

## Electronic Supplementary Information

### Synthesis of Hierarchical Ag<sub>2</sub>ZnGeO<sub>4</sub> Hollow Spheres for Enhanced Photocatalytic Property

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## Experimental Section

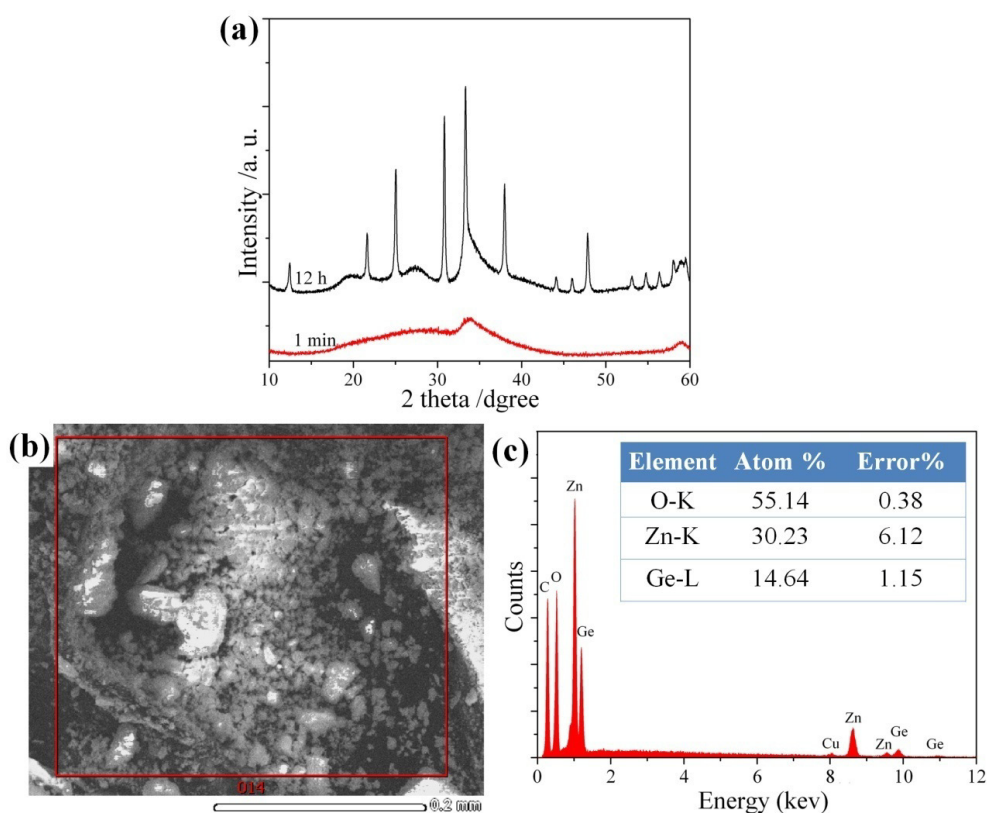
**Materials:** The  $\text{Na}_2\text{GeO}_3$  powders were prepared by solid state reaction way that stoichiometric mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{GeO}_2$  were heated at  $900\text{ }^\circ\text{C}$  for 10 h. The  $\text{ZnAg}_2\text{GeO}_4$  were prepared by ions exchange in aqueous solution. In a typical process, 0.0025 mol  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 50 mL deionized water to form a clear solution. 0.0025 mol as-prepared  $\text{Na}_2\text{GeO}_3$  was dissolved in 50 mL deionized water to form a transparent colloidal suspension of  $\text{Na}_2\text{GeO}_3$  hydrates. The  $\text{Na}_2\text{GeO}_3$  hydrates colloidal suspension was added dropwise to the  $\text{Zn}(\text{CH}_3\text{COO})_2$  solution and white suspension was formed immediately. The suspension was stirred for about 1 min and then 100 mL  $\text{AgNO}_3$  solution ( $100\text{g L}^{-1}$ ) was added. After stirred for about 30 min at room temperature, the mixture was put into an oil bath reactor with magnetic stirring at  $70^\circ\text{C}$  for 2 to 12 hrs. After the reaction, the red precipitate was separated and washed by centrifugation and filtration with distilled water. Finally, the powders were dried at  $70\text{ }^\circ\text{C}$  for 4 h.

**Photocatalytic Activity Test:** A 300W Xe arc lamp was employed as the light source of photocatalytic reactions. Before reaching the reactor, the irradiated light beam was passed through a UV-light cutoff filter (L42,  $\lambda > 420\text{ nm}$ ) and a water filter (removing the infrared ray irradiation). The intensity of the light was about  $9.5\text{ mW/cm}^2$ . About 0.3 g photocatalyst was suspended in 100 mL dye solution in a Pyrex glass reactor. The initial dye concentrations of these solutions were all about 16.0 mg/L. Before irradiation, the suspensions were magnetically stirred in the dark for about 20 min to

ensure an adsorption-desorption equilibrium of dye on the sample surface. During irradiation, the reactor was located in a cooling water bath to maintain the solution temperature at 11-19°C. The intensity of incident light was measured by a spectroradiometer (Ushio, USR- 40, Japan).

**Characterizations:** X-ray diffraction patterns (XRD) were recorded by a RIGAKU Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-K $\alpha$  radiation ( $\lambda=1.54178 \text{ \AA}$ ). Scanning Transmission Electron Microscopy (STEM), and energy-dispersive X-ray elemental mapping (EDS mapping) were performed with a JEOL 2100F field emission transmission electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) patterns were recorded with a JEOL 6700F field emission scanning electron microscopy. UV-visible diffuse reflectance spectrum was recorded with a Shimadzu UV-2500 Spectrophotometer. Brunauer-Emmett-Teller (BET) measurements were carried out in a BELSORP II Surface Area Analyzer.

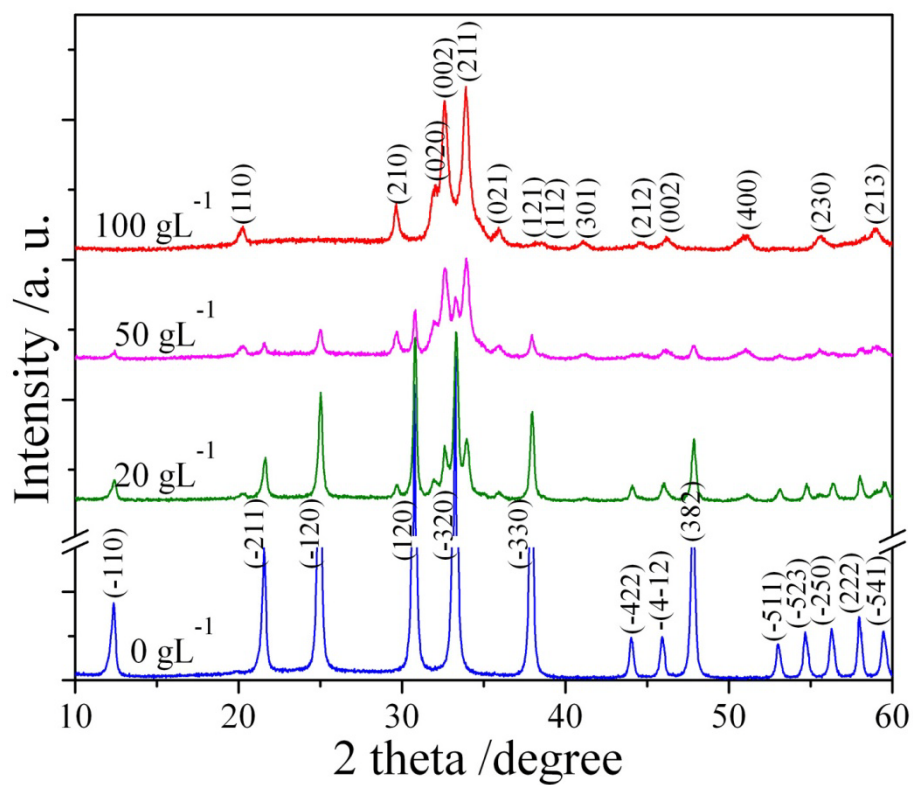
## Figures and Captions



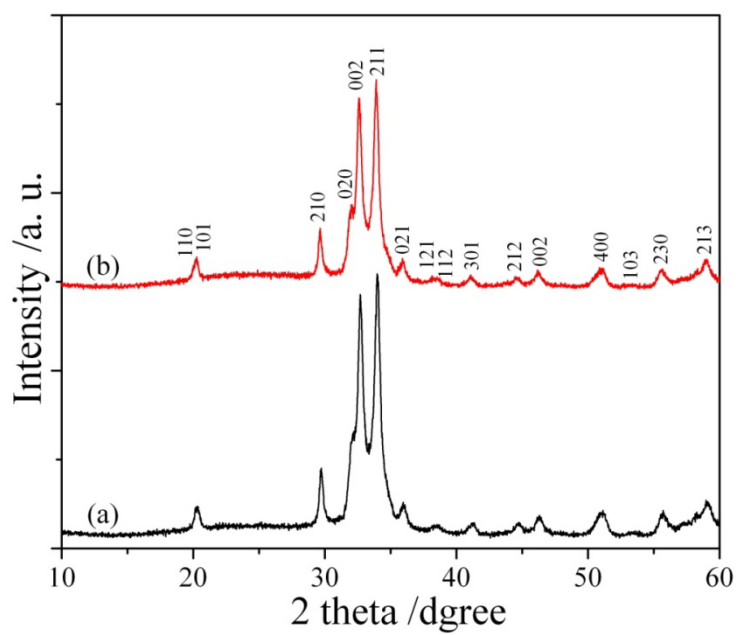
**Fig. S1** (a) XRD pattern of the  $\text{Zn}_2\text{GeO}_4$  prepared at reaction time of 1 min and 12 h; (b) SEM image of the  $\text{Zn}_2\text{GeO}_4$  at reaction time of 1 min in large scale; (c) EDS pattern of  $\text{Zn}_2\text{GeO}_4$  at reaction time of 1 min taken from the red square in (b); the set in (c) is the atom percentage of O, Zn, and Ge.

**Descriptions:** The XRD pattern in Fig. S1a shows that the  $\text{Zn}_2\text{GeO}_4$  prepared at 1 min is amorphous phase, which can be converted to the well crystallized  $\text{Zn}_2\text{GeO}_4$  with elongation of reaction time to 12 h at room temperature. Fig. S1b is the SEM image of the  $\text{Zn}_2\text{GeO}_4$  prepared at 1 min, which reflects the powders in large scale.

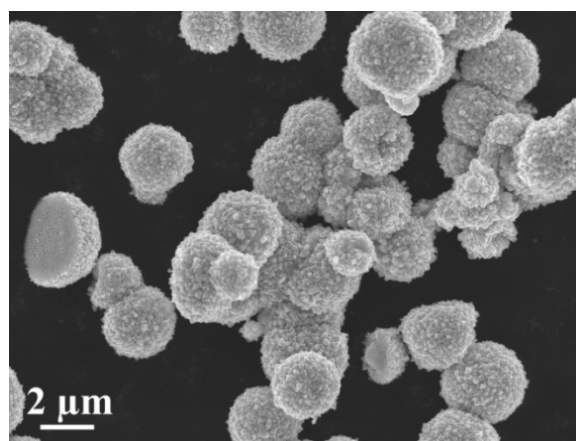
The EDS spectrum in Fig. S1 c is taken from the red square marked in Fig. S1b, which shows that the ratio among the elements of Zn, Ge, and O is about 2: 1: 4.



**Fig. S2** XRD patterns of the product prepared by 0, 20, 50, and 100 gL<sup>-1</sup> AgNO<sub>3</sub> for 12 h.

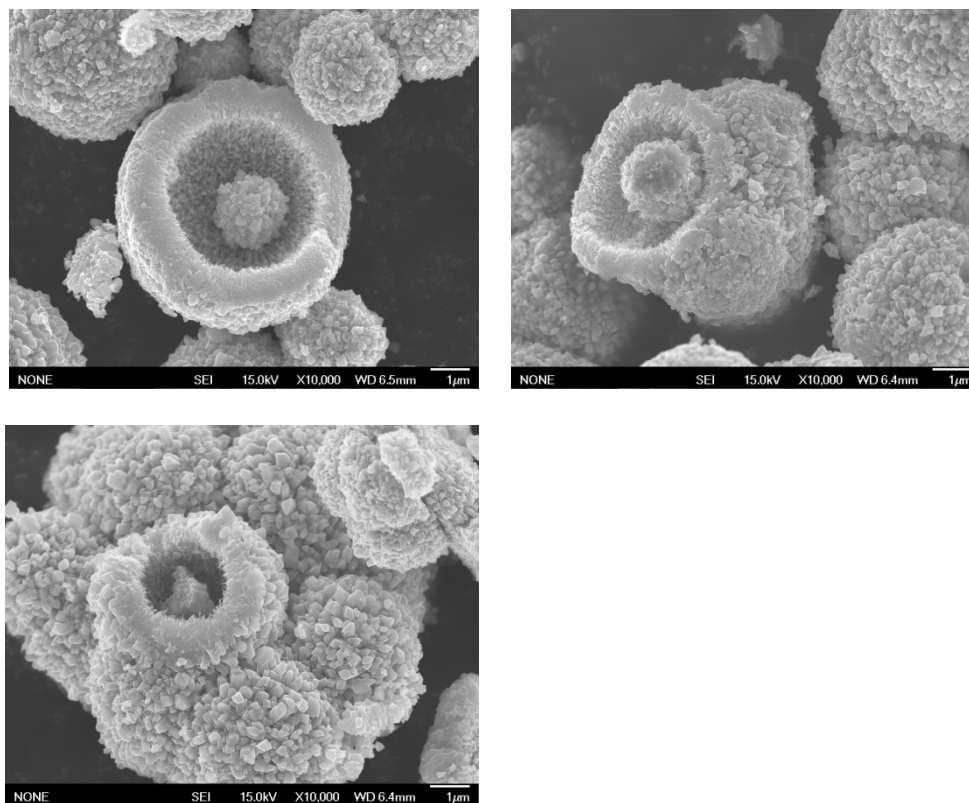


**Fig. S3** XRD patterns of the product prepared by  $100 \text{ gL}^{-1} \text{ AgNO}_3$  for (a) 2 h and (b) 12 h.

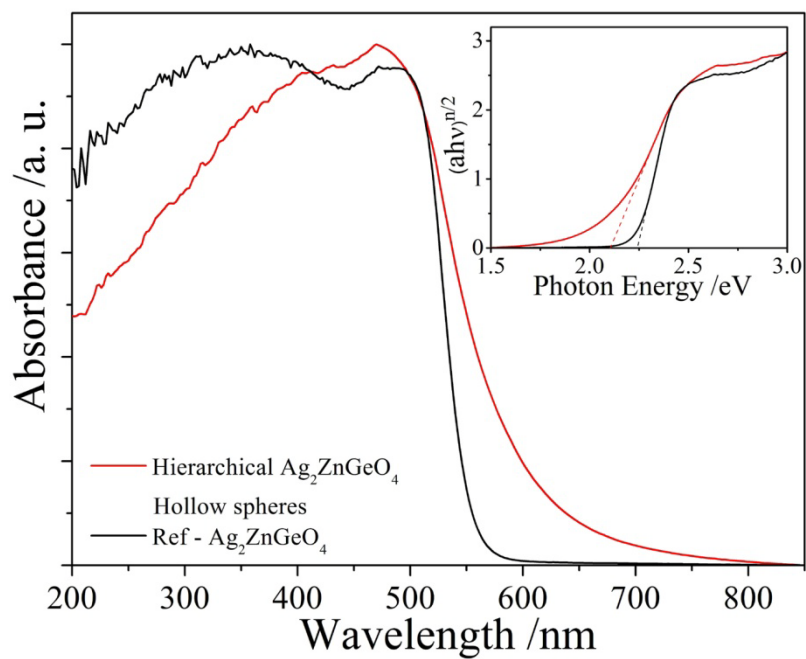


**Fig. S4** The SEM image of the Ag<sub>2</sub>ZnGeO<sub>4</sub> product prepared by 100 gL<sup>-1</sup> AgNO<sub>3</sub> for 2 h.





**Fig. S5** The SEM image of observed core-shell structure in the product prepared by  $100 \text{ gL}^{-1}$   $\text{AgNO}_3$  for 12 h.



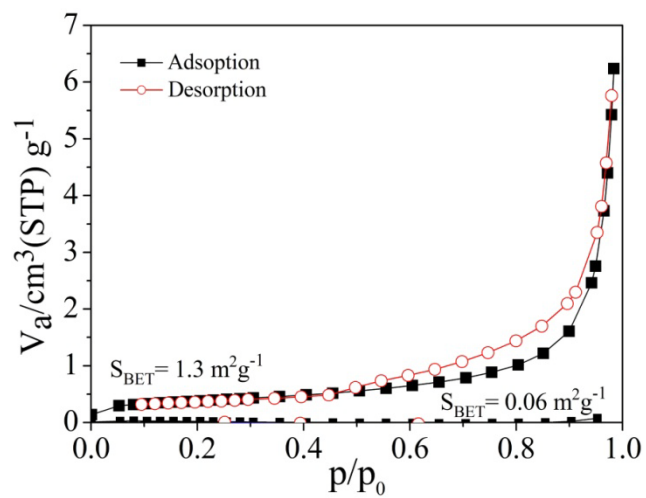
**Fig. S6** UV-visible diffuse reflectance spectrum of hierarchical  $\text{Ag}_2\text{ZnGeO}_4$  and referenced  $\text{Ag}_2\text{ZnGeO}_4$ . Insets are the calculation diagram of their band-gaps.

**Table S1** Characterizations of the  $\text{Ag}_2\text{ZnGeO}_4$  samples

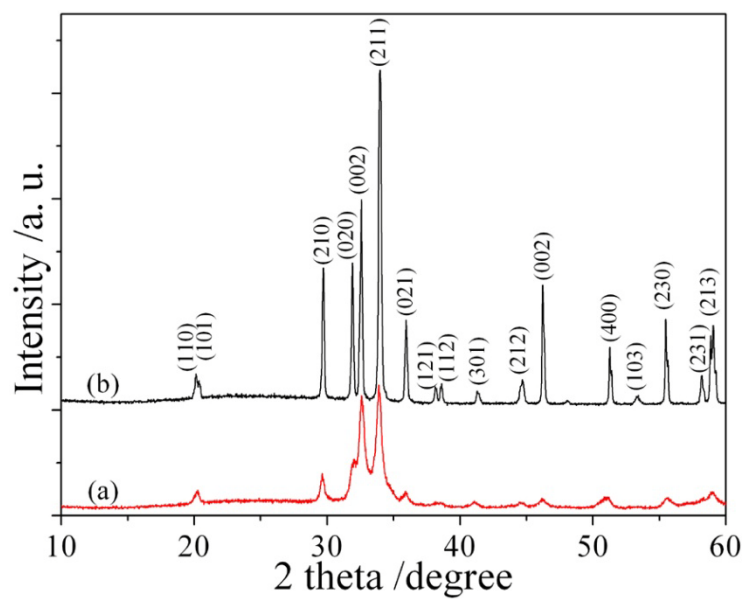
Samples	Element Content (percentages among Ag, Zn, and Ge, at. %)			BET surface areas
$\text{Ag}_2\text{ZnGeO}_4$ (12 h)	49	24	26	$1.3 \text{ m}^2\text{g}^{-1}$
Ref- $\text{Ag}_2\text{ZnGeO}_4$	50	25	24	$0.06 \text{ m}^2\text{g}^{-1}$

**Descriptions:** To find out composition difference between the  $\text{Ag}_2\text{ZnGeO}_4$  hollow spheres and referenced  $\text{Ag}_2\text{ZnGeO}_4$ , the elemental composition was analyzed by ICP-OES, which was shown in Table 1. The ratio of Ag/Zn for the  $\text{Ag}_2\text{ZnGeO}_4$  hollow spheres and referenced  $\text{Ag}_2\text{ZnGeO}_4$  was about 2.04 and 2.00 respectively.

The elemental substitution of Zn by Ag caused the decrease of band gaps from ~4.6 eV of  $\text{Zn}_2\text{GeO}_4$  precursor to ~2.3 eV of  $\text{ZnAg}_2\text{GeO}_4$  material. The bottom of conduction band is composed of hybridized orbitals of Ag 5s5p, O 2p, and Ge 4s4p.<sup>[1]</sup> The valence band is composed orbitals of Ag 4d and O 2p.<sup>[1]</sup> The larger Ag/Zn ratio contribute to the lower bottom of conduction band and subsequently induced the narrower band gap for the hierarchical  $\text{Ag}_2\text{ZnGeO}_4$  hollow spheres.



**Fig. S7** The nitrogen adsorption-desorption isotherms of (upside) the hierarchical  $\text{Ag}_2\text{ZnGeO}_4$  hollow spheres prepared at 12 h and (bottom) referenced bulk  $\text{Ag}_2\text{ZnGeO}_4$  show that the BET surface areas are about  $1.3 \text{ m}^2\text{g}^{-1}$  and  $0.06 \text{ m}^2\text{g}^{-1}$ , respectively.



**Fig. S8** XRD pattern of (a)  $\text{Ag}_2\text{ZnGeO}_4$  product prepared by  $100 \text{ gL}^{-1}$   $\text{AgNO}_3$  for 12 h and (b) the ref- $\text{Ag}_2\text{ZnGeO}_4$ .

## Refernce

- [1] X. Li, S. Ouyang, N. Kikugawa and J. Ye, *Appl. Catal. A-General*, 2008, **334**, 51.