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In situ growth and activation of an amorphous MoS\textsubscript{x} catalyst on Co-containing metal-organic framework nanosheets for highly efficient dye-sensitized H\textsubscript{2} evolution

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Fig. S1 Low-magnification TEM image of Co-BDC NSs.

Table S1 Zeta potentials of different synthetic systems in TEOA aqueous solution (10%, pH 8).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-BDC NSs</td>
<td>-4.69</td>
</tr>
<tr>
<td>MoS₄²⁻</td>
<td>-2.64</td>
</tr>
<tr>
<td>Co-BDC NSs/MoS₄²⁻</td>
<td>-6.54</td>
</tr>
<tr>
<td>ErB/MoS₄²⁻</td>
<td>-1.99</td>
</tr>
<tr>
<td>ErB/Co-BDC NSs/MoS₄²⁻</td>
<td>-3.30</td>
</tr>
</tbody>
</table>

"Co-BDC NSs, 0.1mg mL⁻¹; MoS₄²⁻, 0.1 mM; ErB, 0.1 mM.

Fig. S2 N₂ adsorption-desorption isotherm and pore size distribution (inset) of Co-BDC NSs
**Fig. S3** Enhancement factor of H$_2$ evolution from ErB-TEOA system by comparing MoS$_x$ and Co-BDC NSs/MoS$_x$ catalysts under visible light irradiation. Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 5 mg; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, $\lambda \geq 450$ nm.

**Fig. S4** TONs of H$_2$ evolution catalyzed by free MoS$_x$ and Co-BDC NSs/MoS$_x$ catalysts as a function of MoS$_x$ concentration after 6 h irradiation. Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 5 mg; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, $\lambda \geq 450$ nm.

**Table S2** Photocatalytic H$_2$ evolution activity of Co-BDC NSs/MoS$_x$ catalyst in this work, in comparison with several representative results with high performance non-noble metal based catalysts from recent publications.

<table>
<thead>
<tr>
<th>Photocatalytic H$_2$ evolution system</th>
<th>Light source</th>
<th>H$_2$ evolution activity (mmol·h$^{-1}$·g$^{-1}$)</th>
<th>Apparent quantum efficiency (AQE)</th>
<th>TON$_{cat}$</th>
<th>Ref.</th>
</tr>
</thead>
</table>

s3
<table>
<thead>
<tr>
<th>Material</th>
<th>Amount</th>
<th>Additional Components</th>
<th>pH</th>
<th>Lamp Setup</th>
<th>Luminescence Efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mg Co-BDC NSs, 0.03 mM MoSx, 0.1 mM ErB, 10% TEOA, pH=8</td>
<td>30-W white-light LED lamp (λ≥450 nm)</td>
<td>4.8</td>
<td>15% at 500 nm</td>
<td>105.2</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>10 mg ATP/Co(OH)2, 0.05 mM MoSx, 0.2 mM ErB, 10% TEOA, pH=8</td>
<td>30-W white-light LED lamp (λ≥450 nm)</td>
<td>16.8</td>
<td>47.7% at 500 nm</td>
<td>363</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>5 mg CoAl-LDH NSs, 0.1 mM MoSx, 0.5 mM ErB, 15% TEOA, pH=8</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>21.5</td>
<td>4.3% at 520 nm</td>
<td>174.2</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>10mg GQDs, 8.98×10^{-5} M MoSx, 5.98×10^{-5} M Co^{2+}, 1 mM ErB, 15% TEOA, pH=7</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>17.4</td>
<td>none</td>
<td>118.0</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>100 mg g-C3N4, 0.039 mM MoSx, 0.0125 mM ErB, 0.79 M TEOA, pH=7</td>
<td>400-W High pressure Hg lamp (λ≥420 nm)</td>
<td>0.3</td>
<td>8.3% at 545 nm</td>
<td>32.1</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>50 mg MoSx^- rGO/TiO2 (0.5wt%), 10% methanol</td>
<td>Four LED lamp (3W, 365 nm)</td>
<td>4.1</td>
<td>none</td>
<td>264.4</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>10 mg MoSx^-CdS/Co3O4, 10% lactic acid</td>
<td>5-W light emitting diode lamp</td>
<td>10.8</td>
<td>none</td>
<td>576.2</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>3 mg 0.14 wt%MoS2QD/Bi2S3, 0.5 M Na2S/Na2SO3</td>
<td>500-W Xe arc lamp</td>
<td>17.7</td>
<td>none</td>
<td>24274.3</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>100 mg 0.5 wt% MoS2/PQ, 0.2 M TEOA, pH=7</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>0.08</td>
<td>none</td>
<td>20.4</td>
<td>[8]</td>
<td></td>
</tr>
<tr>
<td>20 mg Zn0.2Cd0.8S/MoS2-3%, Na2S (0.35 M)/Na2SO3 (0.25 M)</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>0.4</td>
<td>none</td>
<td>8.8</td>
<td>[9]</td>
<td></td>
</tr>
<tr>
<td>20 mg MoS2/RGO, 0.4 mM EY, 15% TEOA, pH=7</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>1.9</td>
<td>24% at 460 nm</td>
<td>450.8</td>
<td>[10]</td>
<td></td>
</tr>
<tr>
<td>50 mg rGO1.5/CdS/MoS2 (1.5 wt %), 10% lactic acid, pH=11</td>
<td>350-W Xe lamp (λ≥420 nm)</td>
<td>1.9</td>
<td>none</td>
<td>22.7</td>
<td>[11]</td>
<td></td>
</tr>
<tr>
<td>Co(NO3)2+(NH4)2MoS4=1 mM, (Co:Mo=4:6), 2 mM ErB, 15% TEOA,</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>53.6</td>
<td>none</td>
<td>100</td>
<td>[12]</td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>pH</td>
<td>Lamp Type</td>
<td>Wavelength (nm)</td>
<td>Emission (%)</td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
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<td></td>
</tr>
<tr>
<td>100 mg TiO2, 0.119 mM (NH₄)₂MoS₄, 0.78 mM EY, 10% TEOA, pH=10.7</td>
<td>9</td>
<td>1000-W Xe arc lamp (AM 1.5 G filter)</td>
<td>&gt;400</td>
<td>none</td>
<td>8.1</td>
<td>[13]</td>
</tr>
<tr>
<td>50 mg MoSₓ/CdS-0.2 wt%, 10% lactic acid</td>
<td>9</td>
<td>300-W Xe lamp (λ≥400 nm)</td>
<td>8.1</td>
<td>none</td>
<td>1515</td>
<td>[14]</td>
</tr>
<tr>
<td>4 mM MoSₓ, 2 mM ErB, 10% TEOA, pH=8.1</td>
<td>8.1</td>
<td>300-W Xe lamp (λ≥400 nm)</td>
<td>9.6</td>
<td>none</td>
<td>25</td>
<td>[15]</td>
</tr>
<tr>
<td>17 mg [Mo₃S₁₃]²⁻/MIL-125-NH₂ (0.82 wt%), MeCN:TEA:H₂O=9:16:5</td>
<td>8.1</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>2.1</td>
<td>11.8% at 450 nm</td>
<td>2157.5</td>
<td>[16]</td>
</tr>
<tr>
<td>17 mg 1T-MoS₂/MIL-125-NH₂ (0.82 wt%), MeCN:TEA:H₂O=9:16:5</td>
<td>8.1</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>1.5</td>
<td>5.8% at 450 nm</td>
<td>340.5</td>
<td>[16]</td>
</tr>
<tr>
<td>10 µM [Mo₃S₁₃]²⁻, 100 µM Ru(bpy)₃Cl₂, CH₃CN:H₂O=9:1, 100 mM H₂A</td>
<td>8.1</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>14.5</td>
<td>none</td>
<td>1570</td>
<td>[17]</td>
</tr>
<tr>
<td>40 mg CdS/WSₓ (12 wt%), 10% lactic solution</td>
<td>8.1</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>19.0</td>
<td>14.7% at 420 nm</td>
<td>253.7</td>
<td>[18]</td>
</tr>
<tr>
<td>NiSₓ/graphene (46.7 wt%), 1 mM EY, 10% TEOA, pH=7,</td>
<td>8.1</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>12.4</td>
<td>32.5% at 430 nm</td>
<td>18.5</td>
<td>[19]</td>
</tr>
<tr>
<td>100 mg Cdₒ.₅Znₒ.₅S/NiSₓ, Na₂S (0.35 M)/Na₂SO₄ (0.25 M)</td>
<td>8.1</td>
<td>Xe lamp (λ≥430 nm)</td>
<td>44.6</td>
<td>95% at 425 nm</td>
<td>18374.5</td>
<td>[20]</td>
</tr>
<tr>
<td>200 mg NiSₓ/C₃N₄ (5 wt%), 20% TEOA</td>
<td>8.1</td>
<td>300-W Xe lamp (λ≥420 nm)</td>
<td>2.0</td>
<td>3.2% at 405 nm</td>
<td>59.2</td>
<td>[21]</td>
</tr>
<tr>
<td>50 mg a-MoSₓ/gC₃N₄, 10% lactic acid</td>
<td>8.1</td>
<td>3W-LED (λ≥420 nm)</td>
<td>0.3</td>
<td>none</td>
<td>8.7</td>
<td>[22]</td>
</tr>
<tr>
<td>50 mg Ni(OH)₂/g-C₃N₄ (0.5 mol%), 10% TEOA</td>
<td>8.1</td>
<td>350-W Xe arc lamp (λ≥400 nm)</td>
<td>0.2</td>
<td>1.1% at 420 nm</td>
<td>16.78</td>
<td>[23]</td>
</tr>
</tbody>
</table>
**Fig. S5** H₂ evolution amounts over different Co-BDC NSs/MoSₓ catalysts sensitized by ErB (0.1 mM) from TEOA solution, where different concentrations Co-BDC NSs were added. Reaction conditions: MoSₓ, 0.03 mM; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, λ≥450 nm.

**Fig. S6** (a) UV-vis absorption spectra of ErB in TEOA solution during the photocatalytic H₂ reaction from ErB-sensitized Co-BDC NSs/MoSₓ as a function of light irradiation time. (b) The variations of maximum wavelength and absorbance of ErB during the photocatalytic H₂ reaction as a function of light irradiation time.
Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 5 mg; MoS\textsubscript{x}, 0.03 mM; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, \(\lambda \geq 450\) nm.

**Fig. S7** Digital photos of Co-BDC NSs, [MoS\textsubscript{x}]\textsuperscript{2-}, and Co-BDC NSs/[MoS\textsubscript{x}]\textsuperscript{2-} mixture in TEOA.

**Fig. S8** XPS survey spectra of free MoS\textsubscript{x}, Co-BDC NSs, and Co-BDC NSs/MoS\textsubscript{x} catalysts.
Fig. S9 The stability of photocatalytic H$_2$ evolution over Co-BDC NSs/MoS$_x$ catalysts from ErB-TEOA system. Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 15 mg; MoS$_x$, 0.09 mM; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, $\lambda$$\geq$450 nm.

References


