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Colloidal synthesis of ZnSe nanoparticles at room temperature

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ABSTRACT

Structural, morphological and compositional characterizations of zinc selenide nanoparticles (NPs-ZnSe) are discussed in this work. NPs-ZnSe were obtained by colloidal synthesis in aqueous solution at room temperature, atmospheric pressure and without inert atmosphere. The synthesis was carried out using zinc chloride ($ZnCl_2$) and elemental selenium as precursors. A mix of $Na_5P_3O_{10}$ and NaOH called Extran was used as surfactant. Molar concentration and pH of the aqueous solution were varied to study their effect on the crystalline properties of the nanoparticles. The XRD measurements show that the NPs-ZnSe exhibits a cubic phase structure. The size of the nanocrystals was between 3 nm and 4.7 nm. HRTEM analysis showed that NPs-ZnSe exhibit semi-spherical shape. The presence of zinc and selenium in the NPs-ZnSe was confirmed through EDS measurements.

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1. Introduction

In recent years, there exist great interest in the study of nanoparticles (NPs) in order to improve the performance of electronic and optoelectronic devices. NPs show interesting properties when their size becomes smaller than its exciton Bohr radius due to the quantum confinement effect. These properties can be controlled by means of the particle size [1]. NPs-ZnSe have attracted especial interest by their potential applications in light emitting diodes [2], photodetectors [3], and solar cells [4]. ZnSe is a wide bandgap semiconductor material with a bulk value of 2.7 eV at room temperature, emitting in the wavelength range from blue to UV [5,6]. NPs-ZnSe have been synthesized by different methods, such that colloidal synthesis either in organic solutions [7] or in aqueous solution [8], sonochemical method [9], vapor phase [10], solvothermal route [11]. Among these methods, colloidal synthesis by aqueous solution allows obtaining NPs at low cost and good quality.

In the present investigation, NPs-ZnSe were obtained in aqueous solution by the colloidal method at room temperature, atmospheric pressure and without inert atmosphere. The surfactant used is a solution of sodium hydroxide (NaOH), penta sodium tripolyphosphate ($Na_5P_3O_{10}$) and water (H_2O), commercially called Extran. The synthesis method used is easy to implement and economically feasible by not requiring the use of control equipment very expensive. The synthesized NPs were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS).

2. Experimental

For sample preparation, 1 mmol of $ZnCl_2$ (Baker, 98.2%) was dissolved in deionized water at room temperature with constant stirring. After that, Extran was added. Additionally, 1 mmol of selenium powder (Aldrich, 99.5%) and 2 mmol of sodium borohydride ($NaBH_4$, Sigma 95%) were dissolved in deionized water under constant stirring and maintained for 13 min at 75 °C. Following, the two solutions were mixed during 30 min at room temperature. A cleaning process was performed to eliminate the generated by-products [12], adding 1 ml of HCl (Merck, 37%) in the solution and stirred during 15 min, after, the stirring was stopped and then precipitation of the NPs was produced. Finally, NPs were dried at 45 °C for 2.5 h. The pH of the solutions was varied from 8 to 11 and the Zn:Se molar concentrations were varied as: 3:1, 2:1, 1:1, 1:2, 1:3. XRD measurements were done with a Bruker Axs D8 discover diffractometer with a Cu Kα radiation ($\lambda = 1.5428$ Å). The diffractograms were obtained in the range of 20° to 80° with intervals of 0.02°, step time of 1 s, 40 kV and 40 mA as operation conditions. Morphology and compositional studies were done in a Philips XL30 SEM at 20,000X and 2 kV. A JEOL JEM-2010 HRTEM at

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200 kV was used to confirm the presence of nanoparticles.

3. Results and discussion

The chemical reaction of this solution is carried out at 75 °C because selenium has low solubility in water. The chemical reactions during the process can be formulated as follows:

$$2ZnCl_2 + 6H_2O \rightarrow 2Zn^{2+} + 4HCl + 4H_2O + O_2\uparrow \quad (1)$$

$$2Zn^{2+} + 4HCl + 4H_2O + Na_5P_3O_{10} + 3\ NaOH + 5H_2O \rightarrow Zn_2HP_3O_{10} + 4NaCl + 4NaOH + 8H_2O + 2H_2\uparrow \quad (2)$$

$$2Se + 4NaBH_4 + 12H_2O \rightarrow 2NaHSe + Na_2B_4O_7 + 5H_2O + 14H_2\uparrow \quad (3)$$

$$2NaHSe + Na_2B_4O_7 + 5H_2O \rightarrow 2Na_2Se + 4H_3BO_3 \quad (4)$$

$$2Na_2Se + 4H_3BO_3 \rightarrow 2Se^{2-} + Na_2B_4O_7 + 2NaOH + 3H_2O + 2H_2\uparrow \quad (5)$$

$$Zn_2HP_3O_{10} + 4NaCl + 6NaOH + 11H_2O + 2Se^{2-} + Na_2B_4O_7 \rightarrow 2ZnSe + Na_5P_3O_{10}\ NaCl + Na_2B_4O_7 + NaOH + 14H_2O + O_2\uparrow \quad (6)$$

The chemical reaction involving the use of HCl to eliminate by-products is,

$$2ZnSe + Na_5P_3O_{10} + 4NaCl + Na_2B_4O_7 + NaOH + 14H_2O + HCl \rightarrow 2ZnSe + 5NaClO_3 + Na_2B_4O_7 + 15H_2\uparrow \quad (7)$$

Fig. 1 shows the diffractograms of ZnSe samples obtained with 1:1 M concentration and pH values of 8, 9, 10 and 11. The XRD pattern show peaks at $2\theta = 27.2°$, 45.2° and 53.5 ° related to the NPs-ZnSe. According to the ICDD card number 01–071–5977, the peaks position corresponds to the (111), (220) and (311) orientations, respectively, these results correspond to a cubic phase structure. The ZnSe peaks do not exhibit important variations as the pH value is increased. However, can be observed the presence of peaks at $2\theta = 23.5°$ and 29.7° related to selenium, indicating that a basic solution promotes the formation of ZnSe as well as selenium. The size of the crystallites was estimated by using the Debye-Scherrer equation: $\tau = K\lambda/\beta \cos(\theta)$, where k is 0.9, θ is the diffraction angle, λ is the x-ray wavelength and β is the full width at half maximum. The calculated crystallite size was similar for the range of pH studied and it was about 3.2 nm. Inset in Fig. 1 shows the crystallite size vs pH plot.

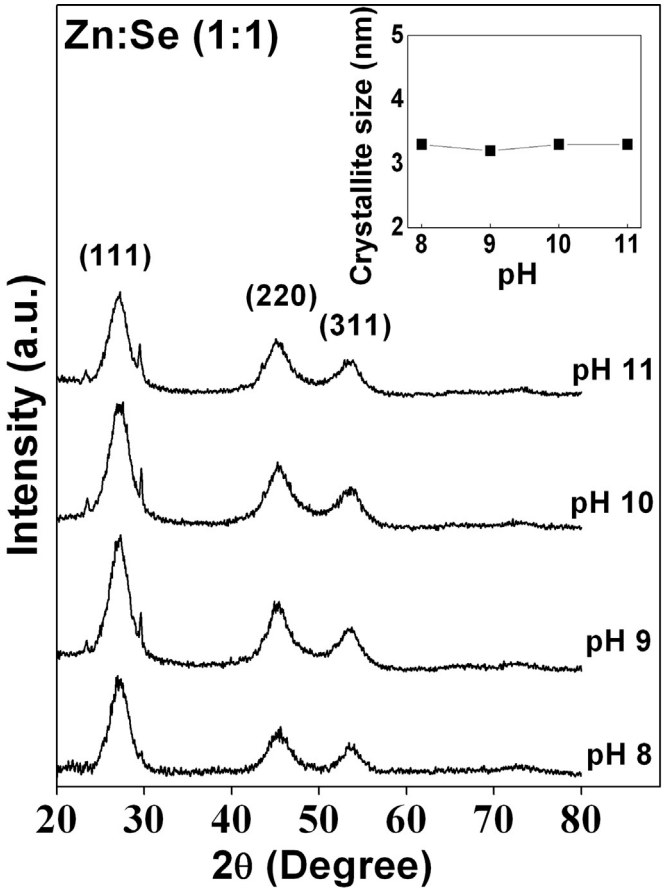

Fig. 1. XRD patterns of NPs-ZnSe samples with Zn:Se molar concentration (1:1). Inset shows the crystallite size vs molar pH plot.

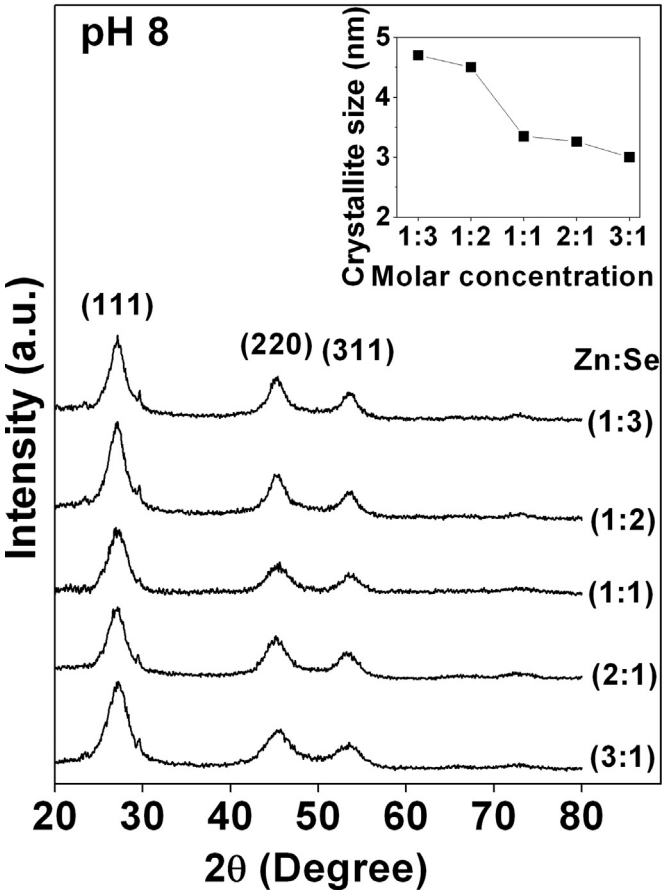

Fig. 2. XRD patterns of samples with pH=8 and different molar concentrations. Inset shows the crystallite size vs molar concentration plot.

Fig. 2 shows the XRD patterns of samples obtained with pH=8 and Zn:Se molar concentrations of 1:3, 1:2, 1:1, 2:1 and 3:1. In all the diffractograms can be observed the peaks of NPs-ZnSe and elemental selenium; and the value of the crystallite size decreases from 4.7 to 3 nm in the range studied as can be seen in the inset of the Fig. 2.

Micrographs show that NPs-ZnSe join to form micrometer-sized agglomerates. It is noted that the surface morphology of the agglomerates depends on the molar concentration. Fig. 3 presents micrographs of samples obtained with pH=8. Fig. 3(a) shows sample obtained with 1:1 as molar concentration. This sample presents roughness surface a high amount of agglomerates. In some cases, particles with irregular shape and some rod-like structures are attributed to the elimination of Zn during the cleaning process. The mechanism is related with the formation of $ZnCl_2$ from the erosion of NPs-ZnSe by HCl [13], therefore a high amount of selenium concentration is obtained, and the morphology is like nanorods even elemental selenium is also formed as nanorods. The surface morphology for the Zn:Se samples with 1:2

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