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Restructuring multi-phase interfaces from Cubased metal-organic frameworks for selective electroreduction of CO_2 to $C_2H_4\dagger$

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Multi-phase interfaces are promising for surmounting the energy barriers of electrochemical CO_2 reduction involving multiple electron transfer steps, but challenges still remain in constructing interfacial microstructures and unraveling their dynamic changes and working mechanism. Herein, highly active Ag/Cu/Cu₂O heterostructures are *in situ* electrochemically restructured from Ag-incorporating HKUST-1, a Cubased metal-organic framework (MOF), and accomplish efficient CO_2 -to- C_2H_4 conversion with a high faradaic efficiency (57.2% at -1.3 V vs. RHE) and satisfactory stability in flow cells, performing among the best of recently reported MOFs and their derivatives. The combination of *in/ex situ* characterizations and theoretical calculations reveals that Ag plays a crucial role in stabilizing Cu(i) and increasing the CO surface coverage, while the active Cu/Cu_2O interfaces significantly reduce the energy barrier of C-C coupling toward the boosted ethylene production. This work not only proves MOFs as feasible precursors to derive efficient electrocatalysts on site, but also provides in-depth understanding on the working interfaces at an atomic level.

Introduction

The electrochemical CO_2 reduction reaction (CO_2RR) powered by renewable electricity provides a sustainable process toward carbon neutrality. 1,2 Compared with C_1 products (e.g., CO, HCOOH, and CH_4), C_{2+} ones (e.g., C_2H_4 and C_2H_5OH) feature higher energy density and market value; however, their productivity is seriously limited by the multi-step hydrogenation competing with a series of side-reactions. $^{3-5}$ So far, Cu is the only metal that can selectively convert CO_2 to C_{2+} thanks to the benign bonding of *CO intermediates, 6,7 and its interfaces with tailored valence states, grain boundaries and unsaturated sites are evidenced to surmount the energy barriers of such multiple electron transfer steps. $^{8-10}$ Although progress has been made in C_{2+} production, it's still challenging to facilely construct active interfaces and effectively stabilize them during electrolysis. 11

Metal-organic frameworks (MOFs) have attracted extensive interest for the electrochemical CO₂RR associated with the high

surface area, controllable pore size/shape, and open metal sites,12-14 but as for the catalytic mechanism debates remain due to the dynamic change of frameworks during the tough electrolysis.15 In particular, Cu-based MOFs containing frangible Cu-O₄ nodes would undergo in situ reconstruction since the electron transport along networks via the copper-ion redox demolishes the coordination extensively.16 The newly formed surface/interfaces, rather than the initial frameworks, should be brought into sharp focus for the mechanism study.17 Following the progressive insights, such electrochemical reconstruction was proved feasible to produce active and selective catalysts on site, 18-22 avoiding the time and energy-consuming preparation of catalysts and working electrodes (e.g., thermally driven epitaxial growth of multi-phase interfaces23,24 and ultrasonic spraying for loading powdery electrocatalysts onto gas-diffusion electrodes25). The in situ derived electrocatalysts inherit the structural merits of MOFs, and more importantly generate plenteous interfaces abundant with coordinatively unsaturated sites under the manipulated electrochemical conditions.26 For example, the single-type Cu2O sites of Cu2O@CuHHTP and coordinatively unsaturated Cu paddle wheel clusters (Cu₂(-HCOO)₃), partially reduced from CuHHTP and HKUST-1 at mild potentials, promoted the selective CO₂RR to CH₄ in H-type reactors, while C₂₊ production was still restricted. ^{17,19} Moreover, the structure-activity relationship under working conditions was inconclusive in the context of the further reconfiguration at more negative potentials and higher current densities adopted for the CO2RR, especially in flow cells. As

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recently highlighted, the deep reconstruction of sulfur-doped HKUST-1 to ligand-free $\text{Cu/Cu}_x\text{S}_y$ interfaces could enable efficient ethylene production;¹⁸ however, such effort was hampered by the difficult control over the exchange of benzenetricarboxylic linkers by thioacetamide ligands in frangible frameworks. In other words, constructing, promoting and stabilizing interfacial active species, *e.g.*, Cu(0)–Cu(i) ensembles and defective sites, *via* elaborative MOF reconstruction are promising for robust C_{2+} production, but still an arduous task under the harsh CO_2RR conditions.^{27,28}

Thanks to the thermodynamic merits of Ag in comparison with Cu, e.g., the relatively higher standard redox potential $(E_{Ag^+/Ag} =$ +0.80 V vs. $E_{\text{Cu}^+/\text{Cu}} = +0.52 \text{ V}$) and the less negative formation enthalpy of oxides $(-31.1 \text{ kJ mol}^{-1} \text{Ag}_2\text{O} \text{ vs.} -169 \text{ kJ mol}^{-1} \text{Cu}_2\text{O})$, introducing foreign Ag atoms is anticipated to stabilize neighboring Cu(1) active for the CO₂RR.²⁹ Moreover, it's also expected to empower tandem electrolysis on the expanded interfaces via available *CO spillover from weakly bonding Ag to Cu(0)-Cu(1) sites capable of C-C coupling.30-32 However, the relevant research is still absent for directional MOF reconstruction. Here, Ag-incorporating HKUST-1 frameworks (Ag_n/HKUST-1, n denotes the molar ratio of Ag/Cu) were for the first time introduced to in situ restructure Ag/Cu/Cu₂O heterostructures under practical electrolysis conditions, which were highly active for CO2-to-C2H4 conversion due to the rich Cu(1) species and $Ag/Cu/Cu_2O$ interfaces. With an optimal loading of $Ag(n_{Ag}:n_{Cu})$ = 0.1), the in situ derived electrocatalysts afforded a high C₂H₄ faradaic efficiency (FE) of 57.2% at -1.3 V vs. RHE, superior to those of HKUST-1 derivatives (17.4%), electro-deposited Ag/Cu/Cu₂O (16.7%), and their recently reported MOF-related counterparts, and maintained satisfactory long-term durability. The combination of in/ex situ characterizations and theoretical calculations confirmed that Ag played a crucial role in stabilizing Cu(1) and increasing CO surface coverage, while the resulting rich Cu/Cu₂O interface significantly reduces the energy barrier of C-C coupling toward boosted ethylene production.

Experimental section

Chemicals

Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, >99.0%), polyvinylpyrrolidone (PVP, MW 58 000) and N,N-dimethylformamide (DMF, 99.8%) were provided by Macklin Co., Ltd (Shanghai, China). 1,3,5-Benzenetricarboxylic acid (H₃BTC, 98%), potassium hydroxide (KOH, 85%) and silver nitrate (AgNO₃, 99.8%) were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Nafion (5 wt%) solution was purchased from Sigma-Aldrich. Ethanol (99.7%) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All aqueous solutions were prepared using ultrapure water (>18 M Ω).

Material synthesis

Synthesis of HKUST-1. HKUST-1 was prepared via the reported method with a slight modification.³³ Typically, 8.6 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 15 mL of deionized water. A

solution of $\rm H_3BTC$ acid (4.8 mmol) in a co-solvent of DMF and ethanol (30 mL, 1:1 by volume) was mixed with 2.0 g of PVP under continuous stirring. After complete dispersion of the reactants, the two solutions were mixed directly. Subsequently, the mixed solution was stirred for 15 min and transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 100 °C for 10 h. After naturally cooling down to room temperature, the product was washed with ethanol three times by centrifugation at 8000 rpm for 5 min. Finally, the blue powder of HKUST-1 was obtained after drying under vacuum at 60 °C overnight.

Synthesis of Ag_n/**HKUST-1.** The Ag_{0.1}/HKUST-1 pre-catalyst was prepared by a wet chemistry method.³⁴ 5.4 mg (0.032 mmol) of AgNO₃ was dissolved in 10 mL of hydroalcoholic solution ($V_{\text{EtOH}}:V_{\text{H}_2\text{O}}=9:1$), and then 70 mg (0.32 mmol) of the as-prepared HKUST-1 was added into the above solution with continuous stirring for 20 h at 85 °C. The precipitate was centrifuged, washed with ethanol and dried in a vacuum oven at 60 °C overnight. Furthermore, varied amounts of AgNO₃ were used to prepare Ag_n/HKUST-1 with different amounts of Ag incorporated.

Synthesis of EtOH reduced HKUST-1 (ER-HKUST-1). HKUST-1 was added to 10 mL of hydroalcoholic solution ($V_{\rm EtOH}$: $V_{\rm H_2O}$ = 9:1) with continuous stirring for 20 h at 85 °C. The precipitate was centrifuged, washed with ethanol and dried in a vacuum oven at 60 °C overnight.

Physical characterization

Transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) and the corresponding elemental mapping were performed on a JEOL 2100F. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were conducted on a ZEISS ULTRA55. X-ray diffraction (XRD) analysis was performed on a Bruker D8 diffractometer using Cu K α radiation (λ = 1.54056 Å). X-ray photoelectron and Auger electron spectroscopies (XPS and AES) were performed on a Thermo Scientific Escalab 250Xi. Fourier transform infrared (FT-IR) spectroscopy was carried out on a PerkinElmer spectrometer with the spectral range of 4000-400 cm⁻¹. Raman investigation was performed on a laser confocal Raman microspectrometer (Horiba HR-800) with an excitation laser wavelength of 532 nm. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was conducted on an OPTIMA 2000DV. X-ray absorption spectroscopy (XAS) was performed at beamline 12-BM of the Advanced Photon Source beamline at Argonne National Laboratory in Illinois, USA.

Preparation of cathode electrodes

5 mg of electrocatalyst was ground to powder and then dispersed into anhydrous ethanol (450 μ L) followed by adding 50 μ L Nafion. After continuous ultrasonication for at least 30 min, a homogeneous ink was achieved. 100 μ L of the ink was pipetted onto a carbon paper electrode (0.5 cm \times 2 cm) with a loading of 1 mg cm⁻². The electrode was then dried at room temperature naturally for the subsequent electrochemical tests.

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Electrochemical test

CO₂ electrolysis was performed in a flow cell. The prepared gas diffusion electrode (GDE) was the working electrode. An electrolyte (1.0 M KOH) was circulated through the flow cell at a rate of 15 mL min⁻¹ under the pressure applied by a peristaltic pump. Anode and cathode chambers were separated by an anion exchange membrane. A platinum electrode and a solid Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. Electrode potentials in the study were converted to the reversible hydrogen electrode (RHE) scale according to the following equation:

$$E_{(vs. RHE)} = E_{(vs. Ag/AgCl)} + 0.059 \times pH + 0.197 V$$

All electrochemical measurements were carried out in a three-electrode system with a CHI660E potentiostat. Linear sweep voltammetry (LSV) curves were obtained to choose the appropriate potential range for the catalysts. The sweeping range was from 0 to $-1.7~\rm V$ (vs. RHE) at a scan rate of 100 mV s $^{-1}$ in 1 M KOH solution with a CO $_2$ flow.

Products analysis

Gaseous products were analyzed using a gas chromatograph (GC, FULI-9790 II) equipped with a flame ionization detector (FID for CO and hydrocarbons) and a thermal conductivity detector (TCD for H₂). Gas-phase products were sampled every 20 min using high-purity nitrogen (N₂, 99.999%) as the carrier gas. The column effluent (separated gas mixtures) was first passed through the TCD where hydrogen was quantified, then CO, CH₄ and C₂H₄ were subsequently quantified by the FID. According to the peak areas in the GC, the partial current densities and FEs of CO, CH₄, C₂H₄ and H₂ were calculated using the following equations:

$$j_x = \frac{\text{peak area of } x}{\alpha} \times \text{flow rate} \times \frac{nF}{V_m} \times (\text{electrode area})^{-1}$$

$$FE = \frac{j_x}{j_{\text{total}}}$$

where x represents one of CO, CH₄, C₂H₄ and H₂, and n represents the number of electrons to be transferred to form the products, which are 2, 8, 12 and 2, respectively; α is the conversion factor for CO, CH₄, C₂H₄ and H₂, respectively, based on the calibration of standard samples; F is the Faraday constant ($F = 96 485 \text{ C mol}^{-1}$), and $V_{\rm m} = 22.4 \text{ L mol}^{-1}$.

The liquid products were quantified using ¹H nuclear magnetic resonance (NMR) (AVANCE III HD 400 MHz), in which 0.1 mL of the electrolyte was mixed with 0.5 mL of D₂O, and DMSO was used as an internal standard.

Theoretical calculations

DFT calculations were performed at the GGA level within the Perdew-Burke-Ernzerhof (PBE) functional using the CASTEP software implemented in Materials Studio. The total energy calculation was performed using a kinetic energy cutoff of 450.0 eV assigned to the plane-wave basis set for calculating the density of states. The self-consistent field (SCF) tolerance was 1 \times 10⁻⁶ eV. The Brillouin zone was sampled using 5 \times 5 \times 1 kpoints. The core electrons were replaced with ultrasoft pseudopotentials. An fcc Cu model was used to further construct Cu-Ag and Cu-Cu₂O. The fcc Cu-Ag was constructed by replacing a Cu atom with Ag. Then, we selected a 3×3 relaxed rhombus $Cu_2O(001)$ bilayer on top of a relaxed 3 × 3 Cu(001) surface to model Cu/Cu₂O heterojunctions, in which O atoms were introduced to saturate the Cu atoms on the Cu(001) thus the surface atoms are well passivated. The Cu(100), Cu-Ag(100) and Cu-Cu₂O(100) surfaces were modeled using five layer slabs to study the CO₂ reduction activity. A vacuum region of 15 Å between any two repeated slabs was used to avoid interactions between repeated slabs along the z-direction.

The binding energy (BE) of an adsorbate was calculated as:

$$BE_{(adsorbate)} = E_{(slab+adsorbate)} - E_{(slab)} - E_{(adsorbate)}$$

where $E_{\text{(slab+adsorbate)}}$, $E_{\text{(slab)}}$ and $E_{\text{(adsorbate)}}$ are the total energy of the slab with an adsorbate, the energy of the pure slab/facet and the energy of the adsorbate in the gas phase, respectively.

The Gibbs free energy (G) of a species was calculated as:

$$G = E + ZPE - TS$$

where E is the total energy of a species obtained from DFT calculations, and ZPE and S are the zero-point energy and entropy of the species, respectively. A potential of 0 V was adopted in the calculation. The change in free energy (ΔG) was calculated as:

$$\Delta G = \Delta E + \Delta Z PE - T \Delta S$$

The transition state search used complete LST/QST in 0.25 eV ${\rm \mathring{A}}^{-1}$ RMS convergence, with the optimized reactant and product geometries as starting points. CASTEP employed algorithms such as the nudged elastic band (NEB) or the dimer method to explore the potential energy surface and locate the transition state structure. The transition state was obtained between reactants and products while minimizing the energy in 10 QST steps.

Results and discussion

An HKUST-1 framework is built up of dimeric Cu units connected by benzene-1,3,5-tricarboxylate linkers. It was fabricated via a previously reported method,³³ and then was incorporated with Ag after reacting with AgNO₃ in a hydroalcoholic solution ($V_{\text{EtOH}}:V_{\text{H}_2\text{O}}=9:1$), where EtOH was the reducing agent that reduced Ag(I) to metallic Ag and partially reduced Cu(II) to Cu(I).³⁴ Accordingly, we also prepared a reference sample via a similar process in the absence of AgNO₃, which was named EtOH reduced HKUST-1 (ER-HKUST-1).

The crystal structure of the as-prepared samples was analyzed by XRD (Fig. 1a). $Ag_{0.1}/HKUST-1$ presented

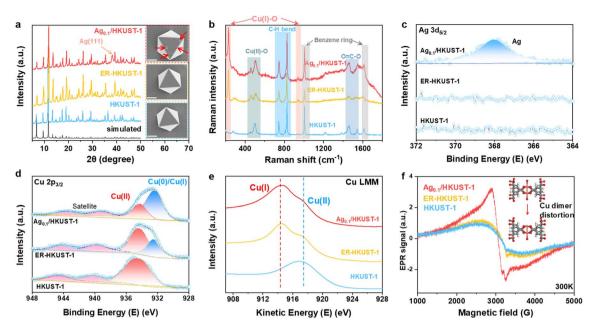


Fig. 1 Structural characterization of HKUST-1, ER-HKUST-1 and Ag_{0.1}/HKUST-1: (a) XRD patterns, (insets of a) SEM images with the scale bar of 1 μ m, (b) Raman spectra, (c) high-resolution Ag 3d_{5/2} XPS, (d) high-resolution Cu 2p_{3/2} XPS, (e) Cu LMM AES and (f) EPR spectra.

a characteristic pattern consistent with those of HKUST-1 and ER-HKUST-1, confirming the well-retained framework after Ag loading and partial reduction. This is also supported by their same absorption bands in FT-IR spectra (Fig. S1, ESI†). A new peak of Ag(111) appearing in Ag_{0.1}/HKUST-1 indicated the successful loading of Ag. An identical octahedral structure was observed in the three samples by SEM (insets of Fig. 1a), and the small nanoparticles (marked by red arrows) on the surface of Ag_{0.1}/HKUST-1 should be assigned to the incorporated Ag. Accordingly, the elemental mapping performed with both SEM and TEM revealed the uniform distribution of O, Cu and Ag elements over Ag_{0.1}/HKUST-1 octahedrons (Fig. S2, ESI†). In the Raman spectra (Fig. 1b), two new bands at 218 and 930 cm⁻¹, responsible for the Cu(I)-O vibrations,34 appeared in ER-HKUST-1 and Ag_{0.1}/HKUST-1, which indicated the partial reduction of Cu(II) to Cu(I).

The chemical composition and element valence state were further studied by XPS and AES. Different from HKUST-1 and ER-HKUST-1, Ag_{0.1}/HKUST-1 displayed a broad Ag 3d peak at 368.1 eV in XPS (Fig. 1c), confirming the successful incorporation of Ag. In the profile of Cu 2p_{3/2}, the peak at 934.5 eV was attributed to Cu(II) species, and that at 932.4 eV could be assigned to Cu(0) or Cu(1) (Fig. 1d).18 AES with the good resolution of Cu(0)/Cu(1) further identified the co-presence of Cu(1) and Cu(II) in both Ag_{0.1}/HKUST-1 and ER-HKUST-1, in comparison with the dominant Cu(II) in HKUST-1 (Fig. 1e). Therefore, the peak at 932.4 eV in the Cu 2p_{3/2} XPS profile should be ascribed to the Cu(1) species in Ag_{0.1}/HKUST-1 and ER-HKUST-1, which was derived from the partial reduction of Cu(II) by EtOH. It's noteworthy that Ag_{0.1}/HKUST-1 showed a relatively higher intensity of Cu(1) in both XPS and AES profiles as compared with ER-HKUST-1, suggesting the stabilization of Cu(1) by additive Ag. The presence of Cu(1) would cause the

distortion of the Cu–Cu dimer, as confirmed by the high signal intensity of Ag_{0.1}/HKUST-1 in EPR (Fig. 1f).³⁵ In addition, a series of Ag_n/HKUST-1 frameworks with an identical structure but different Ag/Cu molar ratios could be obtained after varying the feeding ratio (Fig. S3–S7, ESI†), which showed a volcano relationship between Cu(I)/Cu(II) and Ag/Cu ratios (Fig. S8, ESI†), indicating the enriched Cu(I) at a moderate Ag loading.

We conducted in situ Raman analysis combined with a CO₂RR test at various potentials to assess the reconstruction of such Cu-based MOFs (Fig. S9, ESI†). The bands corresponding to Cu(II)-O and C-H disappeared quickly at the applied bias, indicating the collapse of the metal-organic framework. The emerging band of Cu-CO further suggested the formation of *CO on the in situ formed metallic surface.36 Of particular interest is the appearance of Cu₂O bands at 520 and 610 cm⁻¹ in Ag_{0.1}/HKUST-1 and ER-HKUST-1 compared to HKUST-1,³⁷ whose intensity increased with the negative potentials and reached a maximum at -1.3 V vs. RHE. Thus, the in situ reconstruction of the three samples was further analyzed at -1.3 V vs. RHE in a flow cell. As the model sample, $Ag_{0.1}$ HKUST-1 afforded a fluctuating current density initially in chronoamperometry (Fig. 2a), which afterwards became more stable after 1 h electrolysis, suggesting that the reconfiguration can be completed within the first hour. To observe the reconstruction process more directly, the reconstituted samples were subjected to SEM (Fig. 2b-d). Obviously, the octahedral structure collapsed after only 1 min, and the final morphology of HKUST-1 and ER-HKUST-1 was granular, whereas Ag_{0.1}/HKUST-1 exhibited dendritic nanostructures that can obviously enhance surface hydrophobicity (Fig. S10, ESI†). As previously evidenced,38,39 electrocatalysts with a hydrophobic surface would be favorable for the CO2RR because of the inhibited hydrogen evolution competition. Interestingly, the reconfigured

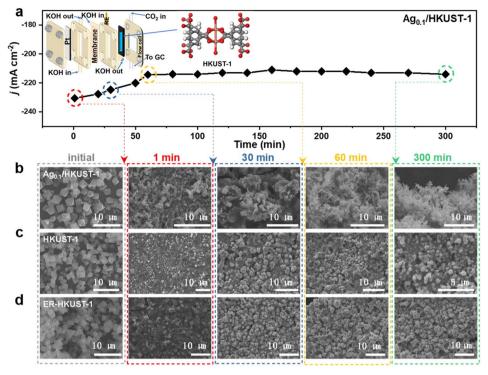


Fig. 2 (a) Chronoamperometry curve of $Ag_{0.1}/HKUST-1$ during in situ electrochemical reconstruction at -1.3 V vs. RHE, and SEM images of (b) $Ag_{0.1}/HKUST-1$, (c) HKUST-1 and (d) ER-HKUST-1 collected at 0, 1, 30, 60, and 300 min.

samples after 1 h and 5 h of electrolysis presented identical nanostructures, further confirming the rapid reconstruction finished within 1 h. Accordingly, the disappearance of the characteristic peaks of the benzene ring in FT-IR indicated that the organometallic framework has been drastically destroyed (Fig. S11, ESI†). This is distinct from the previous reports of ligand-retaining Cu surfaces (e.g., Cu₂O@CuHHTP,¹⁷ Cu₂(HCOO)₃ clusters,¹⁹ PPy/HKUST-1,²¹ and PANI/HKUST-1 (ref. 21)), and guarantees a reliable platform to unravel the structure–activity relationship of *in situ* formed interfaces.

The restructured electrocatalysts from HKUST-1, ER-HKUST-1 and Ag_{0.1}/HKUST-1 after 1 h of CO₂RR were denoted as Cu_H-KUST-1, Cu/Cu₂O_{ER-HKUST-1} and Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1}, respectively. To minimize the impact of oxidation, the samples were immediately transferred to an argon-filled glovebox for further characterization. As depicted in their XRD patterns (Fig. 3a), the diffraction peaks of the original framework disappeared. Instead, typical peaks of Cu(111) and (200) were detected at $2\theta =$ 43.3° and 50.4°, respectively. Besides, the visible Cu₂O(111) and (200) in both Cu/Cu₂O_{ER-HKUST-1} and Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1}, and the Ag(111) and (200) in Ag/Cu/Cu $_2$ O $_{Ag_{0.1}/HKUST-1}$ confirmed the co-presence of multiple phases, i.e., Cu/Cu2O and Ag/Cu/Cu₂O. In the Cu 2p XPS profiles (Fig. 3b), unlike the precatalysts, the peak of Cu(II) was absent in the reconstructed samples, and only the peak at 932.4 eV associated with Cu(0)/Cu(1) was observed, which indicated the reduction of Cu(II) at the applied potential. $Cu/Cu_2O_{ER\text{-}HKUST\text{-}1}$ and Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} showed peaks at 914.3 and 917.3 eV in the AES, corresponding to Cu(1) and Cu(0) species, 40 while only Cu(0) was present on $Cu_{HKUST-1}$ (Fig. 3c), which were consistent with the XRD results. Compared to the pre-catalysts, the peak of Ag 3d on $Ag/Cu/Cu_2O_{Ag_{0.1}/HKUST-1}$ shifted toward a lower binding energy (Fig. S12, ESI†), probably due to Ag aggregation along with the electrochemical reconstruction.⁴¹

The high-resolution TEM (HR-TEM) image of Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} clearly showed the interfaces of Ag/Cu/Cu₂O (Fig. 3d). The lattice fringes of 0.181, 0.204 and 0.245 nm could be indexed to Cu(200), Cu(111) and Cu₂O(111), respectively, and those of 0.204 and 0.235 nm were assigned to

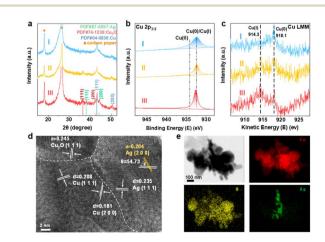


Fig. 3 (a) XRD patterns, (b) high-resolution Cu $2p_{3/2}$ XPS and (c) Cu LMM AES of (I) Cu $_{\rm HKUST-1}$, (II) Cu $_{\rm Cu}_{\rm Cu}_{\rm Ce}_{\rm R-HKUST-1}$ and (III) Ag/Cu/Cu $_{\rm Cu}_{\rm Co}_{\rm Ag_{0.1}/HKUST-1}$. (d) HR-TEM image and (e) elemental mapping of Ag/Cu/Cu $_{\rm Co}_{\rm Ag_{0.1}/HKUST-1}$.

Ag(200) and Ag(111). In comparison, the lattice planes of Cu(111) and $Cu_2O(111)$ were visible in $Cu/Cu_2O_{ER-HKUST-1}$, and only Cu(111) was observed in $Cu_{HKUST-1}$ (Fig. S13, ESI†). In Fig. 3e, the elements of Cu and O were uniformly distributed throughout the nanostructures, while the concentrated distribution of Ag suggested the formation of an $Ag/Cu/Cu_2O$ multiphase with abundant interfaces, rather than Ag-Cu alloys.

Furthermore, the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of Ag/Cu/Cu $_2$ O $_{\mathrm{Ag}_{0.1}\mathrm{HKUST}\text{-}1}$ were analysed to understand the local environments of Ag and Cu (Fig. S14, ESI†). The Ag K-edge overlapped with that of Ag foil, indicating a close-to-zero valence state of Ag in Ag/Cu/Cu₂O_{Ag_{0.1}HKUST-1}. But the white line peak was slightly lower, consistent with the XPS data (Fig. S12, ESI†), which was probably due to the electron transfer from Cu to Ag. The electron transfer between Ag and Cu may lead to the formation of Ag-Cu bonds, as well as the existence of an Ag-Cu interface. 42 Accordingly, the Cu K-edge analysis presented a slightly higher valence state of Cu than that of the Cu₂O reference. Moreover, the k^2 -weighted Ag K-edge EXAFS showed that the bond length and coordination number of Ag in Ag/Cu/ Cu₂O_{Ag_{0.1}HKUST-1} were slightly reduced, suggesting the formation of a heterostructure rather than alloys. Analogously, the increased Cu-O signal in the Cu K-edge EXAFS as compared with that of a Cu reference indicated the considerable amount of Cu₂O in the restructured interfaces, and the lower Cu-O coordination number and the accordingly longer Cu-O bond in

comparison with those of a $\rm Cu_2O$ reference might be due to the presence of heterogeneous interfaces. In addition, wavelet transform analysis highlighted the dominance of Ag–Ag and Cu–O bonds in the heterostructures, while Ag–O and Cu–Cu bonds are negligible, matching well with the EXAFS fitting results (Fig. S15 and Table S1, ESI†).

The electrochemical CO₂RR performance of Cu_{HKUST-1}, Cu/ Cu₂O_{ER-HKUST-1} and Ag/Cu/Cu₂O_{Ago,/HKUST-1} was evaluated in a flow cell with 1.0 M KOH as the electrolyte. The polarization curves showed the highest current densities of Ag/Cu/Cu₂O_{Ag_{0,1}} HKUST-1 among the three samples (Fig. 4a), indicative of the high activity of the restructured Ag/Cu/Cu2O. The electrolyte after reaction was analyzed by using ¹H nuclear magnetic resonance (NMR) spectroscopy, which suggested the negligible formation of liquid products (Fig. S16, ESI†). As evidenced by recent reports,38,43 the higher coverage and transport efficiency of chemisorbed *H derived from abundant H2O on gas-liquidsolid interfaces would benefit the generation of alcohols, the typical liquid products of the CO2RR. Herein, the superhydrophobic surface of the restructured Ag/Cu/Cu₂O (Fig. S10, ESI†) probably prohibits the formation of alcohol products. With further regard to the same key step of *CO coupling shared by ethylene and ethanol formation, we thereby focused on the gas products quantified by on-line GC for the understanding of the restructured interfaces, to avoid the superposition of instrumental errors (e.g., GC and NMR). Potentiostatic measurements at -1.0 to -1.5 V (vs. RHE) showed that Ag/Cu/

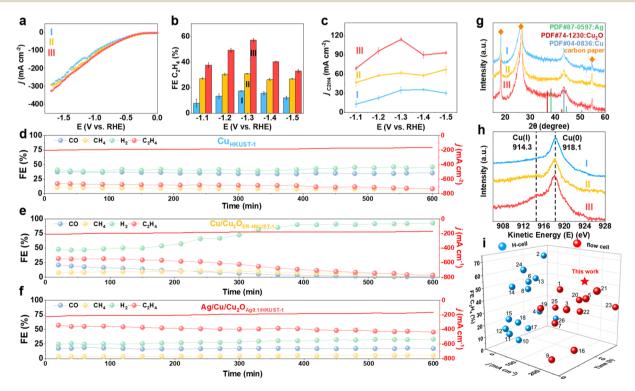


Fig. 4 (a) Polarization curves, (b) FE and (c) partial current density of C_2H_4 at different applied potentials of (l) $Cu_{HKUST-1}$, (II) $Cu/Cu_2O_{ER-HKUST-1}$ and (III) $Ag/Cu/Cu_2O_{Ag_{0.1}/HKUST-1}$ in CO_2 -saturated 1.0 M KOH. Chronoamperometric stability tests of (d) $Cu_{HKUST-1}$, (e) $Cu/Cu_2O_{ER-HKUST-1}$ and (f) $Ag/Cu/Cu_2O_{Ag_{0.1}/HKUST-1}$. (g) XRD patterns and (h) Cu LMM AES of $Cu_{HKUST-1}$, $Cu/Cu_2O_{ER-HKUST-1}$ and $Ag/Cu/Cu_2O_{Ag_{0.1}/HKUST-1}$ after the CO_2RR (600 min). (i) Performance of $Ag/Cu/Cu_2O_{Ag_{0.1}/HKUST-1}$ compared with the recently reported Cu-based electrocatalysts (the numbers of reference samples are obtained from Table S2, ESI^{\dagger}). $^{16.18-20.35,44-64}$

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Cu₂O_{Ag_{0.7}/HKUST-1} produced mainly C₂H₄ with the maximum FE of 57.2% at -1.3 V vs. RHE, while this value was only 17.4% on Cu_{HKUST-1} (Fig. 4b). The reaction profiles of Cu_{HKUST-1}, Cu/ Cu₂O_{ER-HKUST-1} and Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1}, including product FEs and current densities, are depicted in Fig. S17, ESI.† Accordingly, Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} afforded a higher partial current density of C_2H_4 ($j_{C_2H_4}$) than $Cu_{HKUST-1}$ and $Cu_{ER-HKUST-1}$ (Fig. 4c), confirming the promoted ethylene production over Ag/ Cu/Cu₂O heterostructures. For comparison, either the reference sample consisting of physically mixed Cu, Ag and Cu2O nanoparticles or the electro-deposited one delivered a lower FE of C_2H_4 than $Ag/Cu/Cu_2O_{Ag_{0.1}/HKUST-1}$ under the same conditions (Fig. S18, ESI†), which highlighted the key contribution of MOF precursors to construct active Ag/Cu/Cu₂O multi-interfaces. To further unravel the effect of Ag, the CO₂RR performance of a series of Ag/Cu/Cu₂O derived from Ag_n/HKUST-1 frameworks was measured (Fig. S19, ESI†). With the increase of Ag content, the FE of C₂H₄ gradually increased and then tended to decrease, which indicated the benefited synergy of active components on the in situ generated Ag/Cu/Cu₂O interfaces with an optimal composition.

The electrochemically active surface area (ECSA) of the catalysts could be evaluated in terms of double-layer capacitance ($C_{\rm dl}$, Fig. S20, ESI†), on the basis of their proportional correlation. Ag/Cu/Cu₂O_{Ag_{0.7}/HKUST-1} presented a $C_{\rm dl}$ value of 3.24 mF cm⁻², exceeding those of Cu_{ER-HKUST-1} (2.68 mF cm⁻²) and Cu/Cu₂O_{HKUST-1} (2.04 mF cm⁻²), which indicated enriched active-sites after restructuring Ag/Cu/Cu₂O multi-interfaces. Meanwhile, electrochemical impedance spectroscopy (EIS) pointed out the relatively smaller electron-transfer resistance $(R_{\rm ct})$ on Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} (Fig. S21, ESI†), in good accordance with its higher activity.

The long-term stability was evaluated by conducting a chronoamperometric test (Fig. 4d-f). On Cu_{HKUST-1}, the main products were H_2 and CO with FEs of $\sim 40\%$ and $\sim 35\%$, respectively, and the FE of C₂H₄ was lower than 18%. Although the C₂H₄ production was impressively enhanced on $Cu_{ER-HKUST-1}$ ($FE_{C_2H_4}$ ~30%) during the initial reaction, it suffered from a drastic decrease to <20% after 300 min, concomitant with the increase of H_2 production. In sharp comparison, $Ag/Cu/Cu_2O_{Ag_{0,1}/HKUST-1}$ manifested a remarkably stable FE of C2H4 (~50%) within 600 min, which should be ascribed to the Ag additives. In addition, compared to Cu_{HKUST-1}, Cu/Cu₂O_{ER-HKUST-1} and Ag/Cu/ Cu₂O_{Ag_{0.1}/HKUST-1} showed a significantly lower CO yield and higher C2H4 yield during the initial reactions, which was accounted for by the effective consumption of *CO to produce C₂H₄. Afterwards, the CO production suffered a continuous decrease on Cu/Cu₂O_{ER-HKUST-1}, whereas it was almost constant on Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1}, suggesting a dynamic balance of *CO formation and self-coupling on Ag/Cu/Cu₂O interfaces. In other words, *CO generated on Ag sites might spill over onto the Cu/Cu₂O interface to increase the surface coverage of *CO, thereby promoting C-C coupling toward C₂H₄ and retaining the balance with CO formation and consumption.30,32 Furthermore, we characterized the three catalysts after the long-term CO2RR test. The spent Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} showed a well-retained phase composition (Ag/Cu/Cu₂O) in XRD (Fig. 4g). The HR-TEM

images and the elemental mapping of Ag/Cu/Cu₂O_{Ag_a,/HKUST-1} clearly presented the interfaces of Ag/Cu/Cu₂O (Fig. S22, ESI†), indicating the good structural stability. By contrast, the Cu₂O(111) and (200) disappeared on the used Cu/Cu₂O_{ER-HKUST-} 1, consistent with the drastic decrease of C₂H₄ FE. Accordingly, the AES results (Fig. 4h) identified the total disappearance of Cu(I) on Cu/Cu₂O_{ER-HKUST-1}, but the signal on Ag/Cu/Cu₂O_{Ag_{0.1}/} HKUST-1 was still visible after the CO₂RR, which confirmed the promoted stability of Cu(I) assisted by Ag additives. There are two related thermodynamic factors taken into consideration. First, the substantial disparity in the formation enthalpies of $Cu_2O(-169 \text{ kJ mol}^{-1})$ and $Ag_2O(-31.1 \text{ kJ mol}^{-1})$ suggests that any Ag oxide resulting from oxygen exposure will be rapidly reduced by the adjacent Cu.32 Second, Ag, with its higher redox potential relative to Cu, can accept electrons from Cu. In addition, the negligible change of the Ag 3d signal in XPS further underscored the durability of the Ag/Cu/Cu₂O ternary interfaces in Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} (Fig. S23, ESI†).

In further comparison with recently reported Cu-based electrocatalysts (Fig. 4i and Table S2, ESI†), Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} presented an outstanding overall performance with excellent C₂H₄ FE, current output, and service life. Although some previous reports demonstrated the high FE of C₂H₄, they did not gain the high levels of current density and stability synchronously. For example, CuPz2-Act-30 exhibited a high C2H4 FE of 67% in an H-cell, but the performance under high-current conditions such as in flow cells is still unclear.20 S-HKUST-1 displayed a C₂H₄ FE of 57.2% at a current density of -400 mA cm⁻² in a flow cell, but the stability test (480 min) was only conducted at -150 mA cm^{-2} . Similarly, Cu-PzH yielded a C₂H₄ FE of 60% at -1.0 V (vs. RHE) with a large partial current density of 346.46 mA cm⁻² while its stability remained for only 242 min. 59 More counterparts with rich Cu(1) species but prepared via other methods were further taken for comparison. For example, and Cu₂O@SiO₂-NH₂ demonstrated stability exceeding 600 min,61,64 whereas the C2H4 FEs of 35% and 15% were deemed suboptimal. An AgCu single-atom alloy blended with Ag nanoparticles showed a 94 \pm 4% FE towards multicarbon products at a high current density of ~720 mA cm⁻² in a flow cell, but the FE of C₂H₄ was below 40%.⁴² In contrast, Ag/ Cu/Cu₂O_{Ag_{0.1}/HKUST-1} can achieve the superiority of C₂H₄ FE (\sim 50%), current output (>180 mA cm⁻²), and stability (600 min) at the same time, underscoring its promise for practical use. When a membrane electrode assembly (MEA) reactor is rationally designed for such restructured catalysts, we believe greater advances in performance, in particular the greater current density and long-term stability, can be accomplished.65

In situ Raman spectra were obtained and the CO₂RR test was performed to understand the dynamic changes of the restructured interfaces. Different from $Cu_{HKUST-1}$, $Cu/Cu_2O_{ER-HKUST-1}$ and Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} showed the band assigned to Cu(I) species at 520 and 610 ${\rm cm}^{-1}$ (Fig. 5a and b).³⁷ This band was well retained on Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} for 300 min, while it became weaker and disappeared on Cu/Cu2OER-HKUST-1. In the meantime, this evolution was confirmed by the in situ Raman spectra collected at various potentials (Fig. S24, ESI†). Such in situ monitoring, highly consistent with the post-CO₂RR AES analysis

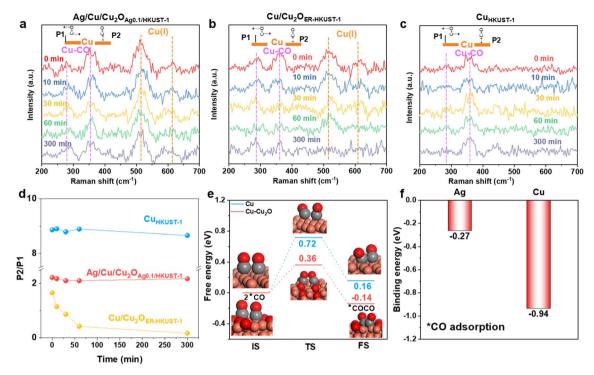


Fig. 5 In situ Raman spectra during the CO₂RR under different reaction times of (a) Ag/Cu/Cu₂O_{Ago,1/HKUST-1}, (b) Cu/Cu₂O_{ER-HKUST-1} and (c) Cu_{HKUST-1}, and (d) the corresponding evolution of P2/P1 ratios. (e) Energy profiles for the initial states (ISs), transition states (TSs) and final states (FSs) of *CO-*CO coupling on Cu and Cu-Cu₂O models. (f) Energy profiles of *CO adsorption on Ag and Cu.

(Fig. 4h), identified again the stabilization of the Cu(1) species by Ag. Furthermore, the peaks at 280 and 364.3 cm⁻¹, corresponding to the restricted rotating (P1) and stretching (P2) models of adsorbed Cu-CO, respectively, could be detected on the surfaces, and the intensity ratio of P2/P1 peaks was a valid measure of the surface coverage of *CO.36 The P2 band was the main peak while the P1 was very weak on Cu_{HKUST-1} (Fig. 5c and d), and their large ratio of 8.5-9.0 indicated the extremely high *CO coverage on the Cu(0)-dominant surface,66 consistent with the main distribution of CO in the products (Fig. 4d). In comparison with $\text{Cu/Cu}_2\text{O}_{\text{ER-HKUST-1}}$, $\text{Ag/Cu/Cu}_2\text{O}_{\text{Ag}_{0.1}/\text{HKUST-1}}$ delivered a larger P2/P1 ratio associated with the higher *CO coverage. More importantly, this ratio was kept at a high level above 2.0 on Ag/Cu/Cu₂O_{Ag_{0.1}/HKUST-1} during the CO₂RR (0-300 min), but it drastically decreased on Cu/Cu₂O_{ER-HKUST-1} (Fig. 5d). According to the recently evidenced tandem electrocatalysis on Ag/Cu interfaces, 67,68 we reasonably assumed that the CO spillover from Ag sites could increase the *CO coverage on Cu(0)-Cu(1) ensembles, leading to the well-maintained P2/P1 ratio on Ag/Cu/Cu $_2\mathrm{O}_{\mathrm{Ag}_{0.1}/\mathrm{HKUST}\text{-}1}$ for the further C–C coupling.

To further understand the contribution of Ag and Cu₂O on the C-C coupling and ethylene production, the model structures of Cu and Cu-Cu₂O were taken for DFT calculations. As a critical step toward C₂₊ products, the coupling of two *CO was brought into focus. As shown in Fig. 5e, the kinetic barrier (0.36 eV) and enthalpy change (-0.14 eV) for the *CO coupling on Cu-Cu₂O are lower than those on Cu (0.72 and 0.16 eV), suggesting that the interfaces of Cu(0)-Cu(1) can effectively boost C2 production. The coupling of two adjacent *CO on Cu-Ag should

be difficult because of the high energy barrier (1.44 eV) (Fig. S25, ESI†), wherein the spillover of *CO from Ag to Cu would be preferred. Numerous studies have found that Ag has a high selectivity for CO in the CO₂RR which can provide adequate *CO for the tandem catalysis toward C2 products. 30-32,67,68 As indicated by the more negative *CO binding energy on Cu (-0.94)eV) than that on Ag (-0.27 eV) (Fig. 5f), the spillover of the asformed *CO from Ag to Cu and even Cu(0)-Cu(1) interfaces is thermodynamically favorable. Therefore, a tandem mechanism is proposed, in which the CO produced by Ag sites can diffuse to the reactive interface of Cu-Cu₂O with a low kinetic barrier for further coupling toward C₂H₄. In addition, Ag can stabilize the Cu(I) species to enable high ethylene production for a long time, which has been well validated by in situ Raman and ex situ XRD and AES.

Finally, we adopted other Cu-MOFs with the varied coordination as the pre-catalysts towards Ag/Cu/Cu₂O interfaces, to examine the applicability of this strategy. With a similar Cu-O₄ structure but a layered crystalline structure, CuBDC (BDC = 1,4-benzenedicarboxylic acid) underwent extensive reconstruction from 2D crystals to smaller nanoparticles, which was beneficial for restructuring Ag/Cu/Cu₂O interfaces when Ag was incorporated (Fig. S26, ESI†). Thanks to the rich interfaces of Ag/Cu/Cu₂O, the reconstructed samples afforded the obviously higher FE of C_2H_4 in comparison with that free from Ag. By contrast, $CuPz_2$ (Pz = pyrazol) with a $Cu-N_4$ structure cannot undergo the reconstruction under these working conditions due to the strong coordination of Cu-N₄ (Fig. S27, ESI†). When Ag was incorporated into CuPz₂, the resulting

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samples unfortunately increased the FE of CO, probably due to the preferred generation of CO on the loaded Ag nanoparticles. The accordingly reduced FE of C₂H₄ also indicated the severely competitive reduction of CO2 on Cu and Ag sites because of the absence of Ag/Cu interfaces. This is indirect proof for the tandem electrolysis towards C₂H₄ over Ag/Cu/Cu₂O_{Ag₂,/HKUST-1} via *CO spillover. It's clear that the coordination of Cu-based MOFs is important for restructuring Ag/Cu/Cu₂O interfaces, although the ligands make negligible influences on the electrocatalytic performance indeed because they have already been removed during the reconstruction (Fig. S11, ESI†). The frangible Cu-O₄ nodes are the prerequisite for the reconstruction, while the strong Cu-N₄ requires more tough conditions (e.g., more negative potentials) to drive the reconfiguration.20

Conclusions

In summary, the directional in situ reconfiguration of Ag incorporating HKUST-1 frameworks was successfully introduced to restructure multi-phase Ag/Cu/Cu₂O electrocatalysts highly active for the CO₂RR. The reconstituted Ag/Cu/Cu₂O exhibited outstanding performance for the selective electroreduction of CO₂ to C₂H₄, with superior FE, current output, and service life to the most of recently reported counterparts. The combination of *in/ex situ* characterizations (Raman, XRD, XPS and AES) and theoretical calculations demonstrated that Ag plays a crucial role in stabilizing Cu(1) and increasing CO surface coverage, while the resulting Cu/Cu₂O interfaces significantly reduced the C-C coupling energy barrier toward the boosted ethylene production. This work not only offered a rational method to prepare highly active catalysts via electrochemical activation, but also deepened the understanding of the working state and mechanism on multi-phase interfaces. It's envisioned to gain further improvement via utilizing booming MOF pre-catalysts with more precise control over the coordination chemistry and dynamic evolution.

Data availability

Data supporting the findings of this study are available within the article ESI.†

Author contributions

Jiye Feng: synthesis, investigations, formal analysis, writing of the original draft, data curation. Wenbiao Zhang: DFT calculation, supervision. Danni Shi: experimental analysis, image polishing. Yingshuai Jia: proofreading of the original draft. Yi Tang: conceptualization, supervision, funding acquisition. Yuying Meng: conceptualization. Qingsheng Gao: conceptualization, supervision, writing - review and editing, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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