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# **Improved electrochemical conversion of CO<sub>2</sub> to multicarbon products by using molecular doping**

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The conversion of CO<sub>2</sub> into desirable multicarbon products such as ethylene and ethanol *via* the carbon dioxide reduction reaction (CO<sub>2</sub>RR) hold promise to achieve a circular carbon economy. The develop of such a technology is currently hampered by the lack of catalysts, which can drive the reaction at industrially relevant current densities with high efficiency and selectivity. Here, we report a novel strategy for increasing the conversion of CO<sub>2</sub> into hydrocarbon molecules with two or more carbon atoms (C<sub>2+</sub>) by modifying the surface of bimetallic silver-copper (Ag-Cu) catalyst with aromatic heterocycles such as thiadiazole and triazole derivatives. By combining *operando* Raman and X-ray absorption spectroscopy with electrocatalytic measurements and analysis of the reaction products, we identified that the electron withdrawing nature of functional groups orients the reaction pathway towards the production of C<sub>2+</sub> species such as ethanol and ethylene and enhances the reaction rates on the surface of the catalyst. As a result, we achieve a maximum Faradaic efficiency for the formation of C<sub>2+</sub> of  $\approx 80\%$  and full-cell energy efficiency of 20.3% with a specific current density of 261.4 mA cm<sup>-2</sup> for C<sub>2+</sub> using functionalized Ag-Cu electrodes, compared to only 33.8% and 70.6 mA cm<sup>-2</sup> for the pristine Ag-Cu electrodes. We anticipate that our strategy can further be extended in order to improve the selectivity of the reaction towards the production of specific multicarbon molecules.

## Main text

The rapid increase in the atmospheric carbon dioxide (CO<sub>2</sub>) levels has motivated the

development of carbon capture, utilization and storage (CCUS) technologies. In this context, the electrochemical reduction of CO<sub>2</sub> to hydrocarbons using renewable energy is regarded as an effective way to close the carbon cycle *via* the conversion of CO<sub>2</sub> into chemical precursors or fuels<sup>1,2</sup>. The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) toward single carbon products has achieved enormous progress<sup>3</sup>, especially for production of C<sub>1</sub> molecules such as carbon monoxide (CO) or methane (CH<sub>4</sub>)<sup>4-7</sup>. Copper (Cu) is one of the few transition metals that can efficiently catalyze the electrolysis of CO<sub>2</sub> to multicarbon products such as ethylene, ethanol, acetate, propanol<sup>8</sup>. Because multicarbon products possess higher market values and are more energy concentrated<sup>1</sup>, intensive efforts have been devoted to improve the reaction selectivity towards the production of C<sub>2</sub> and C<sub>2+</sub> molecules. Examples of strategies for optimizing the Faradaic efficiency towards the production of C<sub>2+</sub> species include alloying<sup>9-12</sup>, surface doping<sup>13,14</sup>, ligand modification<sup>15,16</sup>, and interface engineering<sup>17-20</sup>.

Designing Cu-based catalysts by adapting some of the concept of molecular catalysts in order to finely tailor the behavior of the active sites of metallic surfaces is currently regarded as the long-standing interest for the controlled design of novel electrocatalytic materials. Increasing the oxidation state of copper has been suggested to improve the CO<sub>2</sub>RR performance and notably the formation of C<sub>2+</sub> species<sup>14,21,22</sup>. Various strategies are being explored to prepare Cu<sup>δ+</sup> by using controlled oxidation *via* plasma treatments or doping with boron and halides<sup>14,23-25</sup>. Alternatively, molecular engineering of either the electrolyte or the catalyst surface has recently been proposed for orienting the selectivity of the reaction by stabilizing intermediates, inhibiting proton diffusion, or

acting as redox mediators during the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR)<sup>26-30</sup>. Organic species such as N-aryl pyridinium salts<sup>31,32</sup>, imidazole<sup>33-35</sup>, thiol<sup>36,37</sup> and cysteamine<sup>38</sup> have been reported as effective lever to tune the reaction selectivity toward the formation of specific products. Functionalization of alkyl chains can also lead to better CO<sub>2</sub>RR performance by suppressing the competitive hydrogen evolution reaction (HER) *via* the creation of hydrophobic regions on the surface of the catalyst<sup>37,39,40</sup>.

Here we present an effective strategy to control the surface oxidation state of bimetallic Ag-Cu electrodes by using functionalization for tuning the oxidation state of Cu<sup>δ+</sup>. By combining Auger and X-ray absorption spectroscopies (XAS), we identified that the grafting of aromatic heterocyclic functional groups can efficiently dope the surface of Cu by withdrawing electrons from the metal surface leading to the formation of Cu<sup>δ+</sup> species. Compared to pristine non-functionalized and alkyl-functionalized electrodes, the modified electrodes display a clear improvement of the reaction rates and Faradaic efficiency towards the production of C<sub>2+</sub> products. *Operando* Raman and X-ray absorption spectroscopy (XAS) suggest that the presence of Cu<sup>δ+</sup> with  $0 < \delta < 1$  favors the formation of adsorbed CO with the atop conformation which is a known key intermediate specie involved in the C-C coupling step associated with the formation of multicarbon products. When assembled in a membrane electrode assembly electrolyzer, the catalyst delivers a Faradaic efficiency (FE) for C<sub>2+</sub> products of  $80 \pm 1$  % and a total C<sub>2+</sub> energy efficiency (EE) of 20.3% for the full cell.

## Results

### Catalyst design and characterization

We fabricated the functionalized bimetallic catalyst by using a two-step strategy based on the controlled electrodeposition of Ag and Cu followed by the modification of the catalyst surface *via* functionalization (Fig. 1a). The Ag-Cu electrodes were prepared by firstly depositing Ag on gas diffusion electrodes (GDE) using pulsed electrodeposition. The silver structure grows in the form of a dendritic fish-bone structure with sharp Ag nanoneedles (Supplementary Fig. 1). The Ag layer was then used as a scaffold for the deposition of copper. The final structure of the catalyst on the GDE electrodes is found to be porous where Cu is preferentially deposited on Ag (Figs. 1b and c, Supplementary Fig. 2). We note that the tip of the Ag nanoneedles is typically not covered by the Cu layer and thus remains exposed to the electrolyte during the CO<sub>2</sub>RR. The presence of Ag is anticipated to promote the local formation of CO from CO<sub>2</sub>, which can be readily used in the formation of C<sub>2+</sub> species *via* a cascade reaction mechanism. Systematic investigations of the catalytic performance of the Ag-Cu electrodes revealed an optimum composition of 15 %<sub>at.</sub> Ag-Cu (Supplementary Fig. 2b). To control the oxidation state of Cu, we sought to functionalize the catalyst with thiol molecules *via* dip coating. We selected thiadiazole (N<sub>2</sub>SN) and triazole (N<sub>3</sub>N) derivatives as electron deficient functional molecules to react with the surface of the catalyst<sup>41-</sup><sup>44</sup>(Supplementary Fig. 3). For comparison, the bimetallic electrodes were also modified with 1-propanethiol (C<sub>3</sub>) and cysteamine (C<sub>2</sub>N) as model short alkyl and alkyl amine functional groups (Supplementary Fig. 3, and Supplementary Figs. 6c and d). The

modification of the electrode is clearly visible from the change of the water contact angle that varies between  $86^\circ$  and  $129^\circ$  depending on the nature of the functional groups compared to  $84^\circ$  for the pristine catalyst (Supplementary Fig. 7). To verify the presence of the functional groups, we performed energy-dispersive X-ray spectroscopy (EDS). The corresponding elemental map shows the uniform distribution of S, N and C on Ag-Cu electrode whereas a thin amorphous layer is observed under high resolution TEM on the surface of the catalyst with a thickness of  $\approx 2.5$  nm (Figs. 1d, e, f and Supplementary Fig. 8). The existence of an organic layer on the Ag-Cu electrodes is further confirmed by the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and the electron energy loss spectroscopy (EELS) mapping of the carbon and sulfur elements. Remarkably, the EELS spectrum of the C-K edge displays fine structures characteristics of carbon linked to heteroatoms at  $\approx 292$  eV (Figs. 1 g and h, Supplementary Fig. 9). Raman and Fourier transformed infrared (FTIR) spectroscopies were also used to further confirm the successful attachment of the functional groups on the surface of the catalyst (Fig. 1i and Supplementary Fig. 10). The Raman signatures of the different grafted molecules were detected on the surface of the Ag-Cu electrodes, while strong FTIR bands at  $1303\text{ cm}^{-1}$ ,  $1584\text{ cm}^{-1}$  and  $1622\text{ cm}^{-1}$  are only presented on  $\text{N}_2\text{SN}$ -,  $\text{N}_3\text{N}$ - and  $\text{C}_2\text{N}$ -functionalized Ag-Cu electrodes and attributed to the C-C or C-N stretching, the  $\text{NH}_2$  scissor and the C-N stretching modes respectively <sup>45,46,47</sup> (Supplementary Fig. 10). The successful functionalization with thiadiazole and triazole is further confirmed from the deconvolution of the X-ray photoelectron spectra from the S2p and N1s regions respectively (Supplementary Figs.

11b and c). The peak of S2p was deconvoluted into three doublets at 162.75, 164.23 and 168.31eV for the S2p<sub>3/2</sub>, corresponding to S-H and S-C bonds on both thiadiazole and triazole, respectively<sup>48</sup>. Analogously, the N1s spectrum (Supplementary Fig. 11c) can be divided into two components at 398.24 and 399.63 eV, which reflects the existence of N-N, C-N, and N-H bonds on the surface of functionalized electrodes. The presence of crystalline Ag and Cu on the gas diffusion electrode was further observed from the X-ray diffraction patterns, whereas the presence of distinct peaks from the Ag and Cu facets agrees with the absence of alloy structure of the bimetallic catalyst. (Supplementary Fig. 12). To clarify the orientation of the aromatic heterocycles on the catalyst surface, we carried out density functional theory (DFT) calculations to estimate the total energy and the binding energy of thiadiazole on Cu using a model with 5 Cu (111) slabs (Supplementary Figs. 4 and 5). Among the different configurations tested, the adsorption of thiadiazole is more stable when the N<sub>2</sub>-N<sub>3</sub> nitrogen atoms of the diazole sit on Cu (111) and the binding energy is estimated to -1.08 eV – at least 0.37 eV lower than for the other configurations (Supplementary Table 1).

### **Investigation of the CO<sub>2</sub> electro-reduction**

The functionalized electrodes were electrochemically tested in a H-cell reactor using Argon and CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> electrolyte solutions. Figure 2a shows that thiadiazole (N<sub>2</sub>SN) and triazole (N<sub>3</sub>N) functionalized electrodes exhibit the highest current density and lowest onset potential in CO<sub>2</sub>-saturated solution. We then evaluated

the Faradaic efficiency (FE) by using nuclear magnetic resonance (NMR) and gas chromatography (GC) (See details in the Methods section). H<sub>2</sub>, CO, formate, CH<sub>4</sub> and C<sub>2+</sub> products were formed on the bimetallic electrode (Supplementary Fig.13). Remarkably, the Faradaic efficiency for C<sub>1</sub> and H<sub>2</sub> – obtained *via* the CO<sub>2</sub>RR and HER – decreased after functionalization with thiazole and thiadiazole, while the FE for C<sub>2+</sub> products sharply increases (Fig.2b). Ethylene and ethanol are the major C<sub>2+</sub> products detected, together with trace amount of acetate and n-propanol (Supplementary Fig.14). The FE for C<sub>2+</sub> on N<sub>2</sub>SN- and N<sub>3</sub>N-functionalized electrodes are estimated to 57.3 % and 51.0% at -1.2 V versus the reversible hydrogen electrode (*vs.* RHE) compared to only 18% for the pristine catalyst corresponding to enhancements of 3.1 and 2.8 folds respectively (Fig.2b). The selectivity towards the formation of C<sub>2+</sub> products for both thiazole and thiadiazole functional groups increases continuously with increasing voltage from -0.3 to -1.2 V *vs.* RHE and starts decreasing after -1.3 V, whereas the values of FE for C<sub>1</sub> products and H<sub>2</sub> exhibit a volcano-shaped dependence with the applied potentials (Supplementary Figs.15a and b). This leads to an obvious enhancement of the specific current density for C<sub>2+</sub> products ( $j_{C_{2+}}$ ) up to 5 folds at -1.2 V *vs.* RHE (Fig.2c). Conversely, the functionalization of the Ag-Cu electrodes with short alkyl or amino alkyl chains does not suppress the HER pathway nor improve the CO<sub>2</sub>RR activity (Fig. 2d). C<sub>2</sub>N- and C<sub>3</sub>- modified catalysts clearly display lower activities towards the CO<sub>2</sub>RR, notably with a minimal production of C<sub>2+</sub> species and a relatively large FE for the evolution of H<sub>2</sub>. Our results therefore highlight the importance of the nature of the functional groups on the CO<sub>2</sub>RR performance. To better

evaluate the selectivity of  $C_{2+}$  products on thiadiazole- and triazole-functionalized Ag-Cu electrodes, we calculated the ratio in FE for  $C_{2+}$  products and hydrogen ( $FE_{C_{2+}}/FE_{H_2}$ ) (Fig. 2e). Compared with pristine and alkyl functionalized electrodes, both  $N_2SN$  and  $N_3N$  functional groups present the largest  $FE_{C_{2+}}/FE_{H_2}$  ratios – illustrating that the functionalization with aromatic heterocycles efficiently directs the reaction pathway towards the formation of  $C_{2+}$  products while suppressing the HER. Electrochemical impedance spectroscopy (EIS) measurements were performed to explore the charge transfer processes on the surface of the different electrodes during the electrolysis of  $CO_2$ . The charge transfer resistance of the  $N_2SN$ - and  $N_3N$ -functionalized electrodes is not substantially perturbed compared to that of the pristine bimetallic catalyst (Supplementary Fig.16). On the contrary, the resistance is significantly larger in the case of electrodes functionalized with 1-propanthiol and cysteamine indicating that the charge transfer is strongly affected; likely due to the strong hydrophobicity of the surface of the alkyl-functionalized catalyst.

To gauge the stability of the functionalization, we operated the electrodes at a potential of -1.2 V vs. RHE for more than 20 hours in the H-cell reactor, while recording the current density and continuously analyzing the products of the reaction (Supplementary, Fig. 17). The  $N_2SN$ - and  $N_3N$ -functionalized electrodes demonstrated stable performance with a retention of the current density of 94% and 91% respectively – sharply improved compared to that of pristine Ag-Cu at 78%. The FE for  $C_{2+}$  of  $N_2SN$  and  $N_3N$  functionalized AgCu electrodes remains as high as 54% and 46.5% after 20 hours, which demonstrate that the selectivity for the reaction pathway on the surface of

the electrode is not modified during electrolysis. To further confirm the apparent stability of the functionalized electrode, we performed XPS spectroscopy to evaluate the N:Cu ratio after 30 min, 1 hour, 24 hours and 100 hours. The ratio is found to be virtually constant suggesting a robust grafting of the functional groups on the catalyst surface (Supplementary Figs. 18 and 19, Table 2).

Next we sought to explain the fundamental mechanism responsible for the improved CO<sub>2</sub>RR properties using *ex-situ* X-ray photoelectron spectroscopy (XPS) and *operando* XAS. XPS was firstly used to characterize the surface composition and determine the oxidation state of Cu. From the Cu2p region, no significant change of the oxidation state of Cu can be detected from the functionalized catalysts (Fig. 3a left). For comparison, after exposure to H<sub>2</sub>O<sub>2</sub>, the electrodes are clearly oxidized as confirmed by the apparition of Cu2p3/2 signals at binding energy at 934.6 eV and the satellite peak at 942.6 eV, which is attributed to the formation of Cu<sup>2+</sup><sup>48</sup>. Our XPS results confirm that functionalization does not lead to a dramatic modification of the oxidation state of the surface of the Cu. The small change of binding energy between Cu<sup>1+</sup> and Cu<sup>0</sup> makes the precise identification of Cu<sup>1+</sup> impossible from the Cu2p regions<sup>22</sup>. To overcome this limitation, we therefore used the Cu Auger L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> transition to qualitatively discuss the presence of Cu<sup>1+</sup> in functionalized Ag-Cu as this mode is known to be more sensitive to the modification of the electron density on the d-band of the metals<sup>49,50</sup>. The Cu Auger L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> transition arises from a single L<sub>3</sub> (2p3/2) core-hole decay *via* the Auger process involving two M<sub>45</sub> (3d) electrons for the formation of a final 3d<sup>8</sup>

configuration. The right panel of Figure 3a presents the two final-state terms splitting from L–S coupling  $^1G$  and  $^3F$ . The features of the Cu Auger excitation spectrum ( $^3F$  and  $^1G$ ) reveal the valence configuration of Cu. The most intense peak in each spectrum corresponds the  $^1G$  final-state term, which is due to the  $^1G$  multiplet of the two-localized-hole  $d^8$  final state<sup>51-53</sup>. It has previously been shown that the  $^1G$  peak energy positions of CuO, Cu<sub>2</sub>O, and Cu are located at 917.1, 915.8, and 918.0 eV, respectively<sup>54</sup>.  $^1G$  peak is also broader and at a lower energy for copper oxide compared with that of metal copper<sup>55</sup>, while the  $^3F$  peak is visible in the case of Cu<sup>0</sup> but not for Cu<sup>1+</sup> and Cu<sup>2+</sup><sup>55</sup>. For pristine and C<sub>3</sub>- and C<sub>2</sub>N- functionalized Ag-Cu, we observed that the energy positions of the  $^1G$  peak are located at 918.3 eV(pristine), 915.9 eV (C<sub>3</sub> and C<sub>2</sub>N), respectively, while the distinct  $^3F$  peak is detected at 918.2 eV for both C<sub>3</sub>- and C<sub>2</sub>N-Ag-Cu, in agreement with the existence of Cu<sup>0</sup> (Supplementary Table 3). Conversely, in the case of the N<sub>2</sub>SN- and N<sub>3</sub>N samples, the  $^1G$  peak is identified at 915.8 and 916.0 eV, respectively, which is lower than that for Cu<sup>0</sup> and Cu<sup>2+</sup> and close to that of Cu<sup>1+</sup> (915.8 eV). We also note that the  $^3F$  peak is also visible for both samples pointing out the presence of Cu<sup>0</sup>. These results indicate that the valence state of the N<sub>2</sub>SN and N<sub>3</sub>N samples may be Cu<sup>δ+</sup> with  $0 < \delta < 1$ .

To precisely evaluate the electronic states of copper on functionalized Ag-Cu electrodes, we then performed X-ray absorption near-edge spectroscopy (XANES). The absorption edges of functionalized catalysts reside between those of copper metal (Cu<sup>0</sup>) and Cu<sub>2</sub>O (Cu<sup>1+</sup>) used as references (Fig. 3b). To better compare the influence of the different functional groups, we estimated the copper oxidation state as a function of

copper K-edge energy shift (Fig. 3b). The oxidation state of copper in the N<sub>2</sub>SN- and N<sub>3</sub>N- functionalized Ag-Cu was found to be +0.53 and +0.47 respectively – pointing out the withdrawing properties of the selected heterocycles (Supplementary Table 4). Remarkably, C<sub>3</sub>- and C<sub>2</sub>N- functionalized samples displayed a minimal shift by comparing with pristine Cu electrode and the Cu reference, suggesting the alkyl groups are not prone to modulate the oxidation state nor the coordination environment of Cu. To explore the stability of electron-withdrawing ability of the grafted heterocycles, we measured the oxidation state of Cu *post* CO<sub>2</sub>RR using *ex-situ* XANES. After 30 min of operation at -1.2 V vs. RHE, the oxidation state of copper was estimated be + 0.51 (Inset Fig. 3b and c). This value is similar to that obtained from the freshly prepared samples: +0.53, which demonstrates the stability of the oxidation state of the functionalized Ag-Cu electrodes. Similarly, no obvious shift of the Cu K-edge was observed from the *in-situ* XANES measurements at increasing applied potential up to -1.2 V vs. RHE and the spectra virtually overlap. This confirms the robustness of the oxidation state of the Cu thanks to the stable attachment of the functional groups (Fig. 3c, Supplementary Fig.20). To better understand the role of Cu<sup>δ+</sup> on the CO<sub>2</sub>RR properties, we investigated the influence of the copper oxidation state on the FE for C<sub>2+</sub> and H<sub>2</sub> (Fig. 3d). Remarkably, we identified a strong correlation between the oxidation state and the FE for C<sub>2+</sub>, which points out that the larger oxidation state of Cu benefits the CO<sub>2</sub>RR properties and the formation of C<sub>2+</sub> products in line with recent findings from the literature<sup>51,56</sup>.

It is well known that the formation of multi-carbon products in CO<sub>2</sub>RR proceeds *via* the formation of the \*CO intermediate, and its subsequent dimerization in CO=CO

or \*CO-COH intermediates<sup>57-59</sup>. To gain insight into the C–C coupling mechanism on functionalized and pristine Ag-Cu during CO<sub>2</sub>RR, the surface of the catalysts was probed using *operando* Raman spectroscopy in order to elucidate the interactions between the catalyst surface and the adsorbed \*CO intermediate (Fig. 3e and Supplementary Fig.21, and Supplementary Table 5). The presence of the surface-adsorbed \*CO was identified from the vibration modes at  $\approx 280\text{ cm}^{-1}$  and  $\approx 365\text{ cm}^{-1}$  that originate from the Cu–CO frustrated rotation and Cu–CO stretch, respectively<sup>60,61</sup>. The broad band in the range of  $1900\text{--}2120\text{ cm}^{-1}$  was assigned to the C $\equiv$ O stretch. To confirm that the detected signals are solely due to the CO<sub>2</sub>RR, the Raman spectra were also recorded using Ar-saturated K<sub>2</sub>SO<sub>4</sub> as a controlled experiment and no peaks were detected at these frequencies (Supplementary Fig. 21f). The Raman vibration modes around  $1900\text{--}2120\text{ cm}^{-1}$  have recently been the focus of several studies and there is currently a general agreement that the high frequency region ( $>2000\text{ cm}^{-1}$ ) and the low frequency region ( $1900\text{--}2000\text{ cm}^{-1}$ ) originates to atop-bound CO and bridge-bound CO. Atop (CO<sub>top</sub>) and bridge (CO<sub>bridge</sub>) configurations correspond to a CO bound on top of one Cu atom and between two Cu atoms respectively<sup>50,62,63</sup>. Compared to pristine as well as 1-propanthiol- and cysteamine-functionalized electrodes, N<sub>2</sub>SN- and N<sub>3</sub>N-functionalized Ag-Cu exhibit the relatively intense signals at  $365\text{ cm}^{-1}$  and  $1900\text{--}2000\text{ cm}^{-1}$ . Our systematic investigations revealed that the intensities of both regions are also found to increase with the overpotentials<sup>32</sup> (Supplementary Figs. 21a and b). Importantly, we observed that there is an obvious relationship between the peaks at  $365\text{ cm}^{-1}$  and  $1900\text{--}2100\text{ cm}^{-1}$  and the Faradaic efficiency towards the formation of C<sub>2+</sub> products (Fig.

3f). These results therefore point out the strong correlation between the density of adsorbed \*CO on the catalyst surface and the formation of C-C bonds in agreement with the \*CO being the key intermediate involved in the dimerization reaction and the formation of C<sub>2+</sub> products. We note that 1-propanethiol functionalized Ag-Cu electrodes display the most intense peak at 280 cm<sup>-1</sup> whereas no peaks are detected at 1900–2120 cm<sup>-1</sup>. This indicates the adsorbed \*CO is not present in the form of CO<sub>atop</sub> nor CO<sub>bridge</sub> configurations. We speculate that the hydrophobic surface of the 1-propanethiol functionalized Ag-Cu induces the existence of a high energy barrier for the protons to reach the surface of the catalyst that prevents the stabilization of the \*CO in these bound configurations as previously proposed for other transition metals<sup>50</sup>. Interestingly, we observed a volcano-shaped relationship between the Faradaic efficiency for C<sub>2+</sub> products and the ratio of atop-bound CO to bridge-bound CO on the surface of Ag-Cu (Fig. 3g and Supplementary Fig. 22). The Faradaic efficiency reaches a maximum for a ratio of CO<sub>atop</sub> to CO<sub>bridge</sub> of 0.4-0.5 corresponding to thiadiazole and triazole functionalized catalysts, while the ratio decreases for 1-propanethiol and increases for pristine and cysteamine respectively. We hypothesized that the density of CO<sub>atop</sub> and CO<sub>bridge</sub> on the surface of the catalysts is influenced by the electron withdrawing ability of the heterocycles as suggested by the volcano shaped relationship between the oxidation state of Cu and the ratio of CO<sub>atop</sub> to CO<sub>bridge</sub> (Supplementary Fig. 23). Overall our *ex-situ* and *operando* characterizations of the modified bimetallic catalyst establish an obvious correlation between the electron withdrawing ability of the functional groups and the oxidation state of Cu, which translate into a larger

concentration of adsorbed \*CO on the electrode surface and ultimately a higher probability for \*CO to dimerize.

### **CO<sub>2</sub>RR using a membrane–electrode-assembly (MEA)**

To evaluate the potential of our approach for practical applications towards the electrosynthesis of C<sub>2+</sub> products, we integrated the different functionalized bimetallic electrodes into 4 cm<sup>2</sup> membrane–electrode-assembly (MEA) flow electrolyzers (Supplementary Figs. 24 and 25). The synthesized liquid products at the cathode were collected by using a cold trap connected to the cathode gas outlet. We also analyzed the liquid products in the anolyte to detect liquid products that may have crossed over the membrane electrolyte. We firstly scrutinized the activity of N<sub>2</sub>SN-functionalized Ag-Cu in a MEA electrolyzer by flowing Ar (used as blank experiment) and CO<sub>2</sub> in the cathode compartment (Supplementary Fig. 26) and found that the catalyst can convert CO<sub>2</sub> when operating in a catholyte-free MEA system. We then characterized the current-voltage response of all the functionalized catalysts between -2.8 V and -4.8 V and a constant flow of CO<sub>2</sub> of 10 standard cubic centimeters per minute (sccm) (Fig. 4a). The total current for the different Ag-Cu electrodes increased from 4×10<sup>-2</sup> A up to over 1.6 A. The N<sub>2</sub>SN-functionalized electrodes displayed the largest specific current density for C<sub>2+</sub> at 261 mA cm<sup>-2</sup> together with the maximum FE for C<sub>2+</sub> products and the lowest FE for H<sub>2</sub> at ~80% and 14%, respectively (Fig. 4b , Supplementary Fig. 27a and Supplementary Fig. 28a). Remarkably the selectivity for the C<sub>2+</sub> products increases

together with the electrolysis response when increasing the operating potential of the full cell. The catalytic activity towards the competitive HER concurrently decreases up to -4.55 V (Fig. 4b and Supplementary Fig. 28c). Compared to pristine Ag-Cu, the FE for  $C_{2+}$  products from  $N_2SN$ - and  $N_3N$ -functionalized electrodes demonstrated an average enhancement for  $C_{2+}$  of 3.1 and 2.6 folds respectively over the extended range of full-cell potentials (Fig. 4c and Supplementary Fig. 29). To further assess the performance of the functionalized Ag-Cu electrodes in the MEA devices, we calculated the ratio of  $j_{C_{2+}}$  to  $j_{C_1}$  for the different potential. We found that Ag-Cu functionalized with thiadiazole displays the largest values and the ratio reaches at a maximum value of  $\approx 10$  at a current density of  $261.4 \text{ mA cm}^{-2}$  (Supplementary Fig. 30). These results demonstrate that the controlled orientation of the reaction pathways towards the synthesis of ethanol and ethylene observed in the H-cell reactors can be transposed to the MEA devices (Supplementary Fig. 24). We also found that the total FE for gaseous products gradually decreased with the increase of the full-cell voltage indicating a shift toward the formation of liquid products at high operating potential. The Faradaic efficiency for ethanol and n-propanol reached 16.5% and 6.1% at a voltage of -4.4 V (Supplementary Fig. 27a).

To better understand the influence of operating conditions on the  $CO_2RR$  performance of the MEA device, we varied the  $CO_2$  flow rate from 3 to 100 sccm at a constant full-cell potential of -4.55 V. When using  $N_2SN$ -functionalized Ag-Cu electrodes, the FE for ethylene reached a peak at 56% at  $\sim 10$  sccm (Fig. 4d) together with a sharply reduced FE for  $H_2$  at only 15.2%. The selectivity for ethylene rapidly

drops down to only  $\sim 5\%$  for a  $\text{CO}_2$  flow rate of 3 sccm, suggesting that the feed in  $\text{CO}_2$  is not sufficient to produce enough  $\ast\text{CO}$  to dimerize on the surface of the catalyst. We also estimated the full-cell energy efficiency ( $\text{EE}_{\text{full-cell}}$ ) for  $\text{N}_2\text{SN}$ -functionalized Ag-Cu for the different operating potential. Both the FE and  $\text{EE}_{\text{full-cell}}$  values for  $\text{C}_{2+}$  products increased with the increase of the current density and achieved a maximum  $\text{FE}_{\text{C}_{2+}}$  of  $\approx 80 \pm 1\%$  and an  $\text{EE}_{\text{full-cell}}$  of 20.3% at a specific current density larger than  $260 \text{ mA cm}^{-2}$  for the production of  $\text{C}_{2+}$  (Figs. 4e). By comparing the performance metrics of  $\text{N}_2\text{SN}$ -functionalized Ag-Cu with previous literature benchmarks based on MEA devices, we observed that thiadiazole -functionalized Ag-Cu allows achieving superior performance notably thanks to a record-high  $\text{CO}_2$ -to- $\text{C}_{2+}$  conversion rate of  $785 \mu\text{mol h}^{-1} \text{ cm}^{-2}$  (Fig. 4f).

We finally examined the stability of the  $\text{N}_2\text{SN}$ -functionalized Ag-Cu electrodes in a full-cell MEA electrolyzer under continuous operation at a  $\text{CO}_2$  flow rate of 10 sccm and a cell voltage of -4.55V. The performance of the cell was found to be stable over 100 hours with an average FE of 51% for ethylene and an average current of around 1.6 A (Fig. 4g). After 100 hours, the retention of the FE for ethylene and the current were estimated to be 48% and 1.58A corresponding to retentions of 94% and 99% respectively. The stability of the  $\text{CO}_2\text{RR}$  properties is further accompanied by a high stability of the catalyst morphology and microstructure (Supplementary Fig. 31).

## Conclusions

Our study describes a simple and robust molecular engineering strategy to tune the

oxidation state of Cu electrodes *via* functionalization. We identified that strong electron withdrawing groups based on aromatic heterocycles can effectively orient the pathway of the CO<sub>2</sub>RR reactions towards the synthesis of C<sub>2+</sub> molecules. Functionalization of the surface of a bimetallic Ag-Cu catalyst with thiadiazole and triazole derivatives led to an enhancement of the FE<sub>C<sub>2+</sub></sub> up to  $\approx 80 \pm 1\%$ , corresponding to ratios of FE<sub>C<sub>2+</sub></sub> to FE<sub>C<sub>1</sub></sub> and FE<sub>C<sub>2+</sub></sub> to FE<sub>H<sub>2</sub></sub> of 10 and 5.3 respectively. By combining Auger and XANES spectroscopy we identified that the superior performance towards the CO<sub>2</sub>-to-C<sub>2+</sub> conversion originates from the controlled *p*-doping of the Cu and presence of Cu<sup>δ+</sup> with  $0 < \delta < 1$ . The functionalized Ag-Cu electrodes were found stable, which translates into a prolonged production of C<sub>2+</sub> products for >100h.

## Methods

**Chemicals.** Copper sulfates (CuSO<sub>4</sub>, 99%), silver nitrate (AgNO<sub>3</sub>, 99%), ammonium sulfate (99%), ethylenediamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 99.5%), potassium hydroxide (KOH, 90%), potassium bicarbonate (KHCO<sub>3</sub>, 99.7%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 99.99%), Iridium (III) chloride hydrate (IrCl<sub>3</sub> · xH<sub>2</sub>O, 99.9%), 5-Amino-1,3,4-thiadiazole-2-thiol (C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>S<sub>2</sub>, 95%), 3-amino-1,2,4-triazole-5-thiol (C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>S, 99%), cysteamine (C<sub>2</sub>H<sub>7</sub>NS, 99%) and 1-Propanethiol (C<sub>3</sub>H<sub>8</sub>S, 99%) were purchased from Sigma-Aldrich. Nafion 117 and anion exchange membrane (Fumapem FAA-3-50), gas diffusion layer (Freudenberg, H23C6), and titanium mesh were obtained from Fuel Cell Store. 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>.

**Electrodes preparation.** Before depositing catalysts, gas diffusion electrode (GDE) was treated with sulfuric acid by sonicating 20 minutes. After acid treatment, the remaining acid was rinsed with deionized water for 5 min three times, and gas diffusion layer was dried at room temperature. To obtain the working electrodes, 15 %<sub>at.</sub> AgCu catalysts were prepared through a pulse electrodeposition approach under CO<sub>2</sub> bubbling condition. Firstly, electrochemical deposition of the Ag catalyst was performed using a potentiostat (VSP potentiostat from Bio-Logic Science Instruments). The electrolyte used was composed 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. Ag catalyst was electrodeposited on GDE at a current density of 15 mA cm<sup>-2</sup> with on- and off-time pulsing parameters of 0.25 and 3 s, respectively. Then, the Cu was electrodeposited on Ag at a constant current density of -400 mA cm<sup>-2</sup> for 45 s to obtain the 15 %<sub>at.</sub> AgCu electrode. The solution consisted of 0.2 M CuSO<sub>4</sub> and 1M H<sub>2</sub>SO<sub>4</sub> with continuously CO<sub>2</sub> bubbling.

**Functionalization of the Ag-Cu electrodes.** The different functional groups (organic chemicals(5-Amino-1,3,4-thiadiazole-2-thiol(N<sub>2</sub>SN), 3-amino-1,2,4-triazole-5-thiol(N<sub>3</sub>N), cysteamine(C<sub>2</sub>N) and 1-Propanethiol (C<sub>3</sub>)) were dissolved in ethanol to a fixed concentration of 5 mM. The Ag-Cu electrodes were treated by the different functional solutions *via* dropcasting 20 μL of the solution containing the different thiol reagents on the GDE. After 5 min, the electrode was washed with ethanol and dried under argon flow.

**Physical characterizations.** 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. 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 trimethylsilyl propane sulfonate) 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). 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). An Ag/AgCl electrode and a Pt plate were used as the reference and counter

electrodes respectively. *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 Beijing Synchrotron Radiation Facility (BSRF) on beamline 1W1B and the SOLEIL synchrotron SAMBA beamline, respectively.

***Operando* X-ray absorption spectroscopy (XAS).** *Ex-situ* and *operando* XAS measurements at the copper K-edges were collected at Beijing Synchrotron Radiation Facility (BSRF) on beamline 1W1B and the SOLEIL synchrotron SAMBA beamline, respectively. *Operando* Cu K-edge XAS measurements of functionalized AgCu were obtained by using a 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  $N_2$  (500 mbar)/He (500 mbar) mixture. Two additional ionization chambers filled with 1700 mbar  $N_2$  (in  $I_1$  chamber) and an Ar (150 mbar)/ $N_2$ (850 mbar) mixture (in  $I_1$  chamber) were used for measurements in transmission mode in the case of the reference samples. A custom-built electrochemical cell was used for *operando* XAS measurements. The applied potential was controlled by a VSP potentiostat (Bio-Logic Science Instruments). A platinum wire and Ag/AgCl electrode (3M KCl) were used as counter and reference electrodes, respectively. For the XAS studies, 15%at. Ag-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 drop-coated on the catalyst side, while the other side of the GDL was covered with polyamide tape. The GDL was then tape on a graphite foil and

subsequently, the electrode was mounted in the *operando* cell with the graphite foil acting as a working electrode and window. A 0.5 M solution of  $\text{KHCO}_3$  was used as electrolyte for the  $\text{CO}_2\text{RR}$  and the cell was continuously purged with  $\text{CO}_2$  during the measurements. All measurements were performed at constant potentials of -1.2 V, -1.1 V, -1.0 V and -0.9 V *vs.* RHE. Time-resolved spectra under  $\text{CO}_2\text{RR}$  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 as-prepared catalysts was carried out in R-space in the range from  $R_{\min} = 1 \text{ \AA}$  up to  $R_{\max} = 2.1 \text{ \AA}$ , while for the catalysts in the reduced state,  $R_{\min} = 1.0 \text{ \AA}$  to  $R_{\max} = 3.0 \text{ \AA}$  were used. 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  $\Delta E_0$ . The  $S_0^2$  factors obtained from the deconvoluted EXAFS data of the references were found to be  $0.87 \pm 0.02$  for Cu foil,  $0.32 \pm 0.01$  for  $\text{Cu}_2\text{O}$ .

**Computational details.** All density functional theory (DFT) calculations were carried out in the Vienna Ab-initio Simulation Package (VASP) code with the projector augmented-wave (PAW) method. The exchange–correlation energy was treated using a general gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) formalism. A plane-wave basis with a kinetic energy cutoff of 500 eV was chosen to

expand the electronic wave functions. To investigate the possible binding modes between functional molecular and catalysts, a 5 layers of Cu(111) slab ( $7.7386 \text{ \AA} \times 7.7386 \text{ \AA}$ ), in which the two bottom layers were kept fixed during relaxation, was built with a vacuum space of about  $20 \text{ \AA}$ . For the geometrical optimizations, all atoms were fully relaxed to the ground state with the convergence of energy and forces setting to  $1.0 \times 10^{-5} \text{ eV}$  and  $0.01 \text{ eV \AA}^{-1}$ , where a  $3 \times 3 \times 1$   $\Gamma$ -centered Monkhorst-Pack schemed  $k$ -mesh was used to sample the first Brillouin zone. To compare the bond strength between each group of functional molecular and Cu(111), the adsorption energy ( $E_{ads}$ ) are calculated by using the following formula:

$$E_{ads} = E_{Cu/FM} - E_{Cu} - E_{FM}$$

where  $E_{Cu/FM}$ ,  $E_{Cu}$  and  $E_{FM}$  denote the total electronic energies of an adsorbed system, a clean Cu(111) surface, and the free functional molecular, respectively.

**Electrochemical in H-Cell and MEA configuration.** All electrochemical measurements were carried out at ambient temperature and pressure using a VSP electrochemical station from Bio-Logic 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 reference to the RHE using:

$$E_{RHE} = E_{Ag/AgCl} + 0.197 \text{ V} + 0.0591 * \text{pH}$$

In the H-cell configuration, Ag/AgCl reference electrode (3 M KCl) and Pt plate were used as reference and counter electrodes respectively. The electrolyte consisted in a 0.5 M  $\text{KHCO}_3$  solution (99.9%, Sigma Aldrich), which was saturated with

alternatively CO<sub>2</sub> ( $\geq 99.998$ , Linde) or Ar (5.0, Linde). Prior any experiment, the electrolyte solutions were saturated by bubbling CO<sub>2</sub> or Ar for at least 20 min.

The MEA electrolyzer (Dioxide Materials) was comprised of the Ag-Cu cathode, a Ti-IrO<sub>x</sub> mesh anode and an anion exchange membrane (AEM, Fumasep FAA-3-50, 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>64</sup>.

The AEM was firstly placed between the anode and cathode flow fields and then assembled together (Supplementary Figs. 24 and 25). 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 (Fumapem FAA-3-50) (Dioxide Materials) was activated in 0.5 M aqueous KOH solution for at least 24 hours, washed

with deionized water and used as the anion-exchange membrane(AEM). A 0.1 M  $\text{KHCO}_3$  analyte solution was circulated through the anode side of the electrolyzer with the constant flow rate of 30 ml/min *via* a peristaltic pump, while the fully humidified  $\text{CO}_2$  was supplied to the cathode side with the constant flow rate of 10 standard cubic centimeters per minute (sccm). After three-minutes of initial operation, a full-cell potential of -2.8 V was applied to the electrolyzer and the potential then was gradually increased from -2.8 V with the increments of -0.10 V or -0.05 V. The voltage increments were made upon complete stabilization of the corresponding current, typically 15-20 min.

**Quantification of the  $\text{CO}_2\text{RR}$  products.** The electrochemical data were recorded while simultaneously collecting the  $\text{CO}_2\text{RR}$  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  $^1\text{H}$  NMR spectroscopy (600 Mhz Avance III Bruker 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 test, the MEA electrolyzer was operated at a constant voltage of -4.55 V with a continuous feeding in CO<sub>2</sub>. The gas products were collected at frequent time intervals. The 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 and Energy Efficiency Calculations.** The Faradaic efficiency(FE) of each gas product was calculated as follows:

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

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

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

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

$$R_i = \frac{Q_{total} \times FE_i}{96485 \times z_i \times t \times S}$$

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

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

where  $g_i$  represents the volume fraction of gas product *i*;  $v$  represent 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*; and  $Q_{total}$  represents the charge passed while the liquid products are being collected.  $P_0 = 1.01 \times 10^5$  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 ( $\text{cm}^2$ );  $E_i$  represents the thermodynamic potential (versus RHE) for  $\text{CO}_2\text{RR}$  to species  $i$  and  $E_{\text{cell}}$  represents the cell voltage in two-electrode setup.

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### **Author Contributions**

D.V. conceived the idea, designed the experiments and wrote the manuscript. H.W. designed the experiments with D.V., prepared the electrodes and performed the electrochemical measurements and analyzed the results with D.V. H.W. and D.V. analyzed the data and wrote the manuscript. J. L. discussed the data with H.W and performed the DFT calculations. E.P., C.S. and V.F. carried out the liquid NMR spectroscopy measurements and the XPS/Auger measurements. K.Q., Y.Z. assisted H.W. with the electrochemical and the XANES/HEXAFS measurements. N.O. discussed the reaction mechanism with D.V and H.W.. L.H. and W.W. assisted H.W. with the physical characterizations of the Ag-Cu electrodes. B.R. performed SEM/EDXL. L.L. performed high-resolution TEM on the functionalized Ag-Cu catalysts. P.M. discussed the results with D.V. and H.W.. All of the authors edited the manuscript before submission.

### **Data availability**

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

### **Competing financial interests**

The authors declare no competing financial interests.

### **Additional Information**

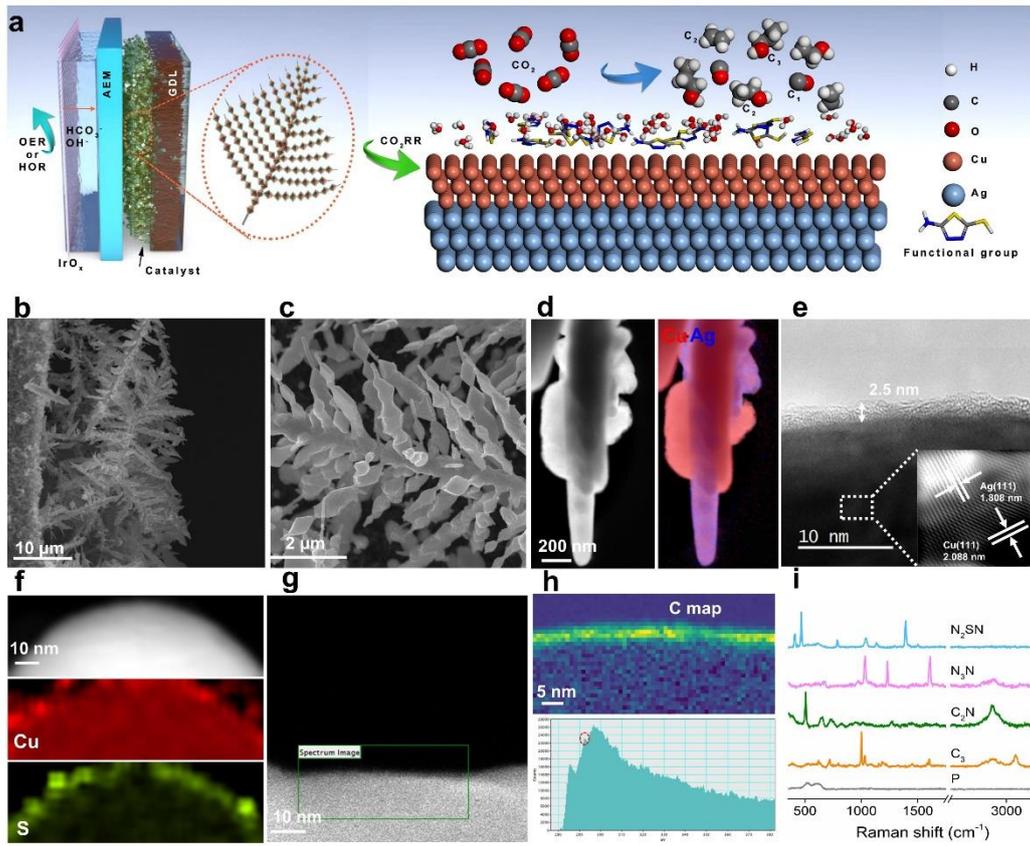
**Supplementary information** and chemical compound information are available in the online version of the paper.

**Correspondence and requests for materials** should be addressed to D.V. (damien.voiry@umontpellier.fr).

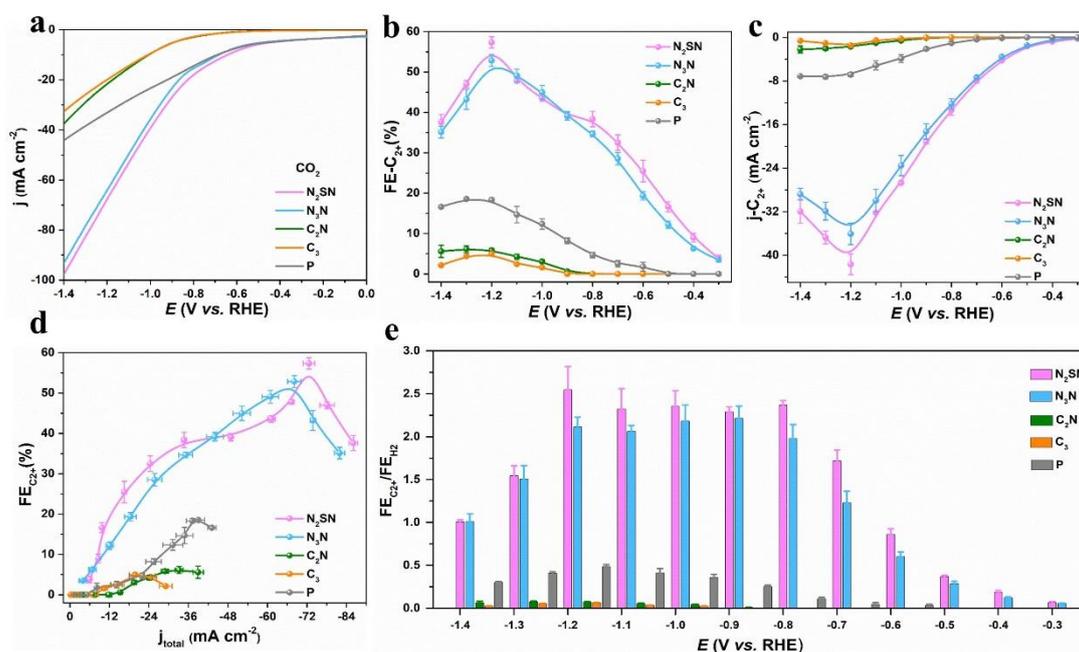
## Figures

### Fig 1 | Structural and elemental composition of the functionalized Ag-Cu catalysts.

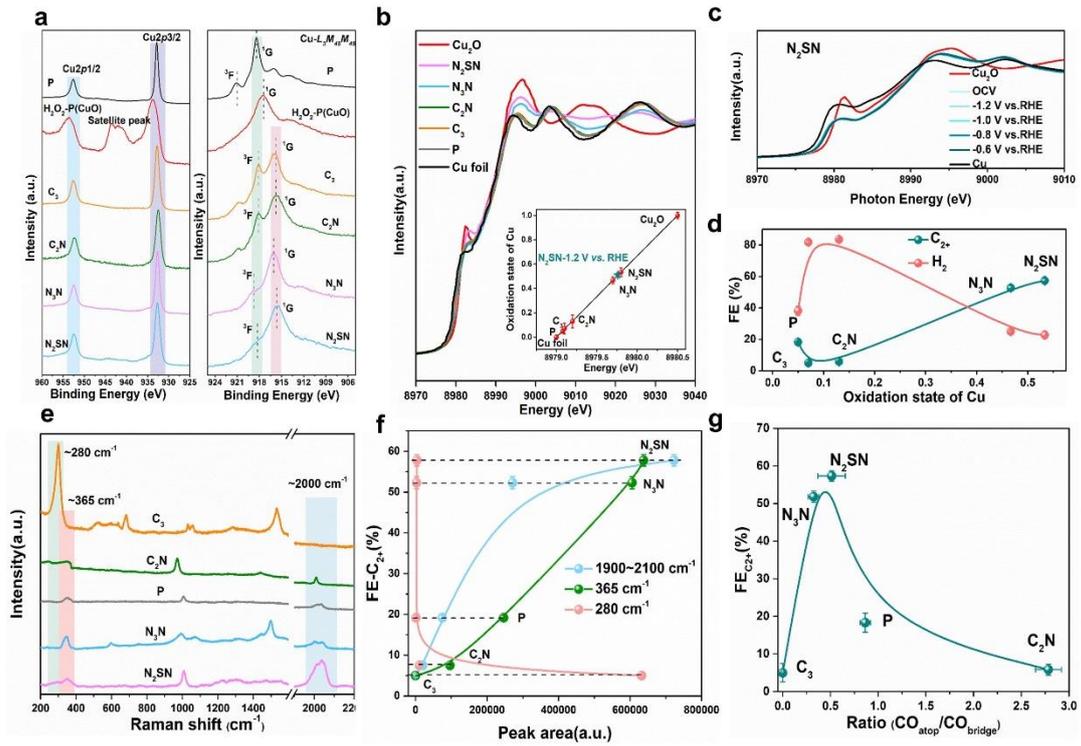
**a**, Schematic representation of the functionalized Ag-Cu electrodes in a membrane. **b**, **c**, Cross-section (**b**) and top-view (**c**) scanning electron microscope (SEM) images of the functionalized hierarchical Ag-Cu catalyst on a gas diffusion electrode (GDE). **d**, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (left) and corresponding Cu and Ag EDS elemental maps of N<sub>2</sub>SN-functionalized Ag-Cu (right). **e**, High-resolution transmission electron microscope (HR-TEM) micrograph of the N<sub>2</sub>SN-functionalized electrode (**e**). **f**, HAADF-STEM image and the corresponding Cu and S EDS elemental maps taken from a section of Cu surface on the N<sub>2</sub>SN-functionalized Ag-Cu electrode. **g**, HAADF-STEM image of the Cu surface of N<sub>2</sub>SN-functionalized Ag-Cu. **h (top)**, Electron energy loss spectroscopy (EELS) elemental mapping of C taken from the area marked by the box in **g**. **h (bottom)**, EELS spectrum of the C-K edge with fine structures characteristics of carbon linked to heteroatoms from N<sub>2</sub>SN layer on the Cu surface. **i**, Raman spectra of pristine (non-functionalized) Ag-Cu (gray), C<sub>3</sub>-functionalized Ag-Cu (orange), C<sub>2</sub>N-functionalized Ag-Cu (green), N<sub>3</sub>N-functionalized Ag-Cu (purple) and N<sub>2</sub>SN-functionalized Ag-Cu (blue).



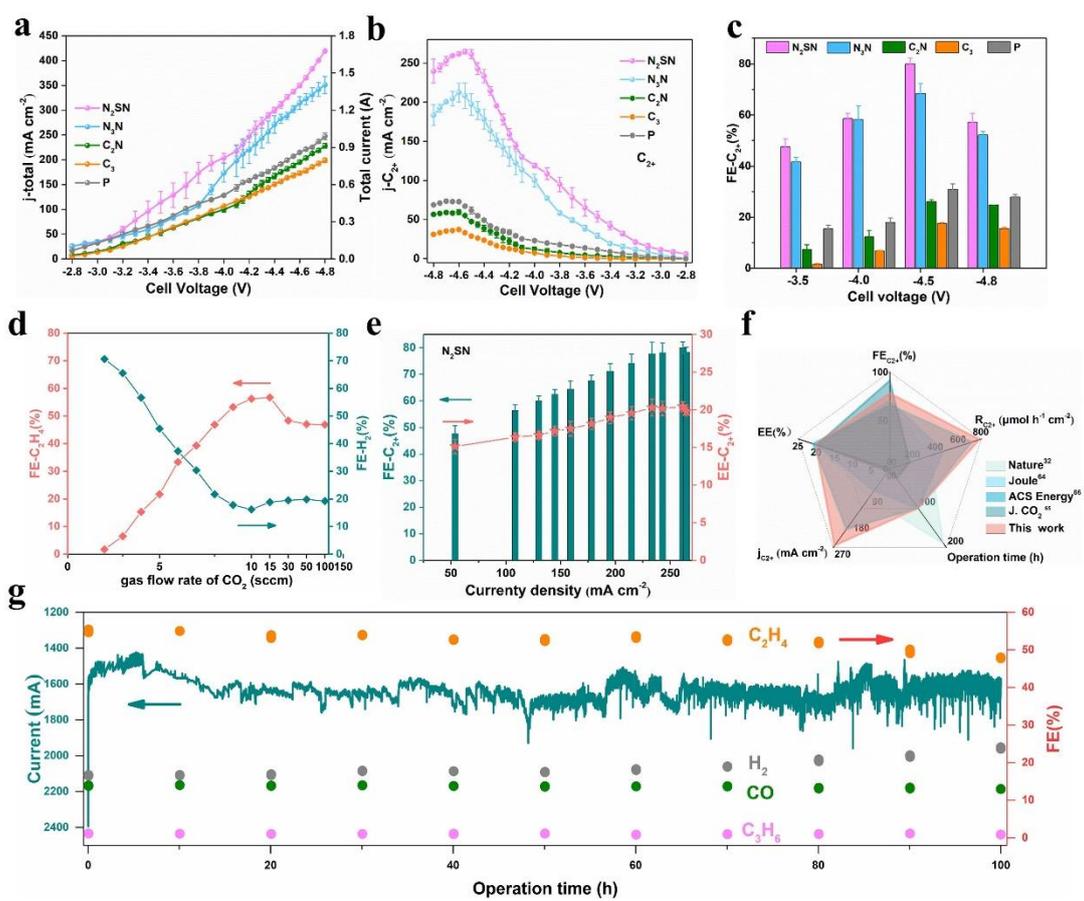
**Fig.2 | CO<sub>2</sub>RR performance of the functionalized Ag-Cu electrodes in a H-cell. a,** Linear scan voltammetry (LSV) curves measured for different samples: N<sub>2</sub>SN, N<sub>3</sub>N, C<sub>2</sub>N, C<sub>3</sub> functionalized Ag-Cu compared to pristine (P) Ag-Cu in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> at electrochemical potential (V) from 0 to -1.4 V vs. RHE. Scan rate, 20 mV s<sup>-1</sup>. **b,** Faradaic efficiency (FE) values for C<sub>2+</sub> products on different samples at various potentials ranging from 0 to -1.4 V vs. RHE and measured in 0.5 M KHCO<sub>3</sub>. **c,** *j*-*j* plots of the partial current densities for the C<sub>2+</sub> products (ethylene and ethanol). **d,** Relationships between the FE for C<sub>2+</sub> and the total current density for all the catalysts **e,** Selectivity for C<sub>2+</sub> products over hydrogen based on the ratio in FEs of C<sub>2+</sub> and hydrogen. The error bars in **b–e** correspond to the standard deviation of three independent measurements.



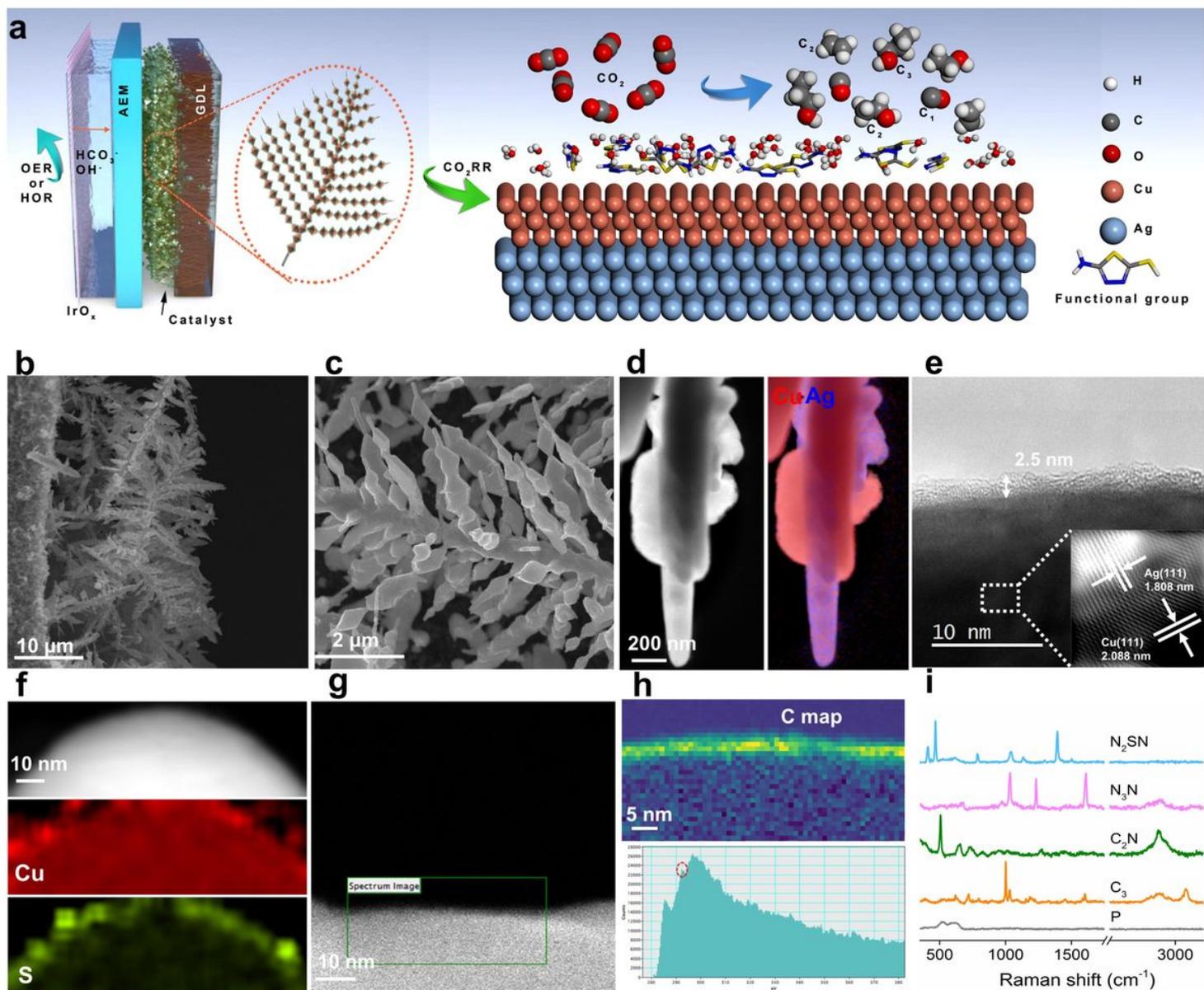
**Fig. 3 | Physical characterizations of the functionalized electrodes using XPS and *operando* Raman and XAS spectroscopy.** **a**, High-resolution spectra of the Cu<sub>2p</sub> regions and Cu L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger transition modes measured by *ex-situ* X-ray photoelectron spectroscopy (XPS) of pristine Ag-Cu sample (P), H<sub>2</sub>O<sub>2</sub>-treated Ag-Cu (H<sub>2</sub>O<sub>2</sub>-P), C<sub>3</sub>-, C<sub>2</sub>N-, N<sub>3</sub>N- and N<sub>2</sub>SN- functionalized Ag-Cu electrodes. **b**, *Ex-situ* and *operando* Copper K-edge X-ray absorption near edge structure (XANES) spectra of pristine and functionalized Ag-Cu electrodes. Inset: Average oxidation state of copper for the corresponding electrodes. **c**, *Operando* Cu K-edge XANES spectra of N<sub>2</sub>SN- functionalized Ag-Cu electrode during CO<sub>2</sub>RR. The measurements were performed after holding the applied potential for 30 minutes. **d**, Evolution of the Faradaic efficiency for C<sub>2+</sub> and H<sub>2</sub> measured at -1.2 V *vs.* RHE with the oxidation state of Cu. **e**, *Operando* Raman spectra for pristine, C<sub>3</sub>-, C<sub>2</sub>N-, N<sub>3</sub>N- and N<sub>2</sub>SN-, functionalized Ag-Cu during CO<sub>2</sub>RR at a fixed potential of -1.2 V *vs.* RHE. The spectra for all the other potentials are presented in Supplementary Fig. 14. **f**, Relationship between the FE for C<sub>2+</sub> products and the Raman peak areas of the frustrated rotational mode of CO at 280 cm<sup>-1</sup>, the Cu–CO stretch at 365 cm<sup>-1</sup> and the C≡O stretch at 1900–2120 cm<sup>-1</sup>, respectively. **g**, Relationship between the FE for C<sub>2+</sub> molecules and the ratio of CO<sub>atop</sub> and CO<sub>bridge</sub> on different Ag-Cu electrodes. The ratio was obtained from the integrated areas of the deconvoluted peaks of the Raman spectra (Supplementary Fig. 22).



**Fig. 4 | CO<sub>2</sub>RR performance of the functionalized Ag-Cu electrodes measured in MEA electrolyzers.** **a**, Relationship between the current and cell voltage relationship of pristine, C<sub>3</sub>-, C<sub>2</sub>N-, N<sub>3</sub>N- and N<sub>2</sub>SN- functionalized electrodes. The error bars represent the standard deviation of the current density of three independent samples during the entire operation and for each cell voltage. The CO<sub>2</sub>RR electrolysis was operated using CO<sub>2</sub> with a flow rate of 10 sccm, 0.1M KHCO<sub>3</sub> anolyte with a flow rate of 30 mL min<sup>-1</sup>. **b**, Corresponding partial current density for the C<sub>2+</sub> products. **c**, Comparison of FEs for C<sub>2+</sub> on the different Ag-Cu electrodes measured at full-cell potentials ranging between -3.5 and -4.8 V. **d**, Evolution of the Faradaic efficiency for C<sub>2+</sub> and H<sub>2</sub> with the CO<sub>2</sub> flow rate. **e**, Evolution of the FEs and full-cell energy efficiency (EE) for C<sub>2+</sub> as a function of specific current densities for C<sub>2+</sub> on the N<sub>2</sub>SN-functionalized Ag-Cu electrode. The error bars represent the standard deviation of three independent samples measured under different current densities. **f**, Comparison of the performance metrics of the MEA electrolyzers based on N<sub>2</sub>SN-functionalized Ag-Cu cathodes with literature benchmark. For each report, the plotted values are those corresponding to the longest duration test<sup>32,64-66</sup>. **g**, CO<sub>2</sub>RR performance of N<sub>2</sub>SN-Ag-Cu catalyst at a full-cell potential of -4.55 V and with a 10 sccm feed in CO<sub>2</sub> over 100 hours. The anolyte consisted in a 0.1 M KHCO<sub>3</sub> solution with a flow rate of 30 ml min<sup>-1</sup>. The blue line represents the current density recorded during the extended CO<sub>2</sub>RR experiment (primary y axis). Each orange, gray, green and purple spheres represent the FEs for C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>, CO and C<sub>2</sub>H<sub>6</sub> averaged from three independent measurements (secondary y axis).



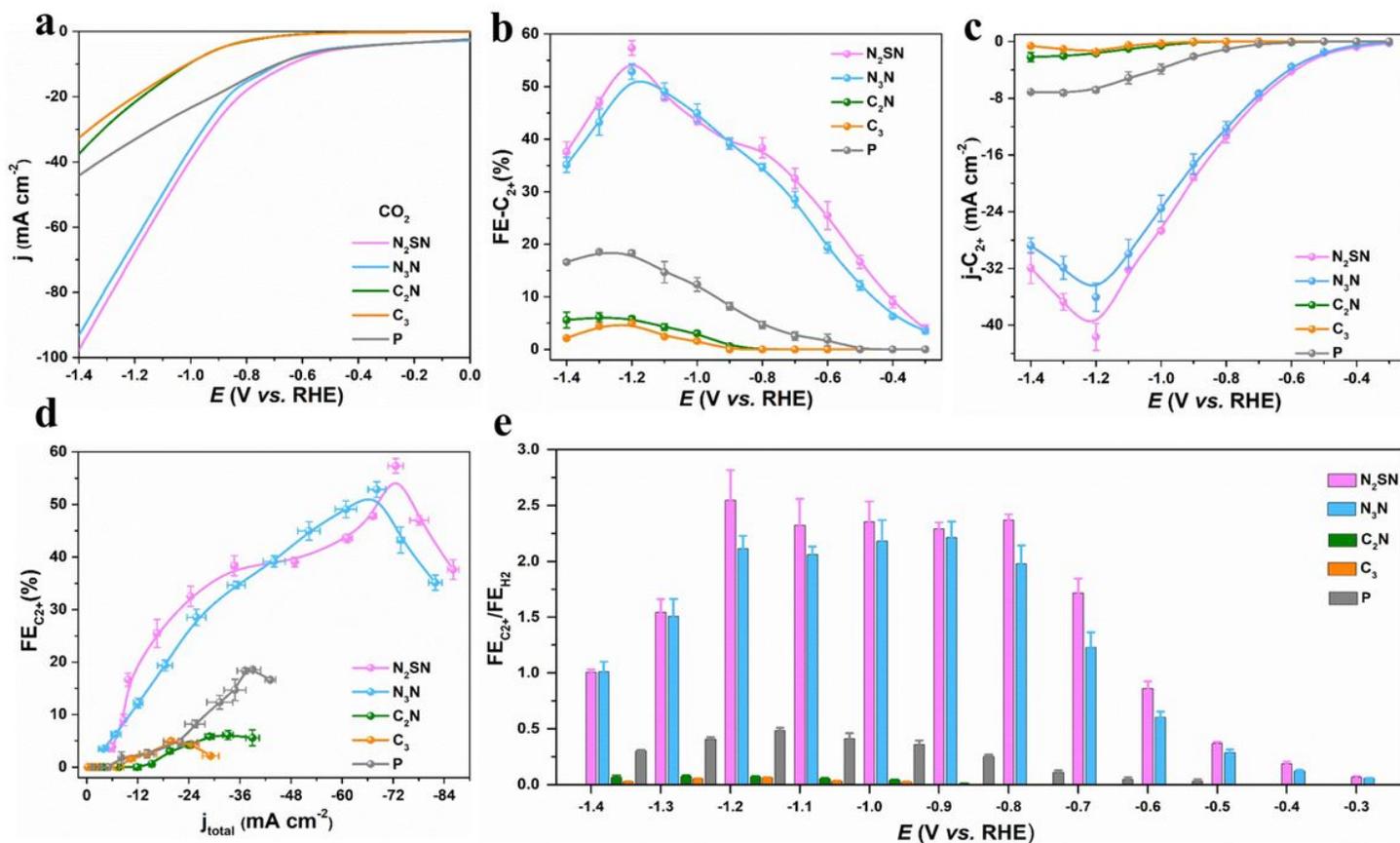
# Figures



**Figure 1**

Structural and elemental composition of the functionalized Ag-Cu catalysts. a, Schematic representation of the functionalized Ag-Cu electrodes in a membrane. b, c, Cross-section (b) and top-view (c) scanning electron microscope (SEM) images of the functionalized hierarchical Ag-Cu catalyst on a gas diffusion electrode (GDE). d, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (left) and corresponding Cu and Ag EDS elemental maps of N<sub>2</sub>SN-functionalized Ag-Cu (right). e, High-resolution transmission electron microscope (HR-TEM) micrograph of the N<sub>2</sub>SN-functionalized electrode (e). f, HAADF-STEM image and the corresponding Cu and S EDS elemental maps taken from a section of Cu surface on the N<sub>2</sub>SN-functionalized Ag-Cu electrode. g, HAADF-STEM image of the Cu surface of N<sub>2</sub>SN-functionalized Ag-Cu. h (top), Electron energy loss spectroscopy (EELS)

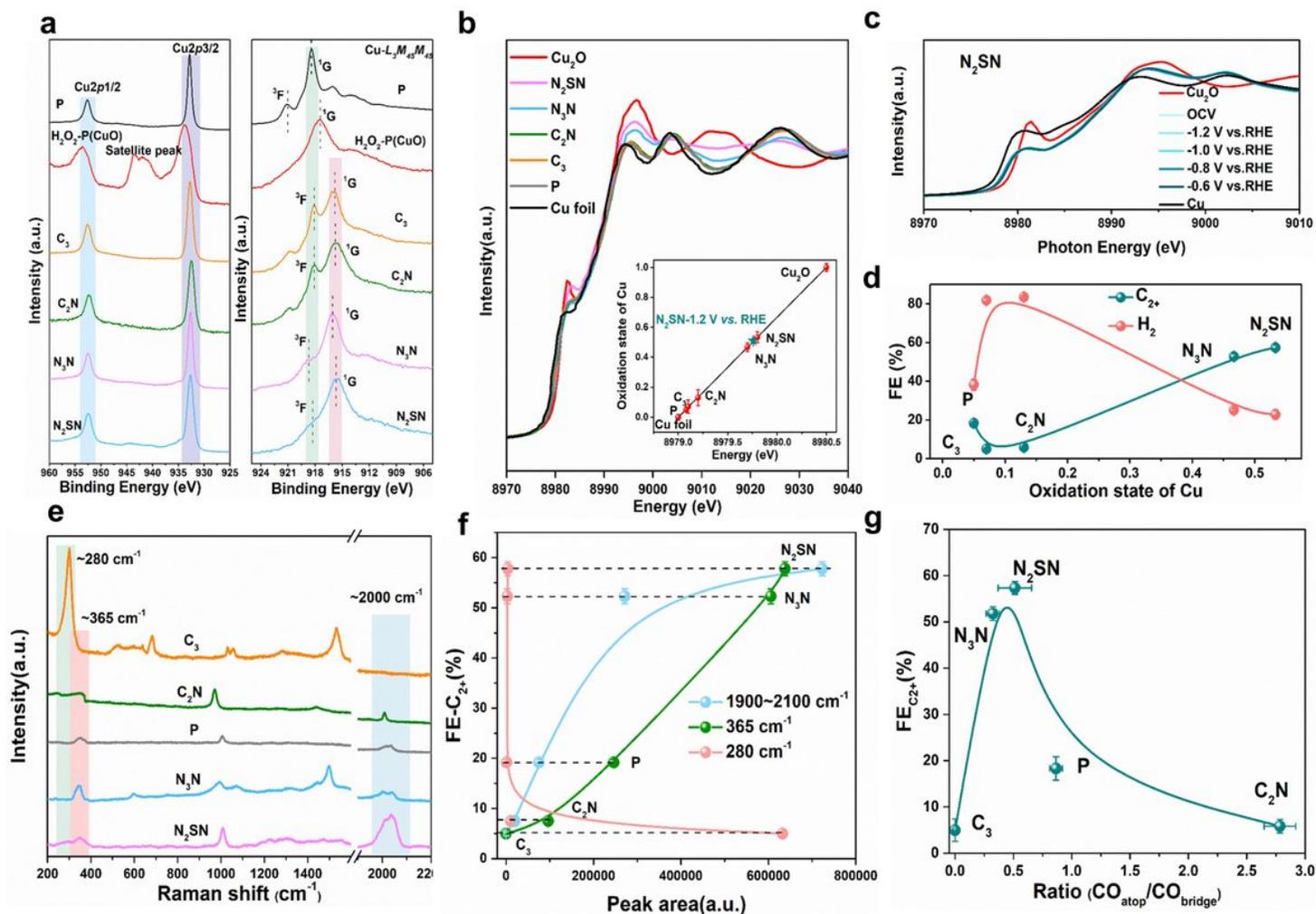
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**Figure 2**

CO<sub>2</sub>RR performance of the functionalized Ag-Cu electrodes in a H-cell. a, Linear scan voltammetry (LSV) curves measured for different samples: N<sub>2</sub>SN, N<sub>3</sub>N, C<sub>2</sub>N, C<sub>3</sub> functionalized Ag-Cu compared to pristine (P) Ag-Cu in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> at electrochemical potential (V) from 0 to -1.4 V vs. RHE. Scan rate, 20 mV s<sup>-1</sup>. b, Faradaic efficiency (FE) values for C<sub>2</sub><sup>+</sup> products on different samples at various potentials ranging from 0 to -1.4 V vs. RHE and measured in 0.5 M KHCO<sub>3</sub>. c, j-V plots of the partial current densities for the C<sub>2</sub><sup>+</sup> products (ethylene and ethanol). d, Relationships between the FE for C<sub>2</sub><sup>+</sup>

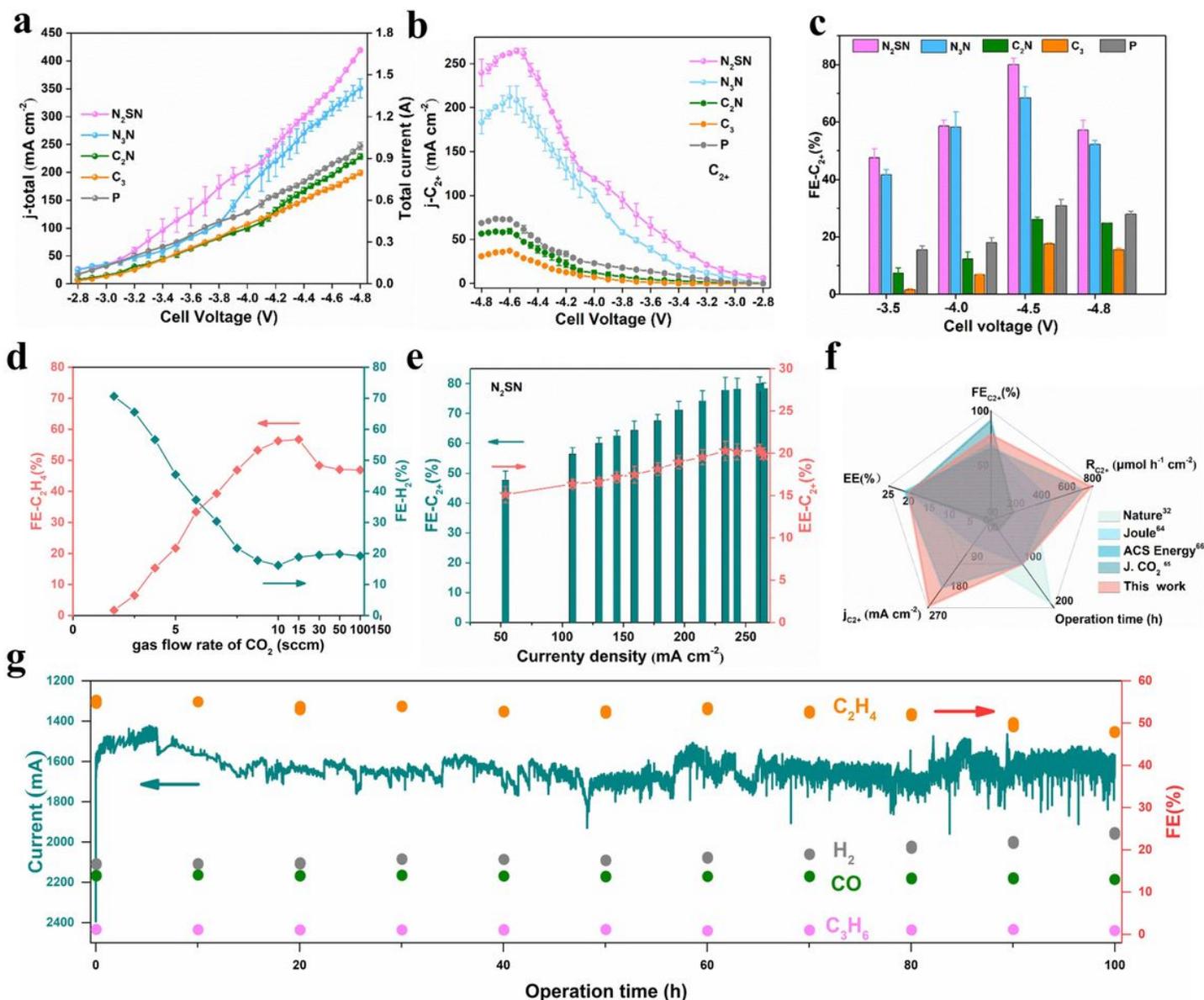
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**Figure 3**

Physical characterizations of the functionalized electrodes using XPS and operando Raman and XAS spectroscopy. a, High-resolution spectra of the Cu<sub>2</sub>p regions and Cu L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger transition modes measured by ex-situ X-ray photoelectron spectroscopy (XPS) of pristine Ag-Cu sample (P), H<sub>2</sub>O<sub>2</sub>-treated Ag-Cu (H<sub>2</sub>O<sub>2</sub>-P), C<sub>3</sub>-, C<sub>2</sub>N-, N<sub>3</sub>N- and N<sub>2</sub>SN- functionalized Ag-Cu electrodes. b, Ex-situ and operando Copper K-edge X-ray absorption near edge structure (XANES) spectra of pristine and functionalized Ag-Cu electrodes. Inset: Average oxidation state of copper for the corresponding electrodes. c, Operando Cu K-edge XANES spectra of N<sub>2</sub>SN- functionalized Ag-Cu electrode during CO<sub>2</sub>RR. The measurements were performed after holding the applied potential for 30 minutes. d, Evolution of the Faradaic efficiency for C<sub>2</sub>+ and H<sub>2</sub> products as a function of the oxidation state of Cu. e, Raman spectra of the samples. f, FE-C<sub>2</sub>+ (%) vs. peak area for different Raman bands. g, FE-C<sub>2</sub>+ (%) vs. the ratio of CO at top and bridge sites.

C2+ and H2 measured at -1.2 V vs. RHE with the oxidation state of Cu. e, Operando Raman spectra for pristine, C3-, C2N-, N3N- and N2SN-, functionalized Ag-Cu during CO2RR at a fixed potential of -1.2 V vs. RHE. The spectra for all the other potentials are presented in Supplementary Fig. 14. f, Relationship between the FE for C2+ products and the Raman peak areas of the frustrated rotational mode of CO at 280 cm-1, the Cu-CO stretch at 365 cm-1 and the C=O stretch at 1900–2120 cm-1, respectively. g, Relationship between the FE for C2+ molecules and the ratio of COatop and CObridge on different Ag-Cu electrodes. The ratio was obtained from the integrated areas of the deconvoluted peaks of the Raman spectra (Supplementary Fig. 22).



**Figure 4**

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## Supplementary Files

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