Journal of Materials Science and Engineering A 9 (7-8) (2019) 153-161
doi: 10.17265/2161-6213/2019.7-8.004

Morphological Characterization with STM and SEM of CdSe Nanostructures in Function of pH

Gabriela Sánchez Legorreta[1], Porfirio Domingo Rosendo Francisco[1], Rebeca Vargas Sanabria[1] and Oscar Olea Mejía[2]

1. Facultad de Ciencias, UAEM, Campus "El Cerrillo, Pierdas Blancas", Carretera Toluca-Ixtlahuaca, Km. 15.5, CP. 50200 Toluca de Lerdo, México

2. Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca-Atlacomulco Km. 14.5, Unidad San Cayetano, C.P. 50200, Toluca de Lerdo, México

Abstract: In this paper, we have interest in the CdSe (cadmium selenide) semiconductor due to their physical and optical properties that depend on their morphology and size, as well as their possible applications in electronic and optoelectronic fields, for example, in the fabrication of solar cells or nanotransistors. For this reason, we synthetized nanoparticles of CdSe using the colloidal method, and varied the pH value: 8 to 12, to know the effect of pH on the samples. The nanoparticles were characterized using the SEM (scanning electron microscope) and STM (scanning tunneling microscope) to know the morphology and electronic cloud on the surface of the samples. In each case, we found different sizes (from 6 to 11.5 nm) and shapes as filaments (fibbers), bars and spheres of CdSe nanoparticles and the 3D-FFT was obtained too.

Key words: CdSe, pH value, colloidal synthesis, SEM, STM.

Nomenclatures

nm:	nanometer
μm:	micrometer
dm:	the shorter diameter
DM:	the largest diameter
I:	current
V:	voltage

1. Introduction

The nanostructured materials of II-VI group have attracted great interest due to theirs optical and electrical properties which depend strongly on their size. This is the case of CdSe (cadmium selenide), where their physical properties (electrical and optical) are better when it is synthesized in nanometric scales which behavior like a quantum dot [1-7].

The CdSe nanocrystals are undoubtedly the most studied due to their tunable emission in the visible range, and the advances in the different techniques of its preparation, the possible uses in industrial and biomedical applications and in other research areas make it a very promising material [2, 8-11]. This material is a *n*-type semiconductor with a direct band gap of 1.74 eV and shows two crystalline phases: hexagonal and cubic [12-16].

Among the existing different techniques to characterizer a material, in this paper we used the SEM (scanning electron microscope, developed in 1928) because it is an instrument available to analyze the morphology of samples. Another is the STM (scanning tunneling microscope), that determines the electronic structure (charge density) of conductors and semiconductors with the objective to know the physical properties of the samples [17-19].

In 1982, Binning and Rohrer [20] published for first time images with resolution atomic of Au (110) and Si (111) surfaces obtained from STM showing the great potential of this microscope, in 1989 Feenstra [21]

Corresponding author: Gabriela Sánchez Legorreta, PhD student, research fields: nanoparticles growth, interaction of radiation with matter.

used the same technique to study the optical properties of gold on the GaAs (110) surface. But in specific with the CdSe nanoparticles, many images obtained from STM did not exist. Recently, the study of nanoparticles of CdSe had been through microscopy and spectroscopy STM showing images of the charge density and the differential conductance (dI/dV) that has correspondence to the DOS (density of states) of the nanocrystals and thus their conduction and valence band edges, respectively, but the spectra is the most used to know their optical properties but not physical [17, 22-24].

In this work, we show different micrographs of CdSe nanostructured using SEM and STM, showing the physical properties of the CdSe.

2. Experimental Setup

The nanoparticles of CdSe were synthesized through a colloidal method using cadmium chloride ($CdCl_2$•$2.5H_2O$) as a cadmium precursor, selenium (Se), sodium borohydride ($NaBH_4$), hydrochloric acid (HCl) and pentasodium tripolyphosphate (called Extran, 2 mL) as surfactant to regulate the pH in solution. The growth of the CdSe nanoparticles was under the following conditions: 15 min of reaction time to obtain the Cd^{2+} ions ($CdCl_2$•$2.5H_2O$ + Extran) and 13 min to Se^{2-} ions (Se + $NaBH_4$), molar concentration 1:1:2 of Cd, Se and $NaBH_4$ respectively; the temperature in solutions must be 75 °C for Se^{2-} and room temperature for Cd^{2+} for each different pH value (8 to 12, increasing one by one). Both solutions are mixed for 30 min to create the CdSe nanoparticles and a clean process was made repeating several rinses with deionized water and HCl for 15 min, all in constant stirring.

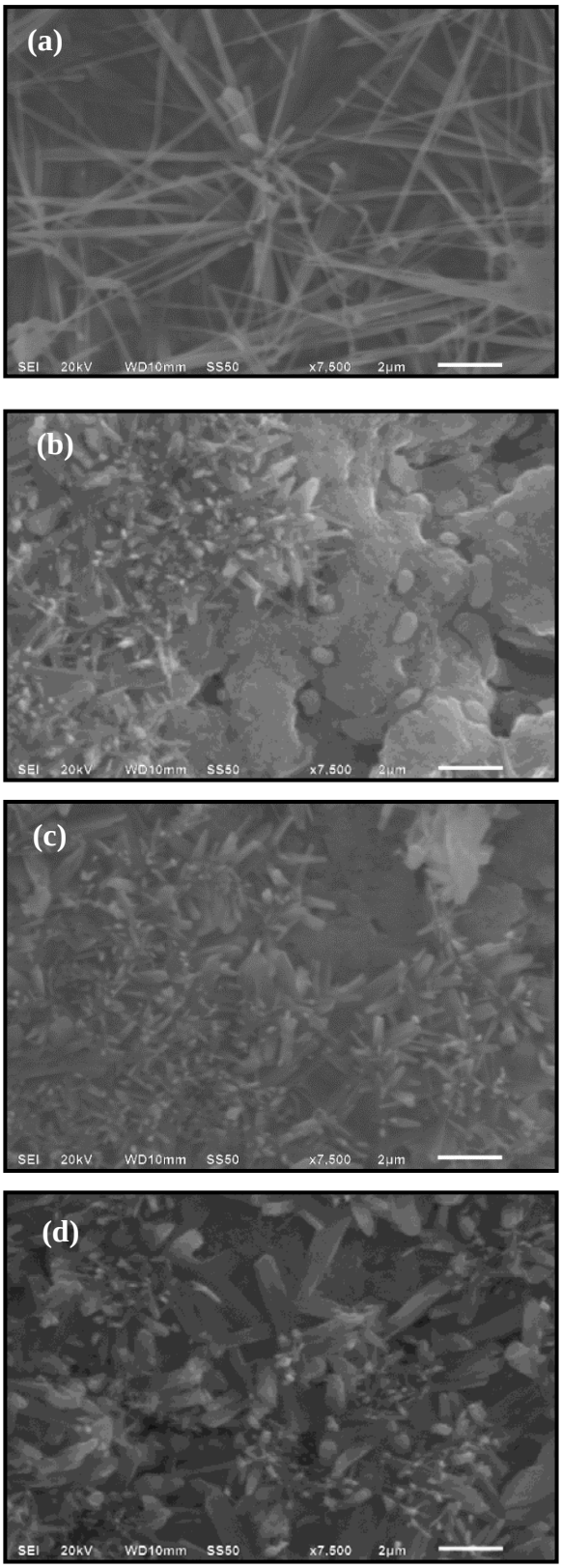
The samples obtained were characterized using the SEM and STM with the objective to measure the size and observe the shape of the particles as well as to know different physical aspects of the surface morphology. The SEM (Jeol JSM-6510lV) uses a thermal emission source, such as a heated tungsten filament to produce electrons, these are focused into a small beam by a series of electromagnetic lenses into the SEM column, the electrons of the beam interact with the sample surface producing various signals, like secondary electrons, backscattered electrons and others, these are recorded for an electron detector forming an image that can be used to obtain information about the external morphology (texture). The STM (Nanosurf easy Scan 2 STM) has a metallic tip (Platinum-Iridium) of 4 mm long; it does a scan on the surface applying a potential difference between it and the sample. When an STM tip approaches a conducting substrate, without touching it, the electrons are presented with an energy barrier between the tip and substrate. The barrier can be broken by applying a tunneling current (I) that is generated by a voltage (V) between the tip and the surface sample which is controlled using the STM software. It is possible to chance the distance in x-, y-, and z-direction too and the images obtained are in nanometric scales, as well, we could obtain the profile of the samples.

3. Experimental Results

The SEM micrographs show the morphological changes on the surfaces from the samples with different pH values (8 to 12), forming filaments (fibbers) and bars (both with different length sizes), and spheres.

At the sample with pH = 8 (Fig. 1a) we can see the formation of long filaments, greater than 10 μm, but with a diameter in tens of nm, when it was grown with pH = 9, 10 and 11 (Figs. 1b-1d respectively), the tendency was to form little rectangular bars with different long sizes between 0.5 and 2 μm, when the pH = 12 we obtained spheres with a diameter from 0.5 to 1.3 μm (Fig. 1e).

The images show the change in the morphology on the surface at the process grown ending. It can be attributed to the pH value, since the potential that exists between the atoms is affected by this parameter, making that the lattice parameter as well as crystalline


(a)
SEI 20kV WD10mm SS50 x7,500 2μm
(b)
SEI 20kV WD10mm SS50 x7,500 2μm
(c)
SEI 20kV WD10mm SS50 x7,500 2μm
(d)
SEI 20kV WD10mm SS50 x7,500 2μm

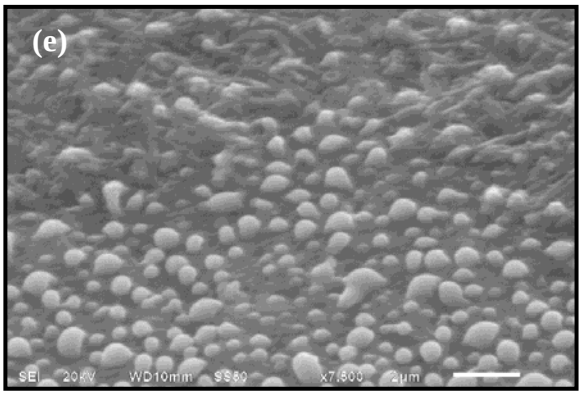


Fig. 1 SEM micrographs of CdSe nanostructured at different pH values. (a) pH = 8, (b) pH = 9, (c) pH = 10, (d) pH = 11 and (e) pH = 12.

structure of system can be modified. In the solution, the pH affects the solubility and precipitation of nanoparticles forming different sizes and shapes; in this work we observed that the nanoparticle size decreases when the pH is higher. In other elements the behaviour is similar, for example in the synthesis of Ag nanoparticles [25, 26], but in some compounds from the II-VI family it is the opposite effect, mostly the particle size tends to increase when the pH is higher, such as the zinc oxide (ZnO) or zinc sulphide (ZnS) [27, 28].

To know the shape and size of the electronic cloud on the nanoparticles at different pH values the micrographs were obtained from the samples using the STM. From these, the formation of circular bars and semi-spheres were observed, however, the size and shape of them are different for each pH value. The tendency of those is to decrease in size when the pH value increases. For example, in the case of pH = 8 (Fig. 2a) the particles were measured on average 11.54 nm, while at pH = 10 (Fig. 2b) it is measured 7.51 nm approximately, see Table 1.

The different shapes and sizes of nanoparticles depend on pH value that acts strongly in the nucleation and grown process of the system [29-31], i.e., having a pH = 8 larger nanoparticles were formed, compared with the other values in which the particle size decreases (Table 1). It is because a higher pH value does not permit that the nucleation process is favored.

Another effect observed in the STM micrographs was the presence of luminescence dots (Fig. 3) on the surface of the sample with pH = 9 (using a potential of -1.4 V on it).

That effect has not been observed before for CdSe and, according to the literature [32, 33], these phenomena can be attributed to the interaction that exists between applied potential by the STM tip and *p* orbital corresponding to Se. In the initial process, when the pH is regulated in the solution, some of the Cd ions are joint with OH^- ions forming Cd-OH, due to its same orbital type (*s*) and because the hydroxyl ions accept protons or positive ions from Cd^{2+}. When the Se ions (*p* orbital) are added, the OH^- ions are replaced by these forming CdSe, but some of them fail to place themselves in those places and remain free, it was recorder like luminescence dots in the STM micrographs (Fig. 4).

This effect is not seen in all regions on the surface due to the form and orientation of the nanoparticles and neither in all samples, an excess of H atoms inhibits this effect. The pH value affects mainly the particle size and is notable on the surface of the samples.

To know the particle size and to be able to quantify them, the profile was obtained in different areas on the surface of the micrograph determining an average of them.

However, in those profiles few perturbations exist in the curves which were removed by smoothing using

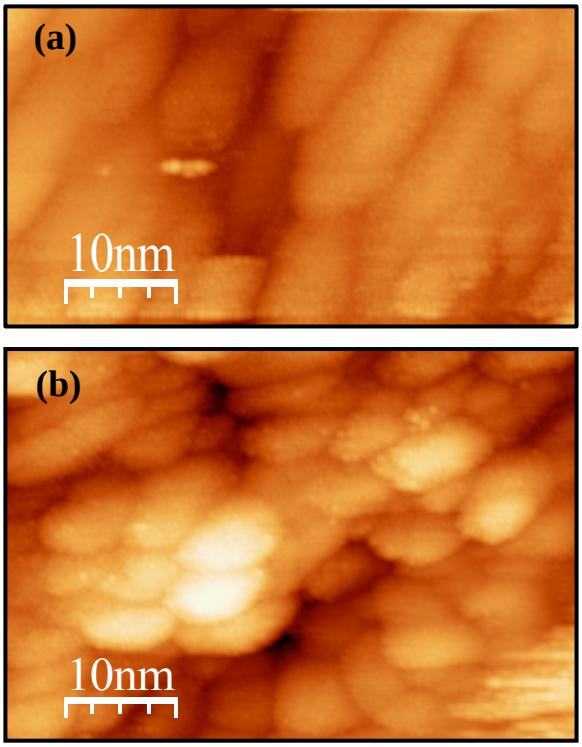


Fig. 2 STM micrographs CdSe. (a) pH = 8, (b) pH = 10.

Table 1 Average size of CdSe for different pH values.

pH	DM (nm)	dm (nm)
8	11.54 ± 1.03	6.07 ± 0.55
9	10.1 ± 0.65	5.71 ± 0.4
10	7.51 ± 0.48	5.09 ± 0.38
11	6.04 ± 0.47	4.38 ± 0.4
12	6.90 ± 0.58	4.05 ± 0.38

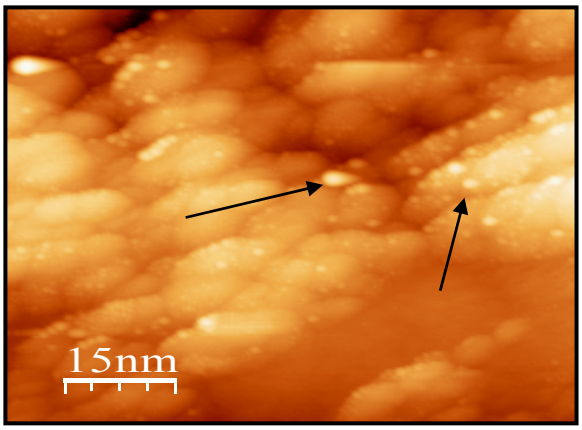


Fig. 3 STM micrographs of CdSe with pH = 9. The narrows in the image identify some of the luminescence dots.

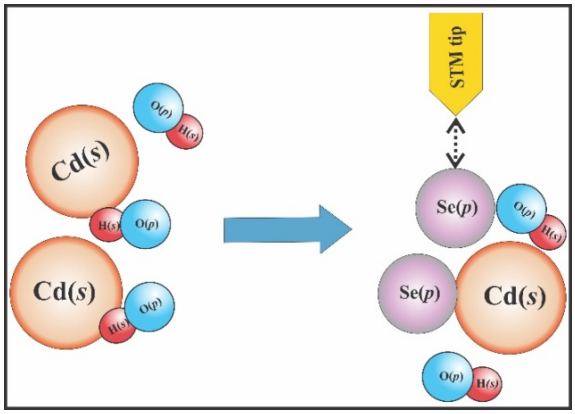


Fig. 4 Schematization of the interaction between Cd (*s*), OH^-, Se (*p*) orbitals and the STM tip.

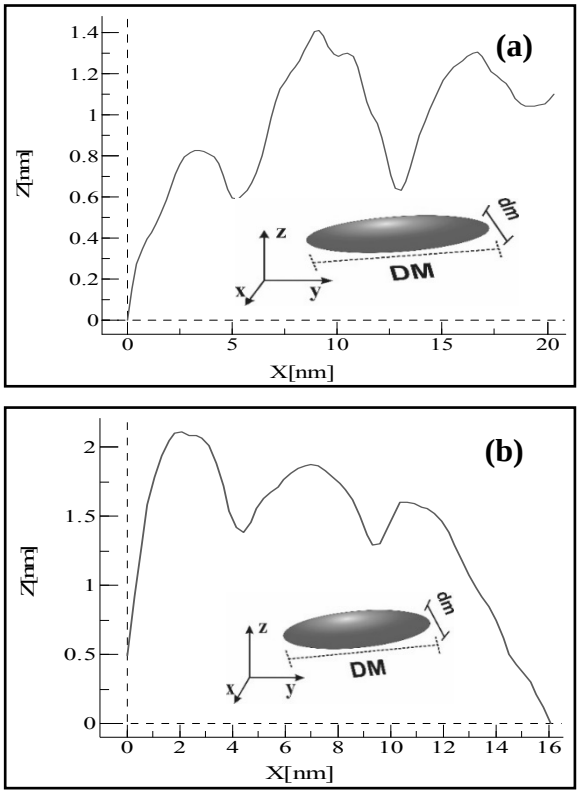


Fig. 5 Profile of the CdSe micrographs corresponding to (a) pH = 8 and (b) pH = 10, where DM and dm represent the largest diameter along the length and width of the particle respectively. The profiles of 9, 11 and 12 have a similar behavior.

the WSxM software, these perturbations are high frequency noise that are easily recorded by the microscope [34, 35], represented like a defect on the surface of the samples.

From the micrographs in Figs. 2a and 2b, we show the surface profile (Fig. 5) to notice the periodicity on the surfaces of the samples, from them it was possible to measure the larger and smaller diameter, recording the following data (Table 1):

With the data shown in Fig. 6, taking the pH = 8 values as a reference, we can see the changes in the size for different pH values, i.e. the size of it is smaller when the pH value increases, nevertheless, in the case with pH = 12 the particle size increases only in larger diameter, because the pH affects the nucleation and the grown process.

To know if the micrographs correspond to periodic arrangement system it was necessary to obtain the FFT

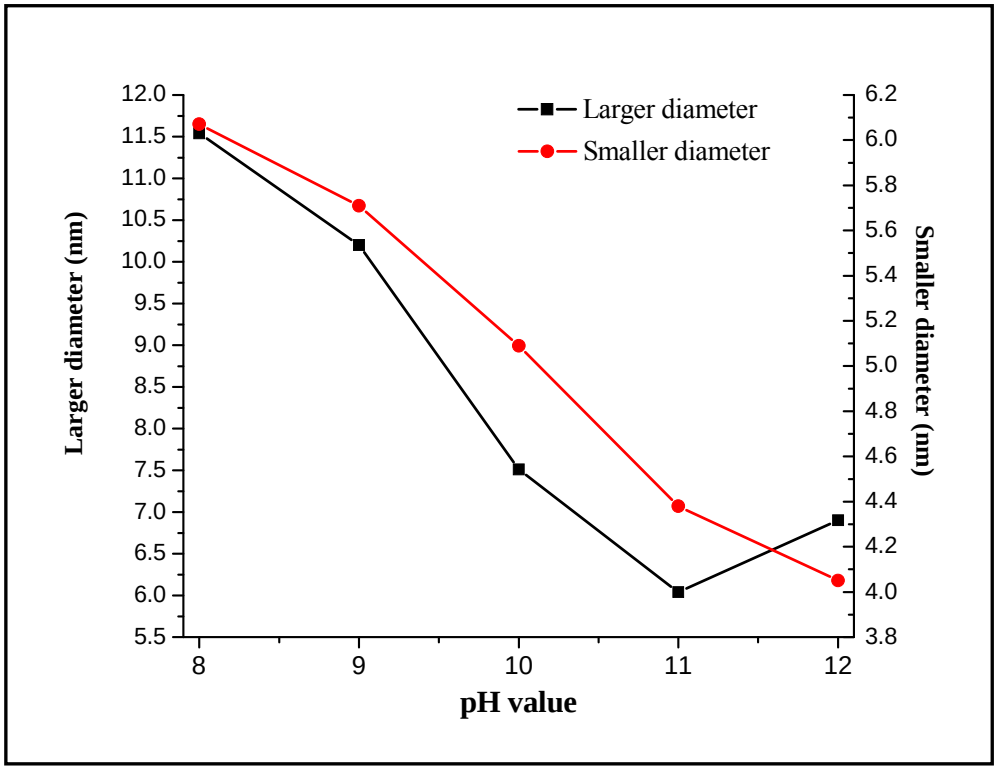


Fig. 6 Larger and smaller diameter size variation in function of pH values.

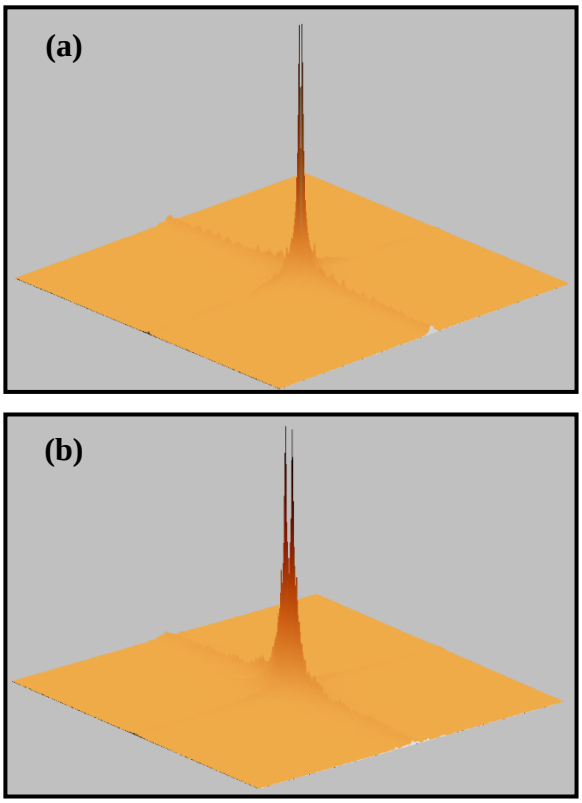


Fig. 7 3D-FFT of CdSe micrographs. (a) pH = 8 and (b) pH = 10.

(Fast Fourier Transform) of each one of them, where two scattering centres were identified which correspond to cubic crystalline structure [36, 37]. The FFT spectra in 3D were obtained from the samples with pH = 8 and pH = 10, in both cases, two peaks appear with high intensity due to most of the elements scatters in one direction, which implies that the system is most crystalline, thus showing the periodicity of the system. In Fig. 7, the pH = 8 peaks are thinner than pH = 10, showing that to increase the pH the periodicity into the system is losing.

According to the behaviour of the spectra found we conclude that the effect of pH is to favour the cubic crystalline phase in the material. It had been working with the characterization and analysis of the samples using XRD (X-ray diffraction) and HRTEM (high-resolution transmission electron microscope) [37].

4. Conclusions

The SEM micrographs obtained showed the grown of nanoparticles to form fibers, bars or hemispheres of different sizes, it depends strongly on the pH value.

STM confirms the formation of nanostructured CdSe of different nanoparticles sizes, which was modified when the pH changed in the synthesis process, they are small at higher pH value, with a maximum size of grain at pH = 8 and minimum at pH = 11.

Acknowledgments

Sanchez-Legorreta thanks CONACYT-Mexico for the scholarship granted for the postgraduate studies; to Laboratory of "Grown and Electro-optical characterization of nanomaterials" FC-UAEMex for the tools to nanoparticles grown and STM-characterization; to CCIQS UAEMex-UNAM for making the structural characterization of samples; finally, to "Red Temática Interacción de Radiación con Materia" for the support.

References

[1] Juárez, B. H. 2011. "Nanopartículas Semiconductoras Coloidales y Aplicaciones." *An. Quím*. 107(3): 229-36.

[2] Barros, P. V., and Villaescusa, V. G. 2011. "Quantum Dots: The New Contribution of Nanotechnology to Research and Medicine." *Revista Complutense de Ciencias Veterinarias* 5: 69-102.

[3] Etxeberria, H., Kortaberria, G., Zalakain, I., Larrañaga, A., and Mondragon, I. 2012. "Effect of Different Aqueous Systhesis Parameters on the Size of CdSe Nanoparticles." *J Mater Sci.* 47: 7167-74.

[4] Acharya, A., Sahu, S., and Balamurgan, S. 2011. "Effect of Doping on Nano Cadmium-Selenide (CdSe)-Assessment through UV-VIS Spectroscopy." *Lat. Am. J. Phys. Educ.* 5: 134.

[5] Tian, L., Yang, H., Ding, J., Li, Q., Mu, Y., and Zhang, Y. 2014. "Synthesis of the Wheat-Like CdSe/CdTe Thin Film Heterojunction and Their Photovoltaic Applications." *Current Applied Physics*. 14: 881-5.

[6] Ananthakumar, S., Ramkumar, J., and Moorthy Babu, S. 2014. "Synthesis of Thiol Modified CdSe Nanoparticles/P3HT Blends for Hydride Solar Cell Structures." *Materials Science in Semiconductor Processing* 22: 44-9.

[7] Cao, G. Z., and Wang, Y. 2011. *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*. 2nd ed. World Scientific Publishing.

[8] Mohammadimasoudi, M., Penninck, L., Aubert, T., Gomes, R., Hens, Z., Strubbe, F., and Neyts, K. 2013. "Fast and Versatile Deposition of Aligned Semiconductor Nanorods by Dip-Coating on a Substrate with Interdigitated Electrodes." *Optical Materials Express* 3 (12): 2045-54.

[9] Gonzáles, J. C., and Chung, A. 2005. "Determinación de las constantes ópticas de una película delgada de CdSe." *Revista de investigación de Física* 8 (1): 5-10.

[10] Romano-Trujillo, R., Rosendo, E., Ortega, M. A., et al. 2012. "Synthesis and Characterization of PbSe Nanoparticles Obtained by a Colloidal Route Using Extran as a Surfactant at Low Temperature." *Nanotechnology* 23 (18): 185602.

[11] Farrow, B., and Kamat, P. V. 2009. "CdSe Quantum Dot Sensitized Solar Cells. Shuttling Electrons through Stacked Carbon Nanocups." *Journal of the American Chemical Society* 131 (31): 11124-31.

[12] He, R., You, X., Tian, H., Gao, F., Cui, D., and Gu, H. 2006. "Synthesis and Characterization of Monodisperse CdSe Quantum Dots in Different Organic Solvents." *Frontiers of Chemistry in China* 1 (4): 378-83.

[13] Burda, C., Chen, X., Narayanan, R., and El-Sayed, M. A. 2005. "Chemistry and Properties of Nanocrystals of Differentshapes." *Chemical Reviews* 105 (4): 1025-102.

[14] Schmid, G. 2011. *Nanoparticles: From Theory to Application*. John Wiley & Sons.

[15] Borkovska, L. V., Korsunska, N. O., Kushnirenko, V. I., Sadofyev, Y. G., and Sheinkman, M. K. 2003. "Influence of Cation Vacancy Related Defects on the Self-assembly Processes in CdSe/ZnSe Quantum Dot Heterostructures." *Semiconductor Physics Quantum Electronics & Optoelectronics* 6 (3): 294-8.

[16] Sung, M. S., Lee, Y. B., Kim Y. J., and Kim Y. D. 2007. "Preparation and Characterization of CdSe Nanoparticles Synthesized Using the Ultrasonic Irradiation." *Solid State Phenomena* 124: 1229-32.

[17] Zhou, W. Z., and Wang, L. 2006. *Scanning Microscopy for Nanotechnology: Techniques and Applications*. Springer.

[18] Hummon, M. R., Stollenwerk, A. J., Narayanamurti, V., Anikeeva, P. O., Panzer, M. J., Wood, V., and Bulović, V. 2010. "Measuring Charge Trap Occupation and Energy Level in CdSe/ZnS Quantum Dots Using a Scanning Tunneling Microscope." *Physical Review B* 81 (11): 115439.

[19] Bakkers, E. P. A. M., Hens, Z., Kouwenhoven, L. P., Gurevich, L., and Vanmaekelbergh, D. 2002. "A Tunneling Spectroscopy Study on the Single-Particle Energy Levels and Electro-Electron Interactions in CdSe Quantum Dots." *Nanotechnology* 13: 1-5.

[20] Binnig, G., and Rohrer, H. 1983. "Scanning Tunneling Microscopy." *Surface Science* 126: 236-44.

[21] Feenstra, R. 1989. "Scanning Tunneling Microscopy and Spectroscopy of Gold on the GaAs (110) Surface." *Journal of Vacuum Science and Technology B* 7: 925-30.

[22] Kundu, B., Chakrabarti, S., and Pal, A. J. 2016. "Temperature Dependent Electron Delocalization in CdSe/CdS Type-I Core-Shell Systems: An Insight from Scanning Tunneling Spectroscopy." *Journal of Applied Physics* 119: 104304.

[23] Gao, B., Kuang, Y.-M., Liao, Y., and Dong, Z.-C. 2012. "Dispersion and STM Characterization of Au-CdSe Nanohybrids on Au (111)." *Chinese Journal of Chemical Physics* 25: 231.

[24] Dey, S., and Pal, A. J. 2013. "Tuning of Band-Edges in Type-I Core-Shell Nanocrystals through Band-Offset Engineering: Selective Quantum Confinement Effect." *Advances, Royal Society of Chemistry* 3: 13225-31.

[25] Qin, Y., Ji, X., Jing, J., Liu, H., Wu, H., and Yang, W. 2010. "Size Control over Spherical Silver Nanoparticles by Ascorbic Acid Reduction." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 372: 172-6.

[26] Alqadi, M., Noqtah, O. A., Alzoubi, F., Alzouby, J., and Aljarrah, K. 2014. "pH Effect on the Aggregation of Silver Nanoparticles Synthesized by Chemical Reduction." *Materials Science* 32: 107-11.

[27] Ikono, R., Akwalia, P. R., Siswanto, W. B. W., Sukarto, A., and Rochman, N. T. 2012. "Effect of pH Variation on Particle Size and Purity of Nano Zinc Oxide Synthesized by Sol-Gel Method." *International Jounal Engineering & Technology* 12: 5-9.

[28] Zhang, H., Chen, B., and Banfield, J. F. 2010. "Particle Size and pH Effects on Nanoparticle Dissolution." *The Journal of Physical Chemistry C* 114: 14876-84.

[29] Sibiya, P. N., and Moloto, M. J. 2014. "Effect of Precursor Concentration and pH on the Shape and Size of Starch Capped Silver Selenide (Ag_2Se) Nanoparticles." *Chalcogenide Letters* 11 (11): 577-88.

[30] Avramescu, M. L., Rasmussen, P. E., Chénier, M., and Gardner, H. D. 2017. "Influence of pH, Particle Size and Crystal Form on Dissolution Behaviour of Engineered Nanomaterials." *Environmental Science and Pollution Research* 24 (2): 1553-64.

[31] Bai, C. 2000. *Scanning Tunneling and Its Applications.* 2nd ed. Springer Science & Business Media.

[32] Bowler, D. R. 1997. "A Theoretical Investigation of Gas Source Growth of the Si (001) Surface." PhD thesis, University of Oxford.

[33] Horcas, I., Fernández, R., Gomez-Rodriguez, J., Colchero, J., Gómez-Herrero, J., and Baro, A. 2017. "WSXM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology." *Review of Scientific Instruments* 78: 013705.

[34] Klaus, S. 2002. *The Energy Gap of Clusters Nanoparticles, and Quantum Dots Handbook of Thin Films Materials.* San Diego: Nanomaterials and Magnetic Thin Films Academic Press.

[35] Li, Y., Han, Q., Kim, T. W., and Shi, W. 2014. "Synthesis of Wurtzite--Zincblende Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ Nanocrystals: Insight into the Structural Selection of Quaternary and Ternary Compounds Influenced by Binary Nuclei." *Nanoscale, Royal Society of Chemistry* 6: 3777-85.

[36] Sung, Y., Lim, J., Koh, J. H., Hill, L. J., Min, B. K., Pyun, J., and Char, K. 2015. "Uniform Decoration of Pt Nanoparticles on Well-Defined CdSe Tetrapods and the Effect of Their Pt Cluster Size on Photocatalytic H 2 Generation." *Cryst. Eng. Comm* 17: 8423-7.

[37] Sánchez-Legorreta, G., Rosendo-Francisco, P., and Vargas-Sanabria, R. To be Published.