Materials Chemistry and Physics 167 (2015) 77–87

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Zinc oxide and zinc hydroxide formation via aqueous precipitation: Effect of the preparation route and lysozyme addition

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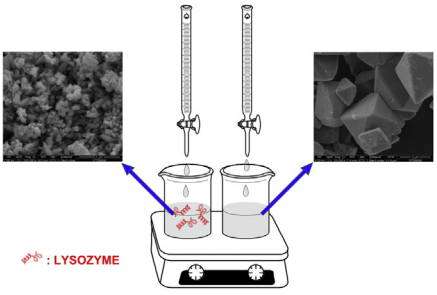
HIGHLIGHTS

- Aqueous precipitation products of $Zn(NO_3)_2$ and NaOH were prepared.
- Synthesis route and lysozyme addition affected morphology of the products.
- ε-$Zn(OH)_2$, β-$Zn(OH)_2$, and ZnO crystal structures were observed.
- Lysozyme-ZnO/$Zn(OH)_2$ composites with ~5–20% lysozyme content were obtained.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 February 2015
Received in revised form
20 August 2015
Accepted 10 October 2015
Available online 24 October 2015

Keywords:
Oxides
Composite materials
Precipitation
Powder diffraction
Electron microscopy
Fourier transform infrared spectroscopy

ABSTRACT

Aqueous precipitation products of $Zn(NO_3)_2$ and NaOH obtained by changing the method of combining the reactants and by using lysozyme as an additive were investigated. In the case of single addition method, octahedral ε-$Zn(OH)_2$ and plate-like β-$Zn(OH)_2$ structures formed in the absence and in the presence of lysozyme, respectively. Calcination of these $Zn(OH)_2$ samples at 700 °C yielded porous ZnO structures by conserving the template crystals. When zinc source was added dropwise into NaOH solution, predominantly clover-like ZnO crystals were obtained independent of lysozyme addition. Mixed spherical and elongated ZnO morphology was observed when NaOH was added dropwise into $Zn(NO_3)_2$ solution containing lysozyme. Lysozyme contents of the precipitation products were estimated as in the range of ~5–20% and FTIR indicated no significant conformational change of lysozyme in the composite. These results suggest that lysozyme-ZnO/$Zn(OH)_2$ composite materials may have a value as an antibacterial material.

1. Introduction

ZnO is a II^b-VI semiconductor with hexagonal wurtzite type crystal structure and currently in use as a filler/additive in rubber, concrete, and cosmetic industries and as a varistor ceramic in electronic industry. It has a band gap of 3.37 eV at room temperature that offers such optoelectronic applications as light-emitting diodes, laser diodes and photodetectors [1–4]. Additionally, ZnO has a great potential as an electron transport material in solar cells, a gas sensor, and an antibacterial material [4–8]. The size and the structure of ZnO have strong effect on its physical and chemical properties and hence, its end-use [9]. For example, compared to the rod-shaped particles, hexagonal plate-like ZnO structures exhibited more than fivefold increase in the photocatalytic activity for the degradation of methylene blue [10]. Similarly, ZnO structures with short nanorod morphology showed

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http://dx.doi.org/10.1016/j.matchemphys.2015.10.013
0254-0584/

higher antibacterial activity than long nanorod and nanoplate morphologies [8].

Aqueous precipitation is a widely employed method in the synthesis of ZnO with different morphologies by simply changing precipitation conditions such as the nature and concentration of zinc source and precipitating agent, pH, temperature, and aging time. Recently, the method of combining the reactants has also been reported to change the morphology [11,12]. For the aqueous precipitation method, different forms of zinc hydroxides, zinc oxide or a mixture of both can be observed depending on the precipitation protocol. Therefore, obtention of the desired precipitation product with desired morphology is perhaps the only challenge of this simple method. The use of additives in aqueous precipitation method as a catalyst and a morphology directing agent has also been successful for providing structural control of the precipitate. A number of additives such as surfactants, and synthetic polymers have been employed to obtain a variety of morphologies including spherical, elongated, hexagonal prismatic, rod-like, ring-like, disk-like and sheet-like structures with different dimensions at mild conditions [13–18]. However, macromolecules from biological origin as additives have not been investigated as much as their synthetic counterparts though their promising activities were reported. One of these macromolecules, dextran, directed the formation of flower-like ZnO structures [19]. Likewise, a positively charged polypeptide, poly-L-lysine, was reported to catalyze ZnO formation at room temperature [20].

Lysozyme is an antibacterial enzyme that can hydrolyze the peptidoglycans in the cell wall of gram-positive bacteria. It was used as a precipitating agent in the synthesis of silica and titania and demonstrated to retain its biological activity in the nanocomposites formed [21]. In this study, it was aimed to test the possibility of preparation of lysozyme containing $Zn(OH)_2$ or ZnO composites via simple aqueous precipitation route. Precipitation conditions were changed systematically to obtain composites with different chemistry and morphology. The role of lysozyme was deduced by comparing the structures and the morphologies in the presence and absence of lysozyme. Additionally, all the precipitates were calcined to obtain the samples with further changed morphologies.

2. Materials and methods

2.1. Materials

In the synthesis of the samples, zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$ (Riedel de Haen, >98%), NaOH (Sigma–Aldrich, 98–100.5%), and lysozyme from chicken egg white (Fluka, ~70,000 U/mg) were used without purification. All the solutions were prepared and washing steps were carried out using deionized water. Potassium bromide, KBr, (Sigma–Aldrich, ≥99%, FTIR grade) was used in the preparation of pellets for Fourier transform infrared (FTIR) spectroscopy experiments.

2.2. Methods

In a typical experiment, stock solutions of 0.1 M $Zn(NO_3)_2.6H_2O$, 0.1 M $Zn(NO_3)_2.6H_2O$ containing 4 mg/ml lysozyme, 0.2 M NaOH, and 0.2 M NaOH containing 4 mg/ml lysozyme were freshly prepared and equal volumes of stagnant solutions (the second column of Table 1) and added solutions (the third column of Table 1) were mixed according to the routes given in Table 1. It is noteworthy to state that the stock solutions were prepared at the stoichiometric ratio of Zn^{2+} and OH^-. The experiments were carried out using a total solution volume of 240 ml. Two different addition procedures were followed: single addition and dropwise addition methods. For the single addition method 120 ml of each solution listed in the last column of Table 1 was poured all onto 120 ml of the relevant stagnant solution at once. In the dropwise addition procedure, on the other hand, the stock solutions were added drop by drop onto the corresponding solutions. The samples were denoted using CX-Y or RX-Y notation in which:

- C corresponds to the samples prepared without lysozyme (control samples) and R denotes the samples synthesized with the aid of lysozyme,
- X is the route number used to distinguish stagnant and added solutions and,
- Y represents the type of addition: SA = single addition or DW = dropwise addition.

After combining the reactants, the solutions were stirred continuously at room temperature for overnight. Next, the solutions were centrifuged to get the precipitates. The precipitates were washed with deionized water several times and dried using a vacuum oven at 40 °C for two days. Finally, some portion of the samples was calcined at 700 °C for 2 h.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were obtained using a Philips Xpert-Pro (Panalytical, Almelo, Netherlands) model diffractometer with an incident CuK_α radiation at 1.54 Å. Crystal phases in the samples were identified qualitatively by using PDF-2 database provided by the International Centre for Diffraction Data (ICDD). The Bragg angle (2θ) was ranged between 5 and 80°. FTIR spectra were recorded using an Excalibur FTS 3000 (Digilab, Randolph, MA) model spectrophotometer by employing KBr disk technique. The spectra were taken between 400 and 4000 cm^{-1} range with 2 cm^{-1} resolution. Morphology of the samples was observed using an FEI Quanta 250 FEG (FEI Company, Hillsboro, OR) model scanning electron microscopy (SEM) system. Thermal gravimetric analyses (TGA) of the samples were carried out by employing a Diamond TG-DTA (Perkin Elmer, Waltham, MA) type instrument. Brunauer, Emmett and Teller (BET) surface area values of the samples were determined using physisorption data of nitrogen at 77 K. Physisorption measurements were performed on an ASAP 2010 (Micromeritics, Norcross, GA) model static volumetric adsorption instrument.

3. Results and discussion

In order to investigate the effect of the addition of lysozyme and the preparation route on the structure and morphology of the precipitation products, the samples given in Table 1 were synthesized. In addition to changing the addition order of the reactants, the rate of combining of the reactants was also investigated by preparing the samples using both single addition and dropwise addition method.

The first group of samples was synthesized by adding NaOH solution into stagnant $Zn(NO_3)_2$ solution. XRD patterns, and SEM pictures of these samples are given in Fig. 1 and Fig. 2a–c, respectively. Conversely, in the synthesis of the second group of samples, $Zn(NO_3)_2$ solution was added into stagnant NaOH solution. SEM pictures and XRD patterns of the second group of as-synthesized samples are given in Fig. 2d–f and Fig. 3, respectively. Additionally, lower magnification SEM pictures for the as-synthesized samples are provided in Fig. S1. Crystal structures and morphologies of all the samples are summarized in Table 2.