Electronic Supplementary Information

Facile Temperature-Controlled Synthesis of Hexagonal Zn_2GeO_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_2GeO_3 solid powders as a new precursor were prepared by heating stoichiometric mixture of Na_2CO_3 and GeO_2 at 900 ^oC for 12 h. For the preparation of Zn_2GeO_4, in a typical procedure, 40 mL of Na_2GeO_3 aquatic solution (0.025 $molL^{-1}$) was added into 40 mL of $Zn(CH_3COO)_2$ (0.05 $molL^{-1}$) aquatic solution. The mixed solution was magnetically stirred and oil bath heated to form Zn_2GeO_4 single crystal nanorod. The Zn_2GeO_4 nanorods were prepared at 40 ^oC for 15h, 60 ^oC for 10h, 80 ^oC for 5h and 100 ^oC for 3h, respectively. The sedimentation was separated by centrifugation, washed with deionized water and dried at 60 ^oC for 2h. A reference sample was prepared by heating stoichiometric mixture of GeO_2 and ZnO at 1300 ^oC for 15 h.

Characterizations

The as-prepared Zn_2GeO_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 microscop (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/P_0 = 0.15. The CO_2 absorption on the catalyst surface was evaluated by the above-mentioned adsorption apparatus under ambient pressure and 0^oC. 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 Zn_2GeO_4 nanorods for overall water splitting were evaluated in a gas-closed circulation system. For the dispersion of RuO_2 particles on Zn_2GeO_4 as a cocatalyst, Zn_2GeO_4 photocatalyst powder of 250 mg was impregnated with ruthenium carbonyl complex, $Ru_3(CO)_{12}$, in THF and oxidized in air at 623 K for 4 h to convert the Ru surface species to RuO_2 particles. RuO_2 was loaded at the rate 1-4 wt % for these as-prepared Zn_2GeO_4. After loading RuO_2, no crystal morphology change and phase transformation were found, suggesting that the Zn_2GeO_4 nanorods have good thermal stability.

For the photocatalytic reactions, the RuO_2 modified Zn_2GeO_4 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 RuO_2 modified Zn_2GeO_4 bulks obtained by solid state reaction at 1300 ^oC for 15h was evaluated as a reference. The gas amounts of H_2 and O_2 from H_2O splitting were determined using gas chromatography (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier).

In the photocatalytic reduction of CO_2, Zn_2GeO_4 powder (0.1 g) was uniformly dispersed on a glass reactor with an area of 4.2 cm^2. 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 CO_2 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 CH_4 concentration analysis with a gas chromatograph (GC-2014, Shimadzu Corp., Japan).

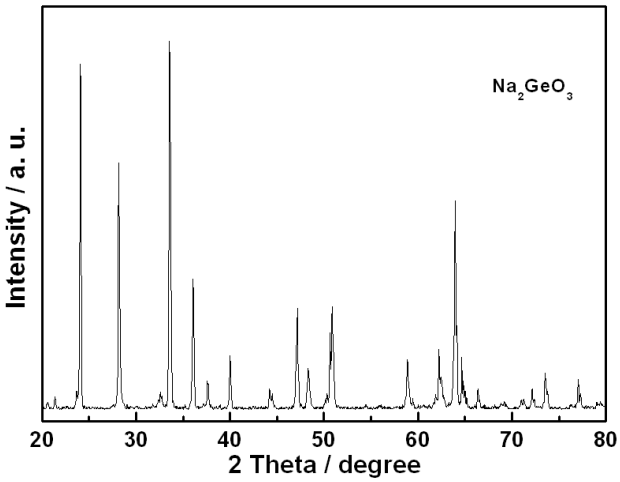

Figure S1. XRD pattern of Na_2GeO_3 powders obtained by heating the stoichiometric mixture of Na_2CO_3 and GeO_2 at 900 ^oC for 12 h. The XRD pattern is in good agreement with JCPDS 70-0754.

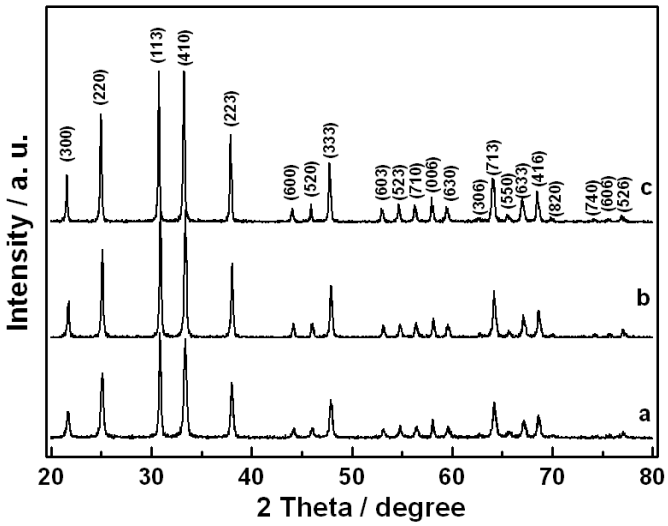

Figure S2. XRD patterns for Zn_2GeO_4 nanorods obtained by solution phase route at 40 ^oC (a) and 100 ^oC (b) and Zn_2GeO_4 bulks prepared by solid state reaction at 1300 ^oC (c).

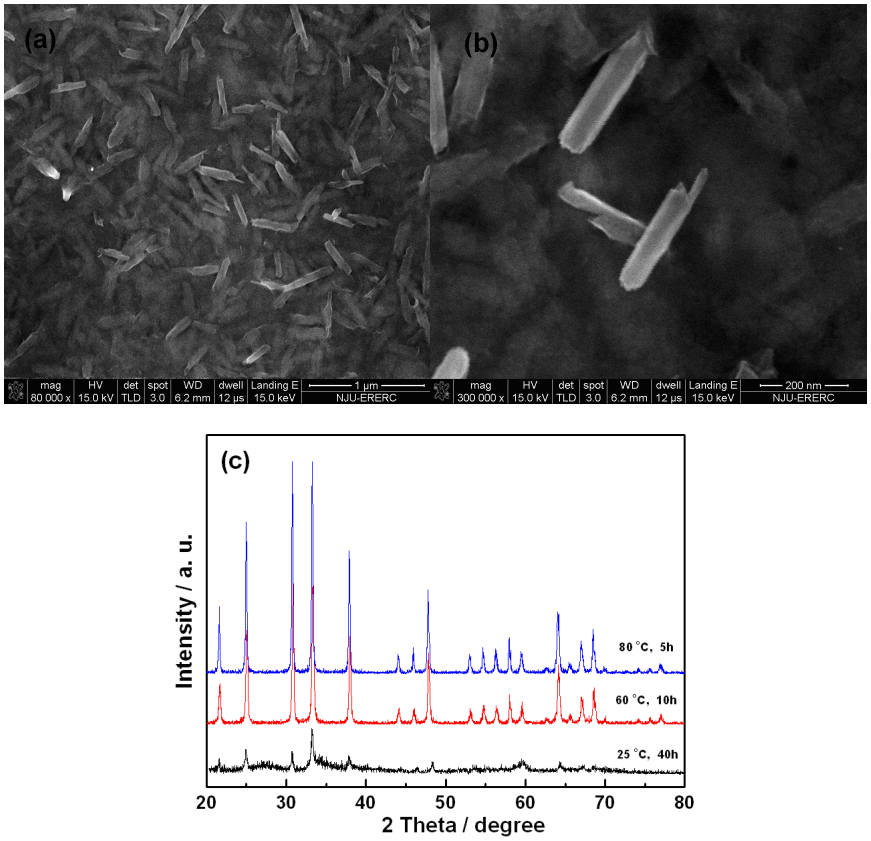

Figure S3. A low-magnification (a) and a high-magnification (b) SEM image of the Zn_2GeO_4 nanorods prepared at 25 ^oC for 40 h. The XRD patterns for the Zn_2GeO_4 nanorods obtained at 25 ^oC for 40 h, 60 ^oC for 10h and 80 ^oC for 5 h (c).

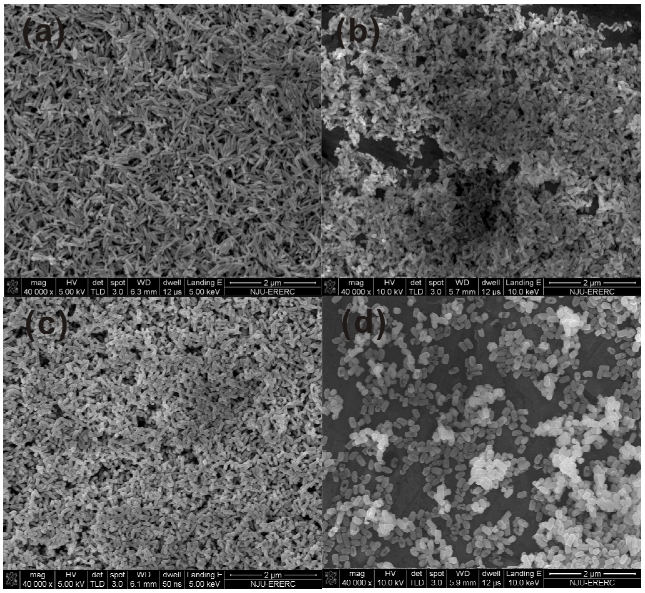

Figure S4. Low-magnification SEM images of Zn_2GeO_4 nanorods prepared at different reaction conditions. (a) 40^oC for 15h, (b) 60^oC for 10h, (c) 80^oC for 5h and (d) 100^oC for 3h.

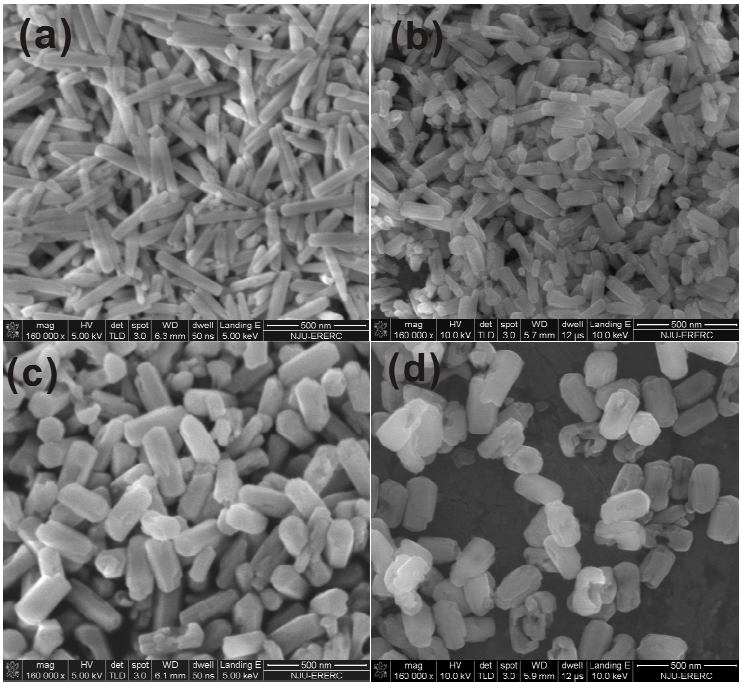

Figure S5. High-magnification SEM images of Zn_2GeO_4 nanorods prepared at different reaction conditions. (a) 40^{o}C for 15h, (b) 60^{o}C for 10h, (c) 80^{o}C for 5h and (d) 100^{o}C for 3h.

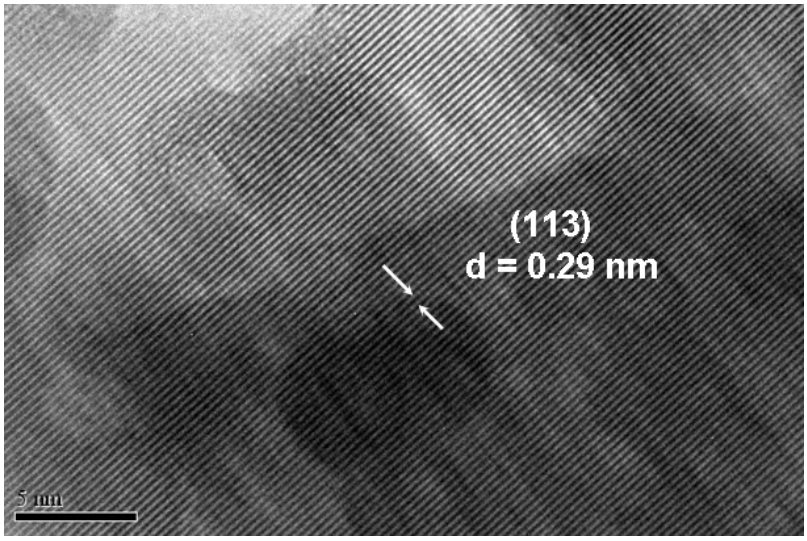

Figure S6. HR-TEM image of the crystal lattice of Zn_2GeO_4 nanorod. The lattice fringe of (113) with an interplanar spacing of 0.29 nm is observed at an angle of 66^{o} to the rod direction.

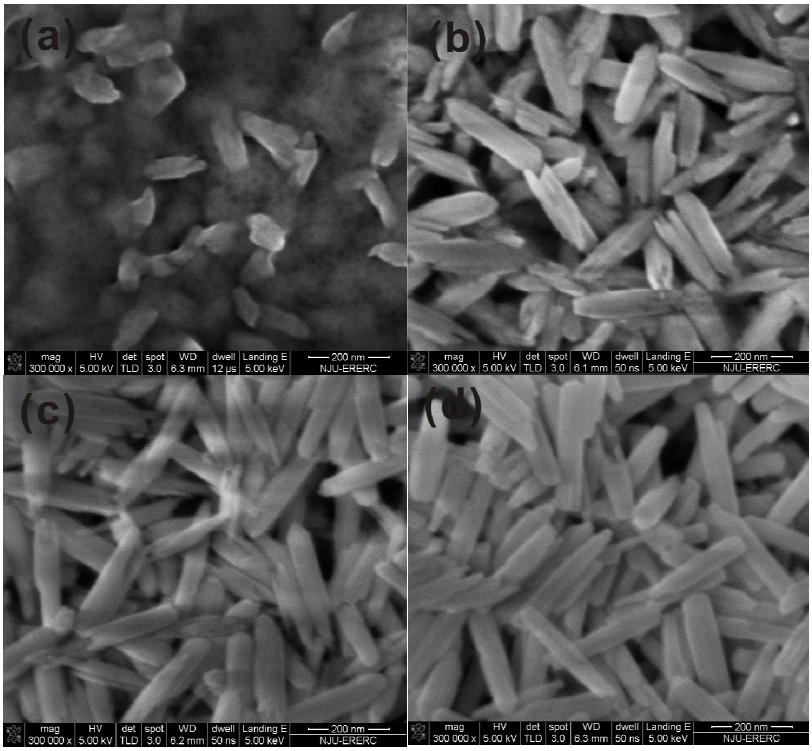

Figure S7. SEM images for different growth stages of Zn_2GeO_4 nanorods. (a) 2h,(b) 4h,(c) 6h, (d) 15h. Reaction temperature: 40^{o}C. Obviously, the formation of hole in nanorod resulted from the growth-rate difference in c-axis direction.

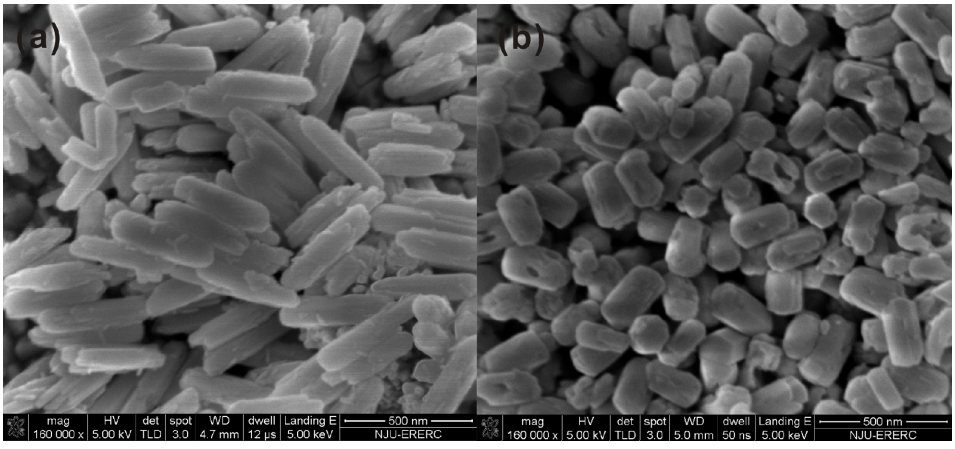

Figure S8. SEM images of 3wt.% RuO_2 loaded Zn_2GeO_4 nanorods. (a) Zn_2GeO_4 obtained at 40 ^{o}C and (b) at 100 ^{o}C. The loading RuO_2 onto Zn_2GeO_4 nanorods was performed at 350 ^{o}C for 4h in muffle furnace.

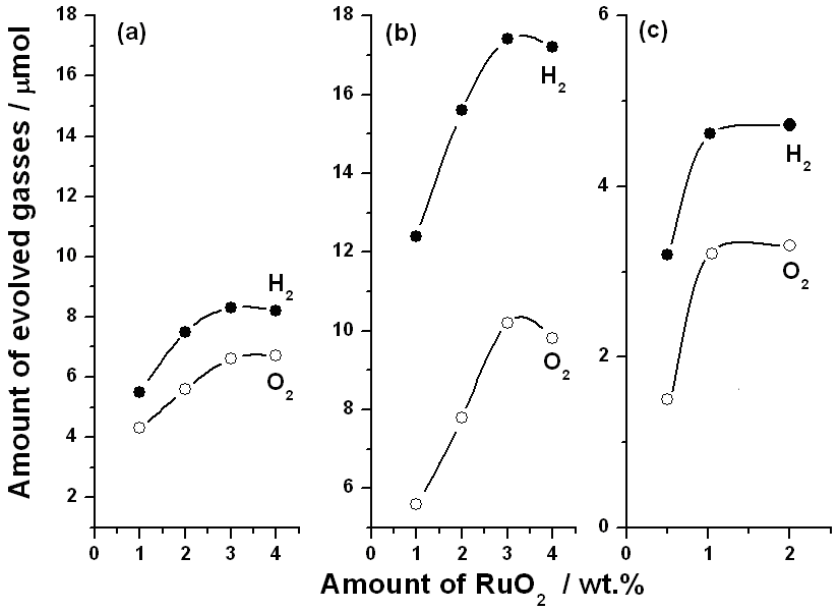

Figure S9. Changes in photocatalytic activity of RuO_2-dispersed Zn_2GeO_4 for H_2 and O_2 production with amount of RuO_2. (a) Zn_2GeO_4 nanorods obtained at 40^{o}C;(b) Zn_2GeO_4 nanorods obtained at 100^{o}C and (c) Zn_2GeO_4 bulk prepared at 1300 ^{o}C.

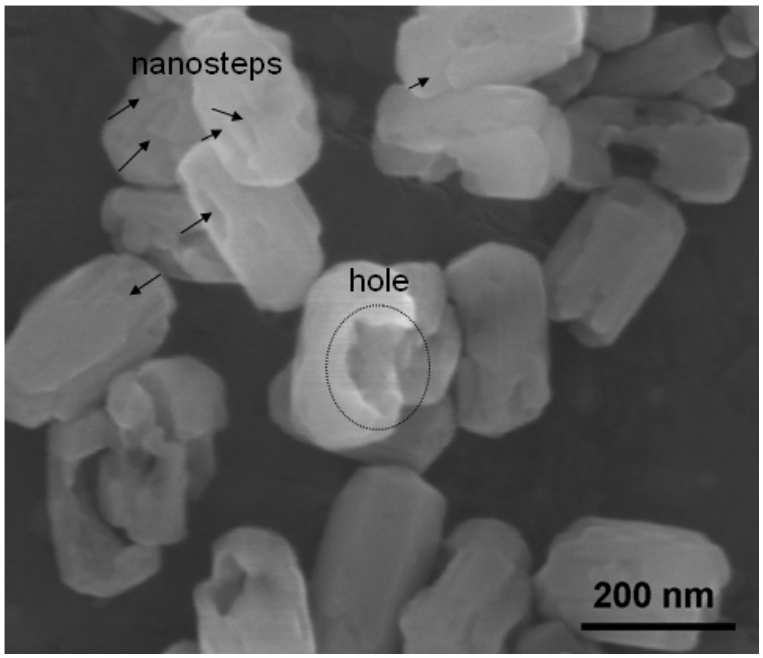

Figure S10. A high-magnification SEM image of Zn_2GeO_4 nanorods obtained at 100 ^{o}C for 3h. The nanosteps formed on the sufarce of Zn_2GeO_4 nanorods.

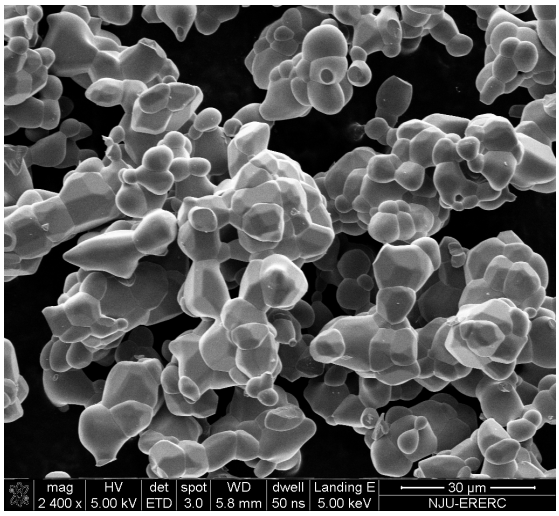

Figure S11. SEM image of Zn_2GeO_4 bulks obtained at 1300 ^oC for 15 h.

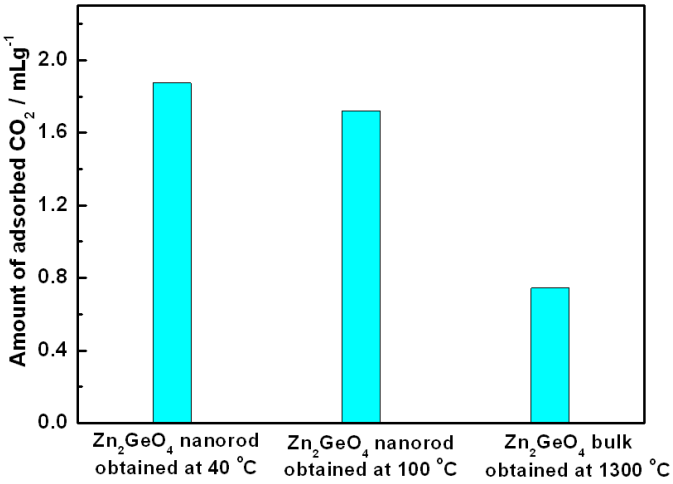

Figure S12. Amount of adsorbed CO_2 on Zn_2GeO_4 nanorods and bulks.

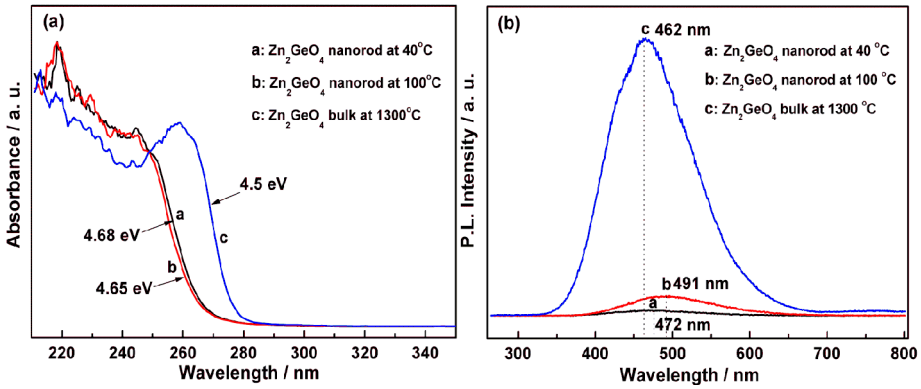

Figure S13. Optical properties of Zn_2GeO_4 obtained by solution phase route and solid state reaction. (a) UV-Vis absorption spectra and (b) room temperature PL spectra with UV fluorescent light excitation of 264 nm.

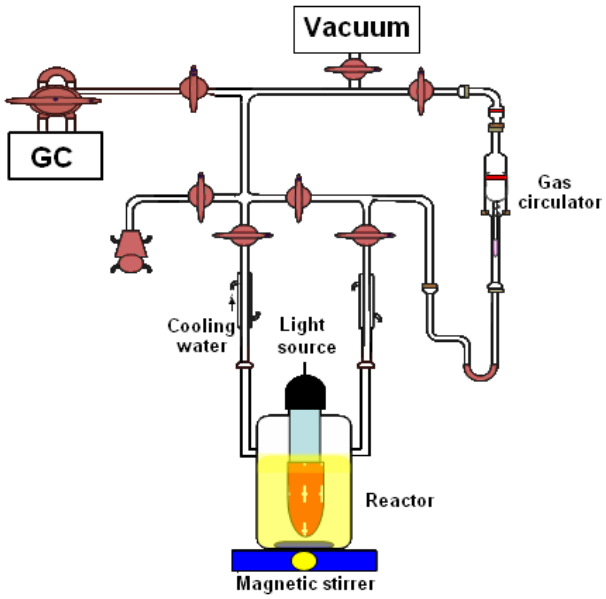

Figure S14. The reaction setup for evaluating the H_2 and O_2 from water splitting over various Zn_2GeO_4.