Supporting Information

P25@CoAl-layered double hydroxide heterojunction nanocomposites for CO\textsubscript{2} photocatalytic reduction

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Apparent quantum yield calculations

The apparent quantum yield (AQY) was measured using the same experimental setup, but with band-pass filters of 365 nm for UV light and 480 nm visible light to obtain monochromatic light and the equation as follows:

\[ \text{AQY} / \% = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100 \]

Moles of incident photons (\(N_{\text{Einstein}}\)) = \(\frac{\text{Number of incident photons (N}_{p}\text{)}}{N_{A}}\)

Number of incident photons \(N_p\) can be calculated by

\[ N_p = \frac{\text{Irradiance (E)}}{\text{Photon energy (E}_p\text{)}} \text{; and} \] Photon energy (\(E_p\)) = \(\frac{hc}{\lambda}\)

\[ E_p = \frac{(6.625 \times 10^{-34} \text{ J.Sec)} \times (3 \times 10^{17} \text{ nm Sec}^{-1})}{\lambda (\text{nm})} = 19.88 \times 10^{-17} \lambda (\text{nm}) \]

\[ N_p = \frac{E}{E_p} = E \times \lambda \times 5.03 \times 10^{15} (\text{m}^{-2}\text{Sec}^{-1}); \]

\[ N_{\text{Einstein}} = \frac{N_p}{N_{A}} = 0.836 \times E \times \lambda (\text{nm}) \times 10^{-8} (\text{mol. m}^{-2}.\text{sec}^{-1}) \]

\[ N_{\text{Einstein}} = 0.836 \times E \times \lambda (\text{nm}) \times 10^{-2} (\mu\text{mol. m}^{-2}.\text{sec}^{-1}) \]

\[ \text{AQY} / \% = \frac{\text{Number of reacted electrons} (\mu\text{mol. sec}^{-1})}{0.836 \times E \times \lambda \times 10^{-2} (\mu\text{mol. m}^{-2}.\text{sec}^{-1})} \times 100 \]

\[ \text{AQY} / \% = \frac{\text{Number of reacted electrons} (\mu\text{mol. h}^{-1})}{0.836 \times 3600 \times E \times \lambda \times 10^{-2}} \times 100 \]

\[ \text{AQY} / \% = \frac{\text{Number of reacted electrons} (\mu\text{mol. h}^{-1})}{30.096 \times E \times \lambda (\text{nm})} \times 100 \]

where Irradiance (E) = light intensity in reactor \(\times\) effective light irradiation area. Light intensity within the reactor was measured using a G & R labs intensity meter over the range 190-750 nm.

E is 0.10 W.cm\textsuperscript{-2} at 365 nm and 0.12 W.cm\textsuperscript{-2} at 475 nm.
**Figure S1.** Spectral output of 300 W Xe light source.
Figure S2. (top) low and (bottom) high resolution TEM images and corresponding EDX element maps of 20 wt% TiO$_2$@CoAl-LDH nanocomposite highlighting relatively high and uniform distribution of P25 throughout LDH matrix.
Figure S3. Powder XRD patterns of P25@CoAl-LDH nanocomposites, and reference patterns from P25, CoAl-LDH and a physical mixture of 20wt%P25+CoAl-LDH.

Figure S4. DRIFT spectra of P25@CoAl-LDH nanocomposites, and reference patterns from P25, CoAl-LDH and a physical mixture of 20wt%P25+CoAl-LDH.
**Figure S5.** N$_2$ adsorption-desorption isotherms of CoAl-LDH, P25@CoAl-LDH nanocomposites and P25.

**Figure S6.** (a) Tauc plot to determine optical band gap of (a) CoAl-LDH and (b) P25 reference materials.
Figure S7. CO productivity during control experiments using (a) P25 and (b) 20 wt% P25@CoAl-LDH.

Figure S8. CO selectivity during aqueous phase CO\textsubscript{2} photoreduction over P25 and CoAl-LDH references and P25@CoAl-LDH nanocomposites under UV-visible irradiation.
Figure S9. Effect of 2-propanol as a hole scavenger on photocatalytic production of (a) gas and (b) liquid phase carbon containing products during UV-visible irradiation under a He atmosphere.

Figure S10. Effect of titania morphology on CO$_2$ photoreduction over 20 wt% P25@CoAl-LDH and 20 wt% anatase nanorod@CoAl-LDH nanocomposites under UV-visible irradiation. 18 nm long anatase nanorods prepared according to reference 11.
### Comparative performance of inorganic heterostructures for the photocatalytic reduction of CO₂

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction conditions</th>
<th>Light source</th>
<th>Surface area / m².g⁻¹</th>
<th>Productivity / µmol.g⁻¹.h⁻¹</th>
<th>AQE / %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrOCo₃⁻IrO₄ SBA-15 wafer</td>
<td>CO₂ and water vapor</td>
<td>355 nm UV light</td>
<td>-</td>
<td>CO=1.74</td>
<td>0.001 (355 nm)</td>
<td>[1]</td>
</tr>
<tr>
<td>Cu₂O/RuO₃</td>
<td>1 bar CO₂ and 0.7M aqueous Na₂SO₃</td>
<td>150 W Xe</td>
<td>-</td>
<td>CO=0.32</td>
<td>-</td>
<td>[2]</td>
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<tr>
<td>Cu²⁺-grafted Nb₂O₆ nanosheets</td>
<td>CO₂ and 0.5 M aqueous KHCO₃</td>
<td>Hg–Xe</td>
<td>-</td>
<td>CO=0.72</td>
<td>-</td>
<td>[3]</td>
</tr>
<tr>
<td>Cu₅O-SrTiO₃</td>
<td>CO₂ and 0.5 M aqueous KHCO₃</td>
<td>Hg–Xe</td>
<td>-</td>
<td>CO=0.35</td>
<td>-</td>
<td>[4]</td>
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<tr>
<td>Ce–TiO₂/SBA-15</td>
<td>CO₂ and water vapor</td>
<td>450 W Xe (450 mW.cm⁻²)</td>
<td>140</td>
<td>0.30 (CO=0.25, CH₄=0.05)</td>
<td>-</td>
<td>[5]</td>
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<tr>
<td>Au@SrTiO₃</td>
<td>CO₂ and water vapor</td>
<td>300 W Xe</td>
<td>72</td>
<td>0.52 (CO=0.35, CH₄=0.17)</td>
<td>-</td>
<td>[6]</td>
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<tr>
<td>Cu-PbS-QDs/TiO₂</td>
<td>CO₂ and water vapor</td>
<td>300 W Xe</td>
<td>-</td>
<td>1.71 (CO=0.82, CH₄=0.58, C₂H₆=0.31)</td>
<td>-</td>
<td>[7]</td>
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<tr>
<td>MgAl-LDO/TiO₂</td>
<td>CO₂ and water vapor &lt;50 °C</td>
<td>450 W Xe</td>
<td>175</td>
<td>CO=1.5</td>
<td>-</td>
<td>[8]</td>
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<tr>
<td>Au@NaTaO₃</td>
<td>CO₂ and water vapor</td>
<td>200 W Hg-Xe</td>
<td>21</td>
<td>0.20 (CO=0.17, CH₄=0.03)</td>
<td>-</td>
<td>[9]</td>
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<tr>
<td>In₂O₃-(OH)₃ Nanocrystal</td>
<td>CO₂ and water vapor</td>
<td>1000 W Hortilux Blue metal halide</td>
<td>159</td>
<td>CO=1.2</td>
<td>-</td>
<td>[10]</td>
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<tr>
<td>P25@CoAl-LDH</td>
<td>1 bar CO₂ and water</td>
<td>300 W Xe</td>
<td>57</td>
<td>CO=2.21</td>
<td>0.10 (365 nm) 0.03 (475 nm)</td>
<td>This work</td>
</tr>
</tbody>
</table>

**References**