

Novel preparation of nanosized ZnO–SnO₂ with high photocatalytic activity by homogeneous co-precipitation method

Maolin Zhang*, Guoying Sheng, Jiamo Fu, Taicheng An, Xinming Wang, Xiaohong Hu

State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

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Abstract

The homogeneous co-precipitation method was proposed to synthesize nanoscale binary mixed oxide ZnO–SnO₂ in the presence of ethyl acetate. The products were characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Their photocatalytic activity was investigated for the liquid-phase photocatalytic degradation of methyl orange (MO) diluted in water under UV light irradiation. It was found that the coupled oxides ZnO–SnO₂ mainly consist of nanosized ZnO and SnO₂, and they have better photocatalytic activity for the degradation of MO than ZnO or SnO₂ alone. Moreover, the calcination temperature had an obvious effect on the size of the coupled oxide particles.

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1. Introduction

In recent years there has been an extensive interest in developing semiconductor photocatalysts with high activities for environmental applications such as air purification, water disinfection, hazardous waste remediation, and water purification [1–4]. However, the high degree of recombination of photogenerated electrons and holes in semiconductors decreased greatly their photocatalytic efficiency and impeded the practical application of photocatalytic technique in the degradation of contaminants in water and air. Thus, a major challenge in heterogeneous photocatalysis is the need to increase the charge separation efficiency of the photocatalyst and its photocatalytic efficiency. Fortunately, the coupling of two semiconductor particles with difference band-gap widths could increase the charge separation and extend the energy range of photoexcitation, so coupled semiconductor photocatalysts

exhibited higher photocatalytic activity for both gas- and liquid-phase reactions than single semiconductor photocatalysts. By far, many research groups have carried out the photocatalytic activity experiments of various coupled semiconductor particle systems [5–9]. However, the preparation of the coupled oxide ZnO–SnO₂ only were little reported [10]. In our previous studies [11,12], the nanosized coupled photocatalyst ZnO–SnO₂ was prepared by the heterogeneous precipitation using NaOH or NH₃·H₂O as the precipitant and its photocatalytic activities were evaluated using MO as a model organic compound. Theoretically, compared to the heterogeneous precipitation, the homogeneous co-precipitation method would lead to more homogeneous distribution and less size-scale of ZnO–SnO₂ species. However, to our knowledge, there was no paper reporting the preparation of the nanosized coupled ZnO–SnO₂ by homogeneous co-precipitation method.

In this paper, we successfully prepared the nanosized coupled ZnO–SnO₂ with 1:1 molar composition by the homogeneous co-precipitation method using ethyl acetate as precipitating agent. This is the first report on the preparation

* Corresponding author. Tel.: +86 20 85290445; fax: +86 20 85290706.

E-mail address: zhangml@gig.ac.cn (M. Zhang).

of the coupled semiconductor photocatalyst ZnO–SnO₂ by the homogeneous co-precipitation route. At the same time, its photocatalytic activities were also evaluated using methyl orange as a model organic compound.

2. Experimental

All of the chemical reagents used in the experiments were analytic grade without further purification and treatment. The synthesis procedures of the coupled ZnO–SnO₂ are as follows: 10 mol l⁻¹ NaOH aqueous solution was added dropwise into 100 ml of 0.5 mol l⁻¹ Zn(NO₃)₂ aqueous solution under vigorous stirring until the solution became transparent, and then 100 ml of 0.5 mol l⁻¹ Na₂SnO₃ solution and a certain volume of distilled water were added. As a result, 300 ml of the mixture solution containing Na₂SnO₃ and Na₂[Zn(OH)₄] was obtained. Subsequently, 200 ml of H₂O, CH₃COCH₃ and CH₃COOC₂H₅ mixture solution with 3:3:2 volume ratio was added into the above mixture solution at room temperature (ca. 25 °C) under vigorous stirring, and the resulting solution was subjected to precipitation by the hydrolysis of ethyl acetate until the reaction mixture attained a pH value between 9 and 10. The precipitate obtained was separated and washed 3 times with distilled water, and dried at 80 °C, then calcined at different temperatures in air to synthesize ZnO–SnO₂ particles. At the same time, the pure SnO₂ and ZnO were also prepared by the same homogeneous precipitation method, i.e., 100 ml of 0.5 mol l⁻¹ Na₂SnO₃ solution and 100 ml of 0.5 mol l⁻¹ Zn(NO₃)₂ solution were diluted, respectively, and the former was diluted to 300 ml by distilled water while the later by adding an appropriate amount of 10 mol l⁻¹ NaOH aqueous solution and a certain volume of distilled water in it under vigorous stirring into 300 ml of the transparent solution of Na₂[Zn(OH)₄]. Subsequently, the experimental process was the same as that of the coupled ZnO–SnO₂.

X-ray diffraction patterns and TEM images were obtained for some calcined samples (A Rigaka D/max-1200 and Jeol JEM-100CX11). The photocatalytic reactions took place in a 100 ml Pyrex glass bottle under irradiation of a 125 W high pressure Hg lamp (GGZ125, Shanghai Yaming Lighting CO., Ltd) with a maximum emission at about 365 nm. The MO concentration was analyzed by UV-VIS spectroscopy (Thermo Spectronic/Heλios α) at its maximum absorption wavelength of 464 nm.

3. Results and discussion

3.1. Characterization of coupled oxides

The XRD patterns of the coupled oxide powders calcined at different temperatures were shown in Fig. 1. Fig. 1 indicated the phases of the prepared ZnO–SnO₂ were the couple of ZnO and SnO₂, but the Zn₂SnO₄ phase emerged in the sample calcined at

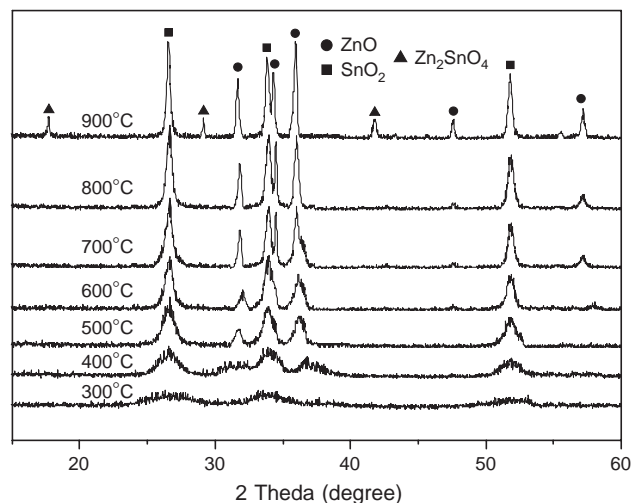


Fig. 1. The XRD patterns of ZnO–SnO₂ calcined at different temperatures.

900 °C. The diffraction peaks are continuously getting sharper with increasing calcination temperature, which reveals that the grain sizes become larger with increasing calcination temperature. The mean sizes of ZnO or SnO₂ in the coupled oxides calcined at 400, 500, 600, 700, 800 and 900 °C for 2 h, respectively could be calculated by the Scherrer formula. Calculated results showed that the mean sizes of ZnO were 3.0, 13.7, 30.3, 53.7 and 90.3 nm, respectively, and those of SnO₂ were 2.8, 8.7, 16.9, 25.1, 39.3 and 57.7 nm, respectively. Compared to our previous studies [11,12], It is also noted that the growth of Zn₂SnO₄ was slower under the present conditions, and Zn₂SnO₄ only appeared in the coupled oxide calcined at 900 °C.

The TEM photographs of the coupled oxide powders calcined at 300, 500, 700, and 900 °C were given in Fig. 2. The TEM photographs showed that the shape of coupled oxide powers was clear and the aggregation was little. At the same time, the TEM photographs also showed that coupled oxide powders were nanometer scale and the sample calcined at 300 °C was almost an amorphous power, which is in reasonable agreement with the results obtained from the XRD. Moreover, it was also easy to see from the TEM photographs that the mean size of coupled oxide particles increased significantly with increase of the calcination temperature.

3.2. Photocatalytic activity of coupled oxides

3.2.1. Adsorption behavior of MO on photocatalysts

In order to investigate the adsorption/desorption behavior of MO on photocatalysts surface, the suspensions were prepared by mixing 100 ml of 20 mg l⁻¹ MO aqueous solution at the natural pH value with 0.25 g sample powers calcined at 600 °C for 2 h or commercial TiO₂ (Degussa P25). The suspensions were kept for given times in the dark under the condition of stirring, and then filtered after being centrifuged. The absorbance of the filtrate was then measured at the maximum band 464 nm of MO to determine the concentration of MO. The experimental results were shown in Fig. 3. From the Fig. 3, it was found that the adsorption/desorption equilibrium of MO on various photocatalysts under 20 mg l⁻¹ initial concentration of MO was reached at about 30 min of equilibration time, and MO couldn't be degraded in the exper-

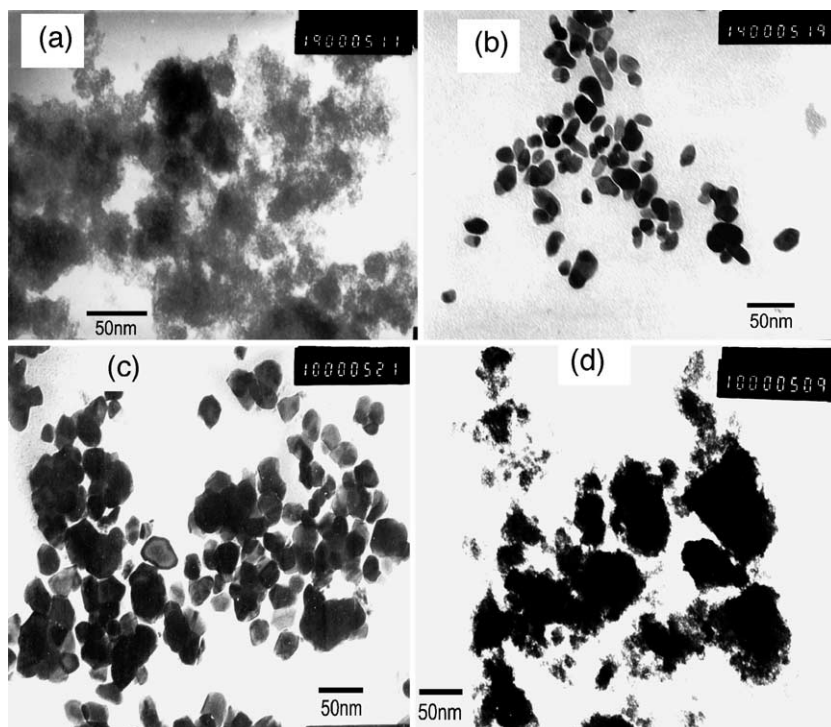


Fig. 2. The TEM photographs of ZnO–SnO₂ calcined at different temperatures. (a) 300, (b) 500, (c) 700, (d) 900 °C.

imental conditions with catalyst but without light irradiation. At the same time, the equilibrium adsorption capacity of these photocatalysts showed the order of sequence: SnO₂>ZnO–SnO₂>ZnO>P25 TiO₂.

3.2.2. Degradation kinetics of MO

The photocatalytic activity of these coupled oxide samples calcined at different temperatures was tested for the degradation of MO aqueous solution. In a typical photocatalytic experiment, 100 ml of 20 mg l⁻¹ MO aqueous solution was mixed with 0.25 g sample powers in a 100 ml Pyrex glass bottle, and the suspension was dispersed ultrasonically for 15 min and then magnetically stirred in a dark condition for 30 min to disperse fully and establish an adsorption/desorption equilibrium. The

mixed solution then was irradiated under UV light, and the high pressure Hg lamp was parallel to the Pyrex glass bottle with 15 cm distance and the reaction temperature was kept at ca. 30 °C by using a fan. The experimental result of the coupled oxide sample calcined at 600 °C for 2 h was shown in Fig. 4. For the purposes of comparison, the photocatalytic degradation of MO was also carried out using P25 TiO₂, and the pure SnO₂ and ZnO prepared by the same homogeneous precipitation method. The experimental results are also shown in Fig. 4. The Fig. 4 showed that the coupled oxide ZnO–SnO₂ had high photocatalytic activity and its photocatalytic efficiency was higher than the pure ZnO or SnO₂ alone, and slightly higher than P25 TiO₂. In addition, the Fig. 4 also showed that the photocatalytic

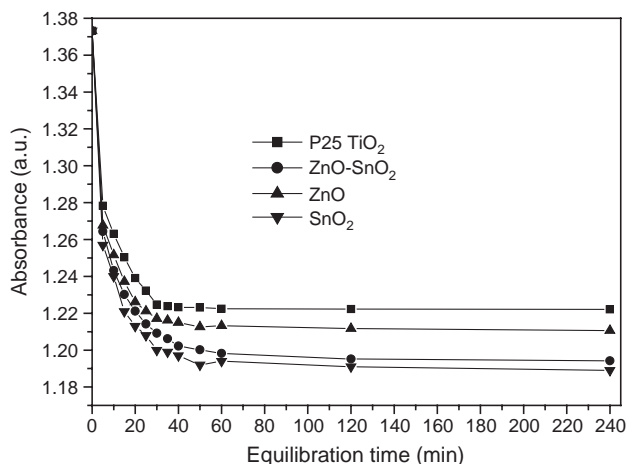


Fig. 3. The adsorption behavior of MO on various photocatalysts.

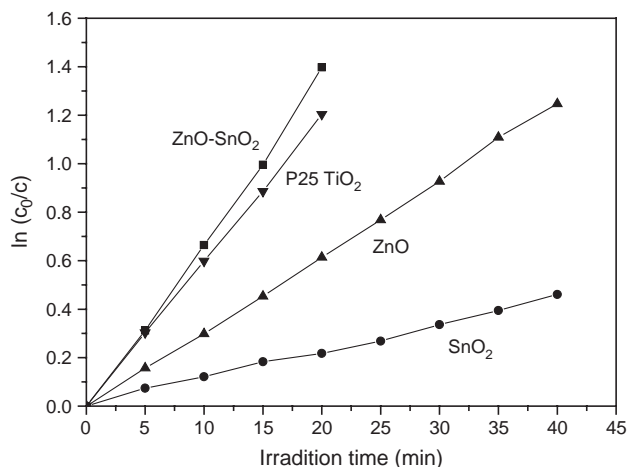


Fig. 4. The photocatalytic activity of commercial TiO₂ and different oxide samples calcined at 600 °C for 2 h.

reaction of MO was the first-order kinetics under the present reaction conditions.

4. Conclusions

The nanosized coupled oxide ZnO–SnO₂ was prepared by the homogeneous co-precipitation method in a short time. The coupled oxide prepared by the method had a better photocatalytic activity than that of either single oxides, ZnO or SnO₂, and its photocatalytic activity was slightly higher than commercial P25 TiO₂.

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