Low temperature synthesis and blue photoluminescence of ZnS submicronparticles

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ARTICLE INFO

ABSTRACT

Submicronparticles of ZnS were synthesized at low temperature using a top-down fabrication process by ultrasonication. The obtained ZnS particles were characterized by scanning transmission electron microscopy (S/TEM), energy dispersive X-ray analysis (EDAX), Fourier transform infra-red spectroscopy (FTIR), UV–visible spectrophotometry (UV), and photoluminescence spectroscopy (PL). The results showed that the formed products are ZnS particles with size less than 200 nm and exhibit a strong luminescence in the blue region. The origin of the blue emission could be attributed to the quantum size effect of ZnS nanocrystals.

1. Introduction

In recent years, nanocrystalline materials have attracted considerable interest due to their unique properties which are different from the bulk materials [1]. Among various II–VI nanostructured materials, zinc sulfide (ZnS) generates great interest for its direct wide band gap in the near ultraviolet range of 3.65 eV (bulk) at room temperature (RT) [2]. ZnS is a promising material for optoelectronic applications such as optical coating, flat panel displays, electroluminescent and infrared devices [2–5]. Recently, ZnS nanostructures have been synthesized by several methods [2–8], among which the chemical methods are most commonly used. The importance of choosing a proper synthetic route in fabricating nanostructured materials 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], and is now a powerful tool in the synthesis process [10]. Here we report a top-down fabrication process of ZnS submicronparticles directly from ZnS powder employing an ultrasound-assisted method at low temperature and pressure. This method has the virtue of simplicity, efficiency, and low-energy cost, which facilitates the synthesis of various kinds of nanomaterials. The structural and morphological properties of the fabricated submicronparticles have been confirmed using scanning transmission electron microscopy (STEM) and infrared (IR) spectroscopy. As well, the optical properties were studied.

2. Experimental details

Materials and fabrication of nanoparticles: Zinc sulfide with purity $\geq \geq 97.0\%$ (Sigma-Aldrich) has been used without further purification. Absolute isopropyl alcohol was used for the sample preparation. Samples of 10 mg of ZnS powder (particle size of 10 μm) were dispersed in a glass recipe containing 10 mL of isopropyl alcohol. The suspension was subject to continuum sonication for 12 h under vacuum (using an oil free vacuum pump /Rocker 300) with the objective of breaking in smaller particles through the mechanical pressure. During the sonication process, the solution temperature was kept at 50 °C. The process was carried out using two ultrasonic baths (Elma E30H and HiLab innovation system) of 2.75 L and 3.0 L in volume. These models operate at a fixed frequency of 37 kHz and 53 kHz with maximum input power of 320 W and 100 W, respectively.

Characterization: The samples were characterized on a Tecnai F20 FEG-S/TEM operated at 200 kV, equipped with an EDAX detector. Specimens of TEM samples were collected on an ultrathin holey carbon-coated Cu grid. IR spectra (KBr pellets) were recorded on a Rayleigh WQF-510A FTIR spectrometer in the 400–4000 cm^{-1} region. Photoabsorbance measurements of the samples were obtained using a Rayleigh UV-1800 UV/vis spectrometer in the range 200–800 nm. Photoluminescence (PL) measurements were

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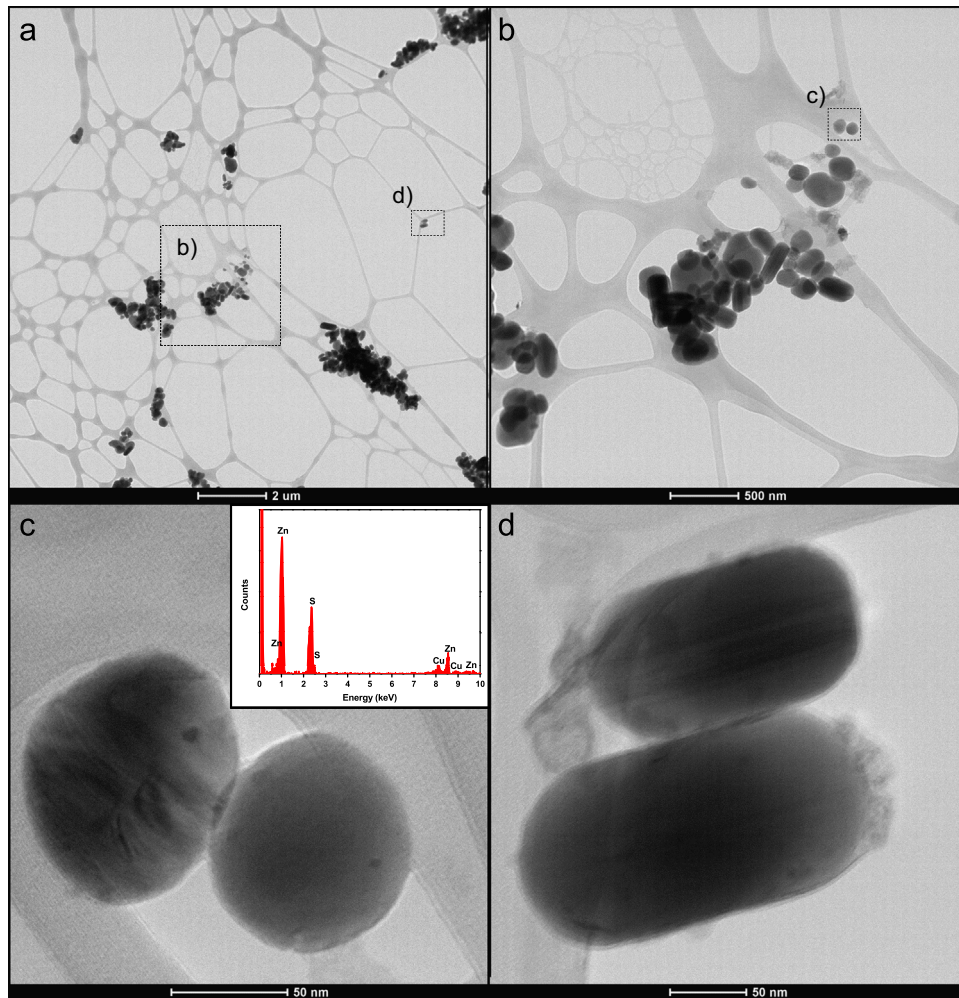*E-mail address:* edemova@ing.uchile.cl (E. Mosquera).

Fig. 1. (a–d) STEM images of ZnS submicronparticles obtained under frequency of 37 kHz. The doted frame in (a) and (b) is shown magnified in (c) and (d). Inset EDAX spectrum.
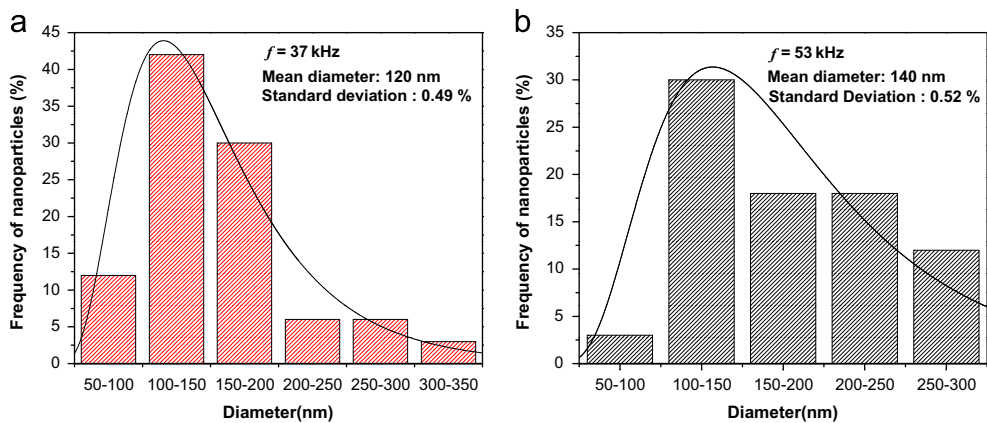

Fig. 2. Particle mean size and particle distribution of ZnS submicronparticles obtained under frequency of: (a) 37 kHz, and (b) 53 kHz.

performed at room temperature in a Perkin-Elmer spectrofluorometer LS-55, equipped with a Xenon lamp. All absorbance/PL measurements were done using a 10 mm/10 mm quartz cuvette.

3. Results and discussion

Fig. 1(a–d) shows a sequence of STEM images at different magnifications of ZnS particles obtained after sonication of ZnS powder dispersed in isopropyl alcohol at 37 kHz. These images clearly reveal that the formed products are submicronparticles with size less than 200 nm. The EDAX analysis of the produced sample (inset in Fig. 1(c)) consists of zinc (Zn) and sulfur (S) elements from obtained submicronparticles except for Cu, which is from copper grid. This confirms that the fabricated product was high purity ZnS.

Through STEM inspection, the size of particles can be determined from image. This analysis is more direct than X-ray line

broadening and less likely to be affected by experimental errors and/or other properties of very small crystals such as strain or a distribution in the size of lattice parameters [11]. As shown in Fig. 1, the particles sizes are in the range of 170 and 50 nm (measured as equivalent diameter by ImageJ 1.46r), respectively. Fig. 2 presents lognormal distribution curve for mean diameter of ZnS particles. The lognormal function used for fit the experimental curves are given by:

$$y = A \cdot \exp\{-[\,Ln\,(x/x_c)^2]/(2w^2)\} \qquad (1)$$

Where A is an arbitrary constant related to particle number, x_c represent the distribution maximum and w is strong correlated with the particle diameter dispersion. The ZnS samples consist of nonhomogeneous particles with a broad size distribution and, with an average diameter of the particle of 120 and 140 nm for 37 kHz and 53 kHz, respectively.

FTIR spectroscopy was performed to study the characteristic functional groups of ZnS samples. In Fig. 3 the broad absorption band observed at $\sim \sim 3450\ cm^{-1}$ corresponds to the O–H stretching vibrations of water present in the KBr. The bands at 2960.2, 2919.7, and 2854.2 cm^{-1} are due to nanostructure formation of the samples, and which correspond to C–H vibrations. The peaks in the range of 1750–1200 cm^{-1} correspond to the C=O stretching modes and O–C–O bonds arising from the absorption of CO_2 on the surface of the submicronparticles [6]. Peaks around 1000–600 cm^{-1} are attributed to ZnS bands corresponding to sulfides [7]. The metal–oxygen stretching mode appearing at $\sim 450\ cm^{-1}$ in the ZnO lattice was not observed [12]. It means that ZnS submicronparticles are not oxidized to ZnO during the preparation.

The UV–visible absorption spectra of ZnS samples prepared under two different frequency intensities of ultrasound are shown in Fig. 4(a). One can see that the optical absorption edge exhibits a blue-shift with respect to that of bulk (340 nm, $E_g = 3.65$ eV). The excitonic peak was observed at 270 nm (4.6 eV), which indicate the blue-shift. In order to verify the direct energy band gap (E_g) of the samples, the nature of the optical transition can be determined on the basis of the dependence of the absorption coefficient (α) and the photon energy ($h\nu$). For allowed direct transitions, the
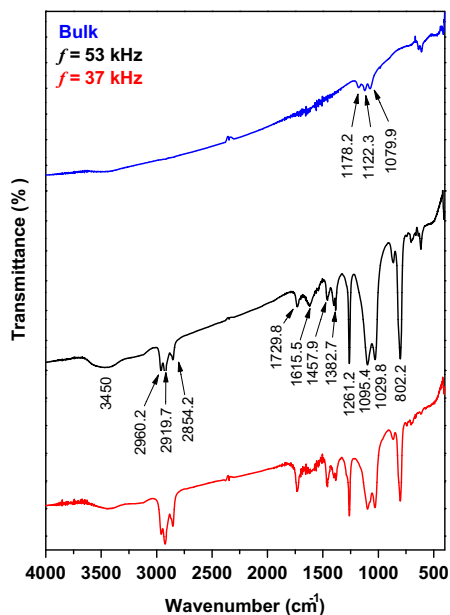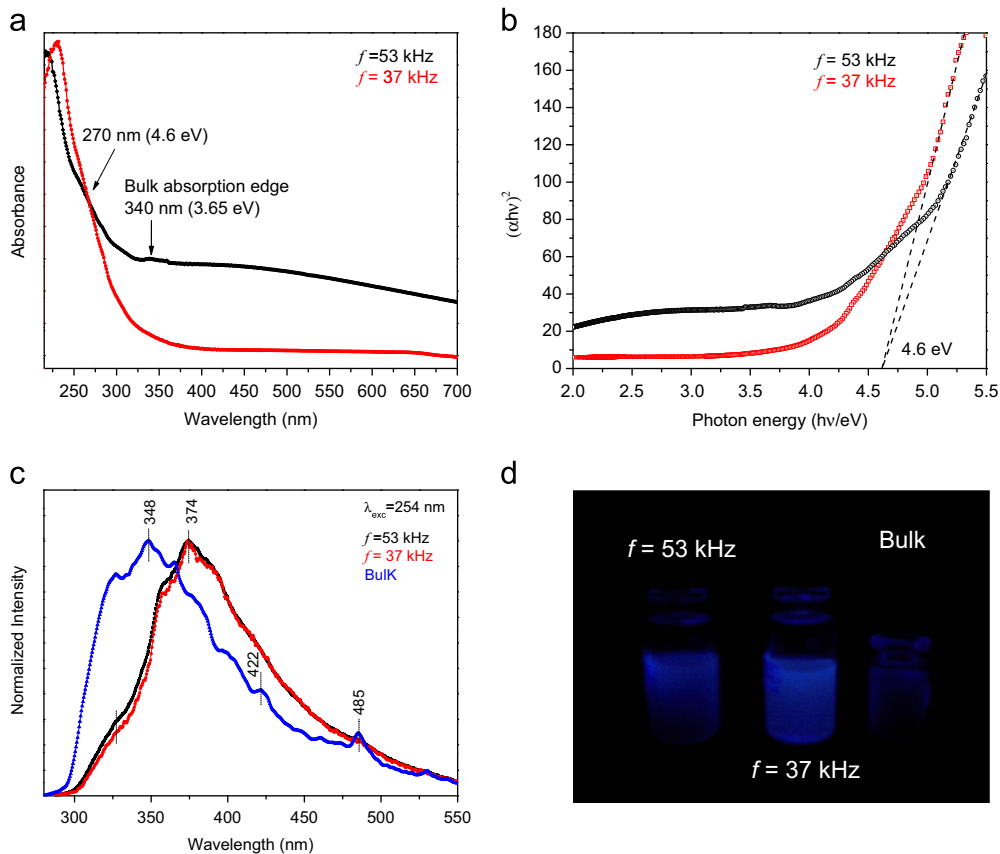

Fig. 3. FTIR spectra of ZnS samples.

Fig. 4. (a) Absorption spectra, (b) direct band gap energy, (c) photoluminescence spectra, and (d) fluorescence spectra of ZnS samples.

following relation is written as [13]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \qquad (2)$$

where B is a proportional factor. The variation of $(\alpha h\nu)^2$ with $h\nu$ for fabricates submicronparticles is shown in Fig. 4(b). The direct energy band gap (E_g) is determined extrapolating the liner portion of the $(\alpha h\nu)^2$ versus $h\nu$ plot to $\alpha = 0$ and found to be 4.6 eV, which show a blue-shift relative to the bulk. The blue-shifts in the absorption edge to shorter wavelength could be explained by the quantum confinement of ZnS nanocristallites [14].

Room temperature photoluminescence (PL) spectra were recorded to study the optical emission characteristic of fabricated ZnS submicronparticles (Fig. 4(c)). The excitation wavelength was fixed at 254 nm and the emission peak of the ZnS submicronparticles was observed at 374 nm (3.32 eV). However, the bulk sample exhibits a strong emission peak at 348 nm (3.6 eV) accompanied by other peaks of relatively lower intensity positioned at 422 nm (2.94 eV), and 485 nm (2.56 eV). The UV-emission at 348 nm contribute to near-band-edge emission originates from the recombination of free excitons of ZnS nanocrystalline size regime. The origin of the blue emission at 422 nm and 485 nm should be assigned to stoichiometric Zn vacancies (defect states) or interstitial impurities, and the peak of 422 nm is attributed to the S vacancies in the lattice [3,8]. While for the submicronparticles, the emission peak at 374 nm (3.32 eV) can be attributed to exciton recombination [15]. The emission is clearly more intense for the submicronparticles than for the micron size particles used as reference (Fig. 4(d)).

4. Summary

Submicronparticles of ZnS have been successfully synthesized through the sonication method using a conventional ultrasonic bath without and additional heater or magnetic stirrer. It was found that the sonication energy has a significant effect on the particle size for a fixed ultrasonic power and frequency. The morphological studies indicate the formation of ZnS submicronparticles with an average diameter of 120 and 140 nm. EDAX ensures the presence of Zn and S and no other impurities. FTIR spectroscopy confirms that ZnS submicronparticles are not oxidized to ZnO during the preparation. The optical properties show that the absorption peaks are blue-shifted due to quantum size effect of ZnS nanocrystals, and the emission peaks of submicronparticles is due to exciton recombination. It is a highly reproducible method for making a large volume of ZnS submicronparticles of consistent quality.

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