# Supplementary information for

## Facile Fabrication of Single-Atom Catalysts by a Plasma-Etching Strategy for Oxygen Reduction Reaction

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#### **MATERIALS AND METHODS**

#### Chemicals.

Cu, Co, Ni, and Fe foams were purchased Kunshan Xingzhenghong Electronic Materials Co., Ltd. Zinc nitrate hexahydrate, methanol, 2-methylimidazole were obtained from Shanghai Macklin Biochemical Co., Ltd. The graphene was purchased from Nanjing XFNANO Materials Tech Co., Ltd. 20 wt. % Pt/C (it is also noted as 20 % Pt/C and Pt/C in the manuscript) and Nafion (5%) were purchased from HESEN Co., Ltd. The Cu, Co, Ni, and Fe foams were washed with the 10% HCl and ultrapure water, and dried at 60 °C before using. Expect the metal foams, all the chemicals were analytical grade and used without further purification.

#### Synthesis of NC.

Following a typical process, a methanol solutions (30 mL) of  $Zn(NO_3)_2 \cdot 6H_2O$ (3.6 g) was mixed with 2-methylimidazole (13 g) methanol solution (70 mL) under vigorous stirring for 24 h. The obtained solid was centrifuged and washed by methanol for five times, and then dried in a vacuum oven at 60 °C for 12 h (the obtained material was named as ZIF-8). Then, the prepared ZIF-8 was heated at 950 °C for 1 h under Ar flowing, the final product was denoted as NC.

#### Synthesis of Cu-SAC/NC.

The Cu foams ( $1 * 1 \text{ cm}^2$ ) and NC powder (100 mg) were placed in the plasmaenhanced chemical vapor deposition (PECVD) in sequence, and then started on the tube furnace of the PECVD with the following parameters, the temperature was 800 °C, holding time was 40 min, and under the N<sub>2</sub> flowing. When the temperature reached the setting value, turn on the PECVD with the following parameters, radio frequency (RF, 13.56 MHz) power was 500 W, the processing time was 40 min, the tube pressure was 50 Pa, and under the  $N_2$  flowing. After the temperature of the tube drops to room temperature, the Cu-SAC/NC was obtained.

## Synthesis of Cu-SAC/G.

The preparation process of Cu-SAC/G was similar to Cu-SAC/NC, excepted the graphene was used as support.

## Synthesis of Fe-SAC/NC, Co-SAC/NC, Ni-SAC/NC.

The preparation process of Fe-SAC/NC, Co-SAC/NC and Ni-SAC/NC was similar to Cu-SAC/NC, excepted Fe foam (1 \* 1 cm<sup>2</sup>), Co foam (1 \* 1 cm<sup>2</sup>), and Ni foam (1 \* 1 cm<sup>2</sup>) were used as the metal precursor, respectively. The duration was changed to 40 mins for Fe-SAC/NC, 45 min for Co-SAC/NC, and 40 min for Ni-SAC/NC. The radio frequency was changed to 450 W for Fe-SAC/NC, 400 W for Co-SAC/NC, and 400 W min for Ni-SAC/NC, respectively.

## Synthesis of FeCo-SAC/NC.

The preparation process of FeCo-SAC/NC was similar to Cu-SAC/NC, excepted Fe foam (1 \* 1 cm<sup>2</sup>) was used as the Fe precursor, and the support was changed to the Co-SAC/NC.

#### Synthesis of SAC-Cu/NC-2.3g.

The preparation process of the Cu-SAC/NC-2.3g is similar as the Cu-SAC/NC, except that three Co foam  $(2 * 2 \text{ cm}^2)$  stacked together are used as the Cu precursor, and the NC changes to 1.3 g. The maximum yield of a single batch is approximately

1.15 g. The 2,3 g was synthesized in two batches.

#### Material characterizations.

X-ray diffraction (XRD) was conducted on an X'Pert-Pro powder diffractometer operated at 30 kV and 20 mA, using a Cu-K radiation source ( $\lambda$ =1.5405Å). Scanning electron microscopy (SEM) was conducted on JEOL JSM-6510 microscope. Transmission electron microscopy (TEM), TEM-EDS data and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL 2100F microscope. High-angle annular dark field (HAADF) images were carried out by using the scanning transmission electron microscopy (STEM) mode on an aberration-corrected FEI Titan G2 60-300 fieldemission TEM (FEI, USA), operated at 300 kV ( $\alpha max = \sim 100 \text{ mrad}$ ). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer employing a monochromated Al-K X-ray source (hv=1486.6 eV). X-ray Absorption Fine Structure (XAFS) spectra at the Cu K-edge were recorded at the BL14W1, Shanghai Synchrotron Radiation Facility. The metal loading of the prepared species was determined by the inductively coupled plasma-optical emission spectrometer (ICP-OES, Aglient 5110). Specific surface area and pore distribution of the prepared catalysts was measured by the N2 adsorption/desorption isotherm curves analyzed by Micromeritics APSP 2460.

## **Electrochemical measurements.**

All the electrochemical measurements were measured on an electrochemical

workstation (Gamry 1100E) at room temperature, using a three electrode electrochemical setup with a rotating rotation disk electrode (RRDE) system. A glassy carbon working electrode (GCE, 5 mm inner diameter, 0.196 cm<sup>2</sup>), a graphite rod counter electrode and a Hg/HgO reference electrode were used for all the tests. The potential at the zero current point was determined to be -0.886 V, so the potential measured with a Hg/HgO electrode can be related by E(RHE) = E(Hg/HgO) + 0.886V. The electrode was prepared as follows. First, a catalyst ink was prepared by ultrasonicating a mixture of catalyst and 1 mL of Nafion/ethanol solution (0.25 wt.%) for 30 min, and then 5 µL of the catalyst ink was pipetted onto the GCE surface, and finally, the GCE was dried under ambient conditions. The catalysts loading was kept at 50 µg cm<sup>-2</sup>, but the catalysts loading of the Pt/C was kept at 25 µg cm<sup>-2</sup>.

Linear sweep voltammetry (LSV) was carried out to determine ORR performance at 1600 revolutions per minute (rpm) at a scan rate of 5 mV·s<sup>-1</sup> in O<sub>2</sub>-saturated 0.1 M KOH. The durability test was conducted via the accelerated durability test (ADT), which cycled the potential from 0.6 to 1.0 V at 100 mV s<sup>-1</sup> for 10,000 cycles. During the test, the oxygen flowing was kept above the electrolyte to ensure  $O_2$  saturation.

Kinetic current density  $(j_k)$  of the prepared catalysts was calculated via the Koutechy-Levich (K-L) function <sup>1</sup>:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_L}$$
(1)

J: Cathodic electrode current.

J<sub>k</sub>: Kinetic current density.

J<sub>L</sub>: Limiting current density.

Tafel slope measurement was calculated based on Tafel function <sup>2</sup>:

$$\eta = a + b \, lgi \tag{2}$$

in which,  $\eta = U - U_0$ ,  $b = 2.3 \text{RT}/(\alpha F)$ ,  $\eta$  is the overpotential, i is the current density, a is the transfer number, b is Tafel slope, R is the gas constant, T is the temperature, and F is the Faraday constant.

## Zinc-Air Battery (ZAB) Test.

The ZAB was assembled by using a zinc plate and 6 M KOH as the anode and electrolyte, respectively. The air-cathode consists of carbon paper dropped with Cu-SAC/NC catalyst. The polarization curve was measured on Gamry 1010E electrochemical workstation. The discharge polarization curve and stability measurement tests were performed using LANHE (CT2001A) battery testing system.

## Density functional theory (DFT) calculation.

Spin-polarized density functional theory calculations were performed by using the Vienna *Ab Initio* Simulation Package (VASP) <sup>3-4</sup>. The Perdew-Burke-Ernzerhof (PBE) <sup>5</sup> functional and the projector augmented wave (PAW) <sup>6-7</sup> potential were employed. An energy cutoff of 500 eV and a convergence criterion of  $10^{-5}$  eV for selfconsistent calculations (SCF) was adopted. All structures were fully relaxed until the total force on each atom was less than 0.05 eV/Å. The solvent effect was included by using the implicit solvation model as implemented in VASPsol code <sup>8-9</sup>. The thickness of the vacuum layer was large than 15 Å. A 6 × 6 × 1 graphene supercell was used to model the Cu-pd-N<sub>3</sub>, Cu-pd-N<sub>4</sub>, and Cu-po-N<sub>3</sub>. The Cu-po-N<sub>4</sub> model was derived from the pyrrole-type FeN<sub>4</sub> model <sup>10</sup>. The Cu-pd-N<sub>2</sub> and Cu-po-N<sub>2</sub> were based on  $6 \times 4\sqrt{3} \times 1$  armchair graphene nanoribbons and Cu-po-N<sub>2</sub> was based on  $3\sqrt{3} \times 8 \times 1$ zigzag graphene nanoribbons, respectively. A Γ-centered k-point with a resolution less than  $0.03 \times 2\pi/$  Å was used. A  $1 \times 1 \times 1$  k-point and the SCF convergence criterion of  $10^{-4}$  eV were adopted in Ab initio molecular dynamics (AIMD) simulations in the NVT ensemble. The simulation's timescale was 5 ps and the time step was set to be 1 fs. VASPKIT code <sup>11</sup> and VESTA software <sup>12</sup> were used for calculation pre-processing and post-processing.

The computational hydrogen electrode (CHE) model <sup>13</sup> was used in our calculations. The Gibbs free energy of molecules and ORR-related absorbates was calculated by  $G = E_{DFT} + ZPE - TS$ , where  $E_{DFT}$ , ZPE, and S were the DFT energy, zero-point energy, and entropy, respectively, and temperature T was adopted as 298.15K. The ORR involves four four-electron pathways on the active sites. The theoretical overpotential at equilibrium potential was determined according to  $\eta = 1.23 - |\triangle G_{max}/e^{-}|$ , where  $\triangle G_{max}$  was the maximum free energy change of adjacent electronic steps.



Fig. S1 SEM image the ZIF-8.



Fig. S2 XRD pattern of the ZIF-8.



Fig. S3 TEM image of the NC.



Fig. S4 XRD pattern of the NC.



Fig. S5 HRTEM image of the Cu-SAC/NC.



Fig. S6 XRD patterns of the Cu-SAC/NC and NC.



Fig. S7 XPS data of the Cu-SAC/NC.



Fig. S8 High-resolution (a) N 1s and (b) Cu 2p XPS peaks of Cu-SAC/NC.



Fig. S9 XRD patterns of (a) Fe-SAC/NC and NC, (b) Co-SAC/NC and NC, (c) Ni-SAC/NC and NC, (d) Cu-SAC/G and G, (e) FeCo-SAC/NC and NC.



Fig. S10 EDS-mapping images of (a) Fe-SAC/NC, (b) Co-SAC/NC, (c) Ni-SAC/NC,(d) FeCo-SAC/NC, (e) Cu-SAC/G.



Fig. S11 Specific surface area (a) and pore distribution (b) data of the Cu-SAC/NC.



Fig. S12 Tafel slope of the prepared catalysts and Pt/C.



Fig. S13 Photo of the assembled ZAB.



Fig. S14 Discharge curve of the Cu-SAC/NC-based ZAB.



Fig. S15 Atomic structures of (a) Cu-pd-N<sub>4</sub>, (b) Cu-po-N<sub>4</sub>, (c) Cu-pd-N<sub>2</sub>, and (d) Cu-po-N<sub>2</sub>.



Fig. S16 Adsorption configurations of the intermediates on Cu-pd- $N_3$  model.



Fig. S17 Adsorption configurations of the intermediates on (a) Cu-pd-N<sub>4</sub> and (b) Cupo-N<sub>4</sub> model.



Fig. S18 Adsorption configurations of the intermediates on (a) Cu-pd-N<sub>2</sub> and (b) Cu-po-N<sub>2</sub> model.



Fig. S19 Free energy diagram of the oxygen reduction reaction at the potential (a) U = 0 V and (b) U = 1.23 V.



Fig. 20 AIMD simulation results of Cu-po- $N_3$  at 1000 K and the atomic structures at the end of AIMD simulations.



Fig. S21 Picture of 2.3 g of the Cu-SAC/NC-2.3g catalyst.



Fig. S22 XRD patterns of the prepared Cu-SAC/NC-2.3g and NC.



Fig. S23 HRTEM image of the Cu-SAC/NC-2.3g catalyst.



Fig. S24 ORR activity of Cu-SAC/NC and Cu-SAC/NC-2.3g catalysts.

sample	Scattering	CN	R(Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0 (eV)$	R factor
	pair					
Cu-SAC/NC	Cu-N*	3.07±0.4	1.943±	0.004±0.0	2.755±1.3	0.012
			0.007	02	50	

Table S1 Structural parameters extracted from the Cu K-edge EXAFS fitting.  $(S_0^2=0.85)$ 

 $S_0^2$  is the amplitude reduction factor; CN is the coordination number; R is interatomic distance;  $\sigma^2$  is Debye-Waller factor;  $\Delta E_0$  is edge-energy shift. R factor is used to value the goodness of the fitting.

\*This value was fixed during EXAFS fitting, based on the known structure.

	Metal loading (wt. %)
Cu-SAC/NC	0.65
Fe-SAC/NC	0.67
Co-SAC/NC	0.51
Ni-SAC/NC	0.35
Cu-SAC/G	0.42
FeCo-SAC/NC	1.10

 Table S2 The metal loading of the prepared catalysts.

	E <sub>onset</sub>	E <sub>1/2</sub>	$j_{L@}$ 0.3 V vs. RHE	j <sub>k</sub> @0.85 V vs. RHE
	(V vs. RHE)	(V vs. RHE)	(mA cm <sup>-2</sup> )	(mA cm <sup>-2</sup> )
Cu-SAC/NC	1.011	0.886	5.759	14.309
NC	0.885	0.745	4.563	0.373
Pt/C	0.938	0.856	5.553	5.545

**Table S3** The ORR data of the prepared catalysts and Pt/C.

	ORR per	formance	ZAB performance			
	E <sub>ONSET</sub>	E <sub>1/2</sub>	Peak power density	Specific capacity	References	
	V vs. RHE	V vs. RHE	mW m <sup>-2</sup>	mAh g <sup>-1</sup>		
Cu-SAC/NC	1.011	0.886	175	715	This work	
Pt/C	0.938	0.856	140	612	This work	
Cu-N/C	0.914	0.813	-	-	Small 2017, 13 (30), 1700740	
Cu-SAs/N-C	1.01*	0.895	-	-	Nat Catal. 2018, 1, 781-786	
Cu-SAs/N-G	0.955*	0.740	-	-	Nat Catal. 2018, 1, 781-786	
Cu-N-C	0.95*	0.869	-	-	Energy Environ. Sci. 2018, 11 (8), 2263-2269	
Cu@Cu-N-C	0.97	0.85	-	-	Small 2019, 15 (43), 1902410	
Cu-N <sub>4</sub> -C	0.915	0.84	-	-	ACS Nano <b>2019,</b> <i>13</i> (3), 3177- 3187	
Cu-MFC60	0.86	0.76	-	-	Small 2020, 16 (12), e1903937	
Cu/NC	0.901	0.793	-	-	Small 2020, 16 (48), e2004855	
SA-CuNC	0.99*	0.78	-	-	<i>Adv. Energy Mater.</i> <b>2021</b> , 11, 2100303	
Cu <sub>3</sub> P@NPPC	0.885*	0.78	110.8	-	Adv. Mater. <b>2018</b> , 30 (6), 1703711	
Cu-SA/SNC	0.990*	0.893	220	780	<i>Energy Environ. Sci.</i> <b>2019,</b> <i>12</i> (12), 3508-3514	
Cu SAC	0.97	0.81	196	618	J. Mater. Chem. A 2019, 7 (28), 16690-16695	
Cu ISAS/NC	1.05*	0.920	280	736	Nat. Commun. 2019, 10, 3734	

**Table S4** Comparisons of the ORR performance both in RDE- and ZAB-level inrecently reported works.

NOTE: \*The data is not given, but excavated from the LSV curves.

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