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Dependence of ZnO Morphology on Zn^{2+} Concentration

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We have succeeded in controlling the morphology of Wulfingite $Zn(OH)_2$ and Wurtzite ZnO at room temperature without using any template or surface ligand through the alteration of zinc ion molarity and the use of the moderately strong cylcohexylamine Brønsted base as a precipitating agent. The morphology was examined by SEM technique while XRD technique was used to identify the precipitated materials. We observed octahedral particles when the [Zn^{2+}] was in the range of 0.09-0.02 Molar, flake-like particles when applying 0.19 Molar of [Zn^{2+}], and mixture of chuncky and spherical particles when using 0.38 Molar of [Zn^{2+}].

Keywords: Zinc ion concentration, Morphology, Wulfingite $Zn(OH)_2$, Wurtzite ZnO.

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1. INTRODUCTION

Zinc oxide (ZnO) is very important material due to its semiconducting, piezoelectric, and pyroelectric multiple properties [1]. ZnO is a wide band gap (Eg) semiconductor, displaying high optical transparency and luminescent properties in the near ultra violet and the visible regions [2]. Owing to these properties, ZnO has found numerous electronic and optoelectronic applications such as solar cells, gas sensors, liquid crystal displays, and heat mirrors [3]. ZnO properties and activity depend on the particle size and morphology, which in turn are dependent of the preparation method [4]. In this context, many synthesis methods have been reported for the production of ZnO such as sol-gel [5], thermal decomposition [6], chemical vapor deposition [7], hydrothermal reactions [8]. However, these methods require heat input. Therefore, we have recently developed a novel, room-temperature, wet chemical procedure for the synthesis of ZnO nanoparticles with different morphologies by varying the reaction media [9-11]. It has also been shown that varying the molar concentration of zinc ions, [Zn^{2+}], is a key parameter for controlling the shape of ZnO nanoparticles using colloid-chemical techniques [12]. Thus, we are reporting herein the effect of [Zn^{2+}] on the morphology of ZnO, prepared by our room-temperature procedure without using any surface ligand or template. X-ray powder diffraction (XRD) was used to identify the crystalline phase, while UV-vis absorption spectroscopy was used to study the optical properties of the prepared ZnO materials. Scanning electron microscopy (SEM) was the main technique to study the morphology of the prepared ZnO materials.

2. EXPEREMENTIAL

2.1 Materials

Zinc nitrate hexahydrate (pure, POCH), cyclohexylamine (CHA, 98+%, Alfa Aesar) were commercially available and were used as received without further purification. Deionized water (DI, 18.2 MΩ.cm) was obtained from a Milli-Q water purification system (Millipore).

2.2 Materials Preparation

Five different molar concentrations of Zn^{2+} (0.38, 0.19, 0.09, 0.05, and 0.02) were prepared by dissolving 30 mmol zinc nitrate hexahydrate in the proper amount of DI at room temperature, under continuous magnetic stir-ring. Upon the obtainment of clear solutions of zinc nitrate, 60 mmol of CHA was added to each solution of Zn^{2+}. White precipitate was observed upon the addition of CHA. The reaction vessels were left stirring for four days, after which they were filtered off and were washed copiously with DI. The precipitates were then air-dried at room temperature, under vacuum for one day. Each precipitate was then suspended in 300 ml DI for one day and then was filtered off, washed with DI, and finally air-dried at room temperature under vacuum. The precipitates were then calcined at 550 °C for three hours.

2.3 Materials Characterization

Solid materials were characterized before and after calcination by UV-vis absorption spectroscopy, X-ray powder diffraction (XRD), and scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSIONS

3.1 XRD Analysis

XRD showed hexagonal wurtzite structure of ZnO for all calcined materials with the highest intensity for the (101) crystallographic phase, followed by the (100), and then by the (002). However, for the highest [Zn^{2+}] of 0.38 M, ZnO was precipitated at room temperature, while orthorhombic Wulfingite structure of $Zn(OH)_2$ was detected by XRD for the other [Zn^{2+}] concentrations. These XRD results are in agreement with the pH

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effect on determining the form of precipitated Zn-containing material [13].

3.2 UV-Vis Analysis

The UV-Vis absorption spectra revealed that all obtained ZnO materials have an E_g of ~3.1 eV, which is comparable to the value of 3.2 eV for the bulk ZnO, irrespective of $[Zn^{2+}]$. Fig. 1 shows the UV-Vis absorption spectra for the ZnO obtained by calcination at 550°C of $Zn(OH)_2$, precipitated from the 0.19 *M* and 0.05 *M* Zn^{2+} solutions, as examples.

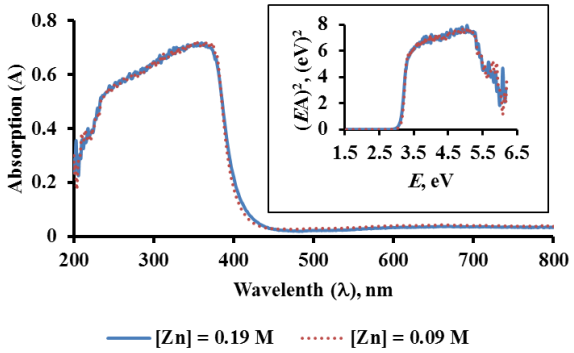

Fig. 1 – UV-Visible absorpation spectra of Wurtzite ZnO obtained by calicnation at 550°C of Wulfingite $Zn(OH)_2$ precipitated at different $[Zn^{2+}]$.

3.3 SEM Images

SEM images (Fig. 1) explicitly revealed a strong influence of $[Zn^{2+}]$ on the morphology of the precipitated materials at room-temperaturethe, which was maintained for the ZnO materials, obtained upon calcination. Connected-Spherical along with chunky particles were obtained for the highest $[Zn^{2+}]$ of 0.38 M. Aggregated Sheet-like morphology was obtained for the materials when applying $[Zn^{2+}]$ of 0.19 M. On the other hand, the other three lower $[Zn^{2+}]$ resulted in octahedron particles with well-defined surfaces and edges. The octahedron particles, obtained at $[Zn^{2+}]$ of 0.09 M, appears to be formed by aggregation of small sphere-like particles. This aspect was clearly noticed after calcination. However, the octahedron particles, obtained at $[Zn^{2+}]$ of 0.05 M, appears to be formed by aggregation of rod-like particles, which make the surface look more smoother. This feature was evidently observed upon calcination. For the octahedron particles, obtained at $[Zn^{2+}]$ of 0.02 M, surfaces made of both sphere- and rod-like particles can be noticed, resulting in rougher surfaces in comparison to those obtained by sphere-like particles only in case of $[Zn^{2+}]$ of 0.09 M or by rod-like particles only in case of $[Zn^{2+}]$ of 0.05 M. The observed morphology of the ZnO materials, prepared in this work, could be ascribed to the "oriented

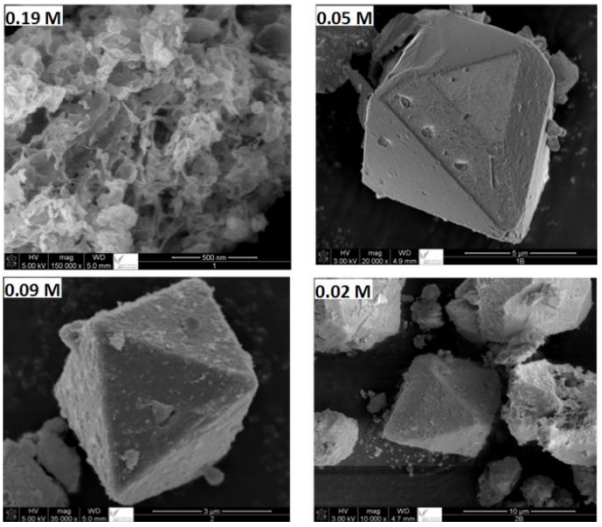

Fig. 2 – SEM images of Wulfingite $Zn(OH)_2$ obtained at different $[Zn^{2+}]$.

4. CONCLUSIONS

We succsued to control the morophology of ZnO by changing $[Zn^{2+}]$ at room temparture without using any surface ligand or template. Octahedron ZnO particles were observed for low $[Zn^{2+}]$ concentration, while chuncky and spherical particles were observed for the high concentration of $[Zn^{2+}]$.

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