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Cation Enrichment Promotes High-rate CO Electroreduction to C₂+ Liquid Products

Chunyu Cui¹, Liang Xu², Peiping Yu², Nan Wang³, Fenglou Ni⁴, Wen Guo¹, Hao Yang², Tao Cheng², and Bo Zhang^{1*}

¹*State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200438, China.*

²*Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, Suzhou, 215123, Jiangsu, China.*

³*Department of Chemistry, Fudan University, Shanghai 200438, China.*

⁴*Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, U.K.*

*Correspondence and requests for materials should be addressed to Bo Zhang (bozhang@fudan.edu.cn) (B.Z.).

Abstract

Electrochemical reduction of CO into valuable multicarbon (C₂₊) liquids is crucial for reducing CO₂ emissions and advancing clean energy, yet mastering efficiency and selectivity in this process remains a tough challenge. Herein, we employ a surface-modification strategy using electrochemically active polymeric 1,4,5,8-naphthalenete-tricarboxylic dianhydride (PNTCDA)-modified copper nanosheets (PM-Cu) to rearrange reactive species in the electric double layer, where the PNTCDA triggers a distinctive enolization that anchor potassium ions (K⁺) onto the cathode surface under reduction condition. Electrochemical analysis and computational simulations revealed that this approach fine-tunes K⁺ distribution in the double layer, making the dehydration of hydrated K⁺ more efficient and reducing active water molecules at the interface, thus inhibiting the hydrogen evolution reaction while concurrently promoting CO reduction *via* enhanced C–C coupling. For the first time, the PM-Cu catalyst demonstrates ampere-scale current densities with the exclusive selectivity of a C₂₊ liquid product yield exceeding 90%. Thus, by tailoring the local microenvironment with electrochemically active organics, it is possible to modulate CO reduction, improve sustainable energy storage, and increase industrial carbon utilization.

Introduction

Recent advancements in carbon-negative technologies, particularly through the conversion of carbon dioxide and carbon monoxide electrolysis reactions (CO_2/COR) into valuable fuels and chemicals using renewable energy-generated electricity, have demonstrated significant potential for practical implementation and beneficial environmental impact.^[1–4] Among various CO_2/COR products, the highly reduced C_{2+} liquid products generated by the proton-coupled multielectron transfer steps are considered ideal due to their high energy density, substantial market value and industrial applicability.^[5,6]

The meticulously engineered catalytic activity of nanostructures, achieved by shaping nanostructures, managing defects, and manipulating oxidation states, has been proven to be highly effective in promoting C–C coupling on copper (Cu) catalysts.^[7–10] Despite notable progress in enhancing C–C coupling, the specificity for producing high-energy C_{2+} liquid-phase products, especially those with significant low ethylene content, remains a challenge.^[11,12] Building upon the intrinsic activity of the catalyst, further modulation of the microenvironment near the catalyst surface is emerging as a key factor in refining the activity and selectivity of C_{2+} liquid products.^[13–18] One crucial aspect of these tailored approaches involves the modification of local concentrations of CO , H_2O , OH^- and alkali cations.^[19] Notably, the electrostatic interaction between alkali cations and the electric dipoles of adsorbates on the electrode surface has been proven to be beneficial for C–C coupling.^[20,21] Concurrently, the augmentation of alkali cations plays a pivotal role in suppressing hydrogen evolution and is thus considered one of the most effective strategies for regulation.^[18]

Therefore, adjusting the electrolyte composition and introducing organic compound layers on the catalyst surface play a key role in tailoring the microenvironment. For instance, potassium ion (K^+) enrichment is achieved by adding a concentrated K^+ -containing solution to the electrolyte while simultaneously modifying the copper electrode surface with an ion-polymer to adsorb K^+ .^[18] Alternatively, a bipolar membrane can be used in an alkaline environment to facilitate the diffusion of K^+ toward the cathode surface.^[22] Or, more directly, by increasing the K^+ electrolyte concentration to enhance C–C coupling and suppress hydrogen evolution.^[23]

However, the physical adsorption of K^+ by organic compounds and polyelectrolyte layers presents limitations because the concentration of K^+ in the electrolyte exceeding 6 mol/L may lead to diminished solution conductivity and lower mass transfer efficiency.^[24] This poses challenges

in further enhancing COR production efficiency, particularly in terms of high current density. To address this issue, we proposed a strategy that directly binds K^+ onto the solid electrode surface using *in situ* electrochemically active organics. This approach aims to enhance C–C coupling and simultaneously suppress hydrogen evolution reaction (HER) while maintaining optimal electrolyte conductivity and mass transfer properties.

Inspired by aqueous K^+ ion batteries, the employment of polyimide-type organic substances as cathode materials has demonstrated promising potential for binding K^+ .^[25–27] In this study, polymeric 1,4,5,8-naphthalene-tricarboxylic dianhydride (PNTCDA) was incorporated *in situ* during the preparation of CuO nanosheet catalysts, and then reduce CuO into metallic Cu, resulting in the innovative PM-Cu electrode. Throughout the charging process, *via* a distinctive barrier-free enolization process, PNTCDA effectively stabilized the adsorption of alkali cations from the electrolyte onto the electrode surface. Additionally, alkali cations within PNTCDA exhibited high migration rates, significantly reducing the migration barrier. This characteristic realizes the directly binding K^+ onto the electrode surface, ensuring sustained enrichment of K^+ , even under the rigorous conditions of industrial current densities exceeding 1 A/cm^2 .

At the same time, the modification of PTNCDA on the surface of the Cu electrode enables precise modulation of the species distribution over the double layer by enriching K^+ at the catalytic interface. Moreover, the process of binding hydrated K^+ into the PNTCDA structure at the reduction potential facilitated the desolvation of hydrated alkali cations. As a result, the density of active water molecules at the reaction interface decreases, thereby inhibiting the occurrence of the HER. Concurrently, this strategy enhances the C–C coupling step toward the production of C_{2+} liquid compounds with yields exceeding 90% from CO electrolysis.

Results and Discussion

PNTCDA was synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) according to previous reports.^[26,28,29] The purity of the as-prepared PNTCDA was confirmed by Fourier transform infrared (FT-IR) spectroscopy (Figure S1). Figure 1a depicts the preparation process of the PNTCDA-modified copper oxide (PM-CuO) electrode. This method involves transferring PM-CuO nanosheets onto a gas diffusion layer (GDL) through a pressure rolling technique. Subsequently, *in situ* electroreduction in a CO atmosphere reduces the PNTCDA-incorporated CuO nanosheets to metallic Cu, forming the PM-Cu electrode. For comparison, a bare Cu electrode was produced using the same method but without PNTCDA modification. Powder X-ray diffraction (XRD) analysis of PM-Cu after COR confirmed the existence of metallic Cu and PNTCDA (Figure S2). The XRD pattern of the PM-Cu electrode revealed an unchanged Cu lattice, akin to that observed in the bare Cu electrode. No metal oxide phases, e.g., CuO or Cu₂O, were identified, suggesting that the CuO was reduced to metallic Cu following CO electrolysis.

Subsequently, high-resolution transmission electron microscopy (HRTEM) was employed to characterize the preelectrolysis PM-CuO nanosheets (Figure 1b and 1c) and the postelectrolysis PM-Cu sample (Figure 1e and 1f). HRTEM images show that postelectrolysis PM-Cu undergoes adaptive reconstruction into Cu nanoparticles composed of small grains with sizes of ~10-20 nm following the electrocatalytic reduction of CO. Figures 1e and 1f display the voltage-induced reconstruction of the Cu surface and the preservation of a coordinated layer on the Cu surface by PNTCDA. The distributions of PNTCDA and Cu in both the PM-CuO precursor and the postelectrolysis PM-Cu samples were analyzed using scanning transmission electron microscopy (STEM) combined with energy dispersive X-ray spectroscopy (EDS) mapping. Due to the distinctive nitrogen composition of PNTCDA, as illustrated in Figures 1d and 1g, the distribution of Cu and PNTCDA remained uniform in the samples, both pre- and postreaction, suggesting its stability during CO reduction.

As shown in Figure 2a, each NTCDA formula unit comprises four oxygen atoms, serving as potential sites for the association and dissociation of K⁺. This feature suggests a high specific capacity, given that each PNTCDA unit has the theoretical potential to transfer four electrons.^[25] According to previous studies,^[26,30] K⁺ are coordinated to the PNTCDA chain *via* an enolization process: (C=O)_n → (C-O)_n. First-principles calculations revealed that the formation of the K⁺-O

bond is barrierless, indicating that the enolization process is readily achievable. Moreover, K^+ exhibit high mobility within bulk PNTCDA, encountering minimal energy barriers.^[27] In the catalytic process of COR, PNTCDA undergoes an enolization reaction at the PM-Cu cathode, wherein K^+ intercalate into its lattice. This chemical interaction facilitates the enrichment of K^+ by enabling effective coordination and electron transfer with the PNTCDA structure.

Voltametric analysis revealed that the reaction at the PM-Cu cathode was scarcely impeded by diffusion (Figure 2b), exhibiting rapid kinetics and distinguished rate capabilities. Significantly, Figure 2b demonstrates that the electrochemical reactions for both the PNTCDA and PM-Cu electrodes occur within the stable window of the aqueous electrolyte. Since PNTCDA undergoes activation in the initial cycle and the as-prepared PM-CuO is in the deficient- K^+ state, the cathode must be preactivated before cell assembly.

To assess the effect of PNTCDA on the kinetics of the cathodic hydrogen evolution reaction, linear sweep voltammetry (LSV) was conducted in a flow cell reactor with Ar gas and 3 M KOH electrolyte. This experiment was carried out with a preactivated PM-CuO electrode. As a control, a preactivated CuO electrode without PNTCDA was tested (Figure 2c). The HER activity decreased in the following order: PM-CuO > CuO. The diminished HER activity suggested that the integration of PNTCDA into the cathode significantly increased the reaction threshold of the HER.

To provide a more concrete demonstration, K^+ from KOH electrolyte can be stably enriched on the cathode surface under reduction potential using the PM-Cu electrode. Both the PM-Cu and CuO electrodes were evaluated in a flow cell with 3 M KOH electrolyte under the same CO reduction conditions. Following the reduction test, the electrodes were analyzed *via* EDS mapping, revealing a more pronounced enrichment of K^+ on the PM-Cu electrode surface, considering the consistent copper content on both electrode types (Figure 2d, Figures S3 and S4). Concurrently, we precisely measured the electrochemical active surface area (ECSA) of each electrode, normalized the K^+ content on each electrode with the ECSA, and found that after ECSA normalization, the K^+ concentration on the PM-Cu electrode is 7.4 times higher than that on the bare Cu electrode (Figure S5, Tables S1 and S2), confirming the effectiveness of the PNTCDA.

In aqueous electrolytes, alkali cations (M^{n+}) are solvated by dipolar water molecules (H_2O), forming a solvation structure – $M(H_2O)_x^{n+}$. The interaction between cations and water prompts electron transfer from H_2O to cations *via* M-OH₂ bonds, leading to a weakened O–H bond within

the H₂O molecule.^[31] As a result, cation-water chemistries play a pivotal role in the HER. Given the influence of cations on the HER, weak cation-water interactions are favorable for suppressing the HER.^[32] Previous studies^[33,34] have demonstrated that bound water is easier to reduce than free water. Therefore, removing bound water from the K⁺ solvation structure further enhances the reduction resistance of the HER.

In view of this, we sought to enrich K⁺ by constructing a conductive polymer, PNTCDA, on a Cu surface that is capable of binding K⁺ under reduction potentials. As depicted in the schematic diagram of Figure 3a, compared to bare Cu, the introduction of PNTCDA realizes the enolization process under reduction potentials, resulting in a significant concentration of partially dehydrated K⁺ on the electrode surface. This phenomenon effectively obstructs the proximity of associated reactive water to the reaction zones on the cathode surface. Consequently, it mitigates the predominant HER at excessive potentials.

Molecular dynamics (MD) simulations, which employ accurately parameterized force fields, yield more reliable statistical data when performed in larger simulation boxes. These simulations are crucial for elucidating species distributions within the electric double layer (EDL). In this study, we investigated the behavior of three distinct 3 M KOH electrolyte environments on an electrode surface with the incorporation of PTNCDA, PTNCDA²⁻, and PTNCDA⁴⁻. These additives were introduced under varying voltage conditions to assess their impact on the EDL structure and dynamics. Representative snapshots of these models are depicted in Figure S6.

Analysis of the species density distributions revealed a pronounced peak in the K⁺ concentration within the EDL region for PTNCDA⁴⁻, as illustrated in Figure S7. Conversely, the concentration of hydroxide ions (OH⁻) was found to be at its minimum in the same system (Figure S8). These observations suggest that the PTNCDA⁴⁻ additive engages in electrostatic interactions with K⁺ while repelling OH⁻, thereby modulating the distribution of species within the EDL. Furthermore, Figures S9 and S10 demonstrate that the concentration of H₂O molecules and H-bonds are significantly greater in the pure KOH electrolyte system than in the systems containing PTNCDA, PTNCDA²⁻, or PTNCDA⁴⁻. This suggests that the introduction of the PTNCDA series of additives, with their rigid planar structures, displaces H₂O molecules and destroys the H-bond structure from the EDL, thereby suppressing the HER, in agreement with the experimental observations. Therefore, PTNCDA⁴⁻ was identified as an optimal additive for enhancing COR efficiency while concurrently inhibiting the HER.

To investigate the influence of PTNCDA on desolvation dynamics, we used a 3 M KOH electrolyte system to elucidate the solvation structure of K^+ . Subsequently, the desolvation energy associated with K^+ was calculated. Utilizing both radial distribution function (RDF) and coordination distribution function (CDF) analyses, we determined that the K^+ is solvated by seven H_2O molecules, a configuration depicted in Figures S11-S15. Notably, RDF analysis of the interaction between K^+ and OH^- indicated an absence of OH^- coordinated with K^+ , leading to a solvation structure of $K[H_2O]_7^+$. After determining the solvation structure, we proceeded to calculate the potential energy of various components, including K^+ and $K[H_2O]_7^+$, the complex formed between K^+ and $PTNCDA^{4-}$ ($K^+-PTNCDA^{4-}$), and the complex formed between the solvated ion and $PTNCDA^{4-}$ ($K[H_2O]_7-PTNCDA^{3-}$). These calculations were instrumental in determining the desolvation energy. Density functional theory (DFT) calculations revealed the desolvation energies associated with the transition from $K[H_2O]_7^+$ to K^+ both in the presence and absence of $PTNCDA^{4-}$. As illustrated in Figure 2b, the desolvation of $K[H_2O]_7^+$ necessitates an energy increase of 2.78 eV, in stark contrast to the desolvation of $K[H_2O]_7-PTNCDA^{3-}$, which requires merely 1.88 eV. These results underscore the significant role of $PTNCDA^{4-}$ in facilitating the desolvation process. Moreover, $PTNCDA^{4-}$ effectively decreases the concentration of water molecules at the EDL, thus suppressing the HER.

To elucidate the catalytic mechanisms underlying the HER kinetics, we employed DFT calculations to assess the adsorption and desorption properties of H_2O molecules, along with the intermediates involved in the elementary reaction steps. These calculations were based on the most stable configurations of a crystalline copper model and a porous copper (PM-Cu) model, as depicted in Figure S16. As demonstrated in Figure 3c, compared with the modified surfaces, the pristine copper surfaces exhibited markedly more significant HER kinetics. Specifically, the activation energy for water molecule dissociation on bare copper was found to be exceptionally low, at 0.65 eV, indicating much lower energy barriers and thus facilitating H_2O dissociation. In contrast, on the PM-Cu surface, the activation energy for H_2O dissociation was greater at 0.85 eV, as shown in Figures S17 and S18, detailed in Table S3. This increase suggests a more challenging water dissociation process on the PM-Cu surfaces.

Subsequent analyses focused on calculating the barrier heights associated with the C–C coupling reaction pathway on both the PM-Cu and pristine copper surfaces. DFT calculations revealed a notable reduction in the energy barrier for the potential-determining step (PDT),

specifically the *CO–*CO coupling leading to C₂⁺ product formation. On the PM-Cu surface, this barrier decreased from 0.73 eV to 0.54 eV, representing a significant enhancement in reaction efficiency compared to that observed on the bare Cu surface. These findings are comprehensively documented in Figure 3d, Figure S19, and Table S4.

Guided by the cation effect on the HER, a strategy for designing an electrode featuring a cation desolvation structure is proposed to address the issue of the HER on the cathode. By incorporating the polymer PNTCDA into the Cu electrode, the bound water in the K⁺ solvation shell is released, resulting in the formation of a cation-type, water-free solvation structure – K⁺-PNTCDA, which effectively suppresses the HER. The present cathode design therefore provides insights into the effect of cations on the HER and delineates a promising approach for employing polymer modification by directly integrating PNTCDA onto the surface of Cu catalysts.

In light of these findings, we evaluated the electrochemical CO reduction performance of PM-Cu and CuO electrodes in a flow-cell reactor employing 3 M KOH as the electrolyte at ambient temperature (Figure 4a, Figure S20, Tables S5 and S6). The LSV polarization curves revealed that the PM-Cu electrode, when flushed with CO, exhibited a significantly higher current density than that in argon, suggesting that the COR efficiency of PM-Cu was superior to that of argon (Figure S21). Subsequently, galvanostatic electrolysis experiments were conducted to investigate the product selectivity. The FEs of the gas products were determined using gas chromatography (GC), while the FEs of the liquid phase products were quantified by nuclear magnetic resonance (NMR) (Figure S22). Figure 4a displays the FEs for all products during COR on both the PM-Cu and CuO electrodes across current densities ranging from 100 to 1600 mA/cm². Notably, PM-Cu exhibited a remarkable selectivity toward C₂⁺ liquid products across various current densities, achieving a peak FE of 96 ± 3%, in contrast to that of the CuO electrode, which showed lower efficiencies between 10 and 30% (Figure 4b). Given that the hydrophobicity of PM-Cu may vary with PNTCDA modification, we added PTFE additives instead of PNTCDA to bare Cu catalyst to match the hydrophobicity of the PM-Cu electrode^[35] (Figure S23). However, the selectivity for C₂⁺ liquid products did not significantly improve with enhanced hydrophobicity (Figure S24 and Table S7).

The PM-Cu electrode achieves a peak current density for C₂⁺ liquid products exceeding 1.4 A/cm² while maintaining the FE close to 90%, representing a significant improvement compared to other state-of-the-art C₂⁺ liquid product-selective catalysts (Figure 4c).^[36–49] Following 80% iR

compensation, an overpotential of only -0.52 V was required to achieve an 89% FE for C_{2+} liquid products at a current density of 1.6 A/cm^2 , highlighting the catalyst's scalability for practical applications (Table S8). Moreover, less than 10% ethylene and negligible amounts of hydrogen were detected at this stage. The inhibition of ethylene may be attributed to the differences in surface oxygenophilic properties between PM-Cu and bare Cu, as the intensity of adsorbed $*OH$ on PM-Cu electrode is higher than that on the bare Cu electrode^[37,50] (Figure S25). The combined metric of exclusive selectivity and high current density signifies a 3-fold increase in performance relative to the best prior reports on CO reduction for C_{2+} liquid electroproduction.

To validate these findings in a practical setting, the PM-Cu electrode was integrated into a zero-gap membrane electrode assembly (MEA) electrolyzer (Figure 4d and Figure S26). Without applying a catholyte to reduce the ohmic loss and maximize the energy efficiency, we operated the electrolyzer at a constant current density of 1 A/cm^2 for 50 hours of continuous COR operation. The system reached a steady FE of $\sim 85\%$ for the C_{2+} liquid products. The partial current density for the C_{2+} liquid products reached 850 mA/cm^2 throughout, which is $7\times$ greater than the full-cell C_{2+} liquid production performance in previously reported CO electroreduction studies (Figure S27 and Table S9).

In summary, we have developed an effective strategy by utilizing polymer modification to directly integrate PNTCDA onto the surface of Cu catalysts. This approach increases the potassium ion concentration on the cathode surface at a reduction potential, facilitating efficient electrosynthesis of C_{2+} liquid products while effectively suppressing the hydrogen evolution reaction, which initiates and eventually dominates with increasing overpotential and current density. The synthesized PM-Cu demonstrates an $\sim 90\%$ selectivity for C_{2+} liquid products at a current density of 1.6 A/cm^2 , surpassing the performance of previously reported state-of-the-art catalysts for C_{2+} liquid product formation. Additionally, theoretical investigations demonstrated that PNTCDA promotes the dehydration of hydrated potassium ions on the surface of the PM-Cu electrode. This effectively inhibits the initiation of the hydrogen evolution reaction and increases the barrier for H_2O dissociation. Additionally, the addition of PNTCDA substantially lowers the kinetic barrier to C–C coupling, thereby promoting the C–C coupling reaction and augmenting the specificity toward C_{2+} liquid products. These findings indicate the potential of utilizing *in situ* molecular modification engineering to improve the conversion efficiency of CO to C_{2+} liquid products.

Experimental section

Chemicals. All chemicals, including precursors, solvents, and ionomers, unless otherwise stated, were used without further purification.

Synthesis of catalysts and cathode preparation

Preparation of CuO nanosheets. We first prepared CuO precatalysts using a hydrothermal method similar to that used in a previous report.^[51] Typically, CuSO₄ 5H₂O (2 g) was first dissolved in a 1 M NaOH solution. The solution was then transferred to a Teflon[®] reactor with a volume of 50 mL and reacted at 130 °C for 12 h. After the reaction, the solution was cooled naturally to room temperature and centrifuged for separation. The precipitate was washed with acetone and deionized water at least three times, dried under vacuum overnight, and then ground into a powder.

Preparation of PNTCDA. PNTCDA was synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and ethylene diamine (EDA).^[28,29] Equimolar NTCDA and EDA were allowed to react under reflux in *N*-methylpyrrolidone (NMP) for 6 hours. The product was filtered, washed with ethanol and NMP several times, dried at 120 °C in air for 12 hours, and then heated in a nitrogen atmosphere for 8 hours at 300 °C.

Preparation of PNTCDA-modified CuO nanosheets (PM-CuO). The PM-CuO catalyst was synthesized via the same hydrothermal method. First, we added 80 μmol of PNTCDA to CuSO₄ 5H₂O (2 g) dissolved in a 1 M NaOH solution. The solution was then transferred to a Teflon[®] reactor with a volume of 50 mL and reacted at 130°C for 12 h. After the reaction, the solution was cooled naturally to room temperature and centrifuged for separation. The precipitate was washed with acetone and deionized water at least three times, dried under vacuum overnight, and then ground into a powder.

Preparation of gas diffusion electrodes (GDEs). For GDE with the PM-CuO precatalyst, 0.6 mmol of PM-CuO precatalyst was subsequently dispersed into 2 mL of ethanol and 80 μL of Nafion[®] solution under ultrasonication for at least 60 minutes to obtain a homogeneous catalyst slurry. Then, the catalyst slurry was loaded on a GDL (2 cm × 2 cm, Freudenberg H23C9) by a

pressure rolling method. We applied a catalyst loading of $\sim 10 \text{ mg/cm}^2$ to prepare the working electrode. Electrodes with CuO precatalysts were prepared by a similar procedure. The subsequent procedures for the preparation were the same as those for the preparation of GDE with the PM-CuO precatalyst.

The as-prepared GDEs were run for 300 s at -0.5 V (vs. RHE) in 3 M KOH until a stable current was reached to ensure that the precatalysts were completely electroreduced to a stable state as the CORR catalysts.

The electrode potentials were rescaled to the RHE reference by the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \text{ pH} + 0.098 \text{ V}$$

Electrochemical measurements

CO electrolysis in a flow cell. Electrochemical measurements were performed in a three-electrode flow cell powered by a potentiostat (Metrohm Autolab PGSTAT302N, equipped with a 10 A current booster); a gas diffusion electrode deposited with the as-prepared catalysts was used as the working electrode, and a Hg/HgO electrode (with 1 M KOH as the filling solution) and a NiFe electrodeposited on Ni foam were employed as the reference and counter electrodes, respectively.^[52] The CO electrolysis performance of various catalysts was evaluated using a homemade flow cell electrolyzer consisting of a gas chamber, a cathodic chamber, and an anodic chamber (Figure S21). The as-prepared working electrode was positioned between the gas and cathodic chambers (with a fixed geometric active surface area of 1 cm^2), with the catalyst layer facing toward the electrolyte. An AEM (Fumatech FAB-PK-130) was used to separate the cathode and anode chambers. The combined GDE, AEM and anode were then positioned and clamped together using silicone spacers such that the alkaline electrolyte could be directed into the chambers between the anode and AEM as well as the cathode and AEM at a speed of 10 mL/min using a peristaltic pump. The CO (Air Liquide, 99.99%) flow was kept constant at 80 mL/min using an Alicat Scientific mass flow controller and directly supplied to the gas chamber. The actual flow rate was determined using a bubble flowmeter at the outlet of the gas chamber.^[53] For each test, the reaction ran for at least 120 s to reach a steady state before the products were collected for analysis.

CO electrolysis in a membrane electrode assembly electrolyzer. For CO electrolysis measurements in an MEA electrolyzer, we applied a similar method to prepare the PM-Cu cathodic GDE as that used in the alkaline flow cell. For MEA cell assembly, we placed the GDE on a flow field with the geometric active area fixed to 1×1 cm. We then directly pressed an AEM (Sustainion X37-50) and an IrO_x-coated Ni foam anode together with the other MEA flow field on top.

For CO electrolysis testing, humidified CO gas at a flow rate of ~4.6 sccm was supplied to the cathode chamber of the MEA electrolyzer. At the anode side, an alkaline electrolyte was introduced into the anode chamber and circulated with a pump at a rate of 1 mL/min. Before sample collection, the cell was activated for 10 minutes at a constant current of 100 mA. The products from the cathode side went through a homemade cold trap to separate the gas and liquid products.

Electrochemical active surface area measurement. The electrochemical surface area (ECSA) was deduced from electrochemical double-layer capacitance (C_{dl}) by dividing a factor of 0.029 mF/cm², according to the previous report.^[54] The measurement of C_{dl} was carried out by cyclic voltammetry (CV) at the non-Faradic region. The catalysts were scanned at a range of 0.30 to 0.45 V vs. RHE using elevated scan rates. The cathodic current at 0 V vs. OCP was plotted against scan rates (Figure S5). Then, linear fitting was adopted to these points, and the average slope of cathodic plots represented the value of C_{dl} .

In situ Raman spectroscopy. The *in situ* Raman measurements were performed using a Horiba Scientific Xplora Raman Microscope in a modified flow cell and a water immersion objective (100×) with a 633 nm laser (NA = 1.0, WD = 2.0 mm; LUMPLFLN-60X/W; Olympus Inc.; Waltham, MA). Each spectrum was acquired using a 5-s integration and an averaged 10 scans. The spectra were recorded and processed using the LabSpec 6.0 software. The same working electrode prepared for electrochemical performance testing was applied for *in situ* Raman analysis. An Ag/AgCl electrode and a graphite rod were used as the reference electrode and the counter electrode, respectively. 3 M KOH aqueous solution was used as the electrolyte. CO gas feedstocks was continuously supplied to the gas chamber during the measurement.

References

- [1] R. F. Service, *Science* **2021**, 371, 6536.
- [2] M. Jouny, G.S. Hutcgings, F. Jiao, *Nat. Catal.* **2019**, 2, 1062-1070.
- [3] Y. Y. Birdja, E. Pérez-Gallent, M. C. Figueiredo, A. J. Göttle, F. Calle-Vallejo, M. T. M. Koper, *Nat. Energy* **2019**, 4, 732-745.
- [4] C. Hepburn, E. Adlen, J. Beddington, E. A. Carter, S. Fuss, N. M. Dowell, J. C. Minx, P. Smith, C. K. Williams, *Nature* **2019**, 575, 87-97.
- [5] W. Deng, P. Zhang, B. Seger, J. Gong, *Nat. Commun.* **2022**, 13, 803.
- [6] P. Wang, H. Yang, C. Tang, Y. Wu, Y. Zheng, T. Cheng, K. Davey, X. Huang, S.-Z. Qiao, *Nat. Commun.* **2022**, 13, 3754.
- [7] R. M. Arán-Ais, F. Scholten, S. Kunze, R. Rizo, B. Roldan Cuenya, *Nat. Energy* **2020**, 5, 317-325.
- [8] B. Zhang, J. Zhang, M. Hua, Q. Wan, Z. Su, X. Tan, L. Liu, F. Zhang, G. Chen, D. Tan, X. Cheng, B. Han, L. Zheng, G. Mo, *J. Am. Chem. Soc.* **2020**, 142, 13606-13613.
- [9] J. Wang, H.-Y. Tan, Y. Zhu, H. Chu, H. M. Chen, *Angew. Chem.* **2021**, 133, 17394-17407.
- [10] W. Ma, S. Xie, T. Liu, Q. Fan, J. Ye, F. Sun, Z. Jiang, Q. Zhang, J. Cheng, Y. Wang, *Nat. Catal.* **2020**, 3, 478-487.
- [11] L. Wang, D. C. Higgins, Y. Ji, C. G. Morales-Guio, K. Chan, C. Hahn, T. F. Jaramillo, *Proc. Natl. Acad. Sci. U.S.A.* **2020**, 117, 12572-12575.
- [12] L. Wang, S. Nitopi, A. B. Wong, J. L. Snider, A. C. Nielander, C. G. Morales-Guio, M. Orazov, D. C. Higgins, C. Hahn, T. F. Jaramillo, *Nat. Catal.* **2019**, 2, 702-708.
- [13] Z. Yin, H. Peng, X. Wei, H. Zhou, J. Gong, M. Huai, L. Xiao, G. Wang, J. Lu, L. Zhuang, *Energy Environ. Sci.* **2019**, 12, 2455-2462.
- [14] C. Kim, J. C. Bui, X. Luo, J. K. Cooper, A. Kusoglu, A. Z. Weber, A. T. Bell, *Nat. Energy* **2021**, 6, 1026-1034.
- [15] M. C. O. Monteiro, F. Dattila, B. Hagedoorn, R. García-Muelas, N. López, M. T. M. Koper, *Nat. Catal.* **2021**, 4, 654-662.
- [16] Z. Yan, J. L. Hitt, Z. Zeng, M. A. Hickner, T. E. Mallouk, *Nat. Chem.* **2021**, 13, 33-40.
- [17] D. Kim, S. Yu, F. Zheng, I. Roh, Y. Li, S. Louisia, Z. Qi, G. A. Somorjai, H. Frei, L.-W. Wang, P. Yang, *Nat. Energy* **2020**, 5, 1032-1042.
- [18] J. E. Huang, F. Li, A. Ozden, A. Sedighian Rasouli, F. P. García de Arquer, S. Liu, S. Zhang, M. Luo, X. Wang, Y. Lum, Y. Xu, K. Bertens, R. K. Miao, C.-T. Dinh, D. Sinton, E. H. Sargent, *Science* **2021**, 372, 1074-1078.
- [19] M. Flores-Granobles, M. Saeys, *Energy Environ. Sci.* **2020**, 13, 1923-1932.
- [20] J. Resasco, L. D. Chen, E. Clark, C. Tsai, C. Hahn, T. F. Jaramillo, K. Chan, A. T. Bell, *J. Am. Chem. Soc.* **2017**, 139, 11277-11287.
- [21] R. B. Sandberg, J. H. Montoya, K. Chan, J. K. Nørskov, *Surf. Sci.* **2016**, 654, 56-62.
- [22] K. Yang, M. Li, S. Subramanian, M. A. Blommaert, W. A. Smith, T. Burdyny, *ACS Energy Lett.* **2021**, 6, 4291-4298.
- [23] C. Peng, S. Yang, G. Luo, S. Yan, M. Shakouri, J. Zhang, Y. Chen, W. Li, Z. Wang, T.-K. Sham, G. Zheng, *Adv. Mater.* **2022**, 34, 2204476.
- [24] R. J. Gilliam, J. W. Graydon, D. W. Kirk, S. J. Thorpe, *Int. J. Hydrogen Energy* **2007**, 32, 359-364.
- [25] L. Chen, W. Li, Y. Wang, C. Wang, Y. Xia, *RSC Adv.* **2014**, 4, 25369-25373.
- [26] X. Dong, L. Chen, J. Liu, S. Haller, Y. Wang, Y. Xia, *Sci. Adv.* **2016**, 2, e1501038.
- [27] J. Wang, F. Li, Y. Qu, Y. Liu, Y. Yang, W. Li, M. Zhao, *J. Mater. Chem. A* **2018**, 6, 24869-24876.
- [28] Ghosh, M. *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, **1996**
- [29] Z. Song, H. Zhan, Y. Zhou, *Angew. Chem. Int. Ed.* **2010**, 49, 8444-8448.
- [30] T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, 24, 6397-6409.
- [31] F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J. A. Dura, K. Xu, C. Wang, *Nat. Mater.* **2018**, 17, 543-549.
- [32] N. Dubouis, A. Serva, R. Berthin, G. Jeanmairet, B. Porcheron, E. Salager, M. Salanne, A. Grimaud, *Nat. Catal.* **2020**, 3, 656-663.
- [33] X. Chen, X. Shen, B. Li, H.-J. Peng, X.-B. Cheng, B.-Q. Li, X.-Q. Zhang, J.-Q. Huang, Q. Zhang, *Angew. Chem. Int. Ed.* **2018**, 57, 734-737.
- [34] Q. Zhang, Y. Ma, Y. Lu, X. Zhou, L. Lin, L. Li, Z. Yan, Q. Zhao, K. Zhang, J. Chen, *Angew. Chem. Int. Ed.* **2021**, 60, 23357-23364.
- [35] T. Deng, S. Jia, C. Chen, J. Jiao, X. Chen, C. Xue, W. Xia, X. Xing, Q. Zhu, H. Wu, M. He, B. Han, *Angew. Chem. Int. Ed.* **2024**, 63, e202313796.

- [36] J. Jin, J. Wicks, Q. Min, J. Li, Y. Hu, J. Ma, Y. Wang, Z. Jiang, Y. Xu, R. Lu, G. Si, P. Papangelakis, M. Shakouri, Q. Xiao, P. Ou, X. Wang, Z. Chen, W. Zhang, K. Yu, J. Song, X. Jiang, P. Qiu, Y. Lou, D. Wu, Y. Mao, A. Ozden, C. Wang, B. Y. Xia, X. Hu, V. P. Dravid, Y.-M. Yiu, T.-K. Sham, Z. Wang, D. Sinton, L. Mai, E. H. Sargent, Y. Pang, *Nature* **2023**, 617, 724-729.
- [37] J. Li, H. Xiong, X. Liu, D. Wu, D. Su, B. Xu, Q. Lu, *Nat. Commun.* **2023**, 14, 698.
- [38] X. Wang, Z. Wang, F. P. García de Arquer, C.-T. Dinh, A. Ozden, Y. C. Li, D.-H. Nam, J. Li, Y.-S. Liu, J. Wicks, Z. Chen, M. Chi, B. Chen, Y. Wang, J. Tam, J. Y. Howe, A. Proppe, P. Todorović, F. Li, T.-T. Zhuang, C. M. Gabardo, A. R. Kirmani, C. McCallum, S.-F. Hung, Y. Lum, M. Luo, Y. Min, A. Xu, C. P. O'Brien, B. Stephen, B. Sun, A. H. Ip, L. J. Richter, S. O. Kelley, D. Sinton, E. H. Sargent, *Nat. Energy* **2020**, 5, 478-486.
- [39] P. Wang, H. Yang, Y. Xu, X. Huang, J. Wang, M. Zhong, T. Cheng, Q. Shao, *ACS Nano*. **2021**, 15, 1, 1039–1047.
- [40] T. T. H. Hoang, S. Verma, S. Ma, T. T. Fister, J. Timoshenko, A. I. Frenkel, P. J. A. Kenis, A. A. Gewirth, *J. Am. Chem. Soc.* **2018**, 140, 17, 5791-5797.
- [41] W. Ma, S. Xie, T. Liu, Q. Fan, J. Ye, F. Sun, Z. Jiang, Q. Zhang, J. Cheng, Y. Wang, *Nat. Catal.* **2020**, 3, 478-487.
- [42] Y. C. Li, Z. Wang, T. Yuan, D.-H. Nam, M. Luo, J. Wicks, B. Chen, J. Li, F. Li, F. P. García de Arquer, Y. Wang, C.-T. Dinh, O. Voznyy, D. Sinton, E. H. Sargent, *J. Am. Chem. Soc.* **2019**, 141, 21, 8584-8591.
- [43] Y. Wang, Z. Wang, C.-T. Dinh, J. Li, A. Ozden, M. G. Kibria, A. Seifitokaldani, C.-S. Tan, C. M. Gabardo, M. Luo, H. Zhou, F. Li, Y. Lum, C. McCallum, Y. Xu, M. Liu, A. Proppe, A. Johnston, P. Todorovic, T.-T. Zhuang, D. Sinton, S. O. Kelley, E. H. Sargent, *Nat. Catal.* **2020**, 3, 98-106.
- [44] J. Li, A. Xu, F. Li, Z. Wang, C. Zou, C. M. Gabardo, Y. Wang, A. Ozden, Y. Xu, D.-H. Nam, Y. Lum, J. Wicks, B. Chen, Z. Wang, J. Chen, Y. Wen, T. Zhuang, M. Luo, X. Du, T.-K. Sham, B. Zhang, E. H. Sargent, D. Sinton, *Nat. Commun.* **2020**, 11, 3685.
- [45] C. Yang, B. Hee Ko, S. Hwang, Z. Liu, Y. Yao, W. Luc, M. Cui, A. S. Malkani, T. Li, X. Wang, J. Dai, B. Xu, G. Wang, D. Su, F. Jiao, L. Hu, *Sci. Adv.* **2020**; 6, eaaz6844.
- [46] M. Jouny, W. Luc, F. Jiao, *Nat. Catal.* **2018**, 1, 748-755.
- [47] W. Luc, X. Fu, J. Shi, J.-J. Lv, M. Jouny, B. Hee Ko, Y. Xu, Q. Tu, X. Hu, J. Wu, Q. Yue, Y. Liu, F. Jiao, Y. Kang, *Nat. Catal.* 2019, 2, 423-430.
- [48] C. Chen, X. Yan, S. Liu, Y. Wu, Q. Wan, X. Sun, Q. Zhu, H. Liu, J. Ma, L. Zheng, H. Wu, B. Han, *Angew. Chem. Int. Ed.* **2020**, 59, 16459-1646.
- [49] M. Jouny, J.-J. Lv, T. Cheng, B. H. Ko, J.-J. Zhu, W. A. Goddard, F. Jiao, *Nat. Chem.* **2019**, 11, 846-851.
- [50] Z. Liu, L. Song, X. Lv, M. Liu, Q. Wen, L. Qian, H. Wang, M. Wang, Q. Han, G. Zheng, *J. Am. Chem. Soc.* **2024**, 146, 20, 14260-14266.
- [51] A. El-Trass, H. ElShamy, I. El-Mehasseb, M. El-Kemary, *Appl. Surf. Sci.* **2012**, 258, 2997-3001.
- [52] X. Lu, C. Zhao, *Nat. Commun.* **2015**, 6, 6616.
- [53] B. Seger, M. Robert, F. Jiao, *Nat. Sustain.* **2023**, 6, 236-238.
- [54] A. Verdager-Casadevall, C. W. Li, T. P. Johansson, S. B. Scott, J. T. McKeown, M. Kumar, I. E. L. Stephens, M. W. Kanan, I. Chorkendorff, *J. Am. Chem. Soc.* **2015**, 137, 9808-9811.

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Author Contributions

B.Z. supervised the project. C.C. conceived the idea, designed and carried out most of the experiments. T.C., L.X., P.Y. and H.Y. performed the theoretical calculations. T.C. and C.C. wrote the related sections. N.W. carried out the XRD measurements. C.C. and B.Z. cowrote the manuscript. N.W., F.N. and W.G. provided fruitful suggestions. All authors discussed the results and assisted during manuscript preparation.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article or from the corresponding author upon request.

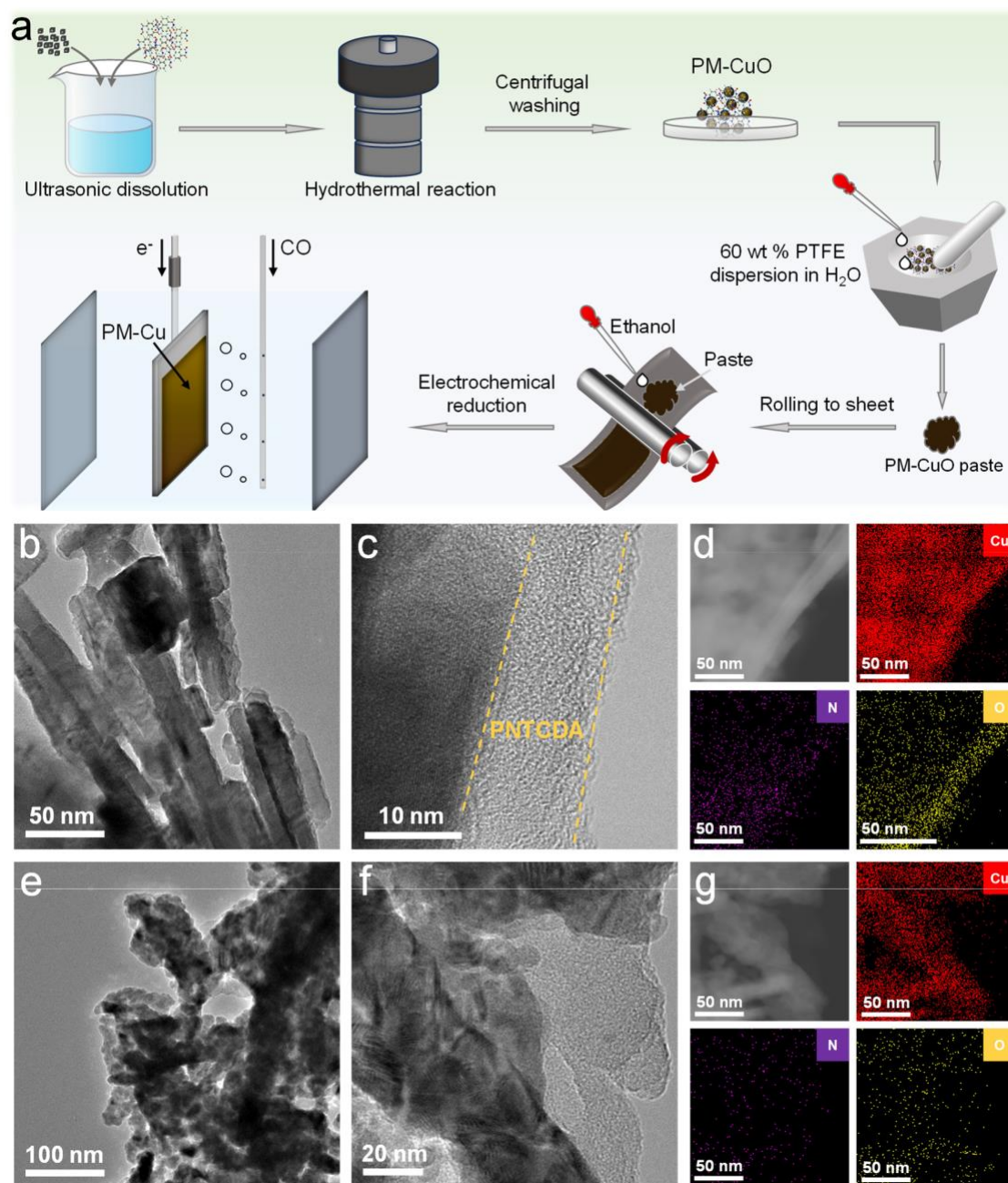


Figure 1. (a) Schematic diagram of the method for the proposed PM-Cu catalyst and the flow cell reactor assembled with the PM-Cu electrode. (b-d) Structural and compositional analyses of the preelectrolyzed PM-CuO nanosheets: (b, c) TEM images, (d) STEM image and corresponding EDS elemental mapping images, showing that Cu and PNTCDA are uniformly dispersed after preparation. (e-g) Structural and compositional analyses of the postelectrolysis PM-Cu catalyst: (e-f) TEM images, (g) STEM image and corresponding EDS elemental mapping images, indicating the stability of PNTCDA during CO reduction.

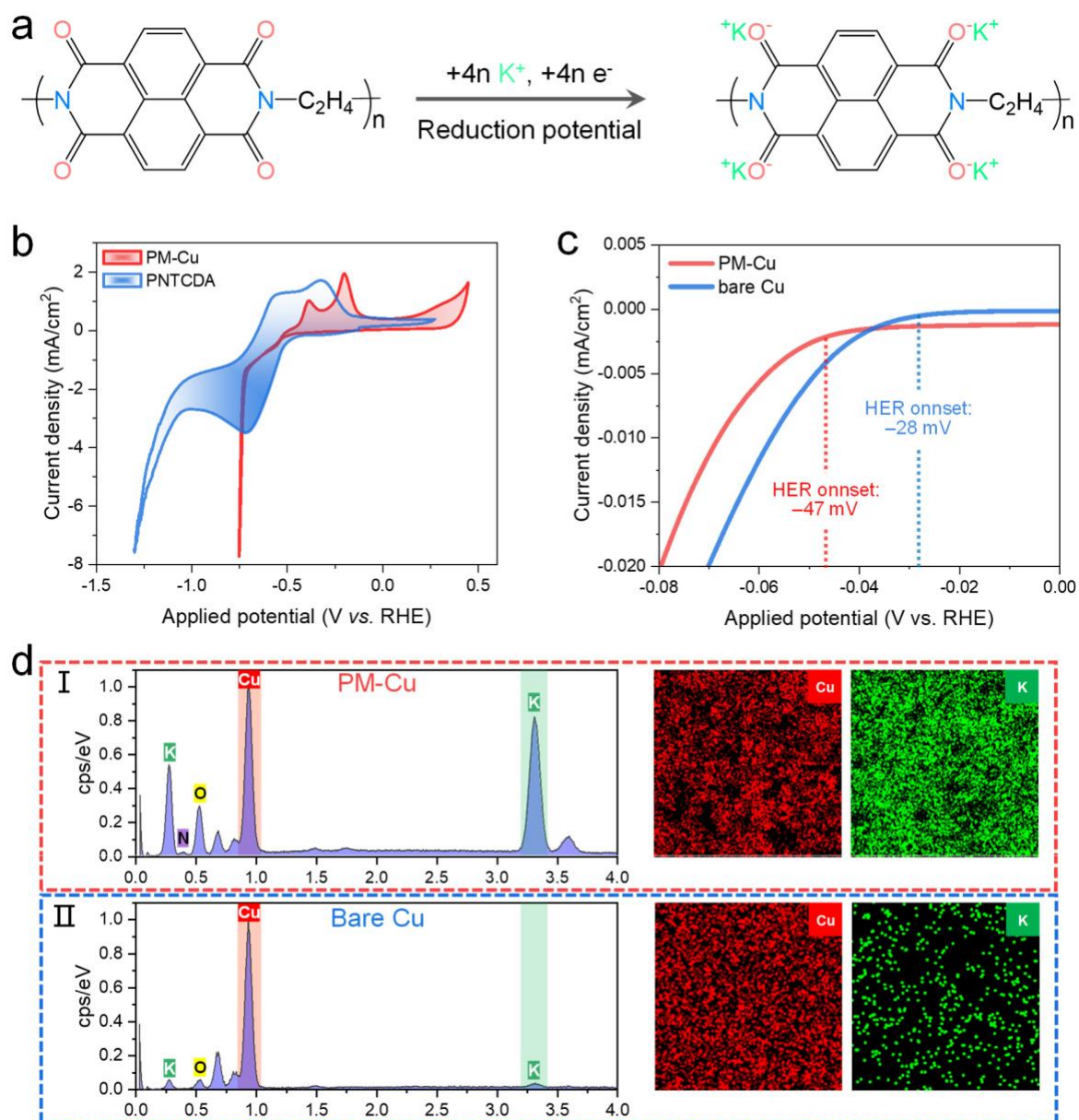


Figure 2. (a) Electrochemical reduction mechanism of PNTCDA. (b) Cyclic voltammetry (CV) curve of the PNTCDA-based electrode in aqueous 3 M KOH electrolyte. (c) Linear sweep voltammetry (LSV) curves of the preactivated PM-Cu electrode and preactivated CuO electrode without the PNTCDA electrode obtained in a flow cell reactor with Ar gas and 3 M KOH electrolyte. (d) EDS mapping of the PM-Cu (I) and CuO (II) electrodes following the reduction test in a flow cell reactor with Ar gas and 3 M KOH electrolyte.

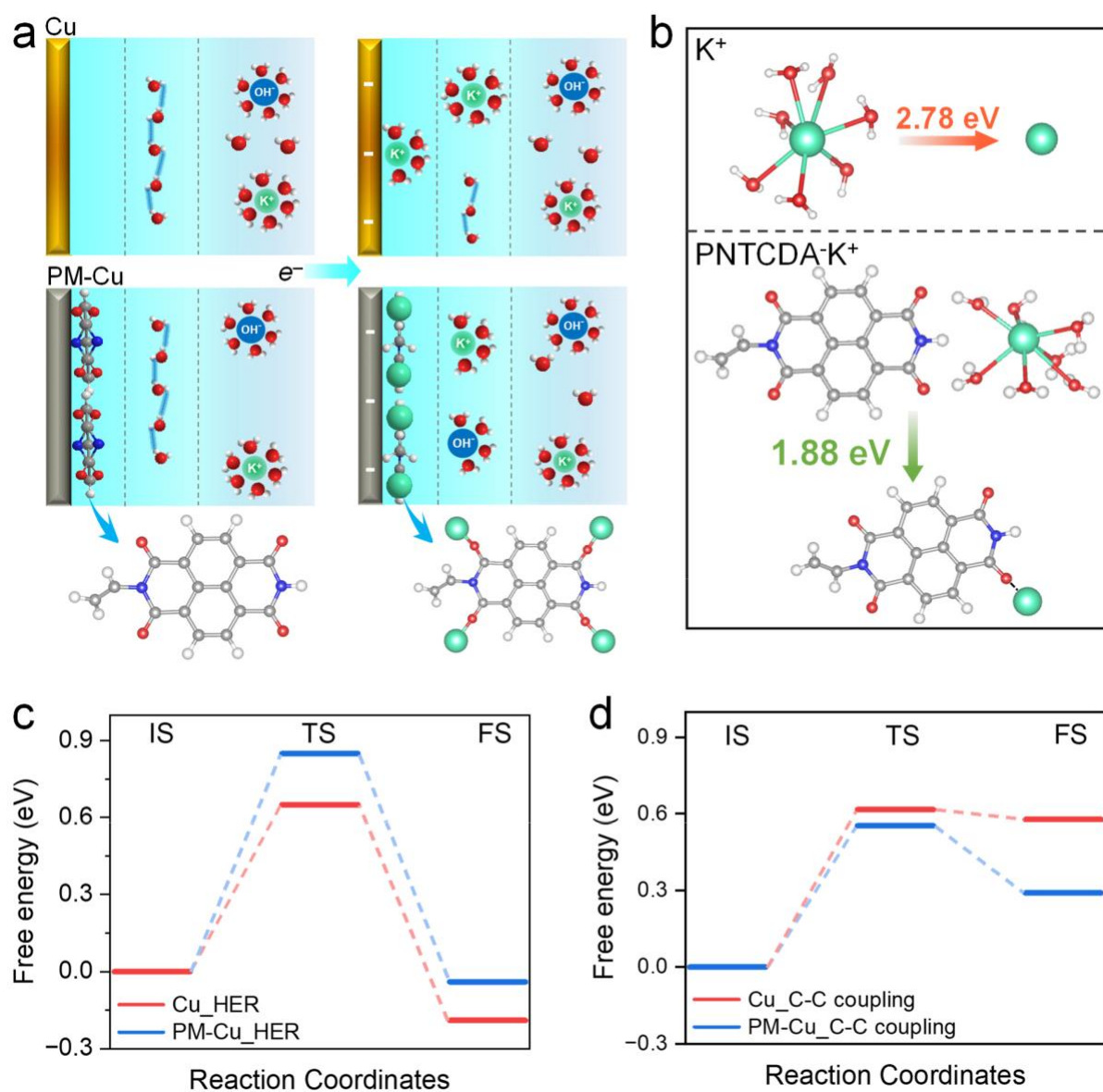


Figure 3. (a) Schematic illustration of the ionic environment and transport near a bare Cu electrode (upper panel) and a Cu electrode functionalized by the PNTCDA polymer (lower panel) and the corresponding solvation structures. (b) Desolvation energy of $K(H_2O)_7^+$ (upper panel) and $K(H_2O)_7^+$ coordinated with an NTCDA molecule (lower panel). (c) Calculated free energies for H_2O dissociation into adsorbed OH and H. (d) Calculated free energies for the C–C coupling pathway on bare Cu and PM–Cu.

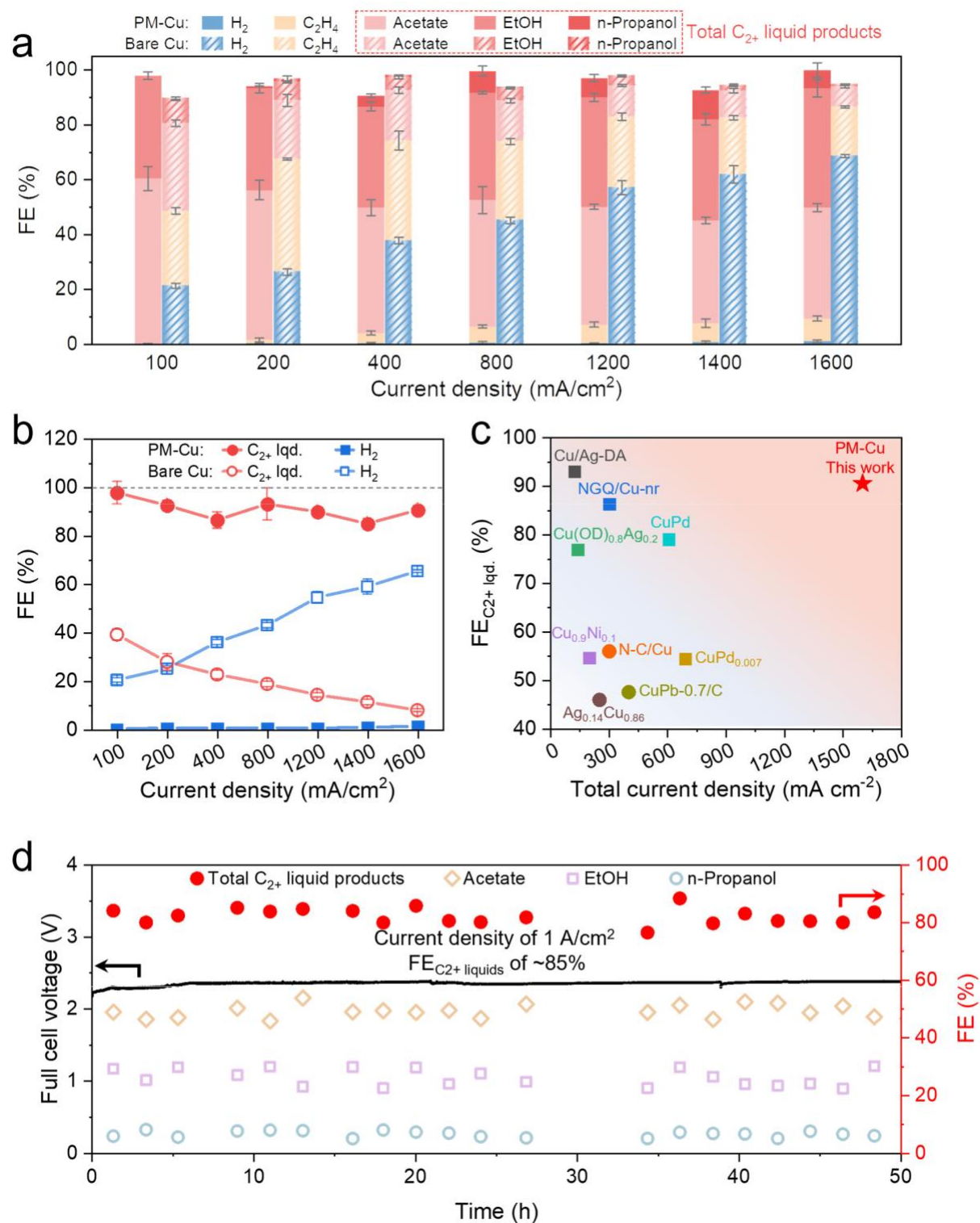


Figure 4. (a) CORR product distribution under various applied current densities on the PM-Cu and bare Cu electrodes. (b) Comparison of the Faradaic efficiencies of C_2+ liquid products (including ethanol, acetate, and n-propanol) and hydrogen for CO reduction at various applied

current densities on the PM-Cu and bare Cu electrodes. (c) Comparison of the maximum C₂+ liquid product FE versus current density between PM-Cu in this work and state-of-the-art catalysts in the literature for the CORR and CO₂RR (see Table S6 for more details). (d) Full-cell voltage and Faradaic efficiencies for C₂+ liquid products after 50 h of electrolysis at a constant current density of 1 A/cm² in a custom-designed MEA electrolyzer with a reaction area of 1 × 1 cm. The error bars represent standard deviations from at least three independent measurements.