Supplementary Information

Zwitterionic polymer assisted asymmetrically coordinated Cu atoms on aligned carbonous microchannels for efficient electroreduction of CO₂ to CO

Congwei Wang^{*, 1,2}, Kun Zhang³, Xiaoxiang Zhang¹, Jianmei Wang⁴, Xinglin Luo³, Gang Li³, Kaiying Wang ^{3,5}

¹ Shanxi Key Laboratory of Carbon Materials, Institute of coal chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China

² School of Energy and Power Engineering, North University of China, Taiyuan 030051, China.

³ Institute of Energy Innovation, College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan, 030024, China

⁴ Key Laboratory of In-situ Property-improving Mining of Ministry of Education, College of Mining Engineering, Taiyuan University of Technology, Taiyuan, 030024, China

⁵ Department of Microsystems, University of South-Eastern Norway, Horten 3184 Vestfold, Norway

* Corresponding Author, E-mail: <u>wangcongwei@sxicc.ac.cn</u>

Experimental Section

Materials

Acrylamide (AM), N, N-methylenebisacrylamide (MBA), potassium persulfate (K₂S₂O₈) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). 3dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS), poly (vinylidene fluoride) (PVDF) and 1-methyl-2-pyrrolidinone (NMP) were supplied from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Copper chloride (CuCl₂), potassium hydroxide (KOH) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used without further purification.

Preparation of directional freezing zwitterionic polymer modified P(AM-co-DMAPS)-Cu²⁺ hydrogels (PADS-Cu)

AM (8.55 g), DMAPS (8.40 g), MBA (23 mg) and different amount of CuCl₂ (0.01, 0.1 and 1 M, respectively) were dissolved in deionized water (50 mL) under stirring for 1 h. Successively, the initiator K₂S₂O₈ (0.2 g) was added into the above solution to obtain precursor solution, which were maintained 15 min to eliminate the air bubbles. The prepared hydrogel precursor solutions were injected into a custom-made mould (Φ 10 mm×10 mm), sealed, and maintained at room temperature for 2 h to obtain semi-crosslinked P(AM-co-DMAPS) (PADS) precursors. Liquid nitrogen was poured into the insulation container as cold chamber/trap. A brass block, whose top surface was polished to ensure a close contact for directional freezing process, was put

into the container for pre-cooling. The mould containing PADS precursor was then placed on the top of brass block for directional freezing. The directional freezing process lasted for 15 min, and then taken out from the cold brass surface and maintained at room temperature until the frozen hydrogel thawing, which is regarded as one complete freeze-thaw cycle. After three cycles, the hydrogels were transferred to a refrigerator and maintained at -10°C overnight to complete the polymerization. The negative groups (-SO₃⁻) in zwitterionic polymer would be effectively anchor Cu ions in the prepared directional frozen PADS hydrogels, obtaining the Cu-anchoring PADS hydrogels, denoted as PADS-Cu-x (x=0.01, 0.1 and 1).

The pyrolysis of directional frozen PADS-Cu hydrogels (Cu@AHPC) and preparation of single Cu atoms supported on alighted hierarchical porous nanocarbons (Cu_{SA}@AHPC)

The directional frozen PADS-Cu hydrogels were subjected to lyophilization and subsequently pyrolyzed at 550°C for 2 h in Ar atmosphere, the as-pyrolyzed samples were denoted as Cu(x)@AHPC (x=0.01, 0.1 and 1). The obtained Cu@AHPC intermediates were then leached with 1M hydrochloric acid and deionized water to remove large particles and impurities, these purified samples were denoted as Cu(x)_{SA}@AHPC (x=0.01, 0.1 and 1). The isotropically undirected PADS-Cu-0.1 hydrogel was also prepared following the same procedure as descripted above without the directional freezing process, the pyrolyzed and leached undirected PADS-Cu-0.1 hydrogels was named as Cu_{SA}@PC. The pure directional freezing PADS hydrogel

without Cu species was also prepared and pyrolyzed as the reference, denoting as AHPC.

Materials characterization

The microstructures of prepared samples were characterized by scanning electron microscopy (SEM) from a Gemini SEM 300 microscope (Zeiss, Germany) under 3.00 kV voltage, which was equipped with energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (JEM-2100EX, JEOL, Japan) operating at 200 kV was utilized to identify the microstructures of pyrolyzed PADS and Cu species. HAADF-STEM was performed on a JEM ARM200F equipped with double aberration correctors in Institute of Physics, Chinese Academy of Sciences, and a cold field emission gun operated at 200 kV. STEM images were recorded using a HAADF detector with a convergence angle of 25 mrad and a collection angle between 70 and 250 mrad. Under these conditions, the spatial resolution is ca. 0.08 nm. The Raman spectra of hydrogels at different temperatures were performed on an Invia Reflex Raman imaging microscope (Renishaw, UK) with a 532 nm excitation laser. X-ray diffraction (XRD) patterns were obtained via an Empyrean 03 diffractometer (Malvern Panalytical, B.V) with Cu K irradiation (λ =1.54 nm) at a scan rate of 5° min⁻¹. X-ray photoelectron spectroscopy (XPS) were performed using Thermo ESCALAB 250 spectrometer, employing an Al-KR X-ray source with a 500 µm electron beam spot. The Brunauer–Emmett–Teller (BET) specific surface area was calculated from the N₂ physical adsorption measurement data that were obtained using an ASAP 2010 Accelerated Surface Area and Porosimetry System. X-ray absorption near-edge structure (XANES) measurements at Cu K-edge in transmission mode were performed at the BL14W1 in Shanghai Synchrotron Radiation Facility. The data analysis was performed using Artemis software package based on the standard analysis procedures. The elemental compositions were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using Thermo ICPA 6300.

Preparation of catalyst loaded electrodes

20 mg prepared catalyst and 25 μ L Nafion solution was dispersed in 1.5 mL ethanol solution, which was then sonicated for 30 min to obtain a homogeneous ink. Subsequently, 200 μ L prepared catalyst ink was drop-casted onto a carbon paper (GC) electrode (1 cm × 1 cm), which was then dried in a vacuum oven at 60 °C for 2 hours. The catalyst loading was determined as the weight difference between this dried GC and raw GC, which were kept consistent as 2 ± 0.3 mg for all prepared GC electrodes.

Electrochemical measurements

All electrocatalytic CO₂RR measurements were carried out in an H-type electrochemical cell and conducted on an electrochemical workstation (CHI 660E, China). The electrolyte was 0.1 M KHCO₃ solution and a Nafion 117 membrane was employed as the separator. The platinum electrode and saturated calomel electrode (SCE) was used as counter electrode (CE) and reference electrode (RE) respectively. The measured SCE potentials in this paper were converted with respect to the reversible hydrogen electrode (RHE) unless otherwise stated based on Nernst equation:

$$E$$
 (vs. RHE) = E (vs. SCE) + 0.244 V + 0.0591 × pH (Equation S1)

Prior to the electrochemical experiment, the electrolyte was bubbled with CO₂ (99.9999%, Dalian Special Gas Co., Ltd.) at a flow rate of 20 mL min⁻¹ for at least 30 min to ensure saturation (pH = 6.8). During CO₂RR experiments, CO₂ were continuously purged and all electrochemical tests were conducted at ambient environment. Linear scanning voltammetry (LSV) measurements were performed for CO₂ reduction experiments using a scan rate of 50 mV s⁻¹.

The double-layer capacitance (C_{dl}) method was employed to calculate the electrochemical active surface area (ECSA) of the electrodes. The double-layer capacitance was determined by measuring the capacitance current associated with bilayer charging according to the cyclic voltammogram (CV) versus scan rate (20, 40, 60, 80, 100 mV s⁻¹). The relationship between the double-layer charging current J_c , the scan rate v and the electrochemical bilayer capacitance C_{dl} can be obtained by equation:

$$J_{\rm c} = C_{dl} \times v \tag{Equation S2}$$

The values of ECSA were linearly proportional to C_{dl} , which can be determined from the linear slope of its current density versus scan rate in a non-faradaic region. ECSA can be proportional to the double layer capacitance, which can be calculated from C_{dl} concerning the specific capacitance C_s by the equation:

$$ECSA = \frac{C_{\rm dl}}{C_{\rm s}}$$
(Equation S3)

Electrocatalytic products analysis

The gaseous products were on-line monitored by gas chromatography (GC, Chongqing Chuanyi Instrument Co., Ltd., China) every 15 minutes, and the content of H_2 was detected by a thermal conductivity detector (TCD) detector and CO was quantified by a flame ionization detector (FID).

The calculation of Faradaic efficiency (FE) for gaseous products was based on the following equation: FE = (The charge of the specific product)/(The total consumed charge)

$$FE = \frac{J_{\text{gas}}}{J_{\text{total}}} = \frac{v_{\text{gas}} \times N \times F}{J_{\text{total}}}$$
(Equation S4)

where J_{gas} is partial current density for specific gaseous product, J_{total} is the total current density, N is the transferred electron number for product (N=2 for CO and H₂), v_{gas} is the gas production rate measured by GC and F is Faradaic constant (96485 C mol⁻¹).

Computational Method

Device Studio program was employed to perform the visualization, modeling and calculation (DS-PAW). The single Cu atom embedded at the vacancy site of either C and nitrogen/sulfur doped C was modeled by replacing the carbon atom with Cu atom or/and N/S atoms in a (6×6) supercell of graphene supercell. For all periodic slab models, a thickness of 15 Å vacuum was placed in the direction perpendicular to the surface, so the interactions between any adjusting molecules can be safely ignored. All density functional theory computations were carried out by employing the plane-wave-based method and periodic slab model. The electron exchange and correlation energy

were used within the generalized gradient approximation (GGA). Projected augmented wave (PAW) potential is employed to describe the electron-ion interaction and a kinetic energy cutoff of 400 eV is selected for the plane wave expansion. The dispersion-corrected DFT-D3 method was employed to deal with long-range van der Waals interactions. For structural optimization, the convergence criterion of total energy was set to 1×10^{-5} eV, and the atoms were relaxed until the force acting on each atom was less than 0.03 eV Å⁻¹. Brillouin-zone was sampled with $3 \times 3 \times 1$ Monkhosrt-Pack grid for slab model calculations. A denser Brillouin-zone grid of $5 \times 5 \times 1$ was employed for the calculation of density of states.

The adsorption model was based on a series of aforementioned surface slab models with different adsorbates representing intermediate reactions. The Gibbs free energy (ΔG) was calculated by correcting the DFT energy with zero-point energy and entropy via equation(E6):

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \qquad (Equation S5)$$

where E is the DFT total energy, ZPE is the zero-point energy, T is the environment temperature, and S is the entropy. For ZPE correction and entropy calculation, the vibrational frequencies were calculated by applying density functional perturbation theory.

Multiphysics Simulations.

The current density and local small molecule distribution were simulated by a two-

dimensional transport model using the COMSOL Multiphysics finite-element-based solver. The "Electric Currents" module was utilized to solve the current density distribution under a specific electrode bias potential. The electric field *E* was determined as the opposite gradient of the electric potential V ($E = -\nabla V$). The polarization loss was calculated based on species transport through migration, with the concentration gradients were represented as a sum of the ohmic loss, diffusion loss, and Nernstian loss. The conductivity of the electrode (graphite) was assumed as 1300 S m⁻¹, the electrolyte conductivity was assumed as 0.1 S m⁻¹. The "Transport of Diluted Species" module was employed to calculate the mass transport of the following species: CO₂, CO and the ions in the electrolyte HCO₃⁻.



Figure S1 SEM image of PADS hydrogel without directional freezing step.



Figure S2 (a) HRTEM image and (b) HAADF-STEM of Cu@AHPC, the Cu_{SA} sites are highlighted in dashed circles.



Figure S3 (a) Raman spectra of Cu_{SA}@AHPC, Cu@AHPC and AHPC, (b) chemical composition of Cu, N and S element, Cu contents were obtained from ICP-OES.



Figure S4 Bonding configurations of PADS derived (a) N element and (b) S element in Cu@AHPC and Cu_{SA}@AHPC.



Figure S5 XPS spectrum of (a) C 1s and (b) O 1s of Cu_{SA}@AHPC.



Figure S6 Detailed FEs of as-pyrolyzed Cu@AHPC with different Cu concentrations, (a) 0.01, (b) 0.1, (c) 1.0 mol L⁻¹, (d) CO Faradaic efficiencies at different potentials.



Figure S7 Detailed FEs of (a) $Cu(0.01)_{SA}$ @AHPC, (b) $Cu(1)_{SA}$ @AHPC, (c) CO

Faradaic efficiencies at different potentials, (d) FEs of Cu-free AHPC catalyst.



Figure S8 The chronoamperometry measurement of Cu_{SA}@AHPC at -0.7 V.



Figure S9 HAADF-STEM of Cu_{SA}@AHPC after durability measurement.



Figure S10 (a) Cu K-edge XANES spectra, (b) Fourier transformed EXAFS spectra,
(c) XPS S 2p spectra of as-prepared Cu_{SA}@AHPC and post-durability tested Cu_{SA}@AHPC-post samples.



Figure S11 N₂ adsorption–desorption isotherms of Cu_{SA}@AHPC and Cu_{SA}@PC.



Figure S12 Measurements of double layer capacitance by cyclic voltammetry (CVs) of

(a) AHPC, (b) $Cu_{SA}@PC$, and (c) $Cu_{SA}@AHPC$.



Figure S13 Atomic models of (a) N doped carbon, (b) Cu_{SA} - C_4 and (c) Cu_{SA} - $N_{4.}$

Sample	Path	CN	R(Å)	$\sigma^{2} (\times 10^{-3} \text{ Å}^{2})$	$\Delta E_0 (eV)$	R-factor
PADS-Cu _{SAC}	Cu-N	4	2.24	4.98	6.65	0.012
	Cu-S	1	2.19	11.78		
Cu foil	Cu-Cu	12	2.63	5.50	3.63	0.005

 Table S1 Summary details of EXAFS fitting parameters.

CN: coordination number; R: interatomic distance between central atom and backscatter atom; σ^2 is Debye-Waller factor; ΔE_0 : potential correction; *R*-factor: indicator of the fit goodness.

Catalwat	Potential	Els stus lats	CO FE	Stability	Def
Catalyst	(V vs. RHE)	Electrolyte	(%)	(h)	Kei
Cu-APC	-0.78	0.2 M NaHCO ₃	92	3	1
Cu SAs/NC	0.7	0.1 M KHCO ₃	92	30	2
Cu-C3N4-CNT	-0.80	0.5 M KHCO ₃	60	5	3
Cu-N4-NG	-1.0	0.1 M KHCO ₃	80.6	NA	4
Cu-N2/GN	-0.50	0.1 M KHCO ₃	81	10	5
Cu-S1N3/Cux	-0.65	0.1 M KHCO ₃	~100	NA	6
Cu-N4-C/1100	-0.70	0.1 M KHCO ₃	96	40	7
Cu-N-CNT	-0.82	0.5 M KHCO ₃	95.7	25	8
Cu _{SA} @AHPC	-0.60	0.1 M KHCO ₃	96.1	80	This work

Table S2 Comparison of reported Cu_{SAC} for electrochemical reduction CO_2 to CO.

	$R_s(\Omega)$	$R_{ct}(\Omega)$
AHPC	26.73	311.8
Cu _{SA} @PC	24.47	315.87
Cu _{SA} @AHPC	24.69	201.40

Table S3 The EIS fitted resistance (R_s, R_{ct})

 Table S4 The potential configurations for *COOH intermediates on catalyst surface.

Cu coordination	Optimized *COOH configuration	Binding energy (eV)	
Cu _{SA} -C ₄		1.216	
		-0.158	
Cu _{SA} -N ₄		0.883	
		0.918	
Cu _{SA} -N ₄ S1		0.547	
		0.542	

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