Electronic Supplementary Information

Facile Temperature-Controlled Synthesis of Hexagonal Zn$_2$GeO$_4$ Nanorods with Different Aspect Ratios toward Improved Photocatalytic Activities for Overall Water Splitting and Photoreduction of CO$_2$†

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Experimental sections and characterizations

Experimental sections

Sample Preparation

Na$_2$GeO$_3$ solid powders as a new precursor were prepared by heating stoichiometric mixture of Na$_2$CO$_3$ and GeO$_2$ at 900 °C for 12 h. For the preparation of Zn$_2$GeO$_4$, in a typical procedure, 40 mL of Na$_2$GeO$_3$ aquatic solution (0.025 molL$^{-1}$) was added into 40 mL of Zn(CH$_3$COO)$_2$ (0.05 molL$^{-1}$) aquatic solution. The mixed solution was magnetically stirred and oil bath heated to form Zn$_2$GeO$_4$ single crystal nanorod. The Zn$_2$GeO$_4$ nanorods were prepared at 40 °C for 15h, 60 °C for 10h, 80 °C for 5h and 100 °C for 3h, respectively. The sedimentation was separated by centrifugation, washed with deionized water and dried at 60 °C for 2h. A reference sample was prepared by heating stoichiometric mixture of GeO$_2$ and ZnO at 1300 °C for 15 h.

Characterizations

The as-prepared Zn$_2$GeO$_4$ were characterized by x-ray diffractions (XRD) for phase identification on the Rigaku Ultima diffractometer and by transmission electron microscope (TEM; FEI Tecnai G2 F30 S-Twin) and field emission scanning electron microscope (FE-SEM; NOVA230, FEI Ltd.) for microstructural observations. The specific surface area was determined by an adsorption apparatus (Micromeritics TriStar 3000, USA) based on the BET method, calculated from the linear part of the BET plot ranging from P/P$_0$ =
0.05 to P/P₀ = 0.15. The CO₂ absorption on the catalyst surface was evaluated by the above-mentioned adsorption apparatus under ambient pressure and 0°C. Ultraviolet visible (UV-vis) diffuse reflection spectra were measured using a UV-vis spectrophotometer (Shimadzu UV-2550, Japan) and converted from reflection to absorbance by the Kubelka-Munk method. The photoluminescence (PL) spectroscopy was obtained by using the Cary eclipse fluorescence spectrophotometer (USA). The Zn/Ga ratio in these as-prepared samples was analyzed on an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima-5300DV, PE, USA).

Photocatalytic activity test

Photocatalytic activities of Zn₂GeO₄ nanorods for overall water splitting were evaluated in a gas-closed circulation system. For the dispersion of RuO₂ particles on Zn₂GeO₄ as a cocatalyst, Zn₂GeO₄ photocatalyst powder of 250 mg was impregnated with ruthenium carbonyl complex, Ru₃(CO)₁₂, in THF and oxidized in air at 623 K for 4 h to convert the Ru surface species to RuO₂ particles. RuO₂ was loaded at the rate 1-4 wt % for these as-prepared Zn₂GeO₄. After loading RuO₂, no crystal morphology change and phase transformation were found, suggesting that the Zn₂GeO₄ nanorods have good thermal stability.

For the photocatalytic reactions, the RuO₂ modified Zn₂GeO₄ nanorods were dispersed in 390 mL of deionized water by a magnetic stirrer in an inner irradiation cell made of quartz. The light source was a 400 W high-pressure mercury lamp (SEN; HL400EH-5). Similarly, photocatalytic water splitting of the RuO₂ modified Zn₂GeO₄ bulks obtained by solid state reaction at 1300 °C for 15h was evaluated as a reference. The gas amounts of H₂ and O₂ from H₂O splitting were determined using gas chromatography (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier).

In the photocatalytic reduction of CO₂, Zn₂GeO₄ powder (0.1 g) was uniformly dispersed on a glass reactor with an area of 4.2 cm². A 300W Xenon arc lamp was used as the light source for the photocatalytic reaction. The volume of the reaction system was about 230 mL. The reaction setup was vacuum-treated several times, and then high-purity CO₂ gas was introduced into the reaction to achieve ambient pressure. Deionized water (0.4 mL) was injected into the reaction system as reducing agent. During the irradiation, about 1 mL of gas was taken from the reaction cell at given intervals for subsequent CH₄ concentration analysis with a gas chromatograph (GC-2014, Shimadzu Corp., Japan).
Figure S1. XRD pattern of Na$_2$GeO$_3$ powders obtained by heating the stoichiometric mixture of Na$_2$CO$_3$ and GeO$_2$ at 900 °C for 12 h. The XRD pattern is in good agreement with JCPDS 70-0754.

Figure S2. XRD patterns for Zn$_2$GeO$_4$ nanorods obtained by solution phase route at 40 °C (a) and 100 °C (b) and Zn$_2$GeO$_4$ bulks prepared by solid state reaction at 1300 °C (c).
Figure S3. A low-magnification (a) and a high-magnification (b) SEM image of the Zn₂GeO₄ nanorods prepared at 25 °C for 40 h. The XRD patterns for the Zn₂GeO₄ nanorods obtained at 25 °C for 40 h, 60 °C for 10h and 80 °C for 5 h (c).

Figure S4. Low-magnification SEM images of Zn₂GeO₄ nanorods prepared at different reaction conditions. (a) 40°C for 15h, (b) 60°C for 10h, (c) 80°C for 5h and (d) 100°C for 3h.
Figure S5. High-magnification SEM images of Zn$_2$GeO$_4$ nanorods prepared at different reaction conditions. (a) 40°C for 15h, (b) 60°C for 10h, (c) 80°C for 5h and (d) 100°C for 3h.

Figure S6. HR-TEM image of the crystal lattice of Zn$_2$GeO$_4$ nanorod. The lattice fringe of (113) with an interplanar spacing of 0.29 nm is observed at an angle of 66° to the rod direction.
Figure S7. SEM images for different growth stages of Zn$_2$GeO$_4$ nanorods. (a) 2h, (b) 4h, (c) 6h, (d) 15h. Reaction temperature: 40°C. Obviously, the formation of hole in nanorod resulted from the growth-rate difference in c-axis direction.

Figure S8. SEM images of 3wt.% RuO$_2$ loaded Zn$_2$GeO$_4$ nanorods. (a) Zn$_2$GeO$_4$ obtained at 40 °C and (b) at 100 °C. The loading RuO$_2$ onto Zn$_2$GeO$_4$ nanorods was performed at 350 °C for 4h in muffle furnace.
Figure S9. Changes in photocatalytic activity of RuO$_2$-dispersed Zn$_2$GeO$_4$ for H$_2$ and O$_2$ production with amount of RuO$_2$. (a) Zn$_2$GeO$_4$ nanorods obtained at 40°C; (b) Zn$_2$GeO$_4$ nanorods obtained at 100°C and (c) Zn$_2$GeO$_4$ bulk prepared at 1300°C.

Figure S10. A high-magnification SEM image of Zn$_2$GeO$_4$ nanorods obtained at 100 °C for 3h. The nanosteps formed on the surface of Zn$_2$GeO$_4$ nanorods.
Figure S11. SEM image of Zn$_2$GeO$_4$ bulks obtained at 1300 °C for 15 h.

Figure S12. Amount of adsorbed CO$_2$ on Zn$_2$GeO$_4$ nanorods and bulks.

Figure S13. Optical properties of Zn$_2$GeO$_4$ obtained by solution phase route and solid state reaction. (a) UV-Vis absorption spectra and (b) room temperature PL spectra with UV fluorescent light excitation of 264 nm.
**Figure S14.** The reaction setup for evaluating the H\textsubscript{2} and O\textsubscript{2} from water splitting over various Zn\textsub{2}GeO\textsub{4}. 