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) mixed-valence MOF with the full light spectrum and a novel topology of (4⁵·6¹²·8⁸)ₐ(4⁵·6¹²·8⁸)ₐ(6⁵·8⁸)ₐ (Cu₄I₂O₂Cu₄(O₄–H₄O)ₒ (pmc)₂(Dabco)₃·2.5DMF·2MeCN)ₐ (NJU-Bai61, NJU-Bai for Nanjing University Bai group; Dabco = 1,4-diazabicyclo[2.2.2]octane), was synthesized stepwise. NJU-Bai61 exhibits good water/pH stabilities and a 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 rate (15.75 μmol g⁻¹ h⁻¹) and a CH₄ selectivity of 72.8%. The CH₄ selectivity is the highest among the reported MOFs in aqueous solution. Experimental data and theoretical calculations further revealed that the Cu₄I₄ cluster may adsorb light to generate photoelectrons and transfer them to its Cu₃OI(CO₂)₃ cluster, and the Cu₄I₄(CO₂)₃ cluster could provide active sites to adsorb and reduce CO₂ and deliver sufficient electrons for CO₂ to produce CH₄. This is the first time that the old Cu(i),X,L₂ coordination polymers' application has been extended for the photoreduction of CO₂ to CH₄ and this opens up a new platform for the effective photoreduction of CO₂ to CH₄.

Introduction

Due to climate change, CO₂ capture and conversion has recently, become one of the greatest concerns.¹ In particular, the photoreduction of CO₂ into value-added chemicals (such as CO, HCOOH, CH₄, and so on) has attracted great attention, because 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 economy.² In the past few decades, diverse photocatalysts have been extensively employed for the photocatalytic CO₂ reduction reaction (CO₂RR).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 (MOFs) may combine the advantages of the traditional homogeneous/heterogeneous catalysts and are emerging as promising platforms for the photocatalytic CO₂RR.⁶ Since 2011,⁷ many MOFs have been designed for the photocatalytic CO₂RR targeting to improve their efficiency, activity and selectivity by 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 its early stages. In terms of the reductive products, most reported MOFs predominantly produce the 2e⁻/2H⁺ products of CO/HCOOH.⁹–¹⁰ Due to the fact that the photocatalytic reduction of CO₂ into CH₄ is more difficult than with other C1 fuels, because it involves a complex 8e⁻/8H⁺ reduction process, i.e., multiple steps of hydrogenation and deoxygenation reactions, and requiring the highest kinetic barrier of up to 818.3 kJ mol⁻¹,¹¹ 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.¹²

The Cu(i),X,L₂ (where X = Cl, 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, and so on. Very recently, their use has been demonstrated for photocatalytic H₂ evolution. Herein the exploration of these polymers as promising platforms for CO₂ capture and conversion is reported. From a simple hetero-N,O ligand pyrimidine-5-carboxylic acid, a Cu₄I₄ and Cu₃Ol(CO₂)₃ cluster based and semiconductive Cu(1)/Cu(II) mixed-valence MOF (NJU-Bai61) with a full light spectrum, which exhibits good water and pH stabilities and the relatively large CO₂ adsorption capacity (29.82 cm³ g⁻¹ at 1 atm, 273 K) was successfully constructed. In addition, NJU-Bai61p could photocatalyze the reduction of CO₂ into CH₄ without additional photosensitizers and cocatalysts and with a high CH₄ production (15.75 mmol g⁻¹ h⁻¹) and CH₄ selectivity of 72.8%. As far as is known, the 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 Cu₃Ol(CO₂)₃ clusters, whereas the Cu₃Ol(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 the Hpmc ligand and using Dabco as the structural directing agent, like many Cu(I)xXyLz, a Cu₄I₄ cluster-based copper(i) coordination polymer, {[Cu₄I₄(Hpmc)₂]}∞ (NJU-Bai61p) was initially obtained. NJU-Bai61p is a 2D layered and 4-connected network with sql topology (Fig. S3, ESI†), in which each Hpmc ligand uses its N-donor center to link to a 4-coordinated Cu(i) in a tetrahedral coordination geometry resulting in a [Cu₄I₄N₄] moiety, leaving its COOH functional group uncoordinated (Fig. S4, ESI†). 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 Cu₃Ol(CO₂)₃ cluster. The Cu₃Ol(CO₂)₃ cluster is 7-connected and surrounded by one Cu₄I₄ cluster, three pmc and three Dabco auxiliary ligands. All the Cu(n) ions in this new cluster adopt 5-coordinated geometry with two O atoms from two independent pmc linkers, one N atom from the Dabco linker, one µ₃-I ion shared by three Cu(n) ions, and one µ₄-O²⁻ ion shared by three Cu(n) ions and one Cu(i) ion from the Cu₄I₄ cluster (Fig. S6, ESI†). Remarkably, the Cu₄I₄ clusters in NJU-Bai61 exist in two different coordination environments. One is the same as that of NJU-Bai61p and can form a 4-connected [Cu₄I₄N₄] moiety, whereas the other is the Cu₄I₄ cluster which is linked by three N atoms from three Dabco linkers and one µ₄-O²⁻ ion to form a 4-connected [Cu₄I₄N₄] moiety (Fig. S5, ESI†). Furthermore, these Cu₄I₄ and Cu₃Ol(CO₂)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 Cu₄I₄ clusters and four Cu₃Ol(CO₂)₃ clusters arranged alternately as vertices and 12 linear Dabco ligands as edges with a diameter of about 8.0 Å (Fig. 1c). The smaller one (cage B) is composed of eight pairs of [Cu₄I₄…Cu₃Ol(CO₂)₃] linkage clusters as vertices and 12 Dabco ligands as edges, in which there exists a square with a diameter of about 6.4 Å based on four pmc linkers and Cu₄I₄ clusters located at the center of the four facets of this cage.

Fig. 1  (a) and (b) Cu₄I₄ and Cu₃Ol(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.
The cages A and B connect alternately with each other to form a 1D channel by sharing quadrilateral windows, whereas the B cages connect with each other to form a 1D cage-stacked chain by sharing the facets including a quadrilateral window and a Cu4I4 cluster (Fig. 1e, f, and S8, ESI†). 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 cage B facets and each cage B shares facets with two cage As and four cage Bs (Fig. 1g and S9, ESI†). From the viewpoint of structural topology, pmc ligands, Cu4I4 and CuI2-OI(CO2)3 clusters could be regarded as 3-connected 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 \( \{4^{1}\text{-}6^{12}\text{-}8^{6}\text{-}6^{14}\text{-}6^{4}\text{-}8^{3}\text{-}6^{6}\text{-}8^{3}\text{-}6^{3}\} \) (Fig. S10, ESI†).

The phase purities and thermal stabilities of NJU-Bai61p and NJU-Bai61 were confirmed using PXRD and TG analyses (Fig. S13 and S14, ESI†). As shown in Fig. S15–S17 (ESI†), the isotopic \(^{13}\text{CO}_2\) tracing experiment was also performed to confirm that the carbon source of CH4 did indeed come from the used CO2 rather than the degradation of organics in the reaction (Fig. 2d). For comparison, the use of NJU-Bai61p as the photocatalyst was also investigated under the same conditions and only CO (1.37 \( \mu \text{mol}, i.e., 17.13 \mu \text{mol g}^{-1} \text{ h}^{-1} \)) and H2 (1.34 \( \mu \text{mol}, i.e., 16.75 \mu \text{mol g}^{-1} \text{ h}^{-1} \)) were detected after 4 h (Fig. S25, ESI†). This result may reveal that Cu3O1(CO2)3 clusters in NJU-Bai61 could provide active sites for CH4 evolution.

Then in-depth research was carried out to discover the reason underlying the high efficiency of CH4 evolution. As for NJU-Bai61, the BET surface area was 248.1 m\(^2\) g\(^{-1}\) and the CO2 uptake at 273 K and 298 K were 29.82 and 19.69 cm\(^3\) g\(^{-1}\), respectively, which was helpful for the subsequent CO2 conversion (Fig. S28–S30, ESI†). The electrostatic potential analysis may further reveal that the Cu(n) centers in CuI2-OI(CO2)3 clusters are the most favorable sites for the nucleophilic attack of CO2 (Fig. S31, ESI†). The local interactions between Cu(n) sites and CO2 molecules were investigated using the \textit{in situ} FTIR technology. The adsorption of CO2 onto the Cu(n) sites in NJU-Bai61 was a 16 cm\(^{-1}\) red shift of the asymmetric stretching mode of CO2 (\( \nu = 2359 \text{ cm}^{-1} \)), indicating the stronger binding between the CO2 and Cu(n) sites (Fig. S33, ESI†).\(^{11b}\) However, for NJU-Bai61p, no shift existed after CO2 adsorption (Fig. S32, ESI†). Moreover, this experimental phenomenon was explained by the DFT calculations in which the peaks were also red-shifted and the adsorbed CO2 molecule takes a slightly bent geometry to facilitate the CO2 activation (Fig. S34 and Table S9, ESI†).\(^{11c}\) Furthermore, its fluorescence was quenched in comparison to NJU-Bai61p, indicating that the photo-excited electrons of the Cu4I4 clusters were transferred to the Cu3O1(CO2)3 clusters, making it act as a photoelectron collector to provide electrons for the adsorbed CO2 (Fig. S35, ESI†).

An energetically feasible reaction pathway was calculated using DFT with the relative free energy, \( \Delta G \), for each step shown in Fig. 3 and S38 (ESI†). Upon light irradiation, the Cu4I4 clusters in NJU-Bai61 may adsorb light to generate the photoelectrons and transfer them to the Cu3O1(CO2)3 clusters, whereas...
Moreover, the stronger CO binding affinity of NJU-Bai61p (which was an endothermic process with the activation energy $E_b = -20.13$ eV) in comparison with that on only Cu(I)-contained MOFs (1.2 eV). In the photocatalytic process, the Cu$_4$I$_4$ cluster could serve as a photosensitizer and donated the energy of 2.16 eV to the conduction band of the MOF. The CO* was reduced to the CH* by accepting two electrons and a proton, and further combined with a total of four electrons and five protons to generate CH$_4$. In the photocatalytic process, the Cu$_4$I$_4$ cluster could serve as a photosensitizer and donated the energy of 2.16 eV to the conduction band of the MOF. The CO* was reduced to the CH* by accepting two electrons and a proton, and further combined with a total of four electrons and five protons to generate CH$_4$.

**Conclusions**

In summary, a novel Cu$_4$I$_4$ and Cu$_3$O$_3$(CO$_2$)$_3$ cluster based and semiconductive Cu(i)/Cu(ii) mixed-valence MOF with the full light spectrum, NJU-Bai61, was successfully produced, which exhibits good water stability, pH stability and a relatively large CO$_2$ adsorption capacity. NJU-Bai61 could photocatalyze the reduction of CO$_2$ into CH$_4$, without additional photosensitizers and cocatalysts, but with a high CH$_4$ production and significantly high CH$_4$ selectivity of 72.8% (the highest among the reported MOFs in aqueous solution). It was revealed that the Cu$_4$I$_4$ and Cu$_3$O$_3$(CO$_2$)$_3$ clusters may play the role of photoelectron generators and collectors, respectively. This work firstly expands the old Cu(i),X,L$_2$ coordination polymers’ application into the reduction of CO$_2$ to CH$_4$ and may open up a new system of MOFs for the reduction of CO$_2$ to CH$_4$ 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), H$_2$SO$_4$ (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 washing 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$_3$I$_3$C$_2$H$_4$N$_2$O$_2$: C 11.89, H 0.80, N 5.54; found: C 11.96, H 1.00, N 5.52.

**Synthesis of NJU-Bai61**

A single crystal of NJU-Bai61p (10 mg), Dabco (4 mg, 0.036 mmol) and Cul (20 mg, 0.11 mmol) were added to 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 d. Dark-red octahedral crystals were obtained and further characterized by PXRD and the results are shown in Fig. S1 (ESI†). 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 Cu$_3$I$_3$C$_4$H$_4$N$_2$O$_2$: C 16.66, H 2.15, N 7.20; found: C 16.87, H 2.30, N 6.98.

**Sample activation**

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

**Photocatalytic reaction**

The photocatalytic CO$_2$ reduction experiments were carried out on an evaluation system (CEL-SPH2N, CEAULIGHT, China), in a 100 mL quartz container. A 300 W xenon arc lamp (300 < λ < 2500 nm) was utilized as the irradiation source. The 20 mg MOFs of NJU-Bai61p or the activated NJU-Bai61 were dispersed in 50 mL of a solution of triethylamine and water (TEA/H$_2$O = 5 : 45 v/v). The suspension was pre-degassed with CO$_2$ (99.999%) for 30 min to remove the air before irradiation. The reaction was stirred constantly with a magnetic bar to ensure the photocatalyst particles remained in suspension. The temperature of the reaction was maintained at 25 °C by a circulating cooling water system. The gaseous product was measured by gas chromatography (GC-7900, CEAULIGHT, China) with a flame ionization detector (FID) and a thermal...
conductivity detector (TCD). An ion chromatography (LC-2010 Plus, Shimadzu, Japan) was used for the detection of HCOO-. The concentration of Cu in the solution before and after catalysis was determined using an ICP-OES system (Optima 5300 DV, PerkinElmer). Before the photocatalytic reaction, the suspension of the activated NJU-Bai61 (220 mg) was pre-degassed with CO2 (99.999%) for 30 min to remove the air, then 2 mL of the filtrate was removed and a Cu concentration of 0.6 mg L-1 was detected. Thus, the concentration of dissolved Cu ions of the activated NJU-Bai61 was 0.05% before catalysis. After the photocatalytic reaction, 2 mL of filtrate was also removed and the concentration of Cu in the filtrate was determined to be 13.8 mg L-1. Thus, the concentration of dissolved Cu ions of the activated NJU-Bai61 was 1.1%. The cycling experiment was carried out as follows: at the end of each run, the suspension was centrifuged and the supernatant was removed. Then the recovered catalyst was washed with distilled water and dried in air at 60 °C before the next cycle.

Conflicts of interest
There are no conflicts to declare.

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