



Fabrication of ZnSe nanoparticles: Structural, optical and Raman Studies



Edgar Mosquera^{a,b,*}, Nicolás Carvajal^b, Mauricio Morel^b, Carlos Marín^c

^a Departamento de Física, Universidad del Valle, A.A. 25360 Cali, Colombia

^b Laboratorio de Materiales Funcionales a Nanoescala, Departamento de Ciencia de los Materiales, FCFM, Universidad de Chile, Beauchef 851, Santiago, Chile

^c Department of General Engineering, University of Puerto Rico, P.O. Box 00680, Mayagüez, Puerto Rico, USA

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ABSTRACT

In this work, a simple, effective, reproducible and green fabrication process for the production of high-quality, pure ZnSe nanoparticles at low temperature is presented. The structural and optical properties of these nanoparticles have been examined by transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), Ultraviolet-Visible spectroscopy (UV-vis), photoluminescence (PL), and Raman spectroscopy. TEM analysis confirms that the formed products are ZnSe particles with size less than 10 nm, respectively. Strong blue shift absorption with energy band gap of 3.85 eV is observed from UV-vis spectrophotometry. Photoluminescence measurements showed that the nanoparticles exhibit a strong UV emission peak at 380 nm. The blue emission could be attributed to the quantum size effect of ZnSe nanocrystals. Raman spectroscopy of the ZnSe NPs showed a clear shift of transverse optical (TO) and longitudinal optical (LO) phonon modes, as well as a broadening of the LO phonon mode.

1. Introduction

In recent years, II-VI semiconductors have been promising candidates for commercial laser diodes and related optoelectronic devices operating in the blue range [1–3]. Among various II-VI nanomaterials, zinc selenide (ZnSe) generates great interest for its direct energy band gap ($E_g = 2.7$ eV) and large binding energy (21 meV), at room temperature [4]. Recently, ZnSe nanostructures have been synthesized by several methods [5–8], among which the chemical methods are most commonly used. The importance of choosing a proper synthetic route in fabricating nanomaterials has been a driving force for the development of new methodologies for several decades. Among variety of approaches, the utilization of ultrasound for nanomaterials synthesis has been extensively examined over many years [9,10], and is now a powerful tool in the synthesis process. In our previous work [10], submicronparticles of ZnS were successfully produced via ultrasound. The effects of ultrasound arise from acoustic cavitation [11], which is the formation, growth and implosion of vapor bubbles generated in a liquid [12]. The collapsing bubbles (in nanoseconds) form a spherical, inward propagating shock in the vapor bubble and due to the symmetry they generate an enormous density of energy at the center. The high temperature (> 5000 K) and pressure (> 20 MPa) that can be created may produce chemical reactions that require very large activation energies in the gas phase molecules. This method has the virtue of simplicity, efficiency, and low-energy cost, which facilitates the synthesis

of various kinds of nanostructures. The present study is focus in producing ZnSe nanoparticles (NPs) employing a top-down fabrication process using ultrasound at low temperature. The structural and optical properties of the fabricated ZnSe nanoparticles have been studied. In addition, the nanoparticles exhibit a strong luminescence in the blue region that could be attributed to the quantum size effect of ZnSe nanocrystals.

2. Experimental details

2.1. Materials and fabrication of nanoparticles

ZnSe with purity $\geq 99.99\%$ (Sigma Aldrich) has been used without further purification. Samples of ZnSe powder (size of $10\ \mu\text{m}$) were dispersed in a glass recipe containing isopropyl alcohol. The suspension was subject to continuum sonication for 8 h under vacuum (using an oil free vacuum pump) with the objective of breaking in smaller particles through the mechanical pressure. During the sonication process, the solution temperature was kept at $50\ ^\circ\text{C}$. The process was carried out using an ultrasonic bath, which operates at a fixed frequency of 37 kHz with a maximum input power.

2.2. Characterization

The samples were characterized on a Tecnai F20 FEG-S/TEM

* Corresponding author at: Departamento de Física, Universidad del Valle, A.A. 25360 Cali, Colombia
E-mail addresses: edemova@ing.uchile.cl, edgar.mosquera@correounivalle.edu.co (E. Mosquera).

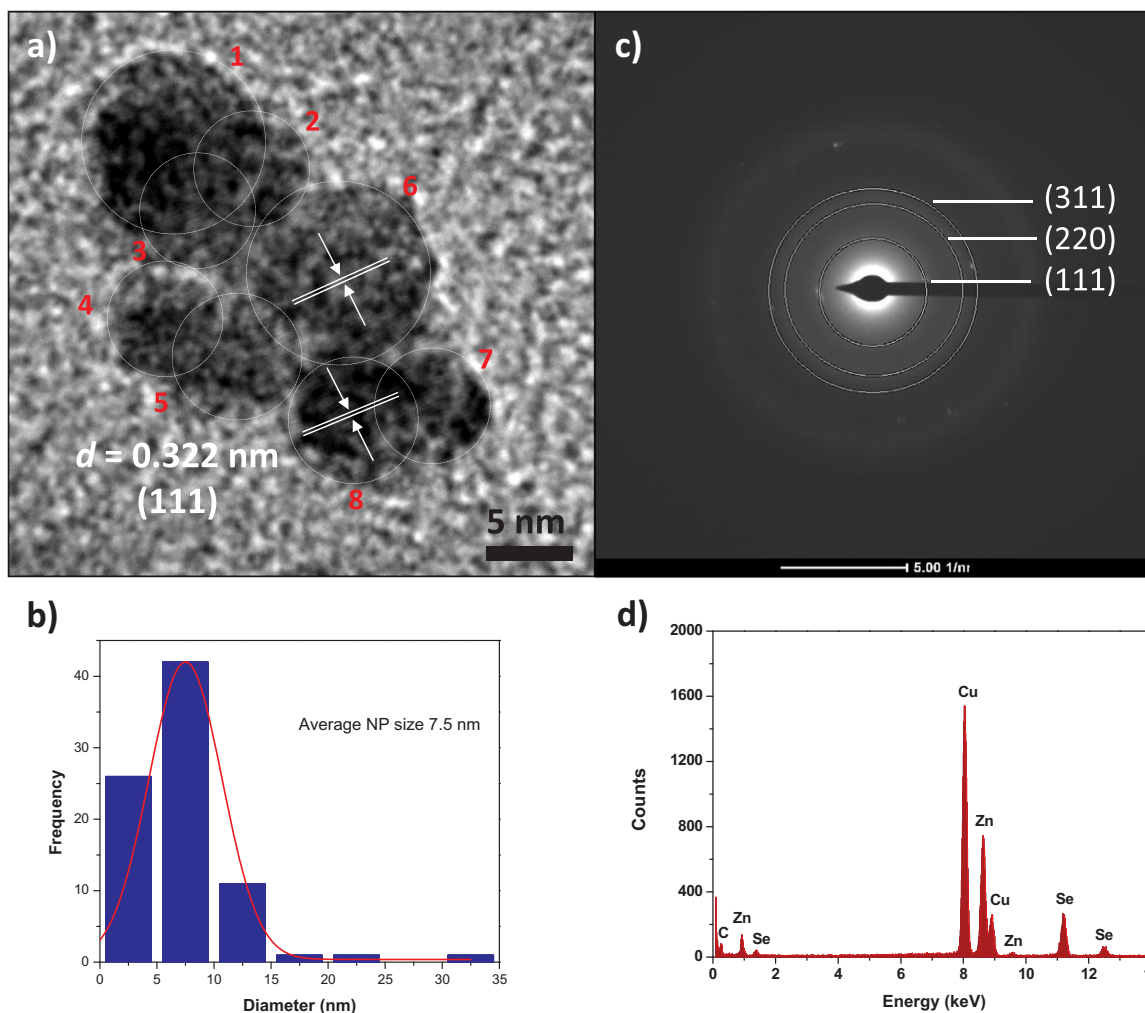


Fig. 1. (a) HRTEM image of the ZnSe nanoparticles. (b) SAED pattern and (c) EDX spectrum of pure ZnSe nanoparticles.

operated at 200 kV, equipped with EDX detector. Specimens of TEM samples were collected on an ultrathin holey carbon-coated Cu grid. Absorbance measurements of the samples were obtained using a Rayleigh UV-1800 UV/Vis spectrometer. Photoluminescence (PL) measurements were performed in a Perkin Elmer spectrofluorometer LS-55 equipped with a Xenon lamp. The absorbance and PL measurements were done using a 10 mm / 10 mm quartz cuvette. The Raman spectra were recorded at room temperature (RT) in a backscattering geometry using a WITec *alpha300R* spectrometer; model CRC200 with spectral resolution less than 2 cm^{-1} . Radiation at $\lambda = 632.8\text{ nm}$ from a He-Ne laser was focused on the sample using a 100x objective.

3. Results and discussion

Fabrication of ZnSe nanoparticles was carried out using a conventional ultrasonic bath. The mechanism employed is previously described in the [Supplementary section](#). A TEM image of ZnSe nanoparticles was shown in Fig. 1(a). The TEM image reveals that formed products are nanoparticles with size less than 10 nm. The interplanar spacing (d) obtained from image in Fig. 1(a) is $d = 0.322\text{ nm}$ along (1 1 1) plane of the ZnSe, which is in agreement with the JCPDS file no. 37–1463 [1], for cubic ZnSe. The selected area electron diffraction (SAED) pattern is shown in Fig. 1(b). As expected, the SAED shows a set of rings due to the random orientations of the nanocrystals, corresponding to the diffraction from different atomic planes. Fig. 1(b) presents the SAED pattern with (1 1 1), (2 2 0), and (3 1 1) diffraction planes of ZnSe cubic structure. The EDX analysis from the produced

particles (Fig. 1(c)) consists of Zn and Se elements except for C and Cu, signal arising from carbon-coated copper grid. This confirms that the fabricated product was pure ZnSe.

The optical properties of the sample were studied, and which are dependent of the size and the shape of the nanoparticles. UV–visible absorption result of the ZnSe nanoparticles is shown in Fig. 2. As can be seen from Fig. 2, the optical absorption edge at approximately 320 nm (3.87 eV) should be ascribed to the first exciton absorption caused by $1S^e-1S_2^h$ transition [8]. However, the absorption edge for the sample is blue shifted ($\Delta E_g = 1.17\text{ eV}$) with respect to the bulk band edge of ZnSe (2.7 eV). The direct energy band gap (E_g) of the sample was determined on the basis of the dependence of the absorption coefficient (α) and the photon energy ($h\nu$). For allowed direct transitions, the following relation is written as $\alpha h\nu = B(h\nu - E_g)^{1/2}$ [10,13], where B is a proportional factor. The variation of $(\alpha h\nu)^2$ with $h\nu$ for fabricated nanoparticles is shown in Fig. 2 (inset). The direct E_g is determined extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ plot to $\alpha = 0$ and found to be 3.85 eV, which show a blue shift relative to the bulk. This blue shift towards higher energy could be attributed to the quantum size effect of ZnSe nanocrystals.

Photoluminescence (PL) spectra of the bulk and ZnSe NPs were recorded to study the optical emission characteristic of fabricated sample (Fig. 3). The excitation wavelength was fixed at 254 nm (Fig. 3(a)) and 312 nm (Fig. 3(b)), respectively. The emission peak of the ZnSe NPs was observed at 380 nm (3.26 eV). However, the bulk sample exhibit emission peaks at 398 nm (3.12 eV), 420 nm (2.95 eV), 493 nm (2.51 eV), and 536 nm (2.31 eV). The emission at 398 nm

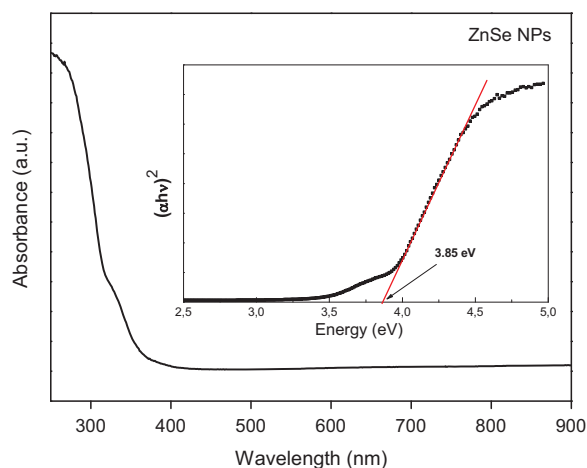


Fig. 2. Absorbance spectrum and energy band gap plot (Inset) of ZnSe nanoparticles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

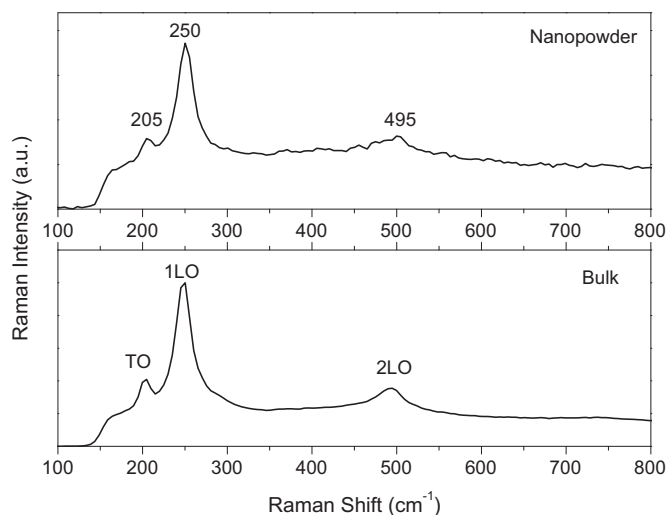


Fig. 4. Raman spectra of ZnSe samples.

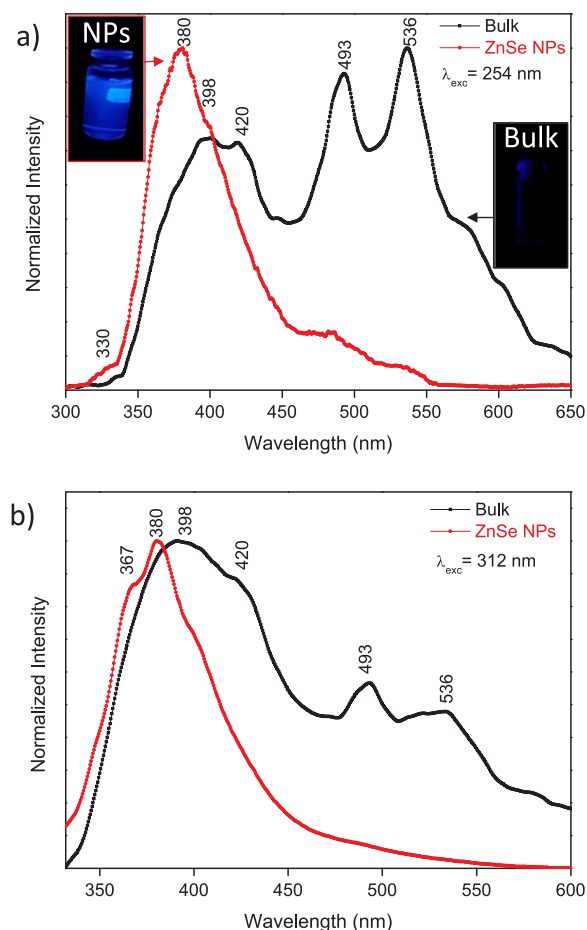


Fig. 3. Normalized PL spectra of the samples excited at (a) 254 nm and (b) 312 nm. Inset in (a) blue emission of ZnSe nanoparticles and Bulk. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contribute to near-band-edge emission originates from the recombination of free excitons of ZnSe nanocrystalline size regime [4]. The origin of the blue emission at 420 nm should be assigned to stoichiometric Zn vacancies or interstitial impurities, whereas the emission at 493 nm is a defect emission [14]. The green emission band at 536 nm is a typical deep defect (DD) related emission [13,15]. This is associated with dislocations and non-stoichiometric defects. While for the ZnSe NPs, the

emission peak at 380 nm was blue shifted ($\Delta E = 0.14$ eV) compared with the peak at 398 nm in the bulk, which is due to exciton recombination [4]. The emission is clearly more intense for the NPs than for the micron size particles used as starting material (Fig. 3(a) inset). The UV-visible absorption and PL emission peaks of the nanoparticles are blue shifted in comparison to the bulk ZnSe due to the quantum size effect of ZnSe nanocrystals.

Raman spectroscopy (RS) was performed for study of vibrational and structural properties of ZnSe nanoparticles. In Fig. 4, we provide the Raman spectra of ZnSe nanoparticles and the bulk crystal. This indicate the presence of transverse optical (TO) and longitudinal optical (LO) phonon modes. As shown in Fig. 4, the obtained Raman bands at 205, 250 and 495 cm^{-1} are attributed to the transverse optical (TO) and longitudinal optical (1LO and 2LO) phonon modes of zinc blende ZnSe crystal, respectively [6]. The crystalline quality was calculated from the full width at half-maximum (FWHM) of the LO phonon mode, which are 11.1 and 9.9 cm^{-1} for the nanoparticles and the bulk, respectively. The LO phonon mode of the ZnSe nanoparticles obtained is 1.2 cm^{-1} more wider than their counterparts of bulk. This broadening of the Raman mode is related to the introduction of defects into the crystal structure and to the decrease in LO-phonon lifetime. The observation is in agreement with the results of Li et al. [7] and Feng et al. [1] for ZnSe nanopowders synthesized by hydrothermal and solvothermal methods. In addition, we found a shift towards low frequency of 5 cm^{-1} of the TO and LO phonon peaks, in comparison with values reported by Feng et al. [1] for polycrystalline ZnSe nanoparticles (210 (TO) and 255 (LO) cm^{-1}), and in between 1 and 2 cm^{-1} of the TO and LO phonon peaks, in comparison with values reported by Li et al. [7] for ZnSe nanopowders (206 (TO) and 252 (LO) cm^{-1}). This shift could be related to the structure and effect of size of the ZnSe nanoparticles. These results also are in agreement with the results of PL.

4. Conclusions

In summary, highly blue luminescent ZnSe nanoparticles have been successfully fabricated by employing a top-down fabrication process using ultrasound. TEM/SAED and RS confirm that the nanoparticles are attributed to a cubic structure. EDX ensures the presence of Zn and Se and no other impurities, which are in agreement with the results of RS. The optical properties show that the absorption and emission peaks are blue shifted in comparison to the bulk. The energy band gap was found to be 3.85 eV, which show a blue shift relative to the bulk (2.7 eV) at room temperature. Appearance of a weak TO band in the Raman spectra indicate that most of the crystal grains in the sample are randomly oriented. In addition, the intensity of the LO modes are related to

the structure and size of the ZnSe particles. The nanoparticles obtained are highly luminescent with respect to the starting material.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlumin.2017.08.017>.

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