

A SIMPLE METHOD FOR THE SYNTHESIS OF CdS NANOPARTICLES USING A NOVEL SURFACTANT

E. C. DE LA CRUZ TERRAZAS^a, R. C. AMBROSIO LÁZARO^{a,d},
M.L. MOTA GONZÁLEZ^a, P.A. LUQUE^b, S. J. CASTILLO^c,
A. CARRILLO-CASTILLO^{a*}

^a*Instituto de Ingeniería y Tecnología, Universidad Autónoma de Ciudad Juárez.
Ave del Charro 450 N Cd. Juárez Chihuahua. CP 32310, México.*

^b*Facultad de Ingeniería, Arquitectura y Diseño, UABC, C.P. 22860 Ensenada,
B.C., México.*

^c*Universidad de Sonora. Hermosillo, Sonora, C.P. 83000, México.*

^d*Benemérita Universidad Autónoma de Puebla, C.P. 72000, México*

In this work, we present the synthesis and characterization of CdS nanoparticles suitable for semiconductor applications using a simple and manufacturable process. The solution based process was synthesized at room temperature using cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ 0.1 M) and a Thioacetamide ($\text{C}_2\text{H}_5\text{NS}$ (TA) 0.5 M) as source of cadmium and sulfur, respectively. The effect of the concentration of polyethyleneimine (PEI) as a surface stabilizer or surfactant for growth control of CdS nanoparticles was studied. The PEI concentrations were varied as 1 M, 0.5 M, 0.25 M, and 0.01 M respectively. Optical properties of CdS were analyzed by UV-Vis spectroscopy; functional groups were identified by Fourier transform infrared spectroscopy (FTIR) and the surface morphology by scanning electron microscopy (SEM). The particle size for CdS nanoparticles were less than 80 nm. An increase in size was observed inversely to the PEI concentration.

(Received February 3, 2015; Accepted April 4, 2015)

Keywords: Cadmium sulfide, nanoparticles, polyethyleneimine effect

1. Introduction

Semiconductor nanocrystals are of great interests for both fundamental research and industrial development. This is due to their unique size-dependent optical and electronic properties and their exciting utilization in the fields of light-emitting diode [1], electrochemical cells [2], laser [3], hydrogen producing catalyst [4] and biological label [5]. The usual preparation technique of nanocrystals are by liquid reaction system at high temperatures for several hours, making those methods either expensive, explosive, moisture sensitive, extreme toxic, and energy consuming. Recently, much attention was paid to develop liquid-liquid approach for synthesis of nanocrystal metals, metal oxides and metal sulfides [6,7]. Particularly, semiconductor nanoparticles have been attracting much attention because of their characteristic properties resulting from the quantum size effect which are significantly different from those of the corresponding bulk material [8-15]. In particular, sulfides of transitional metals acquired attention for applications such as sensors, optical filters, solar cells, and photovoltaic systems among others because the optical properties characteristic of the size and morphology of the crystal, essentially characterized by the transition phase from the electrical conductivity [16].

* Corresponding author: amanda.carrillo@uacj.mx

Semiconducting cadmium sulfide (CdS) has been widely used as a yellow pigment and has been actively studied for application as a photocatalyst for hydrogen generation from water, as a window layer material for CdS/CdTe solar cells, and for various optoelectronic devices.

CdS is one of the most studied materials because it has a well-established relationship between the optical absorption and the size of the particle; the first investigations in this area were focused in the improvement of the synthesis method [17-19]. There are numerous reports on the synthesis of CdS nanoparticles, such as sol-gel [20], chemical vapor deposition [21,22], solvothermal [23, 24], spray pyrolysis [25, 26] and microwave (MW) assisted synthesis [27-29]. However, suspension colloidal synthesis routes offer the advantage such as short time reaction and industrial scalable.

One of the most important goals of materials chemistry is the control of size and nanoparticles stability. Since the nanoparticles are thermodynamically unstable, an agglomeration effect and then a consequent crystal growth are usually observed. To avoid these phenomena, the nanoparticles are stabilized with organic systems that enveloped them and obstruct their agglomeration and the consequent growth.

In this work, we have synthesized CdS nanoparticles using a simple chemical reaction method using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{C}_2\text{H}_5\text{NS}$, PEI, hydrazine 30% (N_2H_4), hydrogen peroxide 3% (H_2O_2) and deionized water. CdS nanoparticles were subsequently analyzed by UV-Vis absorption spectroscopy, Fourier Transform Infrared analysis (FTIR) and scanning electron microscopy (SEM).

2. Experimental details

2.1 Materials

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was used as the cation precursor and $\text{C}_2\text{H}_5\text{NS}$ thioacetamide, TA as anion precursor both from Sigma-Aldrich 98%. Polyethyleneimine (PEI), hydrazine 30% (N_2H_4), hydrogen peroxide 3% (H_2O_2) and deionized water used were of analytical grade.

2.2 Nanoparticles synthesis

The stock solution was prepared by dissolving H_2O_2 , PEI (1M, 0.5M, 0.25M or 0.01M), N_2H_4 and 0.1 M $\text{Cd}(\text{NO}_3)_2$. 1 mL from the stock solution was dissolved to 50 ml of deionized water, followed by the addition of three drops of thioacetamide (TA). The synthesis of CdS nanoparticles in the solutions was conducted at room temperature.

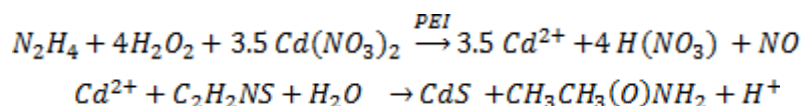
2.3 Characterization

Optical absorption measurements were performed using a Thermo scientific Nanodrop 2000 spectrophotometer in the range from 400 to 700 nm. The Infrared absorption spectra, was recorded by Thermo scientific Nicolet 6700 FT-IR Spectrometer. Powder morphology and nanoparticle size were characterized by Scanning Electron Microscopy (SEM) on JEOL, JSM 7000f microscope.

3. Results and discussions

In the synthesis presented, thioacetamide acts as source of sulfur and cadmium nitrate acts as source of cadmium, H_2O_2 and N_2H_4 act as the alkaline medium in order to yield cadmium and sulfur ions in the solution. In the beginning, a white solution is formed which gradually become transparent, changing from white to orange-yellow, typical color of the cadmium sulfide formation. The color increases with increasing concentration of PEI. Nitrogen atoms from the PEI structure interact with the nanoparticles of CdS, protecting the surface.

The possible mechanism of reaction of the formation of CdS nanoparticles is as follow:



The UV–visible absorption spectra of CdS samples prepared under different concentrations of PEI are shown in Figure 1. It is observed that an absorption edge located at 444 nm occurs when CdS nanoparticles were prepared at 1 M PEI. The maximum absorption for CdS as a bulk material is around 460 nm. This result is in agreement with the value reported [16]. The absorption spectrum of CdS changes with the particle size; and it was observed that the PEI concentration has an inverse relationship to particle size. A shift of the 460 nm absorption compared with the characteristic absorption of bulk CdS may be due to quantum confinement effects.

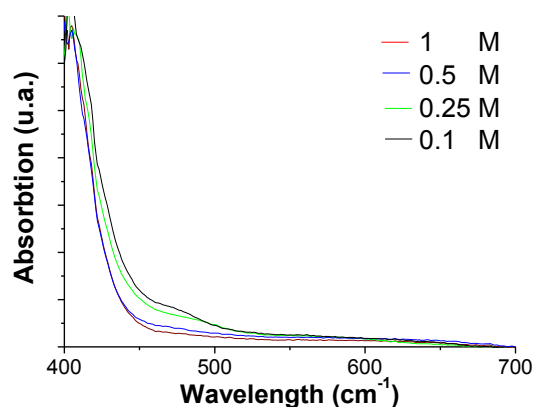


Fig. 1. Absorption spectra for CdS nanoparticles synthesized at different PEI concentration (1M, 0.5M, 0.25M and 0.1M).

The band gap of the as-prepared nanoparticles is determined from the relation $\alpha(h\nu) = A(h\nu - \Delta E_g)^{m/2}$, where A is a constant, ΔE_g is the band gap of the material and α is the absorption coefficient, $h\nu$ is the photon energy and $m = 1$ for a direct transition between bands (valence and conduction band). A plot of $(\alpha h\nu)^2$ vs. energy ($h\nu$) is shown in Figure 2 and the linear portion of the curve is extrapolated to $h\nu$ axis to determine the band gap.

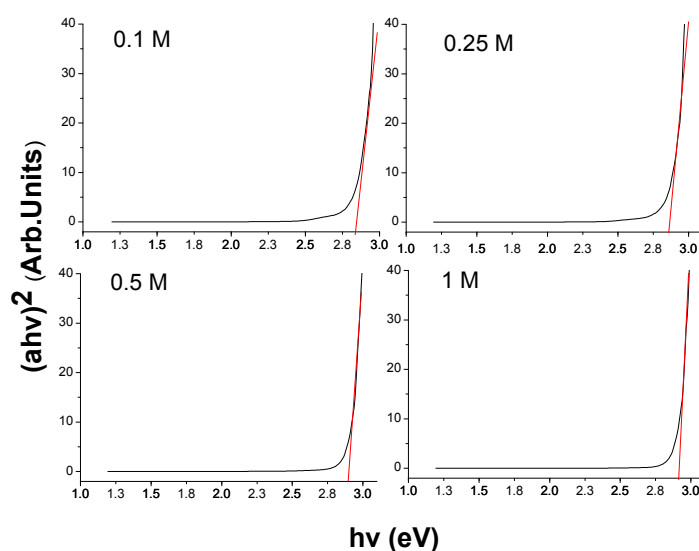


Fig. 2. Estimated band gap from optical absorption spectrum for CdS nanoparticles synthesized at different PEI concentration.

The calculated band gap vs PEI concentration is shown in Figure 3. These results show an increase in the band gap energy as a function of particle size reduction, nevertheless it should be mentioned that the value of band gap energy reported in this work is 2.42 eV. It has been reported previously [30-32]. that the band gap energy of 3.9 eV for nanoparticles of CdS, indicates the presence of quantum-size effects in the prepared CdS nanoparticles [33].

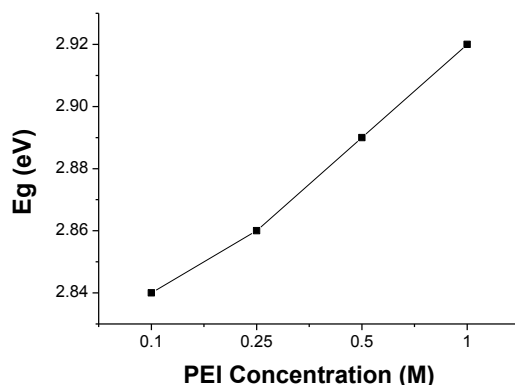


Fig. 3. Effect of PEI concentration on the band gap energy of CdS nanoparticles.

The FTIR spectrum of nanoparticle CdS is shown in the Figure 4. A broad band in the range of 3300-3400 cm^{-1} is due to the N-H and 1607-1645 cm^{-1} is assigned to -NH₂ of hydrazine, which intensity increases gradually with increasing the concentration of PEI. The Cd-S bond is observed at 670 cm^{-1} , indicating the CdS formation.

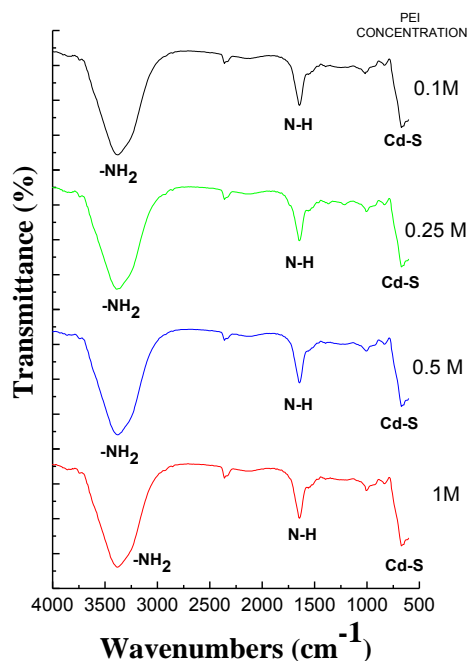


Fig. 4. Infrared spectra for CdS nanoparticles obtained at different PEI concentration.

SEM was performed to obtain direct information about the particle size and morphology of the CdS nanoparticles. Figure 5 shows the SEM image of the CdS nanoparticles obtained at different concentration of PEI. Monodisperse particles were observed with sizes in the range of 59 to 80 nm.

There are been reported several methods for the synthesis of CdS nanoparticles. Yang et al. [34] synthesized size-quantized CdS crystals, which have diameters of 5–15 nm using epitaxial growth. Xu et al. [35] prepared CdS nanoparticles with diameter of 100 nm via hydrothermal synthesis. Zhu et al. [36] produced CdS nanoparticles with 5 – 10 nm by microwave irradiation method. Compared with the results obtained from these preparative routes, the present results demonstrate that this method can easily fabricate CdS nanoparticles with competitive dimensions.

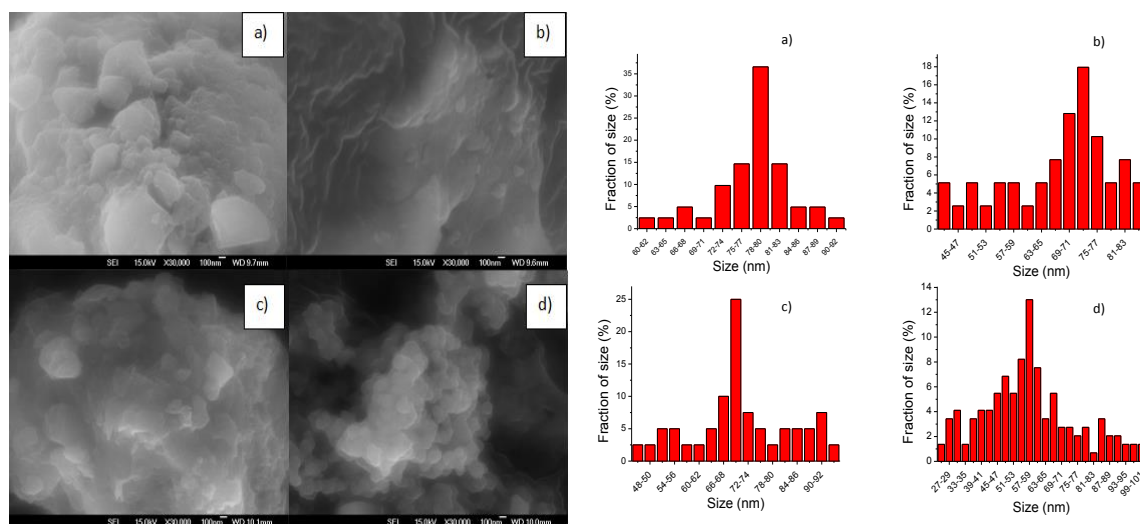


Fig. 5. SEM micrographs for CdS nanoparticles obtained at different PEI concentration: a) 0.1M , b) 0.25M , c) 0.5M d) 1M.

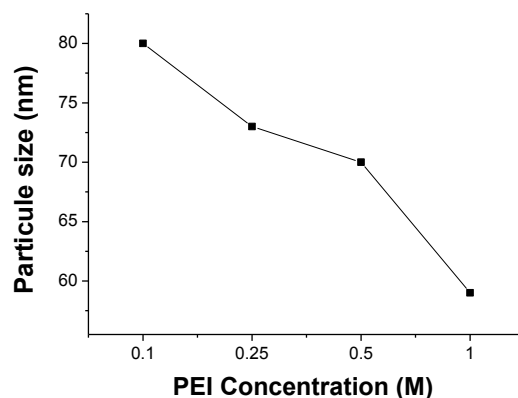


Fig 6. Effect of PEI concentration on the particle size of CdS nanoparticles.

Fig. 6 presents the average size of CdS nanoparticles. 80, 73, 70 and 59 nm where obtained at 0.1M, 0.25M, 0.5M and 1M concentrations of PEI, respectively. The morphology of CdS nanoparticles change as a function of PEI concentration, suggesting that the PEI plays a key role in the tailoring of CdS nanostructures.

4. Conclusions

In the present work, the development of a new method for the synthesis of CdS nanoparticles via a wet process in the presence of a polyelectrolyte cationic of high molecular weight (PEI) is successfully demonstrated. The presented route can easily fabricate CdS nanoparticles with small dimensions in short periods and at room temperature. CdS nanoparticles have been analyzed by SEM, UV-Vis, and FTIR. We demonstrated that the PEI concentration

plays an important role in the formation of CdS nanoparticles. There is a strong relationship between the concentration of PEI and the size of the CdS nanoparticles, as well as with the band gap of the particles. Obtaining a smaller particle (59 nm) energy-band banned from 3.82 eV. An increase in the band gap is also clearly observed by different colorations in the solution due to the quantum confinement effects in the nanoparticles.

Acknowledgements

The authors acknowledge the partial financial support of CONACyT scholarship 2013-2014 as well as the institutional fund Ciencia Básica 2013- IOO17- 221117 and Cátedras CONACyT 2014-01.

References

- [1] J.L. Zhao, J.A. Bardecker, A.M. Munro, M.S. Liu, Y.H. Niu, I.K. Ding, J.D. Luo, B.Q. Chen, A.K.Y. Jen, D.S. Nano Lett. **6**(3), 463 (2006).
- [2] L. Li, W. Wang, H. Liu, X. Liu, Q. Song, S. Ren. J. Phys. Chem. C **113**, 19, 8460 (2009).
- [3] Y.J. Chan, S. Steckel, P.T. Snee, J.M. Caruge, J.M. Hodgkiss, D.G. Nocera, M.G. Bawendi. Appl. Phys. Lett. **86**, 073102 (2005).
- [4] J. Suk-Jang, U. A. Joshi, J. Sung-Lee. J. Phys. Chem. C **111**(35), 13280 (2007).
- [5] M. Bruchez, M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos. Science **281**(5385), 2013 (1998).
- [6] P. Gupta, A. Ulman, S. Fan, A. Korniaikov, K. Loos. J. Am. Chem. Soc. **127**, 1, 4 (2005).
- [7] D. Jian, Q. Gao. Chem. Eng. J. **121**(1), 9 (2006).
- [8] V. Favier, G. R. Canova, S. C. Shrivastava, J. Y. Cavaille. Polymer Engineering & Science, **37**(10), 1732 (1997).
- [9] A.P. Alivisatos. J. Phys. Chem. **100**(31), 13226 (1996).
- [10] A. Henglein. Chem. Rev. **89**(8), 1861 (1989).
- [11] Ch. Tao, S. Zheng, H. Möhwald, J. Li.. Langmuir **19**(21), 9039 (2003).
- [12] Ch. Barglik-Chory, Ch. Remenyi, H. Strohm, G. Müller. J. Phys. Chem. B. **108**(23), 7637 (2004).
- [13] M. E. Wankhede, S. K. Haram. Chem. Mater. **15**(6), 1296 (2003).
- [14] J. Vijay, L. Gary, L. McPherson. Nano Lett. **2**(4), 263 (2002).
- [15] A. Agostiano. J. Phys. Chem. B. **104**(35), 8391 (2000).
- [16] S. Martínez, T. Serrano, A. Gómez, A. Hernández. Bol. Soc. Esp. Coram. **46**(2), 97 (2007).
- [17] C.B. Murray, D. J. Norris, M. G. Bawendi. J. Am. Chem. Soc. **115**, 8706 (1993).
- [18] T. Vossmeier, L. Katsikas, M. Giersig, I. Popovik, K. Diesner, A. Chemseddine, A. Eychmüller, H. Weller. J. Phys. Chem. **98**, 7665 (1994).
- [19] J. R. Lakowicz, I. Gryczynski, Z. Gryczynski, C. J. Murph. J. Phys. Chem. B. **103**, 7613 (1999).
- [20] N.V. Hullavarad, and S.S. Hullavarad. Photonics and Nanostructures. **15**, 156 (2007).
- [21] T. Zhai, Z. Gu, H. Zhong, Y. Dong, Y. Ma, H. Fu, Y. Li, J. Yao. Cryst. Growth Des. **7**(3), 488 (2007).
- [22] B J.K. Dongre, V. Nogiya, and M. Ramrakhiani. Appl. Surf. Sci. **255**(12), 6115 (2009).
- [23] A. Phuruangrat, T. Thongtem, and S. Thongtem. Mater. Lett. **63**(17), 1562 (2009).
- [24] A. Tang, F. Teng, Y. Hou, Y. Wang, F. Tan, S. Qu, and Z. Wang. Appl. Phys. Lett. **96**, 163112 (2010).
- [25] S.J. Ikhmayies and R.N. Ahmad-Bitar. Appl. Surf. Sci. **255**(20), 8470 (2009).
- [26] N. Badera, B. Godbole, S.B. Srivastava, P.N. Vishwakarma, L.S. Chandra, D. Jain, M. Gangrade, T. Shripathi, V.G. Sathe, and V. Ganesan. Appl. Surf. Sci. **254**, 7042 (2008).
- [27] E. Caponetti, D.C. Martino, M. Leone, L. Pedone, M.L. Saladino, and V. Vetri. J. Colloid Interface Sci. **304**(2), 413 (2006).
- [28] F. Atay, V. Bilgin, I. Akyuz, S. Kose. Materials Science in Semiconductor Processing.

- 6**(4), 197 (2003).
- [29] R. Amutha, M. Muruganandham, G.J. Lee, and J.J. Wu. *J. Nanosci. Nanotechnol.* **11**(9), 7940 (2011).
- [30] J. Richard Christman. *Fundamentals of Solid State Physics*. (John Wiley & Sons. 1988).
- [31] N. Kim, S. Ryu, H. Noh, W. Lee. *Materials Science in Semiconductor Processing*, **15**, 125 (2012).
- [32] Shital V. Kahane, R. Sasikala, B. Vishwanadh, V. Sudarsan, S. Mahamuni. *International Journal of Hydrogen Energy*, **38**, 15012 (2003).
- [33] R Banerjee, R Jayakrishnan and P Ayyub. *J. Phys.: Condens. Matter.* **12**, 10647 (2000).
- [34] J.P. Yang, F.C. Meldrum, J.H. Fendler. *J. Phys. Chem.* **99**, 5500 (1995).
- [35] G.Q. Xu, B. Li, S.J. Xu, C.H. Chew, S.J. Chua, L.M. Gana. *J. Phys. Chem. Solids* **61**(6), 829 (2000).
- [36] J.J. Zhu, M.G. Zhou, J.Z. Xu, X.H. Liao. *Mater. Lett.* **47**, 25 (2001).