Steering surface reconstruction of copper with electrolyte additives for CO2 electroreduction

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Electrocatalytic CO2 reduction to value-added hydrocarbon products using metallic copper (Cu) catalysts is a potentially sustainable approach to facilitate carbon neutrality. However, Cu metal suffers from unavoidable and uncontrollable surface reconstruction during electrocatalysis, which can have either adverse or beneficial effects on its electrocatalytic performance. In a break from the current catalyst design path, we propose a strategy guiding the reconstruction process in a favorable direction to improve the performance. Typically, the controlled surface reconstruction is facilely realized using an electrolyte additive, ethylenediamine tetramethylene phosphonic acid, to substantially promote CO2 electroreduction to CH4 for commercial polycrystalline Cu. As a result, a stable CH4 Faradaic efficiency of 64% with a partial current density of 192 mA cm\(^{-2}\), thus enabling an impressive CO2-to-CH4 conversion rate of 0.25 µmol cm\(^{-2}\) s\(^{-1}\), is achieved in an alkaline flow cell. We believe our study will promote the exploration of electrochemical reconstruction and provide a promising route for the discovery of high-performance electrocatalysts.
The continuously increasing carbon dioxide (CO₂) emissions caused by huge fossil fuel consumption lead to severe environmental changes associated with global warming. The CO₂ electroreduction reaction (CO₂RR) is attractive as a sustainable effort to recycle CO₂ into valuable industrial feedstocks and fuels for reducing the greenhouse effect. Among all the catalysts for the CO₂RR, copper (Cu) metal is uniquely capable of producing multi-electron transfer hydrocarbon products with appreciable activity, however, its catalytic activity and selectivity for a certain product are still far from satisfactory. Because of their weak cohesive energy and high surface mobility, metallic Cu catalysts usually undergo reconstruction involving atomic re-arrangement and compositional change during electrocatalysis. Since the electrocatalytic properties have a noticeable dependence on the surface structure, the reconstruction behavior of Cu metal greatly impacts its CO₂ electroreduction performance.

The reconstruction behavior of Cu is a double-edged sword for the CO₂RR. Several studies have shown that the initial well-defined morphology and highly active sites tend to be lost during electrocatalysis because of surface reconstruction, resulting in catalytic performance degradation. Nevertheless, surface reconstruction sometimes generates unique active sites with increased catalytic activity for specific products. Our previous work has shown that the reconstruction of a Cu complex under working conditions causes the formation of Cu nanoclusters with high selectivity for CH₄. Kim et al. found that densely arranged Cu nanoparticles undergo reconstruction to in-situ form a disordered Cu nanostructure with a high selectivity for multicarbons. Unfortunately, previous findings indicate that catalytic activity induced by restructuring is hardly accessible through ex-situ paths. Even if it could be, the well-designed catalysts are still at the risk of oxidation or poisoning in air, or deactivation induced by the restructuring process.

Steering the dynamic reconstruction process in a favorable direction may be a strategy for improving catalytic performance. However, due to the lack of mechanistic understanding, there is currently almost no effective way to control the reconstruction of Cu. Recently, Li et al. showed that the surface atomic migration is driven by the interplay of electric fields and adsorbed reaction intermediates for cathodic metal electrocatalysts. Except for the reaction intermediates, we have shown that surface adsorbed/decorated species can also be introduced artificially to facilitate surface reconstruction. Selective surface-capping additives have been widely used to guide the preferential exposure of crystal faces of the products in chemical synthesis, it is thus of great potential as a simple but effective way to control surface reconstruction of metallic Cu catalysts for a practical CO₂RR technology.

Here, we show our effort on the electrolyte additive way to well guide the surface reconstruction of commercial polycrystalline Cu (poly-Cu), and the additive presented here is ethylenediamine tetramethylenephosphonic acid (EDTMPA) to help achieve an excellent CO₂ electroreduction performance. Experimental and theoretical studies show that EDTMPA molecules are preferentially adsorbed on Cu(110) during the CO₂RR, which not only induces the selective generation of Cu(110) facets that have an inherently high *CO binding strength, but also forms a local environment that promotes proton transfer from water to the Cu(110) facets. Since the rate-determining step of CH₄ formation is *CO + *H → *CHO, the simultaneously increased *CO and proton supplies together with *CHO stabilization caused by EDTMPA result in an excellent electrocatalytic CO₂ reduction performance for CH₄ production. In an H-cell configuration, commercial poly-Cu exhibits a CO₂-to-CH₄ Faradaic efficiency (FE) of 61% with a partial current density of 25 mA cm⁻² at −1.0 V versus a reversible hydrogen electrode (RHE) in a 0.5 M potassium bicarbonate (KHCO₃) electrolyte with 8 ppm EDTMPA, greatly outperforming the EDTMPA-free case. Even in an alkaline flow-cell configuration, where the CO₂-to-CH₄ selectivity is usually completely suppressed according to previous reports, our strategy is still highly efficient in obtaining a nearly constant CH₄ FE of 64 ± 2% at an operating current density of 300 mA cm⁻² over 6 h. Consequently, a CO₂-to-CH₄ conversion rate of 0.25 µmol cm⁻² s⁻¹ is achieved for commercial Cu-based electrocatalysts.

**Results**

**CO₂ electroreduction performance.** Electrocatalysis was performed at −1.0 V versus RHE in CO₂-saturated 0.5 M KHCO₃ electrolytes with/without EDTMPA using an H-cell configuration (Fig. 1 and Supplementary Fig. 1). In the electrolyte with a trace

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**Fig. 1 CO₂ electroreduction performance in an H-cell.** a, b Comparison of average FEs (a) and partial current densities (b) of various products at −1.0 V versus RHE in the electrolytes with and without EDTMPA during one-hour tests. The error bars in a and b represent mean absolute deviation. c, d Stability of FEs (c) and partial current densities (d) of the CO and CH₄ products in the electrolytes with and without EDTMPA.
amount (8 ppm) of EDTMPA, a commercial poly-Cu electrode has a much higher average CH₄ FE and partial current density (61% and 26.6 mA cm⁻²) than those (30% and 7.8 mA cm⁻²) in the EDTMPA-free electrolyte (Fig. 1a, b) during one-hour tests. EDTMPA also greatly increases the catalytic stability of poly-Cu electrodes during continuous electrocatalysis. In the EDTMPA-free case, the poly-Cu electrode retained only 35% and 20% of the initial FE and partial current density of CH₄, respectively, accompanied by gradually increased CO production (Fig. 1c, d). In sharp contrast, with the help of EDTMPA, the poly-Cu electrode showed an impressively stable FE and partial current density of CH₄ and a negligible CO increase (Fig. 1c, d). Considering that surface roughness can affect the electrocatalytic selectivity and activity, the roughness factors of the poly-Cu electrodes were estimated from the cyclic voltammetry (CV) measurements. As a result, both the poly-Cu electrodes become rough and have similar roughness factors of 1.61 and 1.25 after electrocatalysis in the electrolytes with and without EDTMPA, respectively (Supplementary Fig. 2), which eliminates the influence of surface roughness on the increased CO₂ electroreduction performance for CH₄ production.

**Generation of Cu(110) induced by EDTMPA.** Scanning electron microscope (SEM) images confirm that the originally smooth surface of the commercial poly-Cu electrode became rough after electrocatalysis in both electrolytes with and without EDTMPA, however, the resulting surface morphologies are significantly different (Fig. 2a and Supplementary Fig. 3). For the one tested in the EDTMPA-free electrolyte, its rough surface has some aggregated irregular nanoparticles (Supplementary Fig. 3c, d). In sharp contrast, massive uniformly distributed polyhedral nanoparticles were observed for the one tested in the EDTMPA-added electrolyte (Fig. 2a and Supplementary Fig. 3e, f), which is different from the resulting cubic nanoparticles enclosed by {100} facets in previous studies.

Since the commercial poly-Cu electrodes are difficult to prepare for the transmission electron microscope (TEM) characterization, we used electrodeposited Cu TEM grids as poly-Cu electrodes for the CO₂RR and probed their crystal structure before and after electrocatalysis. Representative TEM images of the Cu grid after electrocatalysis in the EDTMPA-added electrolyte show a lot of Cu nanocrystals with hexagonal and cubic outlines, in good agreement with the ideal projections of a rhombic dodecahedron model bounded by (110) facets from different directions (Fig. 2b and Supplementary Fig. 4). The Cu rhombic dodecahedrons are further confirmed by the high-resolution TEM (HRTEM) image and the corresponding selected area electron diffraction (SAED) pattern of the equilateral hexagonal projection shape of Cu nanocrystals along [111] (Fig. 2c). However, irregular Cu nanoparticles without any preferential surface orientation are merely observed for the electrodeposited Cu TEM grids before and after electrocatalysis in the EDTMPA-free electrolyte (Supplementary Figs. 5, 6).

Grazing incidence X-ray diffraction (GIXRD) patterns show no surface phase other than Cu, and that the intensity of the Cu(220) peak at 74.1° (JCPDS No. 04-0836) increases significantly for the poly-Cu electrode tested in the EDTMPA-added electrolyte (Fig. 2d). Its (220) to (111) peak intensity ratio is 4× that of the one tested in the EDTMPA-free electrolyte, which indicates that more Cu(110) surface planes are formed during electrocatalysis in the EDTMPA-added electrolyte.

The surface structure of the poly-Cu electrodes was further probed using the hydroxide (OH⁻) electroadsorption technique. Compared to the poly-Cu electrode tested in the EDTMPA-free electrolyte, the one tested in the EDTMPA-added electrolyte shows a pronounced Cu(110) OH⁻ adsorption peak at ~0.4 V versus RHE in its linear sweep voltammetry profile (Fig. 2e), suggesting a high

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**Fig. 2 Characterization of the poly-Cu electrodes in different electrolytes.** a SEM image of a poly-Cu electrode after electrocatalysis in the EDTMPA-added electrolyte. b, c TEM image (b) and HRTEM image (c) of an electrodeposited Cu TEM grid after electrocatalysis in the EDTMPA-added electrolyte. Inset in c shows the corresponding SAED pattern. d GIXRD patterns of poly-Cu electrodes before/after electrocatalysis in electrolytes with and without EDTMPA. e OH⁻ electroadsorption profiles on the poly-Cu electrodes after electrocatalysis in electrolytes with and without EDTMPA at a scan rate of 100 mV s⁻¹ in 1 M KOH. f DFT-calculated adsorption energies of an MPA molecule on Cu(110), Cu(100) and Cu(111) surfaces. Insets in f are the corresponding atomic structure models.
to understand the role of EDTMPA in the generation of Cu(110).

To simplify the calculations, the energy Cu(110), and thus (110) surfaces are preferentially generated on the poly-Cu electrode during electrocatalysis in the EDTMPA-added electrolyte. Adsorption of EDTMPA molecules on Cu(110). First of all, the stability of EDTMPA molecules is examined by CV tests, which were performed on poly-Cu electrodes between 0.3 V and −1.7 V versus RHE in Ar-saturated 0.5 M KHCO₃ electrolytes without and with a high concentration (100 ppm) of EDTMPA. The CV curves in both electrolytes are nearly identical, which confirms that the EDTMPA molecule is quite stable in the wide electrochemical window (Supplementary Fig. 10). The adsorption of EDTMPA was verified by X-ray photoelectron spectroscopy (XPS). Obvious N and P elements were detected for the poly-Cu electrode tested in the EDTMPA-added electrolyte, but not for the one soaked in the EDTMPA-added electrolyte for the same time at an open circuit potential (Supplementary Fig. 11). It is indicated that EDTMPA has a potential-driven specific adsorption behavior on the Cu surface, which was further confirmed by in-situ Raman measurement (Supplementary Fig. 12). The Cu−O vibration bands (600−620 cm⁻¹) are present in the EDTMPA-added case, and the blue shift occurs as the cathodic polarization increases, indicating that the EDTMPA molecules are coordinated at the Cu surface via Cu−O bonds and the bonding strength is proportional to the cathodic polarization, the same as revealed by DFT calculations (Supplementary Figs. 7, 8 and Supplementary Table 1).

The coverage of EDTMPA molecules on Cu(110) was also investigated to rule out the possibility of blocking the active sites for the CO₂RR. A complete EDTMPA molecule was structurally relaxed on Cu(110) surface with a 2×3 supercell, which represents the close-packed structure of EDTMPA molecules on Cu(110) (Supplementary Fig. 13a, b). Obviously, an adsorbed EDTMPA molecule only occupies up to two Cu atoms per six ones, while other Cu atoms are available for the CO₂RR (marked with green circles in Supplementary Fig. 13a, b). Furthermore, we explored the transfer process of a CO₂ molecule through the EDTMPA adsorption layer on Cu(110) (Supplementary Fig. 13c, d). DFT results show that it is an exothermic process, indicating that CO₂ molecules can approach the Cu(110) surface without obstacle. Therefore, the adsorbed EDTMPA molecules do not block the CO₂RR.

High *CO coverage on Cu(110). Previous studies argued that Cu(111) rather than Cu(110) favors the CH₄ yield during the CO₂RR, whereas Cu(110) seems to promote CH₄ generation in our work. As is widely reported, the rate-determining step for CH₄ production is the reaction (Supplementary Table 2) [21,34,35].

\[ *\text{CO} + \ast\text{H} \rightarrow \ast\text{CHO} \]

Therefore, a higher *CO coverage thermodynamically favors the reaction (Eq. 1) and thus should promote CH₄ production. Among the three low-indexed Cu single crystal surfaces (111, 110, and 100), (110) has the strongest *CO binding strength [36]. To probe the interaction between *CO and the reconstructed Cu(110) facets, in-situ attenuated total reflectance-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) was conducted during the cathodic scan of a poly-Cu-coated Si crystal in a CO₂-saturated 0.5 M KHCO₃ electrolyte with and without EDTMPA from 0.1 to −1.1 V versus RHE. In the vibration region of the linearly-bonded CO absorption band from 2040 to 2080 cm⁻¹ (ref. 37), the spectra in electrolytes with and without EDTMPA are quite different (Fig. 3a). What is first apparent is that the electrode tested with EDTMPA always has a much stronger intensity of the surface-bonded CO peak than the one tested without EDTMPA during the cathodic scanning, as is more obviously seen using the integrated area in Fig. 3b, which shows that the reconstructed Cu(110) facets have much more *CO adsorption sites. When the potential is more negative than −0.47 V versus RHE, the integrated area of the CO peaks begins to decrease, which might be caused by either *CO desorption to deliver CO gas or *CO protonation to form *CHO. Another significant feature of the spectra, in the presence of EDTMPA, is that the CO band position has an initial blue shift and a subsequent red shift during cathodic scanning, which is in stark contrast to the EDTMPA-free case where only a red shift occurs at very negative potentials. The red shift is ascribed to the weakened *CO binding energy caused by the increased charge donation due to the potential-dependent electrostatic field in the double layer [38]. The initial blue shift is attributed to the strong adsorption of CO and hence the high *CO coverage on the reconstructed Cu(110) surfaces in the presence of EDTMPA [39].

In-situ Raman and CO temperature-programmed desorption (TPD) measurements were also conducted to confirm the strong interaction of *CO with the generated Cu(110) surfaces. In the Raman spectra, the peaks located at 280 and 360 cm⁻¹ are assignable to restricted rotation of adsorbed CO (P1) and Cu−CO stretching (P2), respectively [40,41] (Fig. 3c). As the P2-to-P1 intensity ratio is directly proportionate to the increased surface *CO concentration [40], the EDTMPA-added case has obviously higher P2-to-P1 ratios than the EDTMPA-free one, indicating a higher *CO coverage on the reconstructed Cu(110) surface in the EDTMPA-added case. The CO TPD curve of the poly-Cu tested in the EDTMPA-added electrolyte has a pronounced broad CO desorption peak compared to the one tested in the EDTMPA-free case (Fig. 3d), showing a strong *CO binding energy of the generated Cu(110) surfaces. All the above results confirm that the reconstructed Cu(110) surfaces induced by EDTMPA have a high *CO coverage and facilitate *CO stabilization, agreeing well with a previous study [36].

Locally high proton-feeding environment formed by EDTMPA. Although a restructured Cu(110) surface has been shown to have a strong *CO binding ability, the resulting high *CO coverage usually limits the number of *H adsorption sites [42,43], which is in favor of ethanol formation but adverse to the rate-determining step of CH₄ generation (Eq. 1) [44,45]. This is the main reason why Cu(110) has rarely been reported to have a high CH₄ FE. Therefore, in addition to the high *CO coverage, an adequate proton supply is indispensable to the high CH₄ conversion in our work [46,48]. Considering that EDTMPA is a phosphonic acid, its adsorption on Cu(110) might form a local environment that provides a high proton supply.
To explore the function of EDTMPA on this, the CO₂ electro-reduction performance was measured in electrolytes containing different amounts of EDTMPA. As the amount of EDTMPA increased from 0 to 8 ppm, both the FEs and partial current densities of CH₄ increased while those of H₂ remained almost unchanged (Fig. 4a, b). A reasonable interpretation of this is that EDTMPA adsorbed on Cu(110) provides adequate protons to help the protonation of *CO to *CHO rather than the formation of H₂ due to the high *CO coverage on Cu(110). When the amount of EDTMPA was increased to 16 ppm, an excessive proton supply resulted in increased H₂ production (Fig. 4a, b).

DFT calculations were carried out to explore the role of the adsorbed EDTMPA in increasing the number of protons available for CH₄ production. On bare Cu(110), protons are difficult to obtain from H₂O because of the high dissociation barrier (1.32 eV)⁴⁹ (Fig. 4c and Supplementary Fig. 14a). However, more protons are available after contacting EDTMPA with Cu(110). In details, one H atom is transferred from *MPA to Cu(110) with an energy decrease of 0.05 eV and a moderate kinetic barrier of 0.73 eV (Fig. 4d and Supplementary Fig. 14b). Subsequently, the *MPA that loses one H (*MPA−H) captures one H atom from the adjacent H₂O molecule to become an *MPA again (Fig. 4d and Supplementary Fig. 15). Note that this process is barrier free with an energy decrease of 0.10 eV, implying that it is both kinetically and thermodynamically favorable. The above DFT results clearly confirm that the adsorbed EDTMPA serves as a proton-delivering medium that accelerates the conversion of CO₂ to CH₄.

Apart from its high ability to provide protons, the adsorbed EDTMPA also stabilizes the *CHO species through hydrogen bond, which is supported by DFT calculations (Fig. 4e and Supplementary Figs. 16, 17). After introducing *MPA on Cu(110), the *CHO binding energy is significantly increased by about 0.44 eV, and the free energy change from *CO to *CHO (Eq. 1) is reduced from 0.79 to 0.41 eV (Fig. 4e), which suggests that the linear-scaling relations between the two coupled intermediates (*CO and *CHO) are broken, thus improving the kinetics of CH₄ formation. The improved kinetics were experimentally demonstrated by Tafel analysis with a reduced Tafel slope from 144 to 87 mV dec⁻¹ in the presence of EDTMPA (Fig. 4f).

Feasibility study in a flow cell. Since poor CO₂ mass transport through electrolytes significantly limits the current density of the CO₂RR in an H-cell configuration, the scalability of the additive-controlled reconstruction approach was demonstrated in a flow cell configuration for industrial use. The results show that a high CH₄ selectivity is still achieved with the EDTMPA additive in an alkaline flow cell, which is totally different from the previous reports of a high C₂ selectivity in a pure alkaline electrolyte.²³ (Fig. 5a). In a 1 M KOH electrolyte with 13 mM EDTMPA, the poly-Cu gas diffusion electrode (GDE) showed a very stable CH₄ FE of 64 ± 2% with a partial current density of 192 ± 6 mA cm⁻² for 6 h (Fig. 5b), and thus a high CO₂-to-CH₄ conversion rate of 0.25 µmol cm⁻² s⁻¹ was achieved (Fig. 5c). The high CH₄ selectivity indicates that EDTMPA still creates a locally high proton-feeding environment on poly-Cu electrodes even in an alkaline electrolyte, although the conditions were quite different from those in the neutral H-cell. The GIXRD results further illustrate that the surface reconstruction toward Cu(110) is also
achieved in the alkaline flow cell (Supplementary Fig. 18), indicating that the additive-controlled reconstruction approach has general applicability.

Discussion

A controlled surface reconstruction strategy using an EDTMPA additive substantially improves the CO₂ electroreduction performance to CH₄ on a commercial poly-Cu electrode. The CO₂-to-CH₄ conversion is promoted by the increased availability of both *H and *CO substrates and stabilization of the *CHO resultant in the rate-determining step of CH₄ production (Eq. 1), all of which are resulted from surface reconstruction during the CO₂RR. The surface reconstruction involves not only the Cu surface atomic re-arrangement induced by EDTMPA to generate Cu(110) facets, but also the formation of EDTMPA adsorption layer on Cu surface under working potentials.

To illustrate the effects of additives on the surface reconstruction and electrocatalytic performance, we also investigated two analogues of EDTMPA, namely, methylenediphosphonic acid (MDPA) and ethylenediamine tetraacetic acid (EDTA), as electrolyte additives for the CO₂RR. According to SEM and X-ray diffraction (XRD) results, MDPA has an effect on the generation of Cu(110) surface like EDTMPA (Supplementary Fig. 19a, c). However, the CH₄ FE suffers from rapid decay accompanied with increased H₂ FE (Supplementary Fig. 20a), and their partial current densities are both decreased during one-hour electrocatalysis in the MDPA-added electrolyte (Supplementary Fig. 20b). This may be largely attributed to the smaller space structure of MDPA molecules and the resulting higher coverage on Cu surface compared with EDTMPA, which results in an excessive proton supply and limited CO₂ transportation. A substantial stability of the CO₂-to-CH₄ conversion is achieved after adding EDTA into the electrolyte, although the CH₄ FE (~50%) and partial current density (18 mA cm⁻²) are lower than those in the EDTMPA-added case (Supplementary Figs. 1 and 20c, d). This can be attributed to the similar proton-feeding capability of the carboxyl groups in EDTA with the phosphate groups in EDTMPA. The inferior performance for CH₄ production is due to the inability of EDTA to induce the atomic re-arrangement of Cu surface to generate Cu(110) like EDTMPA and MDPA (Supplementary Fig. 19b, c). Therefore, it can be concluded that the additives should be rational selected according...
to the desired products, although the selecting principles are still under exploration. Incidentally, the fact that the electrolyte effects are noticeable at low concentrations highlights that researchers need to pay careful attention to the presence of additives (intentional) or contaminations (unintentional or unknown) in their experiments.

In this work, EDTMPA is presented as a successful example to illustrate the feasibility of manipulating the surface reconstruction of Cu metal by using selective surface-capping additives to achieve an CO2 electroreduction performance. Our results show that the additive-controlled surface reconstruction approach has potentially general applicability. Therefore, we believe that more additives will be targetedly developed to facilitate CO2 electroreduction to other general applicability. Therefore, we believe that more additives will be targetedly developed to facilitate CO2 electroreduction to other desired products, although the selecting principles are still under exploration. Incidentally, the fact that the electrolyte effects are noticeable at low concentrations highlights that researchers need to pay careful attention to the presence of additives (intentional) or contaminations (unintentional or unknown) in their experiments.

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In-situ Raman. In-situ Raman spectra were obtained on a Raman spectrometer (LabRAM HR spectrometer, Horiba) with a laser wavelength of 785 nm. The CO2-adSORbed Cu2O nanocrystals were synthesized using a homogenous method with a CO2-saturated 0.5 M KHCO3 aqueous solution as the electrolyte.

In-situ ATR-SEIRAS. Cu-coated Si ATR crystal was used as the working electrode for in-situ ATR-SEIRAS analysis in a CO2-saturated 0.5 M KHCO3 aqueous solution with and without EDTMPA. A Thermo Fisher Nicolet iS50 spectrometer equipped with a MCT detector and a Pike Technologies VeeMAX III ATR accessory was used to collect the spectra. All spectra were acquired with a resolution of 4 cm⁻¹ by accumulating eight scans.

Electrochemical measurements in the H-cell configuration. Controlled-potential electrolysis was conducted in an H-cell system, which was separated by an anion exchange membrane. An electropolished commercial Cu mesh was used as the working electrode. A graphite rod and a KCl saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The potentials were controlled by an electrochemical working station (IVIUM). All potentials in this study were measured against the Ag/AgCl reference electrode and converted to the RHE reference scale by αRHE = νRHE – E0/2, where E0/RHE and E0/Ce are the total energies of the systems containing the substrate and adsorbate, the substrate, and the adsorbate, respectively. According to this definition, a more negative adsorption energy indicates a stronger adsorption.

Electrochemical measurements in the flow cell configuration. The controlled-current electrolysis was performed in an electrochemical flow cell with a three-electrode system using an electrochemical working station (PARSTAT3000A-DX). 30 mL of 0.5 M KOH solution was used, and without solution, 13 mm EDTMPA additive was circulated through the cathode chamber at a constant rate of 6.4 mL min⁻¹ by a peristaltic pump. An anolyte using 1 M KOH was introduced to the anode chamber by a diaphragm pump. An anion exchange membrane (Fumasep FAB-PK-130) was used to separate the cathode and anode chambers. For the CO2RR, gaseous CO2 (99.999%) was passed through the gas chamber at the back side of the Cu GDE (the exposed geometric area was 1 x 1 cm²) at a flow rate of 14 mL min⁻¹. The CO2 outlet flowrates were recorded by a mass flow detector (Alcatr) for accuracy, which was used for all subsequent efficiency calculations. A piece of Ni foam and a Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. The ohmic loss between the working and reference electrodes was evaluated by electrochemical impedance spectroscopy and 80% IR compensation was applied to correct the potentials manually.

During the reaction, gas phase products were quantified with gas chromatography (SHIMADZU GC-2014), equipped with a thermal conductivity detector and a flame ionization detector. Liquid products were quantified with a 400 MHz 1H NMR spectrometer with water suppression.

The computational hydrogen electrode (CHE) model58 was used to calculate the chemical potential of CO2 to reduction carbon dioxide. Adv. Mater. 28, 3423–3452 (2016).

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