Supplementary Material (ESI) for Chemical Communications

Ion-Exchange Synthesis of Micro/Mesoporous Zn_2GeO_4 Photocatalyst at Room Temperature for Photoreduction of CO_2

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Supporting Information

Experimental Section

Materials preparation: The Na_2GeO_3 powders were prepared by solid state reaction route that stoichiometric mixture of Na_2CO_3 and GeO_2 were heated at 900 °C for 10 h. Mesoporous Zn_2GeO_4 was prepared as follows. 0.01mol $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in 50 mL deionized water to form a clear solution. 0.005 mol as-prepared Na_2GeO_3 was dissolved in 50 mL deionized water to form a transparent colloidal suspension of Na_2GeO_3 hydrates. Then the Na_2GeO_3 hydrates colloidal suspension was added dropwise to the $Zn(CH_3COO)_2$ solution. The mixture was stirred for 3-20 h at room temperature. The white precipitation was separated by centrifugation and then dried under vacuum at room temperature for 4 h. The loading of Pt was performed by a photocatalytic reduction method.[1] For comparison purpose, Zn_2GeO_4 was also obtained by solid-state reaction of ZnO and GeO_2 at 1200 °C for 10 h.

Photoreduction of CO_2: A 300 W Xenon arc lamp was used as the light source. The reaction was performed in a gas-closed system with a gas-circulated pump. The volume of the reaction system was about 360 mL (The scheme of reaction device is shown in Figure S7). In a typical process, Zn_2GeO_4 powder (0.2 g) was uniformly dispersed on a glass reactor with an area of 8.5 cm^2. Deionized water (0.5 mL) was injected into the reaction system as reducing agent. The reaction system was vacuum-pumped and washed with high purity CO_2 gas for several times. Then high purity CO_2 gas was introduced into the reaction system to achieve ambient pressure.

During the irradiation, about 0.5 mL of gas was sampled from the reaction cell at given intervals for subsequent CH_4 concentration analysis with a gas chromatograph (GC-14B, Shimadzu Corp., Japan).

Apparent quantum yield: The apparent quantum yield were measured by inserting 251 nm band-pass filters in front of the reaction cell to supply the irradiant light with wavelength of 251 ± 16 nm. The apparent quantum yield was calculated according to as-below equation,

$$A.Q.Y. = [N(CH_4) \times 8] / N(Photons) \times 100\%$$

in which $N(CH_4)$ and $N(Photons)$ signify the molecular number of generated CH_4 in unit time and the number of incident photons in unit time, respectively. (Generation of one CH_4 molecule will consume 8 photoelectrons, since $CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$.[2])

Characterization: X-ray diffraction patterns were characterized by a RIGAKU Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation (λ=1.54178 Å). Scanning electron microscopy images and energy-dispersive X-ray spectroscopy patterns were recorded with a JEOL 6700F field emission scanning electron microscopy. Transmission electron microscopy and high-resolution were performed with a JEOL 2100F field emission transmission electron microscopy operated at 200 kV. UV-visible diffuse reflectance spectrum was recorded with a Shimadzu UV-2500 Spectrophotometer. Brunauer-Emmett-Teller measurements were carried out in a BELSORP II Surface Area Analyzer. The zeta potential was tested in a BECKMAN COULTER Delsa Nano C Zeta-potential & particle size analyzer.

Reference

1. Z. G. Yi, J. H. Ye, *Appl. Phys. Lett.* **2007**, *91*, 254108.

2. T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature*, 1979, **277**, 637.

Supporting Figures

Figure S1. (a) SEM image, (b) nitrogen adsorption-desorption isotherms of Na_2GeO_3; (c) SEM image, (d) nitrogen absorption-desorption isotherms of the dry gel.

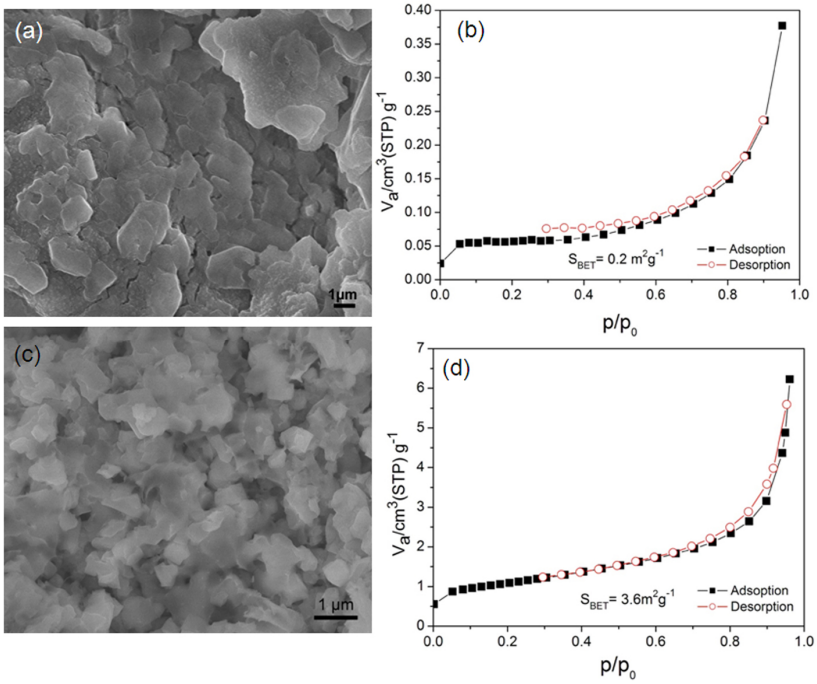

Figure S2. Tyndall scattering effect for colloidal suspension of Na_2GeO_3 hydrates is illuminating with a 635 nm laser beam.

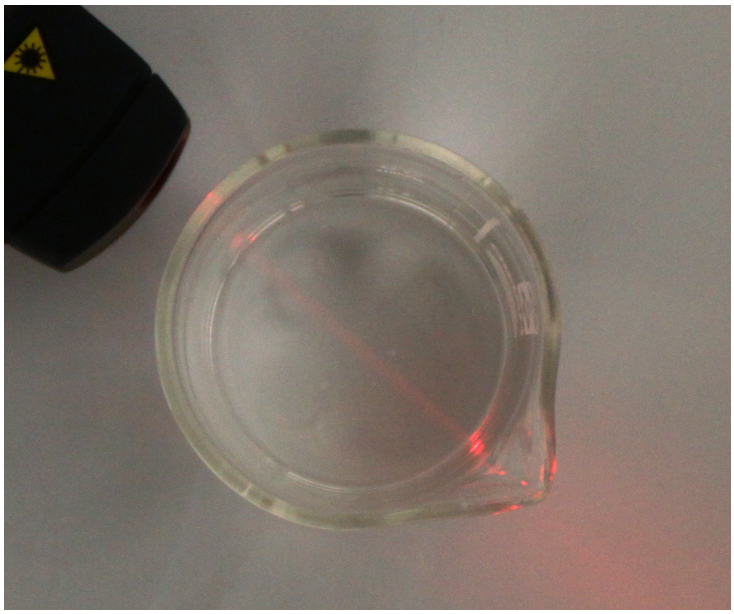

Figure S3. EDS pattern of Zn_2GeO_4 prepared at the reaction time for 12h.

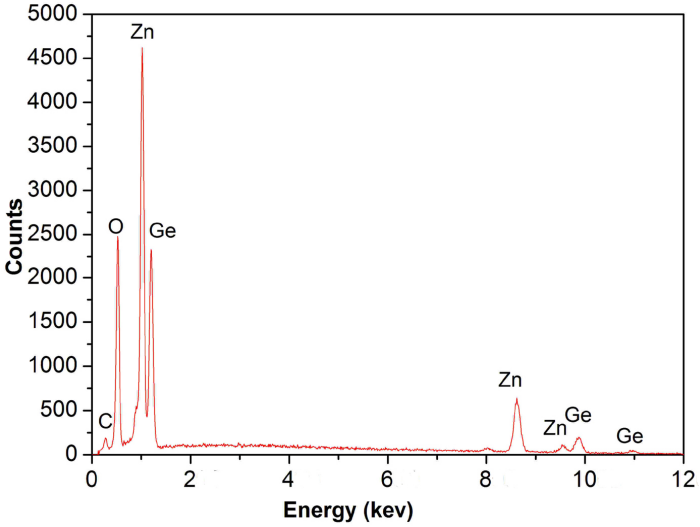

Figure S4. (a) TEM and (b) HRTEM image of Zn_2GeO_4 prepared at reaction time for 3h, which shows the amorphous erosion-like micro/mesoporous structure.

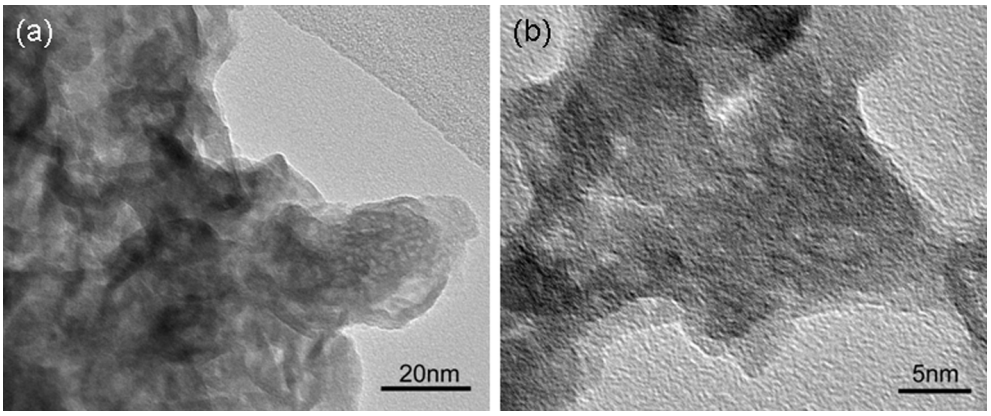

Figure S5. XRD pattern of Zn_2GeO_4 prepared at the reaction time for (a) 3h, (b) 6h, (c) 12h, and (d) 20h, which shows that the amorphous Zn_2GeO_4 gradually transformed into well crystalline Zn_2GeO_4.

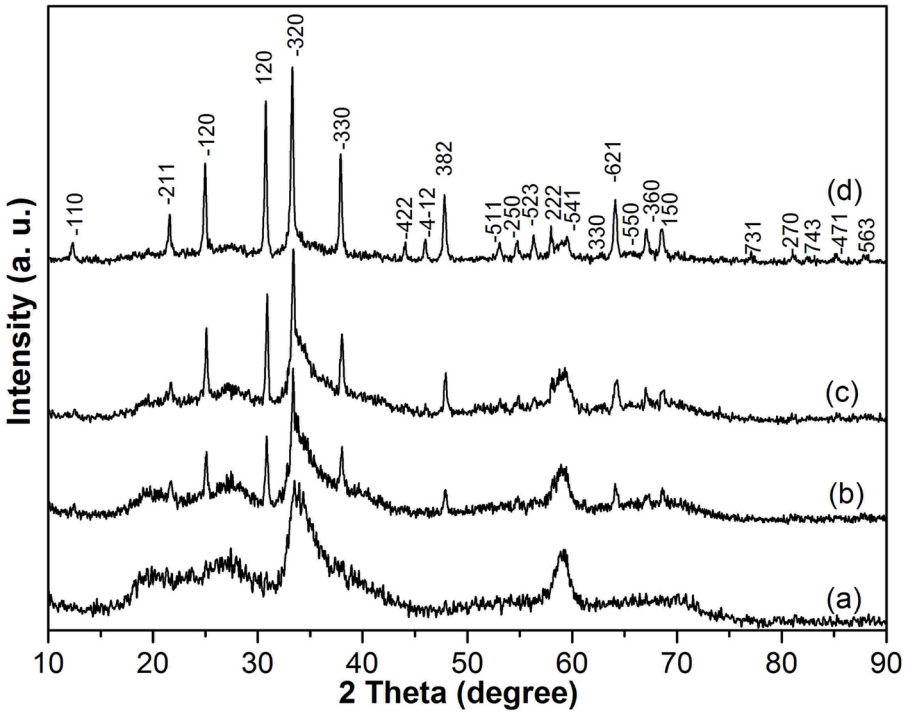

Figure S6. UV-visible diffuse reflectance spectrum of as-prepared micro/mesoporous Zn_2GeO_4 prepared at the reaction time for 12h. The inset is the calculation diagram of its band gap.

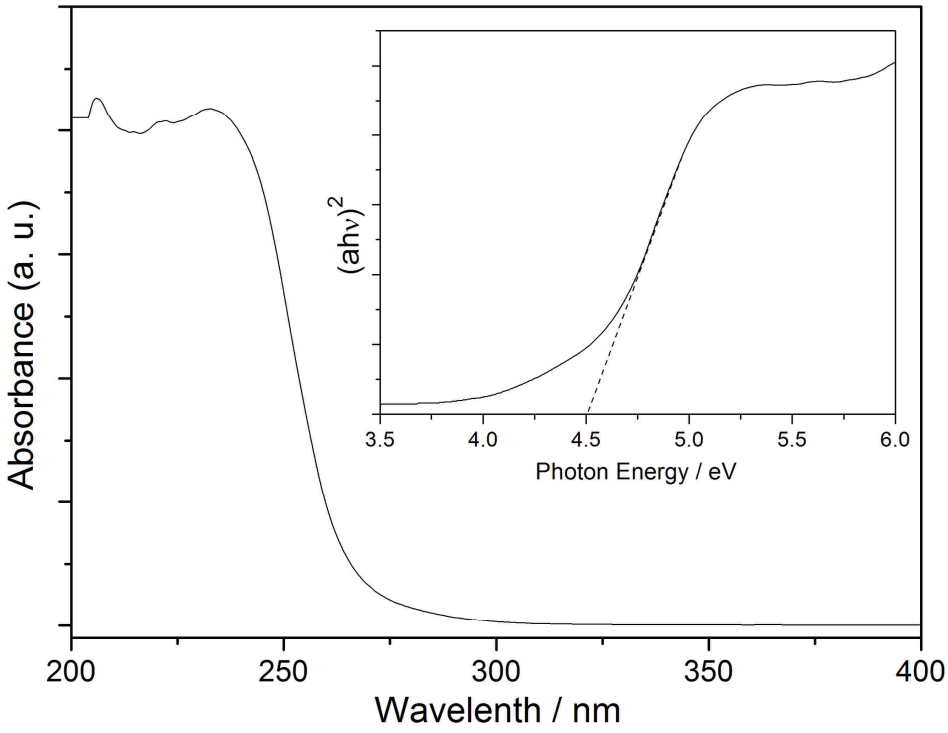

Figure S7. Evaluation System for photoreduction of CO_2

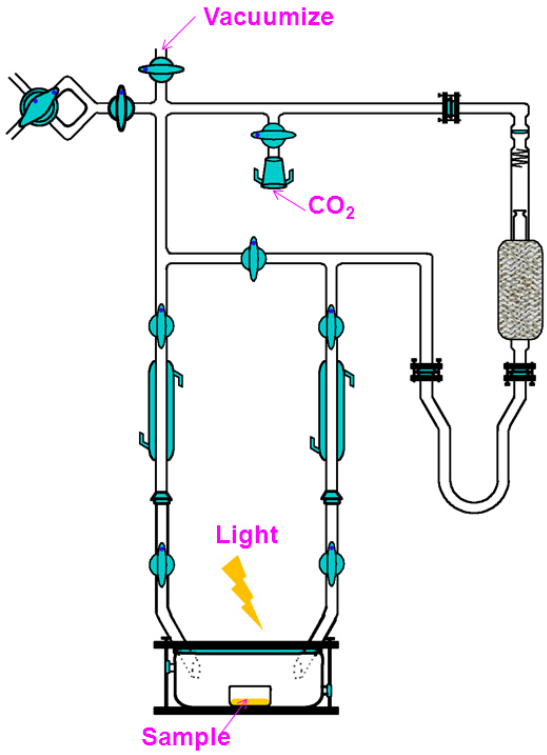

Figure S8. CH_4 evolution rates over micro/mesoporous Zn_2GeO_4 loaded with different concentrations of Pt under full arc Xe lamp irradiation.