Twin-boundary engineering boosted undercoordinated active sites for scalable conversion of CO2 to ethylene

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Article

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Twin-boundary engineering boosted undercoordinated active sites for scalable conversion of CO$_2$ to ethylene

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Keywords

CO$_2$ electroreduction, electrocatalysis, multicarbon product, membrane electrode assembly, twin-boundary, energy efficiency, *operando / in-situ* spectroscopy.
Abstract:

The development of highly selective and energy efficient technologies for electrochemical CO\textsubscript{2} reduction combined with renewable energy sources holds great promise for advancing the field of sustainable chemistry. The engineering of copper-based electrodes provides a pathway for the conversion of CO\textsubscript{2} into high-value multicarbon products (C\textsubscript{2+}). However, the ambiguous determination of the intrinsic CO\textsubscript{2} activity and the maximization of the density of exposed active sites have severely limited the use of Cu for the realization of practical electrocatalytic devices. Here, we report a scalable strategy to obtain a high density of undercoordinated sites by maximizing the exposure of twin-boundary active sites using a direct chronoamperometric pulse method. Our numerical investigations predicted that twin-boundaries modulate the adsorption behavior of *CO on the Cu surface, which acts as a key intermediate species associated with the production of multicarbon species. We investigated the consequence of twin-boundary density on dendric Cu catalysts (TB-Cu) by combining transmission electron microscopy, in-situ Raman and X-ray photoelectron spectroscopy with detailed electrochemical measurements. A linear relationship between the Faradaic efficiency of the C\textsubscript{2+} product and the presence of under-coordinated sites was observed, which allowed to directly quantify the contribution of the twin-boundary in Cu-based catalysts on the CO\textsubscript{2}RR properties and the formation of multicarbon products. Using a membrane electrode assembly electrolyzer, the high twin-boundary density Cu electrodes achieve a maximum Faradaic efficiency of 73.2 % for C\textsubscript{2+} product formation and a full cell energy efficiency of 20.2 % at a specific current density of 303.6 mA cm\textsuperscript{-2}. The TB-Cu was implemented in a 25 cm\textsuperscript{2} MEA electrolyzer and demonstrated selectivity of over 62 % for 70 hours together with current retention of 88.4 % at the applied potential of -3.80 V. The catalysts and electrolyzer were further coupled to an InGaP/GaAs/Ge triple-junction solar cell to demonstrate a solar-to-fuel (STF) conversion efficiency of 8.33 %. This work opens new avenues for the design of an undercoordinated Cu-based catalyst for the realization of solar-driven fuel production.
Introduction

The escalating levels of CO$_2$ in the atmosphere have raised significant concerns about the environmental impact of fossil fuel combustion. This has stimulated interest in exploring innovative technologies to use CO$_2$ as a feedstock for the production of valuable chemical fuels or chemicals.¹ In the search for developing techniques to achieve carbon neutrality and CO$_2$ utilization, electrochemical processes are considered as a potentially economically viable route to reuse CO$_2$ and close the carbon cycle.² Techno-economic analyses have confirmed the potential to produce multicarbon (C$_{2+}$) products due to their higher energy density and commercial value.³ Considering the existing strategies for CO$_2$ to C$_{2+}$ conversion, copper-based electrocatalysts are promising candidates capable of producing C$_{2+}$ products at significant production rates.⁴ Fine tuning of the CO$_2$RR selectivity is currently being explored via oxidation state engineering, molecular functionalization, doping or alloying.⁵ Unfortunately, precise control and efficient scalability of these strategies for CO$_2$ conversion remain a major challenge, while accurate quantification of the catalytic activity and coupling with renewable energy sources remain challenging.⁶ Compared to crystal step edges, which typically undergo continuous dynamic dissolution and reconstruction during catalytic reactions, the twin-boundary (TB) site is one of the most stable and well-defined defects.⁷ In a face-centered-cubic (fcc) structure, the densely packed arrangements at the TB form a low interfacial energy, which endows the structure with exceptional mechanical strength, electrical conductivity, and enhanced thermal stability.⁸,⁹ In addition, the exposed TB atoms have a chemically identical arrangement population, providing a clean and simple catalyst model.¹⁰,¹¹ Although twin boundaries in metallic electrocatalysts have recently been proposed to improve the selectivity and the efficiency of the electrochemical CO$_2$ reduction to methene,¹²,¹³ the limited control of the twin-boundary density on the catalyst surface has hindered realistic applications, while the direct quantification of the twin-boundary contribution to CO$_2$RR remains ambiguous.¹⁴ Here, we report a density-controlled twin-boundary growth strategy for Cu nanostructures via chronoamperometric pulse electrodeposition. We demonstrated the preparation of a high-density twin-boundary dendritic Cu catalyst (TB-Cu) on a porous gas diffusion electrode (GDE) for the direct conversion of CO$_2$. A remarkable Faradaic efficiency (FE) of 46.8 ± 1.2 % for the direct conversion of CO$_2$ to ethylene was observed in an H-cell configuration. By combining the physical characterization of the catalyst with extensive electrocatalytic measurements, we identified a linear relationship between the FE and TB density, together with the significantly enhanced activity confined under nanoscale, providing clear evidence for the quantitative contribution of the uncoordinated TB sites. Our investigations based on in-situ Raman spectroscopy together with ab initio calculations revealed that the presence of TBs can efficiently modulate the adsorption behavior of the key
intermediate: *CO, which triggers the dimerization of *CO during CO\textsubscript{2} reduction.\textsuperscript{15} According to the density functional theory (DFT) results, we predicted that the reaction free energy for the key elementary step over the TB-Cu surface is much lower and the overall reaction is more favorable on the undercoordinated TB site than on the coordinated Cu(111) facet. Finally, we implemented the TB-Cu catalyst in a membrane electrode assembly (MEA) electrolyzer and demonstrated a FE for the C\textsubscript{2+} product formation of 73.2 \% and a full cell energy efficiency of 20.2 \% at a specific current density of 303.61 mA cm\textsuperscript{-2}. This represents a 187 \% and 665 \% increase in FE\textsubscript{C2+} and j\textsubscript{C2+}, respectively, compared to pristine Cu electrodes without TBs. The scalability of TB-Cu electrodes was also validated by successfully fabricating and measuring a 25 cm\textsuperscript{2} MEA flow electrolyzer with a predicted solar-to-fell (STF) conversion rate of \sim 8.33 \%.

**Results and discussion:**

**Design and characterization of the density tunable TB-Cu catalyst**

Twin-boundary density tunable dendritic Cu catalysts were prepared by a pulsed electrochemical deposition method on the surface of a GDE.\textsuperscript{16} Under a constant deposition current density of 100 mA cm\textsuperscript{-2}, the deposition time was set as 50, 100, 200 and 500 ms with a pulse time of 250 ms corresponding to pulse frequencies between 3.3 and 1.3 Hz (Figure 1a). The total deposition charge was set at 15 C cm\textsuperscript{-2} to keep the catalyst loading density on the GDE constant.\textsuperscript{17} We performed extensive qualitative and quantitative analyses of the twin-boundary (TB) density using electron microscopy techniques (Figure 1b, Supplementary Figure 1). We then quantitatively investigated the relationship between the electrodeposition pulse frequency and the TB density. For TB-Cu deposited at a frequency of 1.3 Hz, the prominent twin width is 17 ± 1.4 nm and the corresponding TB density reaches 2.2 ± 0.2 \times 10\textsuperscript{4} cm\textsuperscript{-1} (called hereafter TB-Cu\textsubscript{2.2}) (Supplementary Figure 2). Increasing the pulse deposition frequency leads to a smaller twin width and the TB densities were estimated to be 7.9 ± 0.8 \times 10\textsuperscript{4}, 15.4 ± 0.5 \times 10\textsuperscript{4} and 29.6 ± 1.6 \times 10\textsuperscript{4} cm\textsuperscript{-1}, corresponding to TB-Cu\textsubscript{7.9}, TB-Cu\textsubscript{15.4} and TB-Cu\textsubscript{29.6}, respectively. For comparison, we also observed the pristine Cu catalyst deposited by steady-state electrodeposition and found virtually no twin-boundary (TB-Cu\textsubscript{0}) (Supplementary Figure 3).

As shown in the cross-sectional scanning electron microscope (SEM) image (Figure 1c) and transmission electron microscope (TEM) image (Figure 1d), the dendritic Cu structures were grown in-situ on the surface of GDE. This growth method ensures proper electrical coupling between the catalyst and the electrode, which optimizes the conductivity and facilitates efficient charge transfer.\textsuperscript{18} In the fcc crystal structure of copper, the twin-boundaries are mirror planes along with the <111> direction, which reverses the normal stacking order of the (111) planes.\textsuperscript{19} We attempted to observe the
presence of the TB in the TB-Cu catalyst using high-resolution transmission electron microscopy (HRTEM) (Figure 1e). As shown in Figure 1f, the facet character of the TB-Cu structure was confirmed by the selected area electron diffraction (SAED) pattern, which displays two sets of symmetrical diffraction spots attributed to Cu (111) facets; further confirming the formation of a high-density TB. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image revealed the presence of higher contrast lines parallel to the growth direction of the Cu dendrites (Figure 1g), confirming that the lattice is symmetrically arranged on both sides of the line, showing a typical TB feature in good agreement with the simulated atomic structure.²⁰

**CO₂RR performance in H-cell configuration.**

The CO₂RR electrocatalytic activity was first evaluated using an H-type cell in a standard three-electrode configuration with 0.5 M KHCO₃. Figure 2a shows the linear sweep voltammetry (LSV) curves recorded in both argon (Ar) (dashed line) and CO₂-saturated (solid line) electrolytes for different TB-Cu catalysts and compared with the pristine Cu (TB-Cu₀). It is noteworthy that the onset potential decreases continuously with increasing TB densities. The lowest onset potential is obtained from TB-Cu₂₉.₆ and is estimated to be -0.25 V versus the reversible hydrogen electrode (vs. RHE), which corresponds to a positive shift of 0.21 V with respect to that of the TB-Cu₀, highlighting the improvement of the thermodynamics of the CO₂RR by TB engineering.²¹ To quantify the CO₂RR performance, we performed steady-state chronoamperometric measurements for all the TB-Cu catalysts under different applied potentials between -0.4 and -1.4 V vs. RHE and evaluated the Faradaic efficiency (FE) by using nuclear magnetic resonance (NMR) and gas chromatography (GC) (see details in the Methods section). As shown in Figure 2b and Supplementary Figure 4, hydrogen (H₂), carbon monoxide (CO), formate (HCOO⁻), methane (CH₄) and ethylene (C₂H₄) were detected, confirming the presence of C₁ and C₂ products during the CO₂RR, and the highest FEₐ reaches 46.2 % at -1.1 V vs. RHE. Remarkably, we found that the FEₐ products linearly increase with the TB density at all applied potentials, indicating a rapidly improving selectivity for the *CO dimerization and the production of multicarbon products instead of direct protonation (Figure 2c).

To accurately measure the effect of TB increase on the CO₂RR, we then estimated the electrochemical active surface area (ECSA) using a Pb underpotential deposition method (Supplementary Figure 5). The specific current density for C₂⁺ products was normalized to the ECSA values for the corresponding TB-Cu electrodes under different applied potentials between -0.4 to -1.4 V vs. RHE (Figure 2d). We found that for each applied potential between -0.8 V and -1.2 V vs. RHE, there is a linear scaling relationship between jC₂⁺ and the density of TB on the Cu electrodes, highlighting that the conversion rates benefit from the presence of the TB (Figure 2e). Comparing the
slopes obtained for each potential, we observe a clear increase in the conversion rates, indicating a strong influence of the TB on the CO$_2$RR activity of the Cu electrodes.

The stability for the CO$_2$RR performance of TB-Cu$_{29.6}$ was evaluated over 24 hours at the optimum potential of -1.10 V vs. RHE in 0.5 M KHCO$_3$ with continuous CO$_2$ saturation. The current was continuously measured while the products were collected and quantified by GC and NMR analysis. As shown in Figure 2f, the performance of the TB-Cu$_{29.6}$ catalyst was found to be very stable with a virtually constant cathode current density and minimal drop in FE$_{C_2^+}$. After 24 hours, the current density and FE$_{C_2^+}$ retention reach 96.8% and 94.1%, respectively. For comparison, we operated the MEA system with TB-Cu$_0$ and obtained retentions of 74.3% and 80.2% for the current density and FE$_{C_2^+}$, respectively (Supplementary Figure 6).

**CO$_2$RR performance in SECCM configuration.**

In order to provide direct evidence for the enhancement of the CO$_2$RR properties via the engineering of the twin-boundary, we performed scanning electrochemical cell microscopy (SECCM) experiments in the “hopping mode” (Figure 2g). The SECCM measurements were performed at the interface of TB-Cu$_0$ and TB-Cu$_{29.6}$ catalyst domains grown on the surface of a glassy carbon electrode (see Methods section for more details), and the catalyst layer was polarized between -0.1 V and -1.0 V vs. RHE at a scanning rate of 200 mV s$^{-1}$. The SECCM capillary used for the measurements had an aperture diameter of ~100 nm (inset of Figure 2h). We recorded the LSV curves of the electrodeposited Cu samples TB-Cu$_0$ and TB-Cu$_{29.6}$, under identical SECCM configurations. We found that both the activity and reaction kinetics for CO$_2$RR are greatly improved for TB-Cu$_{29.6}$ compared to TB-Cu$_0$ corresponding to a ~5-fold increase in the current density and a 62 mV positive shift for onset potential (Figure 2h). To assess the electrocatalytic activity of the TB-Cu catalyst, we used activity mapping techniques based on recorded cyclic voltammograms (CVs) at defined potentials (Figure 2i). A grid of 20 × 10 with a hopping distance of 1 µm was used for this analysis. We generated activity maps highlighting different electrocatalytic activity ranges by comparing the recorded CV curves at a constant applied potential (-1.0 V vs. RHE). When comparing the activity map of TB-Cu$_{29.6}$ to that of TB-Cu$_0$, distinct patterns with locally enhanced activity were observed in the map of TB-Cu$_{29.6}$. Overall, our SECCM investigations provide compelling evidence of the positive impact of TBs on the electrocatalytic properties of the Cu surface.

**Investigation of the CO$_2$RR mechanism by in-situ Raman spectroscopy and DFT calculations.**

It is well known that the formation of multicarbon products in CO$_2$RR involves the formation of the *CO intermediate, which has been identified as a critical factor in achieving high conversion efficiency
of CO₂ to multicarbon products.23 Rather, the subsequent dimerization of the *CO intermediate via a C-C coupling step is another key point for the generation of multicarbon than the single-carbon product.24 To gain mechanistic insight into the CO₂RR on TB-Cu electrodes, we probed the surface of the catalysts using in-situ Raman spectroscopy during the reaction to elucidate the interactions between the catalyst surface and the adsorbed *CO intermediate (Figure 3a).25 As shown in Figure 3b, we investigated the relationship between the twin-boundary density and the Raman signals for the *CO intermediate at the optimum potential associated with the formation of C₂H₄. The stretching modes of *CO can be deconvoluted into two components: high- and low-frequency modes below and above 2080 cm⁻¹, corresponding to *CO adsorbed on terrace-like sites (*CO_bridge) and isolated defect-like sites (*CO_atop), respectively.26 It has been previously reported that the optimized ratio of *CO between *CO_bridge and *CO_atop on the Cu surface combined with higher *CO coverage triggers the formation of multicarbon products including ethylene and ethanol.27 We observed a linear relationship between the TB density dependent interplay and the ratio of *CO_atop to *CO_bridge together with FE_C₂⁺ (Figure 3c). This observation underscores the significance of twin boundaries in modulating the CO₂RR process and highlights that the formation of TB sites on the surface of copper induces an enrichment in the population of the *CO_atop on defect-like sites relative to that of *CO_bridge. This enrichment of *CO_atop facilitates the formation of multicarbon products through C-C coupling reactions.28

To further understand the mechanism of CO₂RR process on the TB-Cu catalysts and Cu (111) facets, we performed DFT calculations for each elementary step associated with the CO₂ conversion to ethylene (Figure 3d, Supplementary Figure 7). We note that the main difference between the TB-Cu and Cu (111) facets is the presence of under-coordinated Cu atoms on the TB sites. The energy profile of the CO₂RR predicts that the formation of C₂H₄ is thermodynamically more favorable on TB sites compared to Cu (111) (Figure 3e). As mentioned above, the proposed mechanism for C-C coupling on copper surfaces involves the initial reduction of CO₂ to produce adsorbed *CO intermediates, which are subsequently involved in a dimerization pathway leading to the formation of C₂H₄.29 Our calculations further revealed that the energy barrier associated with the limiting step corresponding to the proton-coupled electron transfer step for the hydrogenation of *CO to *CHO is 18 % lower on TB sites compared with Cu (111) at 1.16 eV and 0.76 eV, respectively. We predict that on TB sites, the C-C coupling proceeds via the dimerization of *CHO and *CO to the intermediate *OCCHO with an associated energy barrier of 0.3 eV. For comparison, the energy barriers for the C-C coupling via the dimerization of *CO to *OCCO and *CHO to *OHCCCHO are predicted to be 1.71 eV and 1.04 eV, respectively.

CO₂RR performance in membrane electrode assembly (MEA) electrolyzer configuration.
To evaluate the scalability of the TB-Cu catalysts towards realistic applications to produce C$_2$H$_4$, we assembled MEA electrolyzers (5 and 25 cm$^2$) using different TB-Cu catalysts and IrOx as cathode and anode catalysts, respectively (Figure 4a, Supplementary Figure 8). First, the current-voltage relationship of the catalysts was evaluated between -3.0 V and -3.9 V at a constant CO$_2$ injection of 10 standard cubic centimeters per minute (sccm) (Figure 4b). As can be seen from the Faradaic efficiency obtained, the selectivity towards C$_2$H$_4$ formation increases rapidly with the TB density, which is in agreement with our H-cell measurements. Consequently, the specific current density for C$_2$H$_4$ increases from -45.10 mA cm$^{-2}$ up to -302.43 mA cm$^{-2}$ for TB-Cu$_0$ and TB-Cu$_{29.6}$, respectively. We then investigated the influence of the CO$_2$ supply on the FE for C$_2$H$_4$ for 5 cm$^2$ MEA cells (Figure 4c). There is a volcano relationship between the FE for C$_2$H$_4$ and the CO$_2$ flow rate, while the FE for H$_2$ decreases continuously with increasing CO$_2$ feed. The correlation between the different product selectivities was demonstrated by the heat maps depicting the ratios of FE$_{C2^+}$ to FE$_{H2}$ and FE$_{C2^+}$ to FE$_{C1}$ at different TB densities and voltages (Figure 4d and 4e, Supplementary Figure 9 and 10). These results show that the best performance for the formation of the multicarbon products is obtained at the TB concentration of 29.6 ± 1.6 × 10$^4$ cm$^{-1}$, while the highest selectivity for C$_2$H$_4$ over H$_2$ and C$_1$ products (CO and CH$_4$) is obtained at an optimal cell voltage of -3.70 V and -3.85 V, respectively. Furthermore, the catalyst achieved an ethylene energy efficiency (EE$_{C2H4}$) of 20.2 % with the MEA configuration at a current density of 303.61 mA cm$^2$.

The device achieved a maximum Faradaic efficiency for the formation of a C$_2^+$ product of 73.2 % with a specific current density of 303.61 mA cm$^2$, which corresponds to a predicted high turnover frequency (TOF) at the twin-boundary sites of 19.8 h$^{-1}$ (Supplementary Table 1). The stability of the C$_2$H$_4$ production was evaluated for both 5 cm$^2$ up to 170 hours and 25 cm$^2$ up to 70 hours. The 5 cm$^2$ MEA cell showed stable current density and Faradaic efficiency with retentions of 93.4 % and 85.2 %, respectively (Figure 4f). For the 25 cm$^2$ MEA configuration, as shown in Figure 4g, the retentions prior to 50 hours are as high as 91.6 % and 90.3 % for $j_{C2^+}$ and FE$_{C2^+}$, respectively, suggesting that the system is highly stable with no apparent degradation in performance. After 50 hours, both the current density and FE decrease slightly due to the inevitable flooding and salting issues at high current (Supplementary Figure 11). Interestingly, the optimal flow rate for CO$_2$ reaches 15 sccm for a 25 cm$^2$ MEA cell compared to 10 sccm for a 5 cm$^2$ MEA cell. This observation highlights the importance of CO$_2$ feeding which will influence the CO$_2$RR performance, particularly for larger electrode sizes (Figure 4h). The robust stability of TB-Cu$_{29.6}$ was confirmed by comparing the HRTEM (atomic structure stability), X-ray photoelectron spectroscopy (XPS) (valence state and phase stability) and Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) (coordination environment...
stability) before and after the 24 h acceleration stability measurements (Supplementary Figure 12 to
13, Supplementary Table 2). Overall, the above data demonstrate the stability of both the catalyst
and the reaction system. Figure 4i shows the J-V characteristic curve of a GaInAs/Ga(In)As/Ge triple-
junction solar cell under 1 sun, achieving a $V_{\text{OC}}$ of ~ 5 V with a solar-to-electric power conversion
efficiency (PCE) of 29.89%. To accurately calculate the solar-to-fuel (STF) conversion efficiency, the
LSV curve under the configuration of MEA was measured. The operating point was determined from
the intersection of the J-V curves of both the solar cell and the MEA reactor. The results show that the
current density and the cell voltage at the operating point reached ~7.22 mA cm$^{-2}$ and 3.96 V,
respectively, as depicted by the red dot in Figure 4i. Using the thermodynamic potential of the reaction,
the electrolysis current, and the Faradaic efficiency (see the Methods section for details of the
calculation), we estimated the STF (C$_2$H$_4$) efficiency to be ~8.33 %, which compares favorably with
the results from the literature (Supplementary Table 3).$^{30-34}$

Conclusion.

In summary, we report a strategy to control the twin-boundary density in Cu catalysts by using a
pulse electrochemical deposition strategy. Our method allowed the preparation of dendritic Cu with a
TB density as high as 29.6 ± 1.6 × 10$^4$ cm$^{-1}$, as confirmed by our electron microscopy studies. The
TB-Cu$_{29.6}$ catalyst showed robust performance towards the electrochemical conversion of CO$_2$ to
ethylene with a selectivity of 46.2 % over a wide potential range. The origin of the high selectivity
towards the formation of C$_2$- products was further elucidated by combining SECCM measurements,
in-situ Raman spectroscopy and DFT calculations. The catalyst was successfully integrated into the
MEA electrolyzer with an electrode size of 25 cm$^2$. The device achieved a maximum Faradaic
efficiency for the formation of a C$_2$- product of 73.2 % with a specific current density of 303.61 mA
cm$^{-2}$, which corresponds to a predicted TOF at the twin-boundary sites of 19.8 h$^{-1}$ – one of the most
active sites ever reported for multicarbon products. We expect our strategy to provide solutions for
scalable CO$_2$-to-ethylene conversion. As a proof of concept, we have integrated the TB-Cu catalyst
into a two-electrode reactor coupled to a photovoltaic cell and achieved an STF conversion efficiency
of ~8.33 %. Our investigations shed light on the precise design of copper-based CO$_2$RR catalysts and
a practical strategy for the realization of photovoltaic-driven electrolysis systems for the selective
production of C$_2$ products.

Data availability

The data that support the findings of this study are available from the corresponding author upon
reasonable request.
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Author Contributions

D.V., K. Q. and Y. Z. designed and directed the research. Y. Z., K. Q. and H. L. W. synthesized the materials and performed the materials property characterization. E. P. carried out the liquid NMR spectroscopy measurements. P. B. L. carried out and analyzed the theoretical results. J. Y. M. performed the hXAS characterization. X. L. Z carried out and analyzed the HAADF-STEM measurements. K. Q., Y. Z. and D. V. wrote the manuscript. D. V. supervised the project and established the final version of the paper. All authors contributed to the manuscript and have approved the final version of the manuscript.

Additional Information

Supplementary information is available for this paper at www.nature.com/nature.

Competing Interests Statement

The authors declare that they have no competing interests.

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Reference:

17 Bentley, C. L., Kang, M. & Unwin, P. R. Scanning electrochemical cell microscopy (SECCM)


Figure 1. Characterization of the twin-boundary rich copper catalysts. a, Electrochemical deposition process for different Cu catalysts. b, Relationship between the electrochemical deposition frequency and the twin-boundary density. c, Cross-sectional SEM images of the TB-Cu\textsubscript{29.6} grown \textit{in-situ} on the surface of GDE. d, TEM image of the TB-Cu\textsubscript{29.6}. e, HRTEM image of the TB-Cu\textsubscript{29.6}. f, The typical SAED pattern of TB-Cu\textsubscript{29.6}. The blue circle marks the matrix diffraction, while the red circles mark the twin-boundary spots. g, Structure illustration and FFT refined aberration corrected HAADF-STEM image of the TB-Cu\textsubscript{29.6}. The light pink atoms represent the twin-boundary Cu sites, while the yellow atom represents the ordinary Cu atoms.
Figure 2. CO\textsubscript{2}RR performance in the H-cell and SECCM configuration. a, CO\textsubscript{2} reduction cathodic linear sweep voltammetry (LSV) results of the Cu-based catalysts with different TB densities. b, Faradaic efficiency for the main CO\textsubscript{2}RR products with the different Cu-based catalysts at different applied potentials. c, Electrochemical active surface area (ECSA) normalized partial current density for the C\textsubscript{2+} products of the Cu with different TB densities. d, Relationship between FE\textsubscript{C2+} and total current density (j\textsubscript{total}) for all the catalysts. e, Selectivity for C\textsubscript{2+} products over hydrogen based on the ratio of FE\textsubscript{C2+} and FE\textsubscript{H2}. f, Long-term stability measurement of TB-Cu\textsubscript{29.6} in CO\textsubscript{2}-saturated 0.5 M KHCO\textsubscript{3} electrolyte under continuous CO\textsubscript{2} feed (10 sccm) at -1.10 V vs. RHE for 24 h. All the above experiments were performed at room temperature (25°C) and the error bars correspond to the standard deviation of three independent measurements. g, Schematic of the SECCM configuration used in the galvanostatic mode with a single channel pipette probe. The arrows indicate the movement of the probe over the substrate (working electrode) surface during a typical scanning protocol. h, LSV curves for the Cu catalysts under CO\textsubscript{2}RR with 100 nm SECCM capillary configuration. i, Spatially resolved electrochemical map derived from the individual LSVs (20 × 10 pixels, covering an area of 20 µm × 10 µm, hopping distance = 1 µm) at different potentials together with the corresponding histogram showing the distribution of the measured electrochemical activity data.
Figure 3. Investigation of the CO₂RR product selectivity mechanism by *in-situ* Raman spectroscopy and DFT calculations. a, Schematic illustration of the design of *in-situ* Raman cell design. b, TB density-resolved *in-situ* Raman spectrum for the Cu-based catalysts during CO₂Rr. b, Potential-resolved *in-situ* Raman heatmaps for TB-Cu<sub>29.6</sub> during CO₂Rr. c, Raman spectrum and peak fitting under different potentials, showing the peak of atop-bonded *CO* (from 2043 to 2095 cm<sup>-1</sup>) and bridge-bonded *CO* (from 1980 to 2030 cm<sup>-1</sup>), respectively. d, Proposed reaction pathways for CO₂ reduction to C₂H₄ over Cu (111) and TB-Cu sites. e, Gibbs free energy diagram of the reaction from the adsorbed intermediate to ethylene over Cu (111) and TB-Cu sites.
Figure 4. CO$_2$RR performance of the Cu electrodes with different TB densities measured under MEA electrolyzers. a, Scheme of the membrane electrode assembly electrolyzer for CO$_2$RR. b, Comparison of $j_{C_2^+}$ on the different Cu electrodes measured at full-cell potentials between -3.5 and -4.0 V. c, Evolution of the FE$_{C_2^+}$ and FE$_{H_2}$ with the CO$_2$ flow rate under the 5 cm$^2$ MEA configuration. d, 2D map of the TB density-dependent FE$_{C_2^+}$ to FE$_{H_2}$ ratio. e, 2D map of the TB density-dependent FE$_{C_2^+}$ to FE$_{C_1}$ ratio. f, Stability measurement of the TB-Cu$_{29.6}$ under 5 cm$^2$ MEA configuration at a full cell potential of -3.80 V and with a continuous CO$_2$ supply (50 sccm) and 50 ml min$^{-1}$ flow of 0.5 M KHCO$_3$ over 70 hours. g, Stability measurement under 25 cm$^2$ MEA configuration with a continuous CO$_2$ supply (10 sccm) and 30 ml min$^{-1}$ flow of 0.5 M KHCO$_3$ over 168 h. h, Evolution of the CO$_2$RR products with the CO$_2$ flow rate under 25 cm$^2$ MEA configuration. i, J-V characteristics of the triple junction solar under simulated AM 1.5G 100 mW cm$^{-2}$ illumination. Polarization curves of the full cell device based on TB-Cu$_{29.6}$ as CO$_2$RR catalyst at the cathode.
Supplementary Files

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