



# Preparation of a high-activity ZnO/TiO<sub>2</sub> photocatalyst via homogeneous hydrolysis method with low temperature crystallization

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## ABSTRACT

The nano-scale ZnO/TiO<sub>2</sub> coupled oxide photocatalyst was successfully synthesized by a two-step method, the homogeneous hydrolysis and low temperature crystallization. The resultant photocatalyst was characterized by ultraviolet–visible absorption spectroscopy (UV–vis), X-ray diffraction (XRD), transmission electron microscopy (TEM), and Brunauer–Emmett–Teller (BET) techniques. The photocatalytic activity of coupled oxides was also evaluated by the degradation of methyl orange (MO) as a model compound. The experimental results showed that the prepared ZnO/TiO<sub>2</sub> at low hydrothermal crystallization temperature exhibited higher photocatalytic activity for the decomposition of MO than either pure phase ZnO or anatase TiO<sub>2</sub>, and even higher than that of the Degussa P25 TiO<sub>2</sub>.

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## 1. Introduction

The semiconductor photocatalysis has been used to mineralize the organics via a series of intermediates into inorganic substances, such as H<sub>2</sub>O, CO<sub>2</sub>, and so on under ambient conditions in the presence of light. Therefore, it appears to be a promising technology and has a number of applications in environmental treatment such as water and air purification as well as hazardous waste remediation [1–3]. To date, many semiconductors have been found to be good photocatalysts to decompose various organics [3]. Among of them, TiO<sub>2</sub> and ZnO have been the dominant photocatalysts [1]. However, the photoinduced charge carrier in single bare semiconductor particles has a very short lifetime because of the high-recombination rate of the photogenerated electron/hole pairs, which reduces photocatalytic efficiency and hinders its further application in industry. Therefore, it is important to prevent the photoelectron/hole recombination before a designated chemical reaction takes place on the surface of semiconductor particles. Numerous efforts have been attempted to improve the photo-excited charge separation and to enhance the photocatalytic activity by modifying the surface or bulk properties of a photocatalyst, such as deposition of metals, doping, surface chelation, and coupling of two semiconductors [4,5]. Among the coupled semiconductors, many efforts have been devoted to combine TiO<sub>2</sub> with other metal oxides such as ZnO [6], SnO<sub>2</sub> [7], Fe<sub>2</sub>O<sub>3</sub> [8], ZrO<sub>2</sub> [9], Cu<sub>2</sub>O [10], etc.

In this study, the ZnO/TiO<sub>2</sub> photocatalyst has been synthesized by the combination method of the homogeneous hydrolysis with the low

temperature crystallization. To optimize the preparation of ZnO/TiO<sub>2</sub>, some factors affecting photocatalytic activity, such as acetic acid concentration, crystallization time and temperature were investigated in detail. The crystal structures and surface properties of coupled oxides were characterized by various techniques including ultraviolet–visible absorption spectroscopy, XRD, TEM and BET techniques. The photocatalytic activity of the photocatalyst was subsequently evaluated by the degradation of methyl orange (MO) as a model compound.

## 2. Experiment

### 2.1. Preparation of ZnO/TiO<sub>2</sub>

All of the chemical reagents used in the experiments were analytical grade without further purification. The nano-sized ZnO/TiO<sub>2</sub> was prepared by the homogeneous hydrolysis method with low temperature crystallization. A typical synthesis procedure is as follows: tetrabutyl titanate, zinc acetate dihydrate and HAc were directly dissolved in ethylene glycol to obtain mixture solution. The mixture was transferred into an autoclave, and heated at 120 °C for 6 h. Uniform hydrolysis of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and Ti(OBu)<sub>4</sub> was accomplished via *in situ* homogeneous generated water by the esterification reaction of ethylene glycol with HAc. For better crystallinity of the nano-particles, the precursor was hydrothermally treated in an autoclave at 180–200 °C for a certain period of time. Subsequently, the product was washed with methanol, filtered, and dried in an electric vacuum drying oven at 60 °C. For comparison, single TiO<sub>2</sub> and ZnO nano-particles were prepared using the same procedure except that the starting materials were Ti(OBu)<sub>4</sub> for TiO<sub>2</sub> and Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O for ZnO, respectively.

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## 2.2. Characterization

The XRD patterns obtained on a Philips MPD 18801 X-ray diffractometer were used to determine phase structures and crystallite size. The morphologies and sizes of the photocatalysts were evaluated by TEM (Jeol JEM-100CX II). The UV–vis spectra were obtained via UV–visible spectrophotometer (UV-1901, China). BET measurements were performed on a Quantachrome NOVA-3000 instrument, and particle size was analyzed on a zetasizer Nano ZS90 (Malvern Instrument, Worcs, UK).

## 2.3. Photocatalytic activity

The photocatalytic activity of all prepared photocatalysts and Degussa P25 were performed at ca. 30 °C in a 50 ml quartz glass reactor. A 125-W high pressure Hg lamp with a wavelength of 365 nm paralleling to the reactor with a 20 cm distance was used as the light source. The initial concentration of MO and photocatalyst powders was 0.02 and 2.5 g/L, respectively. Prior to irradiation, the suspension was stirred in the dark to establish adsorption–desorption equilibrium. Once the concentration of MO has stabilized, the sample was irradiated with UV light, signaling the start of photocatalysis. At given time intervals, sample was collected, centrifuged, and filtered through a 0.2 µm millipore filter. Then the filtrate was analyzed on the UV-1901 UV–visible spectrophotometer at 464 nm.

## 3. Results and discussion

### 3.1. Characterization of photocatalyst

The phase composition of prepared photocatalysts was identified by XRD analysis (see Fig. 1). The photocatalysts were all crystallinity and had obvious diffraction peaks corresponding to ZnO and TiO<sub>2</sub> phases, which indicated that hexagonal ZnO and anatase TiO<sub>2</sub> phases were formed at lower crystallization temperature ( $\leq 200$  °C). Furthermore, HAc concentrations have a significant effect on the phase transformation. With initial concentrations of 9.0 M, only pure anatase TiO<sub>2</sub> nanocrystalline was obtained. Decreasing initial concentration is beneficial to the growth of ZnO phase, which can subsequently restrain the formation of anatase TiO<sub>2</sub> phase (Fig. 1A). Therefore, the nano-scale ZnO/TiO<sub>2</sub> coupled oxides can be formed only at the right range of the initial HAc concentration.

The influence of heat treatment temperature on the phase transformation was shown in Fig. 1B. It reveals that the crystallization degree and the growth rate of ZnO and TiO<sub>2</sub> increased with an increasing crystallization temperature. At 180 °C for 15 h, the obtained material was basically amorphous solid. However, the hexagonal ZnO and anatase TiO<sub>2</sub> phases were formed at 200 °C for 15 h. Besides the crystallization temperature, the retention time also influence the crystallization degree and the growth rate of ZnO and TiO<sub>2</sub>. As shown in Fig. 1C, with an increasing retention time, both the crystal sizes and the crystallization

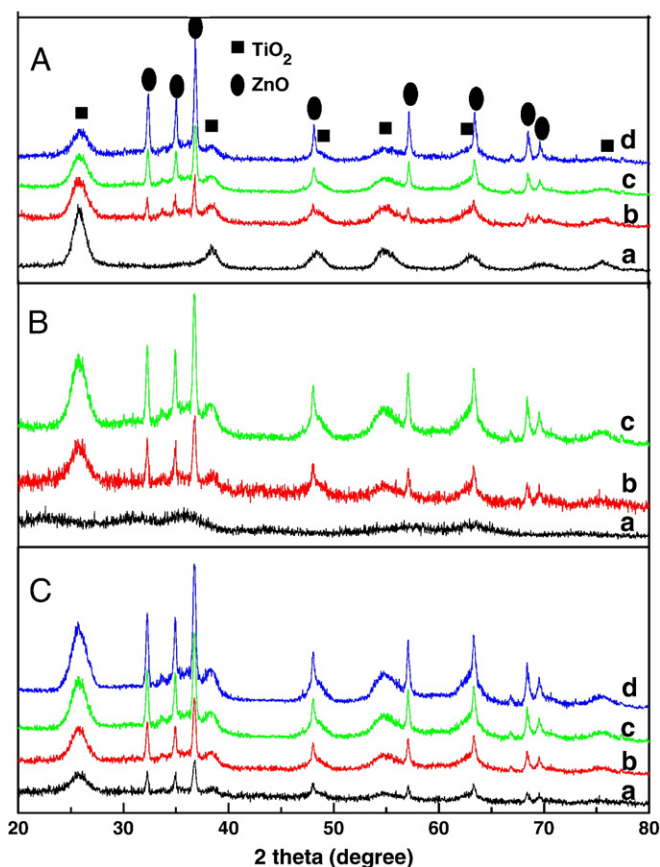


Fig. 1. XRD patterns of prepared ZnO/TiO<sub>2</sub>. (A) Acetic acid concentration (M): (a) 9.0, (b) 4.5, (c) 3.0 (d) 1.5; (B) hold temperature (°C): (a) 180, (b) 190, (c) 200; (C) hold time (h): (a) 8, (b) 12, (c) 15, (d) 24.

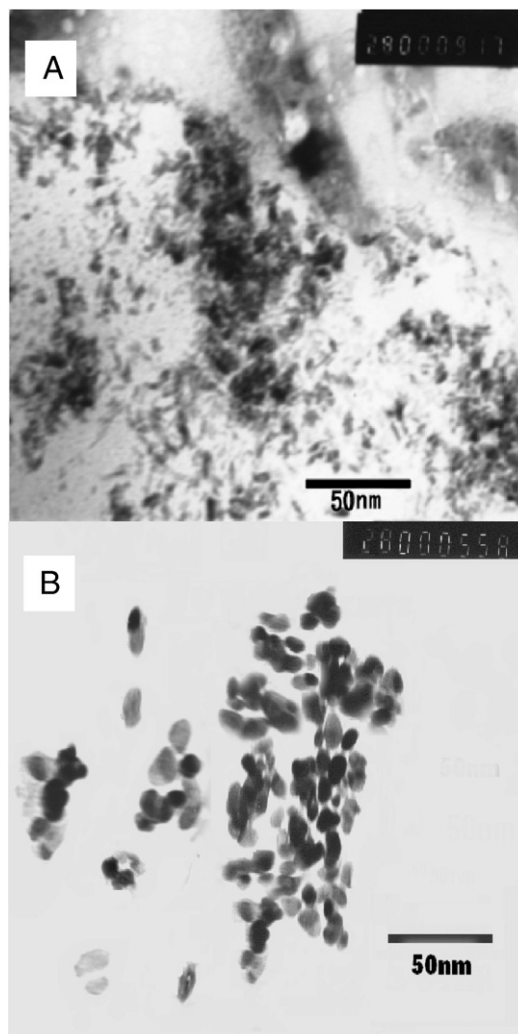


Fig. 2. TEM images of ZnO/TiO<sub>2</sub> prepared at different crystallization temperatures: (A) 180 °C, (B) 200 °C.

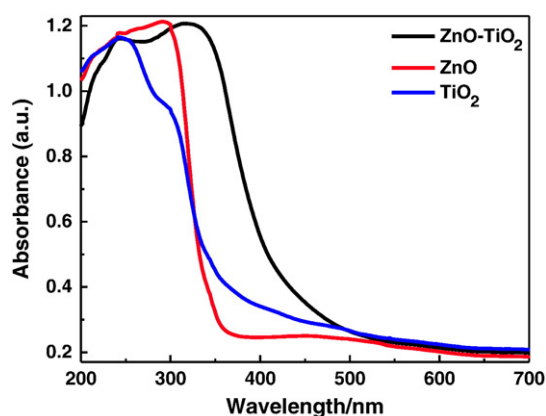


Fig. 3. Ultraviolet–visible absorption spectra of pure ZnO, TiO<sub>2</sub>, and ZnO/TiO<sub>2</sub>.

degree of ZnO and TiO<sub>2</sub> also increased slowly at the same crystallization temperature of 200 °C.

The average particle size of ZnO and TiO<sub>2</sub> determined from the XRD patterns according to the Scherrer equation are 10.1 and 17.3 nm respectively, which was prepared under 3.0 mol/L of HAc and at 200 °C crystallization temperature for 15 h. This indicated that as-prepared materials were composed of nano-sized ZnO and TiO<sub>2</sub>.

Figs. 2A and B show the typical TEM images of the ZnO/TiO<sub>2</sub> samples prepared at the crystallization temperatures of 180 and 200 °C, respectively. Results indicated that the sample prepared at 180 °C is mainly amorphous phase, while the ZnO/TiO<sub>2</sub> mainly becomes crystal material when the temperature is higher than 200 °C, and the particle sizes were all in the range of 10–20 nm. TEM results were in good agreement with the results from the XRD analysis.

Additionally, the particle size and the size distribution of the ZnO/TiO<sub>2</sub> were also measured. As shown in Fig. S1, the particle sizes of ZnO/TiO<sub>2</sub> were in the range of 25–100 nm, with an average particle size of ca. 64 nm. It is worth noting that the particle size measured by the zetasizer was larger than that observed by the XRD and TEM. It is because Malvern Instruments' Zetasizer used light scattering techniques to measure the hydrodynamic size of nano-particles. An increase in the particle size can result in the agglomeration of particles. Simultaneously, the BET specific surface areas of the ZnO/TiO<sub>2</sub> were measured as 206.2 and 97.0 m<sup>2</sup>/g respectively at 180 and 200 °C crystallization temperature. These results showed that the specific surface areas of the ZnO/TiO<sub>2</sub> were greatly decreased with the increase of the crystallization temperature. And BET analysis results were basically in accordance with those from the XRD and TEM analysis.

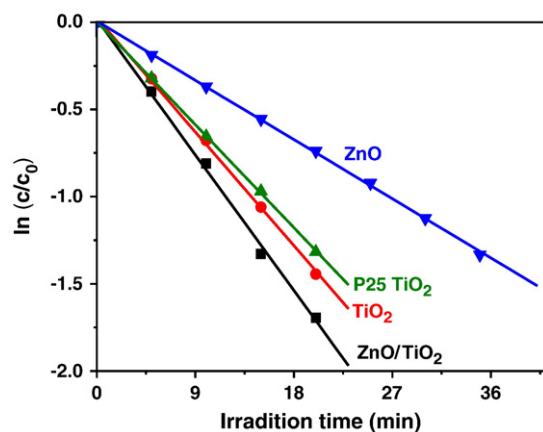


Fig. 4. Photocatalytic degradation of MO by various photocatalysts.

In order to describe the photo-absorption behavior of the ZnO/TiO<sub>2</sub> nanocomposite, a certain amount of samples were uniformly dispersed in a mixture of 50% ethylene glycol and 50% water, and then their UV–vis absorption spectra were recorded. Simultaneously, the UV–vis absorption spectra of ZnO and TiO<sub>2</sub> were also conducted to compare their photo-absorption properties. Fig. 3 shows the UV–vis absorption spectra of ZnO/TiO<sub>2</sub>, ZnO and TiO<sub>2</sub> prepared at 200 °C for 15 h. It can be seen that all the samples had an extremely strong absorption at the wavelength range from 200 to 380 nm, except a relatively strong absorption in the visible region (>400 nm) for ZnO/TiO<sub>2</sub>. It can be observed from Fig. 3 that the UV–vis absorption of the ZnO/TiO<sub>2</sub> sample is red-shifted compare to that of ZnO and TiO<sub>2</sub>. This observed shift can be interpreted as being caused by the Zn<sup>2+</sup> acting as a substitutional dopant in the lattice and on the surface of TiO<sub>2</sub> during the preparation process of the ZnO/TiO<sub>2</sub> sample. And the created defects, which introduce the doping energy level in TiO<sub>2</sub>'s forbidden band gap, can be used to excite electrons to the conduction band to inhibit the recombination of the holes and electrons.

### 3.2. Photocatalytic activity

The photocatalytic activities of all prepared photocatalysts were evaluated by the degradation of MO in aqueous solution. In addition to experiments with the photocatalyst and irradiation, both blank experiments in the absence of irradiation with the photocatalyst or in the presence of irradiation without the photocatalyst were investigated. Both blank experiment results showed that the MO could not be degraded without the photocatalyst or the UV irradiation. However, in the presence of UV irradiation and coupled ZnO/TiO<sub>2</sub> prepared at 200 °C for 15 h, the MO was easily degraded (see Fig. 4).

For comparison, the photocatalytic degradation of MO was also performed using P25 TiO<sub>2</sub>, pure TiO<sub>2</sub> and ZnO prepared at the same procedure. Fig. 4 shows that the coupled ZnO/TiO<sub>2</sub> had high photocatalytic activity and its photocatalytic efficiency was higher than those of the pure ZnO or TiO<sub>2</sub> alone, as well as P25 TiO<sub>2</sub>. Referring to previous literature [11,12], the enhanced photocatalytic activity of ZnO/TiO<sub>2</sub> may be mainly attributed to the presence of the intimately bonded ZnO/TiO<sub>2</sub> surface hetero-structure, which promotes the separation of the photogenerated electrons and holes and thus decreases the electron–hole pair recombination rate. All the time, the photocatalytic activity of ZnO/TiO<sub>2</sub> must be further enhanced from the wide range absorption of incident light.

## 4. Conclusion

The nano-sized coupled ZnO/TiO<sub>2</sub> was prepared by the homogeneous hydrolysis and low temperature crystallization two-step method. This prepared photocatalyst had a better photocatalytic activity than that of either single ZnO or TiO<sub>2</sub>, and P25 TiO<sub>2</sub>.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2010.05.054.

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