rodrgues, P., Muñoz-Aguirre, N., San-Martin, E., Gonzalez, G., 2008. Formation of CdS nanoparticles using starch as capping agent. Appl. Surf. Sci. 255, 740–742.

Santos, B.S., Farias, P.M.A., Fontes, A., Brasil, A.G., Jovino, C.N., Neto, A.G.G.C., Silva, D.C.N., Menezes, F.D., Ferreira, R., 2008. Semiconductor nanocrystal obtained by colloidal chemistry for biological application. Appl. Surf. Sci. 255, 796–798.

Schmitt-Rink, S., Chemla, D.S., Miller, D.A.B., 1989. Linear and nonlinear optical properties of semiconductor quantum wells. Adv. Phys. 38, 89–188.

Tauc, T., Abeies, F., 1970. Optical Properties of solids. IOP Publishing Ltd, North Holland, Amsterdam, p. 903.

Ujjal, K., Gautam, Ram Seshadri Rao, C.N.R., 2003. A solvothermal route to CdS nanocrystals. Chem. Phys. Lett. 375, 560–564.

Wang, G.Z., Wang, Y.W., Chen, W., Liang, C.H., Li, C.H., Zhang, L.D., 2001. Facile synthesis route to CdS nanocrystals at room temperature. Mater. Lett. 48, 269–275.

Xiaoxia, J., Fei, C., Hao, X., Ligong, Y., Weiming, Q., Minmin, S., Mang, W., Hongzheng, C., 2010. Template-free synthesis of vertically aligned CdS nanoroads and its application in hybrid solar cells. Sol. Energy Mater. Sol. Cells 94, 338–344.

Yao, Jian-Xi, Zhao, Gao-Ling, Han, Gao-Rong, 2003. Effect of the ratio of thiourea to Cd^{2+} on the properties of CdS nanoparticles. Microelectron Eng 66, 115–120.