

Evolution of ZnO nanostructures in sol–gel synthesis

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ARTICLE INFO

Article history:

Received 7 April 2008

Received in revised form 19 June 2008

Accepted 21 July 2008

Available online 9 August 2008

PACS:

61.46.Df

81.05.Dz

81.20.Fw

Keywords:

Sol–gel

ZnO

Nanoparticles

Evolution

ABSTRACT

Evolution of the microstructure and optical properties of ZnO nanoparticles in a mild sol–gel synthesis process is studied. The ZnO nanostructures were prepared by reacting zinc acetate dihydrate with NaOH in water at 50–60 °C. Evolution of ZnO nanostructures with reaction time is studied using UV–Vis spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy techniques. During the process of Zn²⁺ hydroxylation, well defined rod-like crystals were formed within 15 min. Further hydroxylation leads to the formation of a gel-like structure within about 45 min. However, XRD, FT-IR and energy dispersive spectroscopy (EDS) confirmed that these initial products were zinc hydroxyl double salts (Zn-HDS), not ZnO. On ageing the reaction mixture, ZnO nanoparticles with wurtzite structure evolved.

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1. Introduction

ZnO nanoparticles have been extensively studied over the past few years because of their size-dependent electronic and optical properties [1]. ZnO is one of the few oxides that show quantum confinement effects in an experimentally accessible size range [2]. ZnO nanostructures find widespread use in varistors, transparent conductors, transparent UV-protection films, chemical sensors and optoelectronic applications [3]. ZnO nanoparticles can be prepared by several ways, of which the sol–gel is a popular method because of its low cost, reliability, reproducibility, simplicity and relatively mild conditions of synthesis (“soft chemistry”). In addition, the nanoparticles produced by this route show good optical properties [4], and the morphology of particles can be tailored by the controlling the relative rate of hydrolysis and condensation reactions. However, it can be difficult to control these reaction rates [5].

In 1993 Na, Walters, and Vannice reported the preparation of high surface area ZnO by allowing ammonium carbonate to react with zinc nitrate hydrate [6]. Formation of ZnO particles from zinc acetate with NaOH in 2-propanol at 0 °C and 65 °C was reported by Wang and co-workers [7]. Tokumoto and co-workers [5] reported

that the products obtained from an ethanolic zinc acetate solution using the sol–gel route depend on catalysts and the temperature of hydrolysis. Unwashed nanoparticulate powders were found to be a mixture of ZnO (Wurtzite), zinc acetate, and zinc hydroxy double salts (Zn-HDS). Use of ethanol as solvent for preparing ZnO nanoparticles by the reaction of zinc acetate and sodium hydroxide in an ice bath was also reported by Peng and co-workers [3]. However, Santilli and co-workers [8] pointed out that the powders extracted from ethanolic zinc acetate sol–gel suspensions were made up of a mixture of nanometre-sized zinc oxide (ZnO) and zinc acetate (ZnAc₂ · 2H₂O). The sequence of formation of these phases was not clear.

In the present work, nanostructured ZnO was prepared from zinc acetate with NaOH in water by a simple sol–gel ageing technique. The structural and optical properties of the as-prepared precipitates were investigated. Evolution of ZnO nanostructures with reaction time in a sol–gel synthesis was studied where no organic solvent or capping agent was used. This method produces pure nanocrystalline ZnO.

2. Experimental details

For the synthesis of ZnO nanostructures, the following procedure was used. 20 ml of aqueous 1 M NaOH solution and 100 ml of aqueous 0.1 M zinc acetate (ZnAc₂ · 2H₂O, Chameleon Reagent,

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99%) solution, prepared using deionized water, were mixed slowly with vigorous magnetic stirring at 50–60 °C to give a reaction mixture with $[\text{OH}]/[\text{Zn}] = 2$. The final pH of the mixture was 6. The reaction mixture was kept at 50–60 °C for 1 h, and then allowed to stand at ambient temperature for 7 days.

UV–Vis absorption spectra of the reaction mixtures were recorded using a UV-3600 SHIMADZU spectrophotometer at different time intervals after mixing. For absorbance measurement, the samples (colloidal) were diluted by adding deionized water in the ratio of 1:10. The morphology of the precipitates obtained by vacuum drying the reaction mixture was observed using a JEM-2500TS transmission electron microscope (TEM) operating at 200 kV. Elemental mapping was carried out under EDX mode using ZnK_α , CK_α and OK_α emission lines. X-ray diffraction (XRD) data of the powder samples were collected using a Rigaku X-ray diffractometer (CuK_α radiation, 40 kV, 20 mA) with step size 0.02° and $4.0^\circ \text{ min}^{-1}$ scanning speed. FT-IR spectra (ATR method) were recorded on a Thermo Electron Nicolet 8700 spectrometer.

3. Results and discussion

XRD results (Fig. 1) shows that as-prepared nanoparticulate powders were not ZnO, as none of the diffraction peaks match the standard diffraction peaks of ZnO. The formed material is believed to be Zn-HDS as reported by Morioka et al. [14] and Tokumoto et al. [5]. The formed material Zn-HDS is further confirmed by

FT-IR spectra (Fig. 6). However, after ageing the reaction mixtures for about one week, the powder isolated by vacuum drying exhibited (Fig. 1) the ZnO crystal structure. All of the diffraction peaks could be indexed to wurtzite ZnO (JCPDS card No. 36-1451, $a = 3.249 \text{ \AA}$, $c = 5.206 \text{ \AA}$).

UV–Vis absorption spectra of the colloidal reaction mixtures at various reaction times are shown in Fig. 2. For reaction times up to about 60 min, the dispersion showed no absorption band to indicate the formation of ZnO. However, the absorbance increased with reaction time. After ageing for one week, there appeared an absorption peak at about 370 nm, which is the characteristic excitonic absorption peak of ZnO nanostructures [9]. The relatively high absorbance at longer wavelengths indicates a large dispersion in size of the ZnO nanostructures and their arbitrary orientations.

TEM images of the ZnO sol-gel samples taken at different reaction times are shown in Fig. 3. Formation of well defined rod-like structures with length of the order $1 \mu\text{m}$ occurs after 15 min of hydroxylation (Fig. 3a). As mentioned earlier, the crystalline material was not ZnO. This observation is in agreement with the observation of Morioka and co-workers [10], however, zinc oxide was obtained by mixing zinc acetate solution with NaOH solution maintaining $[\text{OH}]/[\text{Zn}] > 1$, or by mixing the solutions at 60 °C using an aqueous NaOH solution (0.1 M). In order to have the qualitative idea on composition of the rod-like structures, elemental mapping was performed on the structure presented in Fig. 3a. The results (Fig. 4) show that the rods contain zinc and oxygen,

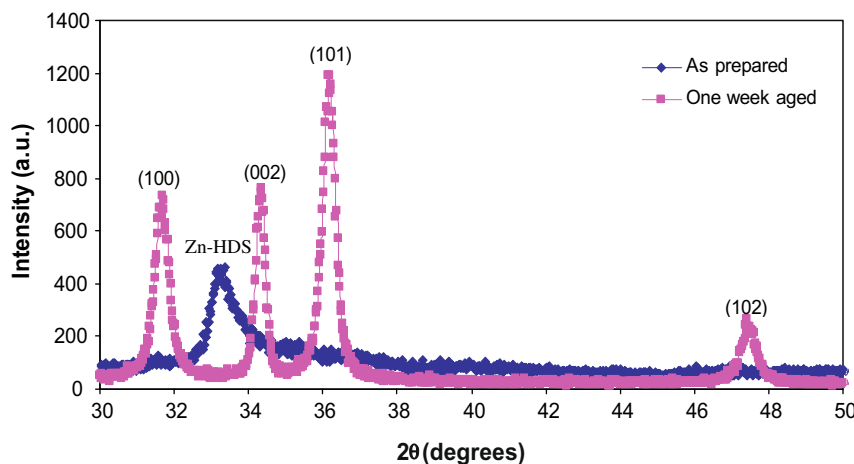


Fig. 1. XRD patterns of the as-prepared and one week aged reaction products. Formation of Wurtzite ZnO is confirmed after prolonged aging.

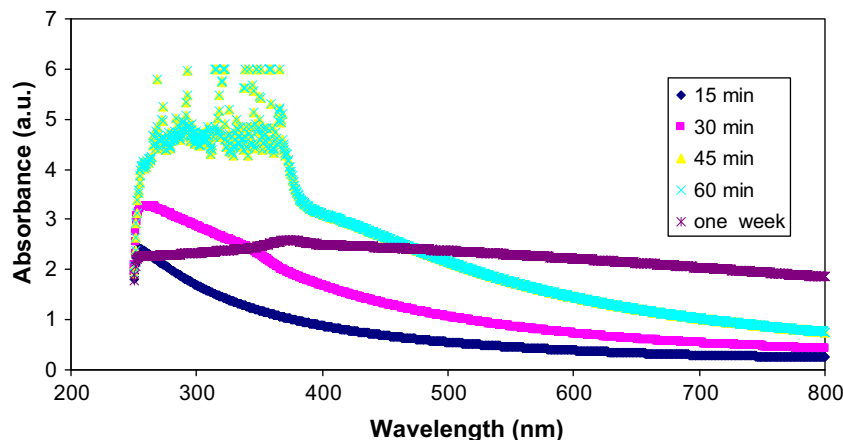


Fig. 2. UV–Vis absorption spectra of the dispersions at different reaction times.

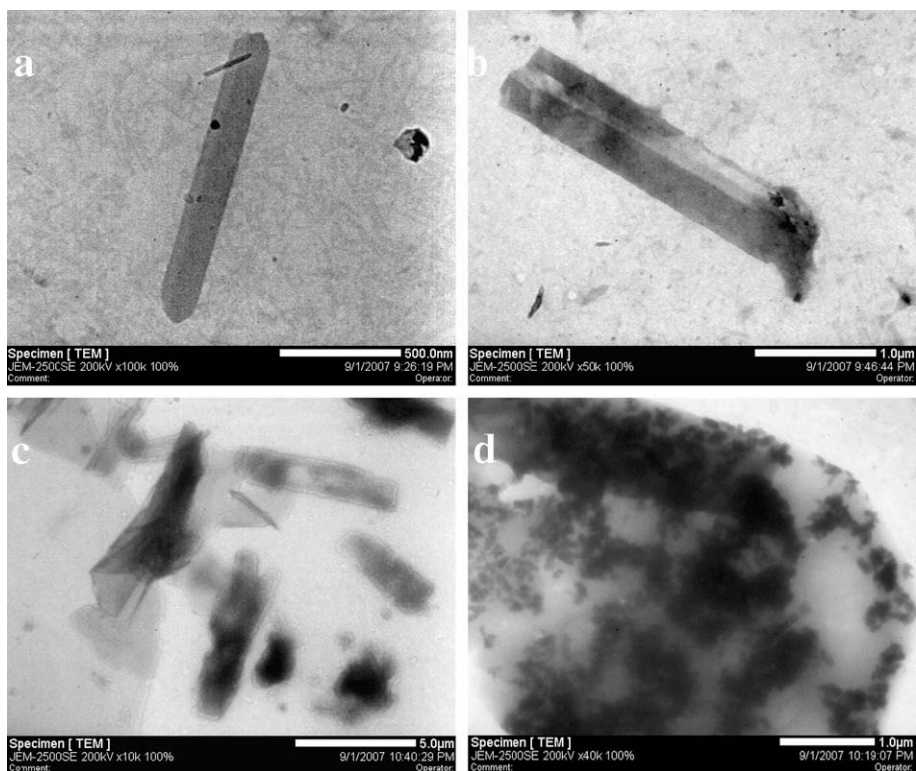


Fig. 3. Typical TEM images of the sol-gel products at different reaction times: (a) 15, (b) 30, (c) 45 and (d) 60 min.

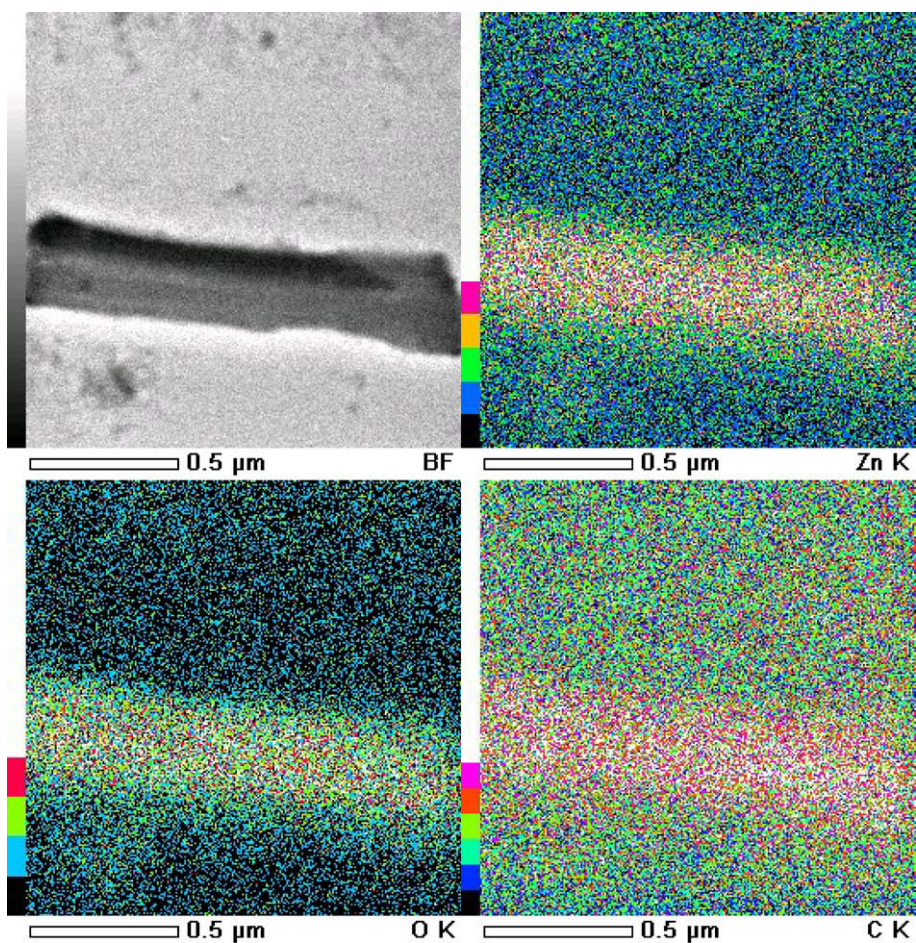


Fig. 4. Elemental mapping of the rod-like sol-gel precipitate recovered after 15 min of reaction. ZnK_{α} , CK_{α} and OK_{α} emission lines were used to map Zn, C and O distributions.

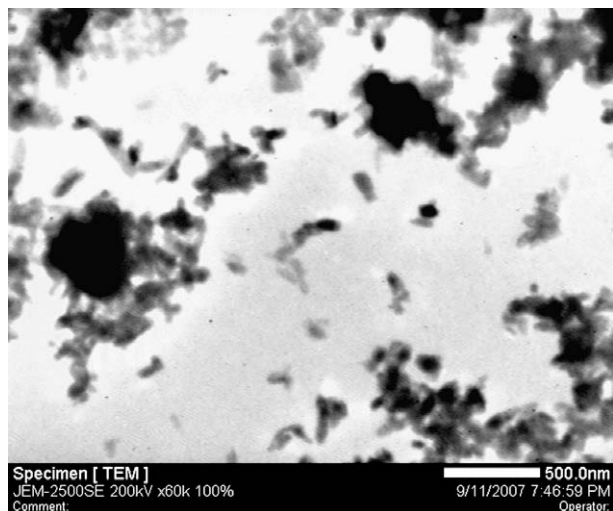


Fig. 5. A typical TEM image of the ZnO nanostructures obtained from aged (1 week) sol-gel precipitate.

together with a high content of carbon. The XRD pattern of the material produced after 15 min of reaction time was very similar to that reported by Tokumoto and co-workers [5] for Zn-HDS, and to the powder diffraction pattern of nickel-zinc hydroxyacetate [11]. Moreover, the diffraction pattern of the crystalline material produced after 15 min reaction time revealed no evidence of the presence of ZnO.

Tokumoto and co-workers [12] have identified $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ as the precursor for the formation of ZnO nanoparticles via the sol-gel route proposed by Spanhel and Anderson [13] in which an ethanolic solution of zinc acetate dehydrate is boiled under reflux. It was subsequently shown [5] that hydrolysis of the precursor solution produces a mixture of ZnO, zinc acetate and Zn-HDS. It is feasible, therefore, that the formation of highly crystalline Zn-HDS that was found in the present work occurred via the soluble $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ species. However, we do not yet have direct experimental evidence for the participation of that species in the formation of Zn-HDS under the experimental conditions.

The structures formed after 15 min of reaction appeared to persist even after 30 min (Fig. 3b). However, after 45 min of reaction (Fig. 3c), the micrometer-scale rod-like structures appeared to be undergoing partial dissolution leading to the formation of a gel-like

structure that evolves to well-defined nanostructured particles after 60 min of reaction (Fig. 3d). The mechanism of the spontaneous, complete conversion of Zn-HDS to nanocrystalline ZnO during ageing at ambient temperature is not very clear at present.

Fig. 5 shows a TEM image of the particles formed after ageing a reaction mixture for one week. Formation of rod-like structures of about 50 nm average diameter and 200 nm average lengths is clear from the image.

To determine the nature of the nanostructures produced at the initial stage of the reaction, FT-IR transmittance spectra of the colloidal reaction mixtures separated at (a) 15 and (b) 60 min of reaction time were recorded (Fig. 6). The bands at about 1551, 1415 and 1344 cm^{-1} correspond to the reported absorption bands of Zn-HDS [14]. The band appeared at about 1675 cm^{-1} corresponds to the deformation vibrational mode of -OH [15]. It can also be observed from the Fig. 6 that the bands attributable to Zn-HDS become stronger as the reaction proceeds.

Our results are in partial agreement with the report of Santilli and co-workers [8], who could not detect the formation of ZnO nanoparticles during the initial period of ethanolic zinc acetate hydrolysis induced by added water, and detected Zn-HDS as the main product. ZnO nanoparticles were detected only at an advanced stage of the reaction. From our XRD analyses, ZnO is found to be formed after ageing the reaction mixture; which suggests that the formation of ZnO nanorods results from a relatively slow but thermodynamically favored dissolution/precipitation process.

4. Conclusions

Wurtzite phase ZnO nanocrystals have been synthesized from zinc acetate with NaOH in water using a sol-gel procedure. The optical and structural characteristics of the precipitates depended on the reaction or ageing time. XRD, EDX and FT-IR analysis revealed that as-prepared materials are Zn-HDS, and the hexagonal wurtzite ZnO nanostructures are formed only after ageing the reaction mixture, which suggests that ZnO results from a relatively slow but thermodynamically favored dissolution/precipitation process. Further research is needed to understand the evolution mechanism in detail.

Acknowledgments

Jim Lee acknowledges the Japan Society for Promotion of Science (JSPS) for providing a JSPS Postdoctoral Fellowship and Nagoya University in Japan. The authors would also like to thank

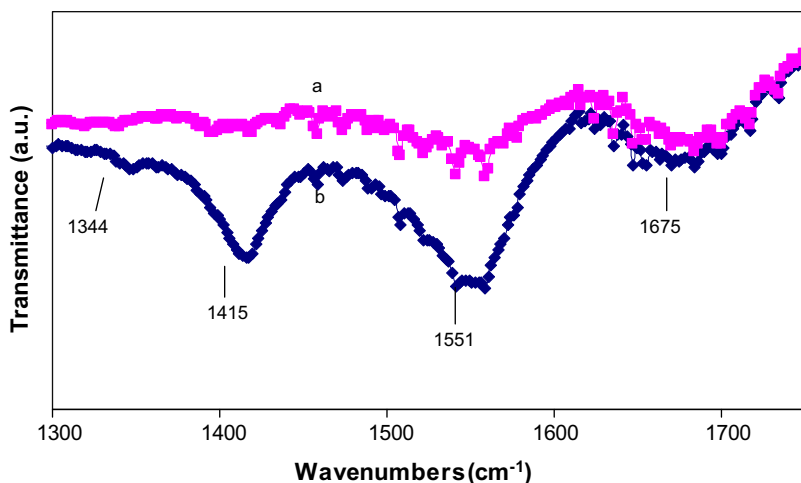


Fig. 6. FT-IR transmittance spectra of the colloidal products obtained after (a) 15 and (b) 60 min of reaction.

Dr. Michel Nieuwoudt and Mr. Shane Crump, Department of Chemistry, the University of Auckland for FT-IR support.

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