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Supporting Information

In Situ Confinement of $CsPbBr_3$ Quantum Dots within COF for Enhanced Photocatalytic CO_2 Reduction

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1. Experimental Details

1.1 Materials and Reagents

All chemicals were purchased from commercial sources and utilized without further purification. 2, 4, 6-Tris(4-aminophenyl) triazine (TTA, 98%, Innochem), tris(4-formylphenyl) amine (TFA, 98%, Innochem), 1,2-dichlorobenzene (C_6H_4Cl, 99%, Innochem), 1-Butanol ($C_4H_{10}O$, 99%, Innochem), Acetic acid ($C_2H_4O_2$, 99%, Innochem), Cesium carbonate (Cs_2CO_3, 99.9%, Innochem), lead bromide ($PbBr_2$, 99.99%, Innochem), 1-Octadecene (ODE, 90%, Innochem), Oleic acid (OA, 90%, Innochem), Oleylamine (OAm, 90%, Innochem), Toluene (C_7H_8, 99%, Innochem), Ethanol (EtOH, 99.9%, Innochem), N, N-dimethylformamide (DMF, 99 %, Aladdin).

1.2 Photocatalytic CO_2 Reduction Measurement

The photocatalytic CO_2 reduction was performed with a liquid–solid heterogeneous reaction mode in a 50 mL quartz reactor at ambient temperature and atmospheric pressure. Typically, a mixture of MOF catalysts (5 mg), water (50 μL) and acetonitrile (MeCN, 10 mL) was added in a gas-closed quartz reactor. The system was thoroughly degassed and then backfilled with pure CO_2 (99.999%, Tenglong Gas) for repeated three times, respectively. After the last degassing, the reactor was backfilled with 1.0 atm of CO_2 and lighted through a 300 W Xenon arc lamp (PLS-SXE300D, Beijing Perfectlight) with a 400–780 nm filter (UVCUT 400, Beijing Perfectlight) for 2 h. During the photocatalytic process, the reaction system was vigorously stirred, and the temperature of the reactor was kept at room temperature with condensate water. The gas products were qualitatively and quantified analyzed by gas chromatography.

1.3 Characterization

Powder X-Ray diffraction (PXRD) patterns were collected on a Bruker D8 ADVANCE diffractometer with Cu Kα radiation (λ =1.54056 Å). Fourier Transform infrared (FT-IR) spectra were acquired on a Bruker Tensor 27 spectrophotometer using KBr pellets in the range of 500–4000 cm^{-1}. Scanning electron microscopy (SEM) images were obtained from a Hitachi SU-8010 SEM. Transmission electron microscopy (TEM) images and energy-dispersive X-ray (EDX) analyses were conducted on an FEI Talos F200X microscope operated at 200 kV. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed on a Thermo Fisher ESCALAB Xi^+ system with

a He Iα excitation source (21.22 eV). UV–vis diffuse reflectance spectra (UV–vis-DRS) were recorded on a Shimadzu UV-3600Plus spectrophotometer using $BaSO_4$ as a reflectance standard. Elemental analyses were carried out via a Vario EL III elemental analyzer and an Agilent 7900 ICP-MS. X-ray photoelectron spectrum (XPS) analyses were carried out on a PHI5000 Versa Probe III spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source. N_2 adsorption-desorption isotherms were recorded on Tristar 3020, and the surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation. CO_2 adsorption-desorption isotherms were assessed on a JW-BK300C instruments. CO_2 temperature programmed desorption (CO_2-TPD) tests were conducted on a Micromeritics AutoChem II 2920 instrument. ^{1}HNMR spectra were recorded using a 400 MHz nuclear magnetic resonance spectrometer (Bruker AV500, TMS as the internal standard). Room-temperature photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) decay dynamics spectra were detected on an Edinburgh instruments Ltd. FLSP920 fluorescence spectrometer.

1.4 Photoelectrochemical Measurements

Transient photocurrent response (*i*−t), electrochemical impedance spectroscopy (EIS), and Mott−Schottky (M−S) plots were carried out using an electrochemical workstation (CHI 660E Chenhua) with a three-electrode cell. There is a Pt foil counter electrode and a saturated Ag/AgCl reference electrode. The working electrode was prepared by a dipcoating method: the photocatalyst (5 mg) was dispersed in a mixed solution of absolute ethanol (0.9 mL) and Nafion (0.1 mL) to form a slurry, and then, the slurry (100 μL) was dip-coated on an ITO conductive glass (1 cm^2). Subsequently, the film was dried in a vacuum oven at 80 °C. Redistilled water solution of Na_2SO_4 (0.1 M) was used as the electrolyte.

2. Supplementary Figures

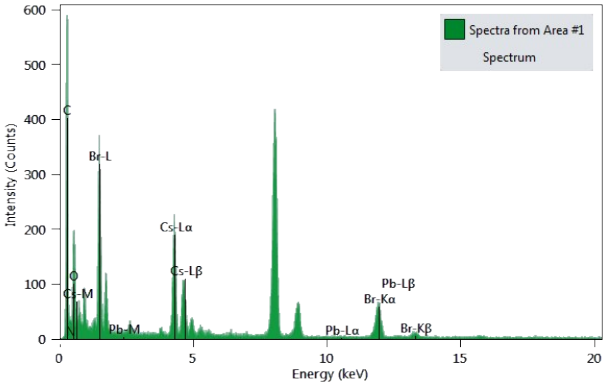

Figure S1. EDX spectrum of the CPB@COF composite.

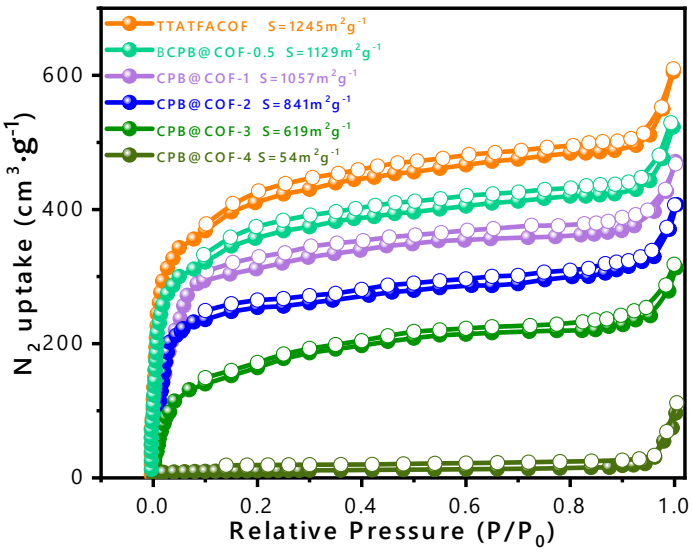

Figure S2. N_2 sorption isotherms of CPB@COF-*x* (*x* = 1, 2, 3, 4)

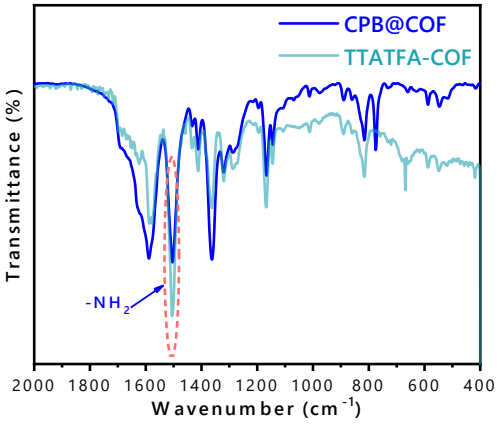

Figure S3. FT-IR spectra of TTATFA-COF and CPB@COF.

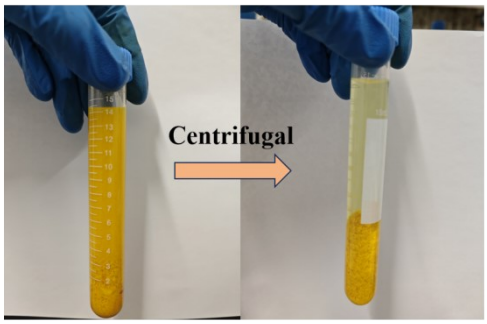

Figure S4. Comparison of photos before and after CPB@COF centrifugation.

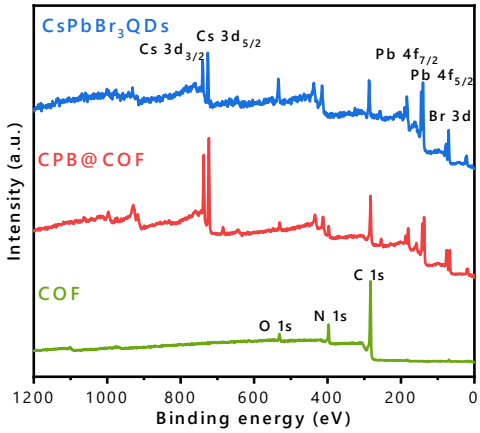

Figure S5. XPS full spectrum of COF, $CsPbBr_3$ and CPB@COF.

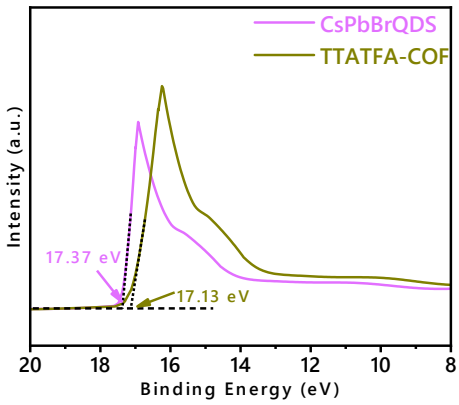

Figure S6. UPS spectra of TTATFA-COF and $CsPbBr_3$ QDs.

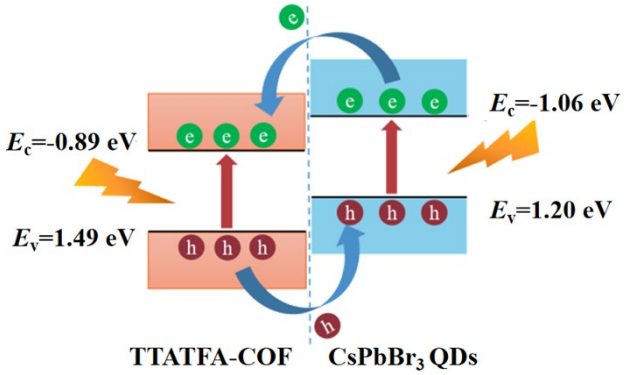

Figure S7. CPB@COF Diagram of type-II heterojunction.

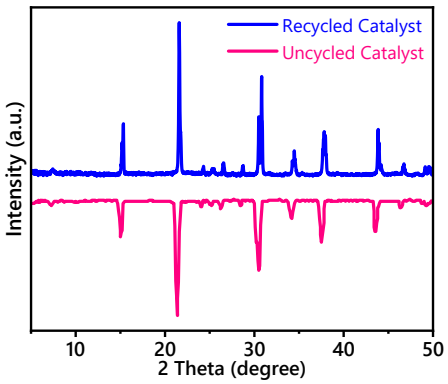

Figure S 8. Comparison of PXRD patterns of the fresh and recycled photocatalyst.

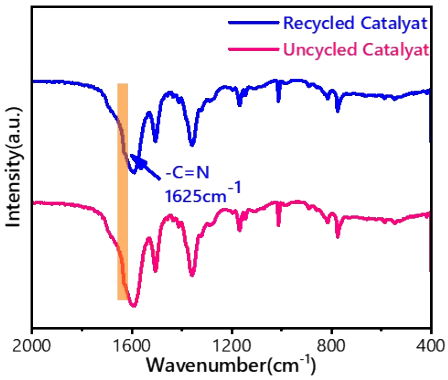

Figure S9. Comparison of FT-IR spectra of the fresh and recycled photocatalyst.

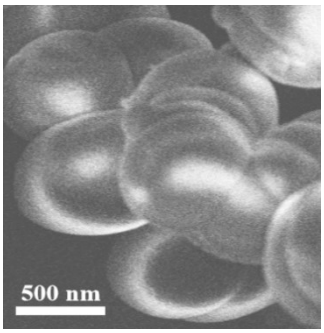

Figure S10. SEM image of CPB@COF after photocatalytic cycling tests.

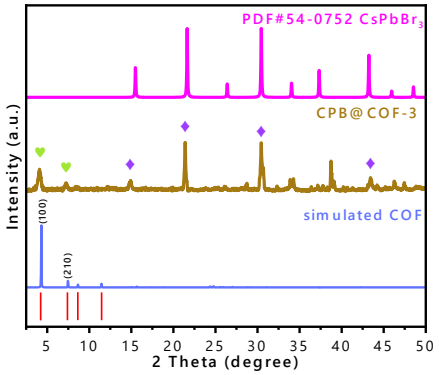

Figure S11. XRD patterns for CPB@COF-3.

3. Supplementary Tables

Table S1. ICP-MS of $CsPbBr_3$ QDs@TTATFA-COF.

Samples/wt%	$CsPbBr_3$	Cs	TTATFA-COF
$CsPbBr_3$ QDs@TTA-TFA-9%	9.25	2.12	90.75
$CsPbBr_3$ QDs@TTA-TFA-12%	12.26	2.82	87.74
$CsPbBr_3$ QDs@TTA-TFA-19%	19.06	4.38	80.94
$CsPbBr_3$ QDs@TTA-TFA-28%	28.43	6.54	71.47
$CsPbBr_3$ QDs@TTA-TFA-37%	37.25	8.72	62.55

Table S2. Multi-exponential fit parameters for the decay plots of TRPL lifetime.

Sample	A_1(%)	τ_1(ns) ($R_{el.}$ %)	A_2(%)	τ_2(ns) ($R_{el.}$ %)	τ_{av} (ns)	χ^2
$CsPbBr_3$	0.74	1.71	0.26	11.99	9.21	1.077
TTA-TFA	0.62	1.67	0.38	8.78	7.07	1.038
$CsPbBr_3$ QDs@TTA-TFA	0.59	1.21	0.41	14.75	13.34	1.016

Table S3. Pb leaching results from the CPB@COF-2 catalyst after different photocatalytic cycles determined by ICP-OES.

Cycle Number	Reaction Time (h)	Pb Concentration in Supernatant (mg/L)
1	6	0.006
2	12	0.007
3	18	0.009
4	24	0.010
5	30	0.010

Note: Experimental conditions for the leaching test: 5 mg of CPB@COF-2 catalyst dispersed in 10 mL of MeCN/H_2O (v/v = 200:1) solution under CO_2 atmosphere. After visible light irradiation for the specified cumulative time, the solution was centrifuged, and the supernatant was digested with concentrated HNO_3 before ICP-OES analysis. The detection limit for Pb is 0.01 mg/L.