Electronic Supplementary Information

Isolated diatomic Zn-Fe in N-doped carbon for electrocatalytic nitrogen

reduction to ammonia

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1. Experimental Section

Synthesis of Zn/Fe-N-C

Zn/Fe-N-C was prepared by modifying previously reported method.¹ 0.8 g chitosan was dispersed in 100ml deionized water and continued stirring for 30 min. Then, 0.8 g ferrous acetate tetrahydrate added into dispersing solution and kept stirring for 2 h. Subsequently, 2.4 g Zinc chloride dissolved in 20 ml deionized water and added into above-mentioned mixture and kept stirring for 6 h. Obtained mixture heated at 80 °C and continued stirring unceasingly until it completely dried. Then, the product was heated by tubular oven to 750 °C with a heating rate of 5 °C min⁻¹ and kept for 4 h in flowing argon atmosphere. The obtained solid was washed with 6 M HNO₃ and deionized water for several times and finally dried at 70 °C under vacuum for overnight. The dried powder sample was heated to 900 °C kept at 900 °C for 2 h at a heating rate of 5 °C min⁻¹ under flowing argon gas.

Synthesis of Fe-N-C and Zn-N-C

The Fe-N-C was prepared with the same procedure as that of Zn/Fe-N-C except without adding Zinc chloride. The Zn-N-C was prepared with the same procedure as that of Zn/Fe-N-C except without adding ferrous acetate tetrahydrate.

Characterization

The morphologies of the as-prepared samples were detected by high angle annular dark field transmission electron microscopy (HAADF-TEM, FEI Talos Tecnai F200x G2 system) and atomic-resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were carried out on Titan Cubed Themis G2 300 microscope at 200 kV. Inductively coupled plasma atomic emission spectrometer (ICP-AES) tests were performed by a PerkinElmer 8300 equipment and all the samples were measured for three times. X-ray diffraction (XRD) patterns were recorded on a Rigaku Mini Flex 600 X-ray diffractometer (Cu K α radiation, $\lambda = 1.5406$ Å). Raman spectra were recorded using

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a confocal Raman microscope (DXR, Thermo-Fisher Scientific) with 633 nm excitation from an argon ion laser. X-ray photoelectron spectroscopy (XPS) measurements were taken with a PerkinElmer PHI 1600 ESCA system. X-ray absorption fine structure (XAFS) spectra at the Fe and Zn K-edge was collected at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF). The electron storage ring of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. Fe-foil, Fe-Pc, Zn-foil and Zn-Pc were used as references. The acquired EXAFS data were extracted and processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k³-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k³-weighted $\chi(k)$ data in the k-space ranging from 2.5–11.2 Å⁻¹ were Fourier transformed to real (R) space using a hanning windows (dK = 1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells.

Preparations of the working electrodes.

For preparing the catalyst ink, 5 mg of the as-prepared catalyst was dispersed in isopropanol and Nafion mixed solution containing 500 μ L isopropanol and 50 μ L Nafion, which formed a homogeneous suspension after sonication for 1 h. Thereafter, the ink was dropped onto a carbon paper with an area of 1 × 1 cm² and dried at room temperature, leading to a loading of 1 mg cm⁻².

Electrochemical measurements

Electrochemical measurements were performed with a H-type cell separated by a Nafion 117 membrane at room temperature and atmospheric pressure. Before NRR tests, the Nafion membrane was pretreated by a previous reported method.² All the electrochemical tests were conducted with an electrochemical workstation (Parstat 4000) using a three-electrode configuration with each as-prepared electrode, a graphite rod and a saturated calomel electrode as the working, the counter and the reference electrodes, respectively. The electrolyte was 0.1 M phosphate buffer solution (PBS, pH=7.2) and the volume of the PBS was 30 mL. All potentials measured were iR-compensated and calibrated to RHE according to the Nernst equation ($E_{RHE} = E_{SCE} + 0.2412 + 0.059 \times pH$). All reported current density values were normalized to the geometric surface area. Prior to each electrochemical measurement, the electrolyte was presaturated with N₂ or Ar gas bubbling for 30 min and continuously bubbled with corresponding gas at a flow rate of 20 sccm during the tests. The scan rate of the linear sweep voltammetry was set at a rate of 1 mV s⁻¹ and the current densities were normalized by geometric

surface areas. The NRR activity of a sample was evaluated using potentiostatic method for 2 h at room temperature.

Ammonia quantification by indophenol blue method

UV-Vis spectrophotometry was employed in detection of NH₃ concentration with indophenol blue method.³ In detail, 1 ml of the post-electrolysis electrolyte was removed from the cathodic chamber and added into 1 mL of M NaOH solution containing 5 wt.% salicylic acid and 5 wt.% sodium citrate. Then 500 µL NaClO solution (0.05 M) and 100 µL sodium nitroferricyanide solution (1 wt.%) were added into the mixture subsequently. After 2 h at room temperature, the absorbance of the mixed solution was detected at λ = 680 nm. In order to calculate the amount of produced NH₃, the calibration curve was fitted using standard ammonia chloride solutions of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1 µg mL⁻¹ in 0.1 M PBS. The fitting curve (y = 0.3678x+0.0431, R² = 0.999) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations (Fig. S8).

The ammonia yield and FE can be calculated as follows:

yield rate (NH₃) = 17×c(NH₃) ×V/(m×t)

 $FE = 3 \times F \times c(NH_3) \times V/(17 \times Q)$

where $c(NH_3)$ is the NH₃ concentration, V is the electrolyte volume, t is the electrolysis time, m is the catalyst weight, F is Faraday constant (96485 C mol⁻¹) and Q is the total charge during electrolysis.

Hydrazine quantification

The hydrazine concentration was estimated by the method of Watt and Chrisp.⁴ A mixture of pdimethylaminobenzaldehyde (4 g), concentrated hydrochloric acid (20 mL) and ethanol (200 mL) was used as a color reagent. 5 ml electrolyte taken out from the cathodic chamber was added into 5 mL color reagent. After 15 min, the absorbance of the resulting solution was measured at 455 nm by using UVvis spectrophotometer. The yields of N₂H₄ were estimated from a concentration-absorbance calibration curve using standard hydrazine monohydrate solution of 0.0, 0.4, 0.8, 1.2, 1.6 and 2 µg mL⁻¹ in 0.1 M PBS. The fitting curve shows good linear relation of absorbance with N₂H₄ concentration (y = 0.5692x+0.0180, R² = 0.999) by three times of independent calibrations (Fig. S11).

Calculations of H₂ amount and FE

The FE was calculated by comparing the amount of measured H₂ generated by cathodal electrolysis with calculated H₂ (assuming 100% FE). GC analysis was carried out on GC-2010 Plus (Shimadzu Co.) with

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thermal conductivity detector and nitrogen carrier gas. FE was calculated according to following equation:

 $FE = 2 \times F \times n/Q$

Where F is the Faraday constant; n is the actually produced H_2 (mol), and Q is the quantity of applied electricity.

Computational details

The spin-polarized density functional theory (DFT) calculations were implemented using the Vienna ab initio simulation package (VASP).⁵ The generalized gradient approximation (GGA) developed by Perdew, Burke and Ernzerhof (PBE) ⁶ was adopted for the exchange-correlation potential and the projector augmented wave (PAW) ⁷ pseudopotentials was applied to treat the core-electron interactions. The kinetic energy cutoff was set to 520 eV. The convergence criterion for geometry optimization was set to 1×10^{-5} eV. The residual force on each atom should be smaller than 0.02 eV Å⁻¹ for structural relaxations. We employed a graphene supercell with surface periodicity of 8 × 8 as a basis, and set Fe and Zn atoms at six sites bonding with N atom. In order to compare the theoretical catalytic activity of bimetallic and monmetallic atomic catalysts, we established graphene supercell with surface periodicity of 5 × 5 as a basis, and made Fe and Zn atoms bonding with four N atoms, respectively. The Gamma-centered Monkhorst-Pack grid with (2 × 2 × 1) and (3 × 3 × 1) k-point samplings were used for bimetallic and monometallic catalyst, respectively. A vacuum of 15 Å was included to isolate interaction between each sheet. In the process of structural optimization, all atoms were fully relaxed. All the structures have been confirmed to be the minimum with no imaginary frequencies.

The adsorption energy (ΔE_{*NN}) for N₂ was calculated as:

 $E_{ad} = E_{substrate+N2} - E_{substrate} - E_{N2}$

The Gibbs free energy change (ΔG) of each elementary reaction was calculated by

 $\Delta G = \Delta E + \Delta Z P E - T \Delta S$

The total energy (E), zero-point energy (ZPE) and the entropy (S) of each adsorbed state were yielded from DFT calculation. Here, the temperature is T = 298.15 K. We use the free energy of $\frac{1}{2}H_2$ as that of (H⁺ + e⁻) by referring the potential to the normal hydrogen electrode. ⁸ The entropies as well as the vibrational frequencies of molecules in the gas phase were in accordance with the NIST database.

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2. Figures and tables



Fig. S1 (a) HAADF-STEM and EDS mapping images of Fe-N-C. (b) Aberration-corrected HAADF-STEM images of Fe-N-C.



Fig. S2 (a) HAADF-STEM and EDS mapping images of Zn-N-C. (b) Aberration-corrected HAADF-STEM images of Zn-N-C.



Fig. S3 HAADF-STEM and corresponding EDS mapping images.



Fig. S4 XRD patterns (a) and Raman spectra (b) of Zn/Fe-N-C, Fe-N-C and Zn-N-C.



Fig. S5 High-resolution N 1s XPS spectra of Zn/Fe-N-C, Fe-N-C and Zn-N-C.



Fig. S6 (a) The Fe K-edge EXAFS k space fitting curves of Zn/Fe-N-C. (b)The Zn K-edge EXAFS k space fitting curves of Zn/Fe-N-C.



Fig. S7 Optimized geometry of the ZnFeN₆ (a), FeN₂ZnN₂ (b), ZnN₄FeN₄ (c) and ZnN₄FeN₄-2 (d) and corresponding total energy.



Fig. S8 UV-vis absorption spectra (a) and corresponding standard curve (b) of the electrolytes stained by the indophenol blue method.



Fig. S9 UV-vis absorption spectra of the electrolytes at various potentials after electrolytic reaction for 2 h.



Fig. S10 NH₃ yield rate and FE under different potentials of Fe-N-C (a) and Zn-N-C (b).



Fig. S11 UV-vis absorption spectra (a) and corresponding standard curve (b) of the electrolytes stained by the Watt and Chrisp method.



Fig. S12 UV-vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp after 2 h electrolysis at -0.3 V using Zn/Fe-N-C as the cathode.



Fig. S13 (a) The amount of produced H₂ at each given potential. (b) The corresponding FE of HER at each given



Fig. S14 (a-c) Cyclic voltammograms for the synthesized samples. (d) Charging current density at 0.15 V difference plotted against scan rate.



Fig. S15 Electrochemical active surface area (ECSA)-normalized LSV curves of Zn/Fe-N-C, Fe-N-C and Zn/-N-C in N2-

saturated 0.1 M PBS solution.



Fig. S16 UV-Vis absorption spectra of the electrolytes stained with indicator under different conditions.



Fig. S17 (a) Time-dependent current density curve of Zn/Fe-N-C at -0.3 V for 30 h. (b) Recycling tests of Zn/Fe-N-C at -0.3 V.



Fig. S18 XRD patterns of the Zn/Fe-N-C before and after NRR stability tests.



Fig. S19 (a) HAADF-STEM and EDS mapping images of the Zn/Fe-N-C after NRR stability tests. (b) Aberrationcorrected HAADF-STEM image and enlarged image of the Zn/Fe-N-C after NRR stability tests.



Fig. S20 High-resolution N 1s spectra of the Zn/Fe-N-C before and after NRR stability tests.



Fig. S21 Optimized geometry and the charge density difference of the N₂-adsorbed configuration via side-on mode on the Zn/Fe-N-C (a), Fe-N-C (b) and Zn-N-C (c). Brown, gray, yellow and taupe spheres refer to C, N, Fe and Zn atoms, respectively. Yellow and cyan shadows represent charge accumulation and depletion around Fe atoms, respectively.



Fig. S22 Gibbs free energy profiles for NRR with two possible pathways on Zn/Fe-N-C (a), Fe-N-C (b) and Zn-N-C (c). The insets are the most stable configurations of intermediates. Brown, gray, yellow, taupe and pink spheres refer to C,

N, Fe, Zn and H atoms, respectively.

 Table S1 ICP-AES analysis results of the as-synthesized catalysts.

Sample	Fe (wt.%)	Zn (wt.%)
Zn/Fe-N-C	0.34	0.29
Fe-N-C	0.36	N/A
Zn-N-C	N/A	0.27

Table S2 Parameters of the EXAFS data fitting results of samples.

Sample	Bond	CN	R (Å)	σ²*10³ (Ų)	R-factor (%)	
Zn/Fe-N-C	Fe-N	3.1±0.3	1.88±0.03	6.82±1.23	1 1	
	Fe-Zn	0.9±0.1	2.50±0.04	7.81±1.69	1.1	
	Zn-N	3.1±0.3	1.96±0.03	5.32±1.87	1 0	
	Zn-Fe	0.9±0.1	2.50±0.04	9.64±1.87	1.2	
Fe-N-C	Fe-N	4.0±0.1	1.90±0.03	3.74±1.16	1.0	
Zn-N-C	Zn-N	4.0±0.1	1.98±0.03	4.01±1.35	1.2	
Fe-foil	Fe-Fe	8.0±0.1	2.46±0.02	4.5±1.28	0.7	
	Fe-Fe	6.0±0.1	2.83±0.02	3.2±1.17	0.7	
Zn-foil	Zn-Zn	6.0±0.1	2.63±0.03	3.9±1.14	0.6	

CN is coordination number, R is distance between absorber and backscatter atoms, σ^2 is Debye-Waller factor to account for both thermal and structural disorders, R-factor (%) indicates the goodness of the fit.

Catalysts	Electrolyte	NH_3 yield rate	FE	Potential	Reference
		(µg h ⁻¹ mg _{cat} -1)	(%)	(V vs. RHE)	hererenee
Zn/Fe-N-C	0.1M PBS	30.5	26.5	-0.3	This work
ISAS-Fe/NC	0.1 M PBS	62.9	18.6	-0.4	[9]
Fe-N/C-CNTs	0.1 M KOH	34.83	9.28	-0.2	[10]
Fe ₂ O ₃ /CNT	0.1 M HCl	34.0	14.6	-0.3	[11]
FeOOH nanorods	0.5 M LiClO ₄	23.32	6.7	-0.7	[12]
FeMoO ₄	0.1 M Na ₂ SO ₄	17.51	10.53	-0.4	[13]
Fe_2O_3 nanorods	0.1 M Na ₂ SO ₄	15.9	0.94	-0.8	[14]
Fe ₃ O ₄ /Ti	$0.1 \text{ M} \text{ Na}_2 \text{SO}_4$	3.42	2.6	-0.4	[15]
SA-Mo/NPC	0.1 M HCl	34.0	14.6	-0.3	[16]
N-doped carbon	0.05 M H ₂ SO ₄	23.8	1.42	-0.9	[17]
Au/TiO ₂	0.1 M KOH	21.4	8.11	-0.2	[18]
B-doped TiO ₂	0.1 M Na ₂ SO ₄	14.4	3.4	-0.8	[19]
VN/CC	0.1 M HCl	15.2	3.58	-0.3	[20]
VNiON	0.05 M H ₂ SO ₄	6.78	5.57	-0.4	[21]

Table S3 Performance comparison of Fe-based and other NRR electrocatalysts in aqueous solutions.

 Table S4 ICP-AES analysis results of blank PBS and electrolyte after stability test (PBS-a).

Sample	Fe (mg/L)	Zn (mg/L)
PBS	<0.01	<0.01
PBS-a	<0.01	<0.01

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