



Original Research Paper

Effect of the mixing rate on the morphology and photocatalytic activity of ZnO powders prepared by a precipitation method

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ABSTRACT

The urchin-like shape of ZnO powders was prepared by mixing of Zn²⁺ and NaOH solutions at various mixing rates. In this work, ε-Zn(OH)₂ was the first precipitant that was subsequently transformed to ZnO in the alkaline medium during heating. The size of the urchin-like shape of the ZnO powder decreased with a decrease of the mixing rate. The large urchin-like shape also had a large diameter of its hexagonal facet (0001) and showed the highest photocatalytic degradative activity on methylene blue.

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1. Introduction

ZnO is an n-type semiconductor that has found many useful applications [1–4]. In recent years, the use of ZnO as a photocatalyst has been one of the more interesting topics because of the concern about environmental problems and energy demand. The ZnO photocatalyst can use sunlight and water for generating reactive species such as hydroxyl radical ($\cdot\text{OH}^-$) or the superoxide anion radical ($\cdot\text{O}_2^-$) that can damage or destroy pollutants in water and air, and reduce the energy consumption in treatment units [5]. However, the charge recombination between photogenerated electrons and holes that occurs in the photocatalyst particles reduces the photocatalytic activity and this is a main problem for industrial usage. Nowadays, improvement of its photocatalytic performance has been a hot topic for investigations.

Control of the morphology of ZnO is a key factor that can change its chemical and physical properties including its photocatalytic activity. From the literature, there are a number of parameters that can affect the ZnO morphology such as the type of the Zn precursors [6], the pH or the concentration of the base [7,8], types of solvent [9], and type of stabilizer or capping agent [10]. The mixing rate is one of the important parameters that can control the shape and size of ZnO powders. Preparation of ZnO by controlling the

mixing rate has many advantages such as no stabilizer requirement, no pH adjustment and easy to handle.

In this work, the effect of the mixing rate between the starting materials on the ZnO morphology has been investigated by a precipitation method. The photocatalytic activity of ZnO particles prepared in various shapes and sizes was studied through the degradation of a methylene blue solution under the irradiation of blacklight fluorescent tubes.

2. Experimental

ZnO powders were prepared through hydrolysis of zinc acetate dihydrate ((Zn(C₂H₃O₂)₂·2H₂O, Fluka) in the presence of sodium hydroxide (NaOH, Merck) in an aqueous solution. The mixing rate was controlled by adjust the stopcock of cylinder column containing NaOH solution and the mixing rate also measured by a decreasing of NaOH per time. In a typical procedure, 150 mL of 1.0 M NaOH was added to 150 mL of a 0.1 M Zn(C₂H₃O₂)₂·2H₂O solution contained in 500 mL of round bottom flask with mixing rates of 30, 5 and 2.5 mL/s and continuously stirred at 450 rpm at room temperature for 10 min. The resulting mixture was then stirred at 450 rpm at 80 °C for 1 h. After being cooled in air to room temperature, the precipitants were filtered, rinsed with distilled water several times, then collected and dried at 100 °C for 1 h in an oven before investigation of their properties.

The structural identification and morphological study of the prepared ZnO powders at several of mixing rates were carried out using an X-ray diffractometer (XRD, X'Pert MPD, Philips) with Cu K_α radiation at a wavelength of 0.15406 nm and with a scanning

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electron microscope (SEM, Quanta 400, FEI), respectively. The UV–Vis diffuse reflectance spectra were recorded on a UV–Vis spectrophotometer (UV-2450, Shimadzu) using BaSO₄ as a reference. The total surface areas of the prepared ZnO powders were analyzed by the Brunauer–Emmett–Teller (BET) method using the surface area analyzer (Autosorb 1 MP, Quantachrome).

The photocatalytic activity was investigated through the degradation of a methylene blue (MB) aqueous solution under irradiation by three parallel blacklight fluorescent tubes (18 W, Sylvania). These tubes efficiently emit UVA at 315–400 nm (peak at 352 and 368 nm, from the data sheet). 150 mg of ZnO was placed into 150 mL of 1×10^{-5} M MB solution contained in 250 mL of beaker (inner diameter ~8 cm). To study the adsorption of MB on the surface of ZnO powders, this mixture was stirred for 30 min in the dark. After that, this mixture was under the blacklight illumination. The suspensions were collected at required times and centrifuged to separate the catalyst powders. The remaining MB concentration after each irradiated period was determined by a UV–Vis spectrophotometer (Lambda 25, Perkin Elmer). The MB degradation was calculated by following:

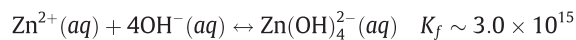
$$\text{degradation (\%)} = [(A_0 - A_t)/A_0] \times 100$$

where A_0 and A_t are the absorbance at 655 nm of initial MB and MB after required irradiation time t , respectively.

3. Results and discussion

3.1. Mechanism of ZnO formation

We have examined the mechanism of ZnO formation by a time-resolved investigation. At the first step, when the NaOH solution was added into the Zn²⁺ solution at a high mixing rate (30 mL/s), the resulting solution produced no precipitant. It is possible that Zn²⁺ reacted with the OH⁻ to form a soluble species such as Zn(OH)₄²⁻. At this mixing rate, 150 mL of NaOH was added completely within 5 s. After the clear solution was continuously stirred for about 3 min at room temperature, (in this work called the delay time) a white suspension (or primary precipitant) appeared and its XRD pattern, (Fig. 1a), matched well with the peaks of ε-Zn(OH)₂ crystallizing in a cubic structure (JCPDS Card No. 38-0385). Therefore, it can be concluded that in this situation Zn²⁺ reacts with OH⁻ to form the Zn(OH)₄²⁻ species and transform to the ε-Zn(OH)₂ species later. This might be explained by the $K_{overall}$ being less than 1 as described below:



When the mixture was then heated at 80 °C for the required heating times, the white products were again characterized by the XRD technique (Fig. 1). The amount of the ZnO phase that corresponded to the peak intensity clearly increased with an increase in the heating time. The XRD pattern showed only a single phase of ZnO without any secondary phase when the heating time was more than or equal to 20 min. In Fig. 2, the SEM images of the solid

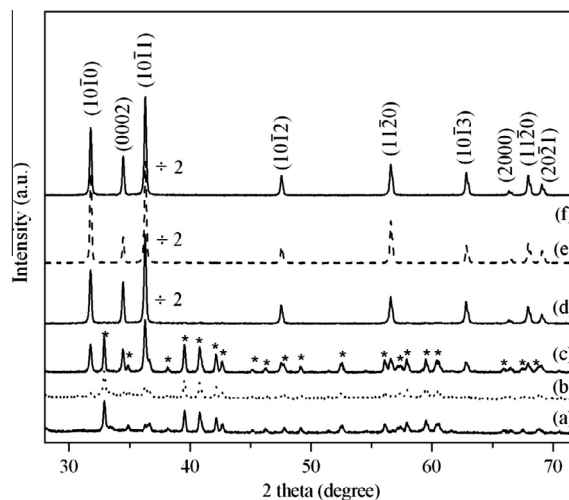
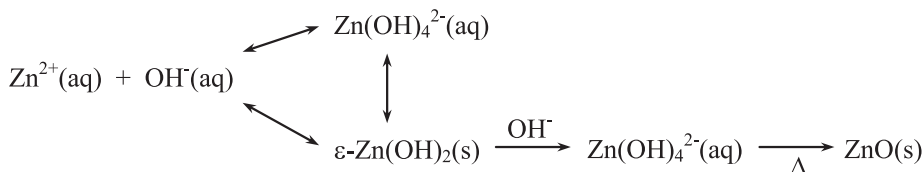


Fig. 1. The time resolved XRD patterns of precipitants after heating at (a) 0, (b) 5, (c) 10, (d) 20, (e) 30 and (f) 40 min at a mixing rate of 30 mL/s. The indexed peaks correspond to the ZnO phase and the peaks marked with * can be assigned to ε-Zn(OH)₂.

powders during different heating times are shown. At first, the primary precipitant, ε-Zn(OH)₂, shows as octahedral prisms (Fig. 3a) and this is a common observation in the literature [11]. This was followed by the surface of ε-Zn(OH)₂ being corroded by OH⁻ (Fig. 2a). When this suspension was continuously heated for 10 min, the urchin-like shape begin to grow from the surface of the octahedral prism of the ε-Zn(OH)₂ crystals (Fig. 2b). Thus, it is possible to conclude that the urchin-like shape observed in the SEM image is that of ZnO because the population of urchin-like shape correlates with the intensity of the characteristic peaks of the ZnO structure as seen in Figs. 1 and 2.

As the ZnO grows from the ε-Zn(OH)₂'s surface, it is possible that ZnO might arise from (1) the decomposition of ε-Zn(OH)₂ or (2) the recrystallization that is known as the redissolution-precipitation mechanism through Zn(OH)₄²⁻. To solve this problem, the primary precipitant, ε-Zn(OH)₂, that comes from the first step, was filtered and added into distilled water. After this suspension was heated at 80 °C for 1 h, the final product showed the major phase of ε-Zn(OH)₂ with a small amount of ZnO (Fig. 4a). In contrast, the ZnO phase without any impurity phase was observed in the XRD pattern when the primary precipitant within the NaOH solution was heated at 80 °C for 1 h (Fig. 4b). This meant that the alkaline medium was a very important factor to transform the ε-Zn(OH)₂ to ZnO and the possibility that the production of ZnO in solution by decomposition of ε-Zn(OH)₂ can be eliminated. From this result, it seems that the surface of ε-Zn(OH)₂ might react with OH⁻ to form Zn(OH)₄²⁻ as a growth species followed by its decomposition to ZnO crystal on the surface of the ε-Zn(OH)₂ particle at a high temperature. When the heating is prolonged, the diameter of the urchin-like shape increased while the amount of ε-Zn(OH)₂ decreased. If the primary precipitant within the NaOH media was stirred for 1 h without heating, the XRD pattern showed a major phase of ε-Zn(OH)₂ with a small amount of the ZnO phase (data are not shown). From this work, we conclude that the mechanism of forming ZnO at a Zn²⁺:OH⁻ = 1:10 might be as follows:



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