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Materials for energy and sustainability

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Electrochemical reduction of CO<sub>2</sub> to ethylene provides a carbon-neutral avenue to convert CO<sub>2</sub> to value-added fuels and feedstocks powered using the intermittent renewable electricity. The exploration of efficient electrocatalysts with high ethylene selectivity and productivity are highly desirable but remain challenging. Here, we present a Cu-based catalyst derived from metal-organic framework (Cu-MOF) with enhanced performance in terms of their porous morphology, complex oxidation state and strong lattice strain. X-ray diffraction, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy are utilized to track the evolution of crystal structure and oxidation state during reaction, the results reveal that the Cu<sup>2+</sup> were rapidly reduced to Cu<sup>+</sup> then slowly to Cu<sup>0</sup>, resulting in Cu@Cu<sub>x</sub>O core@shell structure. The tensile strain caused by distorted grain can benefit the activation of CO<sub>2</sub>. Cu<sup>+</sup>/Cu<sup>0</sup> interfaces formed through stabilized Cu<sup>+</sup> facilitate \*CO-CO dimerization, resulting in promoted C<sub>2+</sub> products conversion and suppressed C<sub>1</sub> products conversion. The optimized catalyst exhibits a 51% Faraday efficiency (FE) for ethylene and 70% FE for C<sub>2+</sub> products, with 20 h operation stability in H-cell configuration and a partial ethylene current density of 150 mA cm<sup>-2</sup> in flow-cell configuration.

## 1. Introduction

Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) provides an attractive paradigm to convert CO<sub>2</sub> to valuable fuels and feedstocks, contributed to storing the intermittent renewable electricity and closing the carbon cycle.<sup>1-3</sup> Compared with C<sub>1</sub> products, C<sub>2</sub> products such as ethylene (C<sub>2</sub>H<sub>4</sub>), offer higher energy density and market value.<sup>4</sup> Despite recent breakthroughs in catalysts and reaction configuration design, the energy efficiency of CO<sub>2</sub>RR cannot fulfill

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the commercial demands. The exploration on improving the selectivity and productivity of ethylene is crucial for the  $\rm CO_2RR$  technologies' marketization.

CO<sub>2</sub>RR to ethylene is 12-electron reduced process, and only copper-based catalysts are reported to show high selectivity.<sup>5</sup> The surface of copper plays a crucial role in determining the reaction pathway, strategies such as enlarging surface area,<sup>6-8</sup> promoting oxidation states,<sup>9</sup> exposing high-index facets,<sup>10</sup> introducing strain effects,<sup>11, 12</sup> and engineering surface reconstruction<sup>13-15</sup> have been explored to improve the product selectivity and lower the reaction energy barrier. However, the synthetic control and characterization of surfaces are challenging.

Copper oxidation states on surface has shown effects on activity and selectivity for  $CO_2RR$  to  $C_2H_4$  conversion.<sup>16</sup> During the  $CO_2RR$ process, the copper oxide can be reduced at negative potentials, resulting in distorted grain, roughened surfaces and complex oxidation states, which are proposed to favor the  $CO_2RR$ . Sargent et al. reported that residual Cu<sup>+</sup> species can stabilize the OCCOH<sup>\*</sup> intermediate, then promote the ethylene conversion while suppress the methane production.<sup>17</sup> Currently, copper oxide catalysts have an average Faradaic efficiency (FE) for ethylene range from 30% to 40%.<sup>9, 17-21</sup> However, due to the complex changes of crystal structure, morphology and chemical state on the surface of copper oxide, the mechanism of their enhancement in  $CO_2RR$  is still under debate.

Surface area of catalyst also has a significant effect on enhancing

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a)

48-1548: CuO

h) TEM EDS imag

ntensity (a.u.)

CO<sub>2</sub>RR. Copper catalysts have been fabricated in different shapes to enlarge their active surface area. Compared with traditional copper film,<sup>21</sup> sputtered copper particles,<sup>22</sup> or nanoparticles,<sup>23-25</sup> metalorganic framework (MOF) has a large surface area with abundance of catalytic sites due to their porous structure, which can provide stronger adsorption with reaction intermediates.<sup>26-28</sup> Moreover, benefiting from the chemical tunability and the porosity/surface topography controllability, the formation of undercoordinated Cu sites in MOF can be promoted to enhance CO<sub>2</sub>RR efficiency, leading to a 45% FE<sub>C2H4</sub>, which is the record for MOF-derived Cu catalysts based on our knowledge.<sup>29</sup>

Inspired by the merits of copper oxide and MOF structure in CO<sub>2</sub>RR, here, we synthesized a Cu-based MOF (HKUST-1) derived catalysts for CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> conversion. The calcination was utilized to simultaneous modify the morphology and oxidization state of catalysts. The pristine catalyst has an octahedral MOF structure, in which copper dimers are separated by adjacent benzene tricarboxylate. After calcination at high temperature, the dissociation of organic ligand happens and the copper oxide phase occurs. When the calcination temperature was 265 ° C, all MOF converted to CuO and Cu<sub>2</sub>O, the mixed phase caused distorted grains with high tensile strain, which might promote the activation of CO<sub>2</sub> molecules. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) were used to track the evolution of catalysts during reaction. The results show that under a negative applied bias, the Cu<sup>2+</sup> is reduced to Cu<sup>+</sup> rapidly, then the Cu<sup>+</sup> is reduced to metallic Cu slowly, leading to a Cu@Cu<sub>v</sub>O core@shell structure. After 10 h operation, trace amount of Cu<sup>+</sup> species remains. The stabilization of Cu<sup>+</sup> benefits the \*CO coupling at Cu<sup>0</sup>/Cu<sup>+</sup> interface to promote the ethylene conversion and suppress the methane production. As a result, the MOF-derived Cu@Cu<sub>x</sub>O exhibited 51% FE for  $C_2H_4$  and 70% FE for  $C_{2+}$  products at -1.58 V versus reversible hydrogen electrode (vs. RHE), with a stability of 20 h in an H-cell configuration. To accelerate the reaction, a flow-cell configuration was performed and a C<sub>2</sub>H<sub>4</sub> partial current density of 150 mA cm<sup>-2</sup> can be achieved with a  $FE_{C2H4}$  of 49.8%.

## 2. Results and discussion

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Precursor HKUST-1 was used for preparing catalysts as described in Fig. 1a. In HKUST-1, Cu cations are stabilized by adjacent oxygen atoms in carboxylate groups (Fig. S1<sup>+</sup>).<sup>30</sup> The calcination process was used to remove the organic ligands, as described by thermogravimetric analysis (Fig. S2<sup>+</sup>). XRD patterns at different temperature showed that when the calcination temperature was 265°C or above 265°C, HKUST-1 was completely converted to inorganic copper oxide (Fig. S3<sup>+</sup>). Therefore, 230, 265, and 500°C was chosen as calcination temperature for pristine HKUST-1 (H-0), and the obtained catalysts were denoted as H-230, H-265 and H-500, respectively.

To determine the crystal structure and morphology of catalysts, XRD and scanning electron microscopy (SEM) measurements were performed on four samples as shown in Fig. 1 and supplementary Fig. S3-4<sup>+</sup>. XRD patterns of H-O show representative peaks corresponding to HKUST-1.<sup>31</sup> The shape of H-0 is octahedral crystals of  $\sim 1 \,\mu$ m in size with nonporous flat surface, which is typical MOF morphology. After calcinated at 230°C, the color of H-0 changed from light blue to dark green, but there were no distinct differences

between H-230 and H-0 in XRD because of the retained organic bonding of HKUST-1. However, the morphology of H-230 was minimally changed and the appearance of porous surface revealed partial degradation of carboxylic moieties. When the temperature increased to 265°C, all HKUST-1 features in XRD disappeared and a mixture of CuO and Cu<sub>2</sub>O phase presented, indicating that MOF phase was completely converted to copper oxide phase (Fig. 1b). <sup>23,</sup> <sup>32</sup> While, the octahedral outline of H-265 remained consistent with H-230, excepting enlarged pore size (Fig. 1e). Further to increase the calcination temperature to 500°C, only CuO features can be observed in XRD, and the sharp peaks demonstrate high crystallinity. SEM image shows the octahedral template was destroyed to irregular aggregated particles and the porosity was lost. Noted that, residual carbon was observed in the calcinated sample (Fig. S5-6<sup>+</sup>),

The crystal structure, oxidation state, and atomic-resolution images of H-265 were further characterized in detail. XRD patterns in Fig. 1b clearly reveal the mix CuO and Cu<sub>2</sub>O phase. The broadening peaks and the 0.1-0.2° negative shifts compared to H-500 demonstrate the diminished crystallinity with smaller grain size. XPS results in Fig. 1c-d confirms that Cu<sup>+</sup> and Cu<sup>2+</sup> coexist in H-265, which agrees with the XRD results. Element mapping images demonstrate that the Cu and O elements distribute homogeneously throughout the whole octahedra (Fig. 1f-h). To further understand the microstructure of H-265, transmission electron microscope (TEM) was performed. High-resolution TEM (HRTEM) images reveal the porous octahedra is constituted of tightly packed  ${\sim}10$  nm nanoparticles (Fig. 1i-j). Atomic-resolution HAADF-STEM images

which agreed with other reports.<sup>27, 28</sup>



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show that some nanoparticle has perfect lattice arrangement, while others have bending lattices due to the distorted grain, which can lead to tensile strain and abundance of uncoordinated Cu sites (Fig. 1k-I).<sup>11</sup> The lattice tensile strain also can be confirmed by the negative peak shifts and broadening peaks of XRD patterns,<sup>33</sup> and the origin of this inhomogeneous lattice bending might be from the lattice mismatch between CuO and Cu<sub>2</sub>O.<sup>34</sup>

In summary, when the calcinated temperature was 230°C, the octahedral mainframe and partial organic bonding remained. When the calcinated temperature was 265 °C, HKUST-1 was completely converted to inorganic Cu<sub>2</sub>O/CuO phase with poor crystallinity and bending lattices. After calcinated at 500°C, the HKUST-1 octahedra was destroyed into irregular aggregated CuO particles with highly crystallinity.

To evaluate the electrocatalytic activity of four samples, CO<sub>2</sub>RR was performed in CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub> in a standard threeelectrode H-cell setup, with graphite rod as counter electrode and Ag/AgCl as reference electrode. The applied potential was in the range from -0.78 to -1.78 V vs. RHE. The gas chromatography (GC) was used to determine the component of gas products and the calibration were shown in Fig. S7<sup>+</sup>. NMR analysis of electrolyte after reaction was used to analyze the liquid products. All samples produced mostly gas products such as H<sub>2</sub>, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>, and small amounts of liquid products such as formic acid, acetate, ethanol and propanol. For the target product C<sub>2</sub>H<sub>4</sub>, H-265 shows a maximum  $FE_{C2H4}$  of 51 ± 3% at a potential of -1.58 V vs. RHE (Fig. 2a), which is comparable to current record (Table S1<sup>+</sup>). Interestingly, the  $FE_{CH4}$  was suppressed to 1%, resulting in a  $C_2H_4$ :CH<sub>4</sub> ratio of 60, which is two order of magnitude higher than that of the pristine H-0 (0.38) as shown in Table S2<sup>+</sup>. The catalytic performance of other samples was shown in Fig. S8<sup>+</sup> and supplementary Table S2<sup>+</sup>. These results suggest that thermal treatment increased the selectivity of  $CO_2RR$  towards  $C_2$  to  $C_1$ , and  $C_2:C_1$  ratio reach maximum when the catalysts calcinated at 265°C, and then declined with further increasing treated temperature. When compared with Cu foil and Cu<sub>2</sub>O samples (Fig. S9-10<sup>+</sup>), MOF-derived catalysts H-265 showed higher selectivity towards  $C_{2+}$  product and suppressed the  $C_1$ conversion, resulting in a 70% total FE toward C<sub>2+</sub> products (Fig. 2b-c and Table S3<sup>+</sup>). More interesting, a n-propanol FE of 3.1% based on our NMR analysis (Fig. S11<sup>+</sup>) was achieved of H-265, while no npropanol product could be detected for H-0, H-230, Cu-foil and  $Cu_2O$ .

In traditional H-cell configuration, the low solubility of CO<sub>2</sub> and the carbonate electrolyte limit the mass transfer and the current density is low. In order to increase the productivity, the flow-cell configuration with a gas diffusion electrode (GDE) (favors the CO<sub>2</sub> transfer) and alkaline electrolyte (favors C<sub>2+</sub> selectivity) was utilized (Fig. S12<sup>+</sup>). In this system, the CO<sub>2</sub> and electrolyte contact on the surface of catalysts, and feed the reaction at the gas-solid-liquid three-phase interface continuously. As shown in Fig. 2d, the production of CH<sub>4</sub> and H<sub>2</sub> was effectively suppressed. The current density was 320 mA cm<sup>-2</sup>, and C<sub>2</sub>H<sub>4</sub> partial current density was 150 mA cm<sup>-2</sup> with a FE<sub>C2H4</sub> of 49.8% (Table S4<sup>+</sup>).

To evaluate the electrochemical stability of the catalysts, the durability during the long-term operation were investigated at constant potential. As shown in Fig. 2e, the results suggest that H-265 was most stable, with negligible decrease of  $FE_{C2H4}$  after 20 h

operation (Fig. S13a<sup>+</sup>). H-500 exhibited a significant Ferther Automation (Fig. S13a<sup>+</sup>). H-500 exhibited a significant Ferther Automation (Fig. S13b<sup>+</sup>). H-0 had poorest stability with a steady low FE<sub>C2H4</sub> dropped from 40% to 30% after 10 h with an increased H<sub>2</sub> production (Fig. S13b<sup>+</sup>). H-0 had poorest stability with a steady low FE<sub>C2H4</sub> and showed a markedly increased of FE<sub>H2</sub> to 43% after 5 h due to its bad water stability (Fig. S13c<sup>+</sup>). These results suggest that mixed Cu<sub>2</sub>O/CuO are more electrochemically stable than pristine MOF or pure CuO.

Journal of Materials Chemistry A



**Fig. 2** Electrochemical CO<sub>2</sub>RR performances of H-265. a) FEs for gas products at virous potentials. b) accumulated bar graph for quantification of products at -1.58 V vs. RHE compared with other catalysts of our experiment, Cu foil and Cu<sub>2</sub>O. c) FEs at various potentials for total products classified by H<sub>2</sub>, C<sub>1</sub>, C<sub>2</sub>+C<sub>3</sub>. d) FEs for products in a flow-cell configuration, catalytic runs were performed with constant current, the pink dots show the partial current density of ethylene. (e) stability of ethylene FE on H-0, H-265, and H-500 samples.

To investigate the high catalytic activity of H-265 is whether from their intrinsic nature or just owing to the enhanced electrochemical surface area (ECSA), we conducted electrochemical double-layer capacitance measurement of these samples (Fig. S14<sup>+</sup> and Table S5<sup>+</sup>). It was found that H-265 did not show highest ECSA as suggested by the double-layer capacitance, excluding the influence of their ECSA.

The excellent CO<sub>2</sub>RR performance of H-265 prompted us to assess the alteration of chemical state of copper before and after CO<sub>2</sub>RR process with XRD, XPS and XAS studied. As shown in Fig. 3a, XRD patterns show that initial H-265 had a prominent CuO phase mixed with Cu<sub>2</sub>O phase. After 1 h CO<sub>2</sub>RR operation, no discernible CuO peaks remained while the enhanced Cu<sub>2</sub>O peaks and features of metallic Cu peak appeared, suggesting all CuO was reduced to Cu<sub>2</sub>O and a small part of Cu. When the reaction continued, Cu<sub>2</sub>O was gradually reduced to Cu, but the XRD features of Cu<sub>2</sub>O still can be observed after 10 h. The similar trend was reproduced by using a flow-cell configuration (Fig. S15<sup>+</sup>). These results suggested that the Cu<sup>+</sup> can be stabilized under an applied potential of -1.58 V vs. RHE and a high current density for several hours, which might facilitate the selectivity towards C<sub>2</sub>H<sub>4</sub>.<sup>17, 35</sup>

XPS spectra were measured to further distinguish the copper' states on the surface of H-265. Cu 2p spectrum clearly shows that  $Cu^{2+}$  with a binding energy at 933.8 eV is the dominated state of the

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Page 4 of 7



Fig. 3 Characterization of H-265 before and after 1 and 10 h of CO<sub>2</sub>RR. a) XRD analysis. b) XPS Cu 2p spectra. c) Auger spectra of Cu LMM. d) Ex-situ Cu L<sub>3</sub>-edge soft X-ray absorption spectroscopy (sXAS). e) Cu k-edge XANES and EXAFS spectra, and f) The Fourier transform magnitudes in R space.

initial H-265,<sup>9</sup> which is reduced to Cu<sup>+</sup> or Cu<sup>0</sup> state during the CO<sub>2</sub>RR process (suggested by the negative shift of binding energy) (Fig. 3b). A small content Cu<sup>2+</sup> residue after 1 and 10 hours of operation were observed, which might originate from the surface oxidation in air. Because the difference of binding energies between Cu<sup>+</sup> and Cu<sup>0</sup> is only 0.1 eV in the Cu 2p peak, it is difficult to distinguish them. Therefore, auger electron spectroscopy (AES) of Cu LMM signal was conducted, which can provide higher spectrum resolution, allowing for acquisition of greater contrast with oxidation state change. It clearly shows after 1 h and 10 h CO<sub>2</sub>RR, Cu<sup>2+</sup> located at 568.5 eV in pristine sample transferred into Cu<sup>+</sup> located at 570.0 eV (Fig. 3c).<sup>36</sup>

To provide a more qualitative investigation of oxidation state evolution during CO<sub>2</sub>RR, Cu L<sub>3</sub>-edge XAS were collected at various reaction time. The transitional metal L-edge (i.e.  $2p \rightarrow 3d$  transition) is highly sensitive to 3d electronic states which is suitable for the electronic structure study here.<sup>37</sup> Total electronic yield (TEY) signal were collected with an average probing depth of around 10 nm.<sup>38</sup> As shown in Fig. 3d, the Cu L<sub>3</sub>-edge XAS spectrum of CuO standard exhibited a single peak at 931 eV, both peak position and line shape match well with previously reported results.<sup>39</sup> The Cu L<sub>3</sub>-edge XAS spectrum of H-265 before reaction has same line shape with that of CuO standard but 0.2 eV energy shift, clearly indicating +2 oxidation state. After applying a constant potential of -1.58 V vs. RHE for 5 min, another higher energy peak at 933.6 eV began to emerge, which is consistent with Cu<sup>+</sup>, suggesting the transition from Cu<sup>2+</sup> to Cu<sup>+</sup> occurs guickly.<sup>39</sup> Remarkably, we found that the peak intensity of Cu<sup>+</sup> increased gradually and then remained stable, indicating Cu<sup>+</sup> may be stabilized under an negative potential for over 10 h during CO<sub>2</sub>RR process.<sup>9, 35</sup> Noted that, the re-oxidation in air cannot be totally exclude in our experiments, which might be the origination of high intensity of Cu<sup>2+</sup> signal in XAS after CO<sub>2</sub>RR operation.

In addition to the surface sensitive Cu L<sub>3</sub>-edge TEY XAS spectrum, we also collected Cu K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra which have deeper probing depth. Cu foil, CuO and Cu<sub>2</sub>O standards were taken as reference. Cu K-edge EXAFS oscillations in k space (k<sup>3</sup>-weighting) image (Fig. S16<sup>+</sup>) show clear oscillations up to k=11, which suggests high data quality. As shown in XANES (Fig. 3e), before reaction, the white line of H-265 at 8979(OR) eV is consistent with CuO, while after 1 h CO<sub>2</sub>RR operation, it is similar to that of the Cu foil, indicating the dominant metallic copper phase in the core of the nanoparticles. Linear combination fitting were conducted as shown in Fig. S17<sup>+</sup> and Table S6<sup>+</sup>. The results suggested the presence of Cu<sup>+</sup> after reduction reaction. In addition, the Fourier transform magnitudes in R space were used to track the associated Cu bonding environment. As shown in Fig. 3f, the Cu-O binding was dominant in pristine H-265, and Cu-Cu binding was dominant after CO<sub>2</sub>RR operation, suggesting the transformation between CuO to Cu. First shell extended edge fitting results suggest consistent transformation in radical distance (Fig. S18<sup>+</sup> and Table S7<sup>†</sup>). Combined with XRD, XPS and sXAS measurements, we can get a conclusion that the initial Cu<sup>2+</sup> in pristine H-265 was reduced to  $Cu^{\scriptscriptstyle +}$  and  $Cu^0$  during  $CO_2 RR$  process, accompanying with a surface reconstruction resulting in a Cu@CuxO core@shell structure. Cu\* was stabilized for over 10 h operation.

In order to explore the reasons for the existence of oxidation valence state, we monitored the chemical state change of oxygen during the reaction process. XPS O 1s peak of pristine H-265 shows feature of the lattic oxygen species ( $O_{latt}$ ) corresponding to CuO phase, which changed into Cu<sub>2</sub>O phase after CO<sub>2</sub>RR

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#### Communication

#### Journal of Materials Chemistry A



Fig. 4 Proposed reaction pathways starting from \*CO on Cu surface in the presence of Cu<sup>+</sup>. Green, blue, and yellow routes are competitive reactions

reaction (Fig. S19<sup>+</sup>).<sup>9, 40</sup> Besides, the atomic concentration ratio of O to Cu (O/Cu) of pristine H-265 was 1.19 and then decreased to 0.46 after 1 h reaction (Table S8<sup>+</sup>). For the control sample H-500, the O 1s peak only showed an adsorbed state after 1 h reaction, and the O/Cu ratio was 0.07, almost 1 order of magnitude lower than that of H-265 (Table S8<sup>+</sup>). Both XRD and XPS of H-500 showed that Cu<sup>2+</sup> was completely reduced to Cu<sup>0</sup> after 1 h reaction (Fig. S20-21<sup>+</sup>). These results demonstrated that the stabilized oxide state on H-265 surface benefits from the oxygen-rich environment, which maybe contributed by the small size nanoparticles and their compact arrangement, thus facilitating rapid oxygen migration along the dense boundaries, then retard the reduction of copper (Fig. S22-24<sup>+</sup>).<sup>41</sup>

To provide mechanistic insights into the high  $C_2H_4$  selectivity of H-265, we firstly used Tafel analysis to explore whether the ratedetermining step (RDS) is the initial one-electron reduction  $CO_2$  to  $CO_2$ .<sup>-</sup> or a chemical reaction occurring after the one-electron activation of an inert  $CO_2$  molecule.<sup>42</sup> According to Fig. S25<sup>+</sup>, the Tafel slope of H-265 sample was 119.5 mV dec<sup>-1</sup>, which was close to 118 mV dec<sup>-1</sup>, implying that the RDS is activation of  $CO_2$ , which has a lower electron transfer resistance during  $CO_2RR$  process as confirmed by the electrochemical impedance spectroscopy (EIS) measurements (Fig. S26<sup>+</sup>).<sup>43</sup> Besides, tensile strain on the surface of catalyst has been reported to shift up the d-band center of surface atoms, thus strengthening the adsorption of  $CO_2$ .<sup>44</sup> Therefore, tensile strain caused by the bending lattice on H-265 is supposed to lower the  $CO_2$  activation energy barrier (Fig. 4).

For the second RDS of  $C_2H_4$  formation, there are three proposed reaction pathways based on previous mechanistic studies as described in Fig. 4.<sup>45, 46</sup> In route 1, \*CH<sub>2</sub> intermediate can directly dimerize to form  $C_2H_4$ , or via the parallel pathway to bond with \*CH<sub>3</sub> to form  $C_2H_6$ , or through a Fischer-Tropsch like CO insertion pathway to form  $C_2H_4$  or CH<sub>3</sub>COO<sup>-</sup> (blue routes).<sup>47</sup> In route 2, \*CO-COH (or \*CO-CHO) coupling can lead to  $C_2H_4$  formation, which is competed with the CH<sub>4</sub> or CH<sub>3</sub>OH formation (yellow routes), and no liquid C<sub>2+</sub> products can be achieved. In route 3, the dimerization of \*CO-CO will be further protonated to facilitate C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, or nC<sub>3</sub>H<sub>7</sub>OH generation (green routes).<sup>48</sup> In our experiments, the products were dominated C<sub>2</sub>H<sub>4</sub> and small amounts of C<sub>2</sub>H<sub>5</sub>OH, n-C<sub>3</sub>H<sub>7</sub>OH, while no C<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub>OH was detected, which match the products from route 3. Moreover, our Cu@Cu<sub>x</sub>O catalyst has abundance of Cu<sup>+</sup>/Cu<sup>0</sup> interface, which have been proved to assist \*CO-CO dimerization due to the opposite electrostatic attraction of charged carbon atoms (+0.11 on Cu<sup>+</sup> and -0.31 on Cu<sup>0</sup>).<sup>49</sup> Based on the final products and catalysts' properties, we propose our reaction pathway follows route 3, in which \*CO-CO coupling promotes the C<sub>2+</sub> conversion while impedes C<sub>1</sub> production. The high selectivity towards C<sub>2</sub>H<sub>4</sub> may be caused by the suitable formation energy barrier, compared with other product such as C<sub>2</sub>H<sub>5</sub>OH and n-C<sub>3</sub>H<sub>7</sub>OH.<sup>45</sup>

## 3. Conclusions

Here, we synthesized MOF derived copper catalyst via calcination in air. XRD, XPS and XAS analysis indicated that the catalyst underwent oxidation state transition and surface reconstruction during the CO<sub>2</sub>RR process and formed a Cu@Cu<sub>x</sub>O structure. The distorted grains lead to lattice strain, which might lower CO<sub>2</sub> activation barrier. The Cu<sup>+</sup>/Cu<sup>0</sup> interface facilitates \*CO-CO dimerization, which promotes the C<sub>2+</sub> products conversion and suppresses the C<sub>1</sub> products conversion, leading to a high selectivity towards C<sub>2</sub>H<sub>4</sub>. The Cu@Cu<sub>x</sub>O catalyst reached 51% FE<sub>C2H4</sub> and 70% FE<sub>C2+</sub> with an operation stability of 20 hours in H-Cell. Moreover, a partial ethylene current density of 150 mA cm<sup>-2</sup> in a flow-cell configuration with a 49.8% FE<sub>C2H4</sub> was achieved. This study will provide new strategies to enhance the selectivity and durability of MOF-derived catalysts for electrochemical CO<sub>2</sub> conversion to valueadded chemicals.

### **Conflict of interest**

The authors declare no conflict of interest.

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