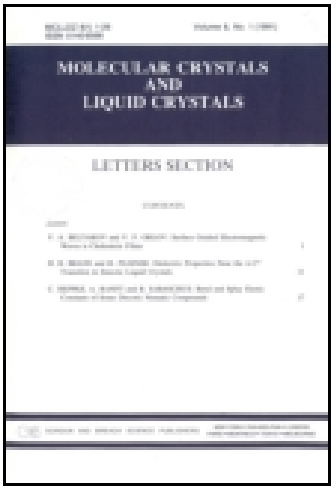

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effects of Growth Temperature on the Properties of CdSe Nano-Crystals Synthesized Eco-Friendly Using Colloidal Route

Chang-Duk Kim[a], Hong Tak Kim[a], Bong-Ki Min[b] & Chinho Park[a]
[a] School of Chemical Engineering, Yeungnam University, Gyeongsan, Korea
[b] Instrumental Analysis Center of Yeungnam University, Korea
Published online: 06 Dec 2014.

To cite this article: Chang-Duk Kim, Hong Tak Kim, Bong-Ki Min & Chinho Park (2014) Effects of Growth Temperature on the Properties of CdSe Nano-Crystals Synthesized Eco-Friendly Using Colloidal Route, Molecular Crystals and Liquid Crystals, 602:1, 151-158, DOI: 10.1080/15421406.2014.944755

To link to this article: http://dx.doi.org/10.1080/15421406.2014.944755

Mol. Cryst. Liq. Cryst., Vol. 602: pp. 151–158, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.944755

Taylor & Francis
Taylor & Francis Group

Effects of Growth Temperature on the Properties of CdSe Nano-Crystals Synthesized Eco-Friendly Using Colloidal Route

CHANG-DUK KIM,[1] HONG TAK KIM,[1] BONG-KI MIN,[2] AND CHINHO PARK[1,*]

[1]School of Chemical Engineering, Yeungnam University, Gyeongsan, Korea
[2]Instrumental Analysis Center of Yeungnam University, Korea

In this study, CdSe nanocrystals (NCs) were synthesized by inexpensive, non-toxic, and eco-friendly method, and the effect of growth temperature on the formation of CdSe NCs was investigated. The NCs were formed using oleic acid, and paraffin liquid instead of environmentally harmful materials typically involved in the NC synthesis. As the growth temperature increased from 140°C to 220°C, the diameter of CdSe NCs was changed from 3 nm to 4.5 nm, and the activation energy for the growth of CdSe NCs was 8.1 J/mol. As-synthesized CdSe NCs had a hexagonal crystal structure with wurtzite phase, and the growth of (101) plane was preferred with increasing growth temperature. The energy band-gap of the NCs was shifted from 2.29 eV to 2.18 eV, and the band-gap shift had a linear relationship with the size increase of the NCs. The growth temperature for the formation of CdSe NCs was an important factor to control the properties of the NCs. The developed method is considered to be an efficient CdSe synthesis method using eco-friendly colloidal route.

Keywords CdSe; colloidal; eco-friendly; hot-injection; nanocrystals

Introduction

The synthesis of high quality nanocrystals (NCs) has been an important subject in the field of materials science, recently [1–3]. Especially, the semiconductor NCs are suitable of applying not only inorganic solar cells but also organic devices. The semiconductor NCs have advantages such as tunable energy band-gap due to quantum confinement effect, high conversion efficiency from excited exciton to electron-hole pair due to high dielectric constant, multiple exicton generation, and wide light absorption above their band-gap [4]. These properties can be useful for utilizing in organic solar cells. Recently, CdSe NCs are the most extensively investigated material among semiconductor NCs since the introduction of the concept of the "size quantization effect" in the earlier eighties [5–7]. High-quality CdSe NCs have attracted broad attention in recent years for the use in a variety of applications including biological fluorescent labels [8], light emitting diodes [9], lasers [10], as well as

*Address correspondence to Chinho Park, School of Chemical Engineering, Yeungnam University, Gyeongsan, 712-749, Korea. E-mail: chpark@ynu.ac.kr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

solar cells [11, 12]. In general, the synthesis of CdSe NCs is carried out in high-boiling mixtures of trioctylphosphine (TOP) and trioctylphospine oxide (TOPO). The TOP/TOPO and thiol-based techniques have been used widely in the synthesis of CdSe NCs, and many results have been reported [13–17]. However, TOP/TOPO and thiol-based materials are very toxic and hazardous to the environment and living organisms [18]. Thus, eco-friendly synthesis methods are needed to produce various NCs including CdSe NCs.

In this study, CdSe NCs were synthesized using eco-friendly colloidal route without using TOP/TOPO and thiol-based materials, and the effects of the growth temperature on CdSe NCs growth were investigated.

Experimental

CdSe NCs were synthesized using colloidal route, and the effects of synthesis temperature were investigated. Cadmium oxide (CdO, Adrich 99%) and selenium (Se, Aldrich 99.9%) were used as precursor materials with the mole ratio of Se to Cd of 1:2. Oleic acid (modified) was used as capping material for Cd, and paraffin oil (OCI) was used as high-boiling solvent material. First, CdO (1 mmol), oleic acid, and paraffin (10 ml) were mixed in three-bottle neck flask at the temperature of 160°C for 1 hr. At the same time, Se (2 mmol) and paraffin (40 ml) were dissolved in three-bottle neck flask at the temperature of 220°C for 1 hr. Both homogeneous solutions were vigorously mixed at different synthesis temperatures for 1 hr, and the synthesis temperature was ranged from 140°C to 220°C. After finishing the growth process, the flask, containing mixed solution, was rapidly cooled down to room temperature using flowing cold water. The cooled solution was centrifuged, and the NCs were washed sequentially with methanol, acetone, and toluene. The purified CdSe NCs were stored in methanol to prevent NCs from oxidation and aggregation.

The structural properties of CdSe NCs were investigated by X-ray diffractometer (XRD, PANalytical MPD) and the transmission electron microscope (TEM, FEI Tecnai G2 F20). The optical properties of the NCs were measured by UV-Vis-NIR spectrometer (Cary 5G) and photoluminescence spectrometer with He-Cd laser (wavelength: 325 nm, power: 1 mW).

Results and Discussion

Figure 1 shows the size distribution of the CdSe NCs according to the different synthesis temperatures (150°C, 160°C, 180°C, 200°C and 220°C). Count of the CdSe NCs size was taken from measurements of low and high resolution TEM images. The size of CdSe NCs linearly increased from 3 nm to 4.5 nm, when the growth temperature increased from 140°C to 220°C. In addition, the sizes of CdSe NCs exhibited narrow distribution, and the NCs were represented in spherical shape at all synthesized conditions. This mono-dispersity is believed to be originated from the structure of oleic acid as a capping material of Cd. The growth probability of CdSe NCs decreases via Se-redox process due to fatty structure of oleic acid, when the oleic acid are weakly bonded to Cd by Van der Waals force. This means that the growth of CdSe NCs proceeds slowly, and the size control is more effective in this method. The activation energy of the CdSe NCs growth is estimated from the Arrhenius plot of the NCs size as a function of inverse temperature, and the equation is given by [19, 20]:

$$g = A \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

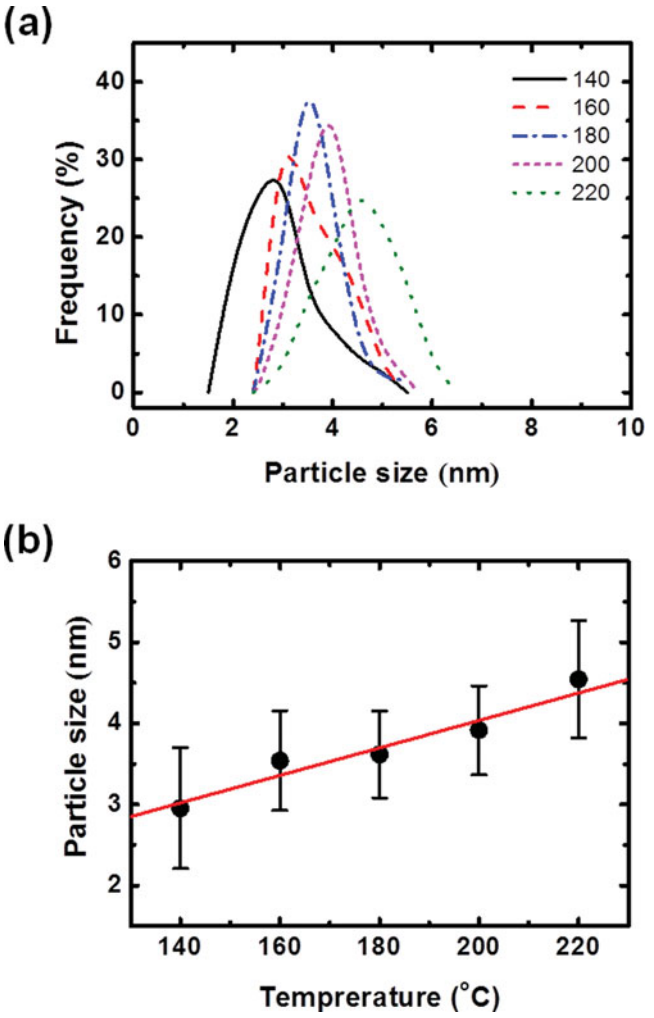

Figure 1. (a) the size distribution of CdSe NCs and (b) particle size (error bar: standard deviation) of CdSe NCs at different conditions.

where g is the growth rate, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. The activation energy can be calculated form the slope of ln(g)-(1/T) plot and estimated to be 8.1 J mole^{-1}. The Arrehnius plot for the growth of CdSe NCs according to the growth temperature is shown in Fig. 2.

Figure 3(a) shows the XRD patterns of the CdSe NCs synthesized at different growth temperatures. Mainly observed peaks were from (100), (002), and (101) crystal planes in all the CdSe NCs obtained in this study, which corresponded to the hexagonal CdSe crystal planes having wurtzite phase. As the growth temperature increased, the (100) preferred orientation of CdSe NCs decreased, and the (101) orientation increased. The degree of growth orientation in synthesized CdSe NCs can be defined as the texture coefficient (TC), and the TC for (100) and (101) peaks, according to the growth temperature, can be calculated

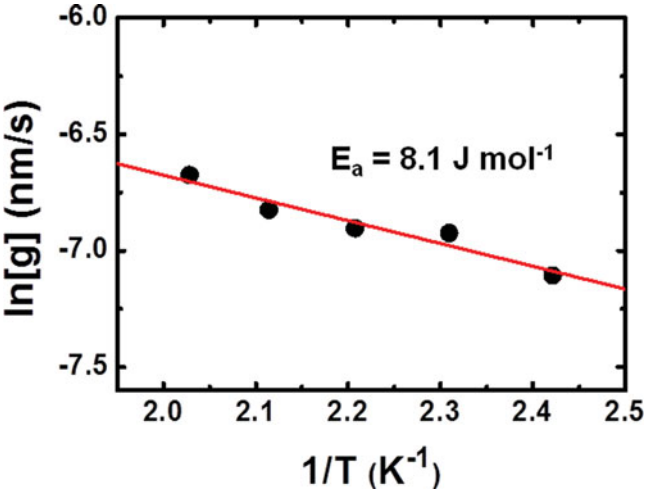

Figure 2. Arrehnius plot for the growth of CdSe NCs.

by the following equation [21–23]:

$$TC_{hkl} = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n}\sum \frac{I(hkl)}{I_0(hkl)}} \tag{2}$$

where TC_{hkl} is the texture coefficient of (hkl) peak, $I(hkl)$ is the relative intensity of (hkl) peak, and $I_0(hkl)$ is the relative intensity of the corresponding orientation, and n is the number of peaks, respectively. As the growth temperature increased from 140°C to 220°C, the (100) orientation of CdSe NCs decreased from 76% to 32%. On the contrary, the (101) orientation of the NCs increased from 24% to 67% with the increase of temperature. This implied that the degree of growth orientation of CdSe NCs changed with respect to the growth temperature.

Figure 4(a) and 4(b) show low and high resolution TEM images of CdSe NCs using eco-friendly colloidal route, respectively (growth temperature: 220°C). The CdSe NCs exhibited mono-dispersed spherical shape, and the existence of well-resolved lattice fringes confirmed the excellent crystalline nature of as-prepared CdSe NCs. The inter-planar distance in the lattice fringe, as shown in Fig. 3(b), was about 0.334 nm, and the d-spacing value calculated from the SAED patterns in Figure 4(c) was about 0.329 nm. These values correspond to the distance of the (101) plane of wurtzite structural CdSe (JCPDS No. 08-0459), and the results of TEM study were consistent with those of the XRD study, as mentioned above.

Figure 5 shows the photoluminesence (PL) spectra of CdSe NCs at different growth temperatures. All the CdSe NCs exhibit the strong excitation peaks and do not show any additional excitation peaks due to impurities. The PL spectra, originating from the band to band transition of the CdSe NCs, can be tuned from 542 nm to 569 nm by changing the growth temperature, since it is closely related to the size of NCs. As shown in Fig. 1(b), the size of the CdSe NCs increased with the rise of the growth temperature, and the increase of the NCs size mainly caused the red shift of the energy band-gap. This result is in good agreement with previous works that the energy band-gap in NCs shifts

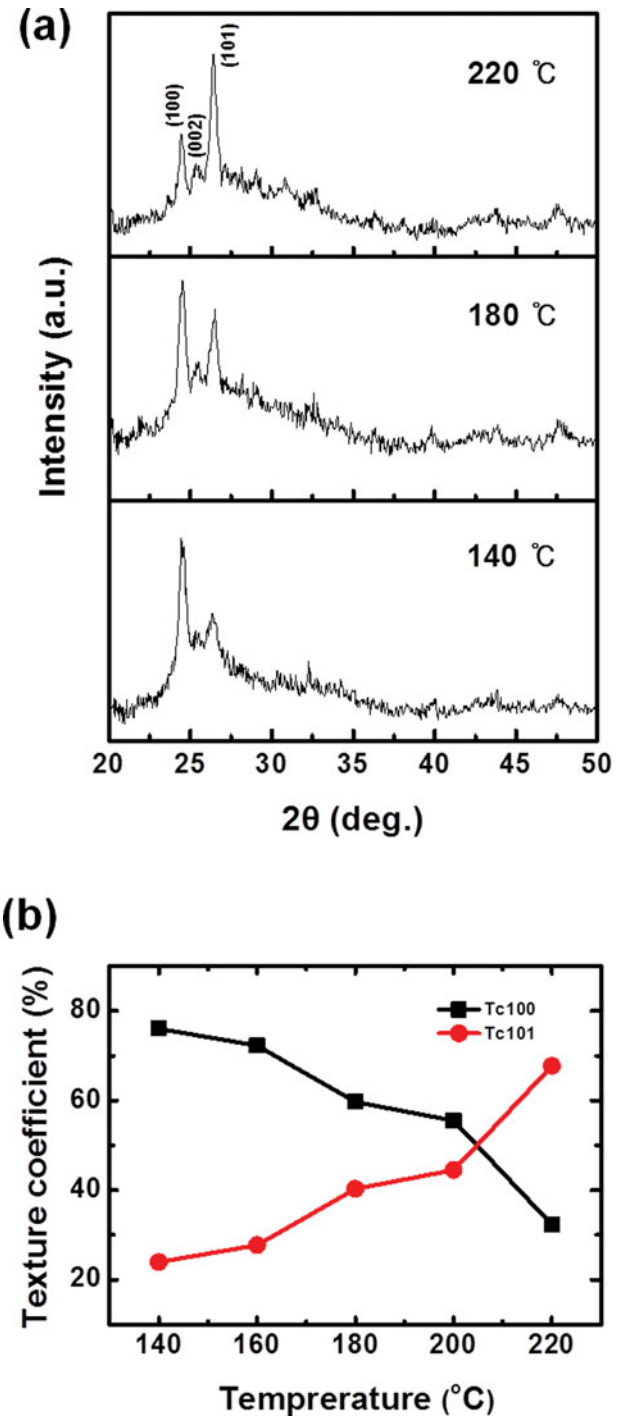

Figure 3. X-ray diffraction (XRD) patterns of CdSe NCs synthesized at different temperatures; (a) XRD patterns of the NCs and (b) texture coefficient of (100) and (101) preferred orientation.

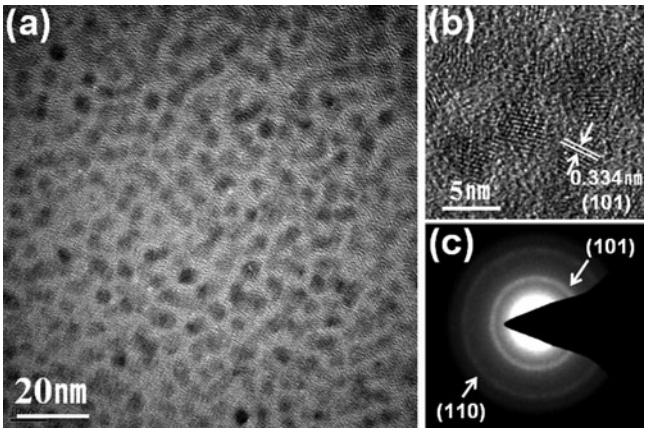

Figure 4. Transmisstion electron microscopic (TEM) images of CdSe NCs synthesized using eco-friendly colloidal route; (a) low resolution TEM image, (b) high resolution TEM image and (c) selective area electron diffraction (SAED) of CdSe NCs (growth temperature: 220°C).

towards higher energy with the reduction of particle size by quantum confinement effect [24]. Using an effective mass approximation, the energy band-gap between bulk and NCs can be expressed simply by [25, 26]

$$E_{NC} = E_g + \frac{\pi^2 \hbar^2}{2\left((m_e^* + m_h^*)/m_e^* m_h^*\right) R^2} - 1.786\frac{e^2}{\varepsilon R} - 0.248E^* \tag{3}$$

where E_{NC} is the energy band-gap of NCs, E_g is the energy band-gap of bulk material, R is the radius of NCs, $m_e{}^*$ is the effective electron mass, $m_h{}^*$ is the effective hole mass, $\hbar$

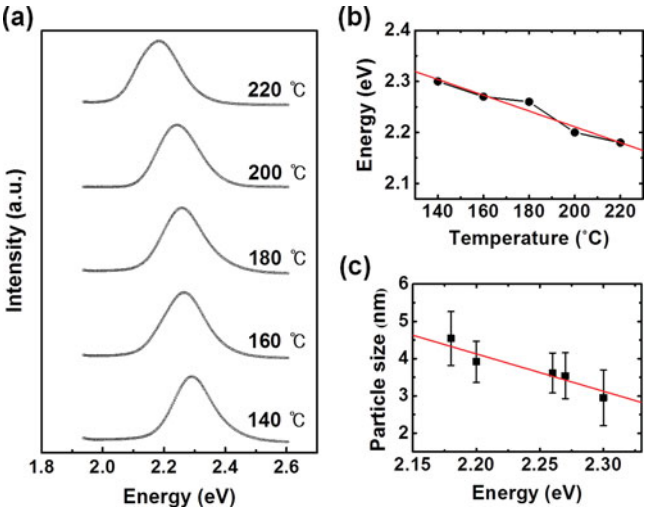

Figure 5. Photoluminescence (PL) spectra of CdSe NCs synthesized at different temperatures; (a) PL spectra of CdSe NCs, (b) energy band gap (E_g) of CdSe NCs, and (c) the relationship between E_g and the particle size of the NCs.

is the Planck constant, e is the electron charge, ε is the permittivity of the vacuum, and E^* is the effective Rydberg energy. In equation 3, the second term on right side represents the energy shift due to the quantum confinement effect and this shows the $1/R^2$ dependence on the energy band-gap. In addition, the third term on right side in Eq. 3 can be usually ignored due to high dielectric constant of NCs. Thus, the energy band-gap of NCs increases compared to that of bulk material when the size of NCs decreases.

Conclusions

The CdSe NCs were synthesized using eco-friendly colloidal route, avoiding the use of environmentally harmful materials such as TOP/TOPO and thiol-based materials, and the effects of the growth temperature on the CdSe NCs formation were investigated in detail. The CdSe NCs were formed using CdO and Se salt as precursor materials, oleic acid as a capping material for CdO, and paraffin liquid as a solvent. As the growth temperature increased from 140°C to 220°C, the size of CdSe NCs was changed from 3 nm to 4.5 nm, and the activation energy for the growth of CdSe NCs was 8.1 J mol^{-1}. The sizes of CdSe NCs exhibited narrow distribution, and the NCs represented spherical shape at all synthesized conditions. The CdSe NCs had a hexagonal crystal structure with wurtzite phase, and the growth direction of the NCs was gradually changed from (100) to (101) plane with increasing growth temperature. The energy band-gap of the NCs was shifted from 2.29 eV to 2.18 eV, and the band-gap shift had a linear relationship with the size of the NCs. From these results, it was found that the growth temperature is a crucial factor to control the opoelectronic and structural properties of CdSe NCs. Consequently, it is expected that the CdSe NCs, synthesized using eco-friendly method, can be applied to eco-friendly manufacture of photovoltaic and light emitting devices.

Funding

This work was supported by the New & Renewable Energy Program (No. 20123010010160) and the Human Resources Development Program (No. 20104010100580) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korean Ministry of Trade, Industry and Energy (MOTIE).

References

[1] Peng, Z. A., & Peng, X. J. (2001). *Am. Chem. Soc.*, *123*, 183.
[2] Wilson, W. L., Szajowski, P. F., & Brus, L. E. (1993). *Science 262*, 1242.
[3] Qu, L., Peng, Z. A., & Peng, X. (2001). *Nano Lett.*, *1*, 333.
[4] Im, S. H. (2012). *Polymer Science & Technology*, *12*, 499.
[5] Efros, Al. L., & Efros, A. L. (1982). *Sov. Phys. Semicond.*, *16*, 772.
[6] Rossetti, R., Nakahara, A., & Brus, L. E. (1983). *J. Chem. Phys.*, *79*, 1086.
[7] Talapin, D. V., Rogach, A. L., Kornowski, A., Haase, M., & Weller, H. (2001). *Nano Lett.*, *1*, 207.
[8] Bruchez, M., Moronne, M., Gin, P., Weiss, S., & Alivisatos, A. P. (1998). *Science*, *281*, 2013.
[9] Chan, W. C. W., & Nie, S. M. (1998). *Science*, *281*, 2016.
[10] Colvin, V. L., Schlamp, M. C., & Alivisatos, A. P. (1994). *Nature*, *370*, 354.
[11] Klimov, V. I., Mikhailovsky, A. A., Xu, S., Malko, A., Hollingsworth, J. A., Leatherdale, C. A., Eisler, H. J., & Bawendi, M. G. (2000). *Science*, *290*, 314.
[12] Greenham, N. C., Peng, X. G., & Alivisatos, A. P. (1996). *Phys. Rev. B*, *54*, 17628.
[13] Deng, Z., Cao, L., Tang, F., & Zou, B. (2005). *J. Phys. Chem. B*, *109*, 16671.

[14] Liu, I., Lo, H., Chien, C., Lin, Y., Chen, C., Chen, Y., Su, W., & Liouc, S. (2008). *J. Mater. Chem.*, *18*, 675.
[15] Park, E., Ryu, J., Choi, Y., Hwang, K., & Song, R. (2013). *Nanotechnology*, *24*, 145601.
[16] Dabbousi, B. O., Rodriguez-Viejo, J., Mikulec, F. V., Heine, J. R., Mattoussi, H., Ober, R., Jensen, K. F., & Bawendi, M. G. (1997). *J. Phys. Chem. B*, *101*, 9463.
[17] Talapin, D. V., Rogach, A. L., Kornowski, A., Haase, M., & Weller, H. (2001). *NanoLett.*, *1*, 207.
[18] Deng, Z., Cao, L., Tang, F., & Zou, B. (2005). *J. Phys. Chem. B*, *109*, 16671.
[19] Huston, P. L. (2001). *Chemical Kinetics and Reaction Dynamics*, McGraw-Hill, New York.
[20] Kim, H. T., Mun, T., Park, C., Jin, S. W., & Park, H. Y. (2013). *J. Power Sources*, *244*, 641.
[21] Barret, C. & Massalski, T. B. (1980). *Structure of Metals*, Pergamon, Oxford.
[22] Montes de Oca Valero, J. A., Petitcorps, Y. L., Manaud, J. P., Chollon, G., Carrillo Romo, F. J., & Lopez M. A. (2005). *J. Vac. Sci. Technol. A*, *23*, 394.
[23] Kim, H. T., Park, J. Y., & Park, Chinho. (2012). *Korean J. Chem. Eng.*, *29*, 676.
[24] Qu, L. & Peng, X. (2002). *J. Am. Chem. Soc.*, *124*, 2049.
[25] Haug, H., & Khoch, S.W. (1993). *Quantum Theory of the Optical and Electric Properties of Semiconductors, World Scientific*, 216.
[26] Vatankhan, C. & Ebadi, A. (2013). *Research J. Recent Sci.*, *2*(1), 21.