Synthesis of ternary oxide for efficient photo catalytic conversion of CO2

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Abstract. Zn2GeO4 Nan rods were prepared by solution phase route. The morphology and structure of the as-prepared products were characterized by scanning electron microscopy (SEM) and Bruner–Emmett–Teller (BET) surface area measurements. The results revealed that Zn2GeO4 Nan rods with higher surface area have higher photo catalytic activity in photo reduction of CO2 than Zn2GeO4 prepared through solid-state reaction.

Keywords. Zn2GeO4, nanostructure, photo reduction.

1. Introduction

Recently, to resolve the problems of energy shortage and environmental pollution by using photo catalysis method, reduction of CO2 into hydrocarbons as well as water splitting into hydrogen are promising green techniques to convert solar energy to chemical energy. Some metal oxides such as TiO2 and etc. [1-3] have been prepared with different phases and morphologies as photo catalysts. For increasing the quantum efficiency of the photo catalysts, complex materials have been prepared and studied. A ternary oxide, zinc orthogermanate (Zn2GeO4), has been prepared and used for deep UV detection [4] and bright white-bluish luminescence [5]. Zn2GeO4 with a wide band gap is accepted to be a good photo catalyst, applied in photo catalytic overall water splitting [6], photo reduction of CO2 and removal of pollutants [7, 8].

Zn2GeO4 with nanostructures exhibit higher photo catalytic activity, in comparison with bulk Zn2GeO4[9] So far, for the application of photo reduction of CO2, Zn2GeO4 with different morphologies such as nan rods or nanowires and etc. have been prepared as photo catalysts[10,11] However, most of the reported routs to prepare nano-Zn2GeO4 had complex process and etc. Recently, under moderate conditions, to synthesize Zn2GeO4 Nan rods, the facile solution route has been reported by Yan et al [12]. In this paper, Zn2GeO4 Nan rods were successfully prepared through a solution phase route at a relatively low temperature under ambient pressure by moderating the ratio of water and ethanol. The as-prepared Zn2GeO4 Nan rods due to the larger surface area show the improved photo catalytic performance in photo reduction of CO2.
2. Experimental

2.1. Synthesis of Zn$_2$GeO$_4$ nanoparticles.
Isotropic solutions were prepared by dissolving different proportion of Na$_2$GeO$_3$ and Zn(CH$_3$COO)$_2$ and EtOH (5 or 20 ml) and H$_2$O (35 or 20 ml). 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. 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 Micrometrics 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. CO$_2$ photo-reduction experiments.
In the photo-reduction of CO$_2$, Zn$_2$GeO$_4$ powder (0.1 g) was uniformly dispersed on a glass reactor with an area of 4.2 cm$^2$. A 300 W Xenon arc lamp was used as the light source for the photo catalytic reaction. The volume of the reaction system was about 230 mL. The reaction setup was vacuum-treated for several times, and then high-purity CO$_2$ gas was introduced into the reaction to achieve ambient pressure. Deionized water (0.4 mL) as reducing agent was injected into the reaction system. During the irradiation, about 1 mL of gas was taken from the reaction cell at given intervals for subsequent CH$_4$ concentration analysis with a gas chromatograph (GC-2014, Shimadzu Corp., Japan).

3. Results and Discussion
The morphology and size information of the as-prepared Zn$_2$GeO$_4$ nan rods sample with 5 mL EtOH were characterized by SEM. Fig. 1 shows the SEM images of Zn$_2$GeO$_4$ product synthesized by 5 mL EtOH. From Fig. 1, Zn$_2$GeO$_4$ nan rods with holes in the middle of the nanorods can be observed. The higher magnified SEM image exhibits the length of Zn$_2$GeO$_4$ nanorods is about 200 nm. The difference in crystallite size between Zn$_2$GeO$_4$ nanorods and SSR-Zn$_2$GeO$_4$ leads to their significant difference in BET surface area: 22.57 m$^2$·g$^{-1}$ for Zn$_2$GeO$_4$ nanorods and 0.85 m$^2$·g$^{-1}$ for SSR-Zn$_2$GeO$_4$ sample.

![SEM image of Zn$_2$GeO$_4$ prepare by 5 mL EtOH](image-url)
Furthermore, the morphology and size information of the as-prepared Zn$_2$GeO$_4$ Nan rods sample by using 20 mL EtOH were characterized by SEM. Fig. 2 shows the SEM images of Zn$_2$GeO$_4$ product synthesized by using 20 mL EtOH. From Fig. 2, Zn$_2$GeO$_4$ Nan rods with holes in the middle of the Nan rods can be observed. The higher magnified SEM image exhibits the length of Zn$_2$GeO$_4$ Nan rods is about 200 nm. The difference in crystallite size between Zn$_2$GeO$_4$ Nan rods and SSR-Zn$_2$GeO$_4$ leads to their significant difference in BET surface area: 23.25 m$^2$·g$^{-1}$ for Zn$_2$GeO$_4$ Nan rods and 0.85 m$^2$·g$^{-1}$ for SSR-Zn$_2$GeO$_4$ sample.

![Fig. 2 SEM image of Zn$_2$GeO$_4$ prepared by 20 mL EtOH](image)

Photo catalytic reduction of CO$_2$ on the as-prepared Zn$_2$GeO$_4$ samples is performed and the result is shown in Fig. 3. Fig. 3 shows that in the presence of water vapor, CO$_2$ can be photo reduced to CH$_4$ by using the Zn$_2$GeO$_4$ Nan rods prepared with 5 mL EtOH and SSR-Zn$_2$GeO$_4$ as photo catalysts. The mechanism of photo reduction of CO$_2$ into CH$_4$ can be described as follows: under UV-vis light irradiation, the photo generated hole on the valence band top [13] of Zn$_2$GeO$_4$ can lead to oxidation of water to produce hydrogen ions via $\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- (E_{\text{redox}}^{\text{valence}} = 0.82 \text{ V vs. NHE})$[11] and the photo generated electron on the conduction band bottom of Zn$_2$GeO$_4$ can drive the reduction of CO$_2$ into CH$_4$ via $\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \rightarrow \text{CH}_4 + \text{H}_2\text{O} (E_{\text{redox}}^{\text{conduction}} = -0.24 \text{ V vs. NHE})$[14]. From Fig. 3, the Zn$_2$GeO$_4$ nan rods obtained by adding 5 mL EtOH (3.49 ppm h$^{-1}$ CH$_4$) exhibit much higher activity than SSR-Zn$_2$GeO$_4$ (0.52 ppm h$^{-1}$ CH$_4$), which is ascribed to more reaction sites arising from high specific surface area.
4. Summary
In summary, by the solution phase route and moderating the proportion of ethanol and water, the Zn$_2$GeO$_4$ Nan rods have been prepared, and compared with the SSR-Zn$_2$GeO$_4$, which exhibit much higher photo catalytic activity in photo reduction of CO$_2$. The high photo catalytic activity of the Zn$_2$GeO$_4$ Nan rods is ascribed to more reaction sites for the high specific surface area.

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