

Electronic supplementary information

Solvent selection and Pt decoration towards enhanced photocatalytic CO₂ reduction over CsPbBr₃ perovskite single crystal

Yi-Xin Chen, Yang-Fan Xu,* Xu-Dong Wang, Hong-Yan Chen and Dai-Bin Kuang*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, Lehn Institute of Functional Materials, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, P. R. China

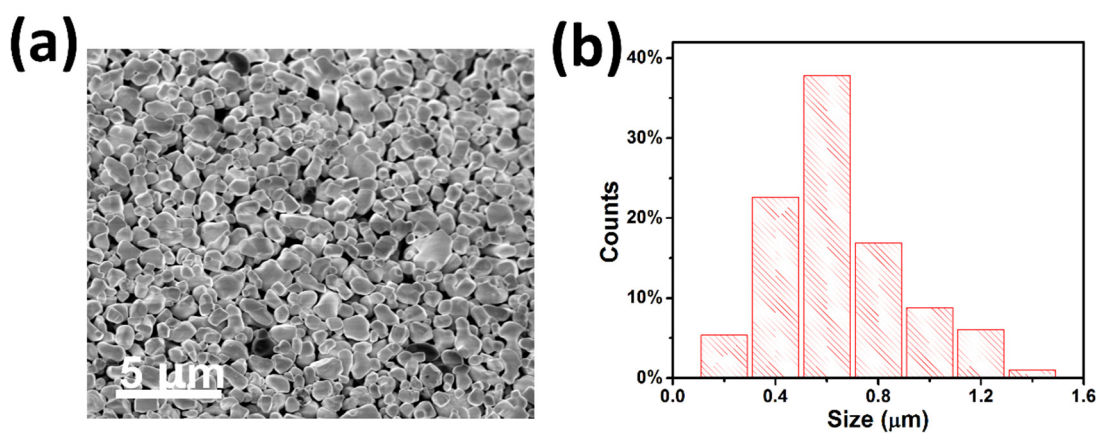


Fig. S1 (a) SEM image and (b) particle size distribution of the as-prepared CsPbBr₃.

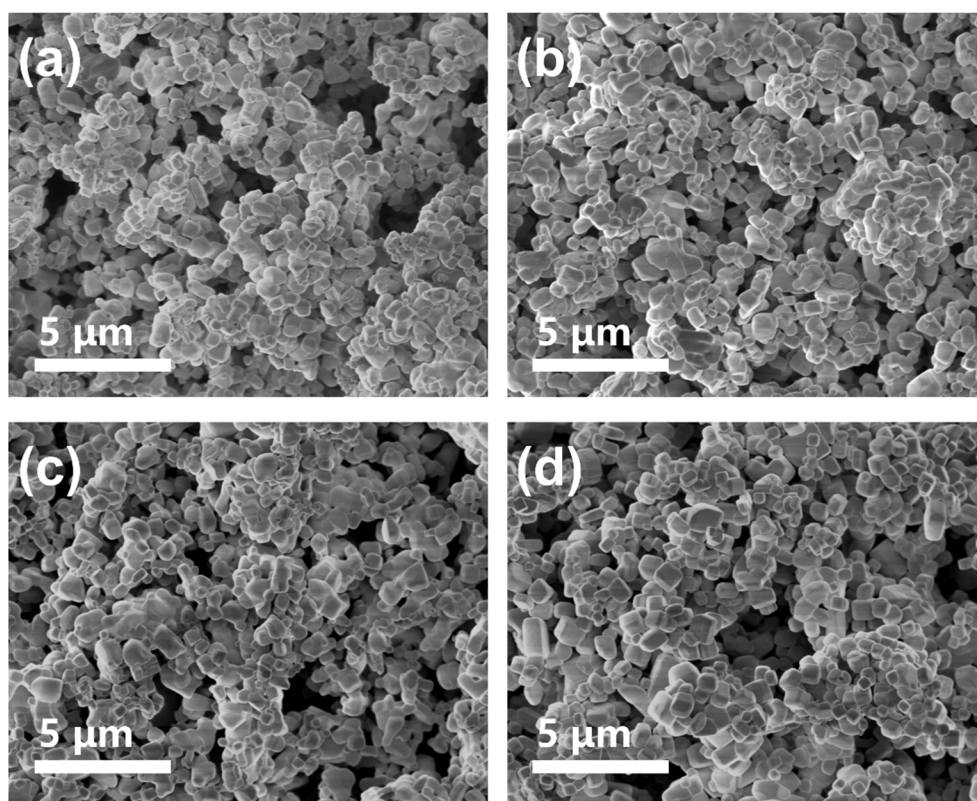


Fig. S2 SEM images of the CsPbBr₃ after 6 h photocatalytic reaction in various solvents: (a) toluene, (b) ethyl acetate, (c) iso-propanol and (d) acetonitrile.

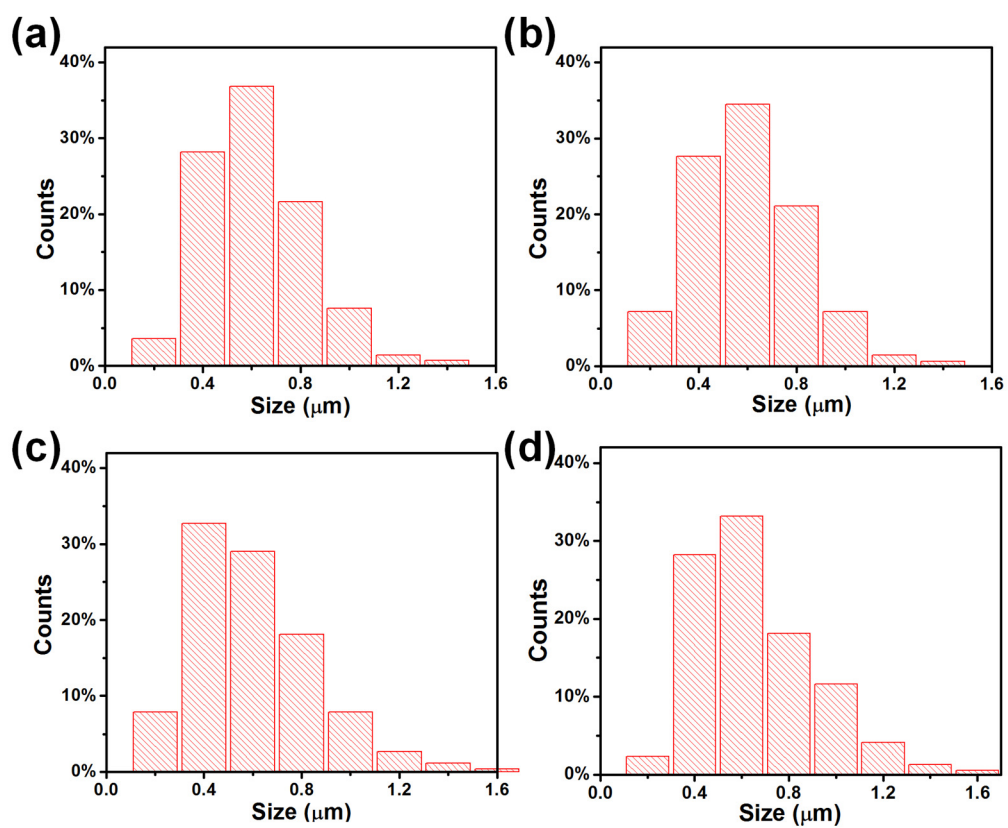


Fig. S3 Size distribution statistics of the CsPbBr₃ crystals after 6 h reaction in (a) toluene, (b) ethyl acetate, (c) iso-propanol and (d) acetonitrile.

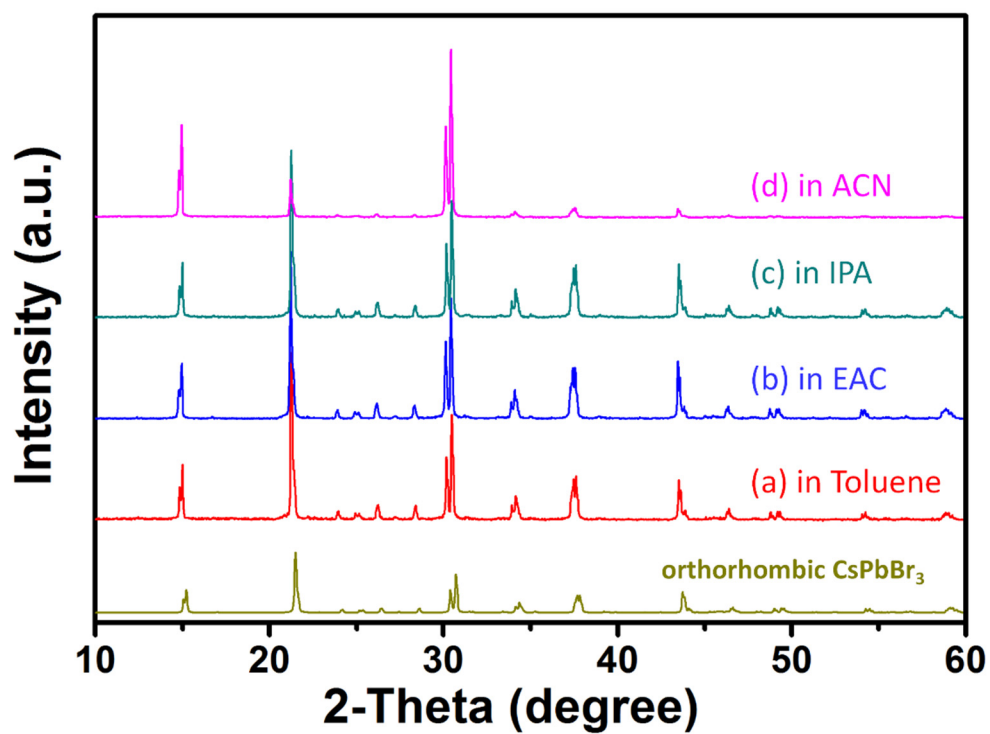


Fig. S4 XRD patterns of CsPbBr₃ storing in various solvents for 50 days: (a) toluene, (b) ethyl acetate, (c) iso-propanol and (d) acetonitrile. Bottom is the standard XRD patterns for orthorhombic phase of CsPbBr₃.

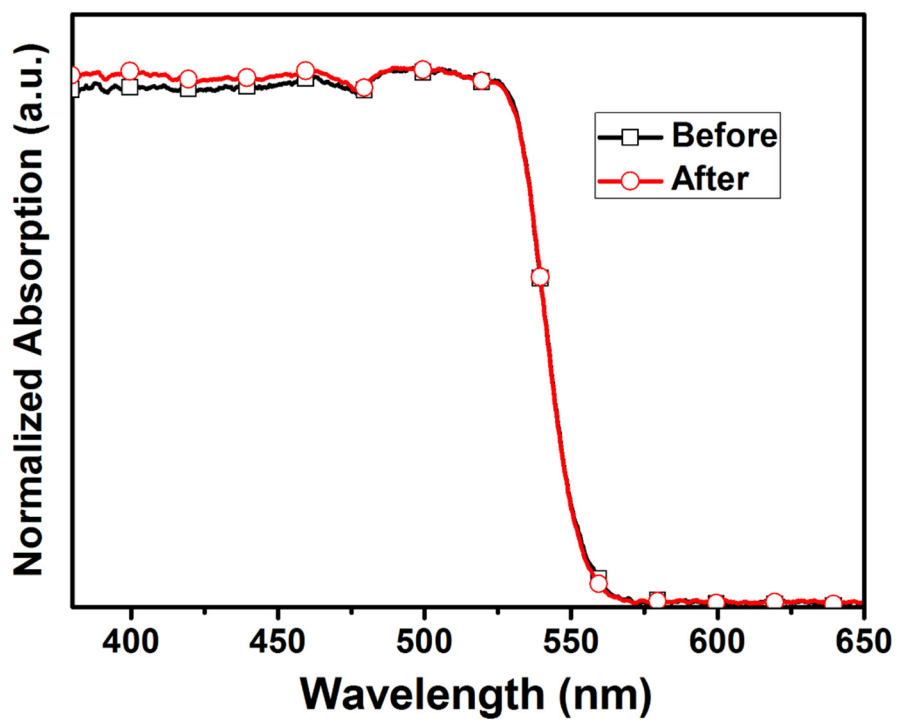


Fig. S5 UV-vis absorption spectra of the CsPbBr₃ before and after photocatalytic reaction of CO₂ in ethyl acetate.

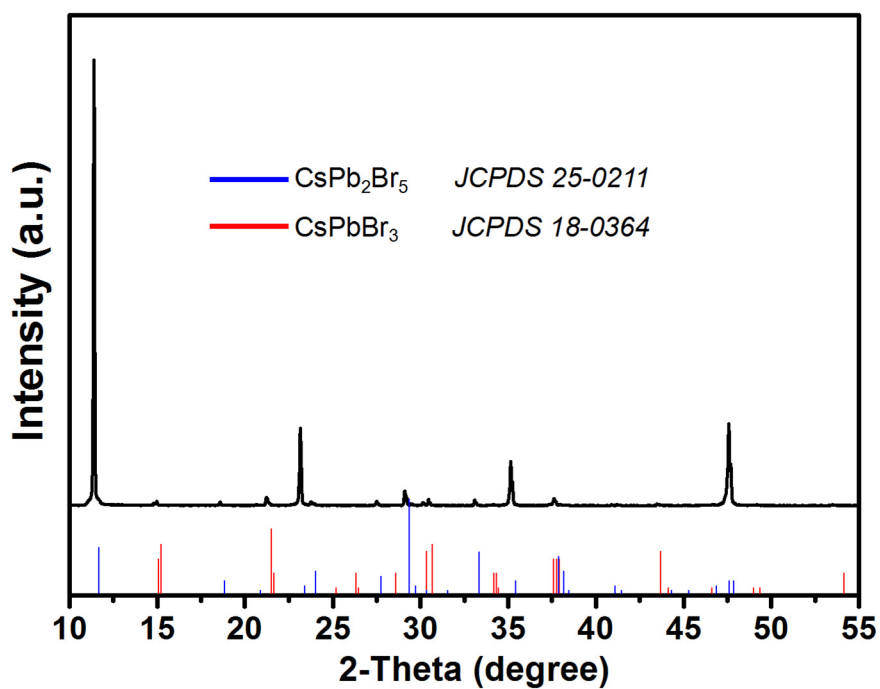


Fig. S6 XRD pattern of the CsPbBr₃ after storing in methanol for 6 h. The evolution from perovskite CsPbBr₃ to tetragonal CsPb₂Br₅ can be illustrated based on the following reaction mechanism: $2\text{CsPbBr}_3 \rightarrow \text{CsPb}_2\text{Br}_5 + 2\text{CsBr}$.

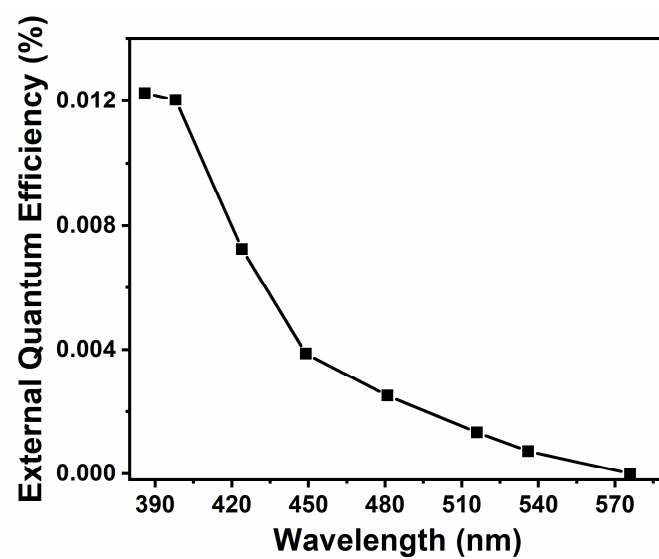
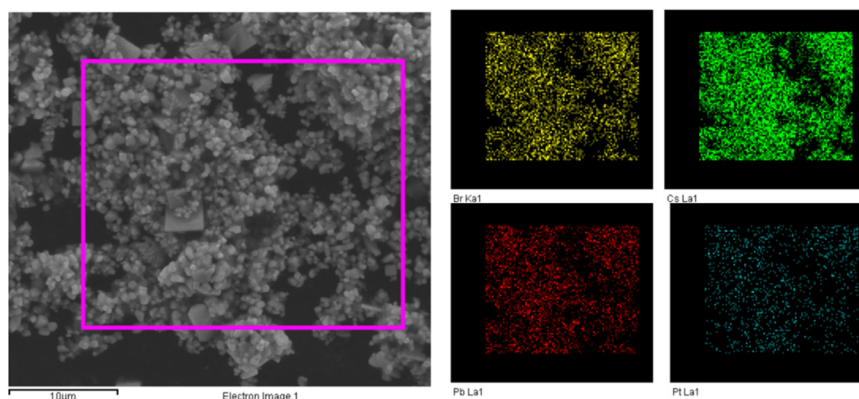


Fig. S7 External quantum efficiencies as a function of wavelength of incident light on CsPbBr₃ photocatalyst in ethyl acetate.

(a)



(b)

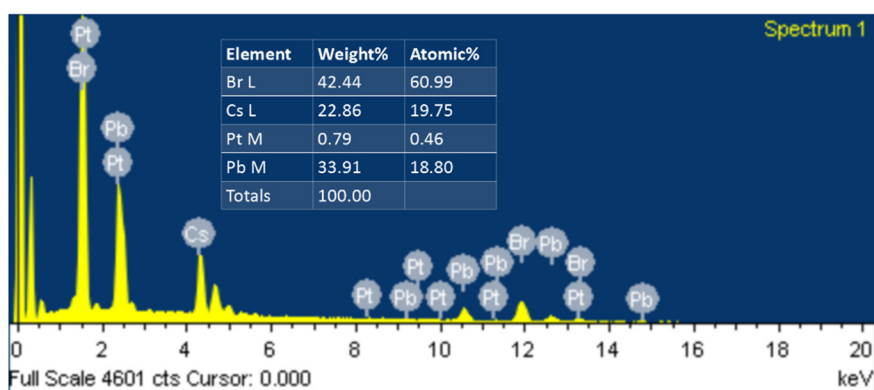


Fig. S8 Energy dispersive X-ray (EDX) analysis: (a) Elemental mapping for the rectangular area (purple box), indicating homogeneous dispersion of Pt on CsPbBr₃. (b) EDX spectroscopy and the related quantitative analysis results.

Table S1. The results of the reference experiments

	R_{CO}
without CsPbBr ₃ photocatalyst	n.d.
CO ₂ replaced by N ₂	0.001 μmol/g h
without illumination	n.d.

CO is not detectable (n.d.) under the absence of CsPbBr₃ or incident light. Moreover, if the saturated CO₂ was replaced by N₂, the CO evolution rate was drastically decreased to 0.001 μmol/g h, implying that the evolution of CO is not originated from the decomposition of the solvents.

Supplementary Note 1. The calculation of the external quantum efficiency (EQE)

The external quantum efficiency (EQE) was performed with the assistance of the Zahner Zennium C-IMPS system (TLS-03). The photosynthesis tests were conducted and detected in an identical process, except the monochromatic incident light provided by a light-emitting diodes (LEDs).

In this study, the EQE is defined as the ratio of the photocatalytic electron consumption (N_{electron}) to the photons flux per hour (N_{photon}) within a specialized wavelength range, which can be illustrate as the followed formula:

$$\text{EQE (\%)} = N_{\text{electron}} / N_{\text{photon}}$$
$$= [2N(\text{CO}) + 8N(\text{CH}_4) + 2N(\text{H}_2)] / N_{\text{photon}}$$

The calculation of N_{electron} is based on the fact that two electrons are required to produce one molecule CO or H₂, while 8 electrons for the one molecule CH₄, according to the equations mentioned in the manuscript. The N_{photon} is calculated using the equation:

$$N_{\text{photon}} = [\text{Light intensity} * \text{Illumination area} * \text{Time}] / [\text{Average single photon energy} * N_A]$$

where the illumination area is controlled to 0.82 cm², N_A is the Avogadro constant and the average single photon energy (E_{photon}) is figured out using the equation:

$$E_{\text{photon}} = hc / \lambda$$

where h is the Planck constant, c indicates speed of light, and λ is the wavelength. The related parameters of the incident light are summarized in Table S2.

Table S2. The information of the incident light used in EQE tests.

Wavelength /nm	Light Intensity /W m ⁻²	Average single photon energy /J	N_{photon} / $\mu\text{mol h}^{-1}$
386	74.1	5.15 E-19	70.61
398	62.5	4.99 E-19	61.41
424	183.98	4.69 E-19	192.57
449	215.2	4.42 E-19	238.52
481	165.4	4.12 E-19	196.39
516	101.7	3.84 E-19	129.54
536	87.6	3.71 E-19	115.91
576	119.49	3.45 E-19	169.90