Supporting information

Tailoring the Catalytic Microenvironment of large-scale Cu foil with

Polyaniline to Enhance CH₄ Selectivity in CO₂ Electroreduction

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Experimental section

Chemicals:

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Aniline, sulfuric acid, Dimethyl sulfoxide (DMSO), Potassium bicarbonate, Deuterium Oxide and Cu foils (thickness 100µm, ~99.99% trace metals basis) were purchased from Sinopharm Chemical Reagent Co., China and Alfa Aesa. All chemicals were of analytical grade and used directly without further purification. Deionized water (18.2 MΩ) was used in all experiments.

Synthesis of Cu-PANI:

The Cu-foil was firstly cut into a size of 1×2 cm and immersed in 1.5 M sulfuric acid for 30 minutes to remove surface oxides and then ultrasonically cleaned with ethanol and acetone several times. After that, the Cu foils were washed with deionized water and dried under N₂ atmosphere. The electro-chemical polymerization of polyaniline was conducted on Shanghai Chenhua-CHI1140C electrochemical workstation under 0-0.9 V vs RHE pulse voltage. 0.2 g aniline monomer was dissolved in 0.5 M sulfuric acid solution as electrolyte. The Cu foil was used both as working electrode and counter electrode. Ag/AgCl was used as reference electrode. After electropolymerized, the Cu foil was cleaned with deionized water, vacuum dried at 70°C for 2 h, and preserved in nitrogen atmosphere.

CO₂RR experiments.

A H-type electrolytic cell equipped with three electrodes and separated by a proton exchange membrane (PEM), nafion composite membranes was used for CO_2RR experiment. Platinum mesh was used as counter electrode in anode chamber, Cu-PANI electrode and Ag/AgCl (RHE in saturated KCl, pH = 6.8) electrode were used as working electrode and reference electrode in cathode chamber, respectively.

The electrolyte solution consisted of a 0.1 M KHCO₃ and 0.1 M KCl mixture, which was saturated with CO₂ to achieve a pH of 6.8. For standardization, all measured potentials were converted to the RHE (Reversible Hydrogen Electrode) scale using the formula: E (RHE)=E (pH=6.8) +0.0591×(Δ PH) –iRu, where Ru accounts for the uncompensated resistance of the solution. All electrochemical experiments were performed using electrochemical workstation (Shanghai Chenhua-CHI1140C). Before electrolysis, the cathodic compartment was purged with gaseous CO₂ at a flow rate of 50 sccm for 30 min to ensure CO₂ saturation. During the test, the flow rate of CO₂ was maintained at 30 sccm.

Gas products were detected by gas chromatography fitted with a thermal conductivity detector and a flame ionization detector (GC-9790plus, Fuli). The liquid solution with DMSO standard was then quantitatively analyzed by NMR (JES-ECZ600S, JEOL). The gas product Faradic efficiency was calculated by the following equation:

$$\frac{p \times v \times f \times 10^{-6} (m^3/ml)}{RT} \times \frac{n_e F}{I \times 60(s/min)} \times 100\%$$

Where p is the pressure $(1.013 \times 105Pa)$; v is the volumetric concentration of gas product determined from GC (in ppm); f is the gas flow rate (20 mL /min); ne is the number of electrons required to generate the product; F is the Faraday constant (96485 C mol⁻¹); R is the ideal gas constant (8.314 J mol-1 K⁻¹); T is the room temperature (298 K); *I* is the total current.

The Faradaic efficiency of liquid product is:

$$_{FE_{liquid}} = \frac{moles \ of \ product}{Q/nF} \times 100\%$$

Where Q is the total charge in a period of reaction time (C); n is the number of electrons required to generate the product; F is the Faraday constant (96485 C mol⁻¹).

ECSA measurement

The electrochemical active surface area (ECSA) measurement was used a traditional Pb underpotential deposition (UPD) method. Typically, a freshly prepared 50 ml electrolyte containing 0.1 M HClO4 with 0.5 mM of PbCl₂ and 50 mM KCl was used. The prepared electrode was held at -0.375 V vs. Ag/AgCl for 10 min. Then, the electrode was tested by sweeping the potential from -0.5 to -0.1 V vs. Ag/AgCl at 10 mV s⁻¹. The charge consumed for the oxidation of Pb adatoms was determined by integrating the current versus time curve. The calculation of copper ECSA was assumed a monolayer of Pb adatoms covering over copper and 2e⁻ Pb oxidation with a conversion factor of 310 μ C cm⁻².

The kinetic isotopic effect (KIE) measurements

The KIE measurements were the same as the CO_2RR measurement, only using D_2O instead of H_2O to prepare the electrolyte. The deuterated gas products were verified through the Gas chromatograph-mass spectrometer. The KIE value was calculated through K_H/K_D , while the reaction rate (K) was converted from the current density.

The in situ ATR-FTIRS measurements

The in situ ATR-FTIR experiments were recorded on a Nicolet 6700 (Thermo Fisher) equipped a liquid nitrogen cooled MCT detector. The measurements were proceeded in the home-made cell under the potential of - 1.3 V vs. RHE. The signal was captured 36 s per time. All spectral resolution was 4 cm⁻¹ and 32 interferograms were co-added for each spectrum if not otherwise mentioned. The CO_2RR reaction time was maintained for 10 min.

Density Functional Thoery (DFT) calculation

To reveal the speculation of Cu-PANI, the mechanism of CO_2RR and HER on the Cu(111) and Cu-PANI were calculated by density functional theory (DFT) through Vienna Ab initio Simulation Package (VASP).¹⁻⁴ The Projector Augmented Wave (PAW) ^{5, 6}in conjunct with the Perdew-Burke-Ernzerh (PBE) flavor⁷ were carried out in optimization calculations. The k-point sampling of (3,3,1) for Cu (111) and Cu-PANI were employed. The convergence criteria was set to 1×10^{-4} eV, and the cutoff energy of plane wave basis was set to 400 eV. The threshold for force was set to $-0.05 \text{ eV} \cdot \text{Å}^{-1}$, and the Van der Waals (v dW) correction was adopted by Grimme (DFT+D3)⁸.

The Cu (111) and Cu-PANI surface were modeled using five-layer slab within (4×4) surface unit cell, respectively. The top four layers and the adsorbates were fully relaxed, and the remaining one layer were fixed. To avoid the periodic interactions of the system, a vacuum region of 20 Å between two repeated slabs was used in the direction perpendicular to the surface. The free energies of all intermediates of the electrochemical reactions were calculated by the computational hydrogen electrode model⁹. The ΔG_0 was calculated at 298.15 K by the VASPKIT package¹⁰, which according to $\Delta G_0 = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S$. The E_{DFT} , E_{ZPE} and S indicates the electronic energy, zero-point energy and entropy, respectively.

Characterization

Scanning electron microscope (SEM) images were obtained by using Hitachi SU-8010 Field Emission Scanning Electron Microscope with a field emission voltage of 5 kV. The element distribution information was obtained by surface scanning using an Energy dispersive spectrometer (EDS). The Raman spectrum was obtained by Horiba Jobin Yvon 's Labram HR Evolution microscopic confocal Raman spectrometer with a 633 nm wavelength light source.Cu Ka radiation ($\gamma = 0.154$ nm) is used to record powder X-ray diffraction patterns on a MiniFlex-600 diffractometer. Atomic force microscopy (AFM) measurements were performed on a Bruker Dimenson ICON .X-ray diffraction (XRD) patterns were collected on a Rigaku MiniFlex-600 diffractometer.X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCCALAB 250 Xi X-ray photoelectron spectrometer (Thermo Fisher) (C-C peak 284.8 eV in the corrected spectrum).

Figures:



Figure S1. SEM image of bare Cu-foil.



Figure S2. SEM of Potentiostatic polymerization PANI on Cu-foil



Figure S3. AFM image of bare Cu-foil surface.



Figure S4. Cu 3d PDOS of Cu-PANI and Cu-foil.



Figure S5. Linear sweep voltammetry of Cu-foil and Cu-PANI with underpotential deposition of Pb monolayer.



Figure S6. (a) Pulse potential treatment of Cu-foil, (b) Potentiostatic polymerization of polyaniline on Cu-foil surface.



Figure S7. Mass spectra results of the CH_4 gas products at (a) CO_2 air atmosphere; (b) ${}^{13}CO_2$ air atmosphere.



Figure S8. The FE of CH_4 and the current density at -1.8 vs.RHE during a 240 min test.



Figure S9. SEM image of Cu-PANI after CO₂RR.



Figure S10. Integrated Projected Density of States of Cu3d for CO₂RR.



Figure S11. Integrated Projected Density of States IPDOS of CO₂ for CO₂RR.



Figure S12. The *in-situ* ATR-FTIR spectra of Cu-foil at $1.3V_{RHE}$.



Figure S13. The CO_2RR pathway toward CH_4 product on Cu (111) facets.

Catalyst	FE _{CH4} (%)	Electrolyte	Reference
Cu-PANI	62	0.1 M KHCO3+0.1M KCl	this work
Cu nanowires (NWs)	55	0.1 M KHCO ₃	(11)
Nanotwined copper	59	0.2 M KHCO ₃	(12)
Single crystal(111)	46	0.1 M KHCO ₃	(13)
Single crystal(110)	50	0.1 M KHCO ₃	(14)
nanoCu	15	0.1 M KHCO ₃	(15)
CuPd nanoalloy	33	0.1 M KHCO₃	(16)
Cu-MOF-74	50	0.1 M KHCO₃	(17)
Cu-N-C	38.6	0.1 M KHCO₃	(18)
Ag-Cu alloy	~60	0.1 M NaHCO_3	(19)
Cu-DBC	56	0.1 M KHCO ₃	(20)
Cu-I	57.2	1M KOH (Flow cell)	(21)

 Table S1. Comparison of the CH4 selectivity with other electrocatalysts reported previously (References including Cu-based metallic catalysts, Cu-based bimetallic catalysts and some other Cu related catalysts).

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