Supplementary Information for:

Engineering of PMo$_{12}$@NiCo-LDH composite via in-situ encapsulation-reassembly strategy for highly selective photocatalytic reduction of CO$_2$ to CH$_4$

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Experimental section

**Chemicals and materials.** Phosphomolybdic acid (PMo$_{12}$), methanol, ethanol, and acetonitrile were obtained from Fuchen (Tianjin) Chemical Reagent Co., Ltd. 2-methylimidazole (2-MIM), terpyridine ruthenium chloride (Ru(bpy)$_3$Cl$_2$·6H$_2$O, 98%), and triethanolamine (TEOA, 99%) were purchased from Energy chemical. Cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99%) and nickel (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99%) were purchased from Sigma-Aldrich trading Co., Ltd. High purity CO$_2$ (99.999%) and $^{13}$CO$_2$ (99%) were obtained from Linde Gas Co., Ltd. All the chemicals were used directly without any further purification.

**Synthesis of PMo$_{12}$@ZIF-67.** The synthesis of PMo$_{12}$@ZIF-67 referenced to the literature with tiny modification[1]. Typically, the mixture of 2.5 mmol Co(NO$_3$)$_2$·6H$_2$O in 25 mL methanol and 10 mL aqueous solution contained certain amount of Keggin-type POMs H$_3$PMo$_{12}$O$_{40}$ (1.2 ×10$^{-2}$ mmol, 25 mg) was stirred continuously at room temperature for 30 min. Subsequently, 40.0 mmol 2-methylimidazole in 25 mL methanol was dropwise added, and a purple suspension was produced. After stirring for 2.5 h, the bluish violet precipitate was collected via centrifugation, washing with methanol for several times, and drying at 60 °C in vacuum overnight. The obtained solid was denoted as PMo$_{12}$@ZIF-67. For comparison, ZIF-67 was prepared by the same method except for the absence of H$_3$PMo$_{12}$O$_{40}$.

**Synthesis of PMo$_{12}$@NiCo-LDH.** Firstly, Ni(NO$_3$)$_2$·6H$_2$O (0.42 mmol, 120 mg) was dissolved in 25 mL ethanol with vigorous stirring for 30 min. Subsequently, 40 mg PMo$_{12}$@ZIF-67 was added into the above solution. After continuous stirring at room temperature for another 2 h, the precipitation was collected via centrifugation, washing with ethanol for several times, and drying at 60 °C in vacuum overnight. The resultant solid was denoted as PMo$_{12}$@NiCo-LDH.

**Synthesis of NiCo-LDH.** NiCo-LDH was prepared by the same method as PMo$_{12}$@NiCo-LDH, except for the replacement of PMo$_{12}$@ZIF-67 to ZIF-67.

**Characterizations.** High-resolution transmission electron microscopy (HRTEM) images were performed on a JEOL JEM-2200FS operating at 200 kV. Elemental mapping EDS spectra were recorded using energy dispersive spectroscopy attached to
JEOL JEM-2200FS. Scanning electron microscopy (SEM) images were performed on a Zeiss Supra55. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out on a Shimadzu ICPS-7500 instrument. Fourier transform infrared (FT-IR) spectra were collected on a Bruker Vector 22 infrared spectrometer using the KBr pellet method at wavenumbers ranging from 4000 to 400 cm$^{-1}$. X-ray diffraction (XRD) patterns were collected by a Rigaku XRD-6000 diffractometer equipped with a Cu Ka radiation ($\lambda = 1.5405$ Å). N$_2$ adsorption-desorption measurements were determined on a Micromeritics ASAP 2020 M surface area and porosity analyzer, with samples pre-degassing under vacuum at 100 °C for 6 h. X-ray photoelectron spectroscopy (XPS) spectra were performed on a monochromatized ALK exciting X-radiation (PHI Quantera SXM), which were calibrated against C 1s at 284.8 eV. Solid-state ultraviolet-visible (UV-vis) diffuse reflectance spectra were collected on a Beijing PGENERAL TU-1901 spectrometer, with wavelength ranging from 200 to 800 nm. In-situ diffuse reflectance infrared Fourier transform spectroscopy (in-situ DRIFT) was performed on a Bruker TENSOR II spectrometer.

**CO$_2$ photocatalytic reduction (CO$_2$PR).** The CO$_2$PR was carried out in a sealed stainless reactor (40 mL) with a quartz top window for light irradiation. In a typical run, 10 mg PMo$_{12}$@NiCo-LDH powder was dispersed in 10 mL solution with CH$_3$CN : H$_2$O : TEOA = 6 : 2 : 2 (v/v/v), following by addition of 4.4 ×10$^{-3}$ mmol (3.3 mg) Ru(bpy)$_3$Cl$_2$·6H$_2$O. The reactor was then sealed and evacuated by a vacuum pump to remove the residual air completely. High purity CO$_2$ was filled into the reactor, with the pressure of 0.18 MPa. Under the irradiation of visible light (400–800 nm) with continuous stirring for 1 h, the gaseous products were collected and analyzed qualitatively and quantitatively by Shimadzu GC-2014 gas chromatography equipped with both flame ionization detector (FID) and thermal conductivity detector (TCD). $^1$H NMR spectra were collected on a Bruker AV400 NMR spectrometer at 400 MHz to detected the possible liquid products. The isotopic-labeled experiments were carried out with $^{13}$CO$_2$ instead of high purity $^{12}$CO$_2$ under the same condition. After irradiation for 1 h, the resultant products were collected and analyzed through gas chromatography-mass spectrometry (GC-MS, QP2020 equipped with Micropacked...
Electrochemical measurements. Electrochemical measurements were all performed on a CHI760A electrochemical workstation (Shanghai Chenhua, China) in a standard three-electrode quartz cell with 0.1 M Na$_2$SO$_4$ aqueous solution as the electrolyte. Electrochemical impedance spectroscopy (EIS) was recorded with carbon paper coated by PMo$_{12}$@NiCo-LDH or NiCo-LDH as a working electrode, Pt foil as a counter electrode, and Ag/AgCl (in saturated KCl) as a reference electrode. Transient photocurrent measurements and Mott-Schottky tests were measured with indium tin oxide (ITO) coated by PMo$_{12}$@NiCo-LDH or NiCo-LDH as a working electrode, Pt foil as a counter electrode, and Ag/AgCl (in saturated KCl) as a reference electrode.
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**Figure S16.** a) Electrochemical impedance spectra (EIS), b) photocurrent–time profiles, c) room-temperature photoluminescence (PL) spectra of NiCo-LDH and PMo$_{12}$@NiCo-LDH.
Figure S17. a) UV-vis spectra and b) bandgaps calculated from Tauc plots of PMo$_{12}$@NiCo-LDH and NiCo-LDH; Mott-Schottky plots of c) PMo$_{12}$@NiCo-LDH and d) NiCo-LDH. e) valance band XPS spectra of PMo$_{12}$@NiCo-LDH and NiCo-LDH; f) conduction band minimum (CBM), valence band maximum (VBM) of PMo$_{12}$@NiCo-LDH and NiCo-LDH.

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**Table S1.** Porosity properties of PMo$_{12}$@ZIF-67 and PMo$_{12}$@NiCo-LDH.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{BET}$ ($m^2\cdot g^{-1}$)</th>
<th>$V_{meso}$ ($cm^3\cdot g^{-1}$)</th>
<th>$V_{micro}$ ($cm^3\cdot g^{-1}$)</th>
<th>$D_p$ (nm)</th>
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<tbody>
<tr>
<td>PMo$_{12}$@ZIF-67</td>
<td>1187</td>
<td>0.15</td>
<td>0.55</td>
<td>1.0, 1.5</td>
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<tr>
<td>PMo$_{12}$@NiCo-LDH</td>
<td>190</td>
<td>0.54</td>
<td>–</td>
<td>6</td>
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**Table S2.** Comparison of CO$_2$PR performance for various photocatalytic systems in this work and in previous literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Photosensitizer co-catalyst</th>
<th>Sacrificial agent</th>
<th>Solvent</th>
<th>Light source</th>
<th>Major product selectivity</th>
<th>Production rate (μmol·g$^{-1}$·h$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NENU-606</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>H$_2$O</td>
<td>300 W Xe ($\lambda &gt; 420$ nm)</td>
<td>CH$_4$: 85.5% CO: 14.5%</td>
<td>1.7478 0.2957</td>
<td>[2]</td>
</tr>
<tr>
<td>3D Fe–Mn POM structures</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>H$_2$O</td>
<td>280 W Xe ($\lambda = 415$ nm)</td>
<td>CH$_4$: 92.6% CO: 7.4%</td>
<td>1.440 0.115</td>
<td>[3]</td>
</tr>
<tr>
<td>TiO$_2$/NiAl-LDH</td>
<td>–</td>
<td>–</td>
<td>H$_2$O</td>
<td>300 W Xe Simulated-solar-light</td>
<td>CH$_4$: 81.8% CO: 9.9%</td>
<td>20.56 2.48</td>
<td>[4]</td>
</tr>
<tr>
<td>Cu$_{2-x}$/Ni-Al-LDH</td>
<td>–</td>
<td>–</td>
<td>H$_2$O</td>
<td>300 W Xe Simulated-solar-light</td>
<td>CH$_4$: 72.8% CO: 27.2 %</td>
<td>14.2 5.3</td>
<td>[5]</td>
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<tr>
<td>System</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>Solvent</td>
<td>Light Source</td>
<td>CH$_4$:</td>
<td>CO:</td>
<td>H$_2$:</td>
</tr>
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<tr>
<td>ZnCr-LDH/Ti$_3$C$_2$Tx</td>
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<td></td>
<td>H$_2$O</td>
<td>300 W Xe</td>
<td>CH$_4$: 14%</td>
<td>CO: 86%</td>
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<tr>
<td>Monolayer NiAl-LDH</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>MeCN-H$_2$O (3 : 1 v/v)</td>
<td>300 W Xe</td>
<td>CH$_4$: 70.3%</td>
<td>CO: 29.7%</td>
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<tr>
<td>HC-NiCo-LDH</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>MeCN-H$_2$O (2 : 1 v/v)</td>
<td>300 W Xe</td>
<td>CH$_4$: 62.7%</td>
<td>CO: 35.6%</td>
<td>H$_2$: 1.7%</td>
</tr>
<tr>
<td>Monolayer NiFe-LDH</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>MeCN-H$_2$O (3 : 1 v/v)</td>
<td>300 W Xe</td>
<td>CH$_4$: 81.75%</td>
<td>CO: 15.68%</td>
<td>H$_2$: 2.57%</td>
</tr>
<tr>
<td>PMo$_{12}$@NiCo-LDH</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>MeCN-H$_2$O (3 : 1 v/v)</td>
<td>300 W Xe</td>
<td>CH$_4$: 74.8%</td>
<td>CO: 19.0%</td>
<td>H$_2$: 6.2%</td>
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<tr>
<td>PMo$_{12}$@NiCo-LDH</td>
<td>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O</td>
<td>TEOA</td>
<td>MeCN-H$_2$O (3 : 1 v/v)</td>
<td>300 W Xe</td>
<td>CH$_4$: 86.2%</td>
<td>CO: 10.5%</td>
<td>H$_2$: 3.3%</td>
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</tbody>
</table>
Reference


