

# Photocatalytic degradation for methylene blue using zinc oxide prepared by codeposition and sol–gel methods

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## Abstract

Zinc oxide nanoparticle was obtained by zinc hydrate deposited on the silica nanoparticle surface and zinc hydrate was dispersed in starch gel. The structure of zinc oxide particle was characterized by nitrogen adsorption–desorption and XRD, the morphology was observed by TEM. The result showed that the zinc oxide nanoparticle deposited on the silica nanoparticle surface was well-dispersed and less than 50 nm, displayed higher photocatalytic activity for methylene blue degradation. However, the zinc oxide nanoparticle in a size of 60 nm was derived from starch gel and showed poorer photocatalytic activity. It provided a simple and effective route to prepare zinc oxide nanoparticle with higher photocatalytic activity through depositing zinc oxide on the silica particle surface, moreover, the catalyst is easier to recover due to its higher density.  
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**Keywords:** Zinc oxide nanoparticle; Surface; Photocatalytic activity; Methylene blue

## 1. Introduction

Nanometer-sized zinc oxide as an important inorganic functional material was widely used in rubber, coat, catalyst, electronic engineering fields [1–3]. In the past two decades, zinc oxide has attracted much attention with respect to the degradation of various pollutants due to its high photosensitivity [4–7], stability and wide band gap [8]. Zinc oxide is thought as a low cost alternative photocatalyst to TiO<sub>2</sub> for degradation of organics in aqueous solutions [9].

The dispersion and surface area of zinc oxide, which depend on the synthesis method, are important factors for determining its photocatalytic activity [10]. Zinc oxide nanoparticles can be prepared by various methods, such as, alkali precipitation [11–13], thermal decomposition [14], hydrothermal synthesis [3], organo-zinc hydrolysis [15], spray pyrolysis [16,17] and

microwave irradiation [18,19], plasma heat-decomposing [20], etc. Composites of zinc oxide and silica nanoparticle could be formed through co-precipitation route; in this case, the zinc oxide could be coated on the silica nanoparticle surface.

Starch gel could be used as template to obtain macroporous material and film [21]. The metal nitrate was added into the starch solution, and heated the mixture to form gel; the porous metal oxide was prepared when the starch was burnt off at air.

In this work, zinc hydrate was formed in the starch gel and silica nanoparticle surface, respectively. Then, it was heated to 600 °C for 4 h to form zinc oxide nanoparticles. Photocatalytic activities of zinc oxide nanoparticles were investigated by measuring the photocatalytic degradation of methylene blue in aqueous solution under the illumination of UV light.

## 2. Experimental

### 2.1. Preparation zinc oxide nanoparticle

The zinc oxide particles were prepared by precipitation and starch gel dispersion methods as following: (1) 0.1 mol

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of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 100 ml of deionic water; then, 100 ml silica colloidal solution (silica content is 20% and particle size is 10–20 nm) was added under vigorous stirring. Sixty milliliters of ammonia (37%) was dropped into the above solution within 10 min under continuous stirring; and a composition deposition was formed and aged 1 day at room temperature. Afterwards it was filtered, washed, dried at 80 °C for 12 h and calcined under air at 600 °C for 4 h. The resulting zinc oxide particles were labeled as ZnO–Si. (2) 0.1 mol of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 100 ml of deionic water, then, 30 g starch was added under continuous stirring, the mixture solution was heated to 90 °C and kept at this temperature for 3 h; then a translucent gel was formed. The gel was cooled down to 4 °C and kept for 24 h, and then water in it was exchanged by 95% alcohol to prevent the network structure from collapse during drying. After that, it was dried at 80 °C for 12 h; the resulting particle was calcined under air at 600 °C for 4 h. The resulting zinc oxide particles were labeled as ZnO–C.

## 2.2. Structure characterization

The pore structure of zinc oxide was determined by nitrogen adsorption–desorption isotherm at 77.4 K using Micromeritics ASAP2010. X-ray diffraction (XRD) patterns were identified by Y-2000 (Dandong, China, 30 kV, 20 mA) at  $2\theta$  (Cu  $K\alpha$  radiation) 10–80°, step size of 0.01°, and scan speed of 0.1°  $\text{min}^{-1}$ . The morphology and size of the ZnO particles were evaluated by transmission electron microscopy (TEM, JEOL at 40 kV).

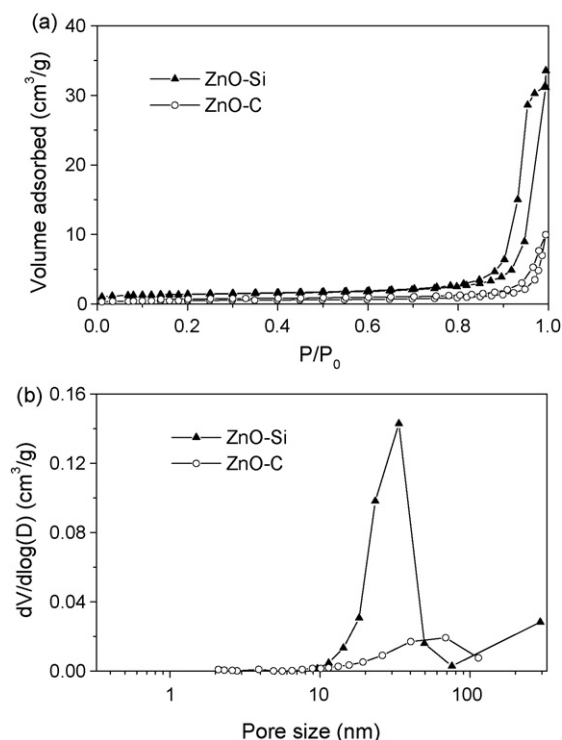


Fig. 1. The nitrogen adsorption–desorption isotherms (a) and pore size distribution (b) of ZnO–Si and ZnO–C.

## 2.3. Evaluation of photocatalytic property

Photocatalytic activity of the zinc oxide particles was evaluated by measuring the photocatalytic degradation of methylene blue in water under the illumination of UV light (high-pressure mercury vapor lamp, 300 W, predominantly wavelength 365 nm). The methylene blue concentration employed was 100 mg/l with 0.1  $\text{kg/m}^3$  ZnO–C or ZnO–Si. In degradation experiments, prior to irradiation, the aqueous solution was stirred continuously in the dark for 30 min to ensure adsorption/desorption equilibrium. The equilibrium concentration of MB was used as the initial value for the photodecomposition processes. Some intermediates would be formed during methylene degradation, and the major absorption band of methylene blue and its degradation intermediates was around 665 nm [22–24]. In order to investigate the photocatalytic activities of ZnO–Si and ZnO–C, the mineralization of methylene blue was evaluated according to the absorption change in this work. The decomposition of methylene blue was monitored by measuring the absorbance of the aliquot solution using the UV–vis spectrophotometer (at 665 nm) in liquid cuvette configuration with de-ionized water as reference.

## 3. Results and discussion

### 3.1. Pore structure characterization

The nitrogen adsorption–desorption isotherms of ZnO–C and ZnO–Si were drawn in Fig. 1. The hysteresis loops of H4 type proved the existence of mesopores, which was observed in the case of aggregates of particles giving rise to pores. The hysteresis loop at a relative pressure between 0.4 and 0.95 is attributed to the stacked of zinc oxide for ZnO–C and ZnO–Si particles. The ZnO–Si showed a relative concentrated pore distribution ranging from 20 to 50 nm; the ZnO–C gave a scattered pore distribution between 3 and 100 nm. The special surface area of ZnO–C and ZnO–Si was 17.7 and 47.3  $\text{m}^2/\text{g}$ , respectively.

### 3.2. X-ray diffraction

The XRD patterns of ZnO–C and ZnO–Si were shown in Fig. 2. All the diffraction peaks can be indexed to be in agreement

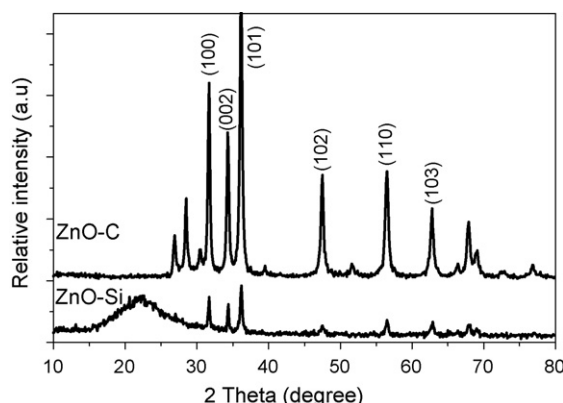


Fig. 2. The X-ray diffraction patterns of ZnO–C and ZnO–Si.

with the hexagonal system structure of ZnO from PDF card 89–1397. The sharpness and intensity characteristic peaks of zinc oxide appeared in ZnO–C; this indicated that the carbon was burnt off at 600 °C in air and the ZnO–C was purity with high crystalline. The diffraction peaks were lower in ZnO–Si. There also showed the peak of SiO<sub>2</sub> (at 15–30°) in ZnO–Si due to the zinc oxide precipitated on the silica nanoparticle surface, the silica oxide was amorphous. The particle size of ZnO–C and ZnO–Si that were estimated by Scherrer equation were 46 and 32 nm, respectively.

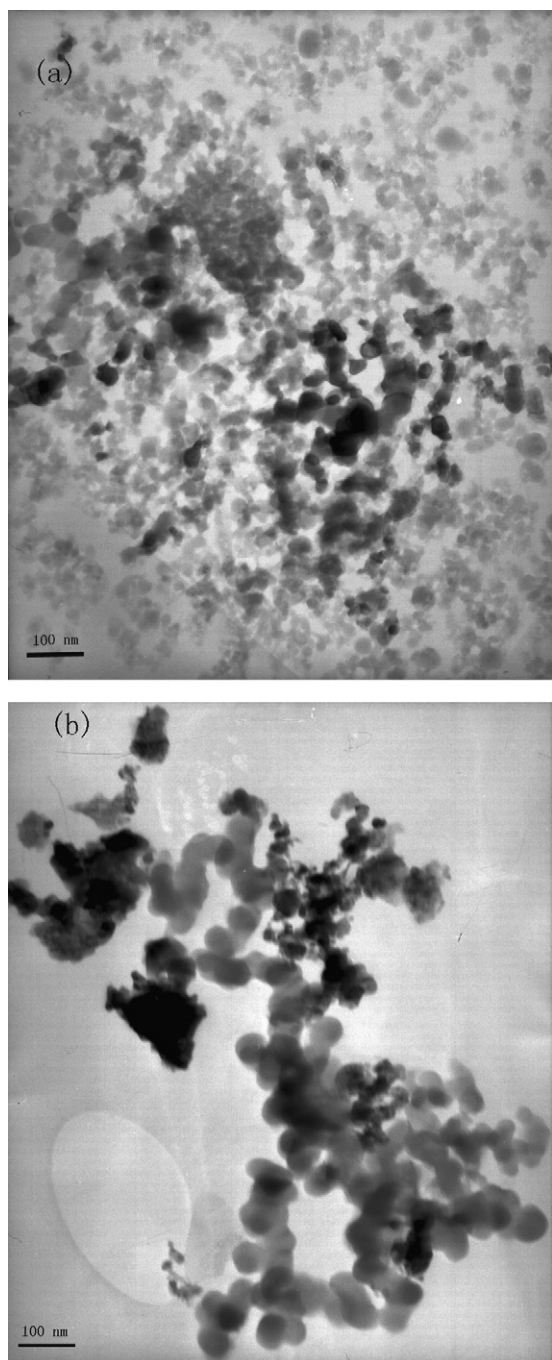


Fig. 3. The TEM images of ZnO–Si (a) and ZnO–C (b).

### 3.3. Transmission electron microscopy

Fig. 3 gave the TEM micrographs of the ZnO–C and ZnO–Si nanoparticles. TEM images showed that the particles are agglomerated up to some extent. The average nanoparticle diameter of ZnO–C was around 60 nm and aggregated to chain; some pores appeared between these particles. The ZnO–Si nanoparticles existed about 20–50 nm. The silica nanoparticles with 20–30 nm were used to disperse the zinc oxide nanoparticle, so, it could deduce that the zinc oxide nanoparticle was well-dispersed on the silica nanoparticle surface and without more aggregation. Also, there are some pores produced among these piled particles. This result was consistent with the pore size distribution derived from nitrogen adsorption–desorption isotherms.

### 3.4. Photocatalytic testing

Since the photocatalytic degradation of methylene blue occurs predominantly on the surface of photocatalyst, studies on the adsorption of the dyes from aqueous solution onto ZnO particles are relevant and important. The equilibrium concentration of the methylene blue ( $C_{eq}$ ) in contact with the catalyst, instead of that of the feed dye solution, represents the true methylene blue concentration in solution at the start of irradiation. For this reason adsorption of the nanoparticles of ZnO in the dark was tested. The equilibrium concentration methylene blue after adsorption by ZnO–C and ZnO–Si was 78 and 69 mg/l, respectively.

Fig. 4 shows the degradation of methylene blue as a function of time using ZnO–C and ZnO–Si. It is clear that the decomposing ratio increased with the degradation time. The decomposition ratio of ZnO–C was very slower and only 20% methylene blue was degraded after 60 min. While the ZnO–Si displayed higher degradation activity, more than 70% and more than 90% methylene blue were decomposed in 20 and 60 min, respectively. The ZnO–Si had less particle size and well-dispersed because it was deposited on the silica nanoparticle surface, and showed higher photocatalytic activity than that of ZnO–C. Moreover, it is easier to separate from solution due to its higher density (2.1 g/cm<sup>3</sup>). This provided a simply route to synthesize zinc oxide with excellent photodegradation property for methylene blue.

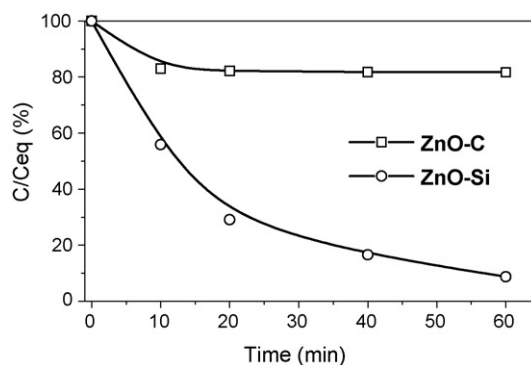


Fig. 4. Photodegradation of methylene blue using ZnO–C (a) and ZnO–Si (b) (initial concentration of methylene blue: 100 mg/l).

#### 4. Conclusion

The structures of zinc oxide prepared through starch gel and deposited on the silica nanoparticle surface were compared; the ZnO–Si displayed higher photocatalytic activity due to its less particle size and better dispersion. Depositing zinc oxide on the silica nanoparticle surface provided a simple and effective route to prepare zinc oxide photocatalyst, which could decompose 90% methylene blue in 60 min.

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