

SYNTHESIS AND CHARACTERIZATION OF CdS NANOPARTICLES BY TWO DIFFERENT FORMULATIONS USING POLYETHYLENIMINE AS COMPLEXING AGENT

J. O. RIVERA-NIEBLAS^{a,b,c}, D. GARCIA-BEDOYA^{d,e*}, M. C. ACOSTA-ENRÍQUEZ^a, R. OCHOA-LANDIN^e, A. APOLINAR-IRIBE^e, F. PARAGUAY-DELGADO^a, R. CASTILLO-ORTEGA^f, S.J. CASTILLO^d

^aCentro de investigación en materiales avanzados. Miguel Cervantes No.120, Complejo industrial. C.P.31109, Chihuahua, Chihuahua, México

^bDepartamento de Metal-Mecánica, Tecnológico Nacional de México, Instituto Tecnológico de Hermosillo, Ave. Tecnológico S/N, Col. Sahuaró, 83170 Hermosillo, Son., México

^cCarrera de Ingeniería Mecatrónica, Universidad Tecnológica de Hermosillo, Blvd. de los Seris Final, Parque Industrial Hermosillo, 83299 Hermosillo, SON, México

^dDepartamento de Investigación en Física, Universidad de Sonora, Apdo. Postal 5-088, CP.83000, Hermosillo, Sonora, México

^e Posgrado en Nanotecnología, Departamento de Física, Universidad de Sonora, Apdo. Postal 1626, CP. 83000, Hermosillo, Sonora, México

^fDepartamento de Ingeniería Industrial, Universidad de Sonora, Apdo. Postal 1626, CP. 83000, Hermosillo, Sonora, México

In this paper we present two different formulations to obtain CdS nanoparticles using polyethylenimine (PEI) and another with ammonium hydroxide as a complexing agent. Chemical composition was obtained by X-ray photoelectron spectroscopy and Raman spectroscopy all of these confirmed the CdS presence. Optics properties such as absorption and transmission were measured. Transmission results were among 20 and 60 percent through 500 y 900 nm and the absorption borders about the order of 487 nm for both formulations. Gap energy was calculated from these absorption values obtaining 2.54 eV for the ammonium hydroxide formulation and 2.55 eV for PEI. On the other hand, a Transmission Electronic Microscope (TEM) determined structural properties, where clusters of different form and orientations (cubical and hexagonal structure) were observed with an average size of 8 nm for both formulations.

(Received April 5, 2016; Accepted June 7, 2016)

Keywords: Nanoparticles, TEM, Polyethylenimine, Cadmium Sulphide.

1. Introduction

Due to the applications there are many studies of nanostructured semiconductors of II-VI and IV-V groups, and they are prepared in form of particles or thin films [1]. One of these materials is the cadmium sulfide (CdS). In nature, cadmium sulfide can be present in the “greenockite” (the most common form of cadmium), this is one of the sulfides group, its color may be from yellow to red orange. Greenockite presents a hexagonal crystal system, bipyramidal, like the “wurzite”, this is why the structure is called w-CdS [2]. The cadmium sulfide is an important semiconductor because the optoelectronic applications, non-linear optics, flat panels display, LEDs, thin-film transistors, among others areas [3, 4, 5]. For nanotechnology it is important to work with unique properties of materials with less than 100 nm [6]. In the case of CdS

* Corresponding author: dgbedoya@gmail.com

nanoparticles, quantum size effects are observed with an obvious difference in color, orange for clusters and yellow for nanoparticles [7]. In this paper, two CdS nanoparticles synthesis formulations are analyzed. Chemical composition was obtained by X ray photoelectron spectroscopy (XPS), Raman spectroscopy and FTIR, while optical properties were determined by UV-Vis spectroscopy and finally, structural properties were measured by Transmission Electronic Microscope (TEM).

2. Experimental

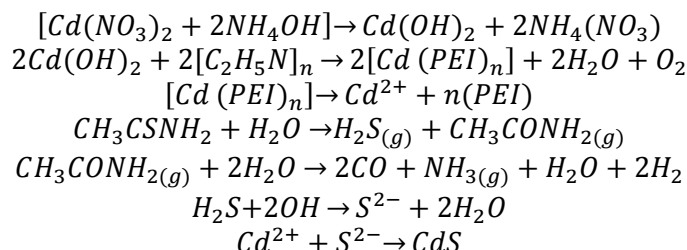
The two formulations performed for the CdS nanoparticles obtaining use analytical grade reagents such as: Cadmium nitrate ($Cd(NO_3)_2$) 0.1M, pH11 buffer, ammonium hydroxide (NH_4OH), thioacetamide(TAA) (C_2H_5NS) 0.1m, deionized water and polyethylenimine (PEI) (C_2H_5N)_n as a complexing agent.

The sequence to obtaining CdS nanoparticles with the pH11 buffer formulation (called FB11) started with 0.5 ml of polyethylenimine in 10 ml of deionized water plus 8ml of the pH11 buffer, 2ml of cadmium nitrate, 5ml of deionized water and 5ml of polyethylenimine.

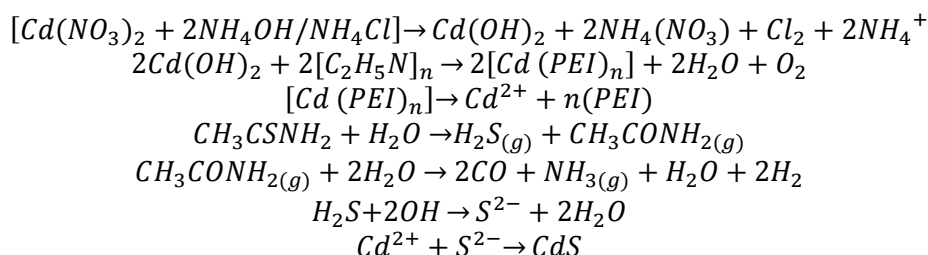
The ammonium hydroxide formulation (called FHA) follows the next arrangement, 0.5ml of polyethylenimine in 10ml of deionized water, 8ml of ammonium hydroxide, 2ml of cadmium nitrate plus 5ml of deionized water and 5ml of thioacetamide. Both formulations were mixed at room temperature and standard pressure conditions.

2.1. Chemical reactions.

The reaction mechanism for CdS nanoparticles with the FHA formulation is the following:



The reaction mechanism for CdS nanoparticles with the FB11 formulation is the following:



Both reactions changed by the PEI addition forming a turbid solution, which is used as complexing agent. In the FHA formulation, the TAA addition turns immediately to yellow, which is characteristic of the CdS compounds, while in the FB11, the TAA addition remains turbid. Both reactions were in an ultrasonic bath for 15 minutes and it has been observed that FB11 turns to yellow after this, this could be due to the ultrasonic bath add energy enough to liberate the Cd complexed by the buffer forming the CdS compound.

2.2.Characterizations

To determine the chemical nanoparticles composition an XPS Perkin-Elmer model Phi-5100 was used. Raman dispersion was obtained with a Micro Raman X'Plora BXT40 a 2400T resolution. FTIR (Fourier Transform Infrared Spectroscopy) was done with a Perkin-Elmer model Spectrum GX. The nanoparticles optical transmission spectrum was measured with a UV-Vis spectrophotometer Perkin Elmer model Lambda 20 and with a spectrophotometer Agilent Technologies Model Cary 60. Structural properties were obtained by a transmission electronic microscope (TEM) JEOL model JEM-2010F Field Emission Electron Microscopy (JEOL Ltd).

3. Results and discussion

3.1. X-ray Photoelectron Spectroscopy (XPS)

For this analysis, nanoparticles were prepared with the drop coating technique over a Corning glass and vacuum dried. This was repeated until a film, thin enough to enter into XPS the vacuum chamber was obtained. This was performed for both formulations. Figure one shows the XPS survey spectra, where the silicon peaks, belonged to the cornig glass, are detected in the 101.25 and 149.5 eV region. The two Auger bands for carbon and oxygen are present in the 995 and 745 eV regions respectively. The grey line with the label "a" corresponds to the FHA formulation and the black line labeled "b" corresponds to the FB11.

An essential difference is the signals corresponding to: Cl 2s at 200 y Cl 2p at 269 eV present in the FB11, which belong to the Ammonium Chloride. Same way the 264 eV signal in the FHA which means Chloride traces due to an impure substrate.

Oxygen peaks are located at 745, 531.75 and 24 eV, where the basic oxygen level (O 1s) is the 531.75 eV and correspond to the O associated to a hydroxide [8]. This could mean that cadmium hydroxide is present in the films due to Cd(OH)₂ is an interval compound in the CdS reaction mechanism.

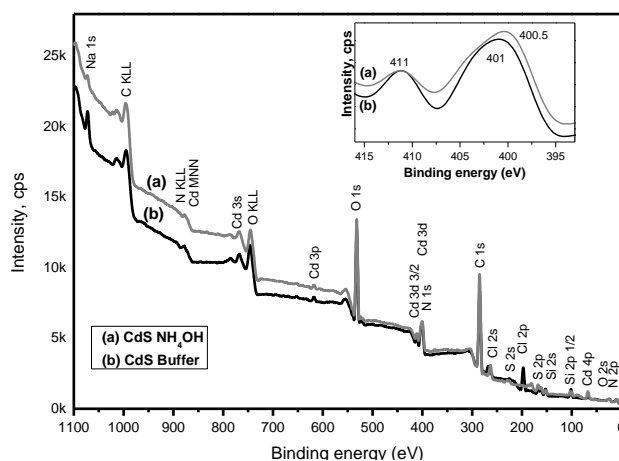


Fig. 1. XPS spectra for CdS nanoparticles (a) FHA synthesized and (b) FB11 synthesized. Inset displays the region for Cd 3d signals.

There are another signals of the spectra that belong to Cd, these are: 879, 769, 617, 410, 404 y 67 eV. The bonding energy observed is characteristic for CdS in the 400.5 eV 3d 5/2 and 411.75 eV 3d 3/2 [9, 10, 11]. Signals 231, 167.4 and 161 eV are from S.

Bonding energy for S 2p 3/2 at 161 eV is indicative of a metal sulfide, CdS in this case [12], while the S 2p 3/2 for S is 167.4 eV corresponding to the SO₂ bond product from the TAA hydrolysis.

Carbon peaks located at 995 and 284 eV, first one is an Auger signal KLL and the second is C 1s signal for a hydrocarbon CH₂[10]. Nitrogen peaks at 882, 401 and 9 eV, correspond to an Auger KLL signal, N 1s and N 2p respectively, this element comes from the reaction precursors.

3.2. Optical properties

In figure 2, the absorption and graphic processes for the energy band gap are shown, the values obtained are 2.54 eV for FHA and 2.55 eV for FB11. In the figure inset Tauc graphic is displayed. As can be observed, for FHA formulation nanoparticles absorption is superior than FB11 nanoparticles. Absorption borders are shown in 487nm for both cases.

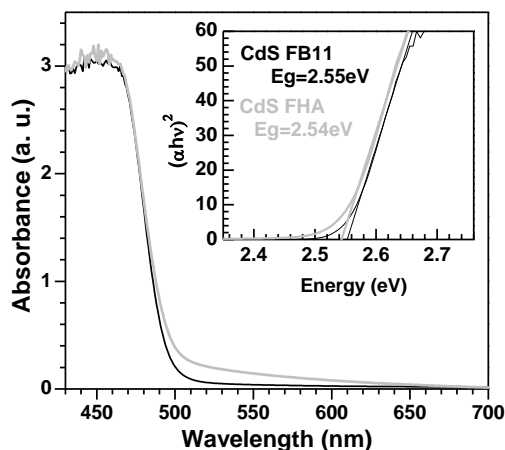


Fig. 2. Absorbance spectrum for CdS (FB11) and (FHA) nanoparticles. The figure inset shows Tauc graphic for energy band gap estimate.

3.3. Structural properties

Figures 3 a) and 4 b) shows the TEM micrograph of synthesized products for formulations FB11 and FHA respectively. TEM images show that the product is composed of nano- particles, which have a size of 5-10 nm for both formulations.

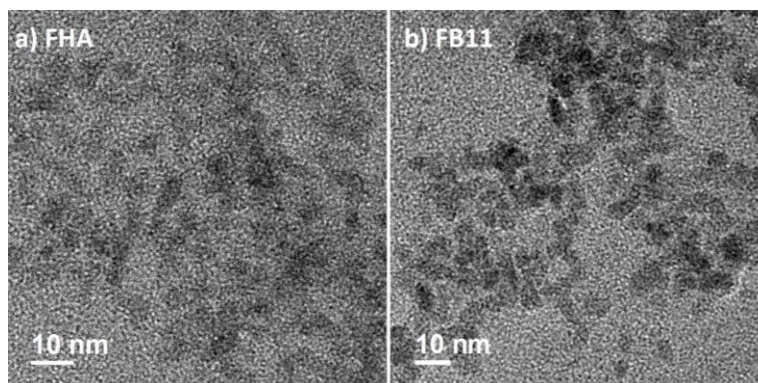


Fig. 3. HRTEM micrographs for both formulations: a) FHA y b) FB11.

Figure 4, with a 5 nm scale, presents two HRTEM contrast micrographs for both formulations (4a for FHA and 4c for FB11). Also in this figure FFT image of the HRTEM are shown FHA (4b) and FB11 (4d). In these micrographs the interplanar distances for different crystalline planes and in certain crystallographic directions are observed allowing the identification of the crystallographic spacing of the CdS NPs. The fringes observed in figure 4a correspond to a cubic system with PDF#10-0454 and a “lattice parameter” 5.818Å; this is corroborated by the

following directions 111, -202 and -113 at zone axis 1-21 (b, FFT image) which interplanar distances 3.302, 2.022 and 1.725 Å respectively (a, HRTEM). On the other hand, an hexagonal system was identified (figure 4 c and d) with a PDF#41-1049 and a lattice parameter of 4.1409x6.7198Å; the directions of this system are 002,1-11,1-13,2-20 and -111at zone axis 110 (d, FFT image) which interplanar distances 3.36, 3.164, 1.899, 1.793 and 3.164 Å respectively (c, HRTEM).

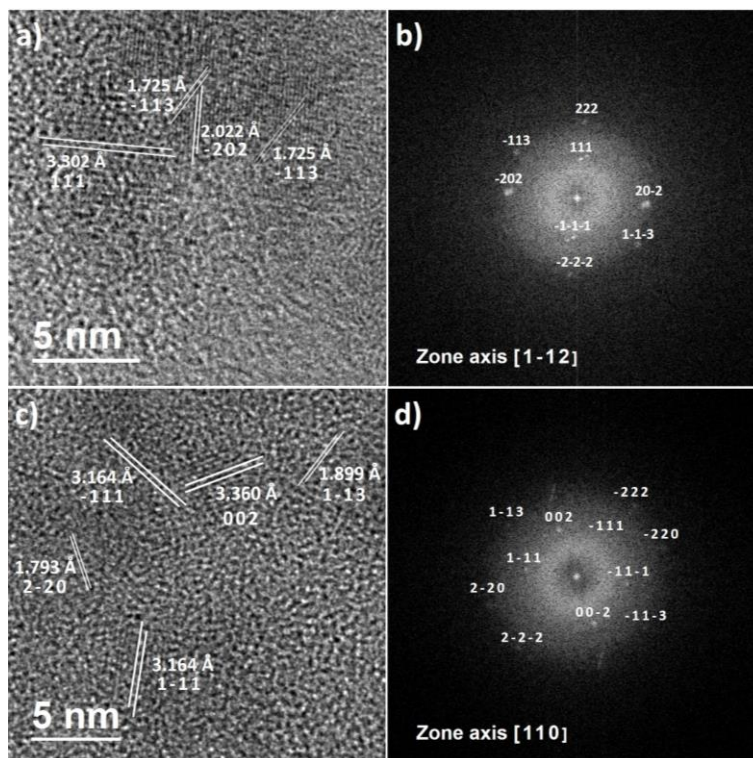


Fig. 4. HRTEM micrographs image(left side) and their corresponding FFT image (right side), for both formulations. FHA (a and b) and FB11 (c and d).

3.4 Raman and FTIR

Figure 5 shows Raman spectra peaks for FHA nanoparticles in aqueous phase obtained with 300 K. The 292 cm^{-1} , 595 cm^{-1} and 895 cm^{-1} are associated to 1LO, 2LO and 3LO respectively [15-19]. These are the first, second and third longitudinal optical modes related to hexagonal CdS nanoparticles. In the case of cubical CdS the Raman spectra shows a high signal at 484 cm^{-1} which has not been reported before. Besides the 1LO, 2LO and 3LO are present, but with a minor insensitivity respect the hexagonal phase. The 1LO+2E and 2LO+2E modes are in the cubical phase. The ratio of I_{2LO}/I_{1LO} is a measure of the interaction phonon-electron, this ratio is 0.5927 and 0.3099 for cubical and hexagonal phases respectively [20-21]. Then the interaction phonon-electron for the cubical structure is higher than hexagonal structure. Furthermore, the interaction phonon-electron depends on temperature and size of the nanoparticles, if the sizes of nanoparticles are increasing the interaction must be bigger [20-21].

In figure 5, the Fourier transform infrared spectroscopy (FTIR) spectra are showed in the inset, for both formulations. The 3414 cm^{-1} for FB11 and 3417 cm^{-1} for FAH correspond to a broad absorption band for O-H bonds, a stretching mode of H_2O absorbed in the surface or NH_4OH present in both formulations [22, 23]. 2150 cm^{-1} peaks correspond to $\text{C}\equiv\text{C}$ stretching bonds for both formulations due to PEI presence and its residual decomposing, this also could mean to a $-\text{N}=\text{C}=\text{S}$ presents in TAA. 1648 cm^{-1} in FB11 and 1645 cm^{-1} of FAH, mean water is present [23]. Also $\text{C}=\text{O}$ stretching mode bonds considerate the presence of aliphatic amides due to the PEI and TAA, these bonds are strong and are represented by the 1630-1695 cm^{-1} peaks, $\text{C}=\text{O}$ (amide band I) and N-H bonds (1-amide) band II between 1590-1650 cm^{-1} [24].

At 1645 cm^{-1} for FAH and 1648 cm^{-1} for FB11 with O-H stretching bond [25].

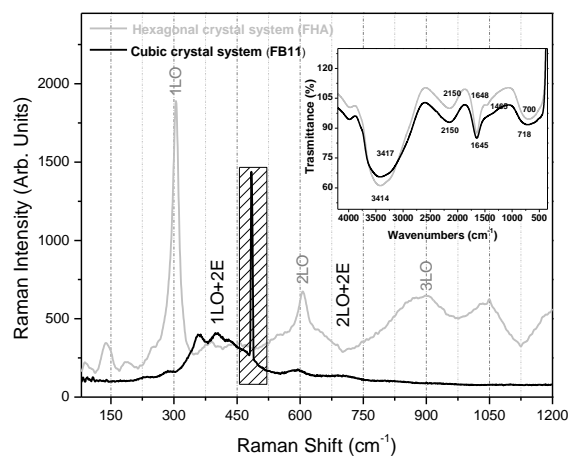


Fig. 5. Raman spectra with 488 nm laser for FHA and 532 nm laser for FB11. In the inset, the FTIR spectra for both formulations are shown.

4. Conclusions

It has been obtained CdS nanoparticles at room temperature with two different formulations, with ammonium hydroxide and pH11 buffer (FHA and FB11). FHA formulation showed a cubic crystallographic structure while FB11 showed an hexagonal crystallographic structure; this is an essential difference between the two materials. Both nanoparticles systems dimensions are about 5 nm or slightly higher. Due to the similarity between the two materials, the energy band gaps have the same confinement values. According Raman spectroscopy the interaction phonon-electron for the cubical structure is higher than hexagonal structure. Raman spectroscopy had concordance with another hexagonal CdS values reported among 300 and 600 cm^{-1} .

Acknowledgements

The authors would like to thanks the support of Universidad de Sonora (UNISON), to M.C. Roberto Mora for the XPS analysis, to Dra. Judith Tanori for the TEM analysis, to Dra. Lorena Armenta and M.C. Ramón Iñiguez for the FTIR analysis. Finally, thanks to the Instituto Tecnológico de Hermosillo (ITH) to ease the use of the absorption and optical transmission equipment.

References

- [1] E. Pentia, L. Pintilie, I. Matei, T. Botila, E. Ozbay, J. Optoelectron. Adv. Mater. **3**, 525 (2001)
- [2] Font: <http://rruff.info/doclib/hom/greenockite.pdf> Consult: February 18, 2014 RRUFF ID: R070325.2
- [3] R. Baron, C.-H. Huang, D. M. Bassani, A. Onopriyenko, M. Zayats and I. Willner, Angew. Chem. Int. Ed., **44**, 4010 (2005)
- [4] E. Katz, M. Zayats, I. Willner and F. Lisdat, Chem. Commun. 2006, 1395–1397.
- [5] Z. Dai, J. Zhang, J. Bao, X. Huang, X. Mo. Facile synthesis of high-quality nano-sized CdS hollow spheres J. Mater. Chem., **17**, 1087 (2007).
- [6] Brushan, Bharat. Handbook of nanotechnology. Ed. Springer-Verlag. Berlin, 2004.
- [7] K. Winkelmann, T. Noviello, S. Brooks J. Chem. Educ. **84**(4). 709 (2007).

- [8] J.F. Moulder, W.F. Strickle, P.E. Sobol, K. D. Bomben, Handbook of X-ray photoelectron spectroscopy, Jill Chastain (Ed), Perkin Elmer, USA, 1992.
- [9] M.D Stoev, J Touskova, J Tousek Thin Solid Films, , **299**(1–2), 67 (1997)
- [10] K. Hota, S. B. Idage, Kartic C. Khilar J. Colloids and surf. , **293**(1-3), 5 (2007)
- [11] P.S. Khiew, S. Radiman, N.M. Huang, Md. Soot Ahmad, Journal of Crystal Growth **254**, 235 (2003)
- [12] Yu X.-R., Liu F., Wang Z.-Y., Chen Y., J. Electron Spectrosc. Relat. Phenom. **50**, 159 (1990)
- [13] Wagner C.D., Taylor J.A. J. Electron Spectrosc. Relat. Phenom., **28**, 211 (1982)
- [14] Xu Y-N, Ching W. Y. Electronic, optical, and structural properties of some wurtzite crystals, Physical Review B - Condensed Matter, **48**, 4335 (1993)
- [15] T. T. K. Chi, G. Gouadec, Ph. Colomban, G. Wang, c L. Mazerollesc, N. Q. Liemb. J. Raman Spectrosc., **42**, 1007 (2011)
- [16] Ramsdell, L. S. Am. Mineralogist, **32**, 64 (1947)
- [17] O. Zelaya-Angel, F.d. L. Castillo-Alvarado, J. Avendaño-Lopez, A. Escamilla-Esquivel, G. Contreras-Puente, R. Lozada-Morales, G. Torres-Delgado, Solid State Comm. **104**, 161 (1997)
- [18] D. Mohanta, G. A. Ahmed, A. Choudhury, Chinese J. Phys. **24**, 740 (2004)
- [19] V. Singh, P. Chauhan, J. Phys. Chem. Sol., **70**, 1074 (2009)
- [20] Sivasubramanian, V., Arora, A. K., Premila, M., Sundar, C. S., & Sastry, V. S. Optical properties of CdS nanoparticles upon annealing. Physica E: Low-dimensional Systems and Nanostructures, **31**(1), 93-98. (2006).
- [21] Kumar, P., Saxena, N., Chandra, R., Gupta, V., Agarwal, A., & Kanjilal, D. Nanotwinning and structural phase transition in CdS quantum dots. Nanoscale research letters, **7**(1), 1 (2012).
- [22] J. Barman, J. P. Borah, K. C. Sarma. J. Optoelect. Adv. Mater. – Rapid Comm., **2**(12), 770 (2008)
- [23] Reddy Veera T., Venkatesu P., Reddy T.S. and Suresh S. Int. J. Res. Chem. Environ. January **2**(1) 218 (2012)
- [24] Aslam Khan Journal of Nanomaterials, Volumen 2012, Article ID 451506, **8** pag
- [25] Aurobinda Acharya, Rajkishore Mishra, G S Roy. Lat. Am. J. Phys. Educ. **4**(3), Sept. 2010