Facile synthesis of ternary oxide and the performance of photo-catalysis

Lijuan Wan¹,²,*, Ming Yang³
¹Nanjing Vocational Institute of Transport Technology, Nanjing, China
²Jiangsu Engineering Technology Research Center for Energy Conservation and Emission Reduction of Transportation, Nanjing, China
³School of Transportation, Southeast University, Nanjing, China

*Corresponding author e-mail: bartty_ym@163.com

Abstract. Nano-structured Zn₂GeO₄ photocatalyst was prepared through solution phase route. The as-prepared products were characterized by Brunauer–Emmett–Teller (BET) surface area measurements and scanning electron microscopy (SEM). The experimental results revealed that for photo-degradation of MO, the nano-structured Zn₂GeO₄ samples with higher surface area have higher photocatalytic performance than bulk Zn₂GeO₄ synthesized through solid-state reaction.

1. Introduction
Recently, photo-degradation of organic pollutants as well as water splitting into hydrogen by using photocatalysis method are promising green techniques to resolve the problems of environmental pollution and etc by some metal oxides photocatalysts.[1-3] With chemical and thermal stability, zinc orthogermanate (Zn₂GeO₄), has been synthesized and used for deep UV detection, and also is excepted to be a good photocatalyst, and etc.[4-8]

Due to the readily tunable properties of the ternary nanostructures, studies of ternary nanostructures are meaningful. Nano-structured Zn₂GeO₄ compared with bulk Zn₂GeO₄ exhibit higher photocatalytic activity [9] The crystallized nano-structured Zn₂GeO₄ samples have rarely been reported. However, most of the reported routes had complex process for the preparation of nano-structured Zn₂GeO₄. Recently, to synthesize nanostructured Zn₂GeO₄, the facile solution route under moderate conditions has been reported. In this paper, at a relatively low temperature under ambient pressure, nano-structured Zn₂GeO₄ were successfully prepared through a solution phase route. The as-prepared nanostructured Zn₂GeO₄ show the improved photocatalytic performance for the degradation of organic compound due to the larger surface area.

2. Experimental

2.1. Synthesis of nano-structured Zn₂GeO₄
Isotropic solutions were prepared by dissolving different proportion of Na₂GeO₃, Zn(CH₃COO)₂, EtOH, H₂O and surfactant F127. The solution was stirred at 60–70 °C for 4–6 h. Then, the as-prepared products were separated by centrifugation and were washed with ethanol and water. Then the samples are dried.
and calcined at 450 °C for 4 h. A reference sample (SSR-Zn₂GeO₄) was prepared at 1300 °C by heating stoichiometric mixture of ZnO and GeO₂ for 15 h.

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

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

3. Results and discussion
The morphology and microstructure of the as-prepared nano-structured Zn₂GeO₄ sample was characterized by SEM. The SEM images of Zn₂GeO₄ product synthesized assisted by the surfactant are shown in Figure 1. As shown in Figure 1, nano-structured Zn₂GeO₄ can be observed. Figure 2 shows the high-resolution SEM image of the as-prepared Zn₂GeO₄ sample. From Figure 2, the morphology of the as-prepared Zn₂GeO₄ sample through solution route with ethanol and the surfactant is uniform. To form nano-structured Zn₂GeO₄ sample, it is necessary to use the morphology-directing reagent. By the influence of the surfactant, the Zn₂GeO₄ nanoparticles are formed.

![Figure 1. SEM image of Zn₂GeO₄ sample.](image-url)
Figure 2. High-resolution SEM image of Zn$_2$GeO$_4$ sample.

The morphology information of the Zn$_2$GeO$_4$ sample prepared for longer reaction time were further characterized by high-resolution SEM. Figure 3 shows the SEM image of the as-prepared Zn$_2$GeO$_4$ product synthesized assisted by the surfactant. From Figure 3, the higher magnified SEM image exhibits the cubic Zn$_2$GeO$_4$ sample with larger size, which may be due to the longer reaction time. The difference in crystallite size between Zn$_2$GeO$_4$ and SSR-Zn$_2$GeO$_4$ sample leads to their significant difference in BET surface area: 19.75 m$^2$.g$^{-1}$ for nano-structured Zn$_2$GeO$_4$ sample and 0.86 m$^2$.g$^{-1}$ for SSR-Zn$_2$GeO$_4$ sample.

Figure 3. High-resolution SEM image of Zn$_2$GeO$_4$ sample.

In addition, on the as-prepared Zn$_2$GeO$_4$ sample and SSR-Zn$_2$GeO$_4$ sample, photocatalytic oxidation of MO is performed. By using the above-mentioned Zn$_2$GeO$_4$ as photocatalysts, it is shown in Figure 4 that the photocatalytic oxidation of MO is investigated. From Figure 4, the nano-structured Zn$_2$GeO$_4$ sample obtained by adding the surfactant exhibit much higher activity than SSR-Zn$_2$GeO$_4$ sample, which is due to the high specific surface area by producing more reaction sites.
Figure 4. Comparison of MO degradation over SSR-Zn2GeO4 (a), as-prepared Zn2GeO4 sample (b).

4. Conclusion
In summary, the nano-structured Zn$_2$GeO$_4$ samples have been prepared by the solution phase route assisted by surfactant. Compared with the SSR-Zn$_2$GeO$_4$ sample, for the photodegradation of MO, the nano-structured Zn$_2$GeO$_4$ samples show higher photocatalytic activity. The high photocatalytic activity of the nano-structured Zn$_2$GeO$_4$ in the photodegradation of MO may be due to the more reaction sites produced from high specific surface area.

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