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# Coupling doped halogen sites in copper(I)–organic frameworks with cuprous oxide for high selectivity CO<sub>2</sub> photoreduction with H<sub>2</sub>O†

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Photoreduction catalysis offers an eco-friendly approach to convert CO<sub>2</sub> into valuable chemicals. However, understanding the influence of halide active sites in metal–organic framework (MOF) catalysts on photoreduction and selectivity remains limited. We report different halogen (X) sites (X = Cl, Br and I) in copper(I)–organic frameworks (CuX–bpy) grown on Cu<sub>2</sub>O for photoreduction of CO<sub>2</sub> without the assistance of additional sacrificial agents and photosensitizers. Impressively, the Cu<sub>2</sub>O@CuCl–bpy–MOF efficiently photo-reduces CO<sub>2</sub> into formate with a high yield of 1520 μmol g<sup>−1</sup> after 12 hours of reaction. Density functional theory calculation results reveal that the effective coordination coupling between the MOF and semiconductor facilitates rapid electron transfer leading to efficient CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation.

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## Introduction

Mimicking natural photosynthesis to convert CO<sub>2</sub> with H<sub>2</sub>O into high-value products offers a promising sustainable solution for decreasing anthropogenic CO<sub>2</sub> emissions and producing renewable chemicals.<sup>1</sup> However, it faces the challenge of coupling the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) and water oxidation reaction into one photosynthetic system and achieving high selectivity of the overall reaction.<sup>2</sup> To address these challenges, combining two components with independent functions to construct catalysts has been considered to be a significant method.<sup>3</sup> Nevertheless, numerous vital aspects are challenging to address simultaneously in a majority of composite systems including efficient light absorption, the separation and rapid migration of photo-generated carriers to redox sites and the rapid adsorption and desorption of CO<sub>2</sub>.<sup>4–8</sup> Consequently, the design and fabrication of composite photocatalysts with well-defined structures to achieve highly selective CO<sub>2</sub> photoreduction is of great significance.

Metal–organic frameworks (MOFs) with excellent structural designability and the presence of both adsorption and active sites have emerged as a promising candidate for the capture and conversion of CO<sub>2</sub>.<sup>9–11</sup> By adjusting appropriate metal nodes and functional organic linkers, MOFs are capable of possessing efficient light absorption and fast separation and migration of photogenerated carriers.<sup>12,13</sup> A variety of MOF-based photocatalysts have been demonstrated for the photocatalytic reduction of CO<sub>2</sub>.<sup>14–16</sup> Inorganic semiconductors such as Cu<sub>2</sub>O,<sup>17</sup> TiO<sub>2</sub>,<sup>18</sup> and α-Fe<sub>2</sub>O<sub>3</sub> (ref. 19) have been reported to be able to achieve highly efficient water photooxidation. On this basis, a feasible strategy is to combine CO<sub>2</sub> reduction MOFs with water oxidation inorganic semiconductors to create composite catalysts to enhance the overall selective reaction in artificial photosynthesis.<sup>20–23</sup>

MOF derived composites, such as the heterojunction of TTCOF and NH<sub>2</sub>-UiO-66 (TTCOF/NUZ),<sup>24</sup> Ni-doped CdS nanoparticles@bimetallic MOF (Ni@CdS@Zn/Co-ZIF),<sup>25</sup> MOF-808 loaded with a molecular photosensitizer (Zr-MBA-Ru/Re-MOF),<sup>26</sup> doped nano-gold@MOF (Au-NC@UiO-68-NHC)<sup>27</sup> and ligand modified Zr-MOF (BUT-110),<sup>28</sup> have been demonstrated to be capable of reduction of CO<sub>2</sub> under light illumination. However, most of these materials primarily yield low-value CO products and require additional photosensitizers and sacrificial agents, which can be economically unfriendly and harmful to the healthy development of the environment. We hypothesize that incorporating a MOF into photosensitive semiconductors may reduce the reliance on photosensitizers and sacrificial agents in the photocatalytic system.<sup>29,30</sup>

Halogens plays a pivotal role in the field of photocatalysis. A substantial body of research has revealed their significance,

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particularly in metal halide perovskite photocatalysts, where halogens profoundly affect the electrolytic transport properties and overall performance.<sup>31</sup> Zhao *et al.* demonstrated that in  $\text{CsCuCl}_2\text{Br}$ , the substitution of  $\text{Cl}^-$  with  $\text{Br}^-$  effectively narrows the bandgap, harnessing a wider range of solar energy and enhancing the transport of photoelectrons and holes.<sup>32</sup> Guo *et al.* also demonstrated the influence of halogens by regulating the ratio of  $\text{Br}^-$  and  $\text{Cl}^-$ , leading to notable changes in the yield of  $\text{CO}$  and  $\text{CH}_4$  (ref. 33). The efficient charge separation and favorable stability in mixed-halide perovskites contribute to their exceptional performance in the  $\text{CO}_2\text{RR}$ . However, in MOF composite materials, relevant research on the impact of halogens on their photocatalytic  $\text{CO}_2\text{RR}$  performance has not yet been reported.

Herein, different halogen (X) sites (X = Cl, Br and I) in copper(I)-organic frameworks *in situ* compounded on cuprous oxide ( $\text{Cu}_2\text{O}@CuX\text{-bpy}$ ; bpy = 4,4'-bipyridine) have been synthesized towards selectively photocatalytic  $\text{CO}_2\text{RR}$  integrated with water photooxidation.  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  achieves efficient photo-reduction of  $\text{CO}_2$  into formate ( $\text{HCOOH}$ ) with a high yield of  $1520 \mu\text{mol g}^{-1}$  in a 12 h photoreduction process without sacrificial agents and photosensitizers. *In situ* spectroscopic results suggest that the prominent photocatalytic performance arises from increased electronegativity, enhancing  $\text{CO}_2$  adsorption and stabilizing  $\text{HCOOH}$  intermediates, and it has been confirmed by density functional theory (DFT) calculation results that the photo-generated electrons rapidly migrate from the semiconductor to the MOF through coordination coupling, accumulating at MOF active sites for the  $\text{CO}_2\text{RR}$ , while holes in the semiconductor

enable  $\text{H}_2\text{O}$  oxidation, mimicking natural photosynthesis.  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  serves as a rational platform for investigating the correlation between halogen sites and photocatalytic efficiency.

## Results and discussion

The synthesis of powdery doped halogen sites in copper(I)-organic frameworks loaded on  $\text{Cu}_2\text{O}$  ( $\text{Cu}_2\text{O}@CuX\text{-bpy}$ ) is schematically illustrated in Fig. 1(a).  $\text{Cu}_2\text{O}$  nanocubes were synthesized by reducing copper oxide nanocubes with ascorbic acid.<sup>34</sup>  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  was obtained through *in situ* recombination of  $\text{CuCl-bpy}$  on the  $\text{Cu}_2\text{O}$  nanocube surface. The  $\text{Cu}_2\text{O}@CuBr\text{-bpy}$  and  $\text{Cu}_2\text{O}@CuI\text{-bpy}$  were synthesized by changing the added cuprous chloride into cuprous bromide and cuprous iodide, respectively.

The X-ray diffraction (XRD) patterns of  $\text{Cu}_2\text{O}@CuX\text{-bpy}$  are shown in Fig. S1.† In Fig. S1(a),† the pronounced diffraction peaks at  $29.5^\circ$ ,  $36.4^\circ$ ,  $42.3^\circ$ ,  $61.4^\circ$  and  $73.5^\circ$  can be indexed to the planes of  $\text{Cu}_2\text{O}$  (JCPDS card no. 05-0667). Taking  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  as an example, the PXRD pattern of the product highly matches with that of the simulated  $\text{CuCl-bpy}$ , indicating the synthesis of the  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  compound (Fig. S1(b)†). To detect the morphology, field emission scanning electron microscopy (SEM) was employed. The SEM image in Fig. 1(b) revealed the formation of a square-shaped morphology for the as-prepared  $\text{Cu}_2\text{O}$  with an average size of  $1 \mu\text{m}$ . As shown in Fig. 1(c)–(e), *in situ* recombination of a two-dimensional sheet-like nanostructure on  $\text{Cu}_2\text{O}$  was observed in  $\text{Cu}_2\text{O}@CuX\text{-bpy}$  as well as distribution at the surface of  $\text{Cu}_2\text{O}$  nanocubes. From

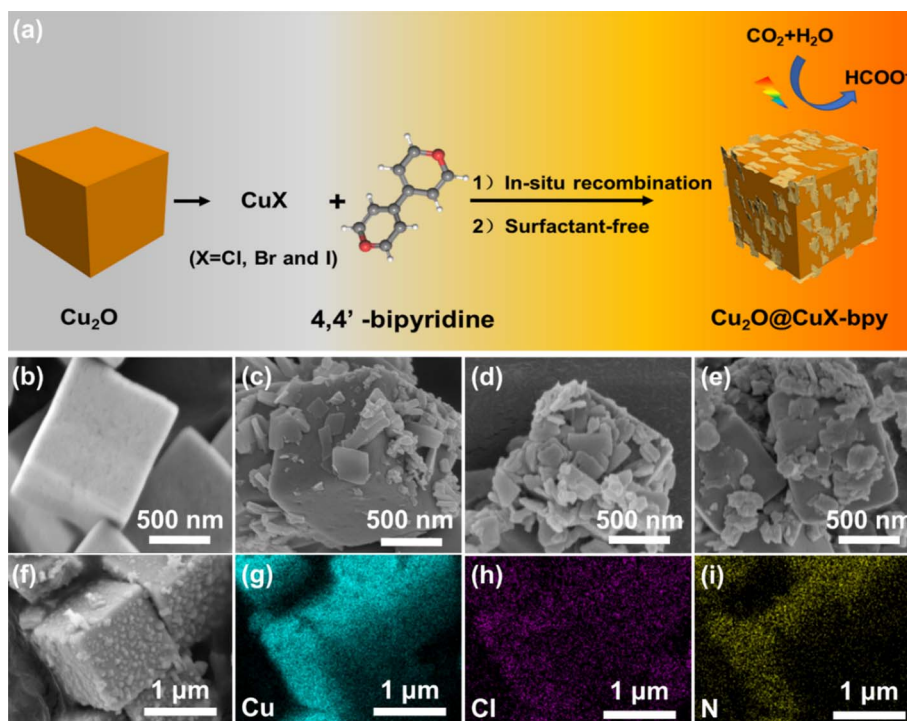


Fig. 1 (a) Schematic illustration of the fabrication method of  $\text{Cu}_2\text{O}@CuX\text{-bpy}$ . SEM images of (b)  $\text{Cu}_2\text{O}$  nanocubes, (c)  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$ , (d)  $\text{Cu}_2\text{O}@CuBr\text{-bpy}$  and (e)  $\text{Cu}_2\text{O}@CuI\text{-bpy}$ . (f–i) SEM image of the  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  and the corresponding element mapping images of Cu, Cl, and N.

Fig. 1(f)–(i) and S2 and S3,<sup>†</sup> the homogeneous distribution of each element was observed by energy-dispersive spectra (EDS) for  $\text{Cu}_2\text{O}@CuX\text{-bpy}$ , indicating successful combination of  $\text{CuX-bpy}$  on the  $\text{Cu}_2\text{O}$  surface.

The chemical composition and valence state of  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  were determined by X-ray photoelectron spectroscopy (XPS spectra) as shown in Fig. 2. The XP spectra results clearly demonstrate the existence of Cu, O, N, and Cl elements within the  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$ . The XP spectra of Cu 2p (Fig. 2(a)) exhibit two main spin-orbit doublets for  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$ . The peaks due to  $\text{Cu}_2\text{O}$  located at 932.4 eV and 952.3 eV can be assigned to  $\text{Cu}^+ 2p_{3/2}$  and  $\text{Cu}^+ 2p_{1/2}$ , respectively.<sup>35,36</sup> In the Cu LMM Auger spectrum presented in Fig. S4,<sup>†</sup> the peak at 569 eV indicates the absence of  $\text{Cu}(0)$ . Compared to  $\text{Cu}_2\text{O}$ , the slight position shift of  $\text{Cu}^+$  for  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  located at 932.1 eV and 952 eV to lower binding energy can be ascribed to the change of local environment charge caused by the presence of halogen element. The chlorine element in  $\text{CuCl-bpy}$  can coordinate with Cu on the  $\text{Cu}_2\text{O}$  surface, which made  $\text{Cu}^+$  move slightly towards lower binding energy. The detailed peak assignments and fitted results are listed in Table S1.<sup>†</sup>

Two types of oxygen are observed for  $\text{Cu}_2\text{O}$  (Fig. 2(b)), *i.e.*, the peaks at 531.3 eV and 530.3 eV, which can be attributed to the adsorbed O and lattice O, respectively.<sup>37</sup> The adsorbed O slightly increased and lattice O significantly decreased for  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  as compared to the adsorbed O and the lattice O for  $\text{Cu}_2\text{O}$ . This results from the successful integration of  $\text{CuCl-bpy}$  with rich adsorption sites onto the  $\text{Cu}_2\text{O}$  surface, and thus decreases the lattice O and increases the adsorbed O within  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$

$\text{bpy}$ . For the XPS N 1s spectrum of  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  in Fig. 2(c), a main peak at 399.1 eV can be observed, assigned to Cu–N bonding.<sup>38</sup> The extra weak peak at 398.5 eV can be assigned to pyridinic N, which did not successfully coordinate with the metal ions during synthesis. The XPS chlorine 2p spectrum of  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$  displayed peaks at 198.7 eV and 197.2 eV that could be assigned to  $\text{Cl}^-$  in chloride (Fig. 2(d)).<sup>39</sup>

For photo-reduction of  $\text{CO}_2$ , the separation behavior of photogenerated charge carriers is one of the vital factors. The optical properties of the samples were analyzed with the UV-vis diffuse reflectance spectra (UV-vis-DRS). They show broad and strong absorption in the region of 400–600 nm (Fig. 3(a) and S5<sup>†</sup>), which indicates the suitable light absorption range and potential photo-response properties of  $\text{Cu}_2\text{O}@CuX\text{-bpy}$ . Using Tauc's relation, the band-gap of  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$ ,  $\text{Cu}_2\text{O}@CuBr\text{-bpy}$  and  $\text{Cu}_2\text{O}@CuI\text{-bpy}$  can be determined to be 1.86 eV, 1.95 eV and 1.97 eV, respectively. The conduction band (CB) positions are estimated by measuring the flat band potential ( $E_{fb}$ ) according to Mott-Schottky (M-S) curves (Fig. S6<sup>†</sup>). Thus, based on the combined UV-vis-DRS and M-S analyses, the energy band structures of  $\text{Cu}_2\text{O}@CuX\text{-bpy}$  are shown in Fig. 3(b). The appropriate energy band structure ensures that they are suitable for photocatalytic reduction of  $\text{CO}_2$  together with oxidation of water to various fuels.

In order to have efficient performance in photocatalytic reactions, the suitable photocatalyst also needs to have prominent charge migration ability. According to the photo-electrochemical (PEC) tests, the  $\text{Cu}_2\text{O}@CuX\text{-bpy}$  samples all display more remarkable photocurrent density in comparison

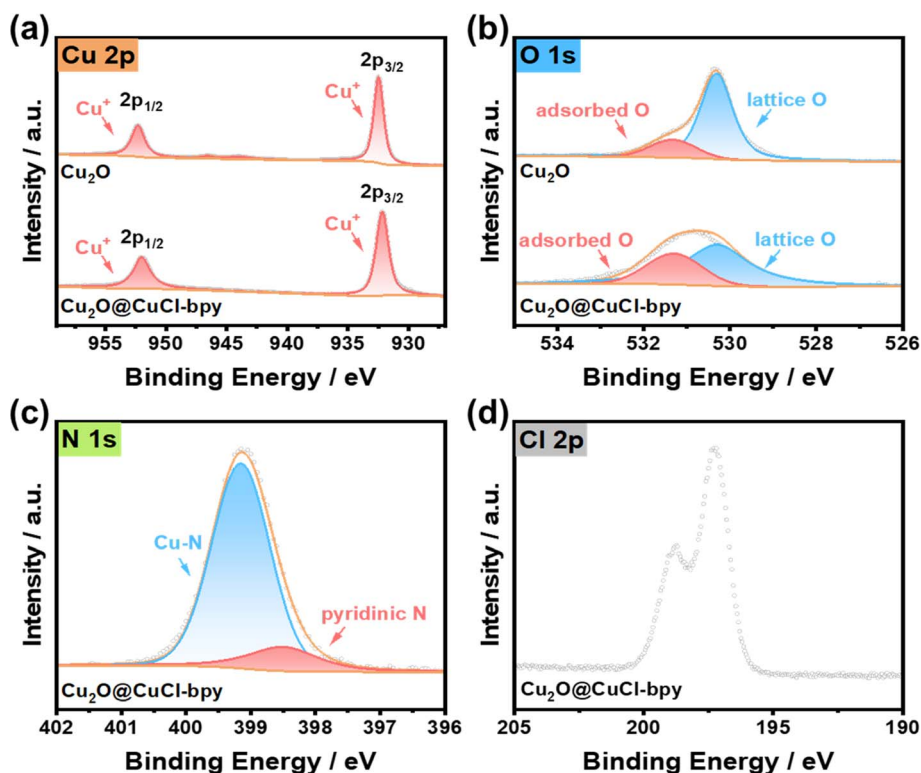


Fig. 2 XPS spectra of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}@CuCl\text{-bpy}$ . (a) Cu 2p, (b) O 1s, (c) N 1s and (d) Cl 2p.



Fig. 3 (a) UV-vis DRS spectra (inset: Tauc plots) of  $\text{Cu}_2\text{O}@CuCl\text{-}bpy$ . (b) The energy band structure of  $\text{Cu}_2\text{O}@CuX\text{-}bpy$ . (c) Transient photocurrent responses. (d) Open-circuit potential decay curves of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}@CuX\text{-}bpy$ . (e) EIS spectra of  $\text{Cu}_2\text{O}@CuX\text{-}bpy$ . (f) Steady-state PL spectra of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}@CuX\text{-}bpy$ .

to  $\text{Cu}_2\text{O}$  (Fig. 3(c)). Especially,  $\text{Cu}_2\text{O}@CuCl\text{-}bpy$  reaches the largest photocurrent density, suggesting efficient carrier transfer and separation. Furthermore, the photoelectron lifetimes of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}@CuX\text{-}bpy$  were determined by the decay of open circuit potentials (Fig. 3(d)). Compared with  $\text{Cu}_2\text{O}$ , the  $\text{Cu}_2\text{O}@CuX\text{-}bpy$  samples (especially  $\text{Cu}_2\text{O}@CuCl\text{-}bpy$ ) present a much more prolonged photoelectron lifetime and a higher photovoltage under irradiation, confirming the more efficient separation of photogenerated electron-hole pairs. On the basis of electrochemical impedance spectroscopy (EIS) spectra and the equivalent circuit (Fig. 3(e)), the EIS spectrum of  $\text{Cu}_2\text{O}@CuCl\text{-}bpy$  presents the smallest semicircle diameter, indicating the lowest charge transfer resistance.

The photochemical properties of compound materials are studied with the help of steady-state photoluminescence (PL)

spectra to display charge migration dynamics. As shown in Fig. 3(f), the  $\text{Cu}_2\text{O}@CuX\text{-}bpy$  samples all show a lower emission peak in comparison to  $\text{Cu}_2\text{O}$ , implying weaker recombination of photoinduced carriers. Particularly,  $\text{Cu}_2\text{O}@CuCl\text{-}bpy$  exhibits the lowest PL intensity, suggesting enhanced charge separation.

Time-resolved transient photoluminescence (TRPL) spectra were further investigated to track the charge dynamics in real time (Fig. S7†). After being fitted by a bi-exponential equation, a long average lifetime is achieved for  $\text{Cu}_2\text{O}@CuCl\text{-}bpy$  ( $\tau_{\text{Cl}} = 48.28$  ns) compared to  $\text{Cu}_2\text{O}$  ( $\tau_{\text{O}} = 1.62$  ns), indicating the suppressed recombination of the photogenerated electrons and holes of  $\text{Cu}_2\text{O}@CuCl\text{-}bpy$ . The efficient charge separation is ascribed to  $\text{CuCl}\text{-}bpy$  loaded on  $\text{Cu}_2\text{O}$  as the charge capture and enrichment center. Combining the analysis results of PL and TRPL, the appropriate introduction of doped halogen sites in

copper(i)-organic frameworks loaded on  $\text{Cu}_2\text{O}$  can shorten the electron-transfer distance, accelerate the transfer dynamics and slow down the photogenerated carrier recombination.

Considering the above discussions of all the characterization results, the  $\text{Cu}_2\text{O}@\text{CuX-bpy}$  samples have an appropriate energy band structure, photoresponse capability and photo-generated carrier separation performance, meeting the needs of photocatalytic reduction of  $\text{CO}_2$  with oxidation of water, which have optimistic application prospects in the field of overall reaction of artificial photosynthesis. Therefore, the photocatalytic assay of the as-prepared  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}@\text{CuX-bpy}$  toward photocatalytic reduction of  $\text{CO}_2$  coupled with oxidation of water was evaluated by using visible-light ( $\lambda > 400$  nm, 200  $\text{mW cm}^{-2}$ ) illumination in  $\text{CO}_2$ -saturated water under mild reaction conditions (25 °C). No additional sacrificial agent and photosensitizer are needed in the reaction process.

After photocatalytic reaction, only HCOOH as a liquid reduction product could be detected by ion chromatography (Fig. S8†) and  $^1\text{H NMR}$  (Fig. S9†). The evolution of HCOOH from  $\text{Cu}_2\text{O}@\text{CuX-bpy}$  as a function of reaction time is shown in Fig. 4(a). The evolution yield of HCOOH exhibits a linear increase behaviour during the initial 12 hour reaction, while no other gaseous and liquid products of the  $\text{CO}_2\text{RR}$  were detected, resulting in a high selectivity. We found that the evolution yield of HCOOH in the photocatalytic  $\text{CO}_2\text{RR}$  over the  $\text{Cu}_2\text{O}@\text{CuX-bpy}$  increased significantly with an increase in the electronegativity of the halogen, suggesting that the halogen modification promotes the reaction steps of HCOOH formation. Notably, it

was found that  $\text{Cu}_2\text{O}@\text{CuCl-bpy}$  is the optimum photocatalyst to achieve the highest evolution yield of HCOOH and the total yield is  $1520 \mu\text{mol g}^{-1}$  after 12 hours of reaction, which is higher than that of the majority of MOF-based photocatalysts (Table S2†). This could be ascribed to the appropriate energy band structure, the best photoresponse performance and charge separation ability of  $\text{Cu}_2\text{O}@\text{CuCl-bpy}$ , which is consistent with the above characterization results.

For comparison, control experiments were conducted under various reaction conditions as displayed in Fig. 4(b). The evolution yield of  $\text{O}_2$  produced by photocatalytic oxidation of water was detected and the HCOOH/ $\text{O}_2$  ratio is close to 2 : 1 as expected, which is consistent with the assumption of the photocatalytic reduction of  $\text{CO}_2$  integrated with oxidation of water in one photoredox cycle. Remarkably, the HCOOH evolution yield with  $\text{Cu}_2\text{O}@\text{CuCl-bpy}$  can reach as high as  $870.6 \mu\text{mol g}^{-1}$  in 6 h, over 7 times higher than that with  $\text{Cu}_2\text{O}$  ( $109.4 \mu\text{mol g}^{-1}$ ) and over 4 times higher than that with  $\text{CuCl-bpy}$  ( $208.1 \mu\text{mol g}^{-1}$ ). In addition, physically mixed control experiments with  $\text{Cu}_2\text{O} + \text{CuCl-bpy}$  composites were performed. The evolution yield of HCOOH is only about five percent that of  $\text{Cu}_2\text{O}@\text{CuCl-bpy}$ , which demonstrates the necessity of the *in situ* recombination of  $\text{CuCl-bpy}$  on the  $\text{Cu}_2\text{O}$  nanocube surface. Additional control experiments demonstrated that negligible reduction products could be detected without the photocatalyst,  $\text{CO}_2$ , or light illumination. These results suggested that those factors were all indispensable for photocatalytic  $\text{CO}_2$  reduction and the generated HCOOH production does indeed originate from the

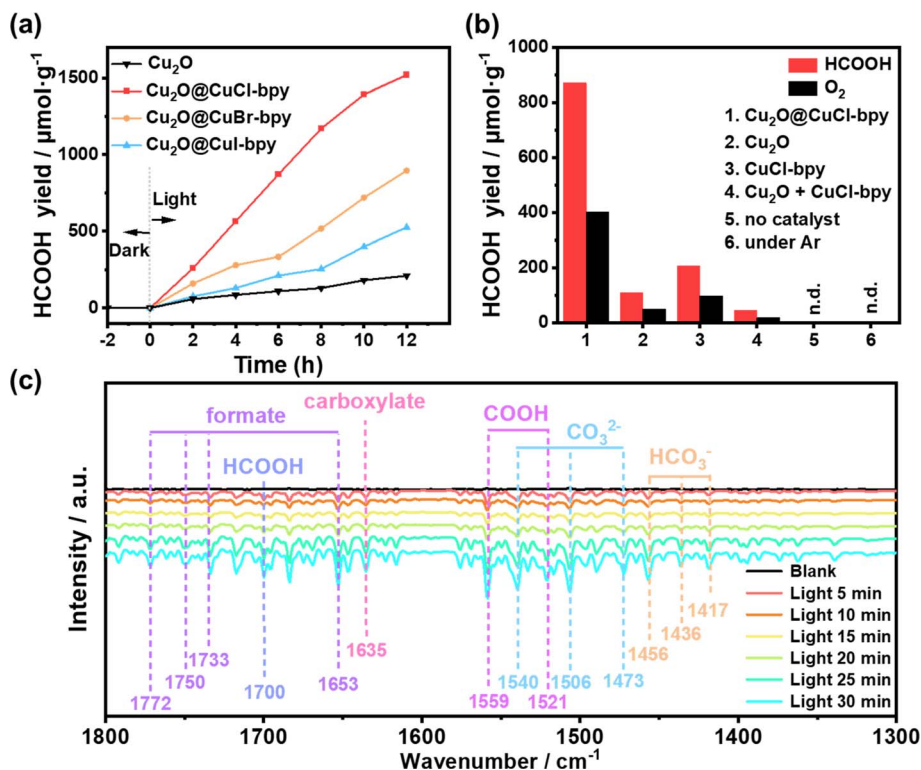


Fig. 4 (a) The yield of HCOOH as a function of the time of visible light illumination over  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}@\text{CuX-bpy}$ . (b) The yield of HCOOH produced with different catalyst and reaction conditions after 6 h of visible light illumination. (c) *In situ* FTIR spectra for the simulated photo-driven  $\text{CO}_2$  reduction process over  $\text{Cu}_2\text{O}@\text{CuCl-bpy}$ .

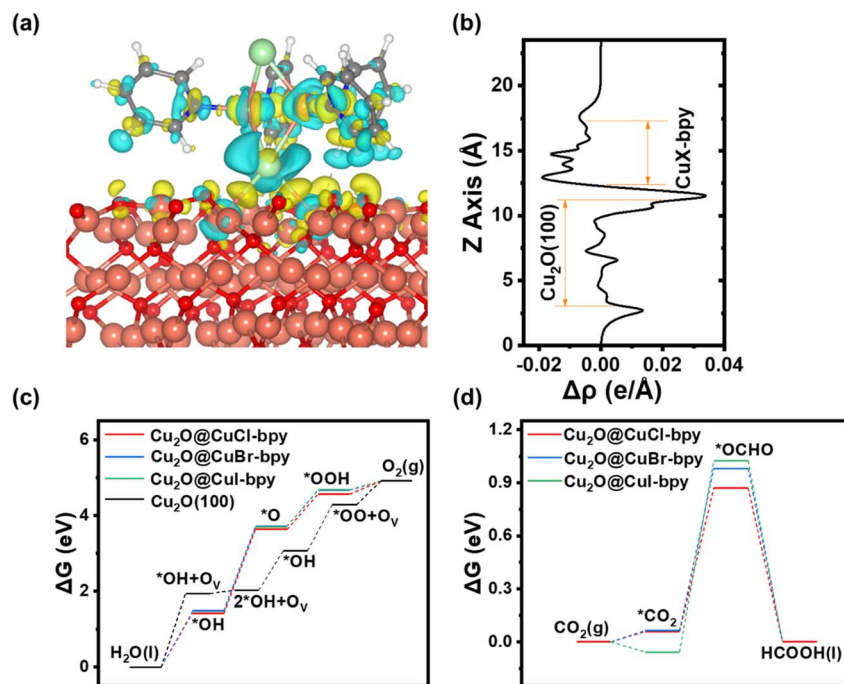


Fig. 5 (a) Charge density difference of Cu<sub>2</sub>O@CuX-bpy (X = Cl, Br, and I, isosurface level = 0.0015 |e| per bohr<sup>3</sup>). Yellow and blue indicate electron accumulation and depletion. (b) Projected charge density difference along the Z axis. Catalytic performance of (c) the OER and (d) CO<sub>2</sub>RR processes.

reduction of CO<sub>2</sub> molecules rather than the photolysis from other carbon-containing species in this photocatalytic system.

In order to further explore the photocatalytic stability of Cu<sub>2</sub>O@CuCl-bpy, the cyclic catalytic performance was examined by running the experiment for five consecutive cycles (Fig. S10†). The Cu<sub>2</sub>O@CuCl-bpy retained the original photocatalytic efficiency for the HCOOH production during three consecutive cycles, indicating the remarkable stability and activity of the photocatalyst. However, in the last two cycles, the performance of Cu<sub>2</sub>O@CuCl-bpy decreases gradually, which may be due to the partial desquamation of CuCl-bpy on the Cu<sub>2</sub>O surface. The structure, morphology, and chemical states of Cu<sub>2</sub>O@CuX-bpy after the photocatalytic reaction were characterized using PXRD, SEM and XP spectra as shown in Fig. S11–S15.† No noticeable change in PXRD between the initial and 12 h catalyzed Cu<sub>2</sub>O@CuX-bpy can be observed, demonstrating that the structure of Cu<sub>2</sub>O@CuX-bpy remains unchanged during the photocatalytic reaction process (Fig. S11†). Furthermore, SEM images show that Cu<sub>2</sub>O@CuX-bpy maintains its basic morphology after photocatalysis and the partial desquamation of CuX-bpy on the Cu<sub>2</sub>O surface can be observed, which is consistent with the previous conjecture (Fig. S12–S14†). After 12 hours of photoreaction, the existence of Cu, O, N and Cl is observed, while adsorbed O slightly increased due to the oxygen generation during the photoreaction process (Fig. S15†). Thus, the above analysis demonstrates the outstanding photocatalytic performance and stability of Cu<sub>2</sub>O@CuX-bpy for application.

To further clarify the reasons for the outstanding photocatalytic performance and HCOOH conversion selectivity, *in situ* FTIR spectroscopy was performed to probe the intermediates of

Cu<sub>2</sub>O@CuCl-bpy during visible light illumination. As shown in Fig. 4(c), new peaks obviously appeared and their intensities gradually increased with the illumination time from 0 to 30 min. The peaks at 1540, 1506 and 1473 cm<sup>-1</sup> are attributed to monodentate carbonate (CO<sub>3</sub><sup>2-</sup>) and the peaks at 1456, 1436, and 1417 cm<sup>-1</sup> are ascribed to bicarbonate (HCO<sub>3</sub><sup>-</sup>).<sup>40–42</sup> The peak intensities of these carbonates increase significantly, indicating that Cu<sub>2</sub>O@CuCl-bpy can chemically adsorb and interact with CO<sub>2</sub> and H<sub>2</sub>O molecules. The emerging peaks at 1653, 1733, 1750, and 1772 cm<sup>-1</sup> may result from formate and the peak at 1635 cm<sup>-1</sup> could be attributed to carboxylate. Moreover, the intensities of the peaks at 1559 and 1521 corresponding to \*COOH increased with the extension of visible light illumination time, which might be possibly caused by the favorable proton capture capability of CO<sub>2</sub> radicals. Notably, the intensity of the peak at 1700 cm<sup>-1</sup> gradually increased with light irradiation and this can be ascribed to \*HCOOH, which is an important intermediate for the formation of HCOOH.<sup>40</sup> For the purpose of comparison, *in situ* FTIR spectroscopy was performed to analyze the intermediates of Cu<sub>2</sub>O@CuBr-bpy and Cu<sub>2</sub>O@CuI-bpy under visible light illumination (Fig. S16†). During the illumination time from 0 to 30 min, the peak intensities of Cu<sub>2</sub>O@CuBr-bpy and Cu<sub>2</sub>O@CuI-bpy obviously appeared and their intensities gradually increased, which is the same as what was observed for Cu<sub>2</sub>O@CuCl-bpy. It is worth noting that the peak intensity of Cu<sub>2</sub>O@CuCl-bpy is the highest while that of Cu<sub>2</sub>O@CuI-bpy is the lowest. We speculate that the increase in electronegativity would increase the interaction between halide anions and intermediates of HCOOH, thus enhancing CO<sub>2</sub> reduction.

Density Functional Theory (DFT) computational methods were used to explain the photoexcitation process and the catalytic reaction mechanism. The model structures established in the calculation and the reaction mechanism are shown in Fig. S17–S22† (details in the Experimental section). To investigate the connection mode between CuX–bpy and the semiconductor Cu<sub>2</sub>O, we investigated the adsorption of CuX–bpy on the Cu<sub>2</sub>O(100) facets through the charge density difference. As shown in Fig. 5(a) and (b), one CuX–bpy molecule is put on the Cu<sub>2</sub>O(100) surface. The halogen element X will bond to two surface Cu atoms to form a tetra-coordinated [ClCu<sub>4</sub>]<sup>3+</sup> structure. There is obvious charge transfer at the interface between CuX–bpy and Cu<sub>2</sub>O(100), where a photoelectron would potentially transfer from Cu<sub>2</sub>O to the CuX–bpy layer.

A comparison graph about the OER and CO<sub>2</sub>RR catalytic performance of CuX–bpy molecules and the Cu<sub>2</sub>O(100) surface is given in Fig. 5(c) and (d). More detailed information is available in Tables S3–S7.† As for the OER process, CuCl–bpy, CuBr–bpy and CuI–bpy all follow the adsorbate evolution mechanism, but exhibit very high free energies of 2.211 eV, 2.222 eV and 2.23 eV, respectively. At  $U = 1.23$  V, their corresponding overpotentials are 0.981 V, 0.992 V and 1 V, respectively. The bare Cu<sub>2</sub>O(100) surface also does not perform well for the OER due to the 3.075 eV free energy. Meanwhile, following the lattice oxygen oxidation mechanism, the Cu<sub>2</sub>O(100) surface exhibits a lower free energy of 1.943 eV, whose corresponding overpotential is 0.713 V. Therefore, the bare Cu<sub>2</sub>O(100) surface plays a role in water oxidation. As for the CO<sub>2</sub>RR process, the \*OCHO adsorbate is more energetically stable than the \*COOH adsorbate in CuX–bpy molecules. Thus, CuCl–bpy, CuBr–bpy and CuI–bpy all follow the formic acid pathway. Their free energies are 0.872 eV, 0.982 eV and 1.083 eV, respectively. In other words, the catalytic performance of CuX–bpy increases with the increase in electronegativity of halogen element X. The adsorption energies of \*CO<sub>2</sub> are all negative in CuX–bpy, which indicates the effortless adsorption beginning of the CO<sub>2</sub>RR. For comparison, the bare Cu<sub>2</sub>O(100) surface can hardly adsorb the \*CO<sub>2</sub> adsorbate due to its 2.058 eV adsorption energy, leading to ultrahigh free energy as well as making it unsuitable for the CO<sub>2</sub>RR. Hence, CuX–bpy molecules play a role in carbon dioxide reduction.

According to the above analysis, we propose a probable photocatalytic mechanism in Cu<sub>2</sub>O@CuX–bpy. Upon visible-light illumination, abundant photo-generated electron–hole pairs are formed in the Cu<sub>2</sub>O@CuX–bpy system. The introduction of halogen sites enables faster migration of photo-induced carriers, achieving long-life carrier separation and stabilizing the formate intermediate to promote the photoredox cycle. Cu<sub>2</sub>O presented excellent visible-light adsorption capacity, which means it can serve as a sensor to absorb light to form photo-generated carriers. The photogenerated electrons in Cu<sub>2</sub>O were further transferred to CuX–bpy loaded on its surface through Cu–Cl coordination bonds. Subsequently, the photogenerated electrons in CuX–bpy were transferred to the Cu active sites, promoting the reduction of CO<sub>2</sub> to HCOOH assisted by halogen sites, whereas the photogenerated holes in Cu<sub>2</sub>O were consumed for the oxidation of water.

## Conclusion

In summary, different halogen (X) sites (M = Cl, Br and I) in copper(i)–organic frameworks *in situ* compounded on cuprous oxide were constructed for outstanding photocatalytic reduction of CO<sub>2</sub> integrated with oxidation of water. The introduction of halogen sites makes the MOF-based catalysts have better photoresponse capability, photo-generated carrier separation and migration capability and photoredox stability. Remarkably, Cu<sub>2</sub>O@CuCl–bpy achieves efficient photo-reduction of CO<sub>2</sub> into formate with a high yield of 1520 μmol g<sup>−1</sup> after 12 hours of reaction. From *in situ* FTIR spectroscopy analysis, the superior photocatalytic performance is attributed to the increase in electronegativity, which would increase the interaction between halide anions and the intermediates of HCOOH, enhancing CO<sub>2</sub> adsorption and stabilizing the intermediates of HCOOH to promote the photoredox cycle. Through comprehensive characterization and DFT calculations, we confirmed that the effective coordination coupling between the MOF and semiconductor enables photo-generated electrons to transfer rapidly between the active sites of the MOF and the semiconductor. This feature results in the photoexcited electrons and holes accumulating in the CuX–bpy and Cu<sub>2</sub>O, respectively, which can be efficiently used for CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation, thus simulating artificial photosynthesis. This work not only affords the rational design strategy of halide active sites in functional MOF catalysts, but also provides fundamental insights into the mechanism of CO<sub>2</sub> photoreduction reaction systems.

## Conflicts of interest

There are no conflicts to declare.

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