Improved electrochemical conversion of CO₂ to multicarbon products by using molecular doping

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The conversion of CO₂ into desirable multicarbon products via the electrochemical reduction reaction holds promise to achieve a circular carbon economy. Here, we report a strategy in which we modify the surface of bimetallic silver-copper catalyst with aromatic heterocycles such as thiadiazole and triazole derivatives to increase the conversion of CO₂ into hydrocarbon molecules. 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 C₂⁺ species (ethanol and ethylene) and enhances the reaction rate on the surface of the catalyst by adjusting the electronic state of surface copper atoms. As a result, we achieve a high Faradaic efficiency for the C₂⁺ formation of ≈80% and full-cell energy efficiency of 20.3% with a specific current density of 261.4 mA cm⁻² for C₂⁺ products.
The rapid increase in the atmospheric carbon dioxide (CO₂) levels has motivated the development of carbon capture, utilization, and storage (CCUS) technologies. In this context, the electrochemical reduction of CO₂ to hydrocarbons using renewable energy is regarded as an effective way to close the carbon cycle via the conversion of CO₂ into chemical precursors or fuels. The electrochemical CO₂ reduction reaction (CO₂RR) toward single carbon products has achieved enormous progress, especially for the production of C₂ molecules such as carbon monoxide (CO) or methane (CH₄). Copper (Cu) is one of the few transition metals that can efficiently catalyze the electrolysis of CO₂ to multicarbon products such as ethylene, ethanol, acetate, and propanol. Because multicarbon products possess higher market values and are more energy concentrated, intensive efforts have been devoted to improve the reaction selectivity towards the production of C₂ and C₃₊ molecules. Examples of strategies for optimizing the Faradaic efficiency towards the production of C₂₊ species include alloying, surface doping, ligand modification, and interface engineering.

Designing Cu-based catalysts by adapting some of the concepts of molecular catalysts in order to finely tailor the behavior of the active sites of metallic surfaces is currently regarded as the longstanding interest for the controlled design of novel electrocatalytic materials. Increasing the oxidation state of copper has been suggested to improve the CO₂RR performance and notably the formation of C₂₊ species. Various strategies are being explored to prepare Cuδ⁺⁺ by using controlled oxidation via plasma treatments or doping with boron and halides. 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 CO₂ reduction reaction (CO₂RR). Organic species such as N-aryl pyridinium salts, imidazole, and cysteamine have been reported as an effective lever to tune the reaction selectivity toward the formation of specific products by stabilizing key reaction intermediates. Functionalization of alkyl chains can also lead to better CO₂RR performance by suppressing the competitive hydrogen evolution reaction (HER) via the creation of hydrophobic regions on the surface of the catalyst.

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 Cuδ⁺⁺. 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 Cuδ⁺⁺ 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 C₂₊ products. 

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 (Fig. 1b, c and Supplementary Fig. 2). The catalytic performance of pure Cu and Ag–Cu electrodes were systematically investigated (Supplementary Figs. 2 and 3), and our results indicated that appropriate loading of Ag contributes to the enhancement of the formation of CO, which may further facilitate C₂₊ production on copper. And the optimum composition is 15% at. Ag in Ag–Cu (labeled as 15%at. Ag–Cu). To control the oxidation state of Cu, we sought to functionalize the catalyst with thiol molecules via dip coating. We selected thiadiazole (N₂SN) and triazole (N₃N) derivatives as electron-deficient functional molecules to react with the surface of the catalyst (Supplementary Fig. 4). For comparison, the bimetallic electrodes were also modified with 1-propanethiol (C₃) and cysteamine (C₂N) as model short alkyl and alkyl amine functional groups (Supplementary Fig. 4 and Supplementary Figs. 5c, d). The modification of the electrode is clearly visible from the change of the water contact angle that varies between 86° and 129° depending on the nature of the functional groups compared to 84° for the pristine catalyst (Supplementary Fig. 6). To verify the presence of the functional groups, we performed energy-dispersive X-ray spectroscopy (EDS) analyses in a SEM. The corresponding elemental maps at low magnification show the uniform distribution of S, N, and C on Ag–Cu electrode. A thin amorphous layer is observed under high-resolution TEM at the surface of the catalyst with a thickness of ≈2.5 nm which also corresponds to an increase of the S signal in the corresponding EDS elemental map (Figs. 1d–f and Supplementary Fig. 7). 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 element. Remarkably, the EELS spectrum of the C–K edge displays fine structural characteristics of carbon linked to heteroatoms at ≈292 eV (Figs. 1g, h and Supplementary Fig. 8). 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. 9). The Raman signatures of the different grafted molecules were detected on the surface of the Ag–Cu electrodes, while strong FTIR bands at 1303, 1584, and 1622 cm⁻¹ are only present on N₂SN-, N₃N- and C₂N-functionalized Ag–Cu electrodes and attributed to the C–C or C–N stretching, the NH₂ scissor and the C–N stretching modes respectively (Supplementary Fig. 9). 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. 10b, c). The peak of S2p was deconvoluted into three doublets at 162.75, 164.23, and 168.31 eV for the S2p½, corresponding to S–H and S–C bonds on both thiadiazole and triazole, respectively. Analogously, the N1s spectrum (Supplementary Fig. 10c) can be divided into three components at 398.24, 399.63, and 400.70 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. 11).
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. 12 and 13). Among the different configurations tested, the adsorption of thiadiazole is more stable when the N2–N3 nitrogen atoms of the diazole sit on Cu (111) and the binding energy is estimated to be $-1.08$ eV—-at least 0.37 eV lower than for the other configurations (Supplementary Table 1).

**Fig. 1 Structural and elemental composition of the functionalized Ag–Cu catalysts.** a Schematic representation of the functionalized Ag–Cu electrodes in a membrane electrode assembly. 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 (red) and Ag (blue) EDS elemental maps of N$_2$SN-functionalized Ag–Cu (right). e High-resolution transmission electron microscope (HR-TEM) micrograph of the N$_2$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$_2$SN-functionalized Ag–Cu electrode. g HAADF-STEM image of the Cu surface of N$_2$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$_2$SN layer on the Cu surface. i Raman spectra of pristine (non-functionalized) Ag–Cu (gray), C$_3$-functionalized Ag–Cu (orange), C$_2$N-functionalized Ag–Cu (green), N$_2$N-functionalized Ag–Cu (purple) and N$_2$SN-functionalized Ag–Cu (blue).

**CO$_2$ electroreduction performance in H cell.** The functionalized electrodes were electrochemically tested in a H-cell reactor using Argon and CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte solutions. Figure 2a shows that thiadiazole (N$_2$SN) and triazole (N$_2$N) functionalized electrodes exhibit the highest current density and lowest onset potential in CO$_2$-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$_2$, CO, formate, CH$_4$, and C$_2$H$_4$ products were formed on the bimetallic electrode (Supplementary Fig. 14). Remarkably, the Faradaic efficiency for C$_1$ and H$_2$—obtained via the CO$_2$RR and HER—decreased after functionalization with thiazole and thiadiazole, while the FE for C$_2$+ products sharply increases (Fig. 2b). Ethylene and ethanol are the major C$_2$+ products detected, together with a trace amount of acetate and n-propanol (Supplementary Figs. 14 and 15). The FE for C$_2$+ on N$_2$SN- and N$_2$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$_2$+ products for both thiazole and thiadiazole functional groups increases
Fig. 2 CO\textsubscript{2}RR performance of the functionalized Ag-Cu electrodes in a H-cell. a Linear scan voltammetry (LSV) curves measured for different samples: N\textsubscript{2}SN, N\textsubscript{3}N, C\textsubscript{2}N, C\textsubscript{3} functionalized Ag-Cu compared to pristine (P) Ag-Cu in CO\textsubscript{2}-saturated 0.5 M KHCO\textsubscript{3} at electrochemical potential (V) from 0 to −1.4 V vs. RHE. Scan rate, 20 mV s\textsuperscript{−1}. b Faradaic efficiency (FE) values for C\textsubscript{2} products on different samples at various potentials ranging from −0.3 to −1.4 V vs. RHE and measured in 0.5 M KHCO\textsubscript{3}. c j-V plots of the partial current densities for the C\textsubscript{2} products (ethylene and ethanol). d Relationships between the FE for C\textsubscript{2} and the total current density for all the catalysts. e Selectivity for C\textsubscript{2} products over hydrogen based on the ratio in FE of C\textsubscript{2} and hydrogen. The error bars in b-e correspond to the standard deviation of three independent measurements.

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\textsubscript{1} products and H\textsubscript{2} exhibit a volcano-shaped dependence with the applied potentials (Supplementary Figs. 16a, b). This leads to an obvious enhancement of the specific current density for C\textsubscript{2} products (j\textsubscript{C2}) up to 5 folds at −1.2 V vs. RHE (Fig. 2c). Conversely, the functionalization of the Ag–Cu electrodes with short alkyl or aminoalkyl chains does not suppress the HER pathway nor improve the CO\textsubscript{2}RR activity (Fig. 2d). C\textsubscript{2}N- and C\textsubscript{3}N-functionalized Ag electrodes, both N\textsubscript{2}SN and N\textsubscript{3}N-functionalized electrodes are not substantially perturbed compared to that of pristine Ag. The charge transfer resistance of the N\textsubscript{2}SN- and N\textsubscript{3}N-functionalized electrodes is not substantially perturbed compared to that of the pristine bimetallic catalyst (Supplementary Fig. 19). 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 h in the H-cell reactor, while recording the current density and continuously analyzing the products of the reaction (Supplementary Fig. 20). The N\textsubscript{2}SN- and N\textsubscript{3}N-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\textsubscript{2} of N\textsubscript{2}SN and N\textsubscript{3}N-functionalized Ag–Cu electrodes remains as high as 54% and 46.5% after 20 h, which demonstrates 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 h, 24 h, and 100 h. The ratio is found to be virtually constant suggesting a robust grafting of the functional groups on the catalyst surface (Supplementary Figs. 21, 22 and Supplementary Table 3).

**Ex situ and in situ mechanistic investigations.** Next, we sought to explain the fundamental mechanism responsible for the
improved CO2RR 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 H2O2, the 1G peak in copper oxide is downshifted in energy and presents a broader shape, while the 3F peak is solely represented by the satellite peak at 942.6 eV, which is attributed to the formation of Cu2+ during CO2RR. The measurements were performed after holding the applied potential for 30 min. d Evolution of the Faradaic efficiency for C2+, C3−, and C3N− and Cu, respectively, functionalized Ag-Cu during CO2RR at a fixed potential of −1.2 V vs. RHE. The different colored shading areas represent the peaks of 280 cm−1 (light green), −365 cm−1 (pink), and −2000 cm−1 (blue), respectively. The spectra for all the other potentials are presented in Supplementary Fig. 26. e Relationship between the FE for C2+, C3−, and C3N− and Cu, respectively, functionalized Ag-Cu during CO2RR at a fixed potential of −1.2 V vs. RHE. The different colored shading areas represent the peaks of 280 cm−1 (light green), −365 cm−1 (pink), and −2000 cm−1 (blue), respectively. The spectra for all the other potentials are presented in Supplementary Fig. 26. f Relationship between the FE for C2+, C3−, and C3N− and Cu, respectively, functionalized Ag-Cu during CO2RR at a fixed potential of −1.2 V vs. RHE. The different colored shading areas represent the peaks of 280 cm−1 (light green), −365 cm−1 (pink), and −2000 cm−1 (blue), respectively. The spectra for all the other potentials are presented in Supplementary Fig. 26. g Relationship between the FE for C2+, C3−, and C3N− and Cu, respectively, functionalized Ag-Cu during CO2RR at a fixed potential of −1.2 V vs. RHE. The different colored shading areas represent the peaks of 280 cm−1 (light green), −365 cm−1 (pink), and −2000 cm−1 (blue), respectively. The spectra for all the other potentials are presented in Supplementary Fig. 26.
Cu^{2+} and close to that of Cu^{1+} (915.8 eV). We also note that the 3F peak is also visible for both samples pointing out the presence of Cu^{0}. These results indicate that the valence state of the N_{2}SN and N_{2}N samples may be Cu^{2+} with 0 < \delta < 1.

To precisely evaluate the electronic states of copper on functionalized Ag–Cu electrodes and eliminate the air effect on the electrode, we then performed in situ X-ray absorption near-edge spectroscopy (XANES). The absorption edges of functionalized catalysts reside between those of copper metal (Cu^{0}) and Cu_{2}O (Cu^{1+}) as 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_{2}SN- and N_{2}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 5). Remarkably, C_{6}- and C_{2}N-functionalized samples displayed a minimal shift by comparing with pristine Ag–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 the electron-withdrawing ability of the grafted heterocycles, we measured the oxidation state of Cu post CO_{2}RR using in situ XANES. After 30 min of operation at −1.2 V vs. RHE in the testing cell, the oxidation state of copper was estimated to be +0.51 (inset Figs. 3b, 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 and Supplementary Fig. 23). To better understand the role of Cu^{2+} on the CO_{2}RR properties, we investigated the influence of the copper oxidation state on the FE for C_{2}H_{4} and H_{2} (Fig. 3d). Remarkably, we identified a strong correlation between the oxidation state and the FE for C_{2}H_{4}, which points out that the larger oxidation state of Cu benefits the CO_{2}RR properties and the formation of C_{2}H_{4} products in line with recent findings from the literature. To finally exclude any hydrophobicity effect on the enhanced selectivity for formation of C_{2}H_{4} products, we sought to prepare functionalized electrodes with similar water contact angles as for pristine Cu counterparts. We identified 1,3,4-thiadiazole-2,5-dithiol, N_{2}SS, that shares the same thiadiazole structure but exhibits a water contact angle of 81° compared to 83.9° for pristine non-functionalized Cu. In H-cell configuration, the Faradaic efficiency for the formation of C_{2}H_{4} molecules on N_{2}SS-Ag–Cu reaches 43.7% at −1.2 V vs. RHE compared to only 18.3% for Ag–Cu (Supplementary Fig. 24). To further demonstrate that the water contact angle has limited influence on the improved C_{2}H_{4} selectivity, we plotted the Faradaic efficiency as a function of the water contact angle. No relationship is clearly observed, emphasizing that the origin of the improved selectivity for C_{2}H_{4} is not primarily due to the surface properties of the Cu electrodes but rather the electron-withdrawing nature of the aromatic heterocycles as evidenced by our operando X-ray absorption spectroscopy measurements (Supplementary Figs. 6, 24 and 25).

It is well-known that the formation of multicarbon products in CO_{2}RR proceeds via the formation of the *CO intermediate, and its subsequent dimerization in CO=CO or *CO-COH intermediates. To gain insight into the C–C coupling mechanism on functionalized and pristine Ag–Cu during CO_{2}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. 26, and Supplementary Table 7). The presence of the surface-absorbed *CO was identified from the vibration modes at \approx 280 and \approx 365 cm^{-1} that originate from the Cu–*CO frustrated rotation and Cu–CO stretch, respectively. The broadband in the range of 1900–2120 cm^{-1} was assigned to the C=O stretch. To confirm that the detected signals are solely due to the CO_{2}RR, the Raman spectra were also recorded using Ar-saturated K_{2}SO_{4} as a controlled experiment and no peaks were detected at these frequencies (Supplementary Fig. 26f). The Raman vibration modes around 1900–2120 cm^{-1} have recently been the focus of several studies and there is currently a general agreement that the high frequency region \{2000 cm^{-1}\} and the low-frequency region \{1900–2000 cm^{-1}\} originates to atop-bound CO and bridge-bound CO. Atop (CO_{bridge}) and bridge (CO_{bridge}) configurations correspond to a CO bound on top of one Cu atom and between two Cu atoms, respectively. Compared to pristine as well as 1-propanthiol- and cysteamine-functionalized electrodes, N_{2}SN- and N_{2}N-functionalized Ag–Cu exhibit the relatively intense signals at 365 and 1900–2000 cm^{-1}. Our systematic investigations revealed that the intensities of both regions are also found to increase with the overpotentials.

The broadband in the range of 1900–2120 cm^{-1} and the Faradaic efficiency towards the formation of C_{2}H_{4} products (Fig. 3f) by following literatures to fit these peaks area. 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_{2}H_{4} products. We note that 1-propanethiol functionalized Ag–Cu electrodes display the most intense peak at 280 cm^{-1} whereas no peak is detected at 1900–2120 cm^{-1}. This indicates the adsorbed *CO is not present in the form of CO_{bridge} or CO_{bridge} 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. Interestingly, we observed a volcano-shaped relationship between the Faradaic efficiency for C_{2}H_{4} products and the ratio of atop-bound CO to bridge-bound CO on the surface of Ag–Cu (Fig. 4g and Supplementary Fig. 27). The Faradaic efficiency reaches a maximum for a ratio of CO_{bridge} to CO_{bridge} 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_{bridge} and CO_{bridge} 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_{bridge} to CO_{bridge} (Supplementary Fig. 28). 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_{2}RR using a membrane electrode-assembly (MEA) flow electrolyzer. To evaluate the potential of our approach for practical applications towards the electrocatalysis of C_{2}H_{4} products, we integrated the different functionalized bimetallic
electrodes into 4 cm² membrane electrode-assembly (MEA) flow electrolyzers (Supplementary Fig. 29). 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 N₂SN-functionalized Ag–Cu in a MEA electrolyzer by flowing Ar (used as a blank experiment) and CO₂ in the cathode compartment (Supplementary Fig. 30) and found that the catalyst can convert CO₂ when operating in a catholyte-free MEA system. We then characterized the current-voltage response of all the functionalized catalysts between −2.8 and −4.8 V and a constant flow of CO₂ of 10 standard cubic centimeters per minute (sccm) (Fig. 4a). The total current for the different Ag–Cu electrodes increased from 4·10⁻² A up to over 1.6 A. The N₂SN-functionalized electrodes displayed the largest specific current density for C₂⁺ at 261 mA cm⁻² together with the maximum FE for C₂⁺ products and the lowest FE for H₂ at ~80% and 14%, respectively (Fig. 4b and Supplementary Figs. 31a, 32a). Remarkably the selectivity for the C₂⁺ 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. 32c). Compared to pristine Ag–Cu, the FE for C₂⁺ products from N₂SN- and N₃N-functionalized electrodes demonstrated an average enhancement for C₂⁺ of 3.1 and 2.6 folds respectively over the extended range of full-cell potentials (Fig. 4c and Supplementary Fig. 33). To further assess the performance of the functionalized Ag–Cu electrodes in the MEA devices, we calculated the ratio of jC₂⁺ to jC₁ for the different potentials. We found that Ag–Cu functionalized with thiadiazole displays the largest values and the ratio reaches at a maximum value of ≈10 at a current density of 261.4 mA cm⁻² (Supplementary Fig. 34). 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. 29). 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. 31a).

To better understand the influence of operating conditions on the CO2RR performance of the MEA device, we varied the CO2 flow rate from 3 to 10 sccm at a constant full-cell potential of ~4.55 V. When using N2SN-functionalized Ag–Cu electrodes, the FE for ethylene reached a peak at 56% at ~10 sccm (Fig. 4d) together with a sharply reduced FE for H2 at only 15.2%. The selectivity for ethylene rapidly drops down to only ~5% for a CO2 flow rate of 3 sccm, suggesting that the feed in CO2 is not sufficient to produce enough CO to dimerize on the surface of the catalyst. The relationships between CO2 flow rates, cell voltages and Faradaic efficiencies for the main gaseous products (H2, CO and C2H4) were explored on N2SN-functionalized Ag–Cu electrodes, and we found that the FE for C2H4 decreases when increasing the CO2 flow rate and the optimal flow rate is 10 sccm even when operating under high voltage and high current density (Supplementary Fig. 35). Conversely, the Faradaic efficiency for H2 increases when increasing the CO2 flow rate, which further demonstrates that the decrease in the C2H4 performance is not caused by insufficient feed in CO2. We also estimated the full-cell energy efficiency (EEfull-cell) for N2SN-functionalized Ag–Cu for the different operating potential. Both the FE and EEfull-cell values for C2H4 products increased with the increase of the current density and achieved a maximum efficiency of ~80 ± 1% and an EEfull-cell of 20.3% at a specific current density larger than 260 mA cm−2 for the production of C2H4 (Fig. 4e).

We finally examined the stability of the N2SN-functionalized Ag–Cu electrodes in a full-cell MEA electrolyzer under continuous operation at a CO2 flow rate of 10 sccm and a cell voltage of ~4.55 V. The performance of the cell was found to be stable over 100 h with an average FE of 51% for ethylene and an average current of around 1.6 A (Fig. 4g). After 100 h, the retention of the FE for ethylene and the current were estimated to be 48% and 1.58 A corresponding to retentions of 94% and 99%, respectively. The stability of the CO2RR properties is further accompanied by a high stability of the catalyst morphology and microstructure (Supplementary Fig. 36).

**Discussion**

Our study describes an original 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 CO2RR reactions towards the synthesis of C2H4 molecules. Functionalization of the surface of a bimetallic Ag–Cu catalyst with thiadiazole and triazole derivatives led to an enhancement of the FE for C2H4 up to ~80 ± 1%, corresponding to ratios of FE for C2H4 to FE for Cu2+ and FE for Cu2+ to FE for H2 of 10 and 5.3, respectively. By combining Auger and XANES spectroscopy we identified that the superior performance towards the CO2-to-C2H4 conversion originates from the controlled p-doping of the Cu and presence of Cu2+ with 0 < δ < 1. The functionalized Ag–Cu electrodes were found stable, which translates into a prolonged production of C2H4 products for >100 h.

**Methods**

**Catalysts.** Copper sulfates (CuSO4·5H2O, 99%), silver nitrate (AgNO3, 99%), ammonium fluoride (99%, ethylendiamine(NH2CH2CH2NH2, 99.5%), potassium hydroxide (KOH, 90%) potassium bicarbonate(KHCO3, 99.7%), sulfuric acid(H2SO4, 99.9%), iodium (III) chloride hydrate (IrrCl3·H2O, 99%), 5-Amino-1,3,4-thiazolaz-2-thiol(C3H4N2S2,95%), 3-aminoc-1,4- triazole-5-thiol(C3H4N4S,99%), cytosine(C6H4N3O3S,99%) and 1-Propanethiol (C3H7S) were purchased from Sigma Aldrich. Naflon 117 and anion exchange membrane (Fumapem EA-3,50) were transposed to the MEA devices (Supplementary Fig. 29). We also treated with sulfuric acid by sonicating 20 min. After acid treatment, the remaining acid was rinsed with deionized water for 3 h followed by gas diffusion layer was dried at room temperature. To obtain the working electrodes, 15%Ag–Cu catalysts were prepared through a pulse electrodeposition approach under CO2 bubbling condition. Firstly, electrochemical deposition of the Ag catalyst was performed using a potentiostat (VSP potentiostat from Bio-Logic Science Technologies). The electrolyte used was composed of 0.01 M AgNO3, 0.6 M (NH4)2SO4, and 0.04 M ethylenediamine. Ag catalyst was electrodeposited on GDE at a current density of 15 mA cm−2 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−2 for 45 s to obtain the 15%Ag–Cu electrode. The electrodeposited Cu catalyst was transposed to the MEA devices which were 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−1.

**Electrodes preparation.** Before depositing catalysts, gas diffusion electrode (GDE) was treated with sulfuric acid by sonicating 20 min. After acid treatment, the GDE was rinsed with deionized water for 3 h followed by gas diffusion layer was dried at room temperature. To obtain the working electrodes, 15%Ag–Cu catalysts were prepared through a pulse electrodeposition approach under CO2 bubbling condition. Firstly, electrochemical deposition of the Ag catalyst was performed using a potentiostat (VSP potentiostat from Bio-Logic Science Technologies). The electrolyte used was composed of 0.01 M AgNO3, 0.6 M (NH4)2SO4, and 0.04 M ethylenediamine. Ag catalyst was electrodeposited on GDE at a current density of 15 mA cm−2 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−2 for 45 s to obtain the 15%Ag–Cu electrode. The electrodeposited Cu catalyst was transposed to the MEA devices which were 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−1.

**Physical characteristics.** A field emission scanning electron microscope (TESCAN Mir3a) was employed to observe the morphology of samples. Abelerration-corrected high-resolution (scanning) TEM imaging (HR-STEM), energy-dispersive X-ray spectroscopy (EDS) and spatially-resolved electron energy-loss spectroscopy (ERELS) 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-PEG gun, a super EDS detector, and an Ultra High Resolution Energy Filter (Gatan Quantum ERS) which allows for working in Dual-ERELS mode. HR-STEM imaging was performed by using high-angle annular dark-field (HAADF) and annular dark-field (ADF) detectors. E-RELS spectra were acquired with the monochromator excited allowing an energy resolution of 1.1 eV with an energy dispersion of 0.4 eV pixel−1. Liquid products were quantified by 1H NMR spectroscopy (600 MHz Avance III Bruker with a cryrobe Prodigy TCI) using deionized water with 0.1% (w/v) of DDS (Sodium dodecylbenzenesulfonate) as internal standard of the quantification of the ethanol and formate. An 1D sequence water suppression with excitation sculpting with gradients (zgsgzg) was used for the acquisition (Number of scan = 32, Delay D1 = 30 s). X-ray photoelectron spectroscopy (XPS) measurements were carried out in a Thermo Electron ESCALAB 250 System using Al Kα X-ray excitation (1486.6 eV) for excitation. Raman measurements were conducted using a Renishaw in Via Raman microscope and an ×50 objective (Leica) equipped with a 633 nm laser. Operando Raman measurements were carried out using a modified liquid-electrolyte flow cell. 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).** 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 XAS measurements of functionalized Ag–Cu electrodes were obtained by using a Si (111) monochromator at the Cu K-edge for energy selection with the beam size of 1 × 0.5 mm. A 13-channel Ge detector was used to collect the signals in fluorescence mode. An ionization chamber (Ic) filled with a mixture of N2/He was used to measure the intensity of the incident radiation. While the measurements in transmission mode were operated in other ionization chambers which were filled with the mixture of N2 and Ar in Ic chamber. A modified electrochemical cell was used for operando XAS measurements. The potentiostat was controlled by a VSP2000 (Bio-Logic Science Instruments). A platinum wire and Ag/AgCl electrode (3 M KCl) were used as counter and reference electrodes, respectively. For the XAS studies, 15%Cu–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 cathode side, while the other 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 three 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 Moliseve 5 Å column continuously. Hydrogen and argon (99.9999%) were used as the carrier gases. Liquid products were quantified by 1H NMR spectroscopy (600 MHz Avance III Bruker with a cryorube Prodigy TCI) using deionized water with 0.1% (w/w) of DSS (Sodium trimethylylpropane-sulfonate) like internal standard for the quantification of the ethanol and formate. An ID-sequenced water suppression with excitation sculpting with gradients (gegseq) was used for the acquisition (Number of scan = 32, Delay DI = 30 s). Owing to the liquid product crossover, the FE values of the liquid products were calculated 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 continuous feeding in CO₂. The gas products were collected at frequent time intervals. The FE values were calculated from the average value obtained from three successive injections. 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:

$$\text{FE}_{\text{gas}} = \frac{\text{FE}_{\text{gas}} \times n_{\text{mol}} \times 100\%}{P_{\text{total}}}$$  

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

$$\text{FE}_{\text{liquid}} = \frac{\text{FE}_{\text{liquid}} \times n_{\text{mol}} \times 100\%}{P_{\text{total}}}$$

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

$$R_i = \frac{Q_{\text{total}} \times \text{FE}_i}{96.485 \times z \times n \times 3}$$

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

$$\text{EE} = \frac{1.23 - E_i \times \text{FE}_i}{E_{\text{cell}}}$$

where $g_i$ represents the volume fraction of gas product $i$; $v$ represents the gas flow rate at the outlet in sccm; $z$ represents the number of electrons required to produce one molecule of product $i$; $I_{\text{total}}$ represents the total current; $R$ represents the number of moles of liquid product $i$; and $Q_{\text{total}}$ represents the charge passed while the liquid products are being collected. $P_f = 0.101 \times 10^5$ Pa, $T_f = 273.15$ K, $F = 96,485$ C mol⁻¹ and $R = 8.314$ J mol⁻¹ K⁻¹; $t$ represents the electrolysis time (h); $S$ represents the geometric area of the electrode (cm²); $E_i$ represents the thermodynamic potential (voltage) for CO₂RR to species $i$ and $E_{\text{cell}}$ represents the cell voltage in two-electrode setup.

### Data availability

The authors declare that all data supporting the results of this study are available within the paper and its Supplementary Information files or from the corresponding authors upon reasonable request.

Received: 11 August 2021; Accepted: 12 November 2021; Published online: 10 December 2021

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**Materials and Methods**

**Quantification of the CO₂RR products.** The electrochemical data were recorded while simultaneously collecting the CO₂RR gas products by using an automatic gas sampler connected to the other 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 three 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 a FID detector. The CO₂RR products were measured using GC-FID and GC-MS. The FE values of the liquid products were calculated 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 continuous feeding in CO₂. The gas products were collected at frequent time intervals. The FE values were calculated from the average value obtained from three successive injections. 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:

$$\text{FE}_{\text{gas}} = \frac{\text{FE}_{\text{gas}} \times n_{\text{mol}} \times 100\%}{P_{\text{total}}}$$  

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

$$\text{FE}_{\text{liquid}} = \frac{\text{FE}_{\text{liquid}} \times n_{\text{mol}} \times 100\%}{P_{\text{total}}}$$

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

$$R_i = \frac{Q_{\text{total}} \times \text{FE}_i}{96.485 \times z \times n \times 3}$$

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

$$\text{EE} = \frac{1.23 - E_i \times \text{FE}_i}{E_{\text{cell}}}$$

where $g_i$ represents the volume fraction of gas product $i$; $v$ represents the gas flow rate at the outlet in sccm; $z$ represents the number of electrons required to produce one molecule of product $i$; $I_{\text{total}}$ represents the total current; $R$ represents the number of moles of liquid product $i$; and $Q_{\text{total}}$ represents the charge passed while the liquid products are being collected. $P_f = 0.101 \times 10^5$ Pa, $T_f = 273.15$ K, $F = 96,485$ C mol⁻¹ and $R = 8.314$ J mol⁻¹ K⁻¹; $t$ represents the electrolysis time (h); $S$ represents the geometric area of the electrode (cm²); $E_i$ represents the thermodynamic potential (voltage) for CO₂RR to species $i$ and $E_{\text{cell}}$ represents the cell voltage in two-electrode setup.

**Data availability**

The authors declare that all data supporting the results of this study are available within the paper and its Supplementary Information files or from the corresponding authors upon reasonable request.

Received: 11 August 2021; Accepted: 12 November 2021; Published online: 10 December 2021

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Acknowledgements
D.V., K.Q., and H.L.W. acknowledge funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement no. 804320). L.L., D.V., and H.L.W acknowledge the use of TEM instrumentation provided by the Nation Facility ELECMII ICTS (‘División de Microscopia Electrónica’, Universidad de Cádiz, DME-UCA). L.L. acknowledges funding from the Andalusian regional government (FEDER-UCA:18-106613), 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). K.Q. and Y.Z. acknowledge financial support from the China Postdoctoral Science Foundation (2018M633127) and the Natural Science Foundation of Guangdong Province (2018A030310602). J.L. acknowledges financial support from the National Natural Science Foundation of China (21808134). We thank Soleil Synchrotron and Andrea Zitolo for allocating beamtime at beamline Samba within the proposal 20200732.

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/EXAFS 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.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-27456-5.

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Peer review information Nature Communications thanks John Flake, Miao Zhong, and the other anonymous reviewer(s) for their contribution to the peer review of this work.

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