Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supporting Information

From Biological Enzyme to Single Atomic Fe-N-C Electrocatalyst for Efficient Oxygen Reduction

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Experimental Section

Synthesis of FeNC catalysts

Fresh coagulated pig blood was available from the local slaughterhouse. For the synthesis of FeNC catalysts, the coagulated pig blood was first dehydrated at 120 ^{o}C in a drying oven. The pristine red curd turned into black solid. The ground black powder was washed to remove soluble impurities, dried, and then heat-treated at 350 ^{o}C for 2 h at a heating rate of 5 ^{o}C/min in an inert atmosphere to preliminarily graphitize the precursor, followed by the pyrolysis at a certain temperature for 1 h. The catalysts pyrolyzed at 900 and 1000 ^{o}C were designated as FeNC-900 and FeNC-1000, respectively.

Characterization

The morphologies of as-prepared FeNC electrocatalysts were characterized by JEM-2100F transmission electron microscopy (TEM) at an accelerating voltage of 200 kV. STEM observation was carried out on a JEOL ARM200F (JEOL, Tokyo, Japan) STEM operated at 200 kV with cold filed-emission gun and double hexapole Cs correctors (CEOS GmbH, Heidelberg, Germany). The attainable spatial resolution defined by the probe-forming objective lens is better than 80 picometers. Raman spectra were recorded on a Thermo Scientific DXR (532 nm laser wavelength). Powder X-ray diffraction (XRD) patterns were recorded on a Regaku D/Max-2500 diffractometer using a Cu Kα radiation. The X-ray absorption data at the Fe K-edge of the samples were recorded at room temperature in the fluorescent mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai), China. The station was operated with a Si(111) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5 GeV and a current between 150-210 mA. The photon energy was calibrated with the first inflection point of Fe K-edge in Fe metal foil. The Fe K-edge extended x-ray absorption fine structure (EXAFS) data were analyzed using standard procedures with the program IFEFFIT.

X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the chemical bonding states using the Thermo Scientific ESCALab 250Xi with 300 W monochromatic Al Kα radiation. The base pressure in the analysis chamber was about 3×10^{-10} mbar. The hydrocarbon C 1*s* line at 284.8 eV from adventitious carbon was used for binding energy referencing. Nitrogen adsorption-desorption isotherms were measured on Quantachrome Autosorb AS-1 at 77 K. Before measurements, the samples were degassed in a vacuum at 150 °C for at least 6 h.

Electrochemical tests

Prior to use, the glass carbon rotating disk electrode (4 mm in diameter, 0.1256 cm^2 in surface area) was polished mechanically with 0.5-0.7 μm down to 0.03-0.05 μm alumina slurry to obtain a mirror-like surface and then washed with Mill-Q water and ethanol and allowed to dry. For all as-prepared FeNC catalysts in this work, in the typical ink preparation procedure, 2 mg catalysts were dispersed in 400 μL ethanol and sonicated for 30 minutes to form a homogeneous ink. 17.6 μL ink was loaded on polished glassy carbon electrode to get catalysts loading of 700 μg /cm^2. A drop of 0.5 wt. % nafion (Sigma-Aldrich) solution was then applied onto electrode surface layer to protect the catalysts dropping out. After dried in the air, the electrode was prepared for test. Before each ORR measurement, background voltammograms were obtained in N_2-saturated electrolyte (0.1 M KOH) and used to be subtracted from that measured in the O_2-saturated electrolyte. For comparison, commercial 20 wt.% Johnson-Matthey Pt/C was also measured with noble metal Pt loading of 25.5 μg /cm^2.

All electrochemical measurements were performed on a RRDE-3A (ALS, Japan) set-up in conjunction with Autolab PGSTAT 302N (Metrohm, The Netherlands) bipotentiostat. All the CV measurements were conducted at a scan rate of 50 mV/s, and the LSV curves were recorded at a rate of 5 mV/s. Before each ORR test, the electrolyte was purging with O_2 at least for 30 min. All RRDE measurements were carried out at a rotation speed of 1600 rpm.

Hydrogen peroxide yields and the electron transfer number (n) were calculated using the equations below:

$$H_2O_2(\%)=200\times\frac{I_R/N}{I_R/N+I_D}$$

$$n=4\times\frac{I_D}{I_D+I_R/N}$$

Herein, I_D and I_R are the disk and ring currents, respectively. N is the ring collection efficiency and the measured N value was 42.4%.

Zinc-air battery was constructed in a configuration of home-built electrochemical cell, where the FeNC-900 catalyst was loaded on a gas diffusion layer (Teflon-coated carbon fiber paper with a catalyst loading of 2.0 mg cm^{-2}) as air cathode and Zn foil was used as anode and 6.0 M KOH as electrolyte. Commercial Johnson-Matthey Pt/C with 20 wt.% Pt loading was also used for comparison with a catalyst loading of 1.0 mg cm^{-2}. All Zn-air batteries were tested under the same experimental conditions.

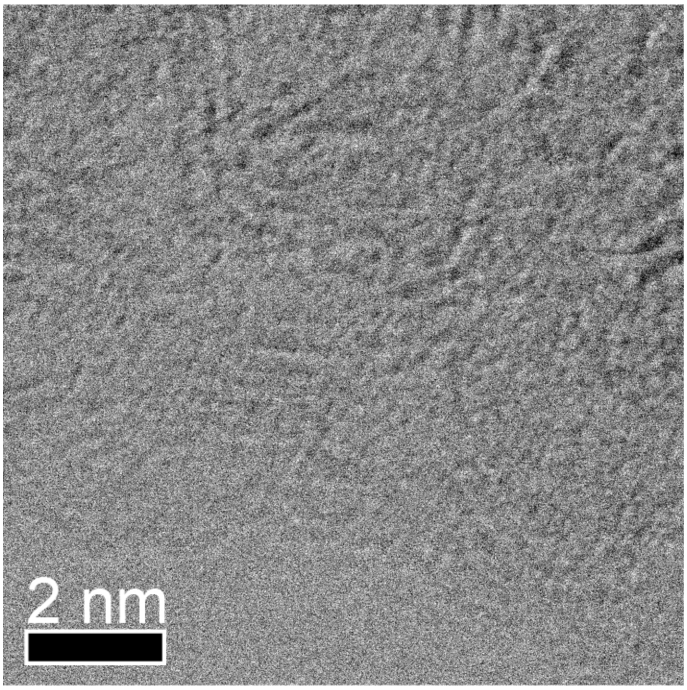

Fig. S1 ABF-STEM image of FeNC-900 sample.

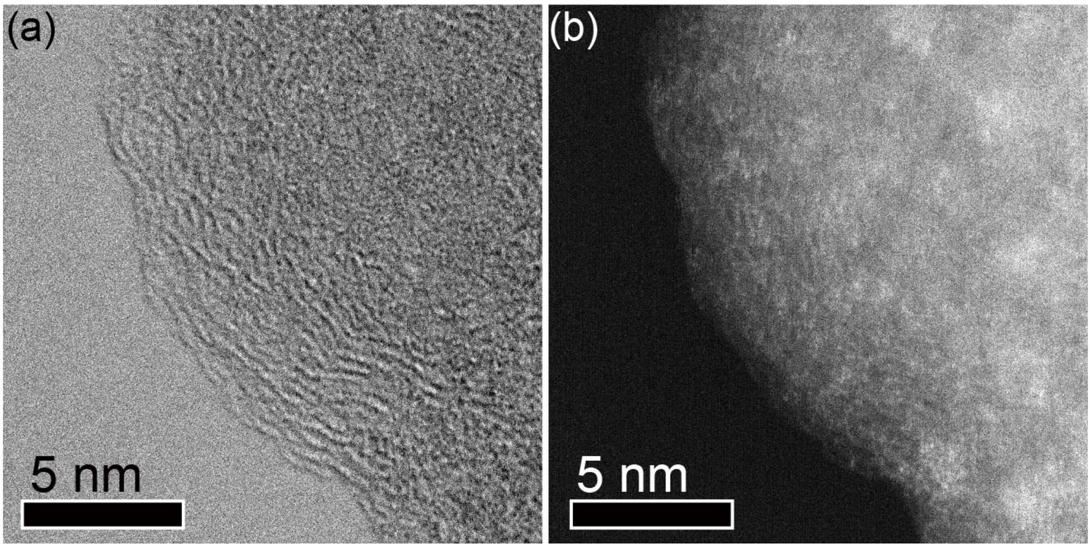

Fig. S2 (a) ABF and (b) HAADF STEM images of FeNC-1000 sample.

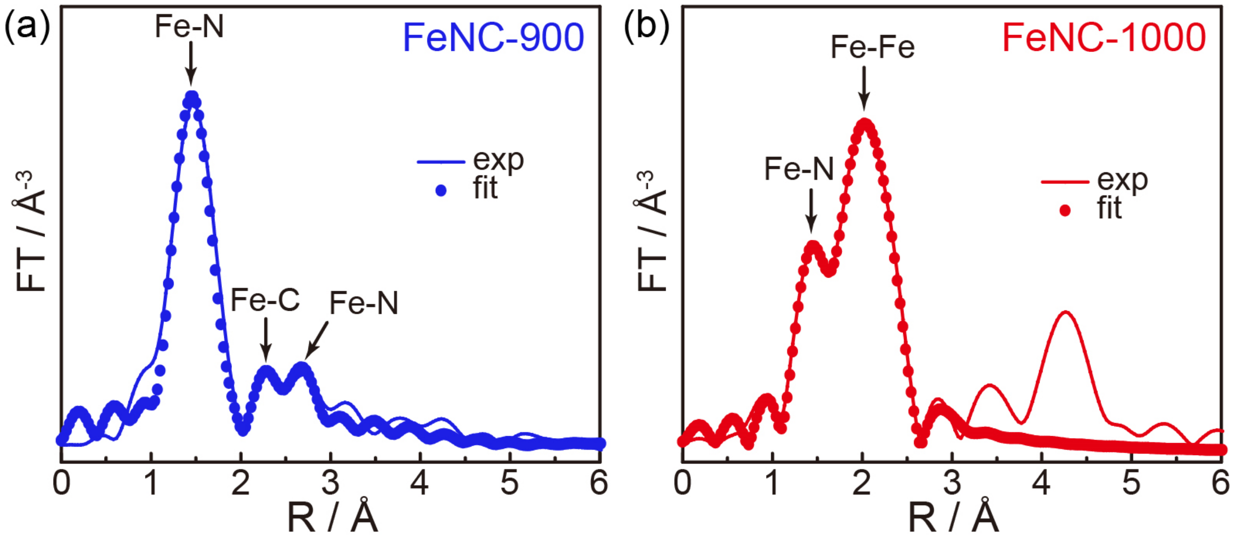

Fig. S3 Experimental Fourier Transformation at the Fe K-edge of EXAFS data and the corresponding fits of (a) FeNC-900 and (b) FeNC-1000 catalysts.

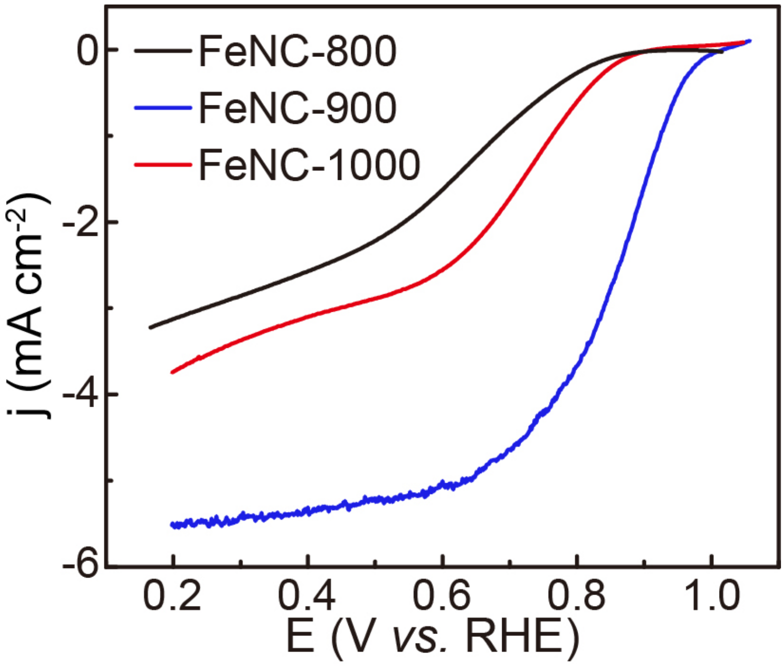

Fig. S4 Steady-state ORR polarization curves of as-prepared catalysts in O_2-saturated 0.1 M KOH solution at a rotation speed of 1600 rpm.

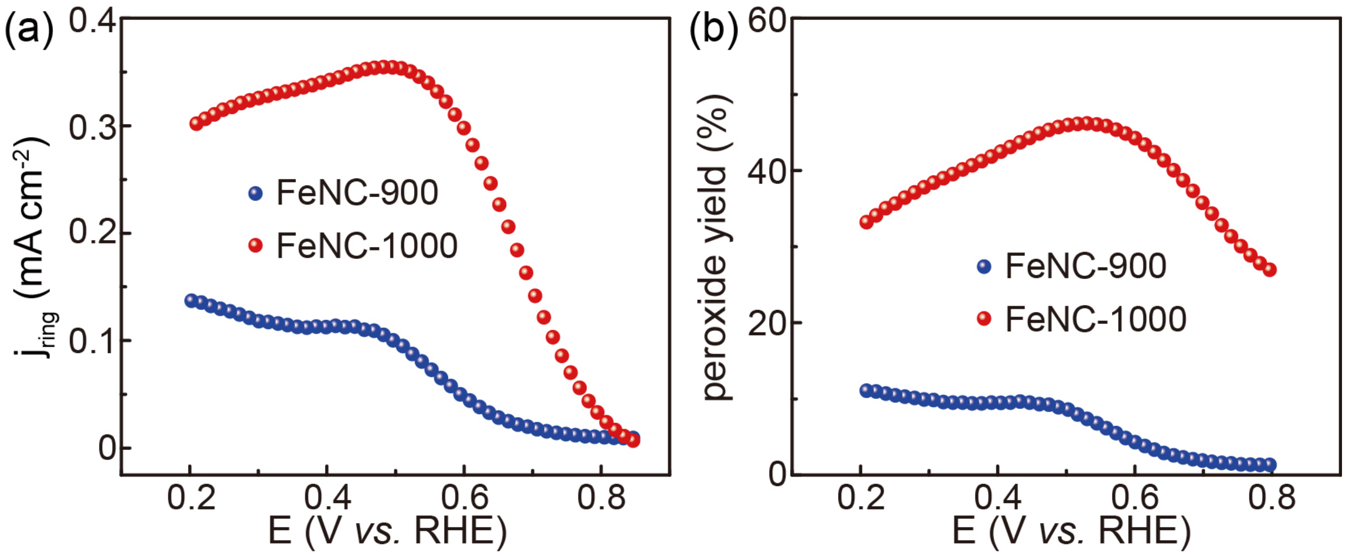

Fig. S5 (a) Ring current density and (b) corresponding peroxide species yield during ORR process for as-prepared catalysts in 0.1 M KOH.

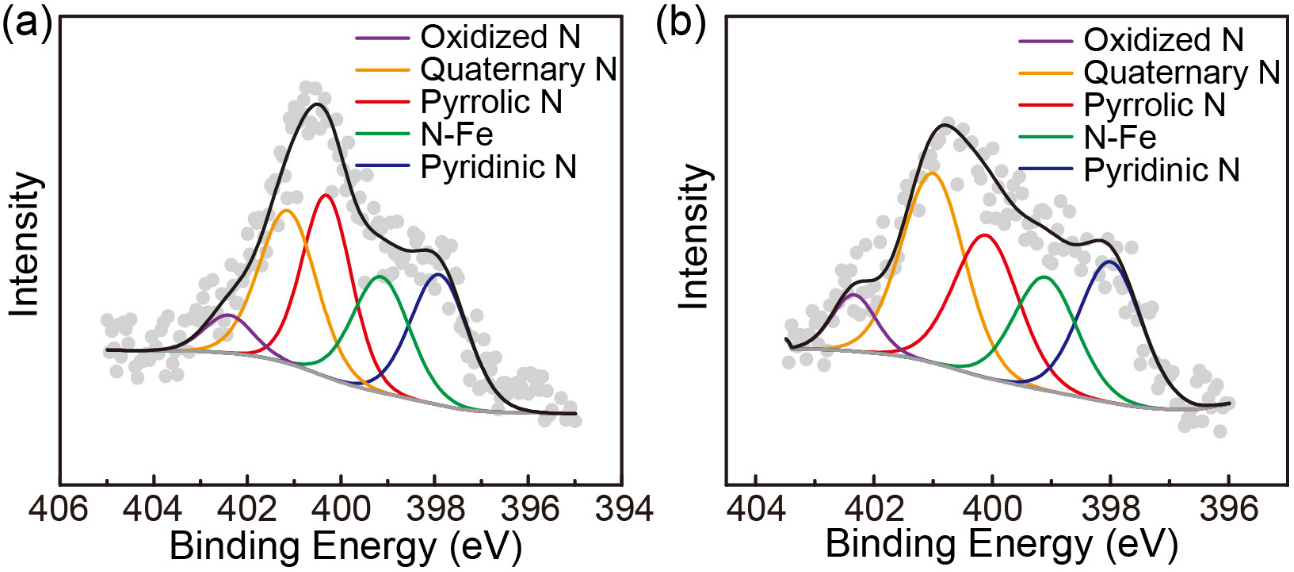

Fig. S6 The deconvoluted N 1s spectra of (a) FeNC-900 and (b) FeNC-1000 catalysts. The quantitative information of different nitrogen configurations was given in Table S2.

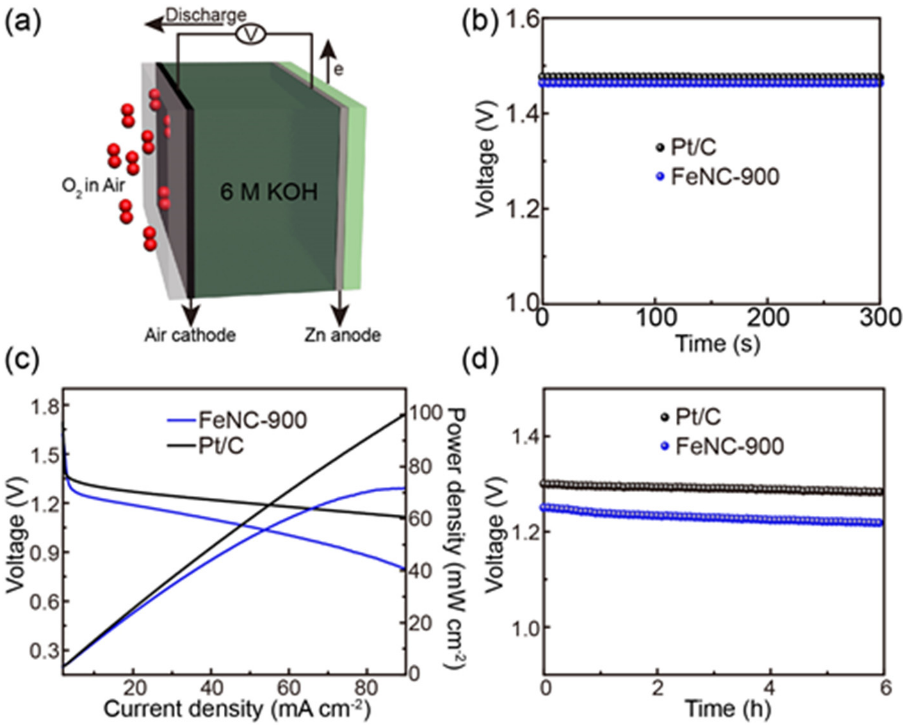

Fig. S7 (a) A schematic diagram of primary Zn-air battery. (b) Time-dependent open-circuit potential, (c) polarization curves and corresponding power density plots, and (d) long-time discharge curves of batteries using FeNC-900 and Pt/C catalysts as cathodes.

Considering the impressive electrocatalytic activity of FeNC-900 for ORR, a laboratory Zn-air battery was thus constructed as schematically shown in Fig. S7a to further explore its potential application in practical energy devices. The battery is composed of FeNC-900 or commercial Pt/C (tested under the same condition for comparison) loaded on carbon paper as cathode and Zn foil as anode. It was measured in a home-built electrochemical cell filled with 6 M KOH electrolyte. As shown in Fig. S7b, the Zn-air battery using FeNC-900 catalyst as cathode continuously outputs an open-circuit potential of 1.46 V, which is only 20 mV smaller than that using commercial Pt/C catalyst, suggesting the good catalytic performance. Fig. S7c shows the polarization curves and corresponding power density plots of the batteries for FeNC-900 and Pt/C catalysts. The power density for FeNC-900 reaches about 72 mW cm^{-2} at 90 mA cm^{-2}. Furthermore, when galvanostatically discharged at a current density of 5 mA cm^{-2} for 6 h, the voltage for FeNC-900 catalyst drops from 1.25 V to 1.22 V, while the voltage for Pt/C catalyst drops from 1.30 to 1.28 V in Fig. S7d. This means FeNC-900 shows a comparable durability under real battery operation conditions. These results indicate that the FeNC-900 exhibits the superior catalytic activity and durability as non-precious cathode in practical Zn-air battery.

Table S1 Parameters of EXFAS fits for FePc and three catalyst Fe@C-FeNCs.

Sample	Bond type	Coordination Number	Bond length R(Å)	Bond disorder $\sigma^2\times10^{-3}$(Å^2)	R factor
FeNC-900	Fe-N	3.8±0.4	1.97±0.02	3.7±0. 8	1%
	Fe-C	3.0±0.6	3.02±0.02	3.0±0.3	
	Fe-N	2.4±0.4	3.30±0.02	2.4±0.7	
FeNC-1000	Fe-N	2.1±0.7	2.00±0.02	5.2±1.0	1%
	Fe-Fe	4.3±0.9	2.49±0.02	4.1±1.5	

Table S2 Nitrogen contents and deconvoluted N 1s peak positions in FeNC-900 and -1000 catalyst from XPS data.

		FeNC-900	FeNC-1000
Nitrogen content (at %)		1.52	1.49
Pyridinic N	Peak position (eV)	397.90	398.03
	Content (at %)	0.34	0.33
N-Fe	Peak position (eV)	399.14	399.10
	Content (at %)	0.30	0.27
Pyrrolic N	Peak position (eV)	400.30	400.10
	Content (at %)	0.40	0.35
Quaternary N	Peak position (eV)	401.13	401.05
	Content (at %)	0.40	0.45
Oxidized N	Peak position (eV)	402.40	402.34
	Content (at %)	0.08	0.09