Electronic Supplementary Information

Mesoporous Zinc Germanium Oxynitride for CO_2 Photoreduction under Visible Light

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Experimental Section

Preparation of Zn_2GeO_4

The microporous Zn_2GeO_4 were prepared by ions exchange between Na_2GeO_3 colloidal suspension and Zn^{2+} solution as we had reported before.[1] Na_2GeO_3 were prepared by a solid state reaction route that stoichiometric mixture of Na_2CO_3 and GeO_2 was heated at 900°C for 10 h. In a typical process, 0.01mol $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in 50 mL deionized water to form a clear solution. 0.005 mol 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 h at room temperature. The white precipitation was separated by centrifugation and then dried under vacuum at room temperature for about 4 h.

Preparation of ZGON

The ZGON materials were papered as follows. The as prepared microporous Zn_2GeO_4 was put in the middle of a ceramic boat. Then the ceramic boat was put into a quartz tube that placed in a horizontal furnace. The microporous Zn_2GeO_4 were heated under NH_3 flow (100 $mL{\cdot}min^{-1}$) at 800°C for 1-15 h. The increase rate of temperature was kept at 10°C per minute.

Preparation of ZGON by solid state reaction route

ZGON solid solutions were prepared by heating a mixture of ZnO and GeO_2 powders at a molar ratio of 5:1 under NH_3 flow (20 $mL{\cdot}min^{-1}$) at 850°C for 15 h.

The loading of Pt on the ZGON

The loading of Pt was performed by a photocatalytic reduction method in a closed gas circulation system. 0.3 g photocatalyst was dispersed in a methanol aqueous solution that composed of about 220 mL distilled H_2O and 50 mL CH_3OH by a magnetic stirrer in a cell with a side-window made of quartz. The platinum co-catalysts (1 wt%) was deposited onto the photocatalyst surface from H_2PtCl_6 methanol aqueous solution by in-situ photodeposition for about 3h under full arc light irradiation. After that, the precipitation was washed with deionized water and then filtrated. At last, the collected powders were dried at 100 °C for about 3 h.

CO_2 Photoreduction

A 300 W of Xenon-arc lamp with a UV-cut-off filter (L-42, Hoya Co. Japan) 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. In a typical process, 0.2 g photocatalyst was uniformly dispersed on a glass reactor with an area of 8.5 cm^2. Deionized water (3 mL) was injected into the reaction system. The reaction system was vacuum-pumped and the atmosphere was exchanged by with high purity CO_2 gas for several times. Then the high purity CO_2 gas was introduced into the reaction system until the pressure achieved about 80 kPa. 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). Before photoreduction, all samples are dried at about 140 °C for about 4 h and then irradiated by full arc light under vacuum-pumped environment for about 5 h to remove the possible adsorbed organics.

Characterizations

X-ray diffraction patterns (XRD) were characterized by a RIGAKU Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation (λ=1.54178Å). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), selected area electron diffraction (SAED) patterns, and energy-dispersive X-ray elemental mapping were performed with a JEOL 2100F field emission transmission electron microscope operated at 200 kV. 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. The chemical composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Iris Advantage, Nippon Jarrell-Ash Co., Japan) and a TC-436AR Oxygen/Nitrogen determinator (LECO Co., United States of America).

Figures and Captions

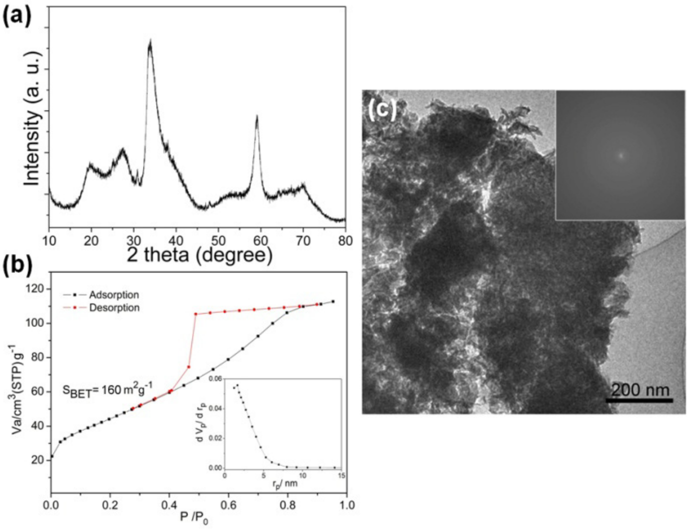

Fig. S1 (a) XRD pattern, (b) Nitrogen adsorption-desorption isotherms and pore size distribution (inset), and (c) TEM image and SAED pattern (inset) of microporous Zn_2GeO_4.

The XRD pattern for the Zn_2GeO_4 prepared by ions exchange at room temperature for 3 h is shown in Fig. S1a, exhibiting that the product is amorphous phase. As we previously reported,[1] the amorphous phase of Zn_2GeO_4 could be converted to well crystallized Zn_2GeO_4 when prolonging the reaction time to 20 h. The nitrogen adsorption-desorption isotherms of the amorphous Zn_2GeO_4 exhibit an obvious porous characteristic (see Fig. S1b). The BET surface area is about 162.7 m^2g^{-1}. The average pore size is less than 1.6 nm calculated from the Barrett-Joyner-Halenda (BJH) method, indicating that micropores exist. The transmission electron microscopy (TEM) image in Fig. c shows that the product is wormhole-like structure. The typical crystal diffraction spots or rings are not observed in the SAED pattern (inset of Fig. S1b), which confirms the amorphous phase property of the microporous Zn_2GeO_4.

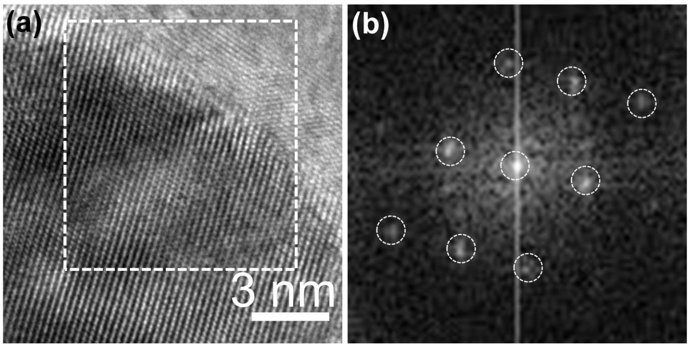

Fig. S2 (a) Magnified HRTEM image and (b) Fast Fourier Transform (FFT) of mesoporous ZGON from the marked square in HRTEM image.

Fig. S2a shows the enlarged HRTEM images of Fig. 1, which exhibits a typical single crystal lattice. The fast fourier transform (FFT) pattern (Fig. S2b) from the marked square of the HRTEM image further confirms that this particle is single crystal.

Table S1. Characterizations of the ZGON samples

Reaction Time (h)	Element Content (at%)					BET areas (m^2g^{-1})
	Zn	Ge	N	O	Chemical Composition	
1	24.16	21.98	42.21	11.64	$Zn_{1.10}GeN_{1.92}O_{0.53}$	35.6
5	22.51	23.19	45.11	9.17	$Zn_{0.97}GeN_{1.95}O_{0.39}$	30.5
10	21.90	24.18	45.33	8.60	$Zn_{0.91}GeN_{1.87}O_{0.36}$	24.4
15	22.43	24.95	47.50	5.13	-	13.9

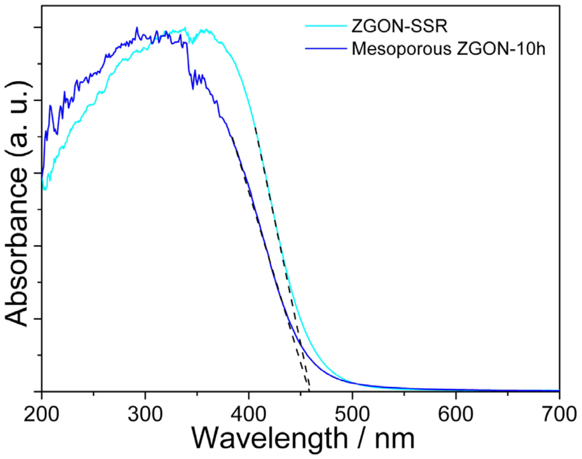

Fig. S3 UV-visible diffuse reflectance spectrum of ZGON-SSR and mesoporous ZGON nitridized at 10 h. The band-gaps were estimated to be 2.70 eV for both ZGON-SSR and mesoporous ZGON nitridized at 10 h.

The adsorption band edge between mesoporous ZGON prepared at 10 h and ZGON-SSR are almost same (from UV-Vis data, at around 459 nm. Therefore bandgaps are estimated to be 2.70 eV) and the BET surfaces area for the mesoporous ZGON was much higher than the ZGON-SSR (24.4 m^2g^{-1} vs. 3.3 m^2g^{-1}). Thus, the higher activity for the mesoporous ZGON prepared at 10 h was ascribed to the strong gas adsorption and greater number of reaction sites, arising from high specific surface area of the meosporous structure.

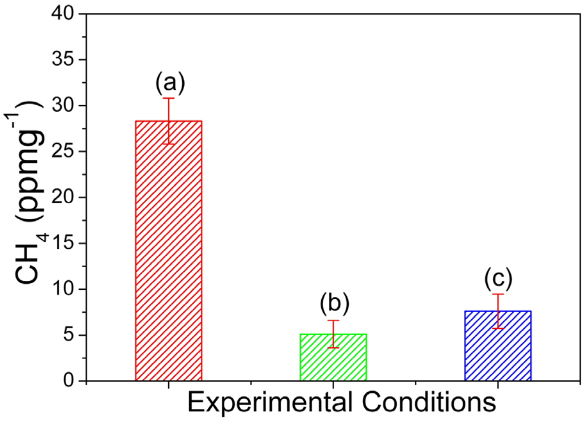

Fig. S4 Detected CH_4 over mesoporous ZGON prepared at 10 h (with 1 wt% Pt loaded) at control experiments in the atmosphere with (a) injection of pure CO_2 gas and 3 mL H_2O; (b) injection of pure CO_2 gas, without H_2O; (c) 3 mL H_2O and injection of pure Ar gas instead of pure CO_2. The control experiments were done under visible light irradiation (300 W Xenon arc lamp, $\lambda > 400$ nm), and the irradiation time was 10 h.

To confirm that the CH_4 was generated from the photoreduction of CO_2 via the protons released from H_2O oxidization and photogenerated electrons, control experiments in the absence of H_2O or pure CO_2 gas injected were performed. Compared with the normal conditions (experiment (a)), there was little CH_4 detected when the reaction proceeded under such conditions (experiment (b) and (c)). The samples could absorb air and desorb it when irradiated by the light. The low content of CH_4 detected in the control experiment (b) was mainly from the desorbed air. In control experiment (c), where there was no pure CO_2 gas injected, about 400 ppm of CO_2 was detected after a 10 hour irradiation time under visible light; the CO_2 gas was most likely released from the surface of the sample which adsorbed during the preparation of materials. Thus, the CH_4 detected in control experiment (c) arose not only as part of the desorbed air, but also as a product of CO_2 photoreduction between H_2O and released CO_2.

About the O_2 evolution during the CO_2 photoreduction

In our experiments, the produced O_2 is calculated to be ~0.9 μmolg^{-1}, according to the equation $CO_2 + 2H_2O = CH_4 + 2O_2$. However, there was no oxygen evolution detected in all of the above CO_2 photo-reduction processes. There are two possible reasons. The first is that the oxygen from CO_2/H_2O seems to be incorporated into the ZGON powder, which is expected to simultaneously result in the consumption of oxygen deficiencies in ZGON materials. That is similar to our previous report.[2] Secondly, as the produced concentration of O_2 is quite low, it is easily absorbed by the ZGON materials by the way of chemical adsorption.

Different amount of water on the CO_2 photoreduction

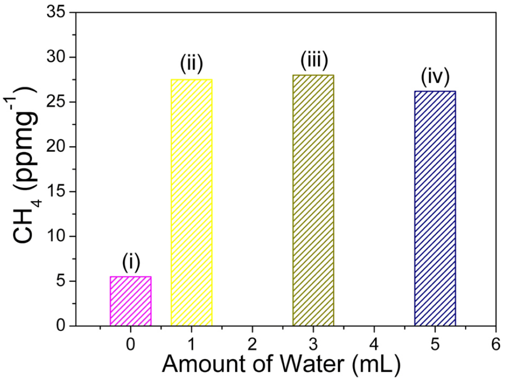

Fig. S5, Detected CH_4 over mesoporous ZGON prepared at 10 h (with 1 wt% Pt loaded) at control experiments in the atmosphere with injection of pure CO_2 gas and different amount of water: (i) 0 mL H_2O, (ii) 1 mL H_2O, (iii) 3 mL H_2O, (iv) 5 mL H_2O. The control experiments were done under visible light irradiation (300 W Xenon arc lamp, $\lambda >$ 400 nm), and the irradiation time was 10 h.

Fig. S5 shows the detected concentration of CH_4 after 10 hrs irradiation under visible light. There was very little CH_4 detected when there was no water added. When 1, 3, and 5 mL water added, the detected CH_4 were almost same. These results indicate that 1 mL H_2O was enough to make the reaction system reach saturated water vapour and more water added cannot improve the production of CH_4.

Reference

1 N. Zhang, S. Ouyang, P. Li, Y. Zhang, G. Xi, T. Kako, J. Ye, *Chem. Commun.* 2011, **47**, 2041.

2 K. Xie, N. Umezawa, N. Zhang, P. Reunchan, Y. Zhang, J. Ye, *Energy Environ. Sci.*, 2011, **4**, 4211.