Electronic Supplementary Information

for

Facile formation of CoN₄ active sites onto SiO₂ support to achieve robust CO₂ and protons reduction in a noble-metal-free photocatalytic system

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1. Chemicals

Tetraethylorthosilicate (TEOS), γ-aminopropyltrimethoxysilane (APTMS), triethylamine, ammonium hydroxide (NH$_3$·H$_2$O, 25%-28%), triethylamine (TEA) and cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) were purchased from commercial suppliers (Sinopharm chemical reagent co., LTD, Adamas and Sigma-Aldrich) and used without further purification. CO$_2$ (99.999%), CO (99.999%), CH$_4$ (99.99%) were purchased from commercial supplier (Huaerwen). $^{13}$CO$_2$ (99% $^{13}$C atom) were purchased from Aldrich. All solvents of analytical grade were purchased from commercial suppliers and used without further purification. $g$-C$_3$N$_4$: $g$-C$_3$N$_4$ were synthesized according to previously reported procedures by heating approximately 5 g of melamine at a rate of 5 K min$^{-1}$ to 823 K and then maintaining this temperature for another 2 h.
2. X-Ray diffraction pattern of g-C$_3$N$_4$

![X-Ray diffraction spectrum of g-C$_3$N$_4$](image)

Figure S1. X-Ray diffraction spectrum of g-C$_3$N$_4$
3. UV-vis diffuse reflectance spectrum of $g$-C$_3$N$_4$

Figure S2. UV-vis diffuse reflectance spectrum of $g$-C$_3$N$_4$
4. UV-vis diffuse reflectance spectra of raw SiO$_2$, NH$_2$-SiO$_2$ and CoN$_4$-SiO$_2$

![UV-vis diffuse reflectance spectra (DRS) of raw SiO$_2$, NH$_2$-SiO$_2$, and CoN$_4$-SiO$_2$](image)

**Figure S3.** UV-vis diffuse reflectance spectra (DRS) of raw SiO$_2$, NH$_2$-SiO$_2$, and CoN$_4$-SiO$_2$
5. IR spectra

Figure S4. IR spectra of raw SiO$_2$, NH$_2$-SiO$_2$, and CoN$_4$-SiO$_2$. 
6. XPS spectra

Figure S5. XPS spectrum of $N\,1s$ of NH$_2$-SiO$_2$
7. Photocatalytic syngas production in CH$_3$CN

**Figure S6.** Long-time photocatalysis in CO$_2$-saturated CH$_3$CN; samples composition: CoN$_4$-SiO$_2$ (5.00 mg), g-C$_3$N$_4$ (10.00 mg), TEA (1.00 mL), total volume = 5.00 mL. The sample was irradiated under visible light (Blue LED, $\lambda_{\text{max}} = 450$ nm).
8. Emission spectra of $g$-$\text{C}_3\text{N}_4$ in the presence of TEA

Figure S7. Emission spectra of $g$-$\text{C}_3\text{N}_4$ in CH$_3$CN in the absence and presence of NH$_2$-SiO$_2$ (up) or TEA (bottom) (excitation wavelength = 380 nm).
9. Comparison of the reported heterogeneous photocatalytic syngas production systems

Table S1. Comparison of the reported heterogeneous photocatalytic syngas production systems

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst / Photocatalyst</th>
<th>Photosensitizer</th>
<th>( n(\text{CO}) ) [( \mu \text{mol} )]</th>
<th>( n(\text{H}_2) ) [( \mu \text{mol} )]</th>
<th>CO/H(_2) ratio</th>
<th>( n/m ) (CO) [( \mu \text{mol} \cdot \text{g}^{-1} )]</th>
<th>( n/m ) (H(_2)) [( \mu \text{mol} \cdot \text{g}^{-1} )]</th>
<th>Lifetime [h]</th>
<th>Ref.</th>
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<td>1(^{[a]})</td>
<td>Co(_{4})-SiO(_2)</td>
<td>g-C(_3)N(_4)</td>
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<td>13.93</td>
<td>1.0 : 1.2</td>
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<td>2786</td>
<td>140</td>
<td>This work</td>
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<td>2(^{[b]})</td>
<td>Co(_{4})-SiO(_2)</td>
<td>g-C(_3)N(_4)</td>
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<td>1.0 : 1.6</td>
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<tr>
<td>4</td>
<td>ReP + CoP/Dye/TiO(_2)</td>
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<td>2.21</td>
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<td>221</td>
<td>10</td>
<td>[c]</td>
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<td>Rh(PD)Au@STO</td>
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<td>26.03</td>
<td>5.3 : 1.0</td>
<td>1846</td>
<td>347</td>
<td>5</td>
<td>[d]</td>
</tr>
</tbody>
</table>

[a]. In CH\(_3\)CN/H\(_2\)O (\( \nu(\text{H}_2\text{O}) = 100 \mu \text{L} \), total volume = 5.00 mL)

[b]. In CH\(_3\)CN (total volume = 5.00 mL)
