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Research Article

Preparation, Characterization, and Photocatalytic Activity of TiO_2/ZnO Nanocomposites

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Nanoparticles of the TiO_2/ZnO composite photocatalysts were prepared via sol-gel process. The crystalline structure, morphology, thermal stability, and pore structure properties of the composite photocatalysts were characterized by XRD, FE-SEM, TG-DTA, and N_2 physical adsorption measurements. The photocatalytic activity of the composite catalysts was evaluated by photocatalytic degradation reaction of methyl orange (MO) in aqueous solution. The best preparation parameters for the composite photocatalysts were obtained through systematical experiments. Furthermore, the photocatalytic degradation reaction of aqueous MO solution followed the first-order reaction kinetics; the relative equation can be described as $\ln(C_0/C) = 0.5689t$, and the calculated correlation constant (R^2) is 0.9937 for the calibration curve.

1. Introduction

Photocatalytic technology has been increasingly demonstrating prominent superiority for the decomposition of organic compounds and pollutants coming from many industries. Among various semiconductor photocatalysts, TiO_2 has been proven to be the most important one due to series of merits such as good photocatalytic activity, good chemical and thermal stability for long term, nontoxicity, and low cost. Thus, it has been widely applied in environmental, optical, and electronic fields [1–7]. ZnO is another promising photocatalyst and suitable alternative to TiO_2 for the wider direct band gap as well as higher solar receive and utilization efficiency for organic pollutants photodegradation [8–15]. Recently, many studies for improving TiO_2 photocatalytic efficiency have become hot topics; one approach is to dope some kind of transition metals into TiO_2, forming doped photocatalyst, which would modify both physical and optical properties of TiO_2 [16], but the results are still unsatisfying. Another one is to couple other oxides in order to achieve higher photocatalytic efficiency, such as WO_3 [17], ZnO [18–20], SiO_2 [21, 22], SnO_2 [23], Fe_2O_3 [24], and MoO_3 [25], and these studies on this aspect are becoming more and more extensively.

In this paper, nanoparticles of TiO_2/ZnO composite catalysts were obtained via sol-gel process. The crystalline structure, morphology, thermal stability, and pore structure properties were characterized by means of XRD, FE-SEM, TG-DTA, and N_2 physical adsorption measurements. The photocatalytic activity of composite catalysts was investigated by photocatalytic degradation experiment of MO in aqueous solution.

2. Experimental

2.1. Materials. The starting materials, tetrabutyl titanate (TBOT), zinc acetate, ethanol absolute, and hydrochloric acid (36.5 wt.%) were purchased from Shanghai Chemical Reagent Company, and they were used to prepare TiO_2/ZnO composite catalysts. The above reagents were of analytic reagent grade, and they were used without further purification. Seven mL TBOT was mixed with 20 mL ethanol absolute and hydrochloric acid which varied from 0.10 mL, 0.15 mL,

0.20 mL, and 0.25 mL to 0.3 mL, respectively, forming solution A. Zinc acetate (for instance, 0.45 g, 0.68 g, 0.90 g, 1.13 g, 1.35 g, and 1.58 g) and 1.5 mL deionized water were mixed with 20 mL ethanol absolute to form solution B. The starting materials ratio was equal to ZnO/TiO_2 (molar ratio) varying from 0.10, 0.15, 0.20, 0.25, and 0.30 to 0.35, respectively. Then, solution B was slowly added into solution A under magnetic stirring for 0.5 h. The mixed sol was aged at room temperature until forming gel, and the mixed gel was dried and calcined. The calcination temperatures were 450°C, 480°C, 500°C, 550°C, and 600°C, respectively. Calcination time was changed among 1 h, 1.5 h, 2 h, 2.5 h, and 3 h when the calcination temperature has been determined. In this way, the nanoparticles of TiO_2/ZnO composite catalysts can be synthesized.

2.2. Characterization. The morphology of TiO_2/ZnO composite catalysts was studied by the field emission scanning electron microscopy (FE-SEM, S4800, Japan), and the pipe pressure was 15 kV. The crystalline structure and crystal phases of the as-prepared composite catalysts were determined by the X-ray powder diffractometer (XRD, Rigaku, Japan) of D/MAX-rB, which was radiated by Cu Kα with the pipe pressure of 40 mV, the wave length (λ) being 0.154056 nm, and the diffraction angle being in the range of 10°–80°. The N_2 adsorption/desorption isotherms, specific surface area, and pore size distribution plots were measured by automatic physical adsorption apparatus (NOVA4000e, Quantachrome, USA), and the thermogravimetric analysis and differential thermal analysis (TG-DTA) curves of the composite catalysts were carried out by CRY-2P and WRT-3P analyzers.

2.3. Photocatalytic Activity Test. 0.1 g powders of TiO_2/ZnO nanocomposite catalysts were put into 100 mL MO aqueous solution; its concentration was 10 mg/L. A 250 W high-pressure mercury lamp was used as the light source. The absorbance of MO aqueous solution was analyzed by the 722s visible spectrophotometer at the wavelength of 465 nm, corresponding to maximum absorption wavelength of MO. The photocatalytic degradation rate of MO aqueous solution can be calculated by the formula

$$D = \frac{(A_0 - A)}{A_0} \times 100\%. \quad (1)$$

In the formula, D represented the photocatalytic degradation rate of MO aqueous solution, A_0 was the absorbance of MO aqueous solution before the photocatalytic reaction, and A was the absorbance of MO aqueous solution after being catalyzed by the TiO_2/ZnO nanocomposite powders at a moment within 5 hours.

3. Results and Discussion

3.1. Physical Properties of TiO_2/ZnO Composite Catalysts

3.1.1. XRD Pattern Analysis of TiO_2/ZnO Composite Catalysts. Figure 1 shows XRD pattern of the prepared TiO_2/ZnO nanocomposite samples. From the XRD pattern and corresponding characteristic 2θ values of diffraction peaks, it can be confirmed that TiO_2 particles in the samples are identified as anatase phase according to the standard card of PDF#21-1272, for the sharp diffraction peaks located at 2θ = 25.3°, 38.0°, 48.1°, 54.1°, 55.1°, 62.8°, 68.9°, and 75.2°, which are corresponding to the (101), (004), (200), (105), (211), (204), (116), and (215) planes, respectively. Meantime, several slight diffraction peaks located at 2θ = 31.7°, 34.4°, 36.3°, and 70.0° are also observed, they are corresponding to the (100), (002), (101), and (201) planes of hexagonal zincite phase ZnO particles according to the standard card of PDF#36-1451. Therefore, it can be suggested that the as-prepared TiO_2/ZnO composites samples are the combination of anatase TiO_2 particles and zincite ZnO particles. In addition, most diffraction peaks in the XRD pattern are sharp and symmetrical Gauss peaks, which further indicate that the particles of TiO_2 and ZnO in the composites samples have high crystallinity. The results are also identified with other research papers [26, 27].

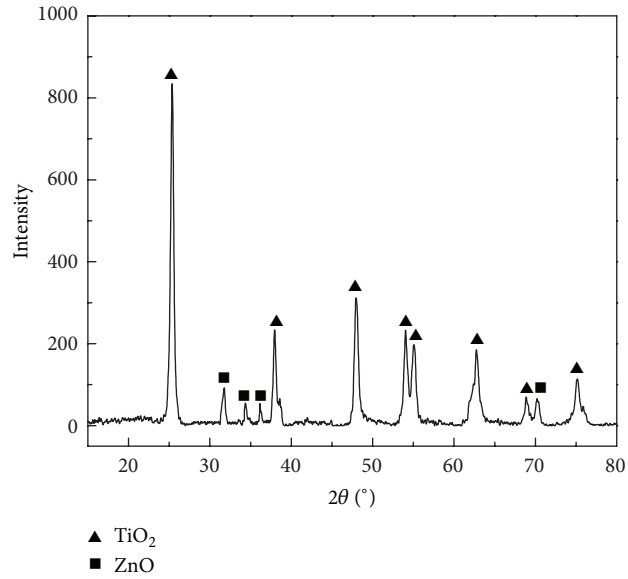

Figure 1: XRD pattern of the TiO_2/ZnO composite catalysts.

3.1.2. FE-SEM Analysis of TiO_2/ZnO Composite Catalysts. Figure 2 has shown FE-SEM image of TiO_2/ZnO composite catalysts. A lot of TiO_2 and ZnO nanoparticles with a granular morphology can be seen clearly from Figure 2. According to the measurement, the particles size of the as-prepared TiO_2/ZnO samples is almost not more than 100 nm. It is also observed that TiO_2 particles are main components in the TiO_2/ZnO composites samples, and ZnO particles were widely dispersed on the surfaces of the obtained TiO_2 bulks, which would be beneficial to improve the catalytic activity of the TiO_2/ZnO composite photocatalysts in essence. Furthermore, some amounts of TiO_2 and ZnO crystalline grains in the samples are aggregated to some extent for their nanoscale particles.

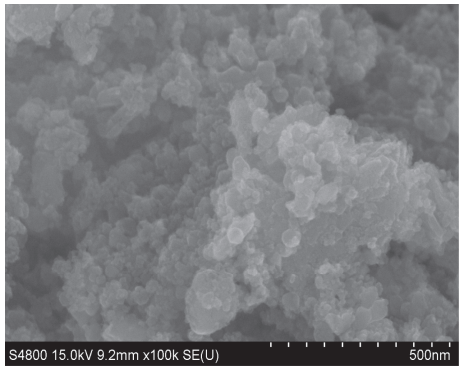

Figure 2: FE-SEM image of the TiO_2/ZnO composite catalysts.

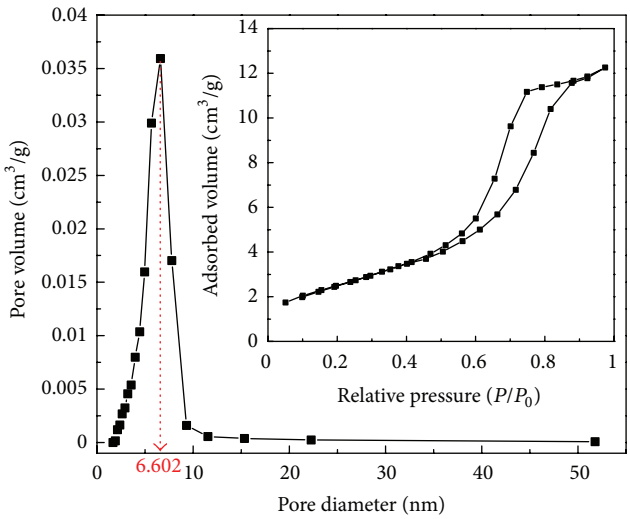

Figure 3: N_2 adsorption/desorption isotherms, pore diameter, and pore distribution plots of the TiO_2/ZnO composite catalysts.

3.1.3. N_2 Physical Adsorption Analysis of TiO_2/ZnO Composite Catalysts. Figure 3 gives the N_2 adsorption/desorption isotherms, pore diameter, and pore size distribution plots of the TiO_2/ZnO composite catalysts. The adsorption/desorption isotherms are corresponding to the typical type-IV isotherms (IUPAC, 1985) which indicate the mesoporous nature of TiO_2/ZnO composite particles. In addition, the desorption hysteresis loop appears when the relative pressure (P/P_0) is in the range of 0.42 to 0.83. The hysteresis type of the isotherms can be classified as H1 which is related to the capillary condensation associated with the mesoporous channels of TiO_2/ZnO composites, and this type of hysteresis loop is normally attributed to the cylindrical pore geometry, and high degree of pore uniformity and connectivity in the composite catalysts [28].

As shown in Figure 3, it also can be seen that the pore diameter is 6.602 nm, the biggest pore volume is 0.0361 cm^3/g, and the average pore volume is 0.0119 cm^3/g. In addition, the average specific surface area is 76.258 m^2/g according to BET calculated results, which are bound up with the morphology and the size of lots of the nanoparticles

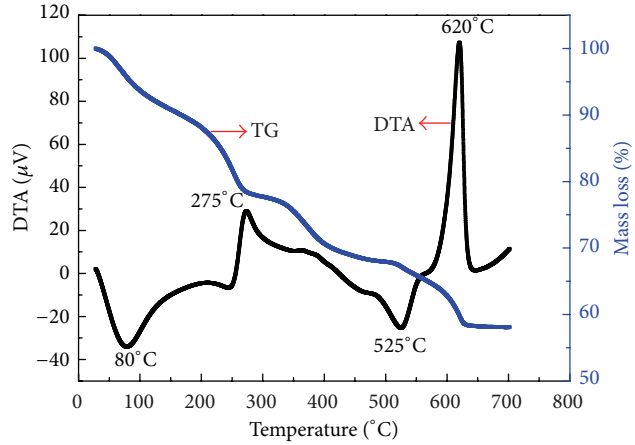

Figure 4: TG-DTA curves of the TiO_2/ZnO composite catalysts.

in the TiO_2/ZnO composite catalysts [29]. These results show that there are rich and uniform pores as well as big specific surface areas in the obtained TiO_2/ZnO composite catalysts.

3.1.4. TG-DTA Curves Analysis of TiO_2/ZnO Composite Catalysts. In order to verify the thermal stability of the TiO_2/ZnO composite catalysts, the TG-DTA analysis was conducted using the dried composites gel. As shown in Figure 4, there is an endothermic peak at 80°C in the DTA curve, and the corresponding mass loss is about 20% in the TG curve, which has inferred that an amount of the absorbed water in the composites samples has been evaporated. When the temperature is increased to 275°C, an obvious exothermic peak can be observed in the DTA curve, and there is a corresponding mass loss in the TG curve, which can be assigned to the dehydroxylation of precursor powders and the formation of some brookite phase TiO_2 particles. There is another endothermic peak appearing at 525°C in the DTA curve, which is attributed to the dehydration of bound water. Then, there is a sharp and strong exothermic peak at 620°C in the DTA curve, which can be attributed to the polymorphic transformation of TiO_2, which is from anatase phase to rutile phase, and this is a steady and slow process. After 650°C, there is no peak in the DTA curve, and the mass of composites samples shows a little change in the TG curve. The total mass loss of the samples is about 40%. The results have shown that the obtained TiO_2/ZnO composite catalysts have good thermal stability.

3.2. Photocatalytic Performance Testing of TiO_2/ZnO Composite Catalysts

3.2.1. Evaluation of Preparation Parameters of TiO_2/ZnO Composite Catalysts. As shown in Figure 5, among the six kinds of the starting materials ratio, when ZnO/TiO_2 (molar ratio) is 0.25, the decolorization rate of MO aqueous solution is the highest; the maximum value is up to 72.34%. The effect of hydrochloric acid dosage on the photocatalytic activity of TiO_2/ZnO composite samples has been shown in Figure 6, when hydrochloric acid dosage is 0.15 mL, the decolorization

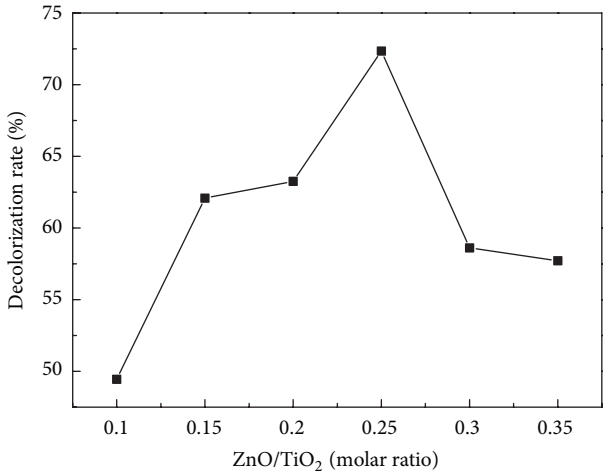

Figure 5: The effect of ZnO/TiO_2 (molar ratio) on the photocatalytic activity of the TiO_2/ZnO composite catalysts.

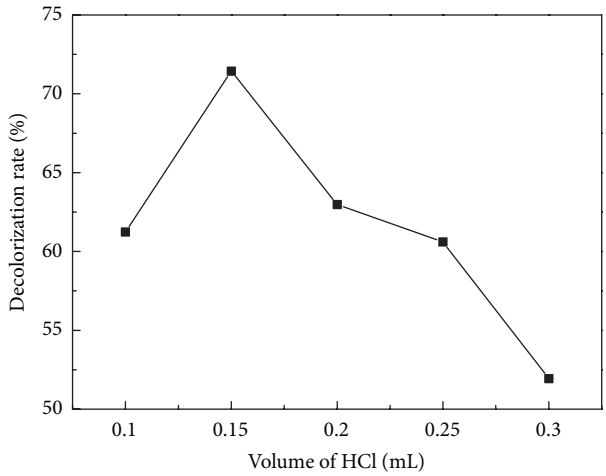

Figure 6: The effect of hydrochloric acid dosage on the photocatalytic activity of the TiO_2/ZnO composite catalysts.

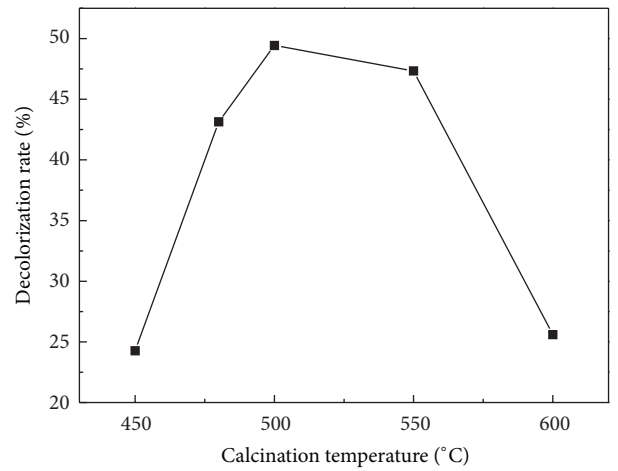

Figure 7: The effect of calcination temperature on the photocatalytic activity of the TiO_2/ZnO composite catalysts.

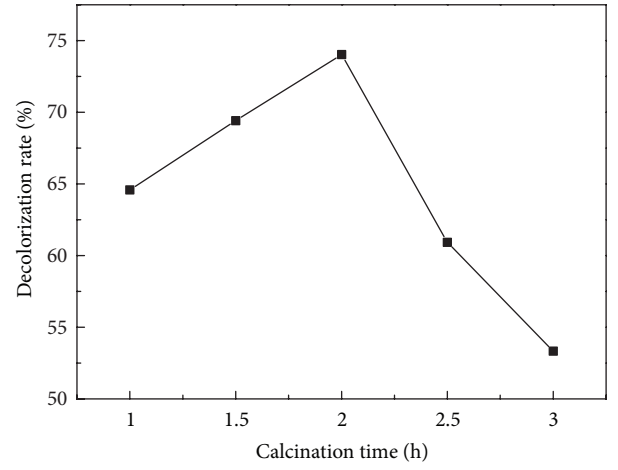

Figure 8: The effect of calcination time on the photocatalytic activity of the TiO_2/ZnO composite catalysts.

rate of MO aqueous solution can be up to the maximum value 71.43%. Through investigating the calcination temperature of TiO_2/ZnO composite catalysts as shown in Figure 7, the most proper calcination temperature is 500°C. Furthermore, the calcination time has been inspected. It can be seen from Figure 8 that when the calcination time is 2 h, the best photocatalytic activity of TiO_2/ZnO composite catalysts has been obtained; at that time, the decolorization rate of MO aqueous solution has reached the highest value 74.03%. From the above, proper preparation conditions of TiO_2/ZnO composite catalysts are as follows: ZnO/TiO_2 (molar ratio), 0.25; hydrochloric acid dosage, 0.15 mL; calcination temperature, 500°C; and calcination time, 2 h.

3.2.2. Photocatalytic Activity of TiO_2/ZnO Composite Catalysts. The photocatalytic activity of TiO_2/ZnO nanocomposites prepared under the best conditions has been shown in Figure 9. When MO aqueous solution alone has been irradiated by high-pressure mercury lamp, its decolorization rate is only 2.22% (Figure 9, MO alone under the light). In the dark condition, TiO_2/ZnO composites have reached the saturation adsorption amount after 0.5 h, the decolorization rate of MO aqueous solution is 4.9% (Figure 9, Adsorption in the dark). Adding TiO_2/ZnO composite catalysts under the same light source, along with the reaction time extending, the photocatalytic decolorization rate of MO aqueous solution increased gradually. When the reaction time is 5 h, the decolorization rate of the MO aqueous solution is up to 93.30% (Figure 9, Photocatalytic reaction), and the increasing tendency of MO decolorization rate turns slowly after 4 h. It can be inferred that the MO aqueous solution would be nearly degraded completely when catalyzed by TiO_2/ZnO composite catalysts in proper time.

3.2.3. Reaction Kinetics of MO Aqueous Solution Catalyzed by TiO_2/ZnO Composite Catalysts. As shown in Figure 10, photocatalytic reaction kinetics of MO aqueous solution has

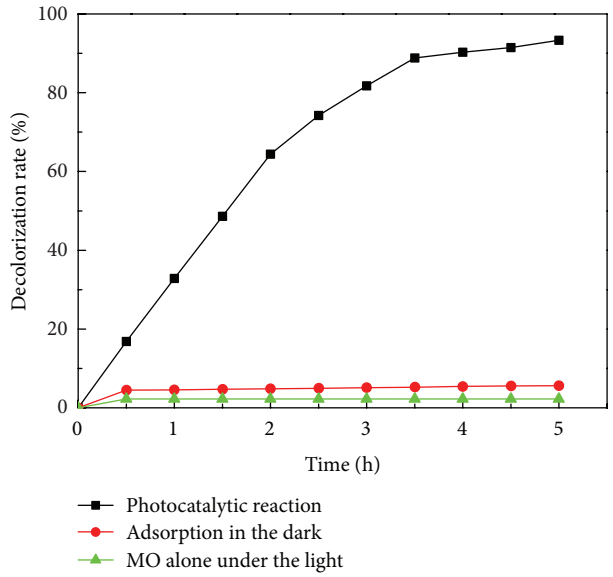

FIGURE 9: The effect of reaction time on MO aqueous solution degradation catalyzed by the TiO_2/ZnO composite catalysts.

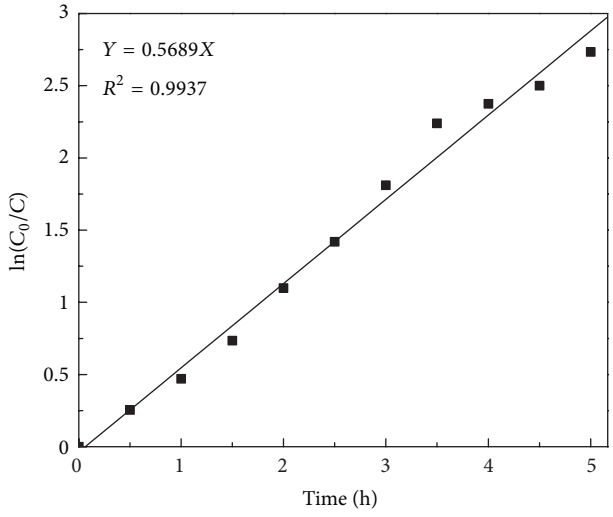

FIGURE 10: The reaction kinetics of MO aqueous solution catalyzed by the TiO_2/ZnO composite catalysts.

been studied, and the good linearity between the MO aqueous solution concentration and the reaction time can be observed. According to calculated results, the reaction kinetics equation can be described as $\ln(C_0/C) = kt$, the reaction rate constant (k) is equal to 0.5689, and the calculated correlation constant (R^2) is 0.9937 for the calibration curve. The above results indicate that the photocatalytic reaction of MO aqueous solution follows the first-order reaction kinetics, which is consistent with the research results of Gao et al. [30].

4. Conclusions

In this study, TiO_2/ZnO composite catalysts were successfully prepared via sol-gel process. According to the above characterization and experiment results, TiO_2/ZnO composite catalysts have a granular morphology, and the particles size is almost not more than 100 nm. The composite catalysts with high crystallinity are the combination of anatase TiO_2 and zincite ZnO particles. The adsorption/desorption isotherms are the typical type-IV isotherm with H1 desorption hysteresis loop in desorption branch curve, which indicates the mesoporous nature of TiO_2/ZnO composite catalysts. The pore diameter is 6.602 nm, the biggest pore volume is 0.0361 cm^3/g, the average pore volume is 0.0119 cm^3/g, and the average specific surface area is 76.258 m^2/g. In addition, the as-prepared TiO_2/ZnO composite catalysts have good thermal stability. Meantime, the better preparation conditions for the TiO_2/ZnO composite catalysts have been obtained, which are as follows: ZnO/TiO_2 (molar ratio), 0.25; hydrochloric acid dosage, 0.15 mL; calcination temperature, 500°C and; calcination time, 2 h. The decolorization rate of the MO aqueous solution is up to 93.30% after 5 h, and the experimental result is better than the research ones of Tian et al. [31] and Zhang and Song [32]. The reaction kinetics equation can be described as $\ln(C_0/C) = 0.5689t$, which follows the first-order reaction kinetics. From the above results, it is reasonable to believe that TiO_2/ZnO composite catalysts will be applied more and more in environmental protection field and other catalytic fields.

Acknowledgments

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