Synthesis and photo-degradation activity of Zn$_2$GeO$_4$ photocatalyst

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Abstract. Through solution phase route, Zn$_2$GeO$_4$ photocatalyst with the morphology of nanoparticle was prepared. The as-prepared products were characterized by scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area measurements. The results revealed that Zn$_2$GeO$_4$ nanoparticles with higher surface area have higher photocatalytic activity in photo-degradation of MO than Zn$_2$GeO$_4$ prepared through solid-state reaction.

1. Introduction

In recent years, to convert solar energy to chemical energy by using photocatalysis method, photo-degradation of organic pollutants as well as water splitting into hydrogen are promising green techniques to resolve the problems of energy shortage and environmental pollution. Some metal oxides with different phases and morphologies such as ZnO and etc.[1-3] have been prepared as photocatalysts. Complex materials have been prepared and studied for increasing the quantum efficiency of the photocatalysts. A ternary oxide with chemical and thermal stability, zinc orthogermanate (Zn$_2$GeO$_4$), has been prepared and used for bright white-bluish luminescence and deep UV detection[4-5]. With a wide bandgap, Zn$_2$GeO$_4$ is expected to be a good photocatalyst, applied in photocatalytic overall water splitting, removal of pollutants and photoreduction of CO$_2$[6-8].

In comparison with bulk Zn$_2$GeO$_4$, Zn$_2$GeO$_4$ with nanostructures such as nano-materials and ect. which has been obtained by different methods including hydrothermal method exhibit higher photocatalytic activity.[9] Zn$_2$GeO$_4$ with different morphologies such as 3-D nanorods, microspheres[10-13], has been obtained by different methods including thermal evaporation method or hydrothermal method chemical[14-16]. Amorphous Zn$_2$GeO$_4$ nanoparticles and hollow Zn$_2$GeO$_4$ nanoparticles have been synthesized, while the crystallized Zn$_2$GeO$_4$ nanoparticles has rarely been reported. Studies of ternary nanostructures are meaningful, due to both more complex functions and readily tunable properties of the ternary nanostructures.

However, for the synthesis of nano-Zn$_2$GeO$_4$, most of the reported routs had complex process, for example, hydrothermal reaction required high temperature and high pressure conditions. Recently, to synthesize nanostructured Zn$_2$GeO$_4$ under moderate conditions, the facile solution route has been reported[17]. In this paper, through a solution phase route at a relatively low temperature under ambient pressure, nanostructured Zn$_2$GeO$_4$ were successfully prepared. Due to the larger surface area, the as-
prepared nanostructured Zn$_2$GeO$_4$ show the improved photocatalytic performance in photo-oxidation of MO.

2. Experimental

2.1. Synthesis of Zn$_2$GeO$_4$ nanoparticles
Isotropic solutions were prepared by dissolving different proportion of Na$_2$GeO$_3$, Zn(CH$_3$COO)$_2$, EtOH, H$_2$O and surfactant F127. The solution was stirred at 80 °C for 3h. Then, the as-prepared products were separated by centrifugation and were washed with water and ethanol, and then the sample is dried and calcined at 450 °C for 4 h. A reference sample was prepared by heating stoichiometric mixture of GeO$_2$ and ZnO at 1300 °C for 15 h (SSR-Zn$_2$GeO$_4$).

2.2. Characterization
The specific surface area of the as-prepared powders was obtained on a Micromeritics TriStar 3000 instrument and Brunauer–Emmett–Teller (BET) equation were used to calculate the specific surface area. The morphology and microstructure were observed using a field emission scanning electron microscope (FE-SEM; NOVA230, FEI Ltd.) with accelerating voltage of 15 kV.

2.3. Photocatalysis test
The methyl orange (MO) dye was used to test the photocatalytic activities of as-prepared samples and the photocatalytic reaction was performed in a Pyrex reactor. The catalyst (0.1 g) was dispersed in 100 mL MO aqueous solution (4.2 mg L$^{-1}$). The light irradiation system contains a 300 W Xe lamp and a water filter to remove heating effects. The reaction solutions of the MO photodegradation for all experiments were first stirred in the dark for 1 h to reach the adsorption–desorption equilibrium of MO on catalysts. The MO degradation efficiency was evaluated using the UV-vis absorption spectra to measure the peak value of a maximum absorption of MO solution at wavelength of 463 nm.

3. Results and discussion
The morphology of the Zn$_2$GeO$_4$ nanoparticles sample was characterized by SEM. Figure 1 shows the SEM image of Zn$_2$GeO$_4$ product synthesized assisted by F127. From Figure 1, Zn$_2$GeO$_4$ nanoparticles can be observed. As shown in Figure 1, in the synthesis of Zn$_2$GeO$_4$ sample through solution route with ethanol and F127, the morphology of the as-prepared Zn$_2$GeO$_4$ sample is nanoparticle which is the same as the morphology of the sample prepared by changing the proportion of ethanol. That indicates that the solvent is not the main effect to form the Zn$_2$GeO$_4$ nanoparticles. The morphology-directing reagent is necessary. By the influence of the surfactant, the Zn$_2$GeO$_4$ nanoparticles are formed.

![Figure 1. SEM image of Zn$_2$GeO$_4$ nanoparticles.](image.png)
The morphology and size information of the Zn$_2$GeO$_4$ sample were further characterized by high-resolution SEM. Figure 2 shows the SEM image of Zn$_2$GeO$_4$ product synthesized assisted by the surfactant F127. From Figure 2, the higher magnified SEM image exhibits the particle size of Zn$_2$GeO$_4$ nanoparticles is about 200 nm. The difference in crystallite size between Zn$_2$GeO$_4$ nanoparticles and SSR-Zn$_2$GeO$_4$ sample leads to their significant difference in BET surface area: 26 m$^2$·g$^{-1}$ for Zn$_2$GeO$_4$ nanoparticles and 0.9 m$^2$·g$^{-1}$ for SSR-Zn$_2$GeO$_4$ sample.

![High-resolution SEM image of Zn$_2$GeO$_4$ nanoparticles.](image)

**Figure 2.** High-resolution SEM image of Zn$_2$GeO$_4$ nanoparticles.

In addition, photocatalytic oxidation of MO on the as-prepared Zn$_2$GeO$_4$ samples is performed. Figure 3 shows that photocatalytic oxidation of MO by using the above-mentioned Zn$_2$GeO$_4$ as photocatalysts. From Figure 3, the Zn$_2$GeO$_4$ nanoparticles obtained by adding F127 exhibit much higher activity than SSR-Zn$_2$GeO$_4$, which is ascribed to high specific surface area which can produce the more reaction sites.

![Comparison of MO degradation over different photocatalysts.](image)

**Figure 3.** Comparison of MO degradation over different photocatalysts, Zn$_2$GeO$_4$ nanoparticles (a) and SSR-Zn$_2$GeO$_4$ (b).
4. Conclusion

In summary, by the solution phase route assisted by F127, the Zn$_2$GeO$_4$ nanoparticles have been prepared, which exhibit much higher photocatalytic activity in photodegradation of MO compared with the SSR-Zn$_2$GeO$_4$ sample. The high photocatalytic activity of the Zn$_2$GeO$_4$ nanoparticles is ascribed to high specific surface area which can produce the more reaction sites.

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