Supporting Information

Self-assembled micro/nano-structured Zn$_2$GeO$_4$ hollow spheres: direct synthesis and enhanced photocatalytic activity

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Experimental Section

Preparation of Zn$_2$GeO$_4$ hollow spheres: A typical synthesis of Zn$_2$GeO$_4$ hollow spheres was as follows: 4.0 g of triethanolamine (TEA) and 0.4 g of NaOH were added to 16 mL of deionized water under stirring in turn. Subsequently, 2.0 mmol of Zn(CH$_3$COO)$_2$·2H$_2$O and 1.0 mmol of GeO$_2$ were added in the above solution, respectively. The mixture was stirred at room temperature to obtain a homogeneous solution, followed by transferring the transparent solution into a 25-mL Teflon-lined stainless steel autoclave, sealed, and maintained at 473 K for 24 h. After naturally cooling to room temperature, the resulted solid product was collected by filtration and washed with distilled water and absolute ethanol for several times. Finally, the solid product was dried in vacuum at 343 K for further use.

Preparation of bulk Zn$_2$GeO$_4$ particles. Bulk Zn$_2$GeO$_4$ particles were prepared by heating a stoichiometric mixture of GeO$_2$ and ZnO at 1473 K (ramp 5°Cmin$^{-1}$) for 15 h using a conventional solid state reaction method.

Preparation of Zn$_2$GeO$_4$ nanorods. Zn$_2$GeO$_4$ nanorods were prepared according to
the hydrothermal process reported by Huang’s group with some minor modification.¹

In a typical synthesis, 0.10 g of cetyltrimethylammonium bromide (CTAB), 0.52 g of GeO₂, and 1.10 g of Zn(CH₃COO)₂·2H₂O were added to 15 mL of deionized water. The pH value of the resulting mixture was adjusted to pH 8 by adding NaOH. The mixture was stirred for 3 h and then transferred to a 25 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 473 K for 24 h, followed by cooling naturally to room temperature. The resulted solid product was collected by centrifugation and washed several times with distilled water and absolute ethanol. The solid was dried in a vacuum oven at 343 K for 12 h.

Characterization

**Physicochemical Characterization:** The phase purity and crystal structure of the sample were characterized by X-ray power diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ=1.541 87 Å). The morphologies and sizes of the samples were examined by field-emission scanning electron microscopy (FE SEM, Nova NanoSEM 230 and S4800). More details about the chemical structure and morphology of the sample were obtained from selected area electron diffraction (SAED) combined with transmission electron microscopy studies (HR TEM, Tecnai G2 F20 S–TWIN transmission electron microscope). The specific surface area of the samples was measured by nitrogen sorption at 77 K on a Micromeritics ASAP 2020 instrument and calculated by the Brunauer–Emmett–Teller (BET) method. The UV–visible diffuse-reflectance spectra (DRS) were obtained by a Cary 500 Scan spectrophotometer.
**Photocatalytic performance:** The photocatalytic hydrogen evolution reaction was performed in a closed gas-recirculation system equipped with a quartz reaction vessel with an inner irradiation. 0.1 g of photocatalyst was dispersed in 155 mL of H₂O by magnetic stirring. Prior to the reaction, the system was evacuated by a mechanical pump and then filled with 101 kPa of high-purity N₂ (>99.99%). This process was repeated three times in order to completely remove O₂ from the system. After that, 5 mL of CH₃OH was introduced into the reactor with a syringe. The suspension was irradiated with a 125–W ultraviolet mercury lamp (Shanghai Yaming Lighting, Model GGZ–125). The temperature of the solution was controlled at room temperature by circulating water. The evolved hydrogen gas was circulated with a microdiaphragm gas pump in the system and its amount was determined using an online gas chromatograph (GC) device. Additionally, the loading of Pt on Zn₂GeO₄ was performed by an *in situ* photoreduction method in the present system.

**Photo-electrochemical measurements:** The measurements were conducted in a BAS Epsilon Electrochemical System with a conventional three-electrode cell. A Platinum plate was used as the counter electrode, and Ag/AgCl electrode (3.0 mol L⁻¹ KCl) was chosen as the reference electrode. 50 mg of Zn₂GeO₄ powder was dispersed in 0.5 mL of ethanol in a centrifuge tube, and sonicated for 30 min to obtain slurry. The working electrode was prepared by spreading the slurry over an area of 0.25 cm² on an indium tin oxide (ITO) glass substrate. The film then was dried in air. The amount of Zn₂GeO₄ loaded on each electrode was ca. 0.9 mg. The electrochemical measurement was conducted with an epsilon (BAS) electrochemical workstation. All electrochemical
potentials are reported vs. NHE. A 500 W xenon lamp fitted by exposure to a UV was used as the light source.

**Figure S1.** Typical XRD pattern of the Zn$_2$GeO$_4$ hollow spheres obtained.

**Figure S2.** Typical FT-IR spectrum of the Zn$_2$GeO$_4$ hollow spheres obtained.
Figure S3. EDX spectrum of the Zn₂GeO₄ hollow sphere.

Figure S4. Typical SEM images of the as-obtained Zn₂GeO₄ hollow spheres.

Figure S5. SEM images of the products obtained at 473 K with different TEA concentrations: (a) 2.0 g, (b) 3.0 g, and (c) 4.0 g.
Figure S6. SEM images of the products obtained at 473 K with different solvothermal treatment times of (a) 30 min, (b) 3 h, and (c) 24 h.

Figure S7. Diffuse reflectance UV-visible spectra of the Zn$_2$GeO$_4$ nanorods and Zn$_2$GeO$_4$ hollow spheres. The inset is the optical band gap energy (Eg) of the corresponding sample.

Figure S8. The periodic on/off photocurrent response of (a) bulk Zn$_2$GeO$_4$ particles, (b) Zn$_2$GeO$_4$ nanorods, and (c) Zn$_2$GeO$_4$ hollow spheres under exposure to UV light.
**Figure S9.** Photocurrent analysis of Zn$_2$GeO$_4$ hollow spheres film electrode under constant light and light/dark illumination cycles.

**Figure S10.** Typical SEM image of the Zn$_2$GeO$_4$ nanorods prepared at 473 K by a CTAB-assisted hydrothermal method.
It should be noted that in Fig. S11, most of the hierarchical Zn$_2$GeO$_4$ hollow spheres were still maintained after photoreaction, but we also observed that some hollow structures have been destroyed in present experimental conditions.

**Figure S11.** SEM image of the as-obtained Zn$_2$GeO$_4$ hollow spheres after the photocatalytic decomposition of water–methanol solution to hydrogen.

**Reference**