Supporting Information

In situ synthesis of ordered mesoporous Co-doped TiO₂ and their enhanced photocatalytic activities and selectivities in reduction of CO₂

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Additional experimental section:

1 Synthesis of reference samples

For purposes of comparison in the same reactor system, we synthesize or buy some typical semiconductors or composites, including Degussa P-25, N-doped TiO₂, Au/TiO₂, C₃N₄, WO₃). The performance and characteristics of these materials are shown in Fig. S8 and Table S2. Degussa P-25(TiO₂) was bought from Evonik-Degussa; ST-01(TiO₂) and WO₃ were bought from Wako pure chemical industries.

Synthesis of N-doped TiO₂: in a typical preparation, a certain amount of ST-01 was annealed in a tubular furnace at 550 °C for 2 h under NH₃ atmosphere. The sample was named as N-TiO₂.

Synthesis of Au/TiO₂: in a typical preparation, ordered mesoporous TiO₂ (OMT) powder was immersed into a certain amount of HAuCl₄ aqueous solution. Then, a small amount of ascorbic acid aqueous solution was added to reduce Au. The theoretical weight percentage of Au is about 7%. The sample was named as Au-OMT.

Synthesis of bulk g-C₃N₄: in a typical preparation, a certain amount of dicyandiamide was annealed in a tubular furnace at 550 °C for 4 h under air atmosphere.
2 Calculation of the quantum efficiency

On the basis of the assumption that a photon must be effectively absorbed, the photocatalytic quantum efficiency (QE) is typically defined as the ratio of the rate of photocatalytic events to the absorbed photons.\(^{2,3}\)

\[
\text{QE} = \frac{N_{\text{photocat. events}}}{N_{\text{absorbed photons}}}
\]

The photocatalytic events have to be summed over the (molar) amounts of all the products, \(N_{\text{photocat. events}} = \sum n_i M_i\). Where \(n_i\) is the number of electrons required to obtain one molecule of product \(M_i\).
Fig. S1 TG/DTA curves of F127 (a) recorded in N₂ and Co-OMT-1 (b) recorded in air
**Fig. S2** (a) The photo of Co$_3$O$_4$ before and after dissolving by HCl. (b) The photos of Co-doped TiO$_2$ dissolving by HCl to remove the Co$_3$O$_4$.

**Table S1** The molar ratio of samples before and after removing the Co$_3$O$_4$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical molar ratio (Co: Ti)$^a$</th>
<th>Practical molar ratio (Co: Ti)$^b$</th>
<th>Doping levels of Co$^{2+}$ (Co: Ti)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMT</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co-OMT-1</td>
<td>0.002</td>
<td>0.0023</td>
<td>0.0020</td>
</tr>
<tr>
<td>Co-OMT-2</td>
<td>0.005</td>
<td>0.0049</td>
<td>0.0021</td>
</tr>
<tr>
<td>Co-OMT-3</td>
<td>0.01</td>
<td>0.013</td>
<td>0.0040</td>
</tr>
<tr>
<td>Co-OMT-4</td>
<td>0.025</td>
<td>0.026</td>
<td>0.0041</td>
</tr>
<tr>
<td>Co-OMT-5</td>
<td>0.05</td>
<td>0.053</td>
<td>0.0049</td>
</tr>
<tr>
<td>Co-OMT-6</td>
<td>0.1</td>
<td>0.12</td>
<td>0.0063</td>
</tr>
<tr>
<td>Co-OMT-7</td>
<td>0.15</td>
<td>0.15</td>
<td>0.0064</td>
</tr>
<tr>
<td>Co-OMT-8</td>
<td>0.2</td>
<td>0.25</td>
<td>0.0045</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] The value is calculated according to the additive amount in the synthetic process.
[b] The value is calculated according to the EDX analysis before removing the Co$_3$O$_4$.
[c] The value is calculated according to the EDX analysis after removing the Co$_3$O$_4$. 
Fig. S3 FE-SEM images of samples: (a) OMT, (b) Co-OMT-1, (c) Co-OMT-2, (d) Co-OMT-3, (e) Co-OMT-4, (f) Co-OMT-5, (g) Co-OMT-6, (h) Co-OMT-7, (i) Co-OMT-8.
Fig. S4 (a) FE-SEM and (b,c,d) TEM images of Co$_3$O$_4$. 
Fig. S5 X-ray photoelectron spectroscopy of samples.
Fig. S6 The Tauc plots of samples.
**Fig. S7** CH$_4$ evolution over Co-OMT-4, Co-OMT-7 and Co-OMT-8 under visible light.
Fig. S8 (a) Wide-angle XRD patterns, (b) UV-vis absorption spectra and (c) N$_2$ adsorption-desorption isotherms of samples.

The wide-angle XRD patterns of samples were shown in Fig. S8a. We can see that P25 presents a mixture of anatase and rutile; N-TiO$_2$ presents anatase; Au-OMT...
presents a mixture of anatase and gold. The characteristic peaks of C₃N₄ are same as the previous reports. UV-visible absorption spectra (Fig. S8b) show that all samples except P25, possess the optical absorption capability in the visible light region. The specific surface areas of P25, N-TiO₂, Au-OMT, C₃N₄, WO₃ were 54.4, 53.6, 181.0, 5.2, 5.4 m² g⁻¹, respectively (calculated by the BET method from N₂ adsorption-desorption isotherms in Figure S8c).

### Table S2 Summary of the various photocatalytic systems employed for CO₂ reduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co-catalyst</th>
<th>Light source</th>
<th>Conditions</th>
<th>Major products</th>
<th>R₂max⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-OMT-4</td>
<td>-</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄ CO</td>
<td>0.09</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UV-Vis light: 300 W Xe lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.33</td>
<td>This study</td>
</tr>
<tr>
<td>P25</td>
<td>-</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.015</td>
<td>This study</td>
</tr>
<tr>
<td>N-TiO₂</td>
<td>-</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.018</td>
<td>This study</td>
</tr>
<tr>
<td>Au-OMT</td>
<td>-</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.031</td>
<td>This study</td>
</tr>
<tr>
<td>C₃N₄</td>
<td>-</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.005</td>
<td>This study</td>
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<tr>
<td>WO₃</td>
<td>-</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.017</td>
<td>This study</td>
</tr>
<tr>
<td>ZnAl₂O₄-modified mesoporous ZnGaNO 0.5 wt% Pt</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.0092</td>
<td>R4</td>
<td></td>
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<tr>
<td>RGO–CdS nanorod composite</td>
<td>-</td>
<td>Visible light: 300 W Xe lamp with a cut-off filter (λ&gt;420 nm)</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>2.51</td>
<td>R5</td>
</tr>
<tr>
<td>P25</td>
<td>-</td>
<td>UV-Vis light: 300 W Xe lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.0027</td>
<td>R6</td>
</tr>
<tr>
<td>Ordered</td>
<td>-</td>
<td>UV-Vis light: 300 W Xe lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄</td>
<td>0.19</td>
<td>R6</td>
</tr>
<tr>
<td>Material</td>
<td>Treated Material</td>
<td>UV-Vis Light</td>
<td>Catalyst</td>
<td>CO Conversion (%)</td>
<td></td>
<td></td>
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<tr>
<td>--------------------------------</td>
<td>---------------------------</td>
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<td></td>
</tr>
<tr>
<td>mesoporous TiO₂</td>
<td>Xe lamp</td>
<td>vapor</td>
<td>CO</td>
<td>0.15</td>
<td></td>
<td></td>
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<tr>
<td>Zn₂GeO₄ nanobelt</td>
<td>1 wt % Pt and 1 wt % RuO₂</td>
<td>UV-Vis light: 300 W Xe lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄ 0.025</td>
<td></td>
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<tr>
<td>Anatase TiO₂ rods with {010} facets</td>
<td>1 wt % Pt</td>
<td>UV-Vis light: 300 W Xe lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄ 0.0057</td>
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<td></td>
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<tr>
<td>Hollow anatase TiO₂ single crystals with {101} facets</td>
<td>1 wt % RuO₂</td>
<td>UV-Vis light: 300 W Xe lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄ 0.0017</td>
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<td></td>
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<tr>
<td>Leaf-architected SrTiO₃</td>
<td>1 wt % Au</td>
<td>UV-Vis light: 300 W Xe arc lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄ 0.28 CO 0.35</td>
<td></td>
<td></td>
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<tr>
<td>NaTaO₃</td>
<td>1 wt % Au</td>
<td>UV-Vis light: 200 W Hg-Xe arc lamp</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄ 0.036 CO 0.17</td>
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<td></td>
</tr>
<tr>
<td>TiO₂ nanorod</td>
<td>Ag</td>
<td>UV light: four 8 W UVA lamps with a wavelength of 365 nm</td>
<td>CO₂ and H₂O vapor</td>
<td>CH₄ 2.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brookite TiO₂ nanorods</td>
<td>0.05 wt% Au</td>
<td>UV light: a light-emitting diode (Nichia, NCCU033), which emitted light at a wavelength of ca. 365 nm</td>
<td>5 mL of 0.2 mol L⁻¹ KHCO₃ aqueous solution saturated with CO₂</td>
<td>CH₃OH 0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In-doped TiO₂</td>
<td>-</td>
<td>UV-vis light: 500W mercury (Hg) flash lamp</td>
<td>CO₂ and H₂O vapor, 0.2 bars reactor pressure, 373K reaction temperature</td>
<td>CH₄ 243.75 CO 81.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO/TiO₂ nanotube film</td>
<td>Pt</td>
<td>UV-vis light: 300W high pressure Hg lamp</td>
<td>0.1 mol L⁻¹ KHCO₃ solution</td>
<td>CH₄ 100.22(b)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Maximum formation rate reported for the major product(s), in μmol g⁻¹ h⁻¹.
[b] In ppm h⁻¹ cm⁻¹.
Fig. S9 GC-MS spectra of the products of photocatalytic $^{13}$CO$_2$ reduction over (a) Co-OMT-4 and (b) Co-OMT-7 after 12 h irradiation.
Fig. S10 Electronic structures of (a) anatase TiO$_2$ and (b) Co$_x$Ti$_{1-x}$O$_2$ (x=0.0625).
Fig. S11 Valence band XPS spectra of samples. The values in Fig. are the relative difference between the Co-OMT-x and OMT.
Fig. S12 Mott-Schottky plots of samples: (a) OMT, (b) OMT, (c) Co-OMT-1, (d) Co-OMT-4, (e) Co-OMT-6, (f) Co-OMT-7.
References


R13. T. Ohno, T. Higo, N. Murakami, H. Saito, Q. Zhang, Y. Yang and T. Tsubot, 

