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Formation of a Mixed-Valence Cu(I)/Cu(II) Metal-Organic Framework with the Full Light Spectrum and High Selectivity of CO₂ Photoreduction into CH₄

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Based upon the hetero-N, O ligand of pyrimidine-5-carboxylic acid (Hpmc), a new semiconductive Cu(I)/Cu(II) mixedvalence MOF with the full light spectrum and a novel topology of $\{4^3\cdot6^{12}\cdot8^6\}_2\{4^3\cdot6^3\}_2\{6^3\}_6\{6^4\cdot8^2\}_3$, $\{(Cu_4I_4)_{2.5}[Cu_3(\mu_4-O)(\mu_3-I)(pmc)_3(Dabco)_3\}_2.5DMF\cdot2MeCN\}_{\infty}$ (NJU-Bai61, NJU-Bai for Nanjing University Bai group; Dabco = 1,4-diazabicyclo [2.2.2] octane), was stepwisely synthesized, which exhibits good water/pH stabilities and the relatively large CO₂ adsorption capacity (29.82 cm³ g⁻¹ at 1 atm, 273 K) and could photocatalyze the reduction of CO₂ into CH₄ without additional photosensitizers and cocatalysts and with a high CH₄ production (15.75 µmol g⁻¹ h⁻¹) and CH₄ selectivity of 72.8%. Its CH₄ selectivity is the highest among the reported MOFs in the aqueous solution. Experimental data and theoretical calculations further revealed that its Cu₄I₄ cluster may adsorb light to generate photoelectrons and transfer them to its Cu₃OI(CO₂)₃ cluster, whereas its Cu₃OI(CO₂)₃ cluster could provide active sites to adsorb and reduce CO₂ and deliver sufficient electrons for CO₂ to produce CH₄. It is the first time to extend the old Cu(I)_xX_yL_z coordination polymers' application into the photoreduction of CO₂ to CH₄ and open up a new platform for the effective photoreduction of CO₂ to CH₄.

Introduction

Due to climate change, recently, CO_2 capture and conversion is one of the highest concerns.¹ In particular, the photoreduction of CO_2 into value-added chemicals (such as CO, HCOOH, CH₄, etc.) has attracted great attention, since it can be considered as a promising approach for solar-to-chemical energy conversion by mimicking the natural photosynthetic process to achieve a carbon neutral economic.² In the past decades, diverse photocatalysts have been extensively employed for the photocatalytic CO_2 reduction reaction (CO_2RR).³ Homogeneous/molecular catalysts exhibit high selectivity and efficiency, but low activity due to catalyst deactivation,⁴ whereas heterogeneous/inorganic catalysts show high activity and efficiency, but low selectivity.⁵ Very recently, due to their high surface area, inorganic-organic hybrid nature, structural and functional diversity and tunability, metal-organic frameworks



Since 2011,⁷ many MOFs have been designed for the photocatalytic CO₂RR targeting to improve their efficiency, activity and selectivity through functionalizing organic ligands, optimizing metal ions/clusters, and making MOF-based composites.⁸ Although, some achievements have been made, research on MOF-based photocatalysts to date is still in their infancy. In terms of the reductive products, most reported MOFs predominantly produce the 2e⁻/2H⁺ products of CO/HCOOH.^{8a,9} Due to that the photocatalytic reduction of CO₂ into CH₄ is more difficult than the other C1 fuels, which involves a complex 8e⁻/8H⁺ reduction process, i.e., multiple steps of hydrogenation and deoxygenation reactions, and requiring the highest kinetic barrier up to 818.3 kJ mol⁻¹,¹⁰ the reported MOF catalysts capable of producing even low or moderate yields of CH₄ are still rare. Thus, design of MOFs with high selectivity for the reduction of CO₂ into CH₄ is a great challenge.¹¹

Cu(I)_xX_yL_z (where X = CI, Br or I; L = N, P or S containing organic ligands) are almost the oldest coordination polymers with diversified structures and interesting properties, such as luminescence and semiconductivity, et al.¹² Very recently, they have been demonstrated for photocatalytic H₂ evolution.¹³ We would like to explore these as the promising platforms for CO₂ capture and conversion. Herein, from a simple hetero-N, O ligand pyrimidine-5-carboxylic acid, we have successfully constructed a Cu₄I₄ and Cu₃OI(CO₂)₃ clusters based and semiconductive Cu(I)/Cu(II) mixed-valence MOF (**NJU-Bai61**) with the full light spectrum, which

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Scheme 1. The schematic view of the preparation for NJU-Bai61.



Figure 1. a) and b) Cu₄I₄ and Cu₃OI(CO₂)₃ clusters are illustrated by two types of tetrahedrons; c) and d) Two types of cubic cages in NJU-Bai61: cage A, lavender; cage B, lime; e) The 1D channel consists of the cages A and B; f) The 1D cage-stacked chain consists of cages B; g) The 3D framework of NJU-Bai61 with the 1D channels and chains.

exhibits good water and pH stabilities and the relatively large CO₂ adsorption capacity (29.82 cm³ g⁻¹ at 1 atm, 273 K). In addition, **NJU-Bai61** could photocatalyze the reduction of CO₂ into CH₄ without additional photosensitizers and cocatalysts and with a high CH₄ production (15.75 μ mol g⁻¹ h⁻¹) and CH₄ selectivity of 72.8%. To the best of our knowledge, its CH₄ selectivity is the highest among the reported MOFs in the aqueous solution. Upon light irradiation, its Cu₄I₄ clusters as photoelectron generators could transfer photoelectrons to the Cu₃OI(CO₂)₃ clusters, while the Cu₃OI(CO₂)₃ clusters could provide active sites for adsorbing and reducing CO₂ and act as photoelectron collectors for delivering enough electrons to CO₂ for CH₄ evolution.

Results and discussion

From CuI and Hpmc ligand and through Dabco as the structural directing agent, like many Cu(I)_xX_yL_z, a Cu₄I₄ cluster-based copper(I) coordination polymer, $\{(Cu_4I_4)(Hpmc)_2\}_{\infty}$ (NJU-Bai61p) was initially afforded. NJU-Bai61p is a 2D layered and 4-connected network with sql topology (Figure S3), in which each Hpmc ligand uses its N-donor center to link a 4-coordinated Cu(I) in a tetrahedral coordination geometry

resulting in a $[Cu_4I_4N_4]$ moiety, leaving its COOH functional group uncoordinated (Figure S4).

Later on, by changing the acid and extending the time, NJU-Bai61p was further transformed into NJU-Bai61 (Scheme 1). Compared with NJU-Bai61p, the Hpmc ligands in NJU-Bai61 were deprotonated, coordinated with Cu(II) ions in a bridging bidentate mode, facilitating the formation of the $Cu_3OI(CO_2)_3$ cluster. The Cu₃OI(CO₂)₃ cluster is 7-connected and surrounded by one Cu₄I₄ cluster, three pmc and three Dabco auxiliary ligands. All Cu(II) ions in this new cluster adopt 5-coordinated geometry with two O atoms from two independent pmc linkers, one N atom from Dabco linker, one μ_3 -I⁻ ion shared by three Cu(II) ions, and one μ_4 -O²⁻ ion shared by three Cu(II) ions and one Cu(I) ion from Cu_4I_4 cluster (Figure S6). Notably, the Cu₄I₄ clusters in NJU-Bai61 exist in two different coordination environments. One is the same as that of NJU-Bai61p to form a 4-connected $[Cu_4I_4N_4]$ moiety, while the other is that the Cu₄I₄ cluster is linked by three N atoms from three Dabco ligands and one μ_4 -O²⁻ ion to form a 4-connected [Cu₄I₄N₃O] moiety (Figure S5).

Furthermore, these Cu_4I_4 and $Cu_3OI(CO_2)_3$ clusters are bridged by pmc and Dabco ligands to form two types of cubic cages. The larger one (cage A) is composed of four Cu_4I_4 This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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Figure 2. a) UV-Vis-NIR absorption spectra of NJU-Bai61p and NJU-Bai61; b) Mott-Schottky plots for NJU-Bai61; c) The amounts of CH₄, CO and H₂ produced as a function of the irradiation time over NJU-Bai61; (d) The Mass spectra analysis of ¹³CH₄ recorded under a ¹³CO₂ atmosphere using NJU-Bai61 as the catalyst.

clusters and four Cu₃OI(CO₂)₃ clusters arranged alternately as vertices and twelve linear Dabco ligands as edges with a diameter of around 8.0 Å (Figure 1c). The smaller one (cage B) is composed of eight pairs of [Cu₄I₄-Cu₃OI(CO₂)₃] linkage clusters as vertices and twelve Dabco ligands as edges, in which there exists a square with a diameter of around 6.4 Å based on four pmc linkers and Cu₄I₄ clusters located at the center of the four facets of this cage (Figures 1d and S7). The cages A and B alternately connect with each other to form a 1D channel by sharing quadrilateral windows, while the cages B connect with each other to form a 1D cage-stacked chain by sharing the facets including a quadrilateral window and a Cu₄I₄ cluster (Figures 1e, 1f, and S8). Therefore, these 1D channels and chains are arranged in an alternating fashion to form a 3D porous framework based on the cages A and B ratio of 1:3, in which each cage A shares facets with six cages B and each cage B shares facets with two cages A and four cages B (Figures 1g and S9). From the viewpoint of structural topology, pmc ligands, Cu₄I₄ and Cu₃OI(CO₂)₃ clusters could be regarded as 3connected triangular nodes, 4-connected tetrahedral nodes, and 7-connected single cap octahedron nodes, respectively. Consequently, NJU-Bai61 is a new (3,4,4,7)-connected network with the point symbol $\{4^3\cdot 6^{12}\cdot 8^6\}_2\{4^3\cdot 6^3\}_2\{6^3\}_6\{6^4\cdot 8^2\}_3$ (Figure S10).

The phase purities and thermal stabilities of **NJU-Bai61p** and **NJU-Bai61** were confirmed by PXRD and TG analyses (Figures S13 and S14). As shown in Figures S15, S16 and S17, they are quite stable under water and other organic solvents. Furthermore, they are also stable under the broad pH value variation ranges.

NJU-Bai61p exhibits a visible light adsorption up to 550 nm due to the Cu₄I₄ cluster to linker charge transfer (CLCT) transition (Figure 2a and Table S2). Very interestingly, **NJU-Bai61** shows the widest absorption band among the reported MOFs with the edge up to 1400 nm, which are mainly dominated by ICT (intra metal cluster transfer), CLCT, and CCCT (metal cluster-to-metal cluster charge transfer) transitions (Figure 2a and Table S3). The bandgaps of semiconductive **NJU-Bai61p** and **NJU-Bai61** were estimated to be 2.33 and 0.92 eV (Figure S18), which could be correlated with the calculated HOMO-LUMO gaps of 2.16 and 1.25 eV for the corresponding cluster models, respectively (Tables S4 and S5). The solid state of **NJU-Bai61** with periodic boundary condition (PBC) model for band gap was further calculated, showing a

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narrow band gap of 0.65 eV (Figure S19). Mott-Schottky measurements further revealed that they were typical n-type semiconductors and their conduction band (CB) were -0.55 and -0.58 V, which are more negative than the reduction potentials for the conversion of CO₂ to CO and CH₄ (Figures 2b and S20).^{8a} Thus, they are very promising for the CO₂ photoreduction.

The photocatalytic reduction of CO₂ over the activated NJU-Bai61 was further investigated. The amount of CH_4 was 1.26 μmol (i.e., 15.75 $\mu mol~g^{\text{-1}}~h^{\text{-1}}$) after 4 h. Except for the small amounts of CO (0.32 μ mol, i.e., 4 μ mol g⁻¹ h⁻¹) and H₂ (0.15 μmol, i.e., 1.87 μmol g⁻¹ h⁻¹), no other products, such as HCOOH, CH₃OH and HCHO, were detected (Figures 2c, S22 and S23). It exhibits the CH₄ selectivity of 72.8% in aqueous solution, which is the highest among the reported MOFs (Table S8). No obvious change of the CH₄ activity occurred during the four continuous runs (Figure S24). The XRD patterns obtained before and after its photocatalytic experiments reveal the structural robustness of the catalyst (Figure S27). The isotopic ¹³CO₂ tracing experiment was also performed to confirm that the carbon source of CH₄ indeed comes from the used CO₂ rather than the degradation of organics in the reaction (Figure 2d).11b For comparison, NJU-Bai61p was also investigated as the photocatalyst under the same conditions and only CO (1.37 µmol, i.e., 17.13 µmol g⁻¹ h⁻¹) and H₂ (1.34 µmol, i.e., 16.75 µmol g⁻¹ h⁻¹) were detected after 4 h (Figure S25). This result may reveal that $Cu_3OI(CO_2)_3$ clusters in NJU₇Bai61, could provide active sites for CH₄ evolution. DOI: 10.1039/D0SC03754K

Then we made an in-depth research to discover the reason underlying the high efficiency of CH₄ evolution. As for NJU-Bai61, the BET surface area is 248.1 m² g⁻¹ and the CO₂ uptakes at 273 K and 298 K are 29.82 and 19.69 cm³ g⁻¹ respectively, which is helpful for the subsequent CO2 conversion (Figure S28-S30). The electrostatic potential analysis may further reveal that the Cu(II) centers in $Cu_3OI(CO_2)_3$ clusters are the most favorable sites for the nucleophilic attack of CO₂ (Figure S31). The local interactions between Cu(II) sites and CO₂ molecules were investigated by the in situ FTIR technology. The adsorption of CO₂ onto the Cu(II) sites in NJU-Bai61 is a 16 cm^{-1} red shift of the asymmetric stretching mode of CO_2 (v = 2359 cm⁻¹), indicating the stronger binding between CO₂ and Cu(II) sites (Figure S33).^{11b} However, for NJU-Bai61p, no shift exists after CO₂ adsorption (Figure S32). Moreover, this experimental phenomenon is rationalized by the DFT calculations in which the peaks are also red-shifted and the adsorbed CO₂ molecule takes slightly bent geometry to facilitate CO2 activation (Figure S34 and Table S9).14 Furthermore, its fluorescence is guenching in comparison with NJU-Bai61p, indicating that the photo-excited electrons of the Cu₄I₄ clusters are transferred to the Cu₃OI(CO₂)₃ clusters, making it act as photoelectron collectors to provide electrons for the adsorbed CO₂ (Figure S35).



Figure 3. A proposed reaction pathway along with free energy difference (ΔG) for the photocatalytic CO₂-to-CH₄ conversion over NJU-Bai61.

An energetically feasible reaction pathway was calculated by DFT with the relative free energy, ΔG , for each step shown in Figures 3 and S38. Upon light irradiation, the Cu₄I₄ clusters in **NJU-Bai61** may adsorb light to generate the photoelectrons and transfer them to the Cu₃Ol(CO₂)₃ clusters, while the Cu₃Ol(CO₂)₃ clusters could supply electrons to the adsorbed CO₂ for CH₄ evolution. In the first step, the adsorbed CO₂ molecule accepts an electron and a proton to generate the COOH*. Then the COOH* combines with the second electron-proton pair to generate CO*. The CO* is reduced to the CHO* by accepting two electrons and a proton, and further

combining with a total of four electrons and five protons to generate CH₄. In the photocatalytic process, the Cu₄I₄ cluster could serve as a photosensitizer and donate the energy of 2.16 eV to the process of CO* to CHO* at the Cu₃Ol(CO₂)₃ cluster which is endothermic process with the Δ G of 1.2 eV. Moreover, the stronger CO binding affinity on **NJU-Bai61** ($E_{\rm b}$ = -20.13 eV) in comparison with that on solely Cu(I)-contained **NJU-Bai61p** ($E_{\rm b}$ = -8.05 eV) may further stabilize the CO@Cu₃IO(CO₂)₃ complex to complete the CO₂-to-CH₄ conversion (Figures S39).

Conclusions

In summary, a novel Cu₄I₄ and Cu₃OI(CO₂)₃ clusters based and semiconductive Cu(I)/Cu(II) mixed-valence MOF with the full light spectrum, NJU-Bai61, was successfully afforded, which exhibits good water stability, pH stability and the relatively large CO₂ adsorption capacity. NJU-Bai61 could photocatalyze the reduction of CO2 into CH4 without additional photosensitizers and cocatalysts and with a high CH_4 production and significantly high CH_4 selectivity of 72.8% (the highest among the reported MOFs in the aqueous solution). It was revealed that the Cu_4I_4 and $Cu_3OI(CO_2)_3$ clusters may play the role of photoelectron generators and collectors, respectively. Our work firstly expands the old $Cu(I)_x X_y L_z$ coordination polymers' application into the reduction of CO₂ to CH₄ and may open up a new system of MOFs for the reduction of CO₂ to CH₄ with high selectivity.

Experimental section

Synthesis of NJU-Bai61p. A mixture of Hpmc (11 mg, 0.09 mmol), Cul (30 mg, 0.16 mmol), Dabco (6 mg, 0.05 mmol), H₂SO₄ (10 µL), DMF (1.0 mL), and MeCN (3.0 mL) was sealed in a 20 mL Pyrex tube and kept in an oven at 85 °C for 1 day. After being washed with DMF, yellow block crystals were obtained. Yield: 2.5 mg (6 %). Selected IR (cm⁻¹): 3036, 2666, 2554, 1713, 1586, 1441, 1398, 1330, 1297, 1202, 1170, 1119, 1090, 1054, 996, 908, 837, 749, 695, 667, 568. Elemental analysis (%) calcd. for $Cu_2I_2C_5H_4N_2O_2{:}\ C$ 11.89, H 0.80, N 5.54; found: C 11.96, H 1.00, N 5.52.

Synthesis of NJU-Bai61. Single crystal of NJU-Bai61p (10 mg), dabco (4 mg, 0.036 mmol) and CuI (20 mg, 0.11 mmol) were added in 1.0 mL of DMF and 3.0 mL of MeCN. To this was added 60 μL of HCOOH with stirring. The mixture was sealed in a Pyrex tube and heated to 85 °C for 2 days. The dark-red octahedral crystals were obtained and further characterized by PXRD in Figure S1. Yield: 8.8 mg (25 %). Selected IR (cm⁻¹): 3392, 3108, 2952, 2883, 2840, 1681, 1652, 1587, 1435, 1377, 1319, 1218, 1170, 1087, 1050, 1000, 924, 840, 805, 764, 700, 612, 583, 468, 420. Elemental analysis (%) calcd. for Cu₁₃I₁₁C_{44.5}H_{68.5}N_{16.5}O_{9.5}: C 16.66, H 2.15, N 7.20; found: C 16.87, H 2.30, N 6.98.

Sample activation. The as-synthesized example of NJU-Bai61 was soaked in MeOH for 5 days with MeOH refreshing every 8 hours. Then, the solvent-exchanged sample was activated at 70 °C and under vacuum for 10 hours to obtain the activated NJU-Bai61.

Photocatalytic reaction. The photocatalytic CO₂ reduction experiments were studied on evaluation system (CEL-SPH2N, CEAULIGHT, China) in a 100 mL quartz container. A 300W xenon arc lamp (300 < λ < 2500 nm) was utilized as irradiation source. The 20 mg MOFs (NJU-Bai61p or the activated NJU-Bai61) were dispersed in the 50 mL solution of triethylamine and water (TEA/H₂O = 5: 45 v/v). The suspension was pre-degassed with CO_2 (99.999 %) for 30 min to remove air before irradiation. The reaction was kept stirring constantly with a magnetic bar to ensure the photocatalyst particles in suspension. The temperature of reaction was maintained at 25 °C by a circulating cooling water system. Gaseous product was measured by gas chromatography (GC-7900, CEAULIGHT, China) equipped with a flame ionization detector (FID) and a thermal conductivity (TCD). The detection of HCOO⁻ was

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analysed using an IC (LC-2010 PLUS, shimadzu.vijapan), The concentration of Cu in the solution before and after that was detected by the Optima 5300 DV ICP. Before the photocatalytic reaction, the suspension of the activated NJU-Bai61 (220 mg), TEA (5 mL) and H₂O (45 mL) was pre-degassed with CO₂ (99.999 %) for 30 min to remove air, then 2 mL of the filtrate was taken to detect the Cu concentration of 0.6 mg/L. Thus, the dissolved Cu ions of the activated NJU-Bai61 was 0.05 % before catalysis. After the photocatalytic reaction, 2 mL of filtrate was also taken and the concentration of Cu in the filtrate was detected to be 13.8 mg/L. Thus, the dissolved Cu ions of the activated NJU-Bai61 was 1.1 %. The cycle experiment was carried out as follows: at the end of each run, the suspension was centrifuged and moved out the supernatant. Then the recovered catalyst was washed with distill water and dried in air at 60 °C for the next cycle.

Conflicts of interest

There are no conflicts to declare.

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A Cu(I)/Cu(II) MOF with the full light spectrum was synthesized, exhibiting the photocatalytic CO_2 -to-CH₄ selectivity of 72.8% in aqueous solution.