

Supporting Information

Self-assembly of MAPbBr₃/Pb-MOF heterostructure with enhanced photocatalytic CO₂ reduction performance and stability

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1. Experimental Section

1.1 Materials

Methylammonium bromide (MABr, 99.5%, CAS 6876-37-5), Lead bromide (PbBr_2 , 99.0%, CAS 10031-22-8), p-Phthalic acid ($\text{C}_8\text{H}_6\text{O}_4$, 99%, CAS 100-21-0) were purchased from Shanghai Macklin Biochemical Co., Ltd, Isopropyl alcohol (99.5%, CAS 67-63-0) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. All chemicals were used without further purification. All of the reagents and solvents were commercially available and could be used without further purification.

1.2 Synthesis of MAPbBr_3

MAPbBr_3 nanocrystals were prepared by high-energy ball milling. MABr and PbBr_2 were weighed in a molar ratio of 1 : 1, and then placed in 3 mL of isopropyl alcohol (IPA) to disperse uniformly by ultrasonic. As a grinding agent, IPA can achieve sufficient grinding. It was then transferred to a 25 mL agate grinding jar containing 5 agate grinding balls, and ground for 120 min at 600 rpm in a glove box under N_2 atmosphere. After ball milling, the orange-yellow perovskite paste was centrifuged and washed with IPA for more than three times to remove unreacted substances, followed by vacuum drying at 60 °C to obtain orange-yellow MAPbBr_3 powder.

1.3 Synthesis of *Pb-MOF*

Typically, 1 mmol of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and 2 mmol of p-Phthalic acid (PTA) were dissolved in 20 mL of IPA and stirred for 1 h. Then, the mixture was moved to a 50 mL Teflon-lined autoclave and heated at 100 °C for 24 h. After centrifugation, washed with IPA for more than three times and placed in a vacuum drying box to dry at 60 °C overnight, the obtained white powder was recorded as *Pb-MOF*.

1.4 Synthesis of $\text{MAPbBr}_3/\text{Pb-MOF}$

100mg of pre-prepared MAPbBr_3 powder was dispersed in 20 mL of IPA, and PTA

was added to the same four solutions according to different molar ratios, and recorded as MP0.05, MP0.5, MP1, MP2 (MAPbBr₃ : PTA = 1:0.05,1:0.5,1:1,1:2), which were recorded as MP0.05, MP0.5, MP1, MP2. The solution was transferred to a 50ml Teflon-lined reaction kettle, kept at 100 °C for 24 h, washed with IPA for more than three times after centrifugation to remove unreacted substances, and dried at 60 °C overnight.

1.5 Materials Characterization

The phase composition of samples was obtained by X-ray diffraction (XRD, D8 Advance) equipped with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$). Fourier transform infrared spectroscopy (FT-IR) was collected on a Thermo Scientific Nicolet iS10 spectrometer. The morphologies of samples were observed on transmission electron microscopy (TEM, JEM-2100Plus). The X-ray photoelectron spectroscopy (XPS) spectra were analyzed by a Thermo Fisher Scientific corporation Escalab 250Xi instrument. N₂ adsorption/desorption isotherms were examined with Brunauer-Emmett-Teller (BET). UV-vis DRS spectra was measured with Shimadzu UV-3600. Steady photoluminescence (PL) emission spectra were tested by luminescence spectrophotometer (QM-400, PTI) with 450 nm excitation wavelength. Transient time resolved PL decay measurements were obtained using a FLS1000 under the excitation of 450 nm. The active species were analyzed by using electron spin resonance (ESR) test (Bruker ESR A-300).

1.6 Photocatalytic Experiments

The photocatalytic CO₂ reduction performance was measured by a gas-solid test system under the visible light of 300W Xe lamp. The powder sample of 20 mg was weighed and placed on sample rack in a quartz reactor filled with CO₂ and water vapor. 0.5 ml of deionized water is placed under the sample in the reactor to avoid direct contact with the sample. Subsequently, the sealed reactor is heated at 60 °C for 30 minutes to ensure that the deionized water becomes water vapor. The water vapor participated in the chemical reaction as a proton source. 1 ml of gas product is extracted

with a syringe every hour and analyzed by gas chromatography (GC-7900, CEAULight, China) with a TCD and FID detector.

1.7 Electrochemical measurements

Photoelectrochemical characterizations were proceeded in Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) solution with a standard three-electrode system on the electrochemical station (SP-150, Bio-Logic). The carbon cloth coated with catalyst, Pt net and saturated Ag/AgCl were served as working electrode, counter electrode and reference electrode, respectively. Typically, a slurry of 4 mg of sample and 1 ml of ethanol were used to make the working electrode. The electrochemical impedance spectroscopy (EIS) was recorded from 0.01 Hz to 100 kHz with a sinusoidal ac perturbation of 10 mV. The impedance potential model was employed to collect the Mott-Schottky plots with the frequency of 500, 1000 and 2000 Hz. I-t curves were recorded using 300 W Xe lamp with a 420 nm cutoff filter.

2. Supporting Figures

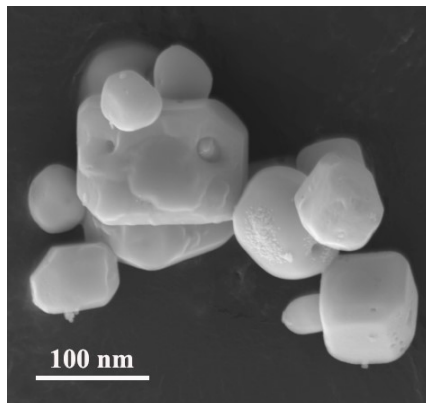


Fig. S1 SEM image of MAPbBr₃.

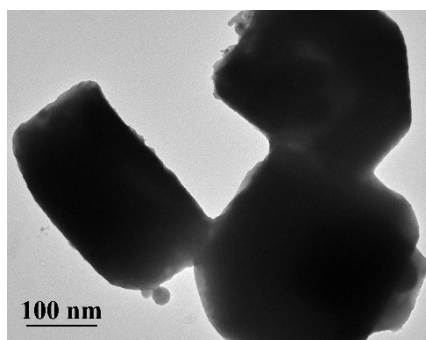


Fig. S2 TEM image of MP0.05.

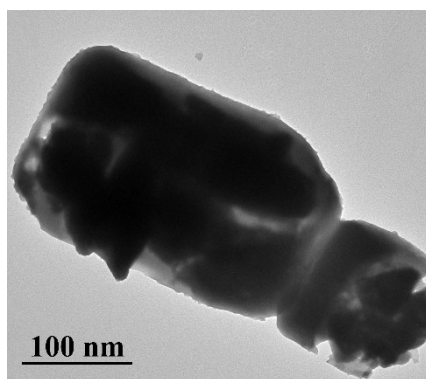


Fig. S3 TEM image of MP2.

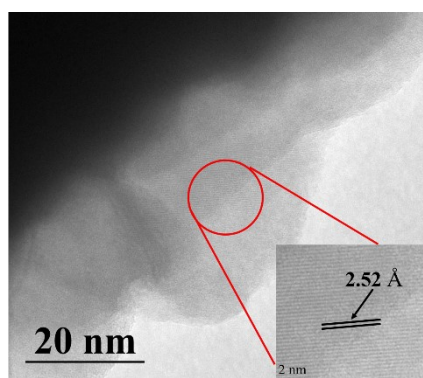


Fig. S4 TEM image of Pb-MOF (inset: HRTEM image of Pb-MOF).

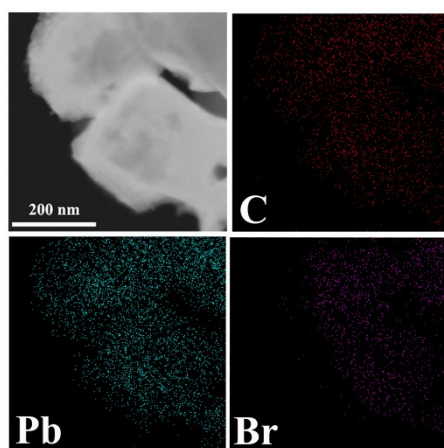


Fig. S5 The corresponding EDX mapping images of MP0.5.

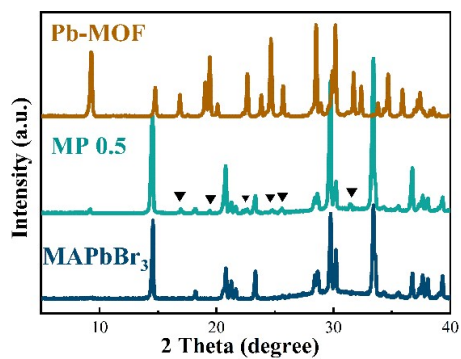


Fig. S6 XRD patterns of MAPbBr₃, Pb-MOF and MP 0.5.

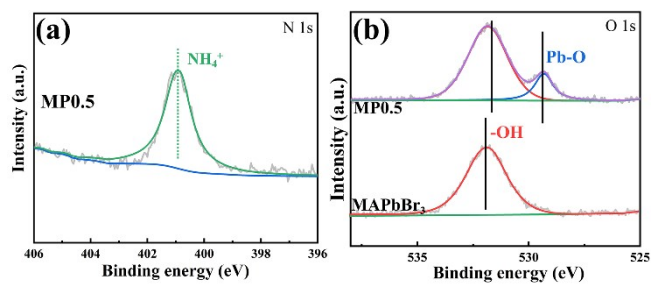


Fig. S7 The high resolution XPS spectra: (a) N 1s of MP0.5, (b) O 1s of MAPbBr₃ and MP0.5.

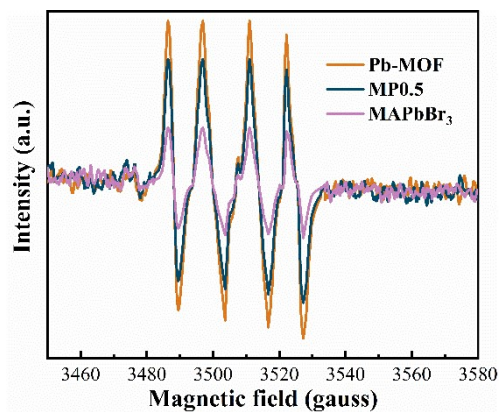


Fig. S8 EPR detection of $\cdot\text{O}_2^-$ under light irradiation of MAPbBr₃, Pb-MOF and MP0.5.

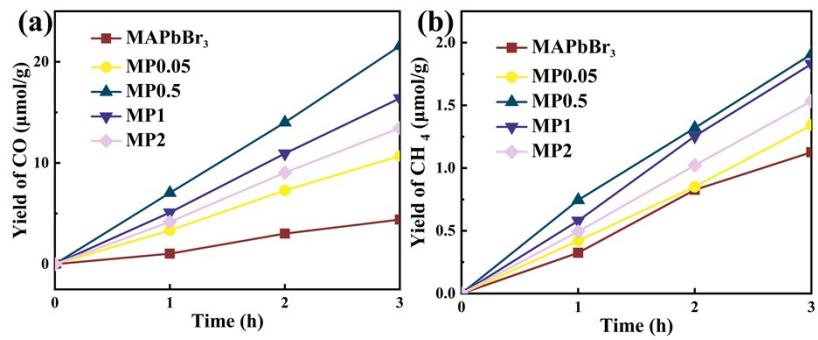


Fig. S9 Photocatalytic reduction of CO₂ products within 3h

3. Supporting Tables

Table S1. The detailed transient fluorescence properties of MAPbBr₃, Pb-MOF and MP samples.

Samples	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	A ₃ (%)	τ ₃ (ns)	Average lifetime τ (ns)
Pb-MOF	71.8	2.59	27.5	2.59	0.7	12.8	2.94
MAPbBr ₃	44.3	1.79	31.8	1.79	23.9	2.05	1.86
MP0.05	78.8	1.64	0.1	17	21.1	0.9	1.72
MP0.5	0.1	6.54	56.1	1.37	43.8	1.37	1.39
MP2	0.4	4.2	67	1.35	32.6	1.79	1.55

Table S2 Specific surface area data of samples

Sample	S _{BET} (m ² g ⁻¹)	S _{Langmuir} (m ² g ⁻¹)
MAPbBr ₃	21.23	81.26
MP0.5	65.47	247.19
Pb-MOF	1769	4501

Table S3 Resistance value (Rs and Rc) of MAPbBr₃, Pb-MOF and MP0.5 samples.

Sample	Rs (Ω)	Rc (Ω)
MAPbBr ₃	117	2994
MP0.5	2.727	542.8
Pb-MOF	125.6	3708

Table S4 The yield of CO and CH₄ productions and the selectivity of CO for photocatalytic conversion of CO₂ over different samples MP0.5 samples.

Sample	Yield of production		Charge selectivity for CO (%)
	CO	CH ₄	
	($\mu\text{mol}\cdot\text{g}^{-1}$)	($\mu\text{mol}\cdot\text{g}^{-1}$)	
MAPbBr ₃	4.39931	1.12604	79.6%
MP0.05	12.92379	1.34288	90.5%
MP0.5	21.56695	1.90779	91.8%
MP1	16.39412	1.83628	89.9%
MP2	13.46413	1.53441	89.7%