

## Photocatalytic Activity of Nanosized ZnWO<sub>4</sub> Prepared by the Sol-gel Method \*

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Nanosized ZnWO<sub>4</sub> photocatalysts were successfully synthesized *via* the sol-gel process in a temperature range of 450—800 °C. The grain size, crystal size, and crystallinity of ZnWO<sub>4</sub> particles increased with the increase of calcination temperature and prolonging calcination time. The photocatalytic activity was measured for the degradation of an aqueous Rhodamine-B (RhB) solution and gaseous formaldehyde (FAD). With the increase of calcination temperature and time, the activities increased to a maximum and then decreased. ZnWO<sub>4</sub> photocatalyst prepared at 550 °C for 10 h showed the highest activity, which is similar to the photocatalytic activity of P25TiO<sub>2</sub> for the degradation of gaseous FAD. High crystallinity, large surface area, and good dispersion are responsible for the high photocatalytic performance of the prepared ZnWO<sub>4</sub>.

**Keywords** Nanosized; Sol-gel method; Photocatalyst; ZnWO<sub>4</sub>

### Introduction

Ever since photocatalytic degradation of harmful pollutants by TiO<sub>2</sub> was reported<sup>[1]</sup>, semiconductor-based photocatalysts have attracted an extensive interest because of their applications in the purification of wastewater and the decomposition of volatile organic compounds<sup>[2,3]</sup>. It is an attractive way because it is environmentally friendly and low in cost<sup>[4]</sup>. Many tungstates are also employed as photocatalysts, for example, WO<sub>3</sub>, Na<sub>2</sub>W<sub>4</sub>O<sub>13</sub>, Bi<sub>2</sub>W<sub>2</sub>O<sub>9</sub>, PbWO<sub>4</sub><sup>[5]</sup>, Bi<sub>2</sub>WO<sub>6</sub>, Ag<sub>2</sub>WO<sub>4</sub>, and AgBiW<sub>2</sub>O<sub>8</sub><sup>[6]</sup>. For these W-oxide materials, 5*d* orbitals of W and 2*p* orbitals of O serve as conduction and valence bands, respectively. ZnWO<sub>4</sub> has been widely used because of its properties of nonhygroscopy, nontoxicity, low cost<sup>[7]</sup>, high chemical stability, average refractive index, and X-ray absorption coefficient<sup>[8]</sup>. Recently, its photocatalytic activity has been studied by our group<sup>[9–12]</sup>. ZnWO<sub>4</sub> has been prepared using several processes, for example, hydrothermal reaction<sup>[9,10]</sup>, solid state reaction<sup>[13]</sup>, heating of ZnO thin film with WO<sub>3</sub> vapor<sup>[14]</sup>, and so on. However, they have many disadvantages. For example, WO<sub>3</sub> has a tendency to vaporize at a high temperature, it is difficult to control grain size, and a high reaction temperature or pressure is always needed. In addition, ZnWO<sub>4</sub> film cannot be obtained. Compared with these methods, the sol-gel method is a kind of potential film preparation process, which possesses the advantages of chemical homogeneity, easy compo-

nents adjustment, low calcination temperature, and low cost.

In this study, ZnWO<sub>4</sub> was synthesized using the sol-gel method at a relatively low temperature. The prepared ZnWO<sub>4</sub> shows a high photocatalytic activity under UV-light for decomposing an RhB solution and FAD gas. Its morphology, crystallinity, and surface area were characterized.

### Experimental

#### 1 Synthesis of ZnWO<sub>4</sub>

5(NH<sub>4</sub>)<sub>2</sub> · 12WO<sub>3</sub> · 5H<sub>2</sub>O powder was dissolved in distilled water, to which stoichiometric amounts of Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O powders were then added. A white precipitation was soon observed. Citric acid [*n*(metal ions):*n*(citric acid) = 1:1.1] was added to the solution as a chelating agent. The pH value of the solution was controlled at 2—3. Then it was dried at about 80 °C until it became a yellow glassy material. The precursors were calcined at different temperatures for different times.

#### 2 Characterization

The crystal structure was analyzed on a D8-Advance X-ray Diffractometer (XRD, Bruker AXS, Germany). The morphology was observed by means of JEM-1010 EX Transmission Electron Microscope (TEM, Jeol Ltd., Japan). The Brunauer-Emmett-Teller (BET) surface areas (SA) of the samples were determined by a nitrogen absorption-desorption isotherm measurement at -196 °C on a ASAP 2010 Nitrogen

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Absorption Apparatus (Micromeritics Instrument Corp., America).

### 3 Photocatalytic Activity Evaluation

The method was reported in a former work by the same authors<sup>[10]</sup>. The aqueous photocatalytic reaction was performed with 100 mg of  $\text{ZnWO}_4$  powder suspended in 200 mL of an aqueous RhB solution under a UV-light lamp of 11 W ( $\lambda = 254 \text{ nm}$ ). The solutions were analyzed on a Hitachi U-3010 UV-Vis spectrophotometer (Hitachi Ltd., Japan) after centrifugation and filtration.

The gaseous photoreactor was a 400 mL cylindrical quartz vessel, which consisted of an inlet, an outlet, and a sample port. The prepared  $\text{ZnWO}_4$  powder of 0.05 g was dispersed uniformly on the slide. Slides with/without catalyst were tested in the vessel perpendicularly under light irradiation. Initially, FAD vapor was allowed to reach an absorption equilibrium with catalysts in the reactor in the dark. Then the reactor was sealed and photocatalytic reaction was started by turning on the UV-lamp. The concentration of FAD was measured on a SP-502 Gas Chromatograph (GC) equipped with a flame ionization detector and a 2-m stainless steel column (GDX-403) at 100 °C.

## Results and Discussion

### 1 Structure of Photocatalyst

There are three exothermic peaks in the DTA of the sample<sup>[12]</sup>. The smaller peak at 157.1 °C is attributed to the desorption of water and decomposition of unbonded citric acid, corresponding to the first weight loss region in TGA. The burning of the organic compounds and the disconnection of the bond between metals correspond to the broad obtuse peak between 157.1 and 485.8 °C. The intense peak at 485.8 °C is because of the formation of the nucleus of  $\text{ZnWO}_4$  crystal. All the organic components are eliminated at 504.2 °C because no further weight loss appears in TGA above the temperature.

Fig. 1 (A) presents the XRD patterns of the decomposition species from the precursor calcined at different temperatures for 10 h.  $\text{ZnWO}_4$  crystal began to form at 450 °C. The crystallinity was improved with in-

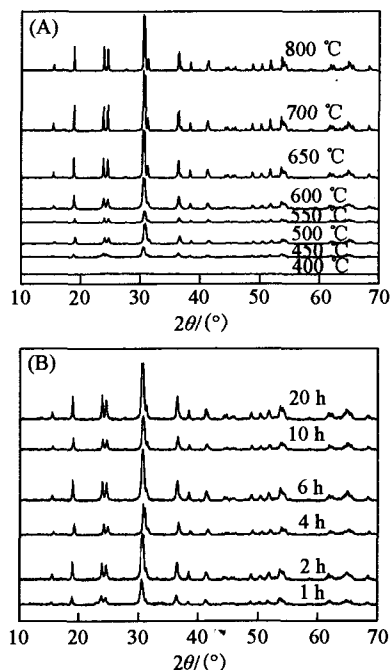


Fig. 1 XRD patterns of  $\text{ZnWO}_4$  powders

(A) Prepared at different temperatures for 10 h;  
(B) prepared at 550 °C for different time.

creasing calcination temperature. Fig. 1 (B) shows the effect of the calcination time on the formation of  $\text{ZnWO}_4$  crystal phase. The samples were calcined at 550 °C for different hours. The number of the peaks of the sample calcined for different time remained constant, suggesting no phase transformation. This condition is more moderate than that required in solid state methods. The XRD pattern could be indexed to the pure phase of monoclinic wolframite (space group:  $P2_1/c$ ;  $a = 0.4689 \text{ nm}$ ,  $b = 0.5724 \text{ nm}$ ,  $c = 0.4932 \text{ nm}$ ) and is in good agreement with the standard data (JCPD No. 15-0774). The differences among the peaks in Fig. 1 (B) are negligible in comparison with those in the Fig. 1 (A), suggesting that the influence of the calcination temperature is more significant than that of the calcination time on the formation of  $\text{ZnWO}_4$  crystal phase. The crystal size was calculated from the peak at  $23.836^\circ$  (011) in XRD patterns according to the Scherrer equation (see Table 1). It varied from 29.17 to 45.04 nm with the increase in calcination temperature.

Table 1 Influence of calcination temperature (calcined for 10 h) on crystal size and grain size

Temperature/°C	450	500	550	600	650	700	800
Crystal size/nm	20.53	26.32	29.17	31.84	35.19	41.21	48.54
Grain size/nm	10—30	20—50	30—40	40—50	100—300	300—500	500—1000

The influences of the calcination temperature and time on the grain sizes and morphologies of  $\text{ZnWO}_4$  were investigated by TEM (Fig. 2). It can be seen that the morphological structure of  $\text{ZnWO}_4$  synthesized by

the sol-gel method is not very homogenous. Some large slices were present in the samples. Fig. 2 (A) and Table 1 show that the grain size of  $\text{ZnWO}_4$  is increased when the temperature becomes higher. It is obvious

that the increase becomes more significant at higher calcination temperatures. Considering the related growth of crystal size, it can be concluded that at a higher temperature the particles tend to interconnect and aggregate to bigger particles, which is difficult to disperse in solution. The grain size of ZnWO<sub>4</sub> is also influenced by calcination time [ Fig. 2 (B), Table 2 ]. It mildly rises with the prolonging of time, suggesting that calcination time plays a less important role in the

growth of grain size than calcination temperature. This is a speciality of the sol-gel method. From the DTA Figure<sup>[12]</sup>, it can be seen that there is some organic group left at 400 °C and no peak in the XRD Figure at this temperature; but all the organic components are eliminated above 504.2 °C and ZnWO<sub>4</sub> crystal peaks present at 450 °C. As a result, the formation of ZnWO<sub>4</sub> significantly depends on the thermal decomposition process of the precursor.

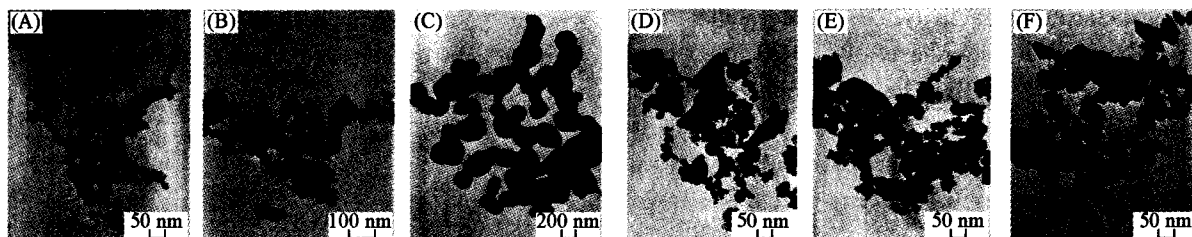


Fig. 2 TEM micrographs of ZnWO<sub>4</sub> powders prepared under different conditions

(A) 450 °C, 10 h; (B) 600 °C, 10 h; (C) 700 °C, 10 h; (D) 550 °C, 2 h; (E) 550 °C, 8 h; (F) 550 °C, 20 h.

Table 2 Influence of calcinations time (calcined at 550 °C) on crystal size and grain size

Heat-treat time/h	1	2	4	6	10	20
Crystal size/nm	24.59	29.39	26.87	28.95	29.17	30.07
Grain size/nm	20—30	30—40	40—50	30—40	30—40	30—50

## 2 Photocatalytic Activity of ZnWO<sub>4</sub>

Fig. 3 compares the degradation rates of RhB over ZnWO<sub>4</sub> catalysts prepared at different temperatures. It was found that RhB concentration decreased by less than 10% after UV-light irradiation for 4 h in the absence of the catalyst. However, the concentration reduced by 90% in 3 h over the ZnWO<sub>4</sub> prepared at 550 °C for 10 h. Fig. 3 shows that the degradation rate is strongly dependent on calcination temperature. The rate increased with temperature at first, reached optimum at 550 °C, and then decreased. The worst activity was achieved at the highest temperature of 800 °C. Ye et al.<sup>[15]</sup> has pointed out that photocatalyst has a saturated surface area (SA) (around 7 m<sup>2</sup>/g) above

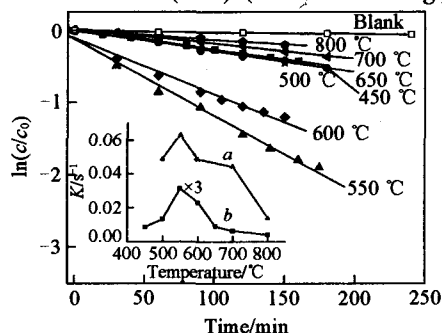


Fig. 3 Photocatalytic degradation of RhB over ZnWO<sub>4</sub> powder prepared at different temperatures for 10 h

Insets: the activity (K) as a function of calcination temperature. a. Gaseous phase; b. liquid phase.

which the crystallinity will be the dominant factor other than the number of activity sites. This is probably because when the surface area is large enough, the migration distance decreases significantly, making it easy for the charge carrier to reach the surface. As a result, the recombination of the electron and the hole during the migration caused by defect in a crystal would determine the photocatalytic activity. The saturated SA value may alter in different experiments, as the exact experiment conditions, for example, solution, organic pollutant, and temperature, are different in each experiment. The SA of as-prepared ZnWO<sub>4</sub> is reduced in the order of 11.86 m<sup>2</sup>/g (500 °C) > 9.33 m<sup>2</sup>/g (550 °C) > 4.92 m<sup>2</sup>/g (600 °C), the photocatalytic activity variation below 550 °C could be explained by the crystallinity according to the results of XRD [ Fig. 1 (A) ]: with enhancing the calcination temperature, the crystallinity of ZnWO<sub>4</sub> increases, so does the photocatalytic activity. The crystallinities of ZnWO<sub>4</sub> powders synthesized at 450 and 500 °C are not sufficient as shown in XRD results, where the activities are poor. Fig. 2 (A) and Table 1 suggest that the grain size grows quickly as the temperature increases. A larger grain size gives a smaller surface area in geometry, which is supported by the previous BET SA results. Larger grain also makes the particle harder to be dispersed than the smaller ones. The long migration distance caused by the large grain size may enhance the chance of recom-

binant and the small SA and poor dispersion may build fewer reaction sites. The reasons can suppress the influence of crystallinity. When the temperature is increased to 600 °C, the SA must reach its saturated value (a value between 9.33 and 4.92 m<sup>2</sup>/g) and begins to govern photocatalytic activity. So the photocatalytic activities decreased with the increasing of temperature above 550 °C.

Fig. 4 shows the relationship between calcination time and photocatalytic activity. The photocatalytic activity is decreased in the order of 10 h > 20 h > 6 h > 4 h > 2 h > 1 h at 550 °C. The crystallinity increases with prolonged calcination time as seen in Fig. 1. It must be the reason why this sample shows high activity primarily. The TEM results illustrate that the average grain size of the powder prepared at 550 °C for 20 h is larger than that prepared for 10 h, causing the decrease of the activity sites and photocatalytic activity.

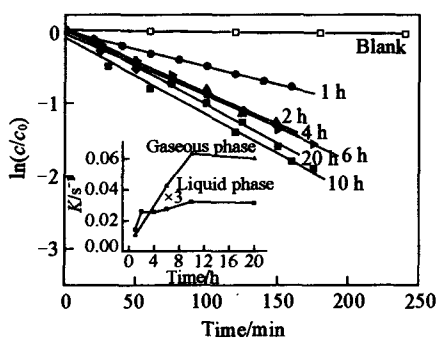


Fig. 4 Photocatalytic degradation of RhB over ZnWO<sub>4</sub> powder prepared at 550 °C for different times

Insets: the activity ( $K$ ) as a function of calcination time.

The photocatalytic activity of ZnWO<sub>4</sub> was also measured for degrading gaseous FAD under UV-light. It can be seen that the concentration of FAD in the reactor is decreased by nearly 100% within 1 h, which suggests the high activity in gaseous phase (Fig. 5). The insets in Figs. 3 and 4 show the rates of degradation of the aqueous RhB solution and gaseous FAD over ZnWO<sub>4</sub> powders. The tendencies of the gaseous decomposing reaction for both temperature and time series accord with what has been acquired in liquid degradation reaction, therefore a high crystallinity and a small surface area must be important factors of the photocatalytic activity under both the conditions. Fig. 5 indicates that the ZnWO<sub>4</sub> powder prepared at 550 °C for 10 h displays the similar photocatalytic activity to that of P25TiO<sub>2</sub>, which is well known as a high activity photocatalyst. However, it is easy to find out that the activity of the same sample is not as high as that of P25TiO<sub>2</sub> in the degradation of aqueous RhB. This is probably

because the aggregate ZnWO<sub>4</sub> particles cannot disperse well in solution, which hinder it from presenting its good activity. However, the particles have the same chance to receive adequate irradiation from the UV-light and enough contact with FAD as P25TiO<sub>2</sub> does in the degradation of gaseous FAD. Thus ZnWO<sub>4</sub> can present its high photocatalytic activity under this condition. It is worth noting that the as-prepared ZnWO<sub>4</sub> has an SA less than 20% SA of P25TiO<sub>2</sub> (63.68 m<sup>2</sup>/g). So the photocatalytic activity will be improved if the surface area is increased, and this work is still under investigation.

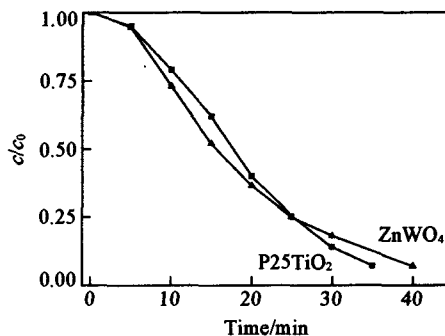


Fig. 5 Comparison of photocatalytic degradation of FAD over ZnWO<sub>4</sub> powder (550 °C, 10 h) and P25TiO<sub>2</sub>

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