Electronic Supplementary Information (ESI) for

Supramolecular confinement synthesis of ultrafine iron nitride nanocrystals for oxygen reduction reaction in Zn-air batteries

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Experimental Section

Preparation of 6-substituted-2,4-diamino-1,3,5-triazine (T monomer)

The 6-substituted-2,4-diamino-1,3,5-triazine (T monomer) was synthesized according to our previous study. Typically, a mixture of dicyandiamide (15 mmol, 1.258 g), sodium hydrogencyanamide (15 mmol, 1.335 g), potassium hydroxide (3 mmol, 0.168 g) and DMSO (10 mL) was added into a Pyrex flask and irradiated using a microwave reactor under 180 °C for 30 minutes. After cooling to room temperature, 150 mL of ethanol was added to the resulted crude mixture. After stirring for 2 hours, the white precipitate (T monomer) was collected by centrifuging, washing with DMF and ethanol, and drying.

Electrochemical measurement

All the electrochemical tests were carried out on a three-electrode system using Biologic SP-300 electrochemical workstation equipped with a high-speed rotator. The graphite rod and Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. To prepare the working electrode, 2 mg of catalyst and 20 μL of 5 wt% Nafion solution were dispersed in 0.5 mL water/ethanol (V/V=4:1) mixture and sonicated for 30 minutes to form a homogeneous ink. 10 μL of the homogeneous ink was dropped on the surface of glassy carbon (GC) (GCE, 0.196 cm^2) and dried at room temperature. The loading of electrocatalysts were 0.2 mg cm^{-2}. All reference potentials were converted to the reversible hydrogen electrode (RHE) according to the Nernst equation (1):

$$E_{RHE} = E_{Hg/HgO} + 0.059\,pH + 0.098 \quad \text{.....(1)}$$

Where E_{RHE} is the potential referenced to a reversible hydrogen electrode, $E_{Hg/HgO}$ is the experimentally measured potential using Hg/HgO as the reference electrode.

The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements for ORR were performed at scan rates of 5 mV s^{-1} in O_2 saturated 0.1 M KOH electrolyte. The rotating disk electrode (RDE) tests were performed at rotation rates from 400 to 1600 rpm with a sweep speed of 5 mV s^{-1}. The electrode stability was tested by chronoamperometric technique at 0.7 V versus RHE for 30000s in 0.1 M KOH. In addition, we reassessed the stability of the electrode by testing chronoamperometric in 3 M methanol.

The hydrogen peroxide yield ($\%H_2O_2$) and electron transfer number (n) were calculated using the following equations:

$$\%H_2O_2 = 200 \times \frac{I_d}{I_d + I_r/N} \quad \text{.....(2)}$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \quad \text{.....(3)}$$

Where I_d is the disk current, I_R is the ring current, and N is the current collection efficiency of the Pt ring.

The Koutecky-Levich equation is (4) and (5):

$$J^{-1} = J_L^{-1} + J_K^{-1} = J_K^{-1} + (B\omega^{0.5}) - 1 \quad \text{.....(4)}$$

$$B = 0.2nF(D_{O2})2/3\ \tau - 1/6C_{O2} \quad \text{.....(5)}$$

Where J represents the measured current density, J_K represents the kinetic current, ω is the rotating rate of the electrode, n is the number of electrons transferred per O_2 molecule, F is the Faraday constant (96485 C mol^{-1}), D_{O2} is the diffusion coefficient of O_2 in the electrolyte (1.9×10^{-5} cm^2 s^{-1}), τ represents the kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1}), and C_{O2} denotes the saturated concentration of O_2 (1.2×10^{-6} mol cm^{-3}) in the aqueous system. 0.2 is a constant to determine B.

Zn-air battery tests

The Zn-air battery was constructed using a Zn plate as the anode electrode, a mixture of 6 M KOH and 0.2 M $Zn(Ac)_2$ as the electrolyte, and the electrocatalyst layer as the cathode electrode. To prepare the cathode electrode, 4 mg of electrocatalyst was dispersed in a mixture of ultrapure water (800 μL), isopropanol (150 μL), and Nafion solution (50 μL) to form a homogeneous ink. The electrocatalyst ink was dropped on the surface of carbon paper. The loading of electrocatalyst is 2 mg cm^{-2} and the available catalyst layer is 2 cm^{-2}. The discharge polarization curve and the corresponding power density curve were measured by LSV with a sweep speed of 10 mV/s on the electrochemical workstation at room temperature.

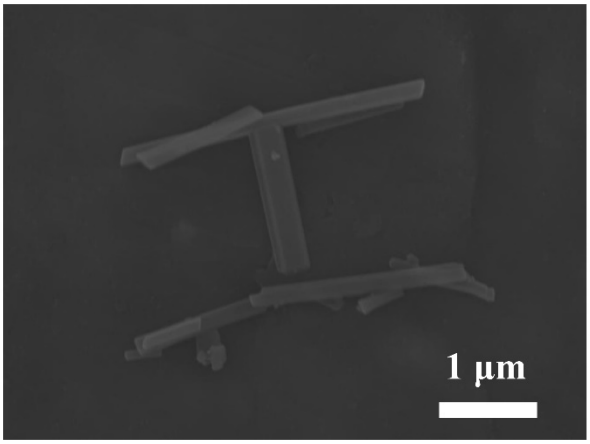

Fig. S1 SEM image of the Fe-CT.

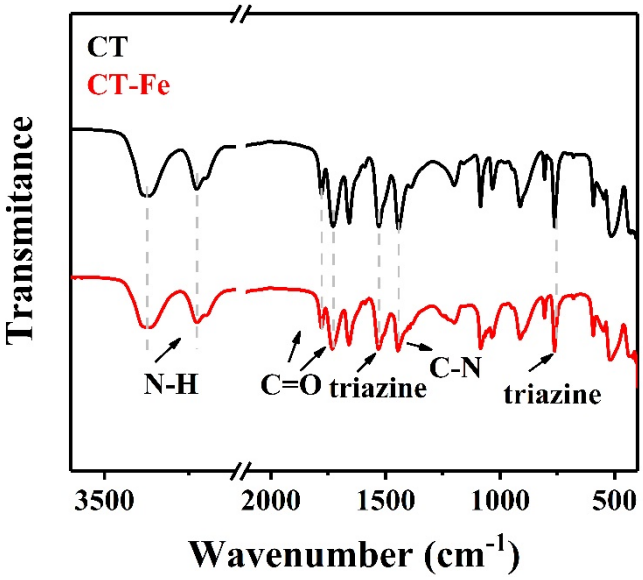

Fig. S2 FT-IR spectra of CT and CT-Fe precursors

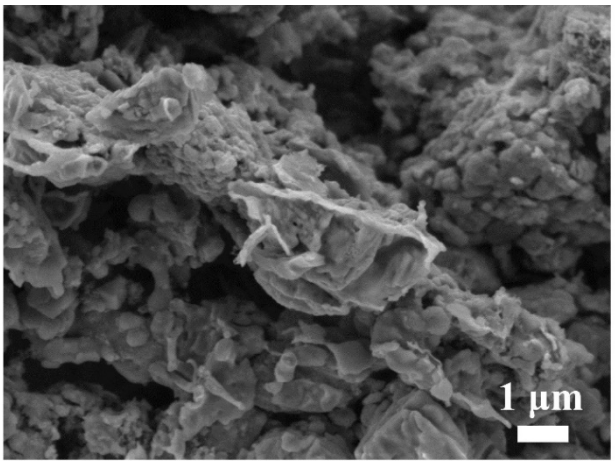

Fig. S3 SEM image of the NC-800.

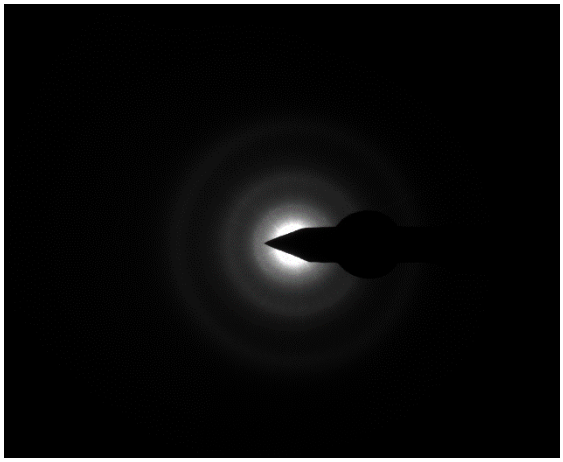

Fig. S4 SAED image of the Fe_3N/NC-800.

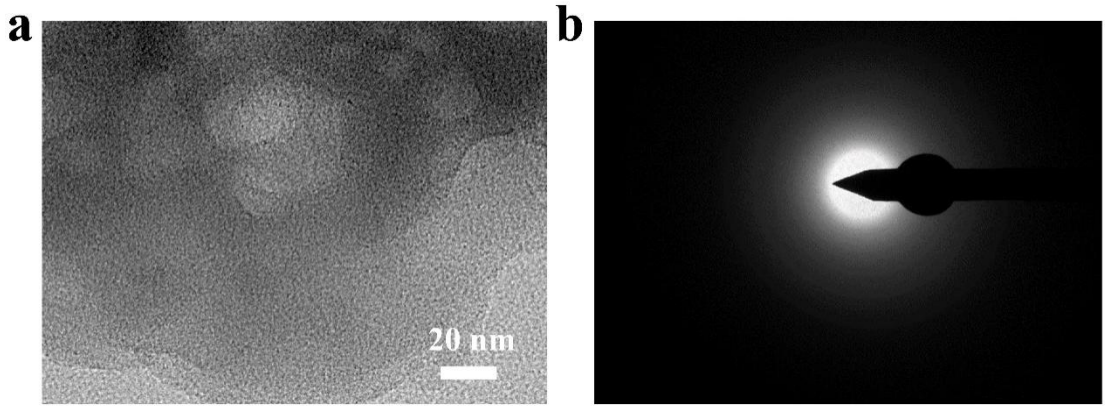

Fig. S5 (a) TEM image of the Fe_3N/NC-700, (b) SAED image of the Fe_3N/NC-700.

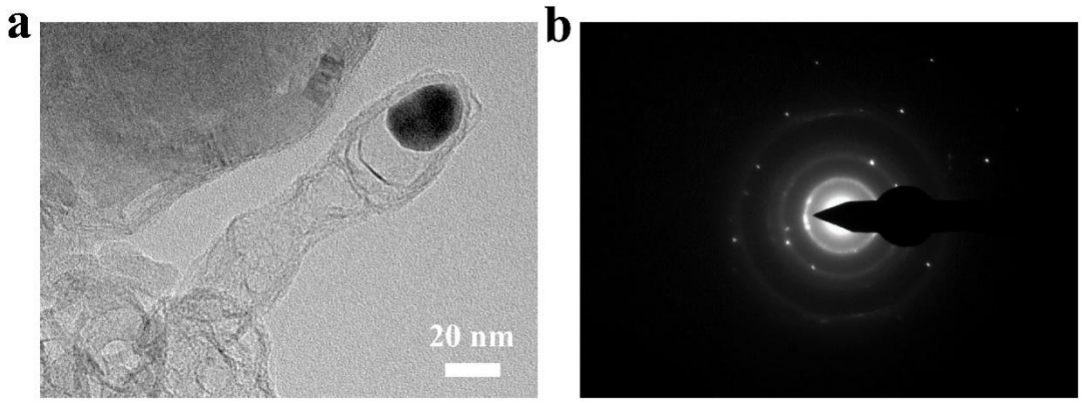

Fig. S6 (a) TEM image of the Fe_3N/NC-900, (b) SAED image of the Fe_3N/NC-900.

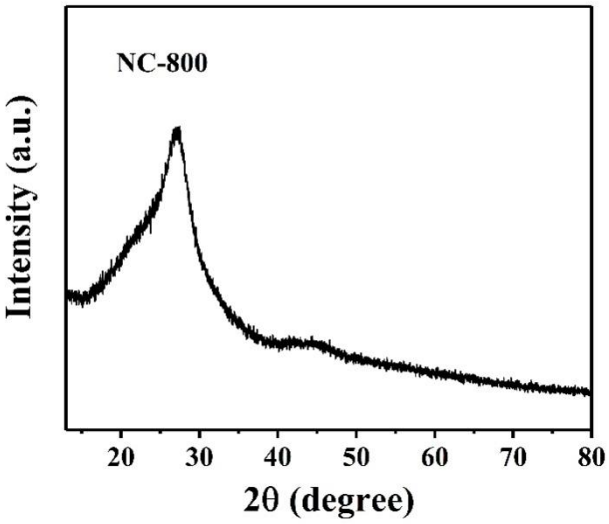

Fig. S7 XRD pattern of NC-800.

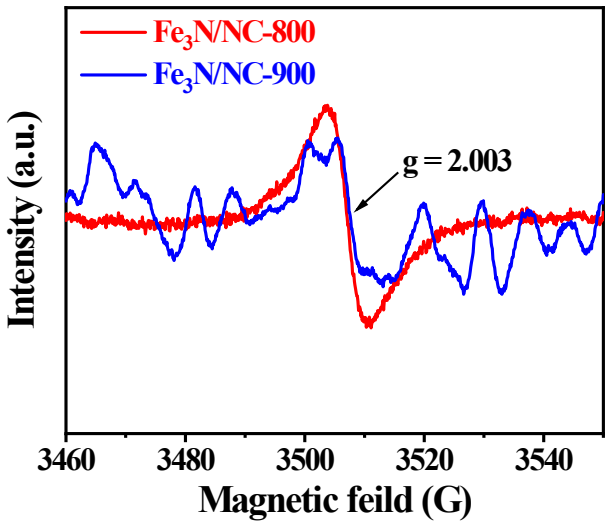

Fig. S8 EPR spectra of Fe_3N/NC-800 and Fe_3N/NC-900.

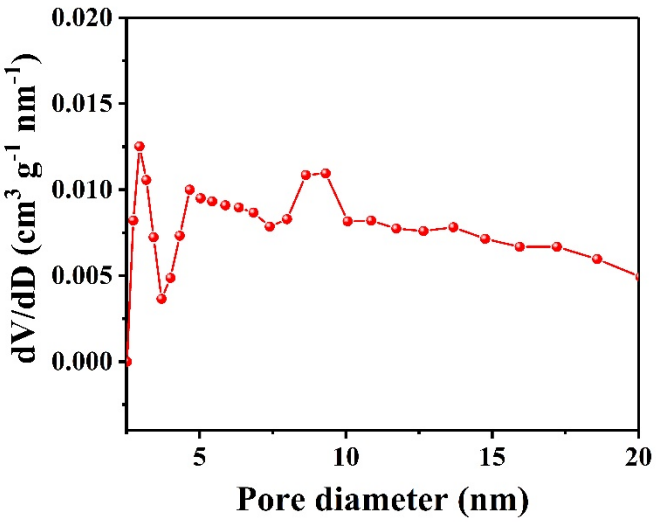

Fig. S9 The corresponding pore-size distribution curve of Fe_3N/NC-800.

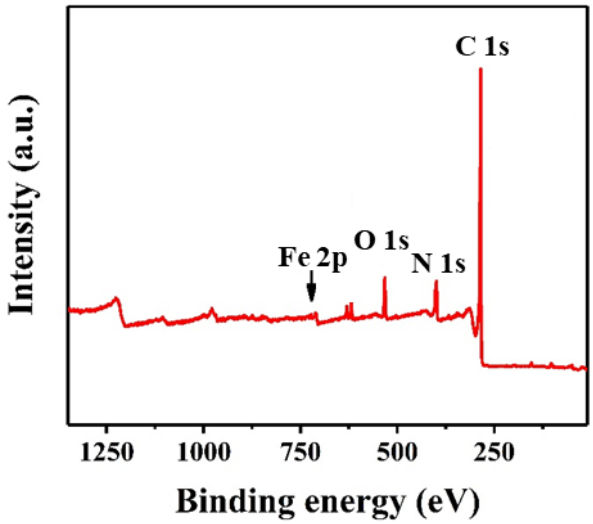

Fig. S10 XPS survey of Fe_3N/NC-800.

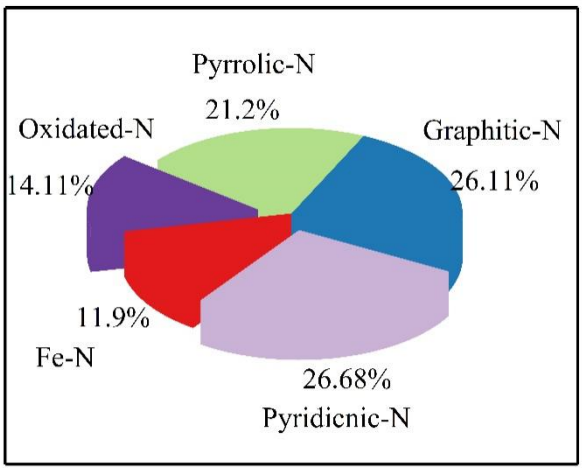

Fig. S11 The corresponding contents of the deconvoluted N species in the Fe_3N/NC-800 catalyst.

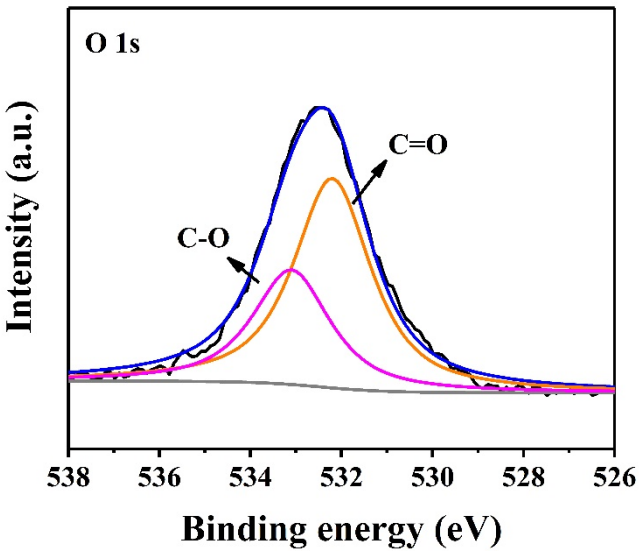

Fig. S12 O 1s XPS spectrum of Fe_3N/NC-800.

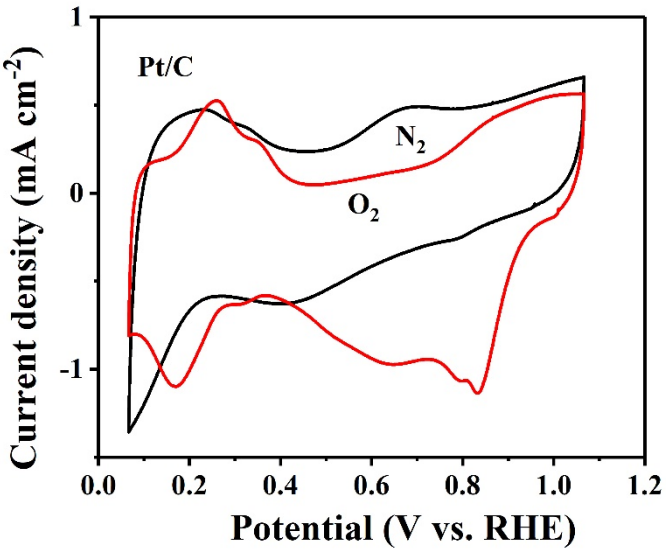

Fig. S13 CV plots of commercial Pt/C in N_2 and O_2-saturated 0.1 M KOH electrolytes.

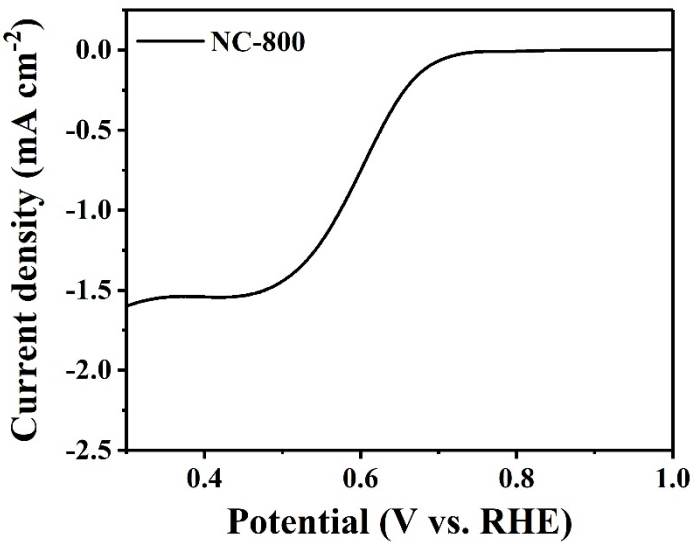

Fig. S14 ORR polarization plots of NC-800 in the O_2 saturated 0.1 M KOH electrolyte.

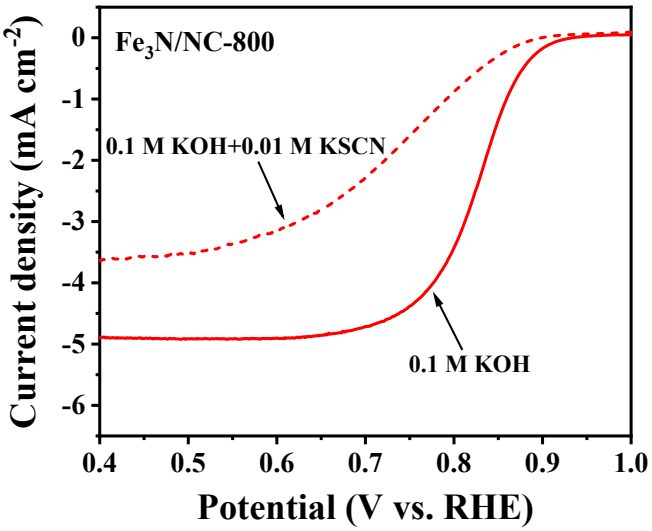

Fig. S15 ORR polarization curves of Fe_3N/NC-800 before and after the addition of 0.01 M KSCN in O_2 saturated 0.1 M KOH.

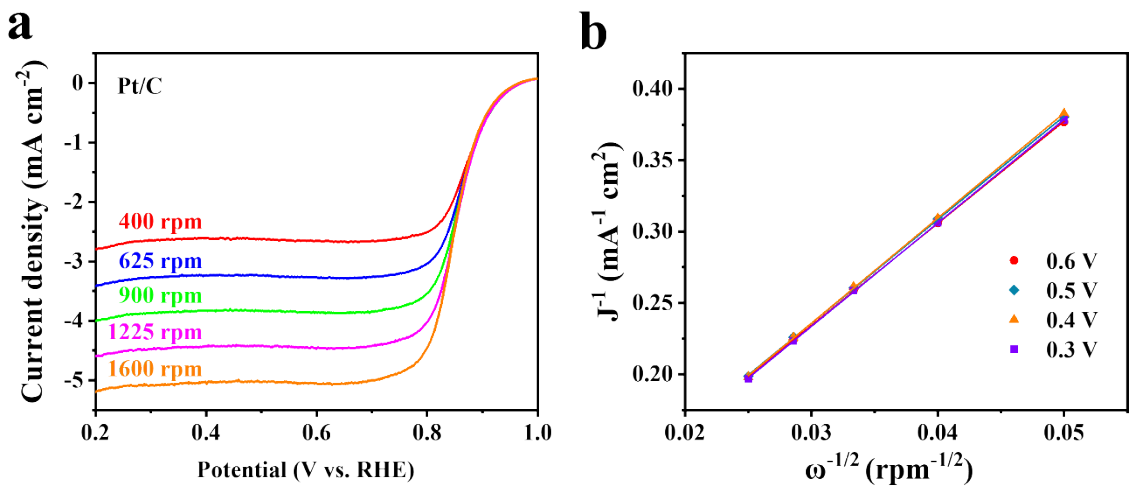

Fig. S16 (a) Polarization plots of commercial Pt/C at different rotating speeds from 400 to 1600 rpm. (b) The K-L plots of commercial Pt/C at different potentials.

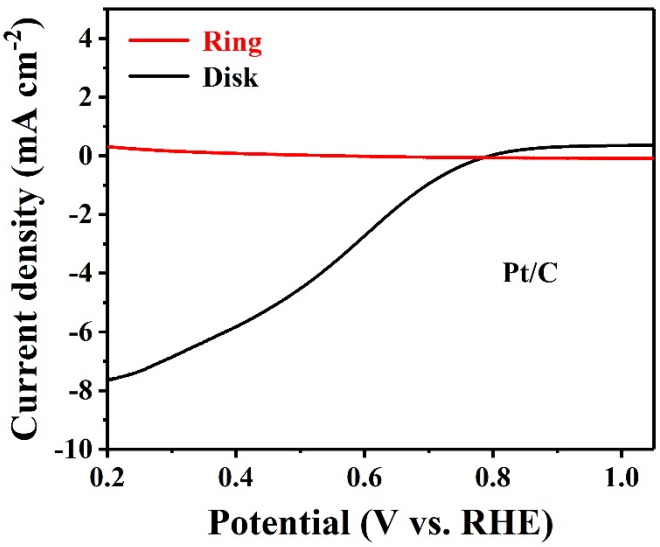

Fig. S17 RRDE curves of Pt/C.

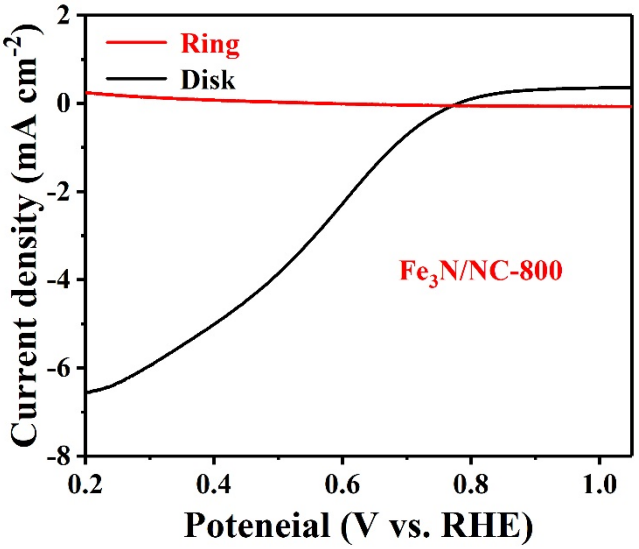

Fig. S18 RRDE curves of Fe_3N/NC-800.

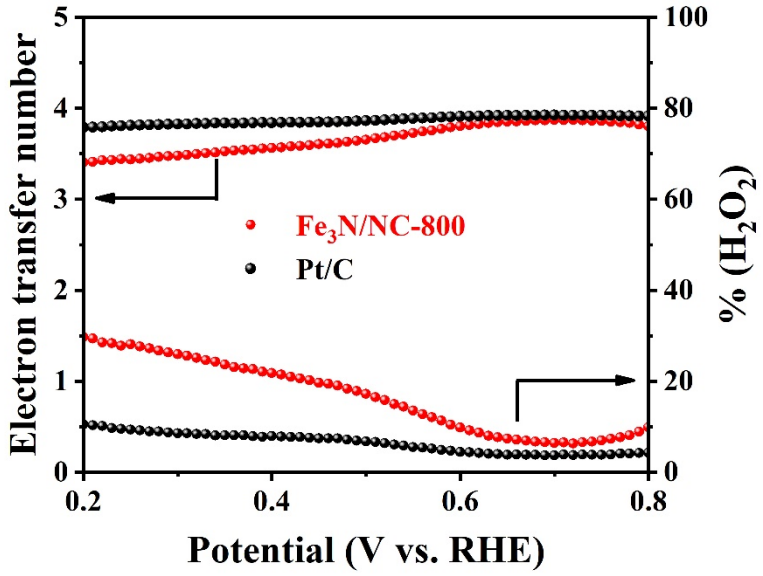

Fig. S19 Electron transfer number and H_2O_2 yield plots of commercial Pt/C and Fe_3N/NC-800 at different potentials.

Table S1. The element content in Fe_3N/NC-800 determined by XPS.

Element content	Atomic %
C	82.39
N	11.31
O	5.49
Fe	0.81

Table S2. The Fe contents in Fe_3N/NC-700, Fe_3N/NC-800 and Fe_3N/NC-900 catalysts determined by ICP-MS.

Sample	Fe_3N/NC-700	Fe_3N/NC-800	Fe_3N/NC-900
Fe content (wt %)	2.26	2.83	7.59