Supplementary Information

High–efficiency photoreduction of CO\(_2\) in low vacuum

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Figure S1. Photocatalytic CO₂ reduction system with online gas analysis. (a) Schematic and (b) photograph.
The total gas pressure:

\[ P_{\text{total}} = P_{\text{CO}_2} + P_{\text{H}_2\text{O}} \]

According to the Ideal Gas Law:

\[ P = \frac{nRT}{V} \]

Where \( P \) is the absolute pressure, \( V \) is the volume, \( T \) is the absolute temperature (T). \( n \) is the number of moles, \( R \) is the universal gas constant, 8.3145 J/mol K.

In this system, \( R \), \( T \) and \( V \) is constant.

If we set,

\[ a = \frac{RT}{V} \]

Then,

\[ P = a \times n \]

Thus,

\[ P_{\text{total}} = P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = a \times n_{\text{CO}_2} + a \times n_{\text{H}_2\text{O}} \]

\[ n_{\text{CO}_2} = \frac{1}{a} \times P_{\text{total}} - n_{\text{H}_2\text{O}} \]

From the linear correlation between the absolute gas pressure and \( \text{CO}_2 \) content in Figure S2, the \( \text{H}_2\text{O} \) content in the system is constant and approximately 0.16 mmol.

**Figure S2.** Absolute gas pressure vs. \( \text{CO}_2 \) content and the approximate \( \text{H}_2\text{O} \) content.
Figure S3. Schematic of the reactor.
Figure S4. Experimental procedure in this work.
Figure S5. Temperature of the titanium oxide covered glass slide during irradiation.
Figure S6. CH₄ yield at 390 K with and without irradiation.
Figure S7. Physical characterizations of the commercial α-TiO₂. (a) XRD pattern of the commercial α-TiO₂. (101) is the most stable lattice plane. (b) Absorption spectrum of the commercial α-TiO₂ covered glass slide. Inset is the Mott-Schottky curve. (c-d) TEM images. Inset is the EDS spectrum. (e) HAADF image and the corresponding elemental mappings of O and Ti.
**Figure S8.** Gas chromatography curves of CH$_4$ in different CO$_2$ ratios.
Figure S9. Calibration curves of the gas chromatography of CH₄ at different pressures.
Figure S10. Gas chromatography curves of CH$_4$ with and without catalysts.
**Figure S11.** CH₄ yield in different vacuum degrees.
Table S1. CH₄ selectivity at various vacuum degrees.

<table>
<thead>
<tr>
<th>Unit (%)</th>
<th>10% CO₂</th>
<th>70% CO₂</th>
<th>100% CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80 kPa</td>
<td>68.52</td>
<td>85</td>
<td>85.89</td>
</tr>
<tr>
<td>-60 kPa</td>
<td>64.89</td>
<td>73.5</td>
<td>89.368</td>
</tr>
<tr>
<td>-40 kPa</td>
<td>23.894</td>
<td>60.14</td>
<td>95.734</td>
</tr>
<tr>
<td>-20 kPa</td>
<td>37.93</td>
<td>95.19</td>
<td>53.987</td>
</tr>
<tr>
<td>0 kPa</td>
<td>46.85</td>
<td>--</td>
<td>95.903</td>
</tr>
</tbody>
</table>

The selectivity of CH₄ in the following discussion is calculated according to the following equation.

\[
\text{Selectivity}_{CH_4} = \frac{n_{CH_4}}{n_{CH_4} + n_{CO}}
\]

where \( n \) is the mole number.

Table S2. CO production rate at different gas pressure and CO₂ content.

<table>
<thead>
<tr>
<th>Unit (nmol g⁻¹ h⁻¹)</th>
<th>10% CO₂</th>
<th>70% CO₂</th>
<th>100% CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80 kPa</td>
<td>180.5</td>
<td>90.63</td>
<td>103.35</td>
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<tr>
<td>-60 kPa</td>
<td>244.97</td>
<td>139.33</td>
<td>33.74</td>
</tr>
<tr>
<td>-40 kPa</td>
<td>51.12</td>
<td>254.33</td>
<td>15.03</td>
</tr>
<tr>
<td>-20 kPa</td>
<td>335.83</td>
<td>6.23</td>
<td>29.84</td>
</tr>
<tr>
<td>0</td>
<td>5.23</td>
<td>6.01</td>
<td>9.34</td>
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Figure S12. Binding energy evolution of the TiO$_2$ photocatalyst upon long-term stability test. (a) XPS survey spectra and (b) high-resolution XPS spectra of Ti 2p.
Figure S13. High resolution XPS spectra of O 1s and C 1s on commercial TiO$_2$ before stability test.
Figure S14. High-resolution XPS spectra of O 1s after running 3.5h and 24 h.
Table S3. Peak fitting parameters of C 1s.

<table>
<thead>
<tr>
<th></th>
<th>Name</th>
<th>Peak BE</th>
<th>FWHM eV</th>
<th>Area (P) CPS.eV</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before test</td>
<td>C-C</td>
<td>284.4</td>
<td>1.33</td>
<td>10197.72</td>
<td>74.94</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>285</td>
<td>1.32</td>
<td>2732.26</td>
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<td></td>
<td>O=C-O</td>
<td>288.1</td>
<td>1.81</td>
<td>678.06</td>
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<tr>
<td>3.5h at -80kPa</td>
<td>C-C</td>
<td>284.4</td>
<td>1.18</td>
<td>18375.97</td>
<td>80.83</td>
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<td>3.37</td>
<td>389.35</td>
<td>1.71</td>
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<tr>
<td>3.5 h at 0kPa</td>
<td>C-C</td>
<td>284.4</td>
<td>1.14</td>
<td>15922.5</td>
<td>85.19</td>
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<td></td>
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<td>1.84</td>
<td>1372.62</td>
<td>7.34</td>
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<tr>
<td></td>
<td>O=C-O</td>
<td>288.1</td>
<td>1.17</td>
<td>339.88</td>
<td>1.82</td>
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<tr>
<td>24 h at -80kPa</td>
<td>C-C</td>
<td>284.4</td>
<td>1.32</td>
<td>8876.62</td>
<td>79.25</td>
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<td>1.45</td>
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<td>1.31</td>
<td>507.98</td>
<td>4.54</td>
</tr>
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<td>24 h at 0kPa</td>
<td>C-C</td>
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<td>1.2</td>
<td>10383.1</td>
<td>78.41</td>
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<td>C-O</td>
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<td>1.35</td>
<td>1970.19</td>
<td>14.88</td>
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<tr>
<td></td>
<td>O=C-O</td>
<td>288.1</td>
<td>3.37</td>
<td>946.72</td>
<td>7.15</td>
</tr>
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</table>
Figure S15. Mechanism of CO$_2$ photoreduction and the fundamental steps of CO$_2$ photoreduction in two pathways.

Generally, there are two pathways of CO$_2$ photoreduction. One is the formation of CO (following the equations S3–S5), the other is the formation of CH$_4$ (following the equations S3–S4, S6–S12). $^{1,2}$

\[
\begin{align*}
\text{Pathway 1: CO formation} \\
\text{CO}_2 + 2\text{H}^\cdot & \rightarrow \text{HCOOH}^* \quad \text{(S3)} \\
\text{HCOOH}^* + \text{H}^\cdot & \rightarrow \text{CO}^* + \text{H}_2\text{O} \quad \text{(S4)} \\
\text{Pathway 2: CH}_4 \text{ formation} \\
\text{CO}^* + \text{H}^\cdot & \rightarrow \text{COH}^* \quad \text{(S5)} \\
\text{COH}^* + \text{H}^\cdot & \rightarrow \text{C}^* + \text{H}_2\text{O} \quad \text{(S6)} \\
\text{C}^* + \text{H}^\cdot & \rightarrow \text{CH}^* \quad \text{(S7)} \\
\text{CH}^* + \text{H}^\cdot & \rightarrow \text{CH}_2^* \quad \text{(S8)} \\
\text{CH}_2^* + \text{H}^\cdot & \rightarrow \text{CH}_3^* \quad \text{(S9)} \\
\text{CH}_3^* + \text{H}^\cdot & \rightarrow \text{CH}_4^* \quad \text{(S10)} \\
\text{CH}_4^* & \rightarrow \text{CH}_4 \quad \text{(S11)} \\
\end{align*}
\]

When CO* on the surface of TiO$_2$ continued to obtain electrons and protons forming COH*, CH$_4$ generated; otherwise, CO generated. The faster those electrons and H$^+$ were transferred, the higher CH$_4$ yield.
Figure S16. CH₄/CO accumulation and yield of the Pt-TiO₂ catalyst at –80 kPa and 0 kPa.
Figure S17. CH$_4$ accumulation and yield from photocatalytic CO$_2$ reduction on Pt–TiO$_2$ catalysts at −80 kPa in pure CO$_2$. CH$_4$ selectivity were 94.71%, 94.18%, 90.49% with 100%, 20% and 5% Pt-TiO$_2$, respectively. For all catalysts, the loading was 20 mg.
References
