Supporting Information

Electroreduction of Acetonitrile to Ethylamine by Thin Carbon Coated Copper Catalysts with Rich Active Interphases

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1. Experimental

1.1 Reagents and chemicals

Acetonitrile (CH₃CN, 99.5%) was purchased from Macklin Biochemical Co. Ltd (Shanghai, China). Copper nitrate hydrate (Cu(NO)₃·3H₂O, 99.0%), trimesic acid (H₃BTC, 98.0%), ethylamine (C₂H₇N, 68.0-72.0%), diethylamine (C₄H₁₁N, 99.0%), triethylamine (C₆H₁₅N, 99.0%), and ethanol (C₂H₅OH, AR) were purchased from Sinopharm Shanghai Chemical Reagent Company. In addition, deuterium oxide (D₂O, 99.9%) was received from Isotope Technology Co. Ltd (Wuhan, China). 1,4-Dioxane (C₄H₈O₂, 99.8%, extra dry) was received from Shanghai Aladdin. All chemicals were directly used without further purification.

1.2 Catalysts preparation

The preparation of this series of Cu@C electrocatalysts was through thermal treatment of Cucoordinated polymer, specifically, here we employed the copper coordinated benzene-1,3,5tricarboxylate (Cu-BTC) framework.

Synthesis of Cu-BTC

Typically, 8 mmol Cu(NO)₃·3H₂O was dissolved in a 100 mL of ethanol-water (1:1 v/v) mixture. Subsequently, 4 mmol of H₃BTC was added, and the solution was stirred continuously for 1 h. The resulting mixture was then transferred to an autoclave and remained at 110 °C for 20 h. After the reaction, the blue precipitate was separated by centrifugation, washed three times with ethanol, and dried before collecting product of Cu-BTC.

Synthesis of Cu@C-x (x refers to thermal treatment duration)

The obtained Cu-BTC was annealed at 800 °C under a 10% H_2/Ar atmosphere for 1 h at 5 °C min⁻¹ to yield Cu@C-1h. By extending the duration to 3 h, Cu@C-3h was obtained.

Synthesis of Cu@C-1h-Ar

By altering the carbonization atmosphere to Ar while keeping other conditions constant, Cu@C-1h-Ar was prepared.

Synthesis of c-Cu NPs

Commercial copper nanoparticles (c-Cu NPs) were treated at 800 $^{\circ}$ C under a 10% H₂/Ar atmosphere for 1 h to ensure the complete reduction of CuO.

Synthesis of bare Cu

Cu@C-1h was first calcined at 500 °C in a muffle furnace for 2 h, followed by annealing at 800 °C under a 10% H_2 /Ar atmosphere for 1 h at 5 °C min⁻¹ to obtain bare Cu.

1.3 Catalysts characterizations

The morphology of the samples was characterized using SU5000 SEM operated at 10.0 kV and JEM-F200 TEM operated at 200.0 kV. The Fourier transform infrared (FT-IR) spectra were acquired from a Thermo Scientific Nicolet 6700 FTIR spectrometer. Raman spectra were recorded

on a DL-2 microscopic Raman spectrometer with a laser (532 nm) as the emission light source. Powder X-ray diffraction (XRD) measurements were conducted with a PANalytical X'Pert3 powder diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). X-ray photoemission spectroscopy (XPS) was performed with a Thermo Scientific K-Alpha system. X-ray absorption fine structure (XAFS) spectroscopy at Cu K-edge was conducted on the BL20U1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF). X-ray absorption near-edge structure (XANES) and Fourier transform extended XAFS (FT-EXAFS) data reduction and analysis were processed by Athena software. The liquid nuclear magnetic resonance spectra (NMR) were collected on a Vaian DLG 400 MHz in deuterium oxide.

1.4 Electrochemical experiments

The electrochemical performance of ACNRR were performed in a three-electrode system using an Ivium-n-Start electrochemical workstation. A reference electrode of Ag/AgCl (saturated KCl) and a titanium plate (3×3 cm²) coated with iridium dioxide (0.5 mg cm⁻²) as the counter electrode were employed. Additionally, the anode and cathode chambers were separated by a Nafion 117 membrane. The working electrode was prepared following a standard procedure: 6 mg of the catalyst was dispersed in 1 mL of isopropanol, followed by the addition of 50 µL of a 5 wt% Nafion ionomer solution to form a catalyst slurry. Subsequently, the catalyst ink was carefully applied to both sides of the hydrophobic carbon paper (TORAY, TGP-H-60), ensuring a uniform catalyst loading of 0.5 mg cm⁻². The potentials were converted to RHE through the Nernst equation: E (RHE) = E (Ag/AgCl) + 0.197 V + 0.0591 × pH. The anolyte consisted of a 1 M KOH aqueous solution, whereas the catholyte was a 1 M KOH solution containing 12 wt% acetonitrile. To evaluate the acetonitrile reduction capabilities of the catalysts, polarization curves were normalized to the corresponding electrode surface areas.

1.5 In-situ Raman spectroscopy

In-situ Raman spectra were recorded using an inVia Qontor confocal microscope with $50 \times$ objective and a custom-made Teflon electrochemical cell. A 532 nm laser was focused on the electrode, and the Raman scattered photons were dispersed by 1800 g cm⁻¹ grating and collected by a spectrometer. *In-situ* spectroelectrochemistry was performed using a CHI620E electrochemical workstation, a Pt wire counter electrode and an Ag/AgCl reference electrode in ~10 mL of 1 M KOH containing 12 wt% acetonitrile. Spectral data were collected at various potentials and different reaction times using chronoamperometry at the fixed potential of 0.5 V vs RHE.

1.6 In-situ FTIR

In-situ FTIR was performed on a Bruker 70 V spectrometer equipped with a liquid N₂-cooled MCT detector and a spectral resolution of 4 cm⁻¹. A glassy carbon electrode coated with catalyst, a Pt wire, and an Ag/AgCl electrode were used as work, counter, and reference electrodes, respectively. The IR window consisted of a ZnSe crystal, and the distance between the working electrode and the crystal should be controlled within 1mm. *In-situ* FTIR spectra was acquired through stepwise varying the potential from -0.4 V to -1.0 V vs RHE in 1 M KOH containing 12 wt% acetonitrile. All FTIR spectra are presented in transmission units by subtracting the background spectrum obtained at open circuit voltage.

1.7 Electrocatalytic performances evaluation

The liquid products from ACNRR were analyzed using ¹H NMR on a Vaian DLG 400 MHz spectrometer. In brief, an internal standard solution was prepared by adding 4 μ L of 1,4-dioxane to 1000 μ L of D₂O. A standard curve for ethylamine in ¹H NMR was established by correlating the peak area ratio of ethylamine to the internal standard solution at varying concentrations. To prepare the test solution, 300 μ L of the reacted electrolyte was mixed with 200 μ L of DI water and 100 μ L of the internal standard solution. ¹H NMR analysis was then performed on this solution, and the integrated peak area of ethylamine was used to determine its Faradaic efficiency by referring to the standard curve.

The Faradaic efficiency (FE) and formation rate are calculated by the following equation:

$$FE = eF \times n/Q$$

Formation rate = n/t

where e is the electrons transfer number and Q (C) is the total charge passed during the electrochemical reaction. n (mol) and F (96485 C mol⁻¹) are the total moles of the product formed and Faraday constant, respectively. t (s) is the reduction time.

Electrochemical active surface area (ECSA) reflects the density of active sites on the surface of catalyst that are effectively involved in electrochemical reactions. The ECSA equation was derived as follows:

$$ECSA = A_{Geom} \times \frac{C_{dl}}{C_s \times m_{cat}}$$

where A_{Geom} (m²) is geometrical area of electrode, m_{cat} (g) is the mass of catalyst loaded, and C_{dl} (μ F cm⁻²) is the measured double-layer capacitance and C_s (40 μ F cm⁻²) is the specific capacitance of standard flat surface.^[1,2]

2. Supporting figures



Fig. S1. SEM images taken at high (a) and low (b) magnifications for sample of c-Cu NPs.



Fig. S2. High-resolution TEM images of (a) Cu@C-1h-Ar and (b) Cu@C-3h. The carbon coating was highlighted with the yellow line.



Fig. S3. TEM images of (a) Cu@C-3h and (b) Cu@C-1h-Ar.



Fig. S4. CO₂ adsorption isotherms of Cu@C-1h and Cu@C-3h at 273 K.



Fig. S5. EXAFS spectra of Cu@C-1h and reference samples. (a) The Fourier transformed (FT) k^3 -weighted EXAFS spectra of Cu Foil, Cu₂O, CuO and Cu@C-1h. (b) The k^3 -weighted EXAFS spectra of Cu Foil, Cu₂O, CuO and Cu@C-1h.



Fig. S6. O 1s XPS spectrum of Cu@C-1h.

The O 1s XPS spectrum is deconvoluted into three peaks situated at 530.5, 532.0 and 533.4 eV, corresponding to the lattice oxygen (O_L), oxygen vacancies (O_V) and surface adsorbed oxygen (O_S) on Cu@C-1h, respectively.



Fig. S7. XPS surveys of (a) Cu@C-1h, (b) Cu@C-3h and (c) Cu@C-1h-Ar.



Fig. S8. XRD patterns of c-Cu NPs, Cu@C-3h, Cu@C-1h, Cu@C-1h-Ar.



Fig. S9. C 1s XPS spectra of (a) Cu@C-1h, (b) Cu@C-3h and (c) Cu@C-1h-Ar.



Fig. S10. ¹H NMR spectra and standard curve of ethylamine. (a, b) ¹H NMR spectra of ethylamine and (c) standard curve of ethylamine. The standard curve of ethylamine shows the good linear relationship and follow the linear equation: y=16.713x+0.0497 (R² = 0.9998).



Fig. S11. ¹H NMR spectra of different mixtures of ethylamine, diethylamine, and triethylamine.



Fig. S12. The catalytic performance of bare Cu. (a) $FE_{ethylamine}$ and $j_{ethylamine}$, (b) formation rate of ethylamine, (c) TEM image of bare Cu.



Fig. S13. The formation rate of ethylamine on Cu@C-1h, Cu@C-3h, Cu@C-1h-Ar and c-Cu NPs.



Fig. S14. Long-term electrolysis. (a) The $FE_{ethylamine}$, current density, and (b) formation rate of ethylamine over Cu@C-1h during reaction for 12 h at -0.5 V_{RHE} .



Fig. S15. Cu 2p XPS spectrum of Cu@C-1h-AE.

We have further analyzed the XPS results of the catalyst after 12 h of electrolysis (denoted as Cu@C-1h-AE). The Cu 2p XPS spectrum shows that Cu species remain predominantly in the Cu⁰ state, with binding energies of 932.6 eV and 952.3 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively. However, compared to the initial state, the proportion of Cu^{2+} species has increased to 37%, indicating that part of the Cu⁰ was oxidized after the reaction, likely due to prolonged electrolysis in the alkaline electrolyte.^[3]



Fig. S16. ECSA-normalized *j*_{ethylamine} of Cu@C-1h, Cu@C-3h, Cu@C-1h-Ar and c-Cu NPs.



Fig. S17. Nyquist plots of c-Cu NPs, Cu@C-1h-Ar, Cu@C-1h and Cu@C-3h.



Fig. S18. *In-situ* FTIR Spectra of Cu@C-1h and c-Cu NPs. (a) *In-situ* FTIR of Cu@C-1h and c-Cu NPs at -1.0 V vs RHE and (b) *In-situ* FTIR of Cu@C-1h and c-Cu NPs under different potentials in wavenumber range of 1400-3800 cm⁻¹.

Two bands at 1650 cm⁻¹ and 3300 cm⁻¹ are observed, which belongs to the bending and stretching vibration of O-H, respectively. Notably, the vibrational band of O-H on Cu@C-1h exhibits a more pronounced peak shift compared to that on c-Cu NPs (1670 cm⁻¹ vs 1627 cm⁻¹, 3350 cm⁻¹ vs 3485 cm⁻¹), indicating the enhanced H₂O adsorption ability on Cu@C-1h due to the effect of carbon shells. Similar observation was reported over oxygen vacancies-rich titanium dioxide nanoarrays catalysts for electrochemical acetonitrile hydrogenation.^[4] Moreover, the O-H vibration intensity of Cu@C-1h continuously increases along with the increase of the overpotential, which is clearly higher than that of c-Cu NPs. This also indicated the higher H₂O consumption during acetonitrile hydrogenation. All these data reveal that the carbon-coated low coordinated Cu sites not only strengthen H₂O adsorption but also facilitate its dissociation, which provided rich active hydrogen species for the targeted acetonitrile hydrogenation.



Fig. S19. In-situ Raman spectra recorded over Cu@C-1h at -0.5 $\mathrm{V}_{\mathrm{RHE}}$ from 240 s to 420 s.

N^a ΔE_0^{d} shell $R(Å^2)^b$ $\sigma_2(\text{\AA}^2)^c$ **R** factor Sample Cu foil Cu-Cu 2.54 0.0087 4.24 ± 0.44 0.0034 12.0 0.0092 Cu@C-1h Cu-Cu 10.1 2.54 $4.18{\pm}0.57$ 0.0038

Tab. S1. EXAFS fitting parameters at the Cu K-edge for various samples.

^{*a*} N: coordination numbers; ^{*b*} R: bond distance; ^{*c*} σ_2 : Debye-Waller factors; ^{*d*} ΔE_0 : the inner potential correction. R factor: goodness of fit. S_0^2 : intrinsic loss. S_0^2 was set to 0.88, according to the experimental EXAFS fit of Cu foil reference by fixing coordination numbers as the known crystallographic value.

Catalysts	Electrolyte	Maximum FE (%)	Ref.
Cu@C-1h	1 M KOH+12 wt% acetonitrile	98.2@-0.8V _{RHE}	This work
Ni/NiO	1 M KOH+1 M acetonitrile	93@-0.67V _{RHE}	ACS Catal. 2024, 14, 6915-6925
PdPtCuCoNi HEAAs	1 M NaOH+1 M acetonitrile	90.75@-0.35V _{RHE}	<i>Adv. Mater.</i> 2024, 36, 2314142
Pd/C	0.5 M H ₂ SO ₄ +8 wt% acetonitrile	66.1@-0.57V _{RHE}	Nat Commun. 2024, 15, 3233
PdCu MAs-400/C	1 M NaOH+8 wt% acetonitrile	88.6@-0.54V _{RHE}	J. Energy Chem. 2024, 89, 216-225
CuNi alloys	1 M NaOH+8 wt% acetonitrile	97@-0.6V _{RHE}	<i>Sci. China Chem.</i> 2023, 66, 3242-
Pd-Ni(OH) ₂	1 M KOH+0.5 M acetonitrile	100@-0.15V _{RHE}	Angew. Chem. Int. Ed. 2023, 62,
OD-Cu NWs	1 M KOH+8 wt% acetonitrile	97.8@-0.32V _{RHE}	Nat. Commun. 2023, 14, 3847
Cu ₃ Ni ₁ NPs	1 M NaOH+8 wt% acetonitrile	95.49@-0.45V _{RHE}	J. Mater. Chem. A. 2023, 11, 2210-
CuNAs/Cu Foil	0.5 M KHCO ₃ -CO ₂ +0.5 M acetonitrile	94@-0.5V _{RHE}	<i>Chem Catal.</i> 2021, 1, 393-406
Cu NPs	1 M NaOH+8 wt% acetonitrile	94.6@-0.29V _{RHE}	Nat. Commun. 2021, 12, 1949

Tab. S2. The comparison of FE of ethylamine for ACNRR over Cu@C-1h and the reported electrocatalysts in literatures.

Catalysts	ECSA (m ² g ⁻¹)	
Cu@C-1h	1.2	
Cu@C-1h-Ar	0.7	
Cu@C-3h	0.7	
c-Cu NPs	0.6	

 Tab. S3. The ECSA of Cu@C-1h, Cu@C-1h-Ar, Cu@C-3h and c-Cu NPs.

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