Electronic Supplementary Information

Synthesis of Hierarchical Ag₂ZnGeO₄ Hollow Spheres for Enhanced Photocatalytic Property

Ning Zhang, a, b Shuxin Ouyang, b Tetsuya Kako,a, b and Jinhua Ye *a, b,c

a, b,c Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, Japan. Fax: (+81)-29-860-4958; E-mail: Jinhua.Ye@nims.go.jp

b Research Unit for Environmental Remediation Materials and International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, Japan.

c TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, P. R. China.
Experimental Section

Materials: The Na\(_2\)GeO\(_3\) powders were prepared by solid state reaction way that stoichiometric mixture of Na\(_2\)CO\(_3\) and GeO\(_2\) were heated at 900 °C for 10 h. The ZnAg\(_2\)GeO\(_4\) were prepared by ions exchange in aqueous solution. In a typical process, 0.0025 mol Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O was dissolved in 50 mL deionized water to form a clear solution. 0.0025 mol as-prepared Na\(_2\)GeO\(_3\) was dissolved in 50 mL deionized water to form a transparent colloidal suspension of Na\(_2\)GeO\(_3\) hydrates. The Na\(_2\)GeO\(_3\) hydrates colloidal suspension was added dropwise to the Zn(CH\(_3\)COO)\(_2\) solution and white suspension was formed immediately. The suspension was stirred for about 1 min and then 100 mL AgNO\(_3\) solution (100 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°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 °C for 4 h.

Photocatalytic Activity Test: A 300WXe 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, \(\lambda > 420\) nm) and a water filter (removing the infrared ray irradiation). The intensity of the light was about 9.5 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-Kα radiation (\(\lambda=1.54178\,\text{Å}\)). 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 Zn$_2$GeO$_4$ prepared at reaction time of 1 min and 12 h; (b) SEM image of the Zn$_2$GeO$_4$ at reaction time of 1 min in large scale; (c) EDS pattern of Zn$_2$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 Zn$_2$GeO$_4$ prepared at 1 min is amorphous phase, which can be converted to the well crystallized Zn$_2$GeO$_4$ with elongation of reaction time to 12 h at room temperature. Fig. S1b is the SEM image of the Zn$_2$GeO$_4$ prepared at 1 min, which reflects the powders in large scale.
The EDS spectrum in Fig. S1c 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\(^{-1}\) AgNO\(_3\) for 12 h.
**Fig. S3** XRD patterns of the product prepared by 100 gL⁻¹ AgNO₃ for (a) 2 h and (b) 12 h.
**Fig. S4** The SEM image of the Ag$_2$ZnGeO$_4$ product prepared by 100 gL$^{-1}$ AgNO$_3$ for 2 h.
Fig. S5 The SEM image of observed core-shell structure in the product prepared by 100 gL⁻¹ AgNO₃ for 12 h.
Fig. S6 UV-visible diffuse reflectance spectrum of hierarchical Ag$_2$ZnGeO$_4$ and referenced Ag$_2$ZnGeO$_4$. Insets are the calculation diagram of their band-gaps.
Table S1 Characterizations of the Ag$_2$ZnGeO$_4$ samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Element Content (percentages among Ag, Zn, and Ge, at. %)</th>
<th>BET surface areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$ZnGeO$_4$ (12 h)</td>
<td>49 24 26</td>
<td>1.3 m$^2$g$^{-1}$</td>
</tr>
<tr>
<td>Ref-Ag$_2$ZnGeO$_4$</td>
<td>50 25 24</td>
<td>0.06 m$^2$g$^{-1}$</td>
</tr>
</tbody>
</table>

**Descriptions:**  To find out composition difference between the Ag$_2$ZnGeO$_4$ hollow spheres and referenced Ag$_2$ZnGeO$_4$, the elemental composition was analyzed by ICP-OES, which was shown in Table 1. The ratio of Ag/Zn for the Ag$_2$ZnGeO$_4$ hollow spheres and referenced Ag$_2$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 Zn$_2$GeO$_4$ precursor to ~2.3 eV of ZnAg$_2$GeO$_4$ material. The bottom of conduction band is composed of hybridized orbitals of Ag 5$s$5$p$, O 2$p$, and Ge 4$s$4$p$.[1] The valence band is composed orbitals of Ag 4$d$ and O 2$p$.[1] The larger Ag/Zn ratio contribute to the lower bottom of conduction band and subsequently induced the narrower band gap for the hierarchical Ag$_2$ZnGeO$_4$ hollow spheres.
Fig. S7 The nitrogen adsorption-desorption isotherms of (upside) the hierarchical Ag₂ZnGeO₄ hollow spheres prepared at 12 h and (bottom) referenced bulk Ag₂ZnGeO₄ show that the BET surface areas are about 1.3 m²g⁻¹ and 0.06 m²g⁻¹, respectively.
Fig. S8 XRD pattern of (a) Ag₂ZnGeO₄ product prepared by 100 g L⁻¹ AgNO₃ for 12 h and (b) the ref-Ag₂ZnGeO₄.
Reference