Research Article

Zhigang Yi*, Tao Jiang, Ying Cheng, and Qiong Tang*

Effect of SiO$_2$ aerogels loading on photocatalytic degradation of nitrobenzene using composites with tetrapod-like ZnO

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Abstract: To study the effect of improved adsorption property of tetrapod-like ZnO (T-ZnO) on its photocatalytic performance, a new composite was prepared by loading silica aerogels (SiO$_2$(AG)) on the surface of T-ZnO via the sol–gel method. Various characterization methods showed that SiO$_2$(AG) was uniformly loaded on the surface of T-ZnO, and the morphology as well as structural characteristics of SiO$_2$(AG) and T-ZnO were not changed. Nitrobenzene (NB) was selected as the model pollutant, and the adsorption and photocatalytic properties of T-ZnO and SiO$_2$(AG)/T-ZnO for NB were studied. The photocatalytic degradation processes of NB using T-ZnO and SiO$_2$(AG)/T-ZnO followed the first-order reaction. Considering the initial moment reaction kinetic, the photocatalytic kinetics of SiO$_2$(AG)/T-ZnO and T-ZnO was consistent with the Langmuir–Hinshelwood kinetic model, and reaction rate constant $K_{\text{SiO}_2(AG)/T-\text{ZnO}}$ > $K_{\text{T-ZnO}}$, adsorption rate constant $K_{\text{ad SiO}_2(AG)/T-\text{ZnO}}$ > $K_{\text{ad T-ZnO}}$, which demonstrated that SiO$_2$(AG) loading could increase T-ZnO adsorption to NB, then promoted its photocatalytic performance.

Keywords: silica aerogels, tetrapod-like zinc oxide, adsorption property, photocatalytic performance, nitrobenzene

1 Introduction

In recent years, large varieties of nanomaterials have become research hotspots in the fields of medicine [1–4], architecture [5–7], energy storage [8,9], and environmental protection [10–14] due to their many special properties such as good chemical stability, microwave absorption, high surface activity, and strong oxidation. Nanomaterials have been investigated in-depth for environmental pollutant treatment [15–19] because of the environmental problems caused by the discharge of persistent organic pollutants with rapid development of industry [20–23].

In the past few decades, more and more attention has been paid to nanomaterial photocatalytic technology, which uses natural/UV light as energy and semiconductor nanomaterials as photocatalysts to degrade organic contaminants via the photocatalytic process on the surface of nanomaterials [24–26]. Among the semiconductors employed, although TiO$_2$ is generally regarded as the best photocatalyst, ZnO has frequently exhibited similar or higher photocatalytic activity compared to TiO$_2$ [27–32]. In addition, ZnO has the advantages of low cost and easy preparation [33]. All of these make ZnO an ideal substitute for TiO$_2$. Previous studies of our research group have found that the microsized tetrapod-like zinc oxide (T-ZnO) had better photocatalytic activity and dispersion than nanosized ZnO with other different morphologies, and was easier to separate from water for reusage [20]. Among different factors affecting the efficiency of photocatalytic degradation of organic matter, the adsorption behaviors of the contaminants onto the surface of photocatalyst were typically considered to play significant roles [34–36]. Plenty of studies have shown that adsorption behaviors were necessary for successful photocatalytic decomposition of organic compounds [37,38]. Thus, improving adsorption property of T-ZnO on the basis of keeping its morphology has been a major consideration to further improve the photocatalytic performance of T-ZnO.
In recent years, porous materials such as activated carbon, zeolites, and SiO$_2$ were actively investigated as advanced sorbents [39]. Many of these porous materials have been used as support materials; loading of TiO$_2$, ZnO, and other semiconductors in the porous materials has improved their adsorption and photocatalytic activity [40–42]. One of the promising porous materials, SiO$_2$ aerogels (SiO$_2$(AG)), is a three-dimensional and multiscaled porous nanomaterial formed by numerous fine particles and networks. The SiO$_2$(AG) materials possess excellent adsorption efficiency owing to high porosity, high specific surface area (SSA), low density, etc. [39,43,44].

To study the effect of improved adsorption property of T-ZnO on its photocatalytic performance, we prepared SiO$_2$(AG)/T-ZnO composites via the sol–gel method, and nitrobenzene (NB) was selected as the model pollutant. The absorption and photocatalytic properties of T-ZnO and SiO$_2$(AG)/T-ZnO for NB were comparatively studied. The Langmuir–Hinshelwood kinetic model was used to calculate the photodegradation kinetic parameter.

2 Experimental

2.1 Reagents and materials

T-ZnO, received from Key Laboratory of Advanced technologies of Materials (Ministry of Education), Southwest Jiaotong University, was prepared by the gas-expanding method using metallic zinc as the raw material [45]. Tetraethyl orthosilicate, anhydrous ethanol (EtOH), trimethylchlorosilane, hexane, HCl, NH$_3$·H$_2$O, and NB were commercially purchased. All reagents were of analytical-grade quality and used without further purification. Deionized water was used in all experiments.

2.2 Preparation of SiO$_2$(AG)/T-ZnO

The SiO$_2$(AG) was synthesized by the solvent-exchanging procedure under ambient pressure as described in our earlier report [20]. The SiO$_2$(AG) powders were dispersed with hexane under ultrasonic assistance to form a fluid sol dispersion [46]. The designated amounts of T-ZnO were mixed into the sol, and after stirring at 60°C for 2 h, the SiO$_2$ gel was deposited onto the surface of T-ZnO. SiO$_2$(AG)/T-ZnO composites were obtained after washing with EtOH and drying at 60°C for 24 h.

2.3 Material characterization

The FESEM (Inspect F; FEI, Holland, the Netherlands) and FETEM (JEM-2100F; JEOL, Japan) were used to investigate the microtopography of fabricated materials. The crystal structure of the materials was analyzed by X-ray diffraction (XRD DX-2500) with Cu Ka-ray generator (40 kV, 40 mA, $\lambda = 0.15406$ nm). The pore structure and the SSA of the prepared materials were determined by the automatic porosity and surface area analyzer (3H-2000PS4; Beishide Instrument Technology Co., Ltd, Beijing, China), respectively, and the detecting conditions of analyzer were as follows: nitrogen as adsorbate, degassing mode of heating vacuum, degassing temperature of 150°C, degassing time of 180 min, saturated steam pressure of 1.0434 bar, and ambient temperature of 14.0°C. UV-VIS diffuse reflectance spectra (UV-VIS DRS) were measured using a TU-1901 spectrophotometer (Purkinje General).

2.4 Research of adsorption performance

Isothermal adsorption experiments were conducted in NB solution with different concentrations (12, 24, 36, 48, and 60 mg/L). The dosage of adsorbent (T-ZnO and SiO$_2$(AG)/T-ZnO) was 2.0 g/L. NB solution of different concentrations (100 mL) was placed in a 250 mL conical flask and shaken at 220 rpm for 24 h under 25°C. The adsorption amount of NB on adsorbent was reflected by measuring the change of concentration of NB in solution via the UV-VIS spectrophotometer (UV-2550; Shimadzu, Japan), which was calculated by:

$$q = \frac{(C_0 - C_e) \times V}{w},$$

where $q$ is the adsorption amount of NB on adsorbent, mg/g; $C_0$ is the initial concentration of NB in solution, mg/L; $C_e$ is the equilibrium adsorption concentration of NB in solution after adsorption equilibrium, mg/L; $V$ is the volume of solution, L; and $w$ is the dosage of adsorbent, g.

2.5 Photocatalytic performance

NB solution with different concentrations (12, 24, 36, 48, and 60 mg/L) was used as simulated wastewater. The dosage of photocatalyst (T-ZnO and SiO$_2$(AG)/T-ZnO) was 2 g/L, respectively. The suspension was stirred for 30 min at room temperature under dark condition, then irradiated
under UV (EA-180, 8w; Spectronics Corporation, America). The sample was fetched at an interval of 30 min, then centrifuged (8,000 rpm, 5 min), and filtered (0.22μm filter membrane). UV-VIS spectrophotometer was used to analyze the concentration change of NB during the photocatalytic degradation process. Formula of photocatalytic removal ratio of NB is as follows:

$$\eta = \frac{C_0 - C}{C_0}, \quad (2)$$

where $\eta$ is the photocatalytic removal ratio of NB; $C_0$ is the initial concentration of NB (mg/L); and $C$ is the concentration of NB after photocatalytic reaction (mg/L).

### 2.6 Photodegradation kinetics

Langmuir–Hinshelwood kinetic models are often used to calculate photodegradation kinetic parameters, which are as follows [47]:

$$r = -\frac{dC}{dt} = \frac{K_{ad}k'C}{1 + K_{ad}C}, \quad (3)$$

$$\frac{1}{r} = \frac{1}{K_{ad}k'C} + \frac{1}{k'}, \quad (4)$$

where $r$ is the photodegradation reaction rate, $k'$ is the rate constant of NB photocatalytic degradation, mg/(L min$^{-1}$); $K_{ad}$ is the adsorption equilibrium constant of NB on catalyst surface, L/mg; $C$ is the concentration of NB in solution, mg/L; and $t$ is the reaction time, min.

The process of photocatalytic degradation begins with the catalyst surface adsorbing organic mass. $C_e$ is the initial moment ($t = 0$) concentration of the solution while in adsorption equilibrium. The reaction time is calculated by the following equation:

$$t = \frac{1}{K_{ad}k'} \ln \left( \frac{C_e}{C} \right) + \frac{1}{k'}(C_e - C). \quad (5)$$

Formulae (3) and (5) can be simplified to formulae (6) and (7), respectively, when the organic content is extremely low. Formula (6) is also used for inefficient adsorption of organic mass. In this case, the reactions are manifested as first-order reactions.

$$r = -\frac{dC}{dt} = K_{ad}k'C = kC, \quad (6)$$

$$\ln \left( \frac{C_e}{C} \right) = K_{ad}k't = kt, \quad (7)$$

where $k$ is the apparent rate constant, min$^{-1}$.

### 3 Results and discussion

#### 3.1 Microtopography of SiO$_2$(AG)/T-ZnO

The microtopography of SiO$_2$(AG) and SiO$_2$(AG)/T-ZnO is demonstrated in Figure 1. As displayed in Figure 1a and c, SiO$_2$(AG) powders were composed of numerous narrow-size-range nanoparticles and presented loose sponge-like porous shapes. The SEM image of SiO$_2$(AG)/T-ZnO nanocomposites (Figure 1b) shows typical structures with four needles extending from the same center, ascribable to the T-ZnO [18] and SiO$_2$(AG) particles uniformly loaded on the surface of these needles. Figure 1(d) shows that the morphology of SiO$_2$(AG) loaded on the surface of T-ZnO has no obvious change.

#### 3.2 Crystal structure of SiO$_2$(AG)/T-ZnO

As shown in Figure 2, a bread-like dispersion peak was observed in 2θ = 20–25°, which is the characteristic peak of amorphous SiO$_2$(AG) [48]. Other peaks corresponded with the characteristic peaks of the wurtzite ZnO structure [18]. The peaks of SiO$_2$(AG)/T-ZnO further indicated that SiO$_2$(AG) and T-ZnO still retained their crystal structural characteristics after forming SiO$_2$(AG)/T-ZnO composites.

#### 3.3 SSA and pore structure of SiO$_2$(AG), T-ZnO, and SiO$_2$(AG)/T-ZnO

SSA and pore structure of SiO$_2$(AG), T-ZnO, and SiO$_2$(AG)/T-ZnO were analyzed via the N$_2$ adsorption–desorption method. As can be seen in Figure 3, N$_2$ adsorption–desorption isotherms of SiO$_2$ (AG), T-ZnO, and SiO$_2$(AG)/T-ZnO were type IV, II, and IV adsorption isotherms, respectively. Figure 3(a) indicates that SiO$_2$(AG) powders were porous materials, and the hole was a narrow tubular pore with open ends and wide mouth [49]. Figure 3(b) shows N$_2$ adsorption behavior on T-ZnO is gas physical absorption, which indicated that T-ZnO was a nonporous material [47]. Figure 3(c) shows that the SiO$_2$(AG) loaded on the surface of T-ZnO still maintained its original shape, and the adsorption of SiO$_2$(AG)/T-ZnO was significantly increased compared with T-ZnO. The SSA, pore size, and pore volume of SiO$_2$(AG), T-ZnO, and SiO$_2$(AG)/T-ZnO are shown in Table 1. Compared to T-ZnO, the SSA, pore size
distribution, and pore volume of SiO\textsubscript{2}(AG)/T-ZnO were significantly improved.

3.4 UV-VIS DRS analysis

SiO\textsubscript{2}(AG), T-ZnO, and SiO\textsubscript{2}(AG)/T-ZnO were characterized by UV-VIS DRS. As shown in Figure 4, SiO\textsubscript{2}(AG) had lower absorbance within the wavelength range between 200 and 800 nm. T-ZnO and SiO\textsubscript{2}(AG)/T-ZnO showed strong absorption between 200 and 400 nm. Within the limits of visible light, the absorption of SiO\textsubscript{2}(AG)/T-ZnO was enhanced slightly. The UV-VIS DRS of SiO\textsubscript{2}(AG)/T-ZnO was similar to that of T-ZnO.

3.5 Adsorption property of T-ZnO and SiO\textsubscript{2}(AG)/T-ZnO

Adsorption isotherms of T-ZnO and SiO\textsubscript{2}(AG)/T-ZnO for NB are demonstrated in Figure 5. In the range of the organic concentration of this experiment, the adsorption amount of SiO\textsubscript{2}(AG)/T-ZnO and T-ZnO to NB grew with the increase of the equilibrium concentration and equilibrium adsorption capacity up to 3.23 and 2.21 mg/g, respectively. T-ZnO had poor adsorption properties for NB because of small SSA of T-ZnO. The adsorption performance of SiO\textsubscript{2}(AG)/T-ZnO was better than T-ZnO, because the SiO\textsubscript{2}(AG) loaded on the surface of T-ZnO has good adsorption for NB [39].
3.6 Kinetic study of NB degradation by T-ZnO and SiO$_2$(AG)/T-ZnO

The NB photocatalytic degradation curves of T-ZnO and SiO$_2$(AG)/T-ZnO are shown in Figure 6. Compared to T-ZnO, SiO$_2$(AG)/T-ZnO had better photocatalytic effect for NB with different initial concentrations. The degradation processes of different initial concentrations of NB were fitted by the pseudo first-order kinetic equation. Figure 7 obviously indicates that the degradation processes of NB by T-ZnO and SiO$_2$(AG)/T-ZnO followed the first-order reaction.

Considering the initial moment reaction kinetic, the curves of $1/C_e$ and $1/r_0$ are displayed in Figure 8, and the relevant fitting equations are as follows:

\[
\text{SiO}_2(\text{AG})/\text{T-ZnO}: \frac{1}{t_0} = \frac{35.397}{C_0} + 4.1307 \quad R^2 = 0.976,
\]

\[
\text{T-ZnO}: \frac{1}{t_0} = \frac{63.695}{C_0} + 6.7816 \quad R^2 = 0.9915.
\]

The degradation kinetics of SiO$_2$(AG)/T-ZnO and T-ZnO were consistent with the Langmuir–Hinshelwood
kinetic model. The degradation rate constant and adsorption constant of NB using SiO$_2$(AG)/T-ZnO and T-ZnO could be calculated, which were $k' = 0.2421 \text{mg/L min}^{-1}$, $K_{\text{ad}} = 0.1167 \text{L/mg}$ and $k' = 0.1475 \text{mg/L min}^{-1}$, $K_{\text{ad}} = 0.1065 \text{L/mg}$. The results indicated that $k'_{\text{SiO}_2(\text{AG})/\text{T-ZnO}} > k'_{\text{T-ZnO}}$ and $K_{\text{ad}}_{\text{SiO}_2(\text{AG})/\text{T-ZnO}} > K_{\text{ad}}_{\text{T-ZnO}}$. According to the phenomenon, we concluded that the loading of SiO$_2$(AG) could increase T-ZnO adsorption to NB, and then promoted photocatalysis.

4 Conclusion

SiO$_2$(AG)/T-ZnO composites were prepared via a simple and controllable method. Various characterization methods showed that the morphology and structural characteristics of SiO$_2$(AG) and T-ZnO were retained after SiO$_2$(AG) loading on the surface of T-ZnO. The photocatalytic degradation processes of NB using T-ZnO and SiO$_2$(AG)/T-ZnO followed the first-order reaction. SiO$_2$
(AG)/T-ZnO had better photocatalytic performance. Considering the initial moment reaction kinetic, the photocatalytic kinetic of SiO2(AG)/T-ZnO and T-ZnO was consistent with the Langmuir–Hinshelwood kinetic model, and reaction rate constant $k_{\text{SiO2(AG)/T-ZnO}} > k_{\text{T-ZnO}}$ adsorption rate constant $K_{\text{ad SiO2(AG)/T-ZnO}} > K_{\text{ad T-ZnO}}$, which demonstrated SiO2(AG) loading could increase T-ZnO adsorption to NB, then promoted its photocatalytic performance. Compared with the conclusions of the important relevant papers of this study, loading SiO2(AG) on the surface of T-ZnO can retain the morphology and structural characteristics of T-ZnO and SiO2(AG) unchanged, and the photocatalysis of SiO2(AG)/T-ZnO composites for NB can be significantly improved. The improvement of the catalytic performance of the material by this method is better than that of other porous materials combined with semiconductor materials.

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**Author contributions:** Zhigang Yi designed the experiments, contributed to characterization of materials, and led the drafting of the manuscript. Tao Jiang and Ying Cheng assisted in the analysis and testing work during the experiments. Qiong Tang designed and supervised the experiments.

**Conflict of interest:** The authors declare no conflict of interest regarding the publication of this paper.

**Data accessibility:** The authors conducted the experiment systematically and reported experimental procedure clearly in Section 2 and provided all necessary data in Section 3 of the manuscript.

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