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## ► To cite this version:

Huali Wu, Lingqi Huang, Janis Timoshenko, Kun Qi, Wensen Wang, et al.. Selective and energy-efficient electrosynthesis of ethylene from CO<sub>2</sub> by tuning the valence of Cu catalysts through aryl diazonium functionalization. *Nature Energy*, 2024, 9 (4), pp.422-433. 10.1038/s41560-024-01461-6 . hal-04747870

**HAL Id: hal-04747870**

**<https://hal.science/hal-04747870v1>**

Submitted on 22 Oct 2024

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**Selective and energy-efficient electrosynthesis of ethylene  
via valence engineering of the Cu sites**

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## Abstract

The electrosynthesis of ethylene ( $C_2H_4$ ) in membrane-electrode-assembly (MEA) cells with high selectivity and large current density is a promising flow process strategy for the conversion of  $CO_2$  or  $CO$  into valuable products. Although considerable progress has been made in meeting industrial requirements in terms of Faradaic efficiency (FE) and formation rate, selectivity towards the formation of a single type of multi-carbon ( $C_{2+}$ ) product has not been demonstrated to date. Here, we evaluated a library of aryl diazonium salts to functionalize Cu catalysts in order to elucidate the influence of Cu valence on the formation of multi-carbon products during the  $CO_2RR$ . By combining density functional theory (DFT) calculations with *operando* Raman and X-ray absorption spectroscopy (XAS), we identified the role of the surface oxidation state of  $Cu^{\delta+}$  with  $0 < \delta < 1$  on the selectivity and the formation rate of  $C_2H_4$ . As a result, we report a FE and a specific current density for  $C_2H_4$  as large as  $83 \pm 2\%$  and  $212 \text{ mA cm}^{-2}$ , respectively on partially oxidized  $Cu^{0.26+}$ . This corresponds to an energy efficiency of 26.9% and an electrical power consumption (EPC) of  $61.4 \text{ kWh N}^{-1}\text{m}^{-3}$ . The conversion performance was further improved by using a perfluorinated sulfonic acid (PFSA) ionomer to reach a record-high FE for  $C_2H_4$  of  $89 \pm 3\%$  at a specific current density of  $536 \text{ mA cm}^{-2}$ . When coupled with an Ag-based MEA cell to generate  $CO$  from  $CO_2$  in a cascade flow process, an energy efficiency of  $\sim 40\%$  with a  $FE_{C_2H_4}$  of  $86 \pm 2\%$  was achieved, corresponding to a record low EPC of  $25.6 \text{ kWh N}^{-1}\text{m}^{-3}$ .

## Introduction

The global consumption of fossil fuels induces profound environmental repercussions and is responsible for colossal emission of  $> 35 \text{ Gt}$  of  $CO_2$  every year. The pledge of net zero emission

by 2050 requires the development of economically viable technologies to reuse the emitted CO<sub>2</sub> and close the carbon cycle. The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) provides a promising and sustainable route to convert CO<sub>2</sub> into valuable chemicals and fuels when powered by renewable electricity<sup>1,2</sup>. Ethylene has been identified as a desirable multi-carbon product of the CO<sub>2</sub>RR owing to its high commercial value and large market size with an annual global production of 140 million metric tons and a market value of 182 billion USD<sup>3</sup>. Techno-economic analyses (TEA) emphasized the necessity to operate CO<sub>2</sub>RR at specific current densities larger than 200 mA cm<sup>-2</sup> while minimizing the power input (or cell voltage)<sup>4</sup>. Although the best reported performance of electrocatalysis of CO<sub>2</sub> to ethylene in liquid flow cells meets industrial requirements with specific current densities >900 mA cm<sup>-2</sup> for ethylene, the stability remains insufficient to compete with traditional ethylene production from fossil sources as well as bio-based ethylene<sup>3,5-9</sup>(Supplementary Fig. 1 and Supplementary Table 1).

Zero-gap membrane electrode assembly (MEA) cells, comprising a cathode, membrane, and anode, offer the potential to achieve industry-relevant current densities with high selectivity and formation rates, while the continuous flow process provides a large mass transfer boundary layer with high local CO<sub>2</sub> concentration near the planar electrodes<sup>10-12</sup>. The absence of catholyte makes MEA cells more stable than traditional liquid flow cells by mitigating the electrode flooding and the precipitation of salts, resulting in greater operating stability and reduced operational expenses (OPEX)<sup>12,13</sup>. The exploitation of MEA cells with high selectivity and high current density for the ethylene production as well as prolonged stability, is thus expected to lower the threshold of economic viability to replace fossil sources for ethylene production. To date, the selectivity and the specific current density for ethylene in MEA systems are however limited to <80% and < 200 mA cm<sup>-2</sup> (Refs.<sup>6,14</sup>).

It has been reported that partially oxidized copper sites: Cu<sup>δ+</sup>, 0<δ<1 facilitate the conversion of CO<sub>2</sub> to C<sub>2+</sub> products by decreasing the energy barrier associated with the CO dimerization and the formation of \*OCCOH intermediate<sup>15-19</sup>. Investigations of the role of Cu<sup>δ+</sup> proved to be tedious, while the intrinsic instability of Cu<sup>δ+</sup> species, especially at high cathodic potentials,

leads to a rapid loss of performance<sup>20</sup>. Recent studies have emphasized the importance of controlling the oxidation state of Cu sites and the presence of Cu<sup>+</sup> species on the electrode surface for efficient CO<sub>2</sub> reduction. Various approaches, such as controlled oxidation, pulse polarization, or molecular doping, have been explored to achieve this goal<sup>6,12,17</sup>.

Aryl diazonium salts are well-known electrophiles that have been extensively used for covalent surface modification since their first demonstration<sup>21-26</sup>. The strong interfacial bonding of aryl groups with the metal surface, which is covalent in nature, makes it much stable and widely applied in various fields<sup>21,26-28</sup>, including biosensors' development<sup>29-31</sup>, antibacterial activity and drug delivery<sup>29,32,33</sup>. The electron withdrawing ability of the aryl group can be adjusted by the nature of the substituents. We hypothesize that the covalent binding of aryl groups onto the Cu surface results in stable valence, making aryl diazonium salts an attractive choice for fine-tuning the valence of surface Cu atoms<sup>21,24,26,28</sup>.

Herein, we report a functionalization strategy based on aryl diazonium salts used as electrophile reagents with a strong affinity for electron-rich copper metal. We identified that the nature of different substituted aryl groups can precisely tailor the oxidation state of surface Cu sites as confirmed by our density functional theory (DFT) calculations. We predict that controlled doping of Cu can facilitate C-O bond breaking followed by C-H hydrogenation of the \*CH<sub>2</sub>CHOH intermediate, which favors the selective formation of ethylene (C<sub>2</sub>H<sub>4</sub>) over ethanol (C<sub>2</sub>H<sub>5</sub>OH) during the CO<sub>2</sub>RR. We corroborated the DFT results by integrating the aryl functionalized catalysts into an MEA flow cell. By tailoring the valence of the Cu sites, we achieved a FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of 83% at a current density of 212 mA cm<sup>-2</sup> for the electrosynthesis of ethylene from CO<sub>2</sub> with an optimal oxidation state for Cu of +0.26. This corresponds to a ~200% increase of the ethylene formation rate compared to the pristine Cu and a C<sub>2</sub>H<sub>4</sub> vs. C<sub>2</sub>H<sub>5</sub>OH selectivity greater than 97% and a sustained stability for 120 hours. When fed with CO, the MEA cell demonstrated a FE for C<sub>2</sub>H<sub>4</sub> of ~86% with a full cell energy efficiency of ~40 %, setting a new benchmark for the formation of ethylene from CO.

## Density functional theory calculations

We first carried out Bader charge analysis to assess how the electron-withdrawing capability of the aryl groups influences the valence of Cu. Our findings revealed that the theoretical valence of the (6x6) Cu supercell can be adjusted by the substituted phenyl groups<sup>34,35</sup> (Fig. 1a-b, Supplementary Figs.2 to 9 and Table 2). To gain understanding, we also analyzed the consequences of functionalization for the surface Cu atoms adjacent to the grafting site. Our results show that the nature of the substituents plays a crucial role in modulating the electron density of copper and the oxidation state of the surrounding atoms, ultimately influencing the catalytic activity of Cu-based systems (Fig.1c, Supplementary Figs.10 to 14 and Tables 3 to 5). We also note that our investigations point out to the formation of new interfaces with different valence states after functionalization with aryl diazonium salts, which originate from the orientation of the molecule on the Cu surface (Fig.1c). Such interfaces are analogous to the previously described Cu<sub>2</sub>O/Cu catalyst proposed by Goddard group<sup>15</sup>.

To clarify how the functional group affect the oxidation state of the Cu atoms and regulate the CO<sub>2</sub> reduction, we calculated the adsorption energy of CO<sub>2</sub> with explicit water molecules. We selected differently specific Cu sites on Cu-NN system with different theoretical valence: -0.018, -0.022, +0.029 and +0.105 for Cu99, Cu105, Cu66 and Cu60, respectively (Fig. 1d, Supplementary Figs.10 and 15, and Table 6). We found that the CO<sub>2</sub> adsorption energy gradually increased with the oxidation state when getting closer to the grafting sites. Among the examined Cu sites, Cu60, located closest to the functional groups, exhibited the highest theoretical valence (+0.105) and the lowest CO<sub>2</sub> adsorption energy (-0.468 eV). Conversely, the farther Cu site (Cu99) demonstrated the highest CO<sub>2</sub> adsorption energy. Our investigations point out that the CO<sub>2</sub> activation and its subsequent electrochemical reduction are likely to occur on the Cu sites in the vicinity of the functional groups, namely Cu60, Cu57 and Cu63, rather than on the outermost Cu99 atom of the Cu-NN catalyst or the directly grafted copper atoms, thanks to more stable adsorption. We calculated the adsorption energy of CO for the different Cu-X systems (See Methods section for details) and found that Cu-NN exhibits the

lowest adsorption energy compared to the other functionalized Cu as well as pristine Cu (Supplementary Fig.16 and Table 7). Our calculations also indicate a reduced energy barrier of CO dimerization on Cu-NN catalyst than pristine Cu and the CO dimerization step typically occur on Cu60, Cu66, Cu63 and Cu57 sites (Fig. 1e, Supplementary Figs.17 to 21 and Table 8). Collectively, our results demonstrate that introducing various electron-withdrawing aryl diazonium groups enables the modulation of the oxidation state (theoretical valence) of Cu. This modulation favors the CO<sub>2</sub> reduction and \*CO dimerization into multi-carbon products by improving the adsorption energy of CO<sub>2</sub> and CO on specific sites near these functional groups. We finally evaluated the free energy of hydrogen adsorption ( $\Delta G_{H^*}$ ) on both pristine Cu and Cu-NN. Our results revealed that  $\Delta G_{H^*}$  on Cu-NN is larger than for Cu indicating that aryl functionalization not only promotes the carbon-carbon coupling but also suppresses the competitive evolution of hydrogen (Supplementary Fig. 22 and Table 9). Overall, our investigations predict that functionalization with electron withdrawing groups favor the adsorption of CO<sub>2</sub> and CO and the reaction preferentially takes on the Cu atoms located near the grafting sites of the aryl diazonium salts.

Ethylene and ethanol are generally considered to share the same initial reaction pathway, starting from \*COCO<sub>H</sub> but branching off from the \*CH<sub>2</sub>CO<sub>H</sub> intermediate<sup>36</sup>. To get insight into the ethylene vs. ethanol selectivity, we explored the role of the oxidation state of Cu<sup>δ+</sup> on the free energy of the successive intermediates along with the ethylene (\*O+C<sub>2</sub>H<sub>4</sub>(g)) and ethanol (\*C<sub>2</sub>H<sub>4</sub>O) pathways (Supplementary Figs.23 to 25). The calculations were systematically performed on pristine and N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, OCH<sub>3</sub>, N, NN, NNN, Br and NO<sub>2</sub> functionalized Cu. Our results reveal a lower free energy for \*O+C<sub>2</sub>H<sub>4</sub>(g) (ethylene pathway) than for \*C<sub>2</sub>H<sub>4</sub>O (ethanol pathway) on Cu-NN. These findings indicate that rational functionalization with substituted aryl groups favors the formation of the \*O+C<sub>2</sub>H<sub>4</sub>(g) intermediate by breaking the C-O bond instead of the direct hydrogenation of the C-H bond to form \*CH<sub>2</sub>CH<sub>2</sub>OH (Fig.1f, Supplementary Fig.26 and Table 10). Of all functionalized Cu catalysts, Cu-NN displayed the lowest free energy of -1.63 eV towards ethylene, suggesting a

large selectivity for ethylene (Fig.1f). We also explored the influence of the electric field on the ethylene selectivity and found that the determining step to produce ethanol is independent on the electric field, while the energy associated to the ethylene formation rapidly decreases and reaction becomes exothermic under negative electric field values as the bias potential is increased<sup>19,37-41</sup> (Supplementary Fig. 27 and Table 11). To exclude any potential influence of the nature of the Cu facet on CO<sub>2</sub>RR performance of Cu-X catalysts, we carried out DFT calculations on Cu (100) and Cu (111). We first calculated the theoretical valence of Cu (100) after functionalization and found that the valence of Cu (100)-X catalysts matches with the result from Cu (111)-X catalysts, suggesting that the influence of aryl diazonium groups on the theoretical valence of Cu is independent of the Cu facets (Supplementary Figs. 28 to 30 and Table 12). We then assessed the energy barrier of \*CO dimerization as well as the energy of hydrogen adsorption on pristine Cu and all Cu-X catalysts (See Methods section for details). Our results demonstrate that the energy barrier for the \*CO dimerization is lower on functionalized Cu (100) compared to that functionalized Cu (111) (Supplementary Figs. 31 to 36, and Table 13). This suggests that the Cu (100) facet has a higher activity towards the formation of multi-carbon products than Cu (111) facet, in agreement with the literature. These predictions are further corroborated by our experimental results on single crystals of Cu (111) and Cu (100), as well as the NN-functionalized Cu (111) and Cu (100) (Supplementary Fig. 37). We also found a higher free energy of hydrogen adsorption on all Cu (100)-X catalysts compared to bare Cu (100) indicating that the aryl groups on Cu (100) lower the HER activity of Cu (Supplementary Figs. 38 and 39, and Table 14).

### **Catalyst synthesis and characterization**

In light of our numerical simulations, we sought to fabricate a series of copper catalysts *via* electrodeposition on a gas diffusion layer (GDL). The Cu catalysts were subsequently modified with aryl diazonium salts and labeled hereafter Cu-X where X represents the grafted aryl groups (Fig. 1a). The reactivity of aryl diazonium salts on copper follows two mechanisms: a direct attachment of the phenyl groups or the formation of new azo groups<sup>26,42-45</sup> (Supplementary Figs.



2 and 3). Based on our XPS analyses, we confirmed that the grafting mechanism involves the formation of azo bonds as evidenced by the presence of the signal at 400 eV. Signals from the N=N bonds were detected on all functionalized copper catalysts, including Cu-Br and Cu-OCH<sub>3</sub>, with an estimated 3:2 molar ratio of Br/OCH<sub>3</sub> to azo (Supplementary Fig. 40 and Supplementary Table 15). The morphology and crystal structure of functionalized Cu catalyst do not substantially change after the modification with diazonium salts, suggesting functionalization does not induce amorphization of the Cu surface (Figs. 2a, b and Supplementary Figs. 41 to 43). In particular, high-resolution electron microscopy analyses showed the presence of a continuously functionalized layer at the surface of the catalysts with a thickness of about 5-8 nm (Figs. 2a, b and Supplementary Fig.44a). In addition, based on our EELS analyses (Fig. 2b and Supplementary Fig. 44b), we confirmed the presence of C and N in the functionalized layer, which highlights the successful grafting of diazonium molecules at the surface of the Cu catalyst. To further improve the gas and ion transport to the active sites in the MEA cell, a perfluorinated sulfonic acid (PFSA) ionomer was spray-coated on the catalyst (Supplementary Fig. 45). The use of ionomers has been recently introduced to promote gas, water, and ion transport due to their hydrophobic and hydrophilic functionalities and ion transport domains, respectively<sup>7,46-48</sup>. The presence of the PFSA ionomer was further confirmed by its characteristic Raman signatures at 733,1005 and 1130 cm<sup>-1</sup>, which are associated with the -CF<sub>2</sub>, C-C, and -SO<sub>3</sub> vibrations modes, respectively<sup>7</sup> (Supplementary Fig. 46)<sup>7</sup>. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping further supports the uniform distribution of ionomer on the surface of Cu-NN catalyst (Supplementary Fig. 47).

To elucidate the relationship between the molecular doping properties of the aryl groups and the behavior of the functionalized catalysts properties, we systematically evaluated the CO<sub>2</sub>RR properties in a zero-gap MEA cell using a 0.5 M KHCO<sub>3</sub> anolyte and 10 sccm of CO<sub>2</sub> as feed for the cathode. Compared to pristine (*i.e.* non-functionalized) Cu, all the Cu-X electrodes exhibited improved Faradaic efficiency for ethylene (Fig. 2c and Supplementary Fig. 48 and Supplementary Table16). We found a volcano relationship between the FE of C<sub>2</sub>H<sub>4</sub> (FE<sub>C<sub>2</sub>H<sub>4</sub></sub>)

and the applied potential and the Cu-NN catalyst exhibits the highest  $FE_{C_2H_4}$  at 83% for a full cell potential of -3.55 V. To explore the influence of the NN thickness on  $CO_2RR$  performance, we assessed the properties of Cu-NN electrodes having different thickness of aryl diazonium (See “Influence of the diazonium thickness” section in the Supporting Materials and Supplementary Fig.49). Our results reveal that thin and uniform coating enhances the formation of ethylene, while larger thickness results in performance degradation due to limited diffusion of  $CO_2$  to the active sites of Cu and non-uniform coating.

To investigate the correlation between the  $FE_{C_2H_4}$  and the oxidation state of different diazonium salts functionalized copper, we plotted the experimental  $FE_{C_2H_4}$  against the valence of the Cu sites predicted by our DFT calculations. We found a volcano trend that peaks at 83% at an average Cu valence of + 0.26, corresponding to the Cu-NN electrodes (Fig. 2d). We also observed a strong correlation between the ratio of  $FE_{C_2H_4}$  to  $FE_{C_2H_5OH}$  as a function of the calculated theoretical valence, confirming the influence of the valence on the selectivity of ethylene over ethanol (Supplementary Fig. 50). A  $FE_{C_2H_4}$ -to- $FE_{C_2H_5OH}$  ratio as high as 38 is obtained on Cu-NN and agrees with our DFT predictions that  $Cu^{\delta+}$  triggers the formation of ethylene rather than ethanol (Supplementary Figs. 50a and b). The performance of both Cu-NN and pristine Cu were further increased in the presence of PFSA ionomer, and the Faradaic efficiency for ethylene reached  $89\pm 3\%$  and  $48\pm 4\%$  at a specific current density of  $C_2H_4$  of  $536\text{ mA cm}^{-2}$  and  $269\text{ mA cm}^{-2}$ , respectively (Supplementary Figs. 51 and 52). To gauge the stability of our functionalization strategy, we operated the MEA cell at a full cell voltage of -3.55 V for 120 h using Cu-NN as  $CO_2RR$  catalyst. We obtained a stable current at approximately 1 A with an average FE for  $C_2H_4$  of 79% corresponding to a retention of 95% in a neutral medium (Fig. 2e). Furthermore, to examine the stability of functional group (NN) on copper, we also characterized the surface of Cu-NN catalyst after 24 hours reaction (hereafter aCu-NN) by using Raman and high-resolution electron microscopy (HRTEM). The Raman signatures of the functional groups are clearly detected, while the HRTEM images of aCu-NN show no significant changes in the morphology and surface coating, highlighting the stability of the

functionalized catalyst (Supplementary Fig. 53).

Next, we sought to evaluate the selectivity, the energy efficiency (EE) and the electrical power consumption (EPC) for the production of C<sub>2</sub>H<sub>4</sub> in a MEA cell. Compared to other literature benchmarks<sup>6,7,9,49-54</sup>, both Cu-NN and Cu-NN/ionomer catalysts demonstrated improved selectivity towards ethylene and higher energy efficiency at the same specific current density of ~200 mA cm<sup>-2</sup> (Figs. 2f and g, Supplementary Table 17). Remarkably, the EPC for the formation of ethylene on Cu-NN is 10% lower compared to the best-reported catalyst tested in the same device configuration, suggesting a lower threshold to meet industrial requirements (Fig. 2h, Supplementary Table 17). To confirm the improvement of the intrinsic CO<sub>2</sub>RR properties after aryl functionalization, we finally estimated the electrochemically active surface area (ECSA) of pristine Cu, Cu-NN and Cu-NN/ionomer catalysts by using the Pb underpotential deposition method (Pb<sub>UPD</sub>) (Supplementary Fig. 54a and Supplementary Table 18). The ECSA-normalized partial current densities for C<sub>2</sub>H<sub>4</sub> measured in the MEA cell are 96 mA cm<sup>-2</sup> and 212 mA cm<sup>-2</sup> for Cu-NN and Cu-NN/ionomer, which are ~2 and ~4.5 times higher than in the case of pristine Cu, respectively (Supplementary Fig. 54b). To rule out any preferential attachment of the aryl groups on the Cu surfaces, we examined the functionalization on Cu(111) and Cu(100) single crystals, and compared their respective surface coverage by assessing their electrochemically active surface areas. Our results revealed that the surface coverage of NN on Cu(111) and Cu(100) single crystals are 20.8% and 22.0%, with estimated ECSAs of 1.20 cm<sup>2</sup>, 1.27 cm<sup>2</sup>, 0.95 cm<sup>2</sup> and 0.99 cm<sup>2</sup> per geometrical cm<sup>2</sup> of Cu(111), Cu(100), Cu(111)-NN and Cu(100)-NN catalysts, respectively. These values are close to the surface coverage obtained for electrodeposited Cu-NN: 18.7%, suggesting that there is no preferential attachment of the aryl groups on Cu (Supplementary Fig. 55 and Supplementary Table 19).

### ***Ex-situ and operando investigations***

To investigate the impact of the aryl functionalization on the oxidation states of copper, we first performed ex-situ X-ray photoelectron spectroscopy (XPS) on the different Cu-X catalysts. When examining the Cu2*p* spectra, the absence of satellites confirms that there is no Cu<sup>2+</sup>

(Supplementary Fig. 56). As it is difficult to distinguish the Cu<sup>+</sup> from the Cu from the Cu2p spectra, we examined the LMM Auger signals from freshly prepared Cu-X samples to precisely evaluate the oxidation state of copper<sup>55</sup>. According to the deconvolution of the Auger LMM spectra, we found that the Cu-NO<sub>2</sub> surface has the largest ratio of Cu<sup>+</sup> to Cu and the average oxidation state is estimated to be +0.75, while Cu-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> has the smallest oxidation state at  $\delta=+0.13$  (Supplementary Table 20).

We then carried out X-ray absorption near-edge spectroscopy (XANES) on the Cu-X catalysts to assess the Cu oxidation state. Before testing, a negative potential (-0.7 to -2.0 V versus reversible hydrogen electrode (RHE), 60 mV s<sup>-1</sup>, 3 cycles) was applied on Cu-X samples to exclude oxygen-containing species. The absorption edges of all Cu-X samples reside between those of pristine copper (Cu<sup>0</sup>) and Cu<sub>2</sub>O used as a reference (Cu<sup>+</sup>) (Fig. 3b and Supplementary Fig. 57). To obtain a direct comparison of the oxidation state of copper in the different Cu-X catalysts, we plotted the copper oxidation state as a function of energy shift of the Cu K-edge (Fig. 3b inset). From the linear fit of the positions for Cu<sup>0</sup> and Cu<sup>+</sup> (Cu<sub>2</sub>O), we determined the average oxidation state of the Cu-X catalysts to range between +0.13 to +0.75 as a function of the electron-withdrawing ability of substituted phenyl groups. Cu-NN exhibits an oxidation state of  $\delta=+0.27$ , which is remarkably close to the calculated theoretical valence of copper ( $\delta=+0.260$ ) (Supplementary Table 21). To further explore the stability of Cu <sup>$\delta$ +</sup> species on Cu-NN, we performed *operando* X-ray absorption spectroscopy (XAS) at applied potentials of -0.93 V, -0.88 V, and -0.83 V vs. RHE (Supplementary Figs. 58 and 59). Close examination of the XAS spectra suggests a minimal perturbation of the oxidation state of Cu during the CO<sub>2</sub>RR. We determined the average oxidation states of copper in Cu-NN to be +0.25, +0.23, and +0.19 at -0.93 V, -0.88 V, and -0.83 V vs. RHE, respectively close to that obtained from our *ex-situ* analyzes (Supplementary Tables 22 and 23).

To increase our understanding of the role of different functional groups in promoting the formation of ethylene, we studied the adsorbed CO on the surface of the Cu-X catalysts using *operando* Raman spectroscopy (Supplementary Figs. 60 to 62). Two different types of defect

sites – isolated defect-like sites and step-edge sites have previously been identified on copper<sup>56</sup> and have been linked to the \*CO dimerization associated with the formation of C<sub>2+</sub> products<sup>6,56-58</sup>. According to previous operando measurements from the literature on well-defined system, \*CO-bound on step-edge sites is usually assigned to the dynamic LFB-\*CO and is related to C-C coupling<sup>56</sup>, whereas the presence of the relative static HFB-\*CO peak at  $\approx 2080\text{ cm}^{-1}$  is ascribed to adsorbed \*CO on isolated defect-like sites and more related to gaseous CO production<sup>56</sup>. Qualitatively, we also observed a linear correlation between the adsorption energy of CO and the CO Raman signals (Supplementary Figs.62 and 63). We then examined the high-frequency band (HFB-\*CO) and the low-frequency band (LFB-\*CO) of CO at  $\sim 2087\text{ cm}^{-1}$  and  $\sim 2060\text{ cm}^{-1}$ , respectively<sup>57,59,60</sup> (Fig. 3c). These bound CO configurations were identified and quantified using *operando* Raman spectroscopy for the different Cu–X catalysts at a fixed potential of -0.88 V vs. RHE (Supplementary Fig. 51 and Supplementary Table 24)<sup>6,57,61,62</sup>. The HFB-\*CO-to-LFB-\*CO ratio on all Cu–X catalysts are larger compared with bare Cu, and presents a clear linear correlation with the average oxidation state of copper (Fig. 3c). We attribute the change in the ratio of HFB-\*CO-to-LFB-\*CO on Cu–X catalysts to the different adsorption energy of CO by the tailored oxidation state of surface copper sites through different substituted aryl groups, as revealed by our calculations of the adsorption energy of CO (Supplementary Fig. 16 and Supplementary Table 7). Our investigations indicate that the average oxidation state of copper should be neither too high nor too low. We found a volcano-shaped relationship between the ethylene selectivity and the HFB-\*CO-to-LFB-\*CO ratio on the Cu–X surfaces, which highlights the importance of the balance between step-edge sites and isolated defect-like sites on Cu for the adsorption of CO and the promotion of the C-C coupling. Cu-NN seats near to the top of the volcano, pointing out to a possible stabilization of HFB-\*CO relative to LFB-\*CO on mildly oxidized Cu <sup>$\delta^+$</sup>  ( $0 < \delta < 1$ ).

We compared the *operando* Raman spectra of Cu-NN and pristine Cu catalysts (Figs. 3d and e) for different potentials. The Raman heat map of the Cu-NN and pristine Cu revealed a clear enhancement of the signals from adsorbed CO in the case of Cu-NN, which qualitatively

indicates that larger amounts of CO intermediates are readily available for the further C-C coupling. We also found that Cu-NN displays strong HFB-\*CO and LFB-\*CO signals for potentials between -0.48 V and -0.7 V vs. RHE up to -0.88 V vs. RHE, while no signals can be detected from pristine Cu (Fig. 3e). This points out to a greater energy barrier to produce CO intermediates, thus limiting the formation of C<sub>2+</sub> products. As the final evidence, we plotted the FE for CO and C<sub>2</sub>H<sub>4</sub> as functions of the potential to visualize the intertwining between the Raman signatures of adsorbed CO and the selectivity for C<sub>2+</sub> products (Figs. 3d and e). To exclude any contribution from the interactions between CO<sub>2</sub> and the substituted aryl groups on Cu, we performed CO<sub>2</sub>-temperature programmed desorption (TPD) on the functionalized Cu catalysts (See “TPD analyses” section in the Supporting Materials and Supplementary Fig.64). The results showed no significant correlation between the interaction of the aryl groups with CO<sub>2</sub> and the catalytic activity, indicating that the valence state of copper is the main factor in promoting CO<sub>2</sub>RR. Moreover, the influences of total current density on the oxidation state of copper and the water contact angle of functionalized copper electrodes on CO<sub>2</sub>RR performance were also examined. No obvious correlation was observed (Supplementary Figs.65 and 66), which further highlights the dominant role of electro-withdrawing functional groups in controlling the valence of copper and enhancing the catalytic performance.

#### **Direct vs. cascade flow processes for the formation of C<sub>2</sub>H<sub>4</sub>**

The electrical power consumption is one the primary obstacle for the development of the CO<sub>2</sub>RR. Although progress has been made in the direct electroreduction of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> in MEA cells with appreciable selectivity and high current density, the requested full-cell potential makes the production cost of ethylene uncompetitive compared to industrial-grade ethylene obtained from steam cracking of oil or natural gas. In addition, the formation of carbonate in the MEA reactor combined to the strongly alkaline conditions leads to poor performance stability and low CO<sub>2</sub> single-pass conversion rate due to the flow of hydroxide ions from anode that reacts with gas CO<sub>2</sub>. Technical-economic analyses have suggested that a high specifically

current density ( $>150 \text{ mA cm}^{-2}$ ), and low operating full-cell potential ( $< 3 \text{ V}$ ) are the necessary requirements to compete with the traditional ethylene production process<sup>50</sup>. CO can advantageously replace CO<sub>2</sub> to produce multi-carbon species *via* the CO reduction reaction (CORR). The CORR is compatible with alkaline electrolytes at the anode to prevent the competitive hydrogen evolution reaction without significant carbonate formation that typically plagues the conversion of CO<sub>2</sub><sup>63</sup>. It is also anticipated that the CORR can improve the charge transfer kinetics and the selectivity towards ethylene, while decreasing the energy footprint of the system<sup>11,12,64</sup>. The realization of cascade flow processes has recently been explored to convert CO<sub>2</sub> to CO and then use CO to produce C<sub>2+</sub> products<sup>65,66</sup>.

In light of this, we sought to develop an integrated flow electrochemical system for the energy-efficient conversion of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> by coupling two MEA cells using Cu-NN as CORR catalyst. Considering the high market price of iridium (at  $\sim 6\text{k}\$$  per once, +375% since Nov. 2020), we thought to replace expensive IrO<sub>x</sub> with NiFe based layered double hydroxide (NiFe LDH) as anode catalyst<sup>67</sup>. We confirmed that NiFe LDH shows a lower overpotential than IrO<sub>x</sub> toward the OER in 1 M KOH (Supplementary Fig. 67). We then estimated the CO<sub>2</sub>-to-CO performance using electrodeposited Ag and NiFe based layered double hydroxide (NiFe LDH) as cathode and anode, respectively. We achieved a 94% FE for CO at the full-cell potential of  $-3.55 \text{ V}$  and a specific current density for CO of  $119 \text{ mA cm}^{-2}$  for an inlet flow rate of 10 sccm of CO<sub>2</sub> (Supplementary Fig. 68, and Supplementary Table 25). We evaluated the single-pass conversion efficiency (SPCE) to be  $\sim 31\%$  at  $-3.55 \text{ V}$ . To achieve an optimal CO feed of  $\sim 4.6 \text{ sccm}$ , we set the full-cell voltage of the first MEA cell to  $-3.8 \text{ V}$  corresponding to a FE and specific current density for CO of  $\sim 84\%$  and  $166 \text{ mA cm}^{-2}$ , respectively. The outlet gas from the Ag-based MEA was purified using a CO<sub>2</sub> capture solution containing 30% ethanolamine and then introduced into the second MEA cell for the CO-to-C<sub>2</sub>H<sub>4</sub> conversion. We tested the CO-to-C<sub>2</sub>H<sub>4</sub> conversion system using pristine Cu, Cu-NN, and Cu-NN/ionomer as cathode, and IrO<sub>x</sub> as anode catalysts. The FE for C<sub>2</sub>H<sub>4</sub> on Cu-NN reached a record-high values for the CORR at  $\sim 86.0\%$  and a full-potential of  $-2.5 \text{ V}$ . Cu-NN clearly outperforms Cu and Cu-NN/ionomer

with  $FE_{C_2H_4}$  of ~67.4% and ~72.1%, respectively (Supplementary Fig. 69 and Supplementary Table 26).

The operating cell voltage ( $E_{Cell}$ ) for the  $CO_2RR$  is known to be responsible for a significant electrical consumption and the oxidation evolution reaction (OER) at the anode brings a high energy penalty to the process<sup>5</sup>. By operating the cascade MEA cells with NiFe LDH and Cu-NN as anode and cathode catalysts, we achieved an optimal  $E_{Cell}$  of -2.3 V for maximizing the production of ethylene with a  $FE_{C_2H_4}$  of ~86% (Fig. 4a and Supplementary Fig. 70 and Supplementary Table 27). We determined a stable full-cell energy efficiency of 39.6% and a 12.3%  $CO_2$ -to- $C_2H_4$  cascade single pass conversion efficiency for the cascade flow process with a specific current density of  $154 \text{ mA cm}^{-2}$ . For comparison, Cu-NN/ionomer and pristine Cu catalysts exhibit EEs of 30.5% and 27.4% and  $CO_2$ -to- $C_2H_4$  cascade conversion rates of 12.9% and ~6.0% at -2.3 V, respectively (Figs. 4b and c, Supplementary Fig. 71 and Table 28). The formation rates of ethylene on Cu-NN/ionomer increased by 191% compared to pristine Cu electrodes. We estimated an EPC value of only  $25.6 \text{ kWh Nm}^{-3}$  for the Cu-NN+NiFe LDH system – lower than for Cu-NN/ionomer and Cu (Fig.4b and Supplementary Table 29). Remarkably, the cascade system maintained a 10.7 %  $CO_2$ -to- $C_2H_4$  conversion rate at an average specific current density of  $140 \text{ mA cm}^{-2}$  for 100 h (Fig.4d and Supplementary Table 29). We finally compared the performance of the Cu-NN and Cu-NN/ionomer catalysts with previous literature benchmarks<sup>6,7,49,50,52,65,66,68-70</sup> and found that Cu-NN display greater energy efficiency and lower EPC for both the direct and the cascade flow processes (Figs. 5a and b).

To validate the proposed concept, we functionalized commercial Cu particles (cCu) (Supplementary Figs. 72 to 74) and examined their performance in MEA electrolyzers. Our results showed that even on the not optimized Cu catalysts, the Faradaic efficiency of ethylene on cCu-NN electrode can reach 42% at -3.7 V compared to  $\approx 20\%$  for the pristine Cu particles. Importantly the energy efficiency and the electrical power consumption were improved by 31 % and 23.5% upon functionalization (Supplementary Table 30). Functionalization of the Ag electrode with NN leads to a slight decrease in the  $FE_{CO}$  (Supplementary Figs. 73 and 75), but



a higher specific current density of CO than pristine Ag (Supplementary Figs. 75c) indicating improved kinetics. Furthermore, we evaluated the role of the counter ion of the aryl diazonium salts on the CO<sub>2</sub>RR properties and found that the nature of the anion has a negligible effect on the CO<sub>2</sub>RR properties (Section “Influence for the anion on the CO<sub>2</sub>RR activity” section in the Supporting Information, Supplementary Fig. 76)

To assess the economic viability of electro-reduction of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> on Cu, Cu-NN, and Cu-NN/ionomer, we carried out techno-economic analyses by comparing the direct conversion route (CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> in a single reactor) with the two steps cascade systems (CO<sub>2</sub>-to-CO, and CO-to-C<sub>2</sub>H<sub>4</sub> in cascade system). We considered a single MEA cell to convert CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> using a neutral 0.5 M KHCO<sub>3</sub> anolyte, while 0.1 M KHCO<sub>3</sub> and 1 M KOH were used as anolytes in the first and the second MEA cells for the CO<sub>2</sub>-to-CO, and CO-to-C<sub>2</sub>H<sub>4</sub> reactions (See Note S1 in the Supplementary Information for details). We determined the OPEX of the direct and the cascade flow processes for the production of 1 ton of C<sub>2</sub>H<sub>4</sub> with/without the use of ionomer. In our calculations, we assumed a catalyst lifetime of one year (8,760 hours) and a total electrode surface of 100 m<sup>2</sup>. Figs. 5c and d show the cost distribution for the different parameters, without considering the CO<sub>2</sub> loss due to carbonate formation and membrane crossover as well as the downstream separation costs. We note that the installation costs and the balance of plant are part of the capitalization expenditure (CAPEX) and are not included in our calculations (See Note S2 in the Supplementary Information file). Among the four different MEA configurations, we found that direct conversion of CO<sub>2</sub> to ethylene using Cu-NN and ionomer is the closest to profitability. Importantly the cost of ethylene production decreases from 12,600 \$ ton<sup>-1</sup> to 4,500 \$ ton<sup>-1</sup> using pristine Cu and Cu-NN/ionomer electrodes, respectively, which corresponds to a 64% reduction. The analysis of the cost breakdown highlights that, in absence of ionomer, the main expense items for the direct production of the C<sub>2</sub>H<sub>4</sub> from CO<sub>2</sub> are the anode catalyst and the membranes for a total of 57.4% of the production cost. The use of ionomer lowers the cost (per ton of C<sub>2</sub>H<sub>4</sub>) of most parameters due to the improvement of the yield rate of the process and the EPC accounts for most of the expenses (32.6%) (Figs. 5c and d). Conversely, in the

cascade configuration, the cost of the anion-exchange membrane (AEM) represents the main expense for Cu-NN and Cu-NN/ionomer conditions at 47.1% and 39.4%, respectively (Figs. 5c and d). These findings point to the opportunity to rapidly improve the profitability of CO<sub>2</sub>RR by decreasing the cost to electrolyte membranes (Supplementary Table 31). Overall, aryl functionalized Cu<sup>+0.26</sup> holds potential to lower the financial gap between the low carbon-footprint CO<sub>2</sub>RR technology and the traditional ethylene production based on fossil resources.

## Conclusions

This work presents a novel approach to orient the CO<sub>2</sub>RR and the CORR towards the production of ethylene with record-high selectivity and formation rate. The origin of the high selectivity for C<sub>2+</sub> products is attributed to the formation of stable Cu<sup>δ+</sup> (0<δ<1) as supported by our *operando* and *ex-situ* physical characterizations using XPS, XAS and Raman spectroscopy. We attributed the near-unity selectivity for C<sub>2</sub>H<sub>4</sub> among the C<sub>2+</sub> products to the lower energy associated with the formation of the \*CH<sub>2</sub>CH intermediate on Cu<sup>0.26+</sup>. When implemented in a neutral MEA cell, the Cu-NN catalyst achieved a FE for ethylene of 83 ± 2 % with a partial ethylene current density of 212 ± 3 mA cm<sup>-2</sup>. The full-cell EE and the conversion efficiency for ethylene can be further increased to 39.6% and 12.3%, respectively, with a low record-low EPC of 25.6 kWh/Nm<sup>3</sup> by replacing CO<sub>2</sub> for CO in a cascade flow process. Our findings provide a route towards practical developments for the CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> conversion reaction using valence engineering of the Cu sites.

## Methods

**Catalyst preparation.** The Cu catalyst was electrodeposited at a constant current of -15 mA cm<sup>-2</sup> for 300 s on an acid-treated gas diffusion layer (GDE, Sigracet 22BB, for characterizations) with CO<sub>2</sub> gas flow (60 sccm). The solution consisted of 0.1 M copper bromide (98%, Sigma-Aldrich), 0.2 M sodium tartrate dibasic dihydrate (purum pro analysis ≥ 98.0% non-aqueous

titration (NT), Sigma-Aldrich), and 1 M KOH. Ag electrodes were prepared by electrodeposition in a solution of 0.01 M AgNO<sub>3</sub>, 0.6 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and 0.04 M ethylenediamine at a current density of 10 mA cm<sup>-2</sup> for 15 min. Nafion 117 and anion exchange membrane (Sustainion® X37-50), gas diffusion layer, and titanium mesh were obtained from the Fuel Cell Store. To prepare the Cu electrodes with commercial copper, 200 mg copper particles (the size of 2~3.5 μm, Sigma 7440-50-8) were firstly dissolved into the solution of 35.3 mg Nafion ionomer, 35.3 mg XC-2 ionomer (Carbon Dioxide) and 4 ml iso-propanol, as well as 4 ml deionized water. Then, the prepared ink was spray coated on a porous gas diffusion layer (Sigracet 22BB) with a loading amount of 1 mg/cm<sup>2</sup>. All chemicals were used as received. All aqueous solutions were prepared using deionized water with a resistivity of 18.2 MΩ cm<sup>-1</sup>.

**Functionalized Electrodes preparation.** The Cu electrodes were functionalized in Ar-saturated aqueous solution containing 3mM corresponding diazonium salt. The used aryl diazonium salts in the experiment are 2-Methyl-4-(2-methylphenylazo)benzenediazonium salt (NN, Fast Garnet GBC sulfate salt, Sigma-Aldrich), 4-Amino-4'-methoxydiphenylamine-diazonium chloride (N, Variamine blue B salt, Sigma-Aldrich), 2,5-Dimethoxy-4-([4-nitrophenyl]azo)benzenediazonium chloride hemi(zinc chloride) salt (NNN, Fast Black K Salt hemi(zinc chloride) salt, Sigma-Aldrich), 4-Methoxybenzenediazonium tetrafluoroborate (OCH<sub>3</sub>, 98%, Sigma-Aldrich), 4-Bromobenzenediazonium tetrafluoroborate (Br, 96%, Sigma-Aldrich), 4-Nitrobenzenediazonium tetrafluoroborate (NO<sub>2</sub>, 97%, Sigma-Aldrich) and 4-Diazo-*N,N*-diethylaniline fluoroborate(N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, abcr. Gute Chemie), 4-Aminodiphenylamine diazonium sulfate (Variamine Blue RT Salt, Sigma-Aldrich). All chemicals were used as received and all aqueous solutions were prepared by using deionized water with a resistivity of 18.2 MΩ cm<sup>-1</sup>. The aryl diazonium salts were electrodeposited onto all electrodes (the electrodeposited Cu-GDL electrode, the spray-coated commercial Cu-GDL electrode and the electrodeposited Ag-GDL electrode) using a three-electrode setup with Cu-GDL electrode, Ag/AgCl (3.5 M KCl) and a Pt plate as working, reference and counter electrodes, respectively. A constant current of 0.70 mA cm<sup>-2</sup> was applied for 100 s on the Cu-GDL electrode (~2.0 × 2.0

cm<sup>2</sup> for MEA) by using a potentiostat (VSP potentiostat from Bio-Logic Science Instruments). After electrodeposition, the electrode was rinsed with DI water, dried under Ar, and stored in glovebox for further use.

**Ionomer deposition.** Cu-NN electrodes were modified by spray-coating a PFSA solution. The PFSA solution were prepared by using 700 mg of ionomer (Nafion perfluorinated resin solution, product #527084-25 ml purchased from Sigma Aldrich) and 25 ml methanol (99.8%, anhydrous, Sigma Aldrich). The optimal loading with ionomer was achieved by tuning the spray-coating conditions in order to reach a desired loading of 1.75 mg cm<sup>-2</sup>. Samples were dried for at least 24 h at room temperature in a vacuum chamber before operation.

**Materials characterization.** A field emission scanning electron microscope (TESCAN Mira3) was employed to observe the morphology of samples. Aberration-corrected high-resolution (scanning) TEM imaging (HR-(S)TEM), energy-dispersive X-ray spectroscopy (EDS) and spatially-resolved electron energy-loss spectroscopy (SR-EELS) were performed using a FEI Titan Cubed Themis microscope which was operated at 80 kV. The Themis is equipped with a double Cs aberration corrector, a monochromator, an X-FEG gun, a super EDS detector, and an Ultra High Resolution Energy Filter (Gatan Quantum ERS) which allows for working in Dual-EELS mode. HR-STEM imaging was performed by using high-angle annular dark-field (HAADF) and annular dark-field (ADF) detectors. SR-EELS spectra were acquired with the monochromator excited allowing an energy resolution of 1.1 eV with an energy dispersion of 0.4 eV/pixel. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Thermo Electron ESCALAB 250 System using Al K $\alpha$  X-ray radiation (1486.6 eV) for excitation. Raman measurements were conducted using a Renishaw in Via Raman microscope and an  $\times 50$  objective (Leica) equipped with a 633 nm laser. *Operando* Raman measurements were carried out using a modified liquid-electrolyte flow cell using a 20 s integration time and averaging 10 scans per region. The spectra were recorded and processed using the Renishaw

WiRE software (version 4.4). Ag/AgCl (3.5 M KCl) and a Pt plate were used as the reference and counter electrodes, respectively.

**X-ray absorption spectroscopy (XAS).** *Ex situ* X-ray absorption spectra at the copper K-edges and Operando X-ray absorption spectroscopy (XAS) measurements at the copper K-edges were collected at ALBA Synchrotron Radiation Facility (Barcelona, Spain) on beamline CLAES and SOLEIL Synchrotron Radiation Facility (Saint-Aubin, France) on beamline SAMBA, respectively. Measurements were performed mainly in fluorescence mode, but transmission XAS data were also collected for comparison.

In SOLEIL Synchrotron Radiation Facility, the beamline is equipped with a sagittally Si (111) monochromator at the Cu K-edge for energy selection. The beam size was  $1 \times 0.5$  mm. The signals were collected in fluorescence mode using a 13-channel Ge detector. The intensity of the incident radiation was measured with an ionization chamber ( $I_0$ ) filled with an N<sub>2</sub> (500 mbar)/He (500 mbar) mixture. Two additional ionization chambers filled with 1700 mbar N<sub>2</sub> (in  $I_1$  chamber) and an Ar (150 mbar)/N<sub>2</sub>(850 mbar) mixture (in  $I_1$  chamber) were used for measurements in transmission mode in the case of the reference samples.

In ALBA Synchrotron Radiation Facility, intensities of the incident radiation and transmitted radiation were measured with ionization chamber detectors  $I_0$  and  $I_1$  filled with pure N<sub>2</sub> ( $I_0$  chamber) or 70:30 N<sub>2</sub> and Kr mixture ( $I_1$  chamber). Fluorescence data were collected using energy selective 6-channel Si drift detector. Si (111) monochromator was used for energy selection. XAS data for Cu foil, Cu<sub>2</sub>O, and CuO reference samples were also collected for comparison and data alignment.

For the XAS studies, Cu was firstly electrodeposited on gas diffusion layer (GDL, Sigracet 22 BB, Fuel Cell Store) used as gas diffusion electrode (GDE) and then functional solutions were modified on the catalyst side, while the other side of the GDL was covered with polyamide tape. The GDL was then taped on a graphite foil and subsequently, the electrode was mounted in our home-built single compartment cell, where the samples on graphite foil acted as a working electrode. Pt mesh and Ag/AgCl were used as counter and reference electrodes,

respectively. The applied potential was controlled with BioLogic potentiostat. As for the electrolyte, we used an aqueous solution of CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> that was continuously circulated through the cell using a peristaltic pump. The electrolyte was continuously purged with CO<sub>2</sub> with a flow rate of 20 ml/min. All measurements were performed at constant potentials of -0.98 V, -0.93 V, -0.88 V and -0.83 V vs. RHE. Time-resolved spectra under CO<sub>2</sub>RR conditions were acquired every 12-15 min until no further changes were observed.

Data alignment and normalization of the X-ray absorption near edge structure (XANES) spectra were carried out using the Athena software. Fitting of the Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra  $\chi(k)k^2$  of the catalysts was carried out in R-space in the range from  $R_{\min} = 1.0 \text{ \AA}$  up to  $R_{\max} = 2.7 \text{ \AA}$ . The Fourier transforms were carried out in the k-range from  $3.0 \text{ \AA}^{-1}$  to  $10.0 \text{ \AA}^{-1}$  with a k-weighting of 1, 2 and 3. Fitting parameters were the coordination numbers N, interatomic distances R, disorder factors  $\sigma^2$  for Cu-O and Cu-Cu paths, as well as the corrections to the photoelectron reference energies  $\Delta E_0$ . Amplitude reduction factor  $S_0^2 = 0.94$  was determined from the fitting of EXAFS spectra for Cu foil.

### **Computational details.**

All density functional theory calculations presented in this paper are performed by using the Vienna Ab-initio simulation software package (VASP)<sup>71</sup> with the projected- augmented-wave (PAW)<sup>72</sup> and the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional methods<sup>73</sup>. The energy cutoff was set to 400 eV and the Brillouin zone was sampled by a Gamma  $1 \times 1 \times 1$  K-point grid for structural optimization, while a  $3 \times 3 \times 1$  K-point grid was used for electronic state analysis. During structural optimization, the position of all the atoms except the bottom layer were relaxed and convergence criterion for the maximum force and energy on each atom was set to  $-0.05 \text{ eV/\AA}$  and  $10^{-4} \text{ eV}$ , respectively. In order to accurately describe the weak interactions, the dispersion-corrected DFT-D3 method<sup>74</sup> was employed to consider the van der Waals (vdW) interaction. For our calculations, we first designed a Cu (111) supercell (4 metal atoms in x direction, 4 metal atoms in y direction and 3 layers in z direction) with different aryl

diazonium salts after considering both experimental results and the steric-hindrance effects from the functional groups on the Cu surface. To accurately evaluate the valence of copper after functionalization, we calculated the valence of copper without solvent, as the strong electron-withdrawing ability of the oxygen atom from water molecules would withdraw some electrons from copper. Next, we calculated the valence of copper with explicit water to better replicate the experimental environment of the reaction. Periodic boundary conditions were used in all directions and 20 Å of vacuum layer was used in the z direction to separate the slabs. The two uppermost slab layers and the adsorbates were allowed to relax.

**Theoretical valence analysis** The theoretical valence of the copper atoms was calculated using the Bader Charge Analysis script written by Henkelman and co-workers<sup>75</sup>. The theoretical valence of the whole Cu super cell was evaluated according to the number of net charge obtained by the grafted aryl diazonium salts. We calculated the net charge (NCharge) of different grafted aryl diazonium groups by getting a sum of net charge of all atoms on aryl diazonium group. For each atom, the net charge (NCharge) is calculated by using the calculated formal Bader charge of the atom (NBader) to subtract the outermost electron number (NValence) of the related atom (1, 4, 5, 6 and 7 for H, C, N, O and Br, respectively), as follows

6,15,19

$$NCharge = NBader - NValence \quad (1)$$

For example, taking one nitrogen atom on NN, the net charge is  $5.536 - 5 = 0.536$ , indicating that the nitrogen atom receives 0.536 electron. After functionalizing with different aryl diazonium salts, the valences of bonded Cu systems – calculated with explicit water – are characterized by positive charges with the values of +0.149 e, +0.206 e, +0.219 e, +0.260 e, +0.497 e, +0.630 e and +0.787 e for  $N(C_2H_5)_2$ ,  $OCH_3$ , N, NN, NNN, Br and  $NO_2$  functional groups, respectively. This compares with the values of +0.173 e, +0.285 e, +0.307 e, +0.341 e, +0.590 e, +0.728 e and +0.843 e for  $N(C_2H_5)_2$ ,  $OCH_3$ , N, NN, NNN, Br and  $NO_2$  functional groups calculated in absence of solvent. The valences of nearby Cu atoms are also characterized by the same methods.

**Calculations of the CO<sub>2</sub>/CO adsorption energy over functionalized Cu.** The adsorption energy of CO<sub>2</sub>/CO molecules over a Cu surface in the presence and absence of functional groups was calculated using Equations (2a, b):

$$E_{ad-CO_2} = E_{(CO_2,slab)} - E_{(slab)} - E_{(CO_2,gas)} \quad (2a)$$

$$E_{ad-CO} = E_{(CO,slab)} - E_{(slab)} - E_{(CO,gas)} \quad (2b)$$

where  $E_{(CO_2, slab)}$  and  $E_{(CO, slab)}$  represent the total energy for CO<sub>2</sub> and CO molecules over the Cu slab;  $E_{slab}$  is the total energy of the bare slab.  $E_{(CO_2, gas)}$  and  $E_{(CO, gas)}$  are the carbon dioxide and carbon monoxide gas phase energy. In our calculations, the more negative value of the adsorption energy represents a stronger binding strength of the CO<sub>2</sub>/CO molecule.

**Relationship between the Cu valence and the CO<sub>2</sub> adsorption energy in Cu-NN system.**

To understand how the functional groups affect the valence of Cu atoms and the related CO<sub>2</sub> adsorption energy near the grafting site, we chose NN-functionalized Cu as a model catalyst. For the calculations, we used a larger (3x3) supercell of Cu (111), including 6 metal atoms in the x direction, 6 metal atoms in the y direction and 3 layers in the z direction. A total of ten models were constructed varying the distance between NN-bonded Cu atom (i.e. the grafting site) and the CO<sub>2</sub> molecule from ~ 3.9 to 9.6 Å.

**Calculations of the energy barrier associated with CO dimerization over functionalized**

**Cu.** To investigate the OC-CO coupling energy barriers on different Cu surfaces, a climbing image nudged elastic band (CI-NEB) method<sup>76</sup> was used to explore the transition state, followed by the dimer method to converge the saddle point within 0.05 eV/Å. Four windows were inserted between the initial state (IS) and the final state (FS) to identify the transition state (TS) when calculating the OC-CO coupling process on both pure Cu and Cu-NN. For all the intermediates and the transition states, five water molecules are added near the surface to take into account the effect of solvation<sup>6,15,19,37,76,77</sup>. Goodpaster, Norskov, Goddard, Neurock, and others have widely explored and simulated electric fields and charging effects by different methods<sup>15,37,39,40,64,77</sup>. We applied the Neugebauer and Scheffler method to include an applied electric field (-0.8 to 0.8 V/Å)<sup>41</sup> parallel to the vacuum layer in order to examine how the applied



electric field influences the selectivity of ethylene and ethanol in the presence of aryl diazonium salt (NN). the Gibbs free energy can be calculated using Equation (3), initially proposed by Nørskov et al<sup>78</sup>,

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S \quad (3)$$

where  $T = 298.15$  K,  $\Delta E$ ,  $\Delta E_{ZPE}$  and  $\Delta S$  are the total electron energy difference, zero-point energy difference and entropy change, respectively. The entropy change being small, its effect can be ignored.

### Calculations based on Cu (100) models

We designed a series of Cu (100) supercells (6 metal atoms in x direction, 6 metal atoms in y direction and 3 layers in z direction) with different aryl diazonium salts after considering both experimental results and the steric-hindrance effects from the functional groups on the Cu surface. We calculated the theoretical valence of Cu, the energy barrier of \*CO dimerization, and the free energy of hydrogen evolution reaction on all Cu (100)-X supercells with the consideration of solvent by using the same method as in calculating Cu (111)-X supercells.

**Electrochemical in H-Cell and MEA configuration.** All electrochemical measurements were carried out at ambient temperature and pressure using a VSP electrochemical station from BioLogic Science Instruments equipped with a 5 A booster and FRA32 module. The cell voltages reported in all figures were recorded without iR correction. All the potentials in the H-cell were converted to values with respect to the RHE potential using:

$$E_{RHE} = E_{Ag/AgCl} + 0.197 \text{ V} + 0.0591 \times \text{pH} \quad (4)$$

In the H-cell configuration, Ag/AgCl (3.5 M KCl) and a Pt plate were used as reference and counter electrodes respectively. The electrolyte consisted in a 0.5 M KOH solution (99.9%, Sigma Aldrich), which was saturated with alternatively CO<sub>2</sub> ( $\geq 99.998$ , Linde) or Ar (5.0, Linde). Prior to any experiment, the anolyte and catholyte solutions were saturated by bubbling CO<sub>2</sub> or Ar for at least 20 min.

The MEA electrolyzer (Dioxide Materials) was composed of the Cu cathode, a Ti-IrO<sub>x</sub> mesh anode and an anion exchange membrane (AEM, Sustainion® X37-50, Fuel cell store). The

anode and cathode flow fields are made of titanium and stainless steel with geometric active areas of 4 cm<sup>2</sup> respectively. The anode was prepared by depositing IrO<sub>x</sub> on a titanium support (0.002'' thickness, Fuel Cell Store) by a dip coating followed by thermal annealing. Briefly, the titanium mesh was firstly degreased with acetone and DI water, then etched in a 6 M HCl (Reagent Grade, Bioshop) solution heated to 80 °C to 90 °C for 45 min before dip coating. The solution used for dip coating consisted of 30 mg of IrCl<sub>3</sub>.xH<sub>2</sub>O (Alfa Aesar) dissolved in 10 mL of an iso-propanol solution with 10% concentrated HCl. The etched titanium mesh was dipped into the IrCl<sub>3</sub> solution, dried in an oven at 100 °C for 10 min before calcination in air at 500 °C for 10 min. The dipping and calcination process was repeated until a suitable loading was achieved (2 mg cm<sup>-2</sup>)<sup>70</sup>.

The AEM was firstly placed between the anode and cathode flow fields and then assembled together. The flow fields were mainly responsible for the effective supply in aqueous anolyte solution and humidified CO<sub>2</sub> over the respective surfaces of anode and cathode electrodes. The anode and cathode gaskets were placed between the flow fields and the respective electrodes to ensure proper sealing. An anion exchange membrane (Sustainion® X37-50) (Dioxide Materials) was activated in 1 M aqueous KOH solution for at least 24 hours, washed with deionized water and used as the anion-exchange membrane (AEM). A 0.5 M KHCO<sub>3</sub> anolyte solution was circulated through the anode compartment of the electrolyzer with the constant flow rate of 30 ml/min *via* a peristaltic pump, while CO<sub>2</sub> was supplied to the cathode side with a constant flow rate of 10 standard cubic centimeters per minute (sccm). After three-minutes of initial operation, a full-cell potential of -3.0 V was applied to the electrolyzer and the potential then was gradually increased with increments of -0.10 V or -0.05 V. The current was stabilized for 15-20 min between two voltage increments.

#### **CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> measurements in the cascade MEA system**

An Ag electrode was used to convert CO<sub>2</sub> into CO in 0.1M KHCO<sub>3</sub> solution. The MEA cell possessed the same geometric active area of 4 cm<sup>2</sup>. The first MEA setup was operated at -3.8 V with a CO<sub>2</sub> inlet flow rate of 10 sccm. The outlet of the first MEA setup was connected to a

CO<sub>2</sub> capture solution using a 30 wt % ethanolamine aqueous solution. Purified CO was then supplied to the second MEA cell for conversion of CO to C<sub>2</sub>H<sub>4</sub>. 1 M KOH was used as the anolyte, and the CO-to-ethylene conversion was evaluated at different potentials from -2.0 to -3.0 V.

**Quantification of the CO<sub>2</sub>RR products.** The electrochemical data were recorded while simultaneously collecting the CO<sub>2</sub>RR gas products by using an automatic sampler connected to the cathode outlet. A cold trap was used to collect the liquid products before the sampler. For each applied potential, the gas products were collected at least 3 times with proper time intervals. The gas aliquots were then injected into an online gas chromatograph (Agilent, Micro GC-490) equipped with a TCD detector and Molsieve 5A column continuously. Hydrogen and argon (99.9999%) were used as the carrier gases. Liquid products were quantified by <sup>1</sup>H NMR spectroscopy (600 Mhz Avance III Bukrer with a cryorobe Prodigy TCI) using deionized water with 0.1 % (w/w) of DSS (Sodium trimethylsilylpropanesulfonate) like internal standard for the quantification of the ethanol and formate. An 1D sequence water suppression with excitation sculpting with gradients(zgesgp) was used for the acquisition (Number of scan = 32, Delay D1=30 s). Owing to the liquid product crossover, the FE values of the liquid products were calculated based on the total amount of the products collected on the anode and cathode sides during the same period.

**Stability measurements in the MEA configuration.** For the stability tests, the MEA electrolyzer was operated at a constant voltage of -3.55 V with a continuous feed in CO<sub>2</sub>. The gas products were collected at frequent time intervals and FE values were calculated from the average value obtained from three successive injections. As for the liquid products, the total liquid products were collected at the end of the experiments.

**Faradaic Efficiency, Selectivity, Energy Efficiency and Energy power consumption**

**Calculations.** The Faradaic efficiency (FE, %) of each gas product was calculated as follows:

$$FE_{gas} = g_i \times v \times \frac{z_i}{RT} FP_0 \times \frac{1}{I_{total}} \times 100\% \quad (5)$$

The Faradaic efficiency (FE, %) of each liquid product was calculated as follows:

$$FE_{liquid} = l_i \times \frac{z_i}{Q_{total}} F \times 100\% \quad (6)$$

The formation rate (R) for each species(*i*) was calculated as follows:

$$R_i = \frac{Q_{total} \times FE_i}{96485 \times z_i \times t \times S} \quad (7)$$

The single-pass conversion rate (SPC, %) of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> was calculated as follows:

$$SPC = \frac{C_{C_2H_4} \times flow\ rate_{outlet}}{C_{CO_2} \times flow\ rate_{inlet}} \times 100 \quad (8)$$

The full-cell energy efficiencies (EE, %) was calculated as follows:

$$EE = \frac{(1.23 - E_i) \times FE_i}{E_{cell}} \quad (9)$$

The selectivity (%) of ethylene was calculated as follows:

$$Selectivity_{C_2H_4} = \frac{2R_{C_2H_4}}{R_{CO} + R_{HCOOH} + 2R_{C_2H_4} + 2R_{C_2H_5OH}} \quad (10)$$

The electrical power consumption (EPC, kWh) characterizes the amount of electric energy (typically expressed in kWh) that is required for producing 1 Nm<sup>3</sup> of product gas, and it was calculated as follows:

$$EPC = \frac{E_{cell} \times n \times F}{FE \times V_m} \quad (11)$$

where  $g_i$  represents the volume fraction of gas product *i*;  $v$  represents the gas flow rate at the outlet in sccm;  $z_i$  represents the number of electrons required to produce one molecule of product *i*;  $I_{total}$  represents the total current;  $l_i$  represents the number of moles of liquid product *i*;  $Q_{total}$  represents the charge passed while the liquid products are being collected;  $C_{C_2H_4}$  and  $C_{CO_2}$  represents the concentrations of C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> measured by online GC.  $P_0 = 1.01 \times 10^5$  Pa,  $T = 273.15$  K,  $F = 96,485$  C mol<sup>-1</sup> and  $R = 8.314$  Jmol<sup>-1</sup>K<sup>-1</sup>;  $t$  represents the electrolysis time (h);  $S$  represents the geometric area of the electrode (cm<sup>2</sup>);  $E_i$  represents the thermodynamic potential (versus RHE) for CO<sub>2</sub>RR to species *i* and  $E_{cell}$  represents the cell voltage in two-electrode setup (-1.15 V for CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub>, and -1.06 V for CO-to-C<sub>2</sub>H<sub>4</sub>);  $V_m$  is the molar volume of ideal gas under normal conditions.

## Acknowledgments

D.V., H. W. and K.Q. acknowledge funding from the European Research Council (ERC) under

the European Union's Horizon 2020 research and innovation programme (grant agreement no. 804320). The authors acknowledge the use of TEM instrumentation provided by the National Facility ELECOMI ICTS ("Division de Microscopia Electronica", Universidad de Cadiz, DME-UCA). L.L. acknowledges funding from the European Union's Horizon 2020 research and innovation program (grant agreement 823717-ESTEEM3) and the Spanish Ministerio de Economía y Competitividad (PID2019-107578GA-I00), the Ministerio de Ciencia e Innovación MCIN/AEI/10.13039/501100011033, and the European Union "NextGenerationEU"/PRTR (RYC2021-033764-I, CPP2021-008986). C.S. acknowledged funding from the French National Agency (ANR, JCJC program, MONOMEANR-20-CE08-0009). The authors acknowledge Martina Rüscher, Felix T. Haase and Lichen Bai for their help on synchrotron tests. We acknowledge SOLEIL for provision of synchrotron radiation facilities and we would like to thank Andrea Zitolo for assistance in using beamline SAMBA within the proposal 20200732. XAS experiments were also performed at CLAESS beamline at ALBA synchrotron with the collaboration of ALBA staff. Patrice Montels and Daniel Valenza are acknowledged for their technical assistance with the MEA cells.

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### Author Contributions

D.V. conceived the idea, designed the experiments. D.R. performed the DFT calculations and discussed the results with D.V. and H.W.. H.W. designed the experiments with D.V., prepared the electrodes and performed the electrochemical measurements. H.W., D.R. and D.V. analyzed the data and wrote the manuscript. L. H. and V.F. performed the XPS and Auger measurements and analyzed the data with H.W.. J.T. and H.W. performed the *ex-situ* and *operando* XAS measurements and analyzed the data. L.L. performed high-resolution STEM, TEM and EELS on the Cu-X catalysts and discussed the results with H.W. and D.V.. S. Y. performed DFT data collections and discussed the results with H.W.. E.P. carried out the liquid NMR spectroscopy measurements. K.Q., Y.Z., assisted H.W. with the electrochemical investigations and the GC analyses. W.W., J. Li and J. Jiu assisted H.W. with the physical characterization of the samples and the *operando* Raman measurements. C.S. and P. M. discussed the electrocatalytic performance with H.W. and D.V.. B.R.C. discussed the XAS data with J.T., H.W. and D.V. All of the authors edited the manuscript before submission.

### Data availability

The data that support the plots and other findings in this study are available from the

corresponding authors upon reasonable request.

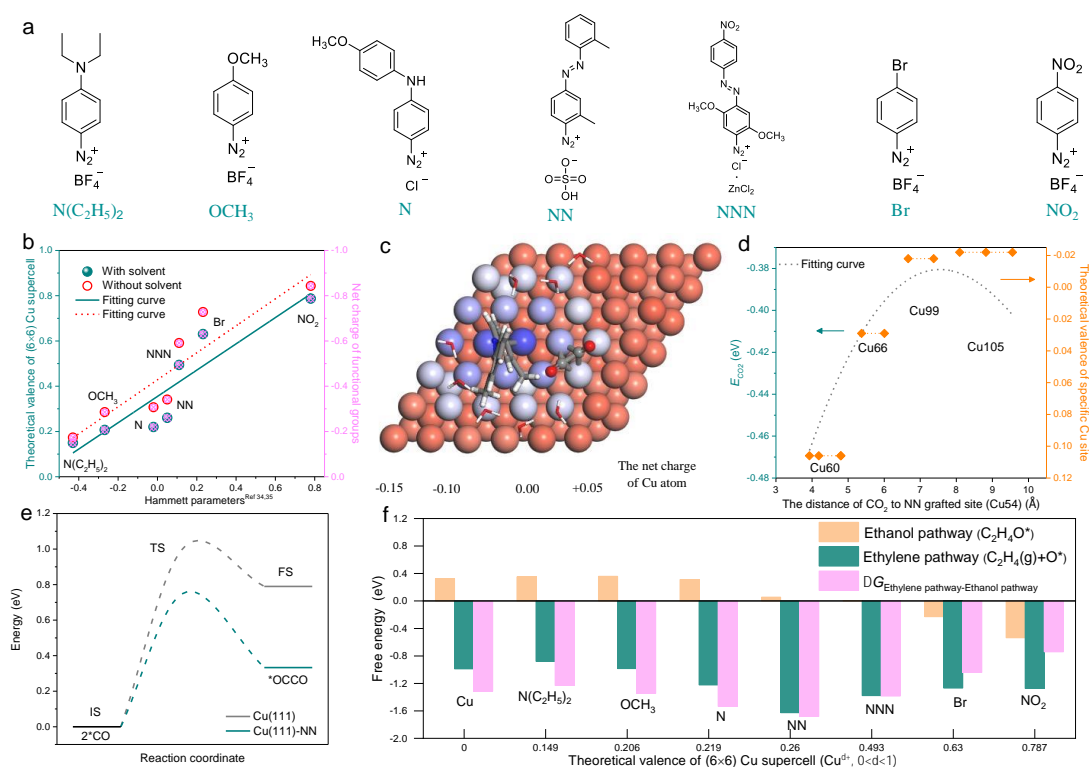
## Competing financial interests

The authors declare no competing financial interests.

## Additional Information

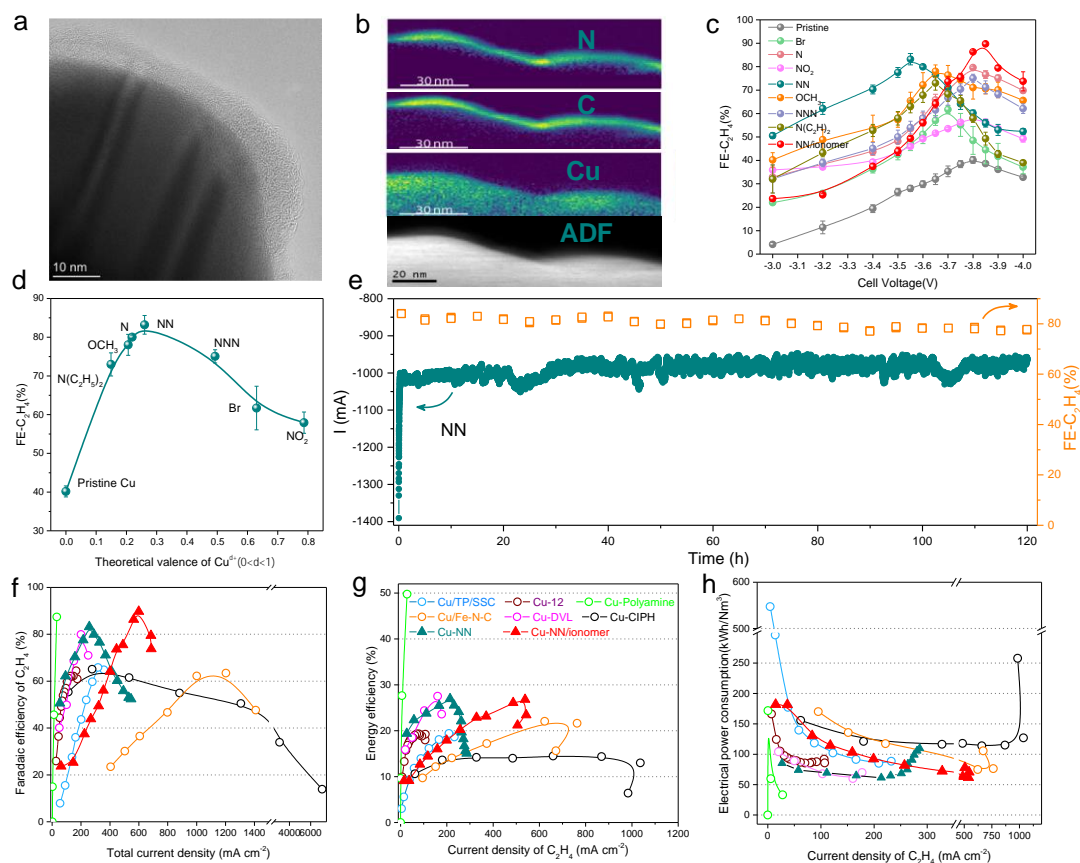
**Supplementary information** and chemical compound information are available in the online version of the paper.

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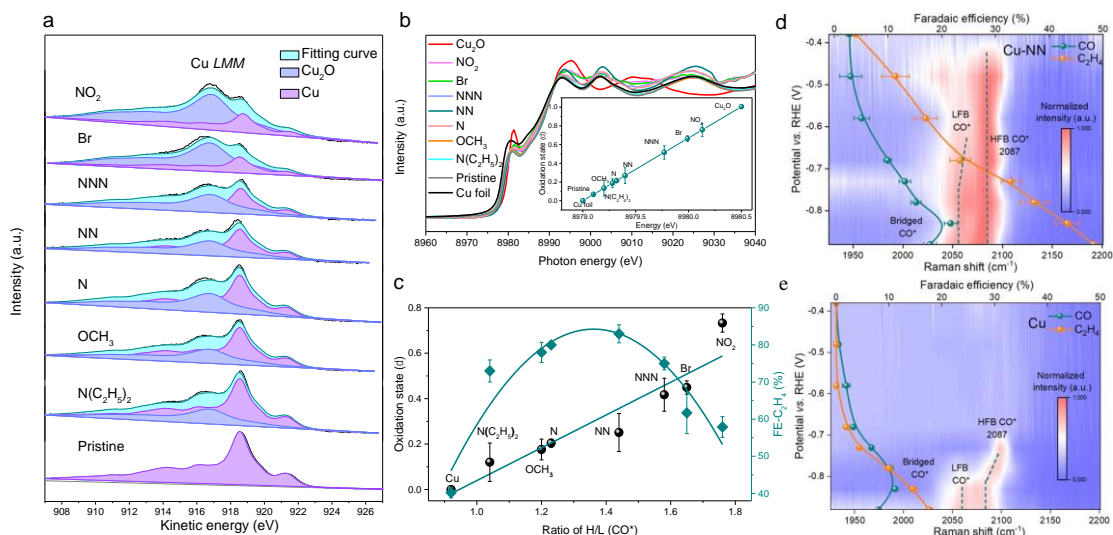
**Fig. 1 Density functional theory calculations.** (a) Molecular structures of different diazonium salts. (b) The relationship between the theoretical valence of the whole (6x6) Cu supercell and the electro-withdrawing ability of different substitutes on phenyl according to Hammett

parameters<sup>34,35</sup>. (c) Heat map of the valence of the top Cu atoms near the NN functional group calculated considering explicit water. Cu, N, C and O atoms are illustrated as orange, blue, grey and red balls, respectively, while water molecules and NN are shown as lines. (d) The relationship between the distance of adsorbed CO<sub>2</sub> to the NN grafted copper atom (Cu54), the theoretical valence of CO<sub>2</sub>-adsorbed specific Cu sites (Cu60, Cu66, Cu99 and Cu105) and the related CO<sub>2</sub> adsorption energy on CO<sub>2</sub>-adsorbed Cu sites. (e) Energy profiles for initial states (ISs), transition states (TSs), and final states (FSs) of CO dimerization on Cu (111) and Cu (111)-NN. (f) Gibbs free energy difference associated with the ethylene and ethanol pathways on Cu-X (X refers to NO<sub>2</sub>, Br, NNN, NN, N, OCH<sub>3</sub> and N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> functional groups), respectively.

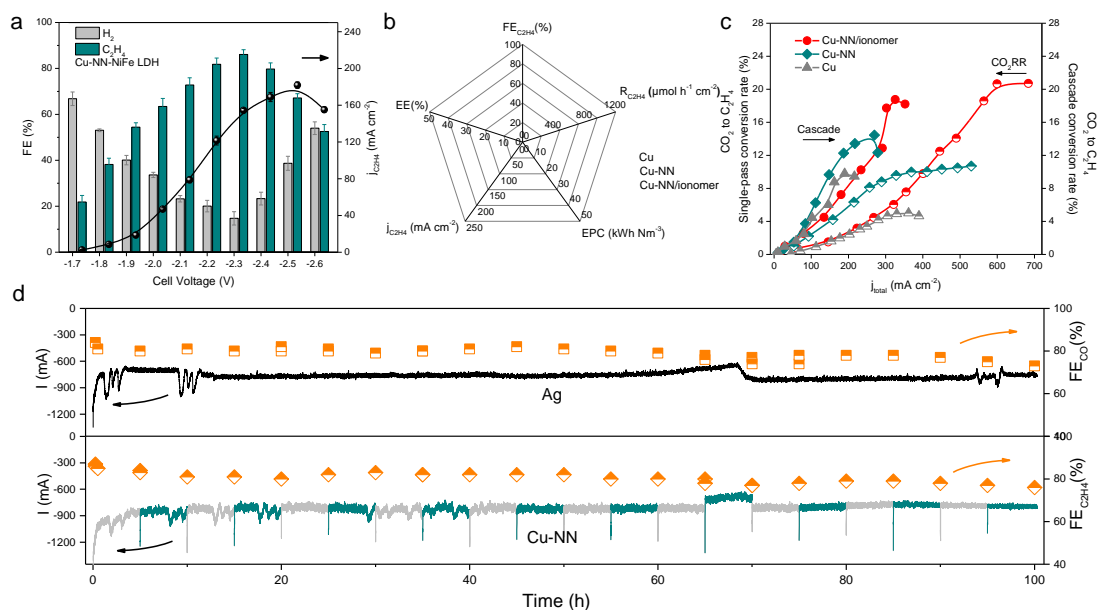


**Fig. 2 Structural, compositional and CO<sub>2</sub>RR performance for the different Cu-X catalysts measured in MEA flow cells.** X refers to NO<sub>2</sub>, Br, NNN, NN, N, OCH<sub>3</sub> and N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> functional groups. (a) HR-TEM image, (b) the corresponding N, C and Cu EELS elemental maps and corresponding ADF image taken from a section of Cu surface on the NN-

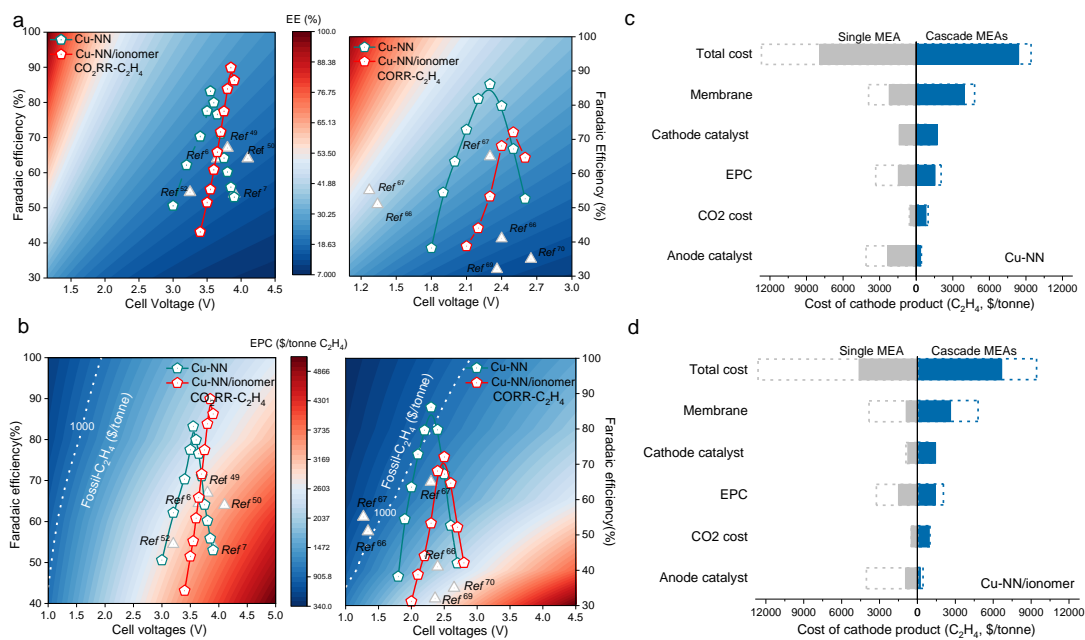
functionalized Cu electrode. **(c)** Comparison of FEs for ethylene on the different Cu electrodes measured at full-cell potentials ranging from -3.0 to -4.0 V and measured in 0.5 M KHCO<sub>3</sub>. **(d)** The relationship between FE<sub>C<sub>2</sub>H<sub>4</sub></sub> and the theoretical valences of the Cu sites on the different catalysts. **(e)** CO<sub>2</sub>RR performance of NN-Cu at a full-cell potential of -3.55 V and with a 10 sccm feed in CO<sub>2</sub> over 120 hours. The anolyte consisted in a 0.5 M KHCO<sub>3</sub> solution circulating at a flow rate of 30 ml min<sup>-1</sup>. The blue line represents the current recorded during the extended CO<sub>2</sub>RR experiment (primary y axis). The empty orange symbols represent the FE for C<sub>2</sub>H<sub>4</sub> averaged from three independent measurements (secondary y axis). Comparison of the selectivity **(f)**, energy efficiency **(g)** and electric power consumption **(h)** for C<sub>2</sub>H<sub>4</sub> based measured on the different Cu-X cathodes with literature benchmarks for MEA electrolyzers. For each reference (Cu-12, Cu-CIPH, Cu/Fe-N-C, Cu-Polyamine, Cu/TP/SSC and Cu-DVL catalysts), the plotted values are those corresponding to the reported best performance<sup>6,7,9,49,53,54</sup> (Supplementary Table 17). The error bars in **c** and **d** correspond to the standard deviation of three independent measurements.



**Fig. 3 XAS, Auger and *operando* Raman characterizations.** (a) The copper *LMM* Auger spectra of the Cu-X electrodes. The amounts of Cu<sub>2</sub>O and Cu contributions were estimated from the integrated area of the corresponding curves. (b) Copper K-edge XANES spectra of Cu-X catalysts after being electrochemically reduced. Inset: average oxidation state of copper in Cu-X obtained from copper K-edge XANES. The edge position of each sample is determined from the intercept of the main edge and pre-edge contributions. The error bars represent the standard deviation of three separate measurements for each sample. (c) The relationship between the FE for ethylene, the oxidation state of copper in Cu-X and the ratio of H/L-\*CO obtained from the *operando* Raman spectra of the Cu-X electrodes at -0.88 V versus RHE. H and L refer high frequency and low frequency modes. (d) The correlations between the FE<sub>CO</sub>, the FE<sub>C<sub>2</sub>H<sub>4</sub></sub> and the *operando* Raman heatmaps of Cu-NN electrode and pristine Cu measured from -0.88 V to -0.38 V vs. RHE. Only the CO region is examined here (1900-2200 cm<sup>-1</sup>). The error bars in **b**, **c**, **d** and **e** correspond to the standard deviation of three independent measurements.



**Fig. 4** CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> performance in the cascade flow process. **(a)** The FE for C<sub>2</sub>H<sub>4</sub> obtained using CO as feed. **(b)** Comparison of different performance of the Cu-X electrodes: Faradaic efficiency (FE), energy efficiency (EE), specific current density ( $j$ ), energy power consumption (EPC) and formation rate ( $R$ ) of C<sub>2</sub>H<sub>4</sub>. **(c)** Comparison of the CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> single-pass conversion measured for a single MEA cell (half-filled sphere) and for the cascade flow process (filled sphere). **(d)** The stability of Ag and Cu-NN catalysts in MEA cells. The error bars in **a** and **c** correspond to the standard deviation of three independent measurements.



**Fig. 5** Techno-economic analyses for the CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> conversion based on the direct and the cascade flow processes. The comparison of energy efficiency (EE) (a) and the cost of the electrical power consumption (b) for the CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> and the CO-to-C<sub>2</sub>H<sub>4</sub> reactions. Comparison of operational costs for production of C<sub>2</sub>H<sub>4</sub> on Cu-NN(c) and Cu-NN/ionomer(d) in both single MEA and cascade MEA systems (the dash line refers to pristine Cu).