**Electronic supplementary information**

**Engineering CsPbBr$_3$-based nanocomposite for efficient photocatalytic CO$_2$ reduction: improved charge separation concomitant with increased activity sites**

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Experimental Section

Materials: Cesium carbonate (Cs₂CO₃, 99%) and lead bromide (PbBr₂, ≥99.9%) were purchased from Xi’an Polymer Light Technology Corp. Oleic acid (OA, 90%) was purchased from Alfa Aesar. N,N-dimethylformamide (DMF, chromatographically pure) and oleylamine (OAm, 80-90%) were purchased from Acros. Ammonium chloride (NH₄Cl, ≥99.5) and dicyandiamide (DCDA, ≥99.5) were purchased from Sinopharm Chemical Reagent Co., Ltd. Titanium (IV) chloride (TiCl₄, 99%) was purchased from Damas-beta. Ethyl acetate (Extra dry, 99.8%), acetonitrile (Extra dry, 99.9%), ¹³CO₂ and H₂¹⁸O were purchased from Innochem. 1-Octadecene (ODE, >90%), tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%) and potassium bromide (KBr, spectral purity) were purchased from Aladdin. All chemicals were commercially available and used without further purification. CsPbBr₃ nanocrystals,¹¹ g-C₃N₄ and TiO-CN nanosheets²² were fabricated according to previous publications.

Preparation of CsPbBr₃@TiO-CN: A certain amount of CsPbBr₃ nanocrystals powder (5 mg, 10 mg or 20 mg) was mixed with TiO-CN powder (10 mg) in 5 mL of hexane to construct CsPbBr₃@TiO-CN composites with different loading amounts of CsPbBr₃ (coded as 1:2, 1:1 and 2:1). Subsequently, the suspension was ultrasonicated for 15 minutes and stirred for 2 hours. After centrifuging at 7000 rpm for 5 min, the color of the suspension gradually became from yellow-green to colorless. Then, CsPbBr₃@TiO-CN composite can be obtained after drying.

Preparation of CsPbBr₃@g-C₃N₄: The CsPbBr₃@g-C₃N₄ was prepared with the same method as CsPbBr₃@TiO-CN, except that TiO-CN was substituted with g-C₃N₄.
**Instrumentation:** UV-Vis absorption spectra were recorded with a U-3900 UV/VIS spectrophotometer (Hitachi). FTIR spectra were performed on a Frontier Mid-IR FTIR spectrometer (Perkin Elmer). Power X-ray diffraction (PXRD) patterns were measured by a SmartLab 9kW with Cu Kα radiation (RIGAKU). X-ray photoelectron spectroscopy (XPS) were measured on an ESCALAB250Xi X-ray photoelectron spectrometer with Al Kα as the excitation source (Thermo scientific). The steady-state photoluminescence spectrum (PL) were performed on a F-4600 Fluorescence spectrophotometer (Hitachi). The time-resolved fluorescence measurements were detected with a FLS-1000 steady state and transient state fluorescence spectrometer (Edinburgh Instruments Ltd.). Excitation wavelength: 450 nm; detection wavelength: 520 nm. Transmission electron microscopy (TEM) images were performed on a Talos F200X transmission electron microscope (FEI). Gas Chromatograph measurements were measured in a GC-2014 Gas Chromatograph instrument (SHIMADZU).

**Photoelectrochemical Experiments:** All the electrochemical measurements were investigated using three-electrode configurations with Ag/AgCl reference electrode, Pt sheet as counter electrode, and FTO (0.5 cm²) coated with prepared samples as photoanode, respectively. Meanwhile, 0.1 M of TBAPF₆ acetonitrile solution was used as electrolyte in all electrochemical measurement. The electrochemical impedance spectroscopy (EIS) tests were carried out in dark with 5 mV AC voltage amplitude and frequency range from 100000 to 1 Hz. The photoresponse of the prepared photoanodes (I-t) were measured by recording the photocurrent densities at a bias potential of −0.4 V (vs. Ag/AgCl). Mott–Schottky plots (M-S) were obtained by measuring the
capacitance of the semiconductor–electrolyte interface with AC voltage amplitude of 0.01 V and frequency of 1000 Hz.

**Photocatalytic Experiments:** The CO$_2$ reduction reaction was performed in a 12 mL sealed Pyrex bottle. First, 2 mg of photocatalysts were evenly dispersed into 5 mL solvent mixture of ethyl acetate/deionized water (200:1 v:v) as reaction system. Subsequently, the reaction system was degassed to remove O$_2$ and refilled with CO$_2$. A 300 W Xe lamp (CEL-HXF300, CEAULICHT) with a 400 nm filter was performed to simulate the solar light irradiation, and the light intensity was adjusted to 100 mW cm$^{-2}$ by calibrating with an NREL-calibrated Si solar cell. The obtained gaseous products were analyzed with SHIMADZU GC-2014 Gas Chromatograph instrument.

**References**


Additional data

**Fig. S1** Optical images of mixed CsPbBr$_3$ and TiO-CN in hexane. Left: initial state; right: after ultrasonic 15 minutes and stirring 2 hours followed by centrifuging.
**Fig. S2** TEM image of CsPbBr$_3$ nanocrystals before loading on the TiO-CN. The average size of CsPbBr$_3$ nanocrystals is ~15 nm.
Fig. S3 TEM image (a) and (b-h) elemental mappings for CsPbBr$_3$@TiO-CN.
Fig. S4 Fourier transform infrared (FTIR) spectra of CsPbBr$_3$, TiO-CN and CsPbBr$_3$@TiO-CN.
Table S1 Multiexponential fit parameters for the decay of photoluminescence lifetime.

Excitation wavelength: 450 nm; detection wavelength: 520 nm.

<table>
<thead>
<tr>
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<th>$\tau_1$ (ns) ($A_1$)</th>
<th>$\tau_2$ (ns) ($A_2$)</th>
<th>$\tau_3$ (ns) ($A_3$)</th>
<th>$\tau_{Ave}$ (ns)</th>
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</thead>
<tbody>
<tr>
<td>CsPbBr$_3$</td>
<td>3.1 (20.5%)</td>
<td>9.2 (57.1%)</td>
<td>40.0 (22.4%)</td>
<td>14.8</td>
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<tr>
<td>CsPbBr$_3$@TiO-CN</td>
<td>0.6 (41.9%)</td>
<td>4.3 (35.4%)</td>
<td>29.2 (22.7%)</td>
<td>8.4</td>
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a. $A_1 + A_2 + A_3 = 1$

b. The calculation formula of average lifetime $\tau_{Ave} = \sum \tau_i * A_i$
Fig. S5 (a) EIS Nyquist plots of CsPbBr$_3$, TiO-CN and CsPbBr$_3$@TiO-CN measured under dark. (b) I-t curves of CsPbBr$_3$, TiO-CN and CsPbBr$_3$@TiO-CN plotted at a bias potential of −0.4 V (vs. Ag/AgCl) under light illumination (100 mW cm$^{-2}$).
**Fig. S6** The yields of CO generated from photocatalytic CO$_2$ reduction based on CsPbBr$_3$@TiO-CN photocatalysts with different loading amounts (mass ratio of CsPbBr$_3$/TiO-CN: 1/2, 1/1, 2/1), after 10 h of irradiation under 300 W Xe-lamp, with the light intensity of 100 mW cm$^{-2}$. 