



Preparation and characterization of dispersive carbon-coupling ZnO photocatalysts

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ABSTRACT

Dispersive carbon-coupling ZnO particles (C/ZnO) with smaller particle sizes and higher specific surface area were produced using a method combining precipitation and combustion techniques. Glucose was added in the production procedure to act as fuel to conduct combustion reaction and as source to form tiny carbon particles in the C/ZnO. Physical and chemical properties of the prepared C/ZnO particles were investigated and photocatalytic abilities of these particles to photocatalytically decompose the methylene blue in water under 365-nm UV light irradiation were kinetically studied. The prepared C/ZnO particles exhibited higher photocatalytic ability than the ZnO particles and the P25. The C/ZnO particles calcined at 900 °C possessed the best photocatalytic performance and had a reaction rate constant (k_m) of $0.859 \text{ L} \cdot (\text{g} \cdot \text{min})^{-1}$, which exhibited much higher photocatalytic ability than the ZnO calcined at 700 °C ($k_m = 0.326 \text{ L} \cdot (\text{g} \cdot \text{min})^{-1}$) and the P25 ($k_m = 0.371 \text{ L} \cdot (\text{g} \cdot \text{min})^{-1}$).

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1. Introduction

ZnO with a hexagonal wurtzite structure is an n-type semiconductor material, which has wide-bandgap energy of 3.37 eV and exciton binding energy of 60 meV. ZnO, aside from TiO_2 , has been considered as a promising material for purification and disinfection of water and air, and remediation of hazardous waste, owing to its high activity, environment-friendly feature and lower cost [1–6]. Several methods have been used to prepare ZnO particles, such as precipitation [7–10], hydrothermal method [11–15], and spray pyrolysis [16–19]. In the application of ZnO photocatalyst, one major problem faced is the fast recombination rate of the photoinduced electrons and electron holes [20,21], which leads to a reduction of photocatalytic activity of the ZnO. Some efforts have been made to improve the photocatalytic activity of ZnO by coupling ZnO with metal or metallic oxide, like Ag [22–24], SnO_2 [25,26], Cu_2O [27] and TiO_2 [28]. ZnO photocatalysts coupled with metal or oxide may retard their electron–hole recombination rates by trapping the photoinduced electrons in the coupling phase and consequently could promote the photocatalytic abilities.

In this study, we proposed a simple method combining precipitation and combustion techniques to prepare carbon-coupling ZnO nanoparticles (C/ZnO). Glucose was used as fuel to carry out the required combustion reaction and as source to form tiny carbon particles to produce dispersive C/ZnO nanoparticles with high photocatalytic reactivity. The characteristics and photocatalytic activities of the C/ZnO

particles were investigated and were compared to those of the ZnO particles without carbons coupling (ZnO) and the P25 (a commercial TiO_2 photocatalyst product; Degussa, Germany).

2. Experimental detail

2.1. Sample preparation

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99% purity, Showa) was dissolved in distilled water to form an aqueous solution of 0.2 M. NH_4OH (28 wt.%, Tedia) was then added dropwise to the stirred aqueous solution until $\text{pH} = 8$. After being continuously stirred for 1 h, the solid precipitates were collected by centrifugal filtration and were dried in an oven at 90 °C. The mixture containing the dried precipitates, distilled water and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, 98% purity, Showa), in weight ratios of precipitates: distilled water: glucose = 1: 1.7: x (where $x = 0$ or 0.85), was ball-milled for 12 h, followed by drying at 90 °C. The added glucose acted as fuel to carry out combustion reaction at the follow-up thermal treatment. The dried ZnO precursor (i.e., $x = 0$) and the C/ZnO precursor (i.e., $x = 0.85$) were then heated up, in a muffle furnace, to different temperatures and isothermally treated at the designed temperature for 3 h.

2.2. Characterization

Thermal behavior of the ball-milled particles was investigated using a thermal analyzer STA 499F3 (Netzsch, Germany), which is capable of performing thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) simultaneously for the same sample. The crystalline phases and crystal structure existing in the specimen were

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examined by X-ray diffraction analysis (XRD; X-ray wavelength 0.154056 nm; D8A; Bruker, Germany). Average crystallite sizes of the obtained ZnO particles were estimated by employing Scherrer's equation in the corresponding profiles of the (101) XRD peak for ZnO. Morphologies and sizes of the particles and the crystallites were observed using scanning electron microscopy (SEM; LEO 1530, Carl Zeiss, USA) and transmission electron microscopy (TEM; H-7100; Hitachi, Japan). Specific surface areas of the calcined specimens were measured using an automated BET sorptometer (Porous Materials, USA), operated at a liquid-nitrogen temperature of around -196°C . To examine the effect of the coupling carbons on the electron-hole recombination rate of the photo-excited ZnO, photoluminescence (PL) spectra of the specimens were measured using a fluorescence spectrophotometer (Hitachi F-2500, Japan), which used Xe lamp as excitation source at room temperature.

2.3. Photocatalytic activity determination

Photocatalytic activities of the ZnO and the C/ZnO particles were estimated by examining their abilities to photocatalytically decompose the MB in water. In a dark chamber, the tested particles of 0.01 g were dispersed in the aqueous solution of MB (10 μM , 200 mL) and the suspension so obtained was vigorously stirred for 10 min to attain the adsorption-desorption equivalence of MB on catalyst, which was confirmed by observing the change of concentration of the $\text{MB}_{(\text{aq})}$ using ultraviolet-visible spectroscopic analysis (UV-vis; Unicam UV500; Thermospectronic, UK). Then, the tested particles were irradiated using 365-nm ultraviolet (UV) lamps (8 W $\times$ 2, Great Tide Instrument, Taiwan). The reaction system was maintained at about 25°C . After every 5 or 10 min UV exposure, 3 mL of the testing MB solution was sampled and was subjected to UV-vis analysis. The absorbance of the MB characteristic band at 664 nm in the obtained UV-vis spectrum was used to determine the concentration of MB in the solution. The concentration changes of $\text{MB}_{(\text{aq})}$ with time under the conditions described above were recorded and examined to determine the photocatalytic activities of the prepared nanoparticles. The specific reaction rate of photocatalyst used (k_m) for photocatalytic degradation of MB under 365-nm UV light was estimated [29] and was used as an index of photocatalytic activity of the prepared photocatalyst.

3. Results and discussion

3.1. Thermal behavior

Fig. 1(a) shows the TG & DSC curves of the ZnO precursor. The ZnO precursor on the course of heating experienced five major endothermic changes and resulted in totally about 34.5% loss in weight. The TG curve of the ZnO precursor was leveled off at the temperature above 300°C . The first endothermic change (the DSC peak with a peak temperature of 42°C) was due to evaporation of the physical adsorbed water. To examine the composition changes caused by the other four endothermic changes, the ZnO precursor was heated up to the predesigned temperatures, without thermal soaking, and the resultant particles were XRD-examined. Fig. 1(b) gives the XRD patterns of the ZnO precursor dried or heated at 90°C , 170°C and 300°C . The major crystalline phases detected in the specimens were $\text{Zn}_5(\text{NO}_3)_2(\text{OH})_8\cdot\text{H}_2\text{O}$ (ICDD # 24-1460) and $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ (ICDD # 52-0627) at 90°C , $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ at 170°C and ZnO (ICDD # 65-3411) at 300°C . Based on the results shown in Fig. 1, the major reactions that occurred during the heating of the ZnO precursor are proposed as follows:

at $90\text{--}152^{\circ}\text{C}$ (corresponding to the DSC peaks at 107°C and 127°C in Fig. 1(a))

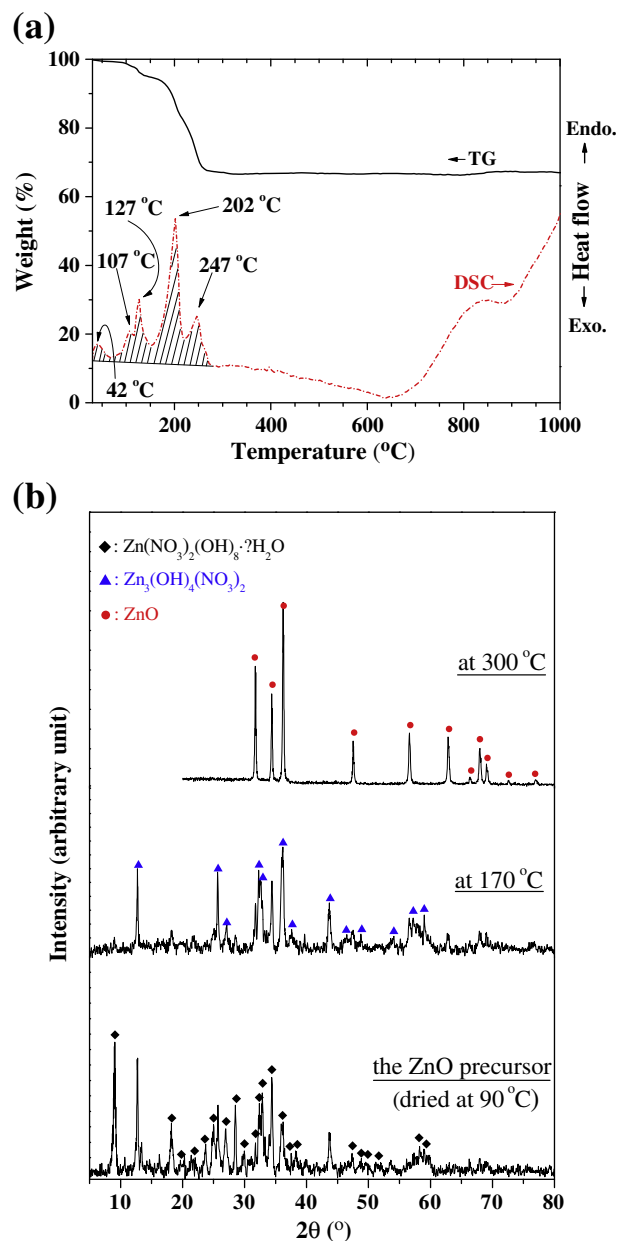
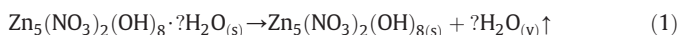
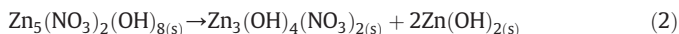
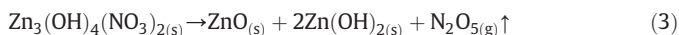


Fig. 1. (a) TG and DSC curves, operating at $4^{\circ}\text{C}/\text{min}$ heating rate and 30 mL/min air flow, of the ZnO precursor and (b) XRD patterns of the ZnO precursor dried or heated at different temperatures.



at $152\text{--}222^{\circ}\text{C}$ (corresponding to the DSC peak at 202°C in Fig. 1(a))



at $222\text{--}300^{\circ}\text{C}$ (corresponding to the DSC peak at 247°C in Fig. 1(a))



Heating the ZnO precursor at temperatures above 300°C produces pure crystalline ZnO with a hexagonal wurtzite structure.

Fig. 2(a) gives the TG & DSC curves of the C/ZnO precursor. During heating, the C/ZnO precursor undertook four endothermic changes and one strong exothermic change, which caused totally about 61.5% loss in weight. XRD analysis (see Fig. 2(b)) indicated that the major crystalline

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