A new 0D-2D CsPbBr$_3$-Co$_3$O$_4$ heterostructure photocatalyst with efficient charge separation for photocatalytic CO$_2$ reduction

Xin Zhong,$^{a,†}$ Xinmeng Liang,$^{a,†}$ Xinyu Lin,$^a$ Jin Wang,*$^{a,b}$ Malik Zeeshan Shahid,*$^a$ and Zhengquan Li,*$^{a,b}$

$^a$Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Normal University, Jinhua, Zhejiang 321004, P. R. China.

$^b$Zhejiang Institute of Optoelectronics, Zhejiang Normal University, Jinhua, Zhejiang 321004, P. R. China.

* The authors contributed equally.

**Corresponding Author**

* E-mail: wangjin@zjnu.edu.cn

* E-mail: zeeshan-nano@zjnu.edu.cn

* E-mail: zqli@zjnu.edu.cn
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1. EXPERIMENTAL SECTION

1.1 Materials
All chemicals were purchased and used without further purification. Lead bromide PbBr$_2$ (99.999%), Cs$_2$CO$_3$ (99.995%), oleic acid (OA, C$_{18}$H$_{34}$O$_2$, 90%), and octadecene (ODE, C$_{18}$H$_{36}$, 99.8%), were purchased from Sigma-Aldrich. Hexane (95%), cyclohexamethylenetetramine (Urotropine, 99.5%, C$_6$H$_{12}$N$_4$), ethanol, and ethyl acetate (EA, 99.8%) were purchased from Aladdin company. Chloride hexahydrate (99%, CoCl$_2$.6H$_2$O) was purchased from Sinopharm chemical reagent. The water used for the experiments was purified by a Millipore Milli-Q system.

1.2 Characterization
Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS) were measured by employing a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. The samples were prepared by using EA solution, and a piece of the carbon-coated copper grid was used on which a drop of suspension (of each sample) was precisely placed. The copper grid was dried under ambient conditions and further used for morphological characterization. Zeta sizer Nano-ZS (Malvern Instruments, U.K.) was used to collect Zeta ($\zeta$)-potential data, for which the samples were prepared by dispersing in EA solutions. Philips X’Pert Pro Super X-ray diffractometer with Cu-K$\alpha$ radiation ($\lambda$ =1.5418Å) was used to record Powder XRD patterns. Shimadzu 2501PC UV-vis spectrophotometer was employed to investigate the UV-vis absorption spectra. FluoroMax-4 spectrofluorometer (HoribaScientific) and analyzed with an Origin-integrated software (FluoroEssencev2.2) was used to measure the steady-state photoluminescence (PL) spectra. The PL decay spectra were recorded on a photoluminescence spectrometer (FLS980, Edinburgh Instruments Ltd.) with a 380-nm excitation wavelength and a 515-nm emission wavelength with the time-correlated single-photon counting (TCSPC) mode. The lifetime data were analyzed with DataStation v6.6 (Horiba Scientific). ESCALab 250 X-ray photoelectron spectrometer with Al-K$\alpha$ radiation was used to record X-ray photoelectron spectra (XPS) data in which the calibration was done with C 1s peak at 284.6 eV.
1.3 Photocatalytic activity measurement
In a typical experiment, the as-prepared photocatalysts (5 mg) were first added to a Pyrex photoreactor without using any sacrificial agent. Next, 50 μL of water was added. Then, a rubber septum was used to seal the photoreactor, and then it was vacuumed and subsequently purged with CO2 for 10~20 min in the dark. The photoreactor was then placed in a water bath maintained at 25 °C, stirred, and irradiated by a 300-W Xe lamp with a 400 nm cutoff filter (Solaredge 700, 100 mW·cm⁻²). The product distribution was quantified through periodic headspace gas analysis (500 μL) by gas chromatography (GC, 7820A, Ar carrier, Agilent). Produced CH4 was measured by a flame ionization detector (FID), and CO was converted to CH4 by a methanation reactor and then analyzed by the FID. The isotope-labelled experiments were performed using ¹³CΟ₂ instead of ¹²CΟ₂, and the products were analyzed using gas chromatography-mass spectrometry (GC-MS, 7890A and 5975C, Agilent). The products were separated with GC in advance and reached the MS at different retention times.

1.4 Photoelectrochemical measurements
The Photoelectrochemical measurements were carried out using a three-electrode cell CHI 760E electrochemical station (Shanghai Chenhua, China) with a Pt foil counter electrode and a saturated Ag/AgCl reference electrode. The working electrode was prepared by the dip-coating method. About 1 mg of the photocatalyst was dispersed in 1 mL of hexane and 10 μL Nafion solution to form a slurry. Next, 30 μL of the slurry was dip-coated on the FTO conductive glass with an exposure area of 0.196 cm². Subsequently, the film was dried in a vacuum oven at 80 °C. Then acetonitrile solution with 0.1 mol/L of tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as the electrolyte. The variation of photoinduced current density versus time (I-t curve) was recorded at a 0 V bias potential under visible light switching on and off mode, λ > 400 nm, 300 W Xe lamp (Solaredge 700). The electrochemical impedance spectroscopy (EIS) results were obtained at the open circuit potential using a frequency ranging from 10⁴ Hz to 10⁻¹ Hz.

1.5 Energy bandgap calculations
In relational expression proposed by Tauc, Devis, and Mott i.e., \( αhν = A (hν− E_g)^n \) symbols are denoted as follows; \( h \): plank constant, \( ν \): frequency of vibration, \( α \): absorption coefficient, \( E_g \): band gap, and \( A \): proportional constant. As both constituents i.e., CsPbBr₃ QDs and Co₃O₄ HPs
in heterostructure are direct allowed transition, the calculation of energy bandgap value was based on n=1/2.
Fig. S1 Schematic illustration for the synthesis of CsPbBr\(_3\) QDs via hot-injection method.
Fig. S2 Schematic illustration for the synthesis of $\text{Co}_3\text{O}_4$ HPs by calcination route.
The desired quantity of $\text{Co}_3\text{O}_4$ HPs was taken (Fig. S3a) and dissolved in absolute ethanol via sonication for 3 minutes (Fig. S3b) to get suspension 1. On the other hand, the required amount of $\text{CsPbBr}_3$ QDs was taken from stock (Fig. S3d), centrifuged (Fig. S3e), and dispersed in ethyl acetate via stirring and sonication for 2 minutes to obtain the suspension 2 (Fig. S3f). This suspension 2 was then placed in the Teflon linen vessel for the subsequent procedure to occur in the dark (Fig. 1c). Next, suspension 1 was swiftly inserted into suspension 2 under vigorous stirring (Fig. 1c), and later on, covered with another Teflon linen vessel directed upside down to achieve a dark environment. The stirring continued for 30 minutes in dark and another 30 minutes in ambient conditions and finally, after washing and drying, the $\text{CsPbBr}_3\cdot\text{Co}_3\text{O}_4$ heterostructure was obtained (Fig. S3g).
**Fig. S4** Zeta potential of pristine Co$_3$O$_4$ HPs and CsPbBr$_3$ QDs in the solution of ethyl acetate. The values endorsing the successful coulomb electrostatic interaction between these components to form the Co$_3$O$_4$-CsPbBr$_3$ heterojunction.
Fig. S5 Color transformations of as-prepared samples (a) without UV light irradiation and (b) under UV light illumination.
Fig. S6 Comparative depiction of catalytic activity during 6 hours in terms of produced gas CO and CH\textsubscript{4} by using as-synthesized CsPbBr\textsubscript{3} QDs, Co\textsubscript{3}O\textsubscript{4} HPs, and CsPbBr\textsubscript{3}-Co\textsubscript{3}O\textsubscript{4} heterostructure.
Fig. S7 Influence of various mass ratios in the CsPbBr₃-Co₃O₄ heterostructure over the production of CO and CH₄.
Fig. S8 Mass spectra showing (a) $^{13}\text{CH}_4$ (m/z = 17) and (b)$^{13}\text{CO}$ (m/z = 29) generated over CsPbBr$_3$-Co$_3$O$_4$ in the photocatalytic $^{13}\text{CO}_2$ reduction.
Fig. S9 The results confirm the oxidation of water to oxygen during the photocatalytic reduction of CO$_2$. 
**Fig. S10** TEM image and XRD pattern of CsPbBr$_3$-Co$_3$O$_4$ after 5 consecutive cycles, displaying the stability of both morphology and crystallinity, beneficial for practical applications.
Fig. S11 Nitrogen adsorption-desorption curves for (e) pristine Co$_3$O$_4$ HPs and (f) Co$_3$O$_4$ HPs decorated with CsPbBr$_3$-QDs, and their corresponding Brunauer-Emmett-Teller BET surface area values are mentioned in Table S1.
**Fig. S12** Control experiments showing steady-state photoluminescence spectra of Co$_3$O$_4$ HPs.

Under an excitation wavelength at about 630 nm, a weak PL signal was obtained. The peak at 670 nm was probably ascribed to deep-level emission in Co$_3$O$_4$. Note that the as-prepared Co$_3$O$_4$ sample did not display the signals for TRPL.
3. SUPPLEMENTARY TABLES S1-3

**Table S1.** The photocatalytic activity of various state-of-the-art photocatalysts in comparison with as-prepared CsPbBr$_3$-Co$_3$O$_4$ heterostructure

<table>
<thead>
<tr>
<th>Entry#</th>
<th>Photocatalyst</th>
<th>CO $\mu$mol g$^{-1}$h$^{-1}$</th>
<th>CH$_4$ μmol g$^{-1}$h$^{-1}$</th>
<th>*R$_{\text{electron}}$ μmol g$^{-1}$h$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CsPbBr$_3$-Co$_3$O$_4$</td>
<td>35.40</td>
<td>29.2</td>
<td>304.4</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>CsPbBr$_3$ QDs</td>
<td>14.23</td>
<td>0.39</td>
<td>31.98</td>
<td>This work</td>
</tr>
<tr>
<td>3</td>
<td>CsPbBr$_3$-BiOBr</td>
<td>2.5</td>
<td>26.1</td>
<td>213.8</td>
<td>[1]</td>
</tr>
<tr>
<td>4</td>
<td>BiVO$_4$/CsPbBr$_3$</td>
<td>17</td>
<td>6</td>
<td>82</td>
<td>[2]</td>
</tr>
<tr>
<td>5</td>
<td>Mn-CsPbBr$_3$</td>
<td>7.5</td>
<td>0.58</td>
<td>19.64</td>
<td>[3]</td>
</tr>
<tr>
<td>6</td>
<td>ZnSe–CsSnCl$_3$</td>
<td>57</td>
<td>2</td>
<td>128.32</td>
<td>[4]</td>
</tr>
<tr>
<td>7</td>
<td>CsPbBr$_3$/CTF-1</td>
<td>48.2</td>
<td>0</td>
<td>96.4</td>
<td>[5]</td>
</tr>
<tr>
<td>8</td>
<td>0D CsPbBr$_3$/2D CsPb$_2$Br$_5$</td>
<td>197.11</td>
<td>1.5</td>
<td>406.22</td>
<td>[6]</td>
</tr>
<tr>
<td>9</td>
<td>CsPbBr$_3$/Bi$_2$WO$_6$</td>
<td>50.3</td>
<td>1</td>
<td>108.6</td>
<td>[7]</td>
</tr>
<tr>
<td>10</td>
<td>CsPbBr$_3$/Bi$_2$WO$_6$</td>
<td>9.3</td>
<td>14.3</td>
<td>133</td>
<td>[8]</td>
</tr>
<tr>
<td>11</td>
<td>CsPbBr$_3$/UiO-66(NH$_2$)</td>
<td>8.21</td>
<td>0.26</td>
<td>18.5</td>
<td>[9]</td>
</tr>
<tr>
<td>12</td>
<td>CsPbBr$_3$/QDs</td>
<td>4.125</td>
<td>1.90</td>
<td>23.72</td>
<td>[10]</td>
</tr>
<tr>
<td>13</td>
<td>CsPbBr$_3$ /GO</td>
<td>4.81</td>
<td>2.46</td>
<td>29.32</td>
<td>[10]</td>
</tr>
<tr>
<td>14</td>
<td>Co$_3$O$_4$ (OVs)</td>
<td>51.7</td>
<td>0</td>
<td>103.4</td>
<td>[11]</td>
</tr>
<tr>
<td>15</td>
<td>Co$_3$O$_4$/Al$_2$O$_3$</td>
<td>48.4</td>
<td>0</td>
<td>96.8</td>
<td>[12]</td>
</tr>
<tr>
<td>16</td>
<td>Hollow Co$_3$O$_4$ Dodecahedron</td>
<td>46.3</td>
<td>0</td>
<td>92.6</td>
<td>[13]</td>
</tr>
<tr>
<td>17</td>
<td>Co$_3$O$_4$ nanoparticles</td>
<td>0.73</td>
<td>10</td>
<td>81.48</td>
<td>[14]</td>
</tr>
</tbody>
</table>

*Formula used to calculate the rate of electron consumed: $R_{\text{electron}} = 2R_{\text{CO}} + 8R_{\text{CH}_4}$

Where $R_{\text{CO}}$ is the rate of CO evolution, and $R_{\text{CH}_4}$ is the rate of CH$_4$ evolution
Table S2. The information of nitrogen adsorption-desorption analysis in terms of BET surface area, average pore size, and total pore volume of as-synthesized Co₃O₄-HPs and CsPbBr₃-Co₃O₄.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m²/g)</th>
<th>average pore size (nm)</th>
<th>total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄ HPs</td>
<td>16.902</td>
<td>31.35</td>
<td>0.1325</td>
</tr>
<tr>
<td>CsPbBr₃-Co₃O₄</td>
<td>5.016</td>
<td>21.21</td>
<td>0.0266</td>
</tr>
</tbody>
</table>
Table S3. PL decay parameters of the CsPbBr\(_3\) QDs in comparison with CsPbBr\(_3\)-Co\(_3\)O\(_4\) heterostructure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_1)</th>
<th>(A_1)</th>
<th>(\tau_2)</th>
<th>(A_2)</th>
<th>(\tau_3)</th>
<th>(A_3)</th>
<th>(\tau_{avg})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbBr(_3)-QDs</td>
<td>2.61</td>
<td>72.9%</td>
<td>14.71</td>
<td>23.7%</td>
<td>104.36</td>
<td>3.4%</td>
<td>47.43</td>
</tr>
<tr>
<td>CsPbBr(_3)-Co(_3)O(_4)</td>
<td>3.38</td>
<td>7.5%</td>
<td>18.21</td>
<td>84.2%</td>
<td>103.52</td>
<td>8.3%</td>
<td>45.04</td>
</tr>
</tbody>
</table>

* Determined using the fitting function \(y = B + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)\)
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