Electronic Supplementary Information

Mesoporous Zinc Germanium Oxynitride for CO₂ Photoreduction under Visible Light

Ning Zhang, a,b Shuxin Ouyang, b Tetsuya Kako, a,b and Jinhua Ye * a,b,c

a Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, Japan.
Fax: (+81)-29-859-2301; E-mail: Jinhua.Ye@nims.go.jp

b Catalytic Materials Group, Research Unit for Environmental Remediation Materials, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki, Japan.

c TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, P. R. China.
Experimental Section

Preparation of Zn$_2$GeO$_4$

The microporous Zn$_2$GeO$_4$ were prepared by ions exchange between Na$_2$GeO$_3$ colloidal suspension and Zn$^{2+}$ solution as we had reported before. Superscript 1 Na$_2$GeO$_3$ were prepared by a solid state reaction route that stoichiometric mixture of Na$_2$CO$_3$ and GeO$_2$ was heated at 900°C for 10 h. In a typical process, 0.01 mol Zn(CH$_3$COO)$_2$·2H$_2$O was dissolved in 50 mL deionized water to form a clear solution. 0.005 mol Na$_2$GeO$_3$ was dissolved in 50 mL deionized water to form a transparent colloidal suspension of Na$_2$GeO$_3$ hydrates. Then the Na$_2$GeO$_3$ hydrates colloidal suspension was added dropwise to the Zn(CH$_3$COO)$_2$ 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$_2$GeO$_4$ 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$_2$GeO$_4$ were heated under NH$_3$ flow (100 mL·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·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$_2$O and 50 mL CH$_3$OH 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$_2$PtCl$_6$ methanol aqueous solution by in-situ photodeposition for about 3 h 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.

**CO₂ 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 cm². 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 CO₂ gas for several times. Then the high purity CO₂ 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 CH₄ 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$_2$GeO$_4$.

The XRD pattern for the Zn$_2$GeO$_4$ 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$_2$GeO$_4$ could be converted to well crystallized Zn$_2$GeO$_4$ when prolonging the reaction time to 20 h. The nitrogen adsorption-desorption isotherms of the amorphous Zn$_2$GeO$_4$ exhibit an obvious porous characteristic (see Fig. S1b). The BET surface area is about 162.7 m$^2$g$^{-1}$. 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$_2$GeO$_4$. 
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

<table>
<thead>
<tr>
<th>Reaction Time (h)</th>
<th>Element Content (at%)</th>
<th>BET areas (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Ge</td>
</tr>
<tr>
<td>1</td>
<td>24.16</td>
<td>21.98</td>
</tr>
<tr>
<td>5</td>
<td>22.51</td>
<td>23.19</td>
</tr>
<tr>
<td>10</td>
<td>21.90</td>
<td>24.18</td>
</tr>
<tr>
<td>15</td>
<td>22.43</td>
<td>24.95</td>
</tr>
</tbody>
</table>
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 m² g⁻¹ vs. 3.3 m² g⁻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 mesoporous structure.
Fig. S4 Detected CH₄ over mesoporous ZGON prepared at 10 h (with 1 wt% Pt loaded) at control experiments in the atmosphere with (a) injection of pure CO₂ gas and 3 mL H₂O; (b) injection of pure CO₂ gas, without H₂O; (c) 3 mL H₂O and injection of pure Ar gas instead of pure CO₂. The control experiments were done under visible light irradiation (300 W Xenon arc lamp, λ > 400 nm), and the irradiation time was 10 h.

To confirm that the CH₄ was generated from the photoreduction of CO₂ via the protons released from H₂O oxidization and photogenerated electrons, control experiments in the absence of H₂O or pure CO₂ gas injected were performed. Compared with the normal conditions (experiment (a)), there was little CH₄ 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 CH₄ detected in the control experiment (b) was mainly from the desorbed air. In control experiment (c), where there was no pure CO₂ gas injected, about 400 ppm of CO₂ was detected after a 10 hour irradiation time under visible light; the CO₂ gas was most likely released from the surface of the sample which adsorbed during the preparation of materials. Thus, the CH₄ detected in control experiment (c) arose not only as part of the desorbed air, but also as a product of CO₂ photoreduction between H₂O and released CO₂.
About the O₂ evolution during the CO₂ photoreduction

In our experiments, the produced O₂ is calculated to be ~0.9 μmol g⁻¹, according to the equation \( \text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2 \). However, there was no oxygen evolution detected in all of the above CO₂ photo-reduction processes. There are two possible reasons. The first is that the oxygen from CO₂/H₂O 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 O₂ is quite low, it is easily absorbed by the ZGON materials by the way of chemical adsorption.
Different amount of water on the CO\textsubscript{2} photoreduction

Fig. S5, Detected CH\textsubscript{4} over mesoporous ZGON prepared at 10 h (with 1 wt\% Pt loaded) at control experiments in the atmosphere with injection of pure CO\textsubscript{2} gas and different amount of water: (i) 0 mL H\textsubscript{2}O, (ii) 1 mL H\textsubscript{2}O, (iii) 3 mL H\textsubscript{2}O, (iv) 5 mL H\textsubscript{2}O. 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\textsubscript{4} after 10 hrs irradiation under visible light. There was very little CH\textsubscript{4} detected when there was no water added. When 1, 3, and 5 mL water added, the detected CH\textsubscript{4} were almost same. These results indicate that 1 mL H\textsubscript{2}O was enough to make the reaction system reach saturated water vapour and more water added cannot improve the production of CH\textsubscript{4}.
Reference
