Electronic supplementary information

Engineering CsPbBr₃-based nanocomposite for efficient

photocatalytic CO₂ reduction: improved charge separation

concomitant with increased activity sites

Xiao-Xuan Guo,^a Shang-Feng Tang,^a Yan-Fei Mu,^a Li-Yuan Wu,^a Guang-Xing Dong^a and Min Zhang^{*ab}

^a Institute for New Energy Materials and Low-Carbon Technologies, Tianjin University of Technology, Tianjin, 300384, China. E-mail: zm2016@email.tjtu.edu.cn.

^b Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin, 300384, China.

Experimental Section

Materials: Cesium carbonate (Cs₂CO₃, 99%) and lead bromide (PbBr₂, \geq 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, \geq 99.5) and dicyandiamide (DCDA, \geq 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, \geq 90%), tetrabutylammonlum 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,^{S1} g-C₃N₄ and TiO-CN nanosheets^{S2} were fabricated according to previous publications.

Preparation of CsPbBr₃@**TiO-CN:** A certain amount of CsPbBr₃ nanacrystals 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 K α radiation (RIGAKU). X-ray photoelectron spectroscopy (XPS) were measured on an ESCALAB250Xi X-ray photoelectron spectrometer with Al K α 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 cm^2) 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 CO₂ 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 O₂ and refilled with CO₂. 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

- S1 J. Li, L. Xu, T. Wang, J. Song, J. Chen, J. Xue, Y. Dong, B. Cai, Q. Shan, B. Han and H. Zeng, *Adv. Mater.*, 2017, 29, 1603885.
- S2 S. Tang, X. Yin, G. Wang, X. Lu and T. Lu, Nano Res., 2019, 12, 457-462.

Additional data



Fig. S1 Optical images of mixed CsPbBr3 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 CsPbBr₃ nanocrystals before loading on the TiO-CN. The average size of CsPbBr₃ nanocrystals is ~15 nm.



Fig. S3 TEM image (a) and (b-h) elemental mappings for CsPbBr₃@TiO-CN.



Fig. S4 Fourier transform infrared (FTIR) spectra of CsPbBr₃, TiO-CN and CsPbBr₃@TiO-CN.

 Table S1 Multiexponential fit parameters for the decay of photoluminescence lifetime.

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

	τ ₁ (ns) (A ₁)	τ ₂ (ns) (A ₂)	τ ₃ (ns) (A ₃)	τ _{Ave} (ns)
CsPbBr ₃	3.1 (20.5%)	9.2 (57.1%)	40.0 (22.4%)	14.8
CsPbBr ₃ @TiO-CN	0.6 (41.9%)	4.3 (35.4%)	29.2 (22.7%)	8.4

a. $A_1 + A_2 + A_3 = 1$

b. The calculation formula of average lifetime $\tau_{Ave}\!=\!\sum\!\tau_i\ast A_i$



Fig. S5 (a) EIS Nyquist plots of CsPbBr₃, TiO-CN and CsPbBr₃@TiO-CN measured under dark. (b) *I-t* curves of CsPbBr₃, TiO-CN and CsPbBr₃@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 CsPbBr₃@TiO-CN photocatalysts with different loading amounts (mass ratio of CsPbBr₃/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.