

Encapsulation of perovskite quantum dots in dual-metal sites metal-organic frameworks for efficient artificial photosynthesis

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ABSTRACT

Metal-organic frameworks (MOFs) have sparked interest in photocatalysis. Unfortunately, they usually exhibit insufficient charge separation and catalytic efficiencies for artificial photosynthesis. Herein, the encapsulation of CsPbBr₃ quantum dots (QDs) into the pores of dual-metal sites MOFs (MOF-919-Cu₂M, M = Cu, Co, Zn) has been achieved to fabricate a series of CsPbBr₃@MOF-919-Cu₂M heterojunctions for CO₂ photoreduction to HCOOH coupled with H₂O oxidation to O₂. The close contact of CsPbBr₃ QDs and MOF-919-Cu₂M shortens the photo-induced electron transfer distance, which dramatically facilitates the charge separation. Meanwhile, the Cu and M dual-metal sites within the Cu₂M clusters exhibit synergistic catalysis effect, which significantly enhances catalytic efficiency of active sites. As a result, CsPbBr₃@MOF-919-Cu₂Co achieves the highest photocatalytic performance with an electron consumption rate of 669.6 μmol g⁻¹ h⁻¹ (selectivity, ~100 %) for HCOOH production, which is 64, 56 and 5 times higher than those of pristine CsPbBr₃ QDs, MOF-919-Cu₃, and the physical mixture of CsPbBr₃ QDs/MOF-919-Cu₂Co, respectively. Experiments and theoretical calculations reveal that the Cu and Co dual-metal sites of CsPbBr₃@MOF-919-Cu₂Co show the optimal synergistic effect due to the strongest binding strength between Cu/Co and HCOO* intermediate, which can drastically decrease reaction energy barrier of the rate-determining step, thus explaining the enhanced photocatalytic activity.

1. Introduction

The large-scale usage of fossil fuels leads to the excessive emissions of carbon dioxide (CO₂) into the atmosphere, which has caused serious environmental issue [1,2]. More and more countries have proposed the carbon neutral schedule. The exploration of effective strategies for CO₂ conversion is an urgent need. Inspired by natural photosynthesis, the conversion of CO₂ and H₂O into value-added fuels and O₂ using sunlight is regarded as a potential solution to achieve carbon neutral goal [3–5]. However, achieving this overall reaction with high efficiency is still challenging owing to the high chemical inertness of both CO₂ and H₂O molecules, as well as multielectron and multiproton transfer processes for both CO₂ reduction and H₂O oxidation reactions [6–11]. Therefore, the development of efficient photocatalysts to realize the artificial photosynthesis is highly desirable.

Metal-organic frameworks (MOFs), as a class of crystalline porous material, which are constructed by metal ions/clusters and organic

ligands, have demonstrated great potential in artificial photosynthesis due to their periodic and tailorable structures, high surface area, semiconductor-like behavior and well-exposed active sites, etc [12–16]. Nevertheless, they usually exhibit insufficient charge separation and catalytic efficiencies, and thus poor photocatalytic performance. Over the past several decades, various strategies have been developed to improve catalytic activity for MOF-based photocatalysts. Among them, the construction of composite photocatalysts by integrating semiconductors and MOFs is considered to be an effective strategy as the charge separation efficiency of composites can be significantly enhanced over single component [17–24]. In particular, the encapsulation of semiconductors in the pores of MOFs to form composite photocatalysts has attracted more and more attentions because the photo-induced electron transfer distance between MOFs and semiconductors can be dramatically shortened compared with their simply physical mixture, thus can further boost charge separation efficiency [23,24].

In addition to increasing charge separation efficiency, a series of

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dual-metal sites MOFs with appropriate M...M separations have been designed and fabricated to enhance catalytic efficiency via the dinuclear metal synergistic catalysis (DMSC) effect. In photocatalytic CO₂ reduction reaction, CO₂ adsorption and activation are two important steps with high reaction energy barriers, which may determine the reactive dynamics. For dual-metal sites MOFs, two metal centers can bind a CO₂ molecule simultaneously with bridge mode to promote the activation of CO₂ molecule, which can lower the reaction energy barriers of the rate-determining step compared with the single-metal site counterparts [25–27]. In this context, the regulation of dual-metal sites of MOFs is expected to modulate dual-metal synergistic effect to further boost catalytic efficiency for CO₂ photoreduction, while the related report has not been documented so far. Therefore, it is meaningful to encapsulate semiconductors in the pores of MOFs and regulate dual-metal sites of MOFs to improve both charge separation and catalytic efficiencies.

Based on the above in mind, we rationally constructed three CsPbBr₃@MOF-919-Cu₂M (M = Cu, Co, Zn) heterojunction photocatalysts by encapsulating CsPbBr₃ quantum dots (QDs) in the pores of dual-metal sites MOF-919-Cu₂M for visible-light-driven CO₂ reduction to HCOOH coupled with H₂O oxidation to O₂. The close contact of CsPbBr₃ QDs and MOF-919-Cu₂M shortens the photo-induced electron transfer distance, thus greatly enhances charge separation efficiency. Meanwhile, the Cu and M dual-metal sites within the Cu₂M clusters exhibit synergistic catalysis effect, which significantly enhances catalytic efficiency of active sites. Among which, the Cu and Co dual-metal sites of CsPbBr₃@MOF-919-Cu₂Co show the optimal synergistic effect due to the strongest binding strength between Cu/Co and HCOO* intermediate, resulting in the highest catalytic activity for photocatalytic CO₂ reduction to HCOOH.

2. Experimental section

2.1. Materials and equipments

All chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (XRD) were collected on D8 ADVANCEX-Ray Diffractometers with Cu K α radiation (λ = 1.54 Å). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and energy dispersive spectroscopic (EDS) mapping were acquired on transmission electron microscope with a LaB6 Gun (Tecnai G2 Spirit TWIN and Talos F200 X, FEI, USA) at an acceleration voltage of 120 kV. Gas sorption measurements were conducted using a multi-station specific surface micropore and vapor adsorption analyzer (BELSORP-Mas, Microtrac BEL, Japan). X-ray photoelectron spectroscopy (XPS) spectra were carried out using an X-ray spectrometer (ESCALAB 250 Xi spectrometer, Thermo Scientific, USA) with Al K α as the excitation source. Solid-state UV–vis absorption spectra were obtained on a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan). Photoluminescence (PL) spectra were measured with an F-4600 fluorescence spectrometer. Time-resolved PL (TRPL) spectra were acquired on an FLS1000 fluorescence spectrometer. Electron paramagnetic resonance (EPR) spectra were collected on EMXplus-6/1 and JEOL JES-FA200 EPR spectrometers. *In situ* fourier transform infrared spectroscopy (FTIR) spectra were recorded on Nicolet iS50 IR spectrometers, and samples were tableted with KBr as support. The contents of metals were quantified by inductively coupled plasma mass spectrometry (ICP-MS) (iCAP RQ, Germany). Transient absorption (TA) spectra were measured on the LP980 laser flash photolysis instrument (Edinburgh). The catalytic product in gaseous phase of the reaction system was analyzed by gas chromatography (GC-2014 +ATF, 230 C, Shimadzu, Japan) equipped with two automated gas sampling valves, which contain a thermal conductivity detector (TCD) and a flame ionization detector (FID). The liquid products were analyzed using ion chromatography (Eco IC) and nuclear magnetic resonance (NMR, Bruker AVANCE AV III 400) spectroscopy. The isotopes of ¹⁸O for O₂ were analyzed using mass spectrometry (HPR-20 QIC). Photocurrent, electrochemical impedance

spectroscopy (EIS), Mott-Schottky plots, electrochemical active surface areas (ECSA), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed on CHI 660E and CHI 760E electrochemical workstations.

2.2. Synthesis of MOF-919-Cu₂M

MOF-919-Cu₃ was synthesized according to the literature [28]. Typically, ScCl₃·6 H₂O (76.2 mg), Cu(NO₃)₂·3 H₂O (135.6 mg), 1H-pyrazole-4-carboxylic acid (H₂PyC, 34.8 mg) and *N,N*-dimethylformamide (DMF) (10 mL) were added in a 20 mL Pyrex vial, which was heated at 100 °C for 15 h. After cooling to room temperature, the green product was collected by filtration, immersed in DMF for 3 days, and followed in ethanol for 3 days. The product was dried under vacuum at 60 °C for 12 h to yield MOF-919-Cu₃. Then, 20 mg MOF-919-Cu₃ was added in 5.0 mL 0.5 M DMF solution of Zn(NO₃)₂·6 H₂O or Co(NO₃)₂·6 H₂O, which was heated at 90 °C for 24 h to yield gray product of MOF-919-Cu₂Zn or dark gray product of MOF-919-Cu₂Co. Afterwards, MOF-919-Cu₂Zn and MOF-919-Cu₂Co were soaked in DMF and ethanol respectively for 3 days, filtrated and dried under vacuum at 60 °C for 12 h. Finally, MOF-919-Cu₂M (M = Cu, Zn, Co) were further dried under vacuum at 150 °C for 12 h to yield the activated MOF-919-Cu₂M.

2.3. Preparation of CsPbBr₃@MOF-919-Cu₂M

20 mg activated MOF-919-Cu₂M was dispersed in 5.0 mL 0.005–0.016 M DMF solution of PbBr₂, and stirred for 2 h. The PbBr₂@MOF-919-Cu₂M were collected by filtration and washing with a mixed solvent of DMF/ethanol (v:v = 1:1). Afterwards, PbBr₂@MOF-919-Cu₂M was dispersed in 1.0 mL toluene. On the other hand, 21.3 mg CsBr was dispersed in 10 mL methanol and stirred at 60 °C for 1 h. Then, 1.0 mL CsBr methanolic solution was added quickly to the toluene solution of PbBr₂@MOF-919-Cu₂M, and stirred at room temperature for 5 min. The CsPbBr₃@MOF-919-Cu₂M were collected by filtration and washing with n-hexane for five times.

2.4. Preparation of CsPbBr₃@MOF-919-Cu_xCo_y

The CsPbBr₃@MOF-919-Cu_xCo_y with different atomic ratios of Cu: Co were prepared following the same procedure as CsPbBr₃@MOF-919-Cu₂Co except for the different exchange time (Table S1).

2.5. Synthesis of CsPbBr₃ QDs

A mixture of Cs₂CO₃ (0.41 g), octadecene (ODE, 20 mL) and oleic acid (OA, 1.3 mL) was added in a 50 mL three-neck flask, and heated at 120 °C in Ar atmosphere for 1 h, followed at 150 °C for 30 min to yield Cs-OA solution. Moreover, a mixture of PbBr₂ (0.70 g), ODE (50 mL), oleylamine (OM, 5.0 mL) and OA (5.0 mL) was added in a 250 mL three-neck flask, heated at 120 °C in Ar atmosphere for 1 h, followed by heating at 170 °C for 10 min. Then, 4.0 mL of prepared Cs-OA solution was swiftly added, followed by cooling in liquid nitrogen. The yellow precipitate was obtained by centrifuging and washing with ethyl acetate for three times, followed by washing with hexane to remove aggregated particles. Finally, the CsPbBr₃ QDs was obtained by filtration and washing with ethyl acetate.

2.6. XAS measurements

The X-ray absorption spectroscopy (XAS) measurements were carried out on the sample at 21 A X-ray nano diffraction beamline of Taiwan Photon Source (TPS), National Synchrotron Radiation Research Center (NSRRC). This beamline adopted 4-bounce channel-cut Si (111) monochromator for mono-beam X-ray nanodiffraction and X-ray absorption spectroscopy. The end-station equipped with three ionization chambers and Lytle/SDD detector after the focusing position of KB mirror for

transmission and fluorescence mode X-ray absorption spectroscopy. The photon flux on the sample is range from $1 \times 10^{11} \sim 3 \times 10^9$ photon/sec for X-ray energy from 6 to 27 keV.

2.7. Photocatalytic experiments

The photocatalytic CO₂ reduction measurements were carried out in a 16 mL sealed Pyrex bottle. 1.0 mg catalyst, 5 mL acetonitrile and 20 μ L deionized water were added in the sealed Pyrex bottle, degassed with CO₂ to remove O₂ and other gases, followed by a 300 W Xe lamp irradiation with a 420 nm filter (light intensity, 80 mW cm⁻²). The generated gaseous products were analyzed by gas chromatography, and liquid products were analyzed by NMR spectroscopy and ion chromatography.

2.8. AQE measurements

The apparent quantum efficiency (AQE) was measured in an identical experimental condition as photocatalytic CO₂ reduction except for the incident light resource. The catalytic system was irradiated by light emitting diode (LED) light for 1 h with wavelengths of 395, 425 and 450 nm, respectively (80 mW cm⁻², irradiation area 0.8 cm²). The generated products were quantitatively detected by ion chromatography. The value of AQE was calculated by the below expression:

$$\text{AQE} = \frac{\text{Total number of consumed electrons}}{\text{Total number of incident electrons}}$$

2.9. Photoelectrochemical measurements

Photocurrent, EIS and Mott-Schottky plots measurements were performed using a three-electrode system in 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile/water (v:v = 100:1) solution. The working electrode was prepared by depositing 1.0 mg photocatalyst on the surface of fluorine-doped tin oxide (FTO, 0.5 $\times$ 0.5 cm²). Pt plate and Ag/AgCl were used as the counter electrode and reference electrodes, respectively. Photocurrent measurements were recorded at -0.4 V (light intensity, 80 mW cm⁻²). EIS measurements were carried out at -0.6 V in the dark. Mott-Schottky plots were recorded at frequencies of 300, 600 and 900 Hz, respectively. CV and LSV measurements were performed using a three-electrode system in acetonitrile/water (v:v = 4:1) solution. Pt silk and Ag/AgNO₃ (0.1 M) were used as the counter electrode and reference electrodes, respectively. For CV measurements, the working electrode was prepared by depositing 40 μ g photocatalyst on the surface of glassy carbon electrode. For LSV measurements, the working electrode was prepared by depositing 1.0 mg photocatalyst on the surface of FTO (0.5 $\times$ 0.5 cm²).

2.10. TA spectra measurements

1.0 mg CsPbBr₃@MOF-919-Cu₂M was dispersed in 3.0 mL acetonitrile, which was degassed with Ar to remove O₂ and other gases. The TA spectra measurements were carried out at room temperature.

2.11. In situ FTIR spectra experiments

A mixture of 1.0 mg CsPbBr₃@MOF-919-Cu₂M and 50 mg KBr was ground for 10 min. Then the mixture was sealed in the chamber for purging with N₂ for 20 min. The *in situ* FTIR spectra were collected under light irradiation with the incremental time upon the introduction of a mixture of CO₂/CH₃CN/H₂O vapour.

2.12. Lifetime analysis

The average lifetime of the excited state ($\tau_{\text{Ave}} = \sum \tau_i A_i$) was obtained by fitting the TRPL spectra with the triple exponential decay function ($I_{\text{PL}} = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$ (where A_i

represents the amplitude coefficient and τ_i represents the lifetime). Here, three components were used to analyze the average lifetimes of CsPbBr₃, CsPbBr₃@MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M, namely, $\tau_{\text{Ave}} = \tau_1 A_1 + \tau_2 A_2 + \tau_3 A_3$ ($A_1 + A_2 + A_3 = 1$).

2.13. DFT calculations

The spin-polarized density functional theory (DFT) calculations were performed based on the Vienna ab initio simulation package (VASP) [29]. The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerh (PBE) [30] functional was applied to describe the exchange-correlation interaction. The projected augmented wave (PAW) method [31] was used to describe the electron-ion interaction. And the electron wave functions were expanded by a plane wave basis set with an energy cutoff of 400 eV. In addition, the DFT-D3 method was applied to describe the van der Waals interactions. The convergence criteria for the energy and residual force were set to 10⁻⁵ eV and 0.03 eV/Å, respectively. During the calculations, the Brillouin zone integration was carried out with a single gamma point. The Gibbs free energy of each species in the simulated pathway was calculated as follows:

$$G = E_{\text{DFT}} + E_{\text{ZPE}} + \int C_V dT - TS$$

Where E_{DFT} is the electronic energy directly obtained from DFT calculations, E_{ZPE} is the zero-point vibrational energy, $\int C_V dT$ is the heat capacity, T is the temperature (298.15 K), and S is the entropy (Tables S2 and S3).

3. Results and discussion

3.1. Synthesis and characterization

MOF-919-Cu₃ with Cu₃ cluster was first synthesized according to the reported procedure [28]. The powder XRD pattern of MOF-919-Cu₃ is basically identical to its simulated one, demonstrating the high phase purity (Fig. 1a). The N₂ adsorption isotherm of MOF-919-Cu₃ shows a reversible type IV isotherm with the saturated N₂ uptake of 593.9 cm³ g⁻¹ (STP) and the corresponding Brunauer-Emmett-Teller (BET) surface area of 1061.3 m² g⁻¹ (Fig. S1). Moreover, MOF-919-Cu₃ shows three types of pores with the sizes of about 2.0, 3.4 and 5.7 nm respectively, which are in agreement with its crystal structure (Figs. S2 and S3). Afterwards, MOF-919-Cu₂Co and MOF-919-Cu₂Zn were prepared through ion exchange strategy, in which MOF-919-Cu₃ was immersed in DMF containing Co(NO₃)₂·6 H₂O and Zn(NO₃)₂·6 H₂O respectively at 90 °C [32]. Taking MOF-919-Cu_xCo_y as a representative (x and y represent the amounts of Cu and Co, respectively), the ICP-MS measurements show that the content of Co increases along with the incremental soaking time, and the atomic ratio of Cu:Co is 2:1 at the soaking time of 24 h (Table S1), with the color change from green to dark gray (Fig. S4). Additionally, the results of DFT calculations demonstrate that the exchange energy for the exchange of the first Cu in Cu₃ cluster with Co (Cu₃ + Co $\rightarrow$ Cu₂Co + Cu, -0.45 eV) is lower than those for the second (0.14 eV) and third (0.15 eV) ones, revealing that it prefers to form Cu₂Co cluster during the process of ion exchange [33,34]. All the above results indicate that one Cu in the Cu₃ cluster prefers to be exchanged by one Co to form a Cu₂Co cluster in MOF-919-Cu₂Co at the soaking time of 24 h.

Powder XRD pattern, N₂ adsorption isotherm and pore size distribution of MOF-919-Cu₂Co are similar to those of MOF-919-Cu₃ (Figs. 1a, S1 and S2), demonstrating that its crystallinity and porous structure are well kept. To elucidate the microstructural information of Co in MOF-919-Cu₂Co, XAS was carried out. As shown in Fig. 1b, the Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectrum of MOF-919-Cu₂Co for Co exhibits a prominent peak at 1.51 Å, corresponding to the Co-N/O scattering paths. No Co-Co scattering path

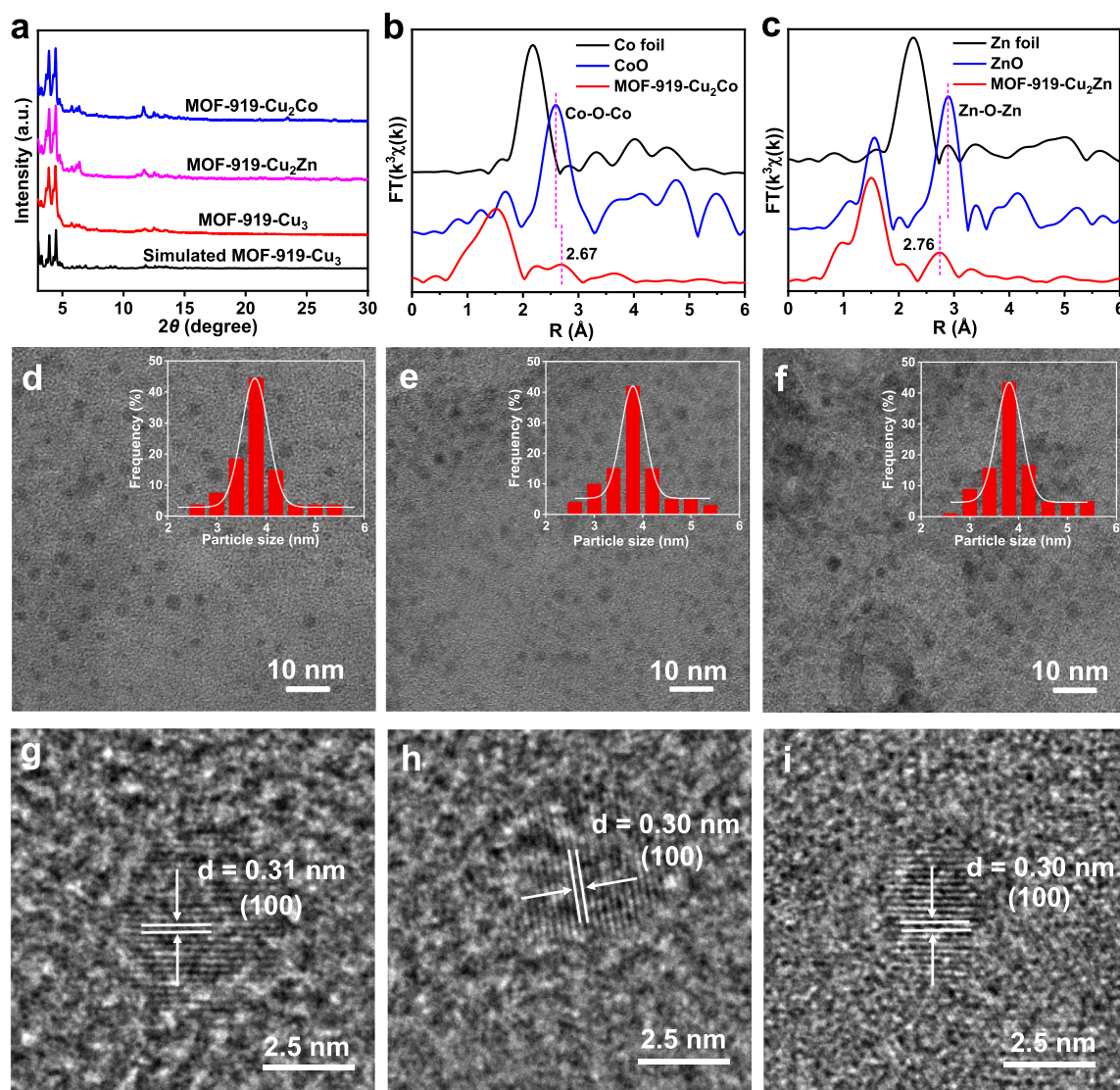


Fig. 1. (a) Powder XRD patterns of the synthesized MOF-919-Cu₃, MOF-919-Cu₂Zn and MOF-919-Cu₂Co, and simulated MOF-919-Cu₃. (b) Co K-edge EXAFS spectra of Co foil, CoO and MOF-919-Cu₂Co at R space. (c) Zn K-edge EXAFS spectra of Zn foil, ZnO and MOF-919-Cu₂Zn at R space. (d-f) TEM images of CsPbBr₃@MOF-919-Cu₃ (d), CsPbBr₃@MOF-919-Cu₂Co (e) and CsPbBr₃@MOF-919-Cu₂Zn (f), the black dots are CsPbBr₃ QDs. Inset: the particle size distribution of CsPbBr₃ QDs. (g-i) HRTEM images with lattice fringes of CsPbBr₃ QDs in CsPbBr₃@MOF-919-Cu₃ (g), CsPbBr₃@MOF-919-Cu₂Co (h) and CsPbBr₃@MOF-919-Cu₂Zn (i).

(2.18 Å) was observed, confirming that Co disperses atomically in MOF-919-Cu₂Co. It is worth noting that another scattering signal was present at 2.67 Å, which shows a slight shift compared with the Co-O-Co signal (2.58 Å) in CoO, thus can be assigned to the Co-O-Cu path [35,36]. The results of the best EXAFS fitting reveal that there are two Cu atoms around the second shell of Co (Fig. S5 and Table S4), which further supports the above conclusion that one of Cu in Cu₃ cluster was exchanged by one Co to form Cu₂Co cluster at the soaking time of 24 h. Furthermore, the best fitting results of Co-N/O shell demonstrate that each Co is coordinated by four atoms, which can be assigned to two O and two N atoms (Table S4) [28]. Similar to MOF-919-Cu₂Co, one of Cu in Cu₃ cluster was exchanged by one Zn to form Cu₂Zn cluster in MOF-919-Cu₂Zn at the soaking time of 24 h (Figs. 1a, c, S1, S2, S4 and S6, Tables S1 and S4).

Subsequently, the encapsulation of CsPbBr₃ QDs in the pores of MOF-919-Cu₂M to form CsPbBr₃@MOF-919-Cu₂M composites was achieved by immersing the activated MOF-919-Cu₂M in 0.01 M DMF solution of PbBr₂, followed by immersing in methanol solution of CsBr [37]. Powder XRD patterns show that the skeleton of MOF-919-Cu₂M are well kept after the encapsulation of CsPbBr₃ QDs (Fig. S7). Furthermore, no

powder XRD characteristic peak of CsPbBr₃ was observed in CsPbBr₃@MOF-919-Cu₂M composites due to the small size of CsPbBr₃ (Fig. S7) [37]. The results of TEM images demonstrate that the CsPbBr₃ QDs are distributed uniformly in MOF-919-Cu₂M with the similar size of about 3.8 nm (Figs. 1d-f and S8). The HRTEM images show lattice fringes of about 0.31 nm (Fig. 1g-i), which can be attributed to the (100) crystal face of CsPbBr₃ QDs [24]. EDS mappings disclose the homogeneous distribution of Cs, Pb, Br, Sc, Cu, Zn and Co elements in CsPbBr₃@MOF-919-Cu₂M composites (Figs. S9-S11). The N₂ adsorption isotherms of CsPbBr₃@MOF-919-Cu₂M composites demonstrate that the saturated N₂ uptakes are sharply reduced compared with those of MOF-919-Cu₂M, and the corresponding pore size distributions and BET surface area also display this trend (Figs. S1, S2, S12 and S13, Table S5). These results confirm that the CsPbBr₃ QDs are successfully encapsulated in the pores of MOF-919-Cu₂M [24,37]. Despite this, CsPbBr₃@MOF-919-Cu₂M still exhibit CO₂ adsorption performance, in which the CsPbBr₃@MOF-919-Cu₂Co displays the highest CO₂ uptake (Fig. S14). This may be attributed to the large BET surface area (Table S5). In addition, the results of ICP-MS analysis show that the ratios of Cs:Pb are about 1:1 and the amounts of CsPbBr₃ QDs are about

4.4 wt% in CsPbBr₃@MOF-919-Cu₂M composites (Table S6). For comparison, the CsPbBr₃ QDs stabilized by OA and OM were also prepared (Fig. S7) [24].

To investigate the metal valence states of Cu₂M clusters in MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M, as well as the interfacial interaction between MOF-919-Cu₂M and CsPbBr₃ QDs in CsPbBr₃@MOF-919-Cu₂M, the XPS was carried out. As shown in Figs. S15 and S16, the Cu 2p XPS spectra of MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M show two kinds of Cu 2p_{3/2} binding energies at about 932.8 and 934.8 eV, respectively, with the Auger peaks at about 570.8 eV, unveiling the mixed Cu⁺/Cu²⁺ valence state of Cu species in these catalysts [28,38]. The XPS spectra of MOF-919-Cu₂Co and CsPbBr₃@MOF-919-Cu₂Co display Co 2p_{3/2} and Co 2p_{1/2} characteristic peaks with two corresponding satellite peaks, demonstrating that the valence state of Co species is also +2 (Fig. S17) [39]. For Zn atom in MOF-919-Cu₂Zn and CsPbBr₃@MOF-919-Cu₂Zn, the binding energy difference between Zn 2p_{3/2} and Zn 2p_{1/2} is about 23.1 eV, revealing the valence state of Zn species is +2 in the two catalysts (Fig. S18) [40]. Additionally, the binding energies of Cu 2p, Co 3d and Zn 2p of CsPbBr₃@MOF-919-Cu₂M display negative shift compared with those in MOF-919-Cu₂M (Figs. S15, S17 and S18), suggesting that MOF-919-Cu₂M in CsPbBr₃@MOF-919-Cu₂M obtains electrons. The binding energies of Pb 4f and Br 3d of CsPbBr₃@MOF-919-Cu₂M show positive shift compared with those in CsPbBr₃ QDs, revealing that CsPbBr₃ in CsPbBr₃@MOF-919-Cu₂M loses electrons (Figs. S19 and S20). These results demonstrate that electron transfer happens from CsPbBr₃ QDs to MOF-919-Cu₂M in CsPbBr₃@MOF-919-Cu₂M.

The solid UV-vis absorption measurements of CsPbBr₃ QDs, MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M were performed to investigate their light absorbance ability. As shown in Fig. S21, the pristine CsPbBr₃ QDs displays strong light absorbance ability in both ultraviolet and visible light ranges. By contrast, the pristine MOF-919-Cu₂M mainly absorbs ultraviolet and weak visible light (Figs. 2a, S22 and S23). After the encapsulation of CsPbBr₃ QDs in the pores of MOF-919-Cu₂M, the

resulting CsPbBr₃@MOF-919-Cu₂M composites exhibit obviously improved light-harvesting ability compared with the pristine MOF-919-Cu₂M (Figs. 2a, S22 and S23). The band-gap energies (E_g) of the pristine CsPbBr₃ QDs, MOF-919-Cu₃, MOF-919-Cu₂Co and MOF-919-Cu₂Zn are 2.27, 2.67, 2.74 and 2.67 eV respectively, which are estimated by the Kubelka-Munk (KM) method based on their solid UV-vis absorption spectroscopy (Figs. S24-S27) [39]. Moreover, the lowest unoccupied molecular orbitals (LUMO) of the pristine CsPbBr₃ QDs, MOF-919-Cu₃, MOF-919-Cu₂Co and MOF-919-Cu₂Zn are -1.03, -0.87, -0.76 and -0.78 V vs. normal hydrogen electrode (NHE), respectively, as determined by the results of Mott-Schottky measurements (Figs. 2b and S28-S30) [39]. Therefore, the highest occupied molecular orbitals (HOMO) of them are calculated to be 1.24, 1.80, 1.98 and 1.89 V vs. NHE, respectively (Figs. 2c, S31 and S32). Obviously, the LUMO of CsPbBr₃ QDs and MOF-919-Cu₂M are more negative compared with some photocatalytic products of CO₂ reduction such as CO (-0.53 V), HCOOH (-0.61 V) and CH₄ (-0.24 V). Furthermore, the HOMO of them are more positive than the oxidation potential of H₂O/O₂ (0.81 V) [39]. All potentials are with reference to NHE with pH = 7. These results imply that the pristine CsPbBr₃ QDs and MOF-919-Cu₂M are theoretically feasible for photocatalytic CO₂ reduction and H₂O oxidation. Additionally, we note that CsPbBr₃ QDs and MOF-919-Cu₂M show staggered band structures, suggesting the type-II or Z-scheme heterojunctions on CsPbBr₃@MOF-919-Cu₂M composites may be formed upon light irradiation (Figs. 2c, S31 and S32) [41,42].

To identify the type of CsPbBr₃@MOF-919-Cu₂M heterojunctions, the *in situ* XPS measurements in the dark and under the light irradiation were performed [43]. The results show that the binding energies of Cs 3d, Pb 4f and Br 3d display positive shift upon light irradiation compared with those in the dark, suggesting that the CsPbBr₃ loses electrons (Figs. 2d, e and S33-S35). By contrast, the binding energies of Cu 2p (Cu²⁺) show negative shift upon light irradiation compared with those in the dark, hinting that MOF-919-Cu₂M obtains electrons (Fig. 2f, S36 and S37). Furthermore, the EPR measurements of CsPbBr₃ QDs,

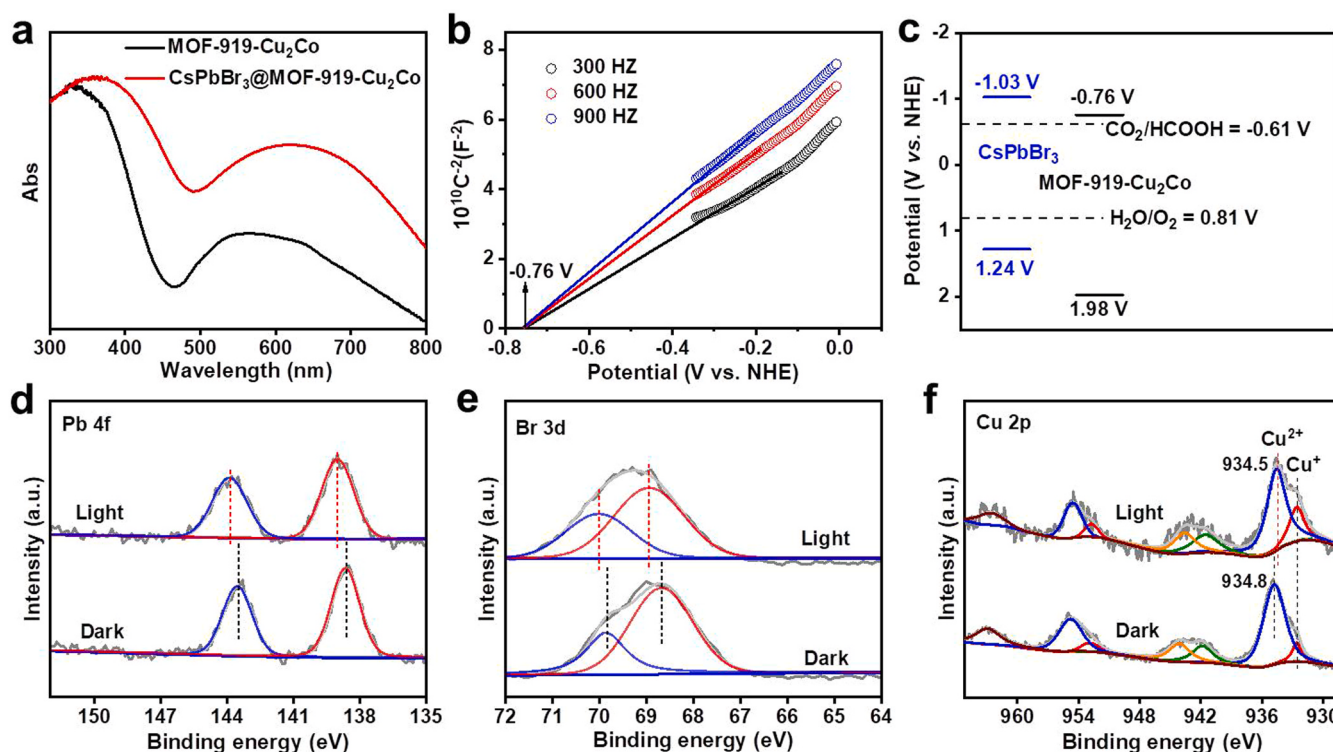


Fig. 2. (a) UV-vis spectra of the pristine MOF-919-Cu₂Co and CsPbBr₃@MOF-919-Cu₂Co. (b) Mott-Schottky plots of MOF-919-Cu₂Co. (c) Band-structure diagram for the pristine CsPbBr₃ and MOF-919-Cu₂Co before contact. (d-f) XPS spectra for Pb 4f (d), Br 3d (e) and Cu 2p (f) of CsPbBr₃@MOF-919-Cu₂Co in the dark and upon light irradiation.

MOF-919-Cu₂Co and CsPbBr₃@MOF-919-Cu₂Co with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as probes were performed to monitor the generation of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ species. As shown in Fig. S38, the characteristic signals of DMPO- $\cdot\text{O}_2^-$ for the pristine CsPbBr₃ QDs and MOF-919-Cu₂Co, as well as CsPbBr₃@MOF-919-Cu₂Co were detected under light irradiation, in which CsPbBr₃@MOF-919-Cu₂Co exhibits stronger signals than the pristine CsPbBr₃ QDs and MOF-919-Cu₂Co. These results suggest that MOF-919-Cu₂Co of CsPbBr₃@MOF-919-Cu₂Co possesses more photogenerated electrons than the pristine MOF-919-Cu₂Co, indicating the occurrence of electron transfer from CsPbBr₃ QDs to MOF-919-Cu₂Co. Moreover, the weak characteristic signals of DMPO- $\cdot\text{OH}$ for the pristine MOF-919-Cu₂Co were observed under light irradiation, while no characteristic DMPO- $\cdot\text{OH}$ signal was observed for CsPbBr₃@MOF-919-Cu₂Co. This result hints that the pristine MOF-919-Cu₂Co has more photogenerated holes than MOF-919-Cu₂Co of CsPbBr₃@MOF-919-Cu₂Co, demonstrating that the hole transfer occurs from MOF-919-Cu₂Co to CsPbBr₃ QDs in CsPbBr₃@MOF-919-Cu₂Co. These results demonstrate that the type-II heterojunctions between CsPbBr₃ QDs and MOF-919-Cu₂M were formed in CsPbBr₃@MOF-919-Cu₂M composites, which might facilitate charge separation and transfer efficiencies in photocatalytic CO₂ reduction compared with the pristine CsPbBr₃ QDs and MOF-919-Cu₂M. For comparison, the type-II heterojunctions of CsPbBr₃/MOF-919-Cu₂M were also fabricated by physical mixture of CsPbBr₃ QDs and

MOF-919-Cu₂M (Figs. S39-S44).

3.2. Photocatalytic CO₂ reduction experiments

Encouraged by the above analysis, the photocatalytic CO₂ reduction experiments of CsPbBr₃ QDs, MOF-919-Cu₂M, CsPbBr₃/MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M were performed in CO₂-saturated acetonitrile solution with small amount of H₂O under visible-light irradiation, in absence of additional photosensitizers and sacrificial agents. The results demonstrate that MOF-919-Cu₂M, CsPbBr₃/MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M can reduce CO₂ to HCOOH (Fig. S45) [16], while the pristine CsPbBr₃ QDs can reduce CO₂ to CO. Firstly, the relationship between catalytic activity and the content of Co was investigated for CsPbBr₃@MOF-919-Cu_xCo_y. As shown in Fig. S46 and Table S1, the HCOOH production rate was linearly increased along with the increase of Co content, and reached a maximum value at the Cu:Co atomic ratio of 2:1. Further increasing the Co content caused the decrease of HCOOH production rate. Secondly, the relationship between catalytic activity and the amount of CsPbBr₃ QDs encapsulated in the pores of MOF-919-Cu₂Co was also investigated. CsPbBr₃@MOF-919-Cu₂Co exhibits the enhanced HCOOH generation rate along with the increased amount of CsPbBr₃ QDs when it is less than 4.4 %. However, the HCOOH production rate drops with further incremental CsPbBr₃ QDs, which may be attributed to the obstacles of mass transfer for CO₂

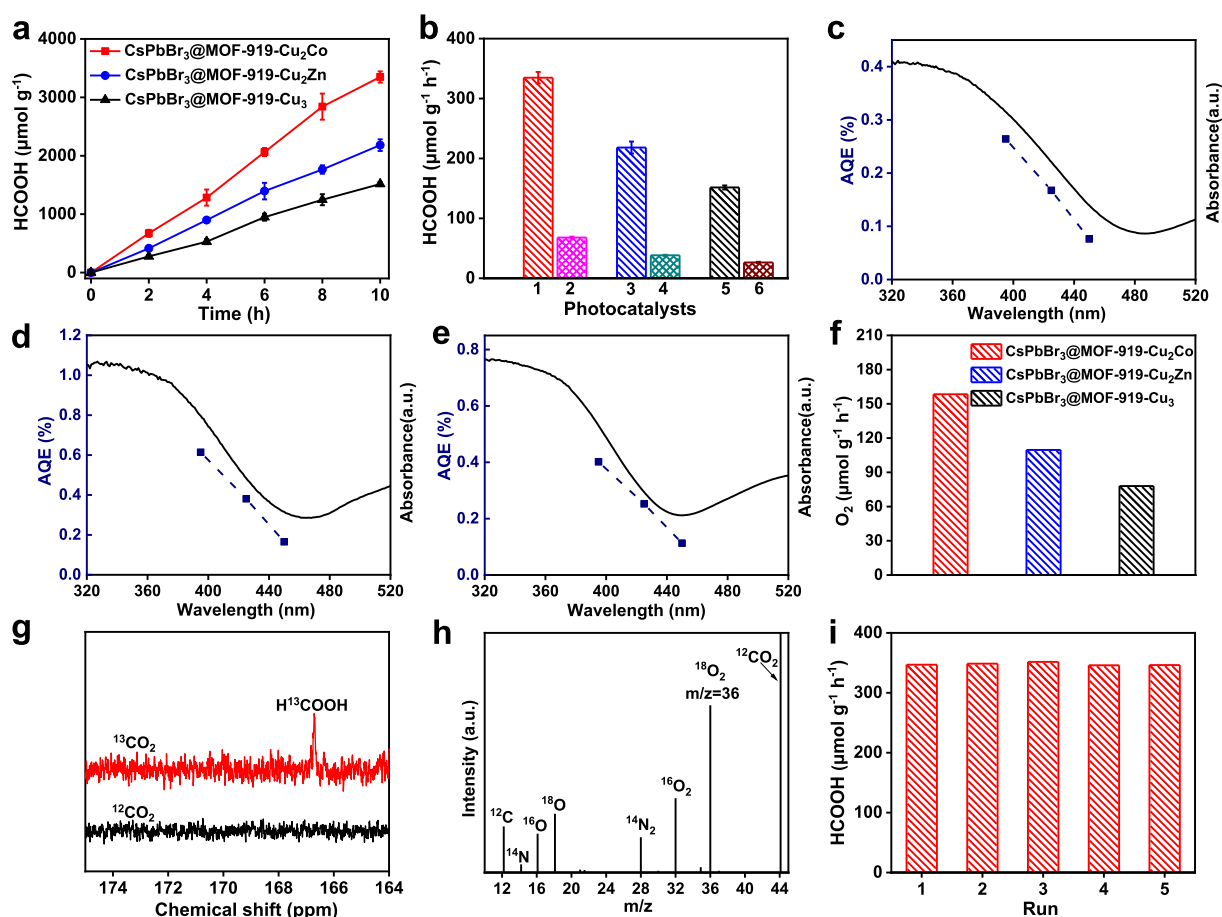


Fig. 3. (a) Time-dependent HCOOH generation of photocatalytic CO₂ reduction over CsPbBr₃@MOF-919-Cu₂M. (b) HCOOH production rates of CsPbBr₃@MOF-919-Cu₂M and CsPbBr₃/MOF-919-Cu₂M (1: CsPbBr₃@MOF-919-Cu₂Co; 2: CsPbBr₃/MOF-919-Cu₂Co; 3: CsPbBr₃@MOF-919-Cu₂Zn; 4: CsPbBr₃/MOF-919-Cu₂Zn; 5: CsPbBr₃@MOF-919-Cu₃; 6: CsPbBr₃/MOF-919-Cu₃). (c-e) UV-vis absorption spectra and AQE values of CsPbBr₃@MOF-919-Cu₃ (c), CsPbBr₃@MOF-919-Cu₂Zn (d) and CsPbBr₃@MOF-919-Cu₂Co (e). (f) The O₂ production rates of CsPbBr₃@MOF-919-Cu₃, CsPbBr₃@MOF-919-Cu₂Zn and CsPbBr₃@MOF-919-Cu₂Co. (g) ¹³C NMR spectra for the product obtained from photocatalytic reaction over CsPbBr₃@MOF-919-Cu₂Co with ¹³CO₂ instead of ¹²CO₂. (h) Mass spectrum of gaseous product generated in the photocatalytic oxidation of H₂¹⁸O over CsPbBr₃@MOF-919-Cu₂Co. (i) HCOOH production rates in five consecutive photocatalytic cycles over CsPbBr₃@MOF-919-Cu₂Co (4 h for each run).

photoreduction due to too many CsPbBr₃ QDs encapsulated in the pores of MOF-919-Cu₂Co (Fig. S47 and Table S7). Therefore, the photocatalytic activities of CsPbBr₃@MOF-919-Cu₂Co show volcano-type trends on the whole, and CsPbBr₃@MOF-919-Cu₂Co presents the highest HCOOH generation rate of 334.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ at the Cu:Co atomic ratio of 2:1 and CsPbBr₃ QDs amount of about 4.4 % (Figs. 3a and 3b). Moreover, the HCOOH generation rates of CsPbBr₃@MOF-919-Cu₃ and CsPbBr₃@MOF-919-Cu₂Zn are 151.6 and 218.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively (Fig. 3a and b). In sharp contrast, the pristine CsPbBr₃ QDs, MOF-919-Cu₃, MOF-919-Cu₂Zn and MOF-919-Cu₂Co display significantly decreased CO and HCOOH production rates of 5.2, 6.0, 12.4 and 15.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively (Figs. 3a, b and S48). Obviously, CsPbBr₃@MOF-919-Cu₂Co achieves the highest photocatalytic activity with the electron consumption rate (R_{electron}) of 669.6 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for HCOOH production, which is 64 and 56 times higher than those of the pristine CsPbBr₃ QDs and MOF-919-Cu₃, respectively. Moreover, the photocatalytic performance of CsPbBr₃@MOF-919-Cu₂M are much higher than those of CsPbBr₃/MOF-919-Cu₂M (Fig. 3b), suggesting that the encapsulation of CsPbBr₃ QDs in the pores of MOF-919-Cu₂M could accelerate charge transfer efficiency. It's also worth noting that the catalytic activity of CsPbBr₃@MOF-919-Cu₂Co is superior to most of the reported MOF/COF-based photocatalysts for artificial photosynthesis (Table S8). Furthermore, the AQE of CsPbBr₃@MOF-919-Cu₂M was measured at 395, 425 and 450 nm [44]. As shown in Fig. 3c-e, they exhibit different AQEs at the tested wavelengths, following the sequence of CsPbBr₃@MOF-919-Cu₂Co > CsPbBr₃@MOF-919-Cu₂Zn > CsPbBr₃@MOF-919-Cu₃, among which the AQE of

CsPbBr₃@MOF-919-Cu₂Co was 0.38 % under 425 nm. These results also demonstrate that the CO₂ photoreduction activity can be boosted simply via regulating the dual-metal sites in Cu₂M cluster-based MOFs. Moreover, O₂ was detected in the catalytic system, with O₂ generation rates of 77.0, 109.6 and 158.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for CsPbBr₃@MOF-919-Cu₃, CsPbBr₃@MOF-919-Cu₂Zn and CsPbBr₃@MOF-919-Cu₂Co, respectively (Fig. 3f). The stoichiometric ratios of HCOOH and O₂ for CsPbBr₃@MOF-919-Cu₂M are all close to 2:1. In addition, no other reduction product such as CO, CH₄, CH₃OH, C₂H₄, C₂H₅OH and H₂ was detected, suggesting the electrons generated through H₂O oxidation are all used to the reduction of CO₂ to HCOOH and the HCOOH selectivities are nearly 100 %.

To confirm the sources of HCOOH and O₂, a series of control experiments over CsPbBr₃@MOF-919-Cu₂Co were carried out. The results show that no HCOOH was detected without catalyst, CO₂, H₂O or light irradiation, indicating that these factors are all indispensable and H₂O is the electron source for CO₂ photoreduction to HCOOH. Moreover, ¹³CO₂ and H₂¹⁸O isotope trace experiments were further performed. As shown in Fig. 3g, the ¹³C NMR spectrum displays an obvious signal at 166.7 ppm, which can be attributed to the H¹³COOH, unambiguously confirming that the carbon source of HCOOH indeed originates from CO₂ reduction [39]. The result of MS shows a peak at $m/z = 36$, corresponding to ¹⁸O₂ (Fig. 3h), verifying that the electron source of CO₂ photoreduction comes from water oxidation [24]. The photocatalytic durability of CsPbBr₃@MOF-919-Cu₂Co was evaluated by consecutive recycling experiments. The HCOOH production rates can be well retained during the five consecutive cycles (Fig. 3i). Additionally, the

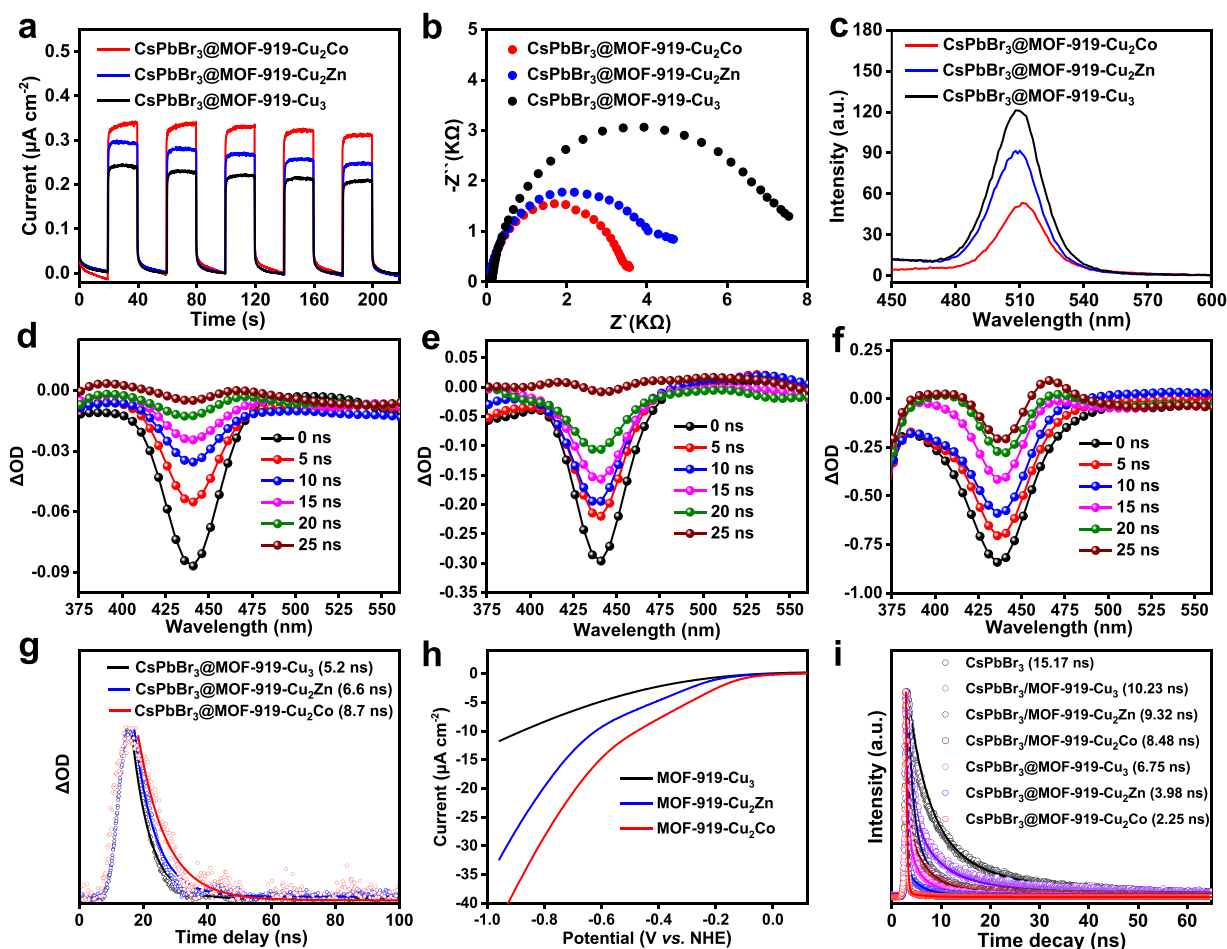


Fig. 4. (a) Photocurrent responses, (b) EIS plots and (c) PL spectra of CsPbBr₃@MOF-919-Cu₂M. (d-f) TA spectra at different delay times for CsPbBr₃@MOF-919-Cu₃ (d), CsPbBr₃@MOF-919-Cu₂Zn (e) and CsPbBr₃@MOF-919-Cu₂Co (f). (g) TA kinetic traces of CsPbBr₃@MOF-919-Cu₂M at 440 nm. (h) The LSV profiles for MOF-919-Cu₂M. (i) Time-resolved PL spectra of CsPbBr₃ QDs, CsPbBr₃/MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M.

results of powder XRD patterns show no loss of crystallinity for CsPbBr₃@MOF-919-Cu₂M after photocatalysis (Figs. S49–S51). The TEM images of CsPbBr₃@MOF-919-Cu₂M demonstrate that the sizes of CsPbBr₃ QDs are hardly changed after photocatalysis (Figs. S52–S54). These results demonstrate that CsPbBr₃@MOF-919-Cu₂M possesses good stability in artificial photosynthesis.

The photocurrent response, EIS and PL emission spectra of CsPbBr₃ QDs, MOF-919-Cu₂M, CsPbBr₃/MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M were tested to study charge separation and transfer efficiencies, as well as to illustrate the different photocatalytic performance [45]. As shown in Figs. 4a and S55, all catalysts exhibit obvious photocurrent signals, among which the CsPbBr₃@MOF-919-Cu₂Co possesses the strongest response intensity, indicating the best separation of photo-generated electrons and holes. The results of EIS spectra reveal that CsPbBr₃@MOF-919-Cu₂Co shows the smallest semicircle radius, suggesting the fastest electron transfer (Figs. 4b and S56). Moreover, the PL spectra demonstrate that CsPbBr₃@MOF-919-Cu₂Co displays the weakest emission intensity, also disclosing the most efficient charge separation (Figs. 4c and S57). In addition, the TA spectra of CsPbBr₃@MOF-919-Cu₂M were carried out to investigate charge-separated state [46,47]. As shown in Fig. 4d–g, the strong bleaching signals around 440 nm were observed upon pulsed laser excitation, and the lifetimes of the charge-separated state were found to be 5.2, 6.6 and 8.7 ns for CsPbBr₃@MOF-919-Cu₃, CsPbBr₃@MOF-919-Cu₂Zn and CsPbBr₃@MOF-919-Cu₂Co, respectively. These results certify again that CsPbBr₃@MOF-919-Cu₂Co shows the most efficient charge separation. Besides, the LSV measurements of MOF-919-Cu₂M were performed in CO₂ atmosphere to study the thermodynamics of CO₂ reduction [14]. It is apparent that the onset overpotential of MOF-919-Cu₂Co is the lowest (Fig. 4h), suggesting that MOF-919-Cu₂Co is thermodynamically superior to MOF-919-Cu₃ and MOF-919-Cu₂Zn for CO₂ reduction. The ECSA of MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M were also performed. As shown in Figs. S58 and S59, CsPbBr₃@MOF-919-Cu₂Co displays the largest ECSA, implying its highest photocatalytic activity. All the results above unambiguously explain the highest catalytic performance of CsPbBr₃@MOF-919-Cu₂Co for CO₂ photoreduction to HCOOH.

To further illustrate the much higher photocatalytic performance of CsPbBr₃@MOF-919-Cu₂M than those of CsPbBr₃/MOF-919-Cu₂M, the electron transfer rates between CsPbBr₃ QDs and MOF-919-Cu₂M were evaluated. The TRPL spectra of CsPbBr₃ QDs, CsPbBr₃/MOF-919-Cu₂M and CsPbBr₃@MOF-919-Cu₂M under excitation at 450 nm were carried out to calculate the electron transfer rate constant (k_{et}) by the below expression [48]:

$$k_{et} = \frac{1}{\tau_{(\text{heterojunction})}} - \frac{1}{\tau_{(\text{CsPbBr}_3)}}$$

Here, τ is the average lifetime. As shown in Fig. 4i, the τ values of CsPbBr₃/MOF-919-Cu₃, CsPbBr₃@MOF-919-Cu₃, CsPbBr₃/MOF-919-Cu₂Zn, CsPbBr₃@MOF-919-Cu₂Zn, CsPbBr₃/MOF-919-Cu₂Co and CsPbBr₃@MOF-919-Cu₂Co are 10.23, 6.75, 9.32, 3.98, 8.48 and 2.25 ns respectively, corresponding to the k_{et} values of 3.18×10^7 , 8.21×10^7 , 4.13×10^7 , 1.85×10^8 , 5.19×10^7 and 3.78×10^8 s⁻¹, respectively. Obviously, CsPbBr₃@MOF-919-Cu₂M exhibit larger k_{et} values than those of CsPbBr₃/MOF-919-Cu₂M, revealing the faster electron transfer from CsPbBr₃ QDs to MOF-919-Cu₂M. These results demonstrate that the CsPbBr₃@MOF-919-Cu₂M exhibits more efficient charge separation and transfer than CsPbBr₃/MOF-919-Cu₂M. Additionally, DFT calculations were carried out to further study the charge transfer between CsPbBr₃ QDs and MOF-919-Cu₂M. Taking CsPbBr₃@MOF-919-Cu₂Co for an example, when the CsPbBr₃ QDs were close to the MOF-919-Cu₂Co, the charge transfer between them was more efficient (Fig. S60) [37]. All the above results unambiguously show that the encapsulation of CsPbBr₃ QDs in the pores of MOF-919-Cu₂M greatly facilitates the charge transfer efficiency, thus significantly improving the catalytic activity for CO₂ photoreduction.

3.3. Photocatalytic mechanism

The possible mechanism for CO₂ photoreduction coupled with H₂O oxidation over CsPbBr₃@MOF-919-Cu₂M was elucidated by *in situ* EPR measurement. The results demonstrate that CsPbBr₃@MOF-919-Cu₃ shows a strong Cu²⁺ signal at $g = 2.10$ in the dark (Fig. 5a), which is obviously decreased upon light irradiation, suggesting that Cu²⁺ was reduced to Cu⁺ [49,50]. CsPbBr₃@MOF-919-Cu₂Zn also exhibits a strong signal at $g = 2.10$ in the dark, which can be assigned to Cu²⁺ because the Zn²⁺ do not generate EPR signal. This signal shows an evident decrease upon light irradiation, hinting that Cu²⁺ is transformed to Cu⁺ (Fig. S61) [49,50]. For CsPbBr₃@MOF-919-Cu₂Co, a strong EPR signal can be observed at $g = 2.13$ in the dark, which can be assigned to the combined signals of Cu²⁺ and Co²⁺ [49–51]. Upon light irradiation, this signal shows a slight decrease, which may be attributed to the reduction of only Cu²⁺ to Cu⁺, owing to its insufficient conduction band potential (-0.76 V vs. NHE) for the reduction of Co²⁺ to Co⁺ (-1.10 V vs. NHE) (Fig. 5b and f) [49–51]. These results suggest that MOF-919-Cu₂M obtains electrons upon visible light irradiation, which are agree well with the results of *in situ* XPS (Fig. 2f, S36 and S37). Considering the type-II heterojunction of CsPbBr₃@MOF-919-Cu₂M, the reaction pathways were proposed. Upon light irradiation, both CsPbBr₃ QDs and MOF-919-Cu₂M absorb light to generate electrons and holes. The photogenerated holes in the HOMO of MOF-919-Cu₂M are transferred to the HOMO of CsPbBr₃ QDs to oxidize H₂O to O₂ (Fig. S62). The O₂ formation at the CsPbBr₃ QDs has been previously identified as a water nucleophilic attack (WNA) mechanism with the following steps [52]: 1) H₂O + * → *OH + H⁺ + e⁻; 2) *OH → *O + H⁺ + e⁻; 3) H₂O + *O → *OOH + H⁺ + e⁻; 4) *OOH → O₂ + H⁺ + e⁻ + * (* stands for an active site). Moreover, the photogenerated electrons in the LUMO of CsPbBr₃ QDs are transferred to the LUMO of MOF-919-Cu₂M to reduce CO₂ to HCOOH (Fig. S62).

To see if the HCOOH generated by MOF-919-Cu₂M will be oxidized by CsPbBr₃ QDs in the catalytic process. The photocatalytic experiment over CsPbBr₃@MOF-919-Cu₂Co was performed under the N₂ atmosphere in the presence of H¹³COOH (0.2 μL). As shown in Fig. S63, negligible ¹³CO₂ peak was detected by the mass spectrum, suggesting that no H¹³COOH was oxidized by CsPbBr₃ QDs, which may be attributed to the much lower concentration of H¹³COOH than H₂O (20 μL) in the photocatalytic system. Moreover, the influence of O₂ generated by CsPbBr₃ QDs to CO₂ photoreduction on Cu₂M sites was also investigated. Taking CsPbBr₃@MOF-919-Cu₂Co as an example, the reaction solution with DMPO as the trapping agent after the CO₂ photoreduction was collected for the EPR measurement [53]. The characteristic signals of DMPO–O₂⁻ were almost negligible, suggesting that the generated O₂ was hardly reduced (Fig. S64), which may be attributed to the much higher CO₂ concentration around Cu₂M clusters than that of O₂. These results demonstrate that the retarding effects of HCOOH on H₂O oxidation and O₂ on CO₂ photoreduction can be avoided, which guaranteed the proceeding of artificial photosynthesis [53]. To detect the key intermediates in the process of CO₂ photoreduction, *in situ* FTIR measurements of CsPbBr₃@MOF-919-Cu₂M were carried out. The results show that the new infrared absorption peaks at 1633, 1640 and 1639 cm⁻¹ were detected for CsPbBr₃@MOF-919-Cu₃, CsPbBr₃@MOF-919-Cu₂Zn and CsPbBr₃@MOF-919-Cu₂Co respectively (Figs. 5c, S65 and S66), which can be assigned to the key intermediates of HCOO* for HCOOH generation [54]. The intensities of these peaks gradually increase along with the incremental irradiation time, demonstrating the increased concentration of HCOO* intermediates during the CO₂ photoreduction.

DFT calculation was further performed to elucidate how the CO₂ photoreduction activity being regulated by the dual-metal sites, and the origin of the outstanding photocatalytic performance of CsPbBr₃@MOF-919-Cu₂Co. The primitive part of MOF-919-Cu₂M were picked out for model building as the CO₂ photoreduction was occurred at MOFs only [37,55]. The photocatalytic CO₂ reduction to HCOOH involves a

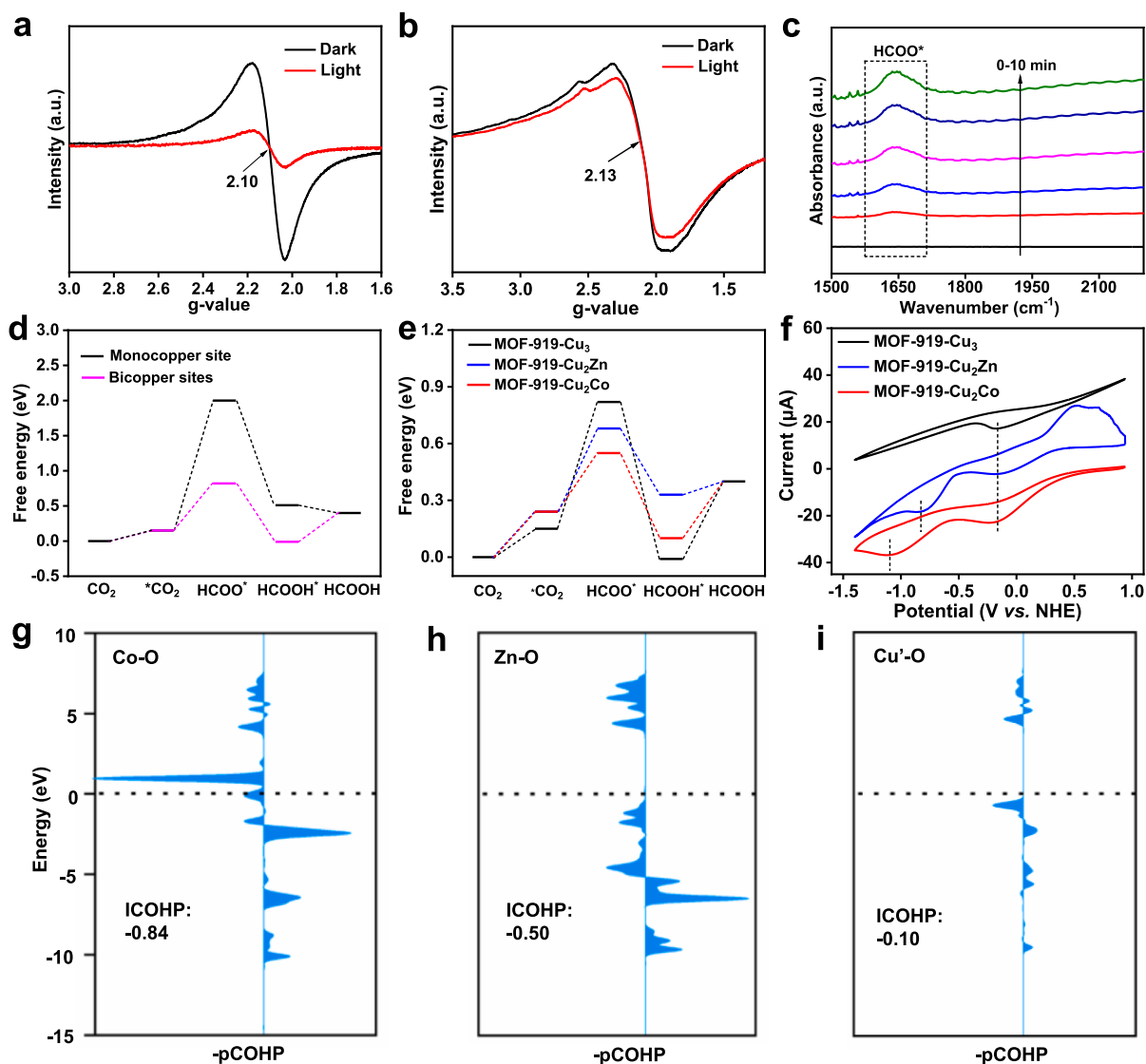


Fig. 5. EPR spectra of CsPbBr₃@MOF-919-Cu₃ (a) and CsPbBr₃@MOF-919-Cu₂Co (b) in the dark and light irradiation. (c) *In situ* FTIR spectra of CsPbBr₃@MOF-919-Cu₂Co in the process of photocatalytic CO₂ reduction. (d) Free energy profiles for the photoreduction of CO₂ to HCOOH for MOF-919-Cu₃ with monocopper and bicopper sites. (e) Free energy profiles for the photoreduction of CO₂ to HCOOH by MOF-919-Cu₂M. (f) CV curves of MOF-919-Cu₂M. (g-i) The COHP analysis between Co/Zn/Cu' and adjacent O atom of HCOO* intermediate for MOF-919-Cu₂Co (g), MOF-919-Cu₂Zn (h) and MOF-919-Cu₃ (i).

two-electron and two-proton transfer process [56]. First, CO₂ is adsorbed at the catalytic site and receive an electron and a proton to form HCOO*. Subsequently, the hydrogenation of HCOO* happens on one O atom to form HCOOH*. Finally, HCOOH desorption occurs. To see if the dimetallic centers is beneficial for CO₂ photoreduction, taking MOF-919-Cu₃ as an example, the free-energy change (ΔG) of CO₂ photoreduction on monocopper and bicopper sites were calculated, respectively (Fig. S67). As shown in Fig. 5d, the ΔG values of the rate-determining step (RDS) for the formation of HCOO* are 1.85 and 0.67 eV for monocopper and bicopper sites respectively, suggesting the photocatalytic CO₂ reduction by MOF-919-Cu₃ prefers to follow a dual-metal synergistic catalysis process. After the exchange of one Cu with one Zn or Co, the ΔG values of RDS decrease from 0.67 eV for MOF-919-Cu₃ to 0.44 for MOF-919-Cu₂Zn and 0.31 eV for MOF-919-Cu₂Co respectively, suggesting the strengthened synergistic catalysis effect between Cu and Zn/Co (Figs. 5e, S68 and S69a). In addition, we calculated the ΔG of CO₂ photoreduction for MOF-919-CuCo₂ with CuCo₂ cluster (Fig. S69b). The RDS for MOF-919-CuCo₂ is the desorption of HCOOH* with ΔG value of 0.48 eV, which is larger than that of MOF-919-Cu₂Co (Fig. S70). These results explain the highest catalytic

activity of CsPbBr₃@MOF-919-Cu₂Co among the all tested catalysts.

To understand why MOF-919-Cu₂Co displays the lowest ΔG value of 0.31 eV for photocatalytic CO₂ reduction, the CV of MOF-919-Cu₂M was firstly measured in Ar atmosphere. As shown in Fig. 5f, the CV of MOF-919-Cu₃ shows a reduction wave at -0.19 V vs. NHE, which is assigned to the reduction of Cu²⁺ to Cu⁺ [57–59]. By contrast, the CV of MOF-919-Cu₂Zn displays two reduction waves at -0.16 and -0.82 V vs. NHE, corresponding to the reduction of Cu²⁺ to Cu⁺ and Zn²⁺ to Zn, respectively [57–59]. Moreover, the CV of MOF-919-Cu₂Co also shows two reduction waves at -0.21 and -1.10 V vs. NHE, which are assigned to the reduction of Cu²⁺ to Cu⁺ and Co²⁺ to Co⁺, respectively [57–59]. Obviously, Co²⁺/Co⁺ exhibits the lowest reduction potential and Co²⁺ cannot be reduced by the photo-induced electron with a reduction potential of only -0.76 V (Fig. 2c), thus cobalt keeps Co²⁺ valence state in the process of CO₂ photoreduction. The CV results are further supported by *in situ* XPS. As shown in Fig. 2f, S36 and S37, the binding energies of Cu 2p (Cu²⁺) display obviously negative shift and the molar ratios of Cu²⁺:Cu⁺ decrease in CsPbBr₃@MOF-919-Cu₂M upon light irradiation compared with those in the dark, suggesting that part of Cu²⁺ were reduced to Cu⁺. However, the binding energies of Zn 2p only show

slightly negative shift under the light irradiation, and Co 2p spectra are identical in the dark and light irradiation (Figs. S71 and S72), indicating only small amount of Zn^{2+} was reduced, and Co keeps + 2 valence state during the photocatalytic CO_2 reduction process. Therefore, we can conclude that the interaction between Cu/Co and HCOO^* intermediate is stronger than Cu/Zn and Cu/Cu, as the high-valence state metals usually show stronger interaction to O than low-valence state metals [60]. Moreover, the crystal orbital Hamilton population (COHP) analysis was conducted to further evaluate the binding strengths between dual-metal sites and HCOO^* [61]. The integrated COHP (ICOHP) was obtained by integration of COHP over all levels up to the Fermi level, which can evaluate the binding strength (the more negative value of ICOHP, the stronger binding strength). As shown in Figs. 5g–5i, the values of ICOHP for Co–O, Zn–O and Cu–O in MOF-919- Cu_2Co , MOF-919- Cu_2Zn and MOF-919- Cu_3 are -0.84 , -0.50 and -0.10 eV, respectively (Cu–O represents the Cu site in Cu_3 cluster corresponding to Zn and Co sites in Cu_2Zn and Cu_2Co clusters, respectively, see Fig. S67a). However, the values of ICOHP for Cu–O in the three samples are similar (Fig. S73). These results demonstrate that the binding strengths between Cu/Co and HCOO^* is the strongest, which agrees well with the results of CV, XPS and DFT calculation. All the above results solidly verify that the dual-metal synergistic effect between Cu and Co is stronger than those of Cu/Zn and Cu/Cu, which promote CO_2 photoreduction to generate the best photocatalytic CO_2 reduction performance.

4. Conclusion

In summary, by encapsulating CsPbBr_3 QDs into the pores of dual-metal sites MOFs, three CsPbBr_3 @MOF-919- Cu_2M composite catalysts were successfully constructed, which exhibit outstanding catalytic activities for CO_2 photoreduction to HCOOH coupled with H_2O oxidation to O_2 . Among which, CsPbBr_3 @MOF-919- Cu_2Co shows the highest photocatalytic performance with a HCOOH production rate of $334.8 \mu\text{mol g}^{-1} \text{h}^{-1}$, 64-, 56- and 5-fold higher than those of pristine CsPbBr_3 QDs, MOF-919- Cu_3 , and CsPbBr_3 /MOF-919- Cu_2Co , respectively. Experimental and DFT calculation results reveal that the significantly enhanced photocatalytic activity of CsPbBr_3 @MOF-919- Cu_2Co is not only attributed to the efficient charge separation due to the close contact of CsPbBr_3 QDs and MOF-919- Cu_2Co , but also due to the strengthened dual-metal synergistic catalysis effect between Cu and Co for dramatically lowering the RDS ΔG value. This work demonstrates that the photocatalytic performance of CO_2 reduction can be significantly promoted by combining efficient charge separation and dual-metal-synergistic catalysis.

CRedit authorship contribution statement

Di-Chang Zhong: Writing – original draft, Conceptualization. **Tong-Bu Lu:** Supervision, Funding acquisition. **Hong-Juan Wang:** Software. **Jing-Jing Wang:** Data curation. **Jing-Yi Liu:** Methodology. **Yun-Nan Gong:** Writing – review & editing, Supervision, Investigation, Conceptualization. **Hao-Yu Yang:** Data curation. **Chong-Jiu Lu:** Investigation.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2025.125878.

Data Availability

Data will be made available on request.

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