Supplementary Information

N-doped Mesoporous Bio-carbon Electrocatalyst Efficient in Zn-air Battery by *In-situ* Gas-foaming Strategy

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1. Experimental

Typically, sodium alginate (J&K Scientific LTD) and ammonium chloride (Sigma-Aldrich) were added into 50 mL of deionized water to form a homogeneous and transparent solution under ultrasonication, followed by violently stirring for 2 h at room temperature (25°C). Subsequently, the above solution was rotary evaporated and dried at 60°C for 12h to obtain a solid. After the solid was ground, the obtained powder was carbonized at 900°C for 3h under Ar atmosphere at a heating rate of 5°C min^{-1}. The black powder was obtained after being washed with 0.5 M H_2SO_4 aqueous solution at 80°C overnight, followed by filtration, rinsed with distilled water and dried at 60°C. The samples were detonated as NC-1, NC-2 and NC-3 in light of the ratio of sodium alginate to ammonium chloride of 1:10, 1:7 and 1:5, respectively.

For comparison, sodium alginate itself under the same conditions to finally obtain black powder, noted as C. With the same pretreatment, sodium alginate was then sent to tubular furnace with ammonia floating between 189.2°C and 273.4°C (the decomposition temperature range of NH_4Cl)and changed with Ar atmosphere to 900°C at a heating rate of 5°C min^{-1}, followed by the same operation to gain the black powder, noted as NC.

2. Material characterization

Field emission scanning electron microscope (FESEM) were carried out on ZEISS Gemini SEM 300. Transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 S-TWIN TMP

field emission transmission electron microscope. The structure of the sample was analyzed on a Rigaku MiniFlex 600 X-ray powder diffractometer (XRD) with Cu-K$_\alpha$ radiation (λ=1.5406Å). The diffraction pattern was collected at a rate of 5°s^{-1} to record the pattern in the 2θ range of 10-80°. The nitrogen adsorption experiment was measured by Micromeritics ASAP 2020 HD88 Surface Area and Porosity Analyzer. Samples were heated and vacuumed at 120°C for over 6 hrs before measurement. X-ray photoelectron spectroscopy (XPS) were measured on Thermo Fisher ESCLAB Xit with a monochromatic Al K$_\alpha$ X-ray beam (1486.6 eV). All binding energies were normalized to the C1s peak energy at 284.8 eV. Raman spectra were measured by using Thermo Fisher DXR RAMAN MICROSCOPE. FT-IR test was carried on PerkinElmer FT-IR Spectromer.

3. Electrochemical measurement

All electrochemical data was obtained by PINE rotating disk electrode (RDE) with an electrochemical workstation (CH Instruments 760E). All of the electrochemical measurements were performed in a conventional three-electrode system at room temperature. A glassy carbon (GC electrode, 3mm in diameter, PINE: AFE5T050PT), a KCl-saturated Ag/AgCl electrode and a Pt foil (0.25 cm^{-2}) was used as working electrode, reference electrode and counter electrode, respectively. 0.1 M KOH and 0.5 M H$_2$SO$_4$ aqueous solution were served as electrolyte in the process of electrochemical measurements and deaerated by high purity O$_2$ and N$_2$ (99.99% pure) according to the concrete conditions. In this work, all potentials are relative to that of the reversible hydrogen electrode (RHE).

The working electrodes were prepared by applying catalyst ink onto glassy carbon (GC) disk electrodes. Briefly, the catalyst ink was made by dispersing 3~5 mg catalyst in 400 uL ethanol and 5 uL 5 wt% Nafion solution. The ink was sonicated for 30 min and agitated overnight before usage. Before each test, the working electrode was polished with 0.05 um alumina powder and rinsed with distilled water. Then, the suspension was transferred onto the GC disk, leading to a loading of 0.6 mg cm^{-2}, and the solvent was evaporated at room temperature. (For commercial Pt/C, the mass loading of the catalyst was 0.025 mg cm^{-2}.) In order to remove possible surface contamination, all the electrodes were firstly subjected to 30 potential cycles between 0 and 1.2V in 0.1 M KOH or 0.5 M H$_2$SO$_4$ aqueous solution at a sweep rate of 50 mV s^{-1} prior to ORR activity testing.

The activities of catalysts were performed by recording linear sweep voltammetry (LSV) curves in the O$_2$-saturated 0.1 M KOH or 0.5 M H$_2$SO$_4$ aqueous solution at a scan rate of 10 mV s^{-1}. The

rotation speed was controlled at 1600 rpm.

During the rotating ring-disk electrode (RRDE) experiment, the ring-disk electrode containing a glassy carbon disk (d=4mm) and a Pt ring (5 mm inner diameter, 7mm outer diameter) was served as the working electrode with the same sample loading. The electron transfer number (n) and the hydrogen peroxide yield [H_2O_2 (%)] were obtained from the following two equations:

$$n = 4 \times I_D/(\frac{I_R}{N} + I_D) \quad \text{(S1)}$$

$$H_2O_2(\%) = 200 \times (I_R/N)/(\frac{I_R}{N} + I_D) \quad \text{(S2)}$$

Where I_D corresponds to the disk current, I_R is the ring current, and N represents the ring collection efficiency (N=0.37).

Rotating disk electrode (RDE) measurements were conducted at rotation speeds from 100 to 2500 rpm. RDE measurements were conducted in O_2-saturated 0.1M KOH electrolyte at 10mV s^{-1} scan rate. The electron transfer number (n) was analyzed on the basis of Koutecky-Levich equations:

$$\frac{1}{J} = \frac{1}{J_D} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad \text{(S3)}$$

$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6} \quad \text{(S4)}$$

In which J is the measured current density, J_K and J_D are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the disk (ω=2 π N, N is the linear rotation speed), n is the overall number of electrons transferred in ORR, F is the Faraday constant (F=96485 C mol^{-1}), C_0 is the bulk concentration of O_2, v is the kinematic viscosity of the electrolyte, and k is the electron transfer rate constant. According to Equations (S3) and (S4), the number of electrons transferred (n) and J_K can be obtained from the slope and intercept of the Koutecky-Levich plots, respectively. By using the value C_0=1.2*10^{-3} mol L^{-1}, D_0=1.93*10^{-5} cm s^{-1} and v=0.01 cm^2 s^{-1} in 0.1 M KOH .

The stability test in 0.1 M KOH or 0.5 M H_2SO_4 aqueous solution was done by chronoamperometry at 0.8V (vs. RHE) with a duration of 20000s. The methanol tolerance was studied under the same LSV condition except for the addition of 0.5 M methanol into the electrolyte.

4. Zn-air test

Zn-air battery was constructed in a configuration of home-built electrochemical cell with a circulating electrolyte flowed past the electrodes in a planar configuration, where NC-2 catalyst was loaded on a gas diffusion layer (Teflon-coated carbon fiber paper with a catalyst loading of 0.5 mg

cm^{-2}) as air cathode; Zn foil was used as anode and 6.0 M KOH as electrolyte. Commercial Johnson-Matthey Pt/C was also used to replace NC-2 at the same mass loading on carbon paper electrode to prepare the Zn-air battery. The flowing-electrolyte design helped to alleviate performance and degradation issues concerning both the zinc electrode and the air electrode. For the zinc electrode, the large volume of circulating electrolyte avoided the problems of dendrite formation, shape change and passivation by improving current distribution and reducing concentration gradients. On the air-electrode side, precipitated carbonates or other unwanted solids could be rinsed away by the flowing electrolyte and removed by an external filter. As a consequence, this provided higher operational and cycling lifetimes in comparison to conventional configurations with a static electrolyte. As a result, we did not use the separator.[1] The electrolyte volume in Zn-air battery approximately equaled to that of the electrolytic cell, *i.e.* 5 mL. All Zn-air batteries were tested under the same experimental condition.
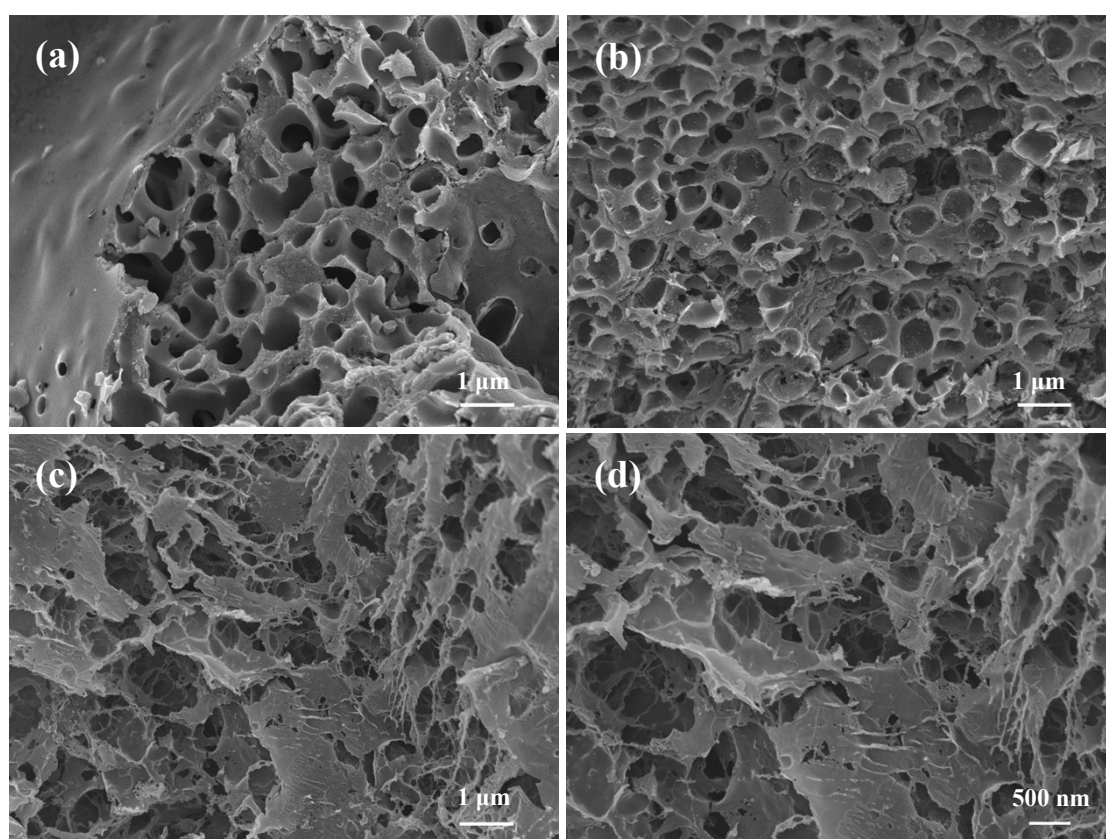
Fig.S1 Field emission scanning electron microscope (FESEM) images of C (a); NC (b); NC-2 (c and d).
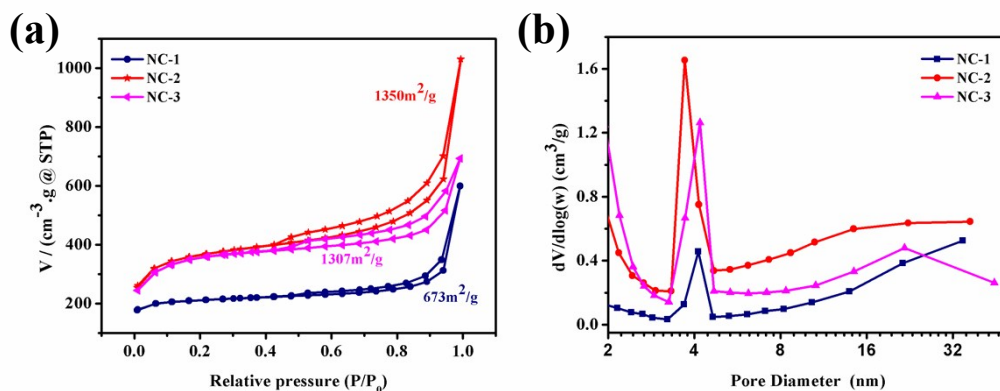
Fig. S2 (a) N2 adsorption and desorption isotherms; (b) Pore size distribution of NC-1, NC-2 and NC-3.
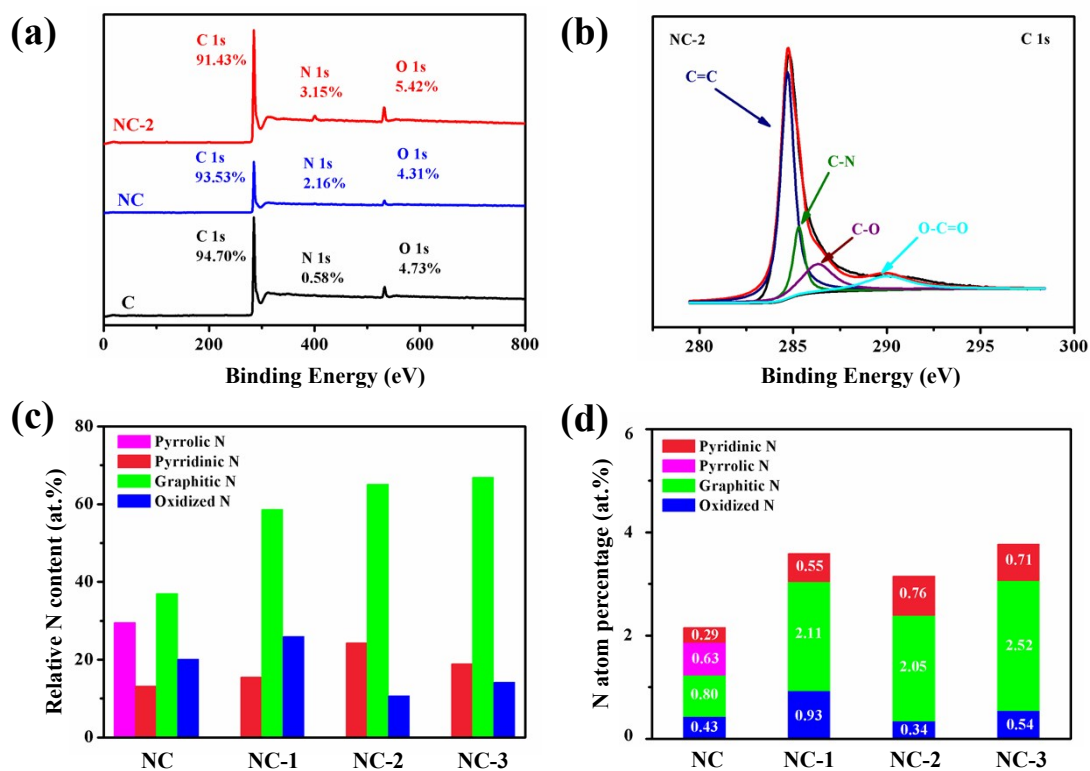

Fig. S3 (a) XPS survey spectra of C, NC and NC-2. (b) High resolution C 1s XPS spectra of NC-2. (c) Relative N content of different nitrogen species in NC, NC-1, NC-2 and NC-3. (d) N atom percentage of different nitrogen species in NC, NC-1, NC-2 and NC-3.
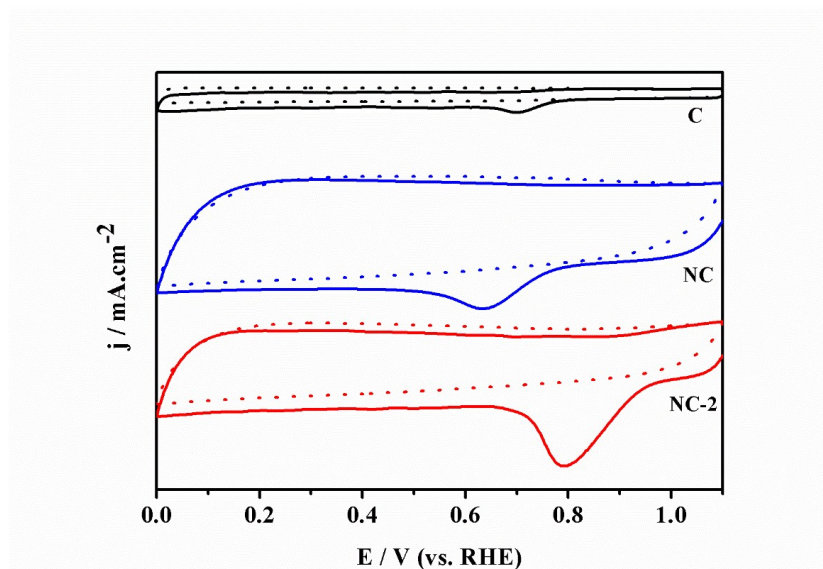
Fig. S4 CV curves of C, NC and NC-2 in N$_2$-(dash line) and O$_2$-(solid line) saturated 0.1 M KOH solution with a scan rate of 50 mV s^{-1}.
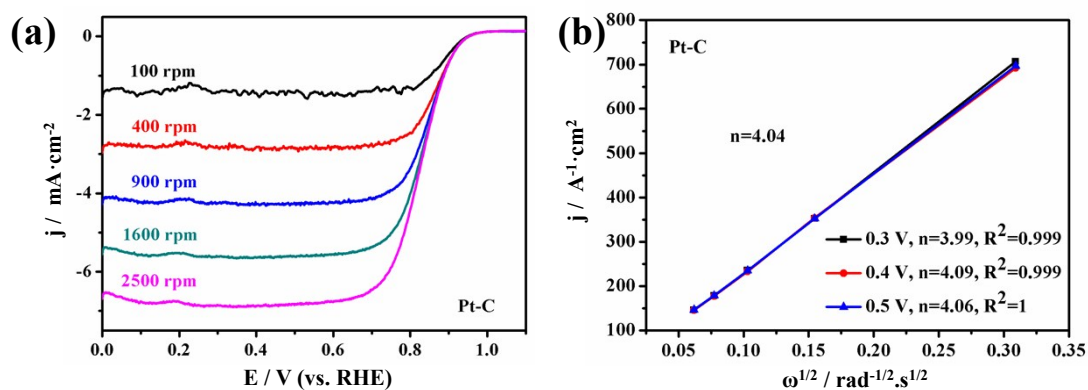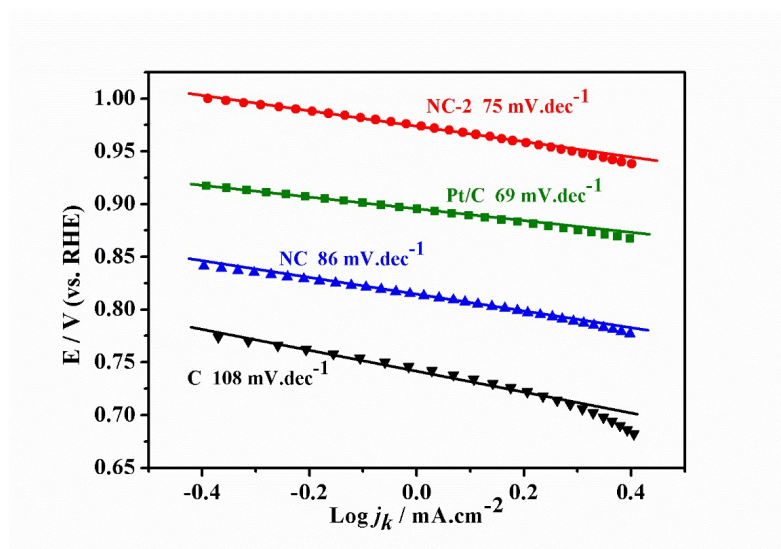
Fig. S5 Tafel plots of C, NC, NC-2 and Pt/C in O2-saturated 0.1 M KOH electrolyte.

Fig. S6 LSVs (a) and K-L plots (b) at different rotating speeds of Pt-C in 0.1 M KOH electrolyte.
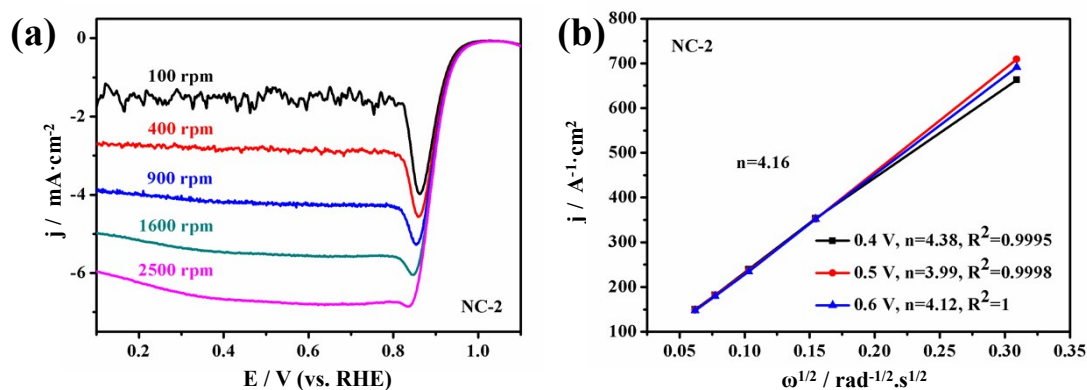
Fig. S7 LSVs (a) and K-L plots (b) at different rotating speeds of NC-2 in 0.1 M KOH electrolyte.

Table S1 Elemental composition of the NC-2 before and after chronoamperometric test obtained from XPS results.

Sample	C(at.%)	N(at.%)	O(at.%)
NC-2	92.60	3.05	4.36
NC-2 after	84.01	3.27	12.72
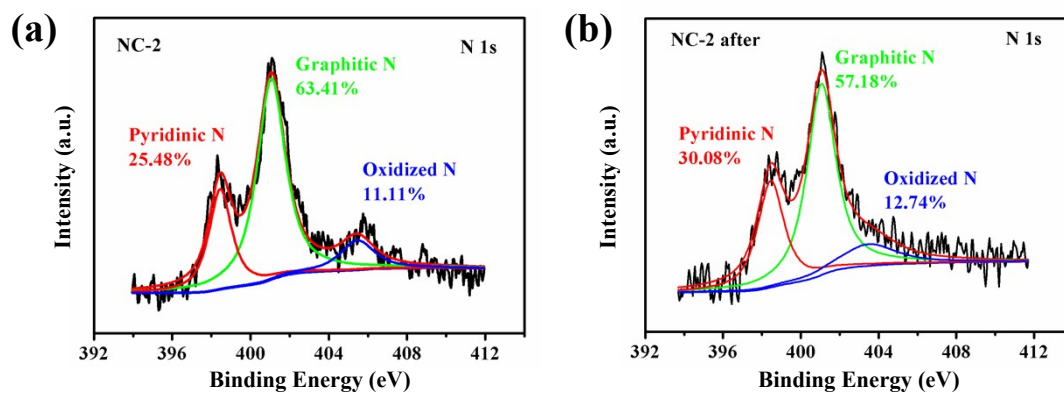
Fig. S8 N 1s XPS spectra of NC-2 (a) before ORR and (b) after ORR.
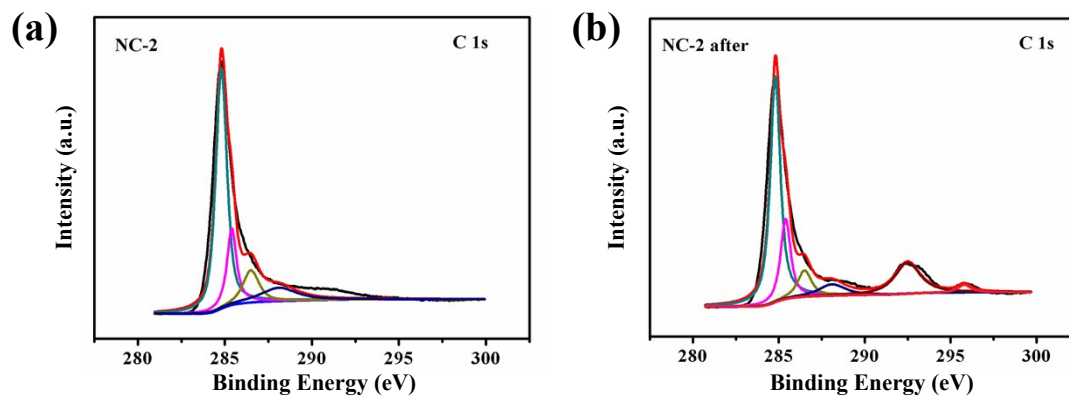
Fig. S9 C 1s XPS spectra of NC-2 (a) before ORR and (b) after ORR. The fitted peaks are C-C/C=C at 284.8 eV, C-OH at 285.4 eV, C-O-C at 286.5 eV, and C=O at 288.1 eV. Peaks at 292.5 eV and 295.8 eV fitted to Nafion contribution.[2]
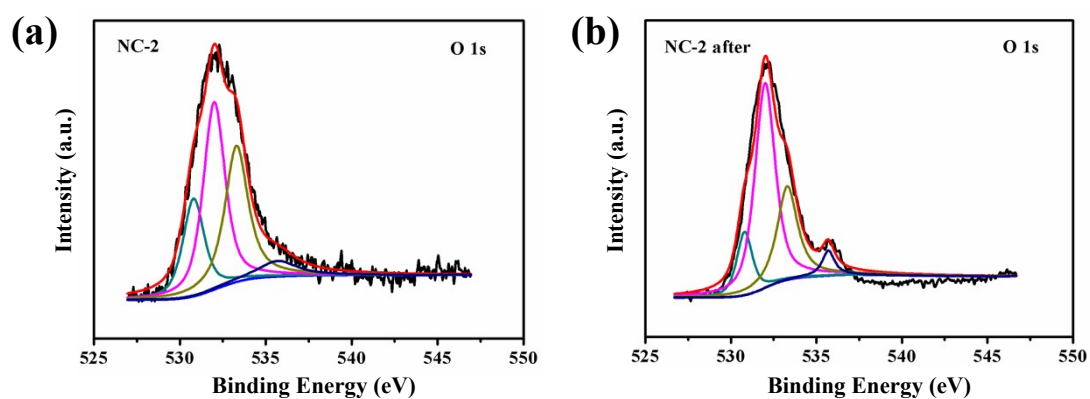
Fig. S10 O 1s XPS spectra of NC-2 (a) before ORR and (b) after ORR. The fitted peaks are C=O at 530.8 eV, C (aliphatic)-OH/C(aliphatic)-O-C(aliphatic) at 532.0 eV, C(aromatic)-OH at 533.3 eV, and chemisorbed water molecules at 535.7 eV.
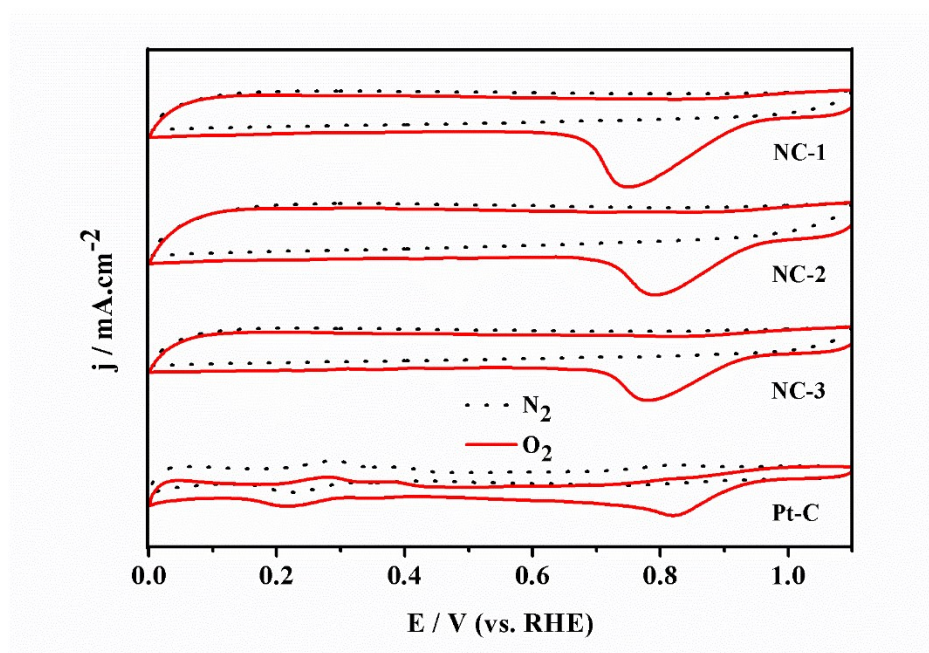

Fig. S11 CV curves of NC-1, NC-2, NC-3 and Pt/C in N_2-(dash line) and O_2-(solid line) saturated 0.1 M KOH solution with a scan rate of 10 mV s^{-1}.
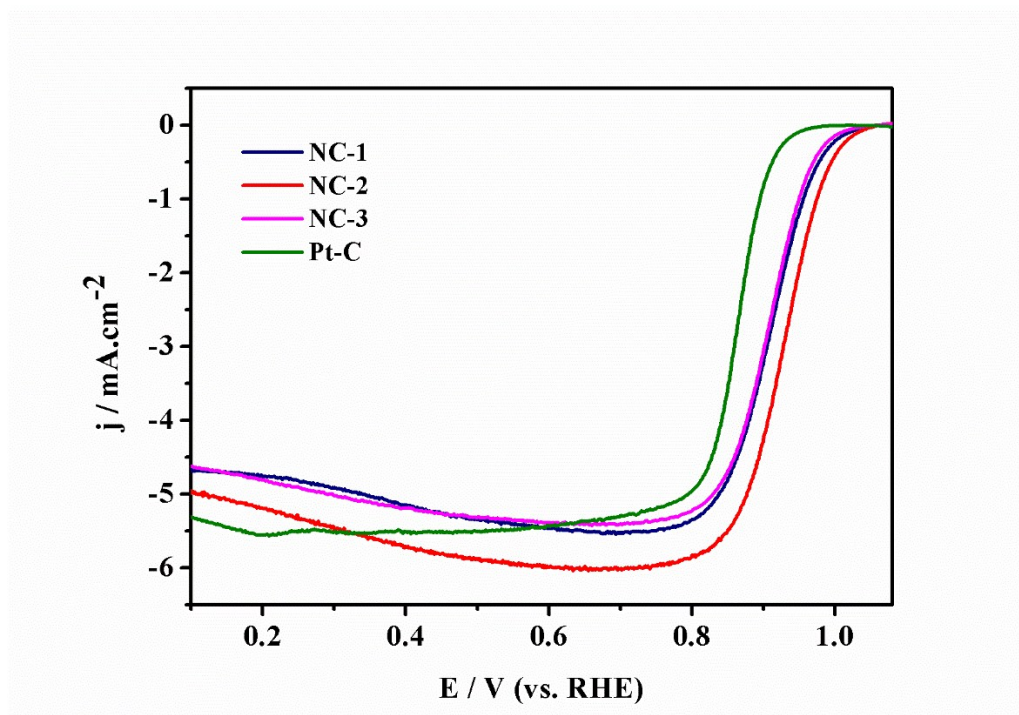
Fig. S12 LSV curves for NC-1, NC-2, NC-3 and Pt/C in O_2-saturated 0.1 M KOH electrolyte at a rotation speed of 1600 rpm with a scan rate of 10 mV s^{-1}.
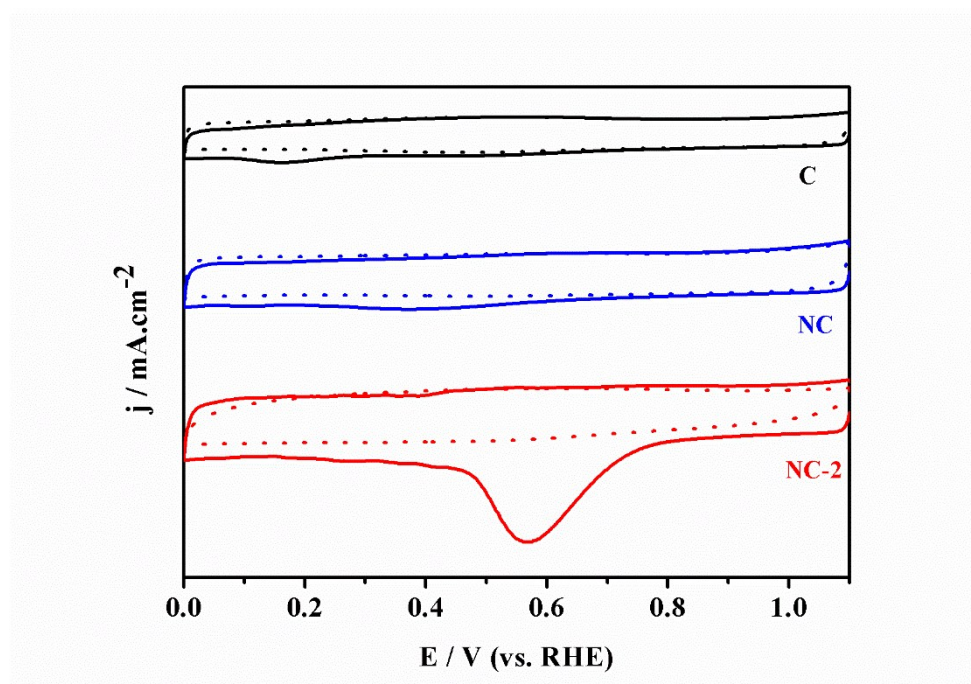

Fig. S13 CV curves of C, NC and NC-2 in N_2-(dash line) and O_2-(solid line) saturated 0.5 M H_2SO_4 solution with a scan rate of 10 mV s^{-1}.
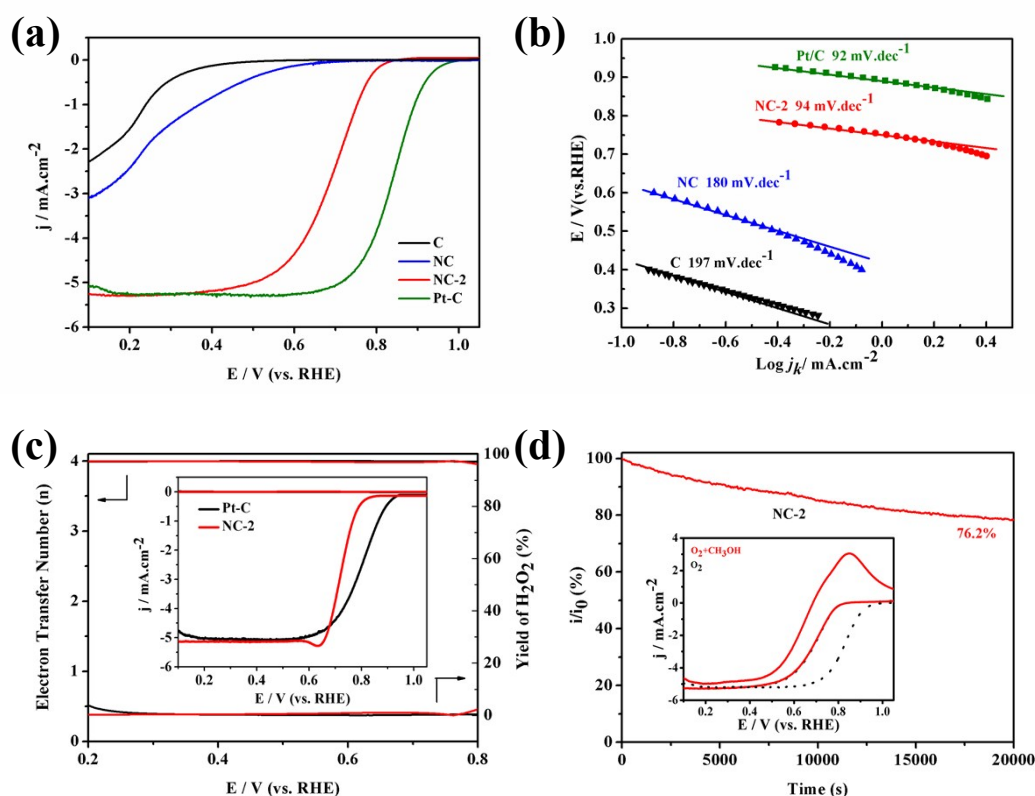
Fig. S14 (a) LSV curves of C, NC, NC-2 and Pt/C in O_2-saturated 0.5 M H_2SO_4 electrolyte at a rotation speed of 1600 rpm with a scan rate of 10 mV s^{-1}. (b) Tafel plots of C, NC, NC-2 and Pt/C in O_2-saturated 0.5 M H_2SO_4 electrolyte. (c) The corresponding electron transfer numbers and peroxide percentages of NC-2 (red line) and commercial Pt/C (black line) catalysts; inset: RRDE curves at 1600 rpm. (d) The chronoamperometric response at 0.8V (vs. RHE) at a rotation speed of 1600rpm; inset shows the LSV curves of NC-2 and Pt/C in O_2-saturated 0.5 M H_2SO_4 electrolyte with or without 0.5 M methanol at a scan rate of 10 mV s^{-1}.
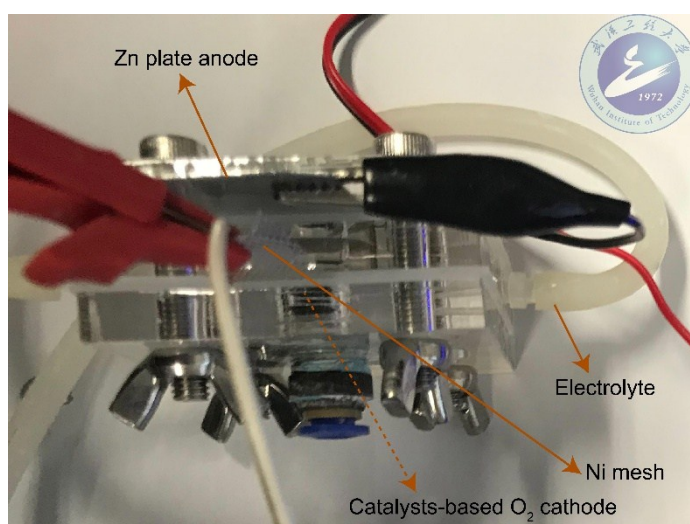

Fig. S15 Digital picture of the customized Zn-air battery based on NC-2.

References

1. J. Fu, Z. P. Cano, M. G. Park, A. Yu, M. Fowler and Z. Chen, *Adv. Mater.*, 2017, **29**, 1604685.

2. T. Xing, Y. Zheng, L. H. Li, B. C. Cowie, D. Gunzelmann, S. Z. Qiao, S. Huang and Y. Chen, *Acs Nano*, 2014, **8**, 6856-6862.