

Supporting Information

Bottom-up Pore-generation Strategy Modulated Active Nitrogen Species for Oxygen Reduction Reaction

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 - **Figure S16.** The LSV curves of holey-NC with different ratio for melamine and bisphenol AF under 1000 ° C of pyrolysis temperature.
- The specific meaning of each catalyst is shown in Table S3.
- **Figure S17.** The LSV curves of three repetitions. Repeatability test is a performance test based on the same conditions for different batches of holey-NC1000 catalysts.
 - **Figure S18.** The key components (anode, cathode, membrane, and catalytical layer, current collector) of Zinc-air battery assembly.
 - **Figure S19.** Photographs of the assembly processes for the

fabrication of a rechargeable zinc-air battery.

● **Table S1.** Specific surface areas and Pore Radius of NC1000, holey-NC800, holey-NC900, holey-NC1000, and holey-NC1100.

● **Table S2.** The $J_k@0.85$ V and $E_{1/2}$ of NC1000, holey-NC800, holey-NC900, holey-NC1000, and holey-NC1100.

● **Table S3.** The naming rules for catalysts.

● **Table S4.** Comparison of ORR performances of our holey-NC1000 catalyst with the recently reported highly active metal-free carbon.

Experimental Section

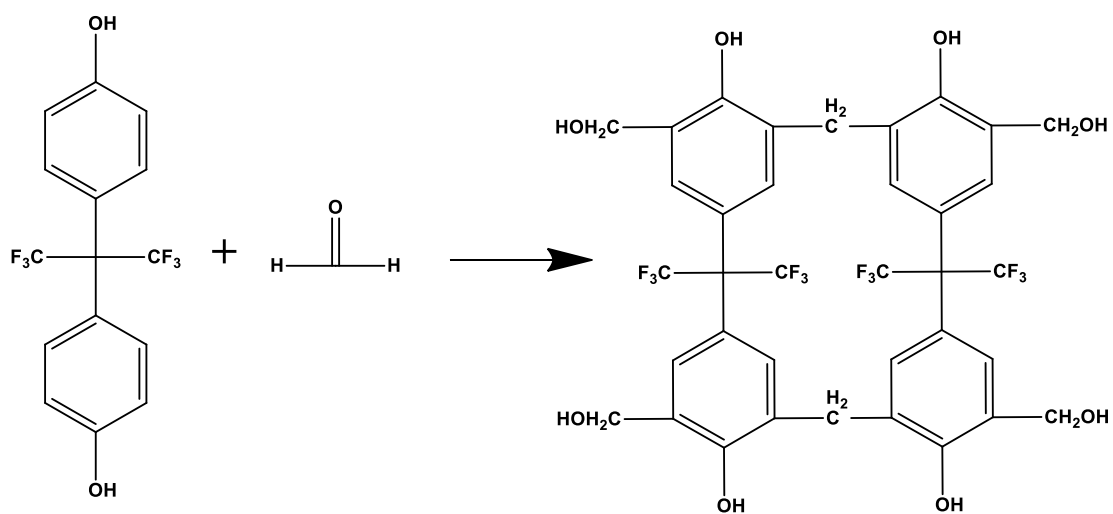
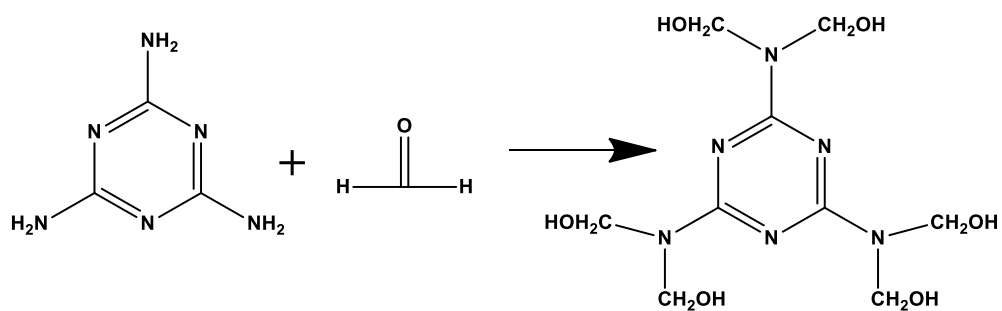
Materials

Bisphenol AF (2, 2-Bis (4-hydroxyphenyl) hexafluoropropane, 95%, Matrix Scientific), Melamine ($C_3H_6N_6$, 99%, Alfa Aesar (China) Chemicals), Formaldehyde (CH_2O , 37%, Alfa Aesar), Nafion perfluorinated resin solution (5 wt%) is purchased from Sigma-Aldrich, 20% Pt/C (20 wt% platinum supported on Vulcan XC-72 carbon) are purchased from TianJin AIDA. All the reagents are analytical grade and used without further purification.

Synthesis of holey-NC catalysts

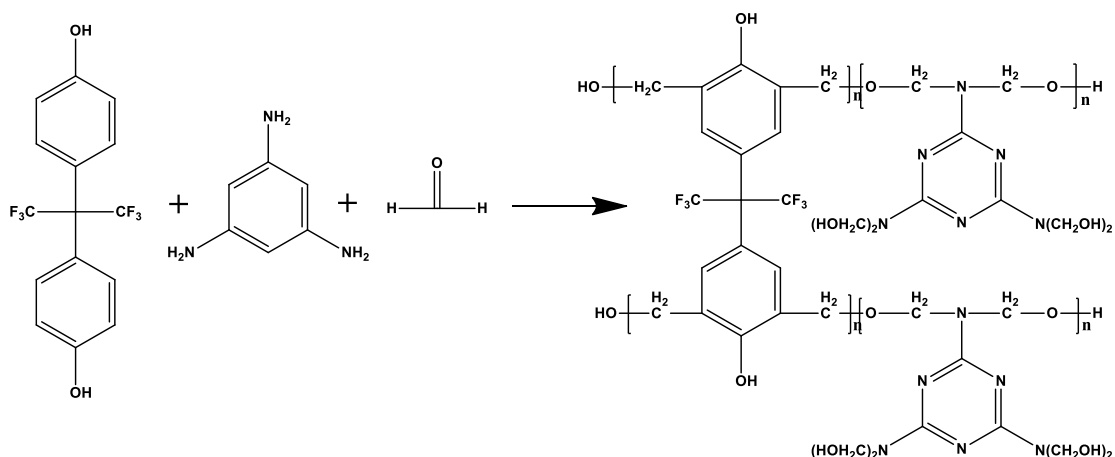
In a typical process, 0.6 g of melamine was dissolved into 15.0 ml formaldehyde solution with constantly stirring for ~ 1.5 h under 70 °C to get a clear solution, and 0.64 g of bisphenol AF (BPAF) was added into

15 ml ethanol under stirring to obtain a homogeneous solution. The above two solution were mixed under vigorous stirring for 15 min, then the mixture (molar ratio of melamine to BPAF was 2.5:1) was transferred into a Teflon-lined autoclave which was put into an oven of 180 °C for 7 h. The possible paths are as follows:



(1)

(2)



The final product was filtered, washed with ethanol and dried in vacuum drying oven at 60 °C. Then the obtained polymers grinded in mortar were pyrolyzed at different temperatures (800 °C, 900 °C, 1000 °C, 1100 °C) for 2 h under nitrogen atmosphere. The final samples with different pyrolysis temperatures were named holey-NC800, holey-NC900, holey-NC1000, holey-NC1100, respectively. And the NC1000 was also synthesized with melamine and formaldehyde under the same conditions. The naming rules are summarized in Table S3.

Characterization

The SEM measurements were conducted using a scanning electron microscope (SEM) (Hitachi-SU8010). The XRD patterns were performed on BRUKERD&ADVANCE with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an AXIS Supra. The binding energies obtained in the X-ray photoelectron spectral analysis were corrected for specimen charging by referencing the C1s to 284.8

eV(standard peak of contaminated carbon). Raman spectroscopic measurement was carried out by Renishaw inVia reflex instrument with an excitation wavelength of 633 nm. N₂ adsorption-desorption isotherms at 77 K were recorded using a Quantachrome NOVA 1000e Surface Area & Pore Size Analyzer. Before the measurements, the samples were outgassed under vacuum at 300 °C for 4 h. And the distribution of holes' diameter was calculated by Barrett-Joyner-Halenda (BJH) method. The C K-edge and N K-edge X-ray absorption near-edge structure (XANES) were performed by total electron yield (TEY) mode at the beamline 4W7B station of the Beijing Synchrotron Radiation Facility (BSRF). XANES spectra were recorded in total electron yield mode with an experimental resolution of 0.2 eV and at room temperature. The obtained data were normalized to the incident photon flux (I₀), which was measured with a refreshed gold mesh at a spherical grating monochromator (SGM) before the measurement, and were then normalized to the absorption edge jump.

Electrochemical measurements

Electrochemical measurements were performed using a SP-200 electrochemical workstation (Bio-Logic SA, Claix, France) with a standard three-electrode system, which was used to record the catalytic activity of samples in an O₂-saturated 0.1 M KOH solution at room temperature. The as-prepared samples, a platinum mesh and

Ag/AgCl/KCl (sta'd) acted as the working, auxiliary and reference electrodes, respectively. The working electrode was a glassy carbon RDE with a diameter of 4 mm. Before being used, the glassy carbon was consecutively polished with 1.0, 0.3 and 0.05 μm alumina slurries. For comparison, commercial catalyst powders (20% Pt/C) were loaded on pretreated glassy carbon RDE with a loading mass of $2.0 \text{ mg}\cdot\text{cm}^{-2}$ via drop-casting of a catalyst ink. The catalyst ink was a 500 μL of ethanol solution that consisted of 5 mg of catalyst powder and 10 μL of Nafion solution (2 wt%) under sonication for 30 min. Then, 10 μL of the catalyst ink was carefully coated onto the polished glassy carbon rotating disk electrode (4 mm). Before testing, the electrolyte was saturated with N_2 . For cyclic voltammetry, data were first collected under N_2 , then the gas was replaced by an O_2 flow until saturation. All measurements were conducted at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$.

The Koutecky-Levich (K-L) plots calculated from ORR polarization data with the number of electrons transferred per O_2 molecule (n). The n value was calculated from the K-L equation:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} = -\frac{1}{nFkc_{\text{O}_2}^b} - \frac{1}{0.2nFAD_{\text{O}_2}^{2/3}\nu^{-1/6}\omega^{1/2}c_{\text{O}_2}^b}$$

Where I , I_k and I_d are the experimentally measured current, the kinetic and diffusion-limited currents, respectively, F is the Faraday constant, k is the electrochemical rate constant for O_2 reduction, A is the geometric

electrode area, c is the concentration of O_2 , D is the diffusion coefficient of O_2 , ω and ν are the electrode rotation rate and the kinematic viscosity. Tafel plots were obtained from the extrapolation of the linear region of a plot of the overpotential versus current density. Chronoamperometric measurements were recorded at cathode oxygen reduction potential for 10k s.

Rechargeable Zinc-air battery

A home-made liquid rechargeable Zn-air battery was prepared by pairing a polished zinc plate (~ 0.5 mm of thickness) and carbon fiber paper casted the obtained catalysts ink as anode and air electrode. The catalyst-coated carbon paper (electrode area = 1.0 cm^2) with the catalysts loading of 1 mg cm^{-2} was dried at $60 \text{ }^\circ\text{C}$ for at least 5 h. And 6 M KOH with 0.2 M zinc acetate was used as electrolyte of the rechargeable Zn-air battery. All the battery performances were tested in ambient atmosphere at room temperature. The V-i discharge polarization curves were plotted at scanning rate of $5 \text{ mV}\cdot\text{s}^{-1}$. The charge/discharge curves were tested at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ (10 min discharge and 10 min charge, along with 1 min pause each time).

Supplementary Figures



Figure S1. Molecular structure of three precursors used to synthesize N-doped carbon material catalysts.

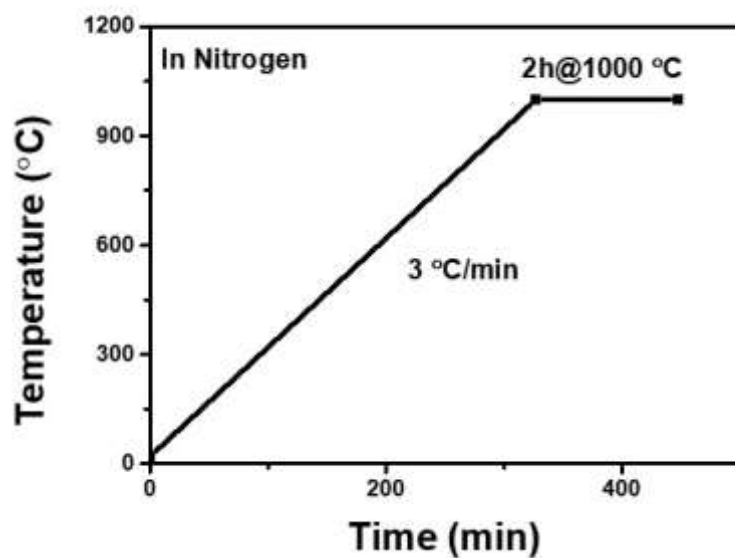


Figure S2. Temperature and time profile of pyrolysis and carbonization process.

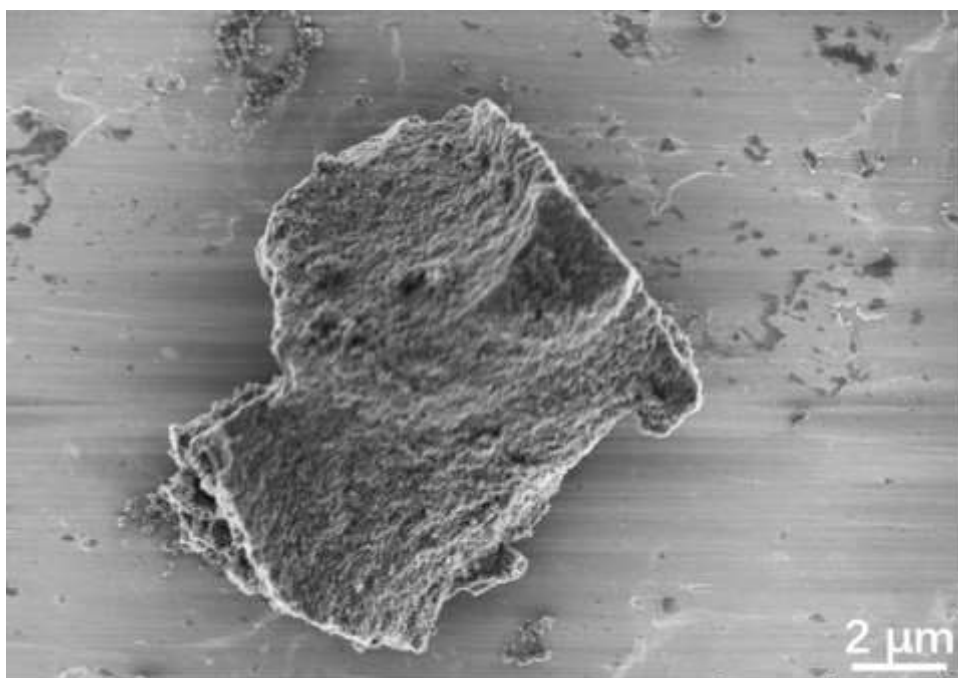


Figure S3. The SEM image of NC1000.

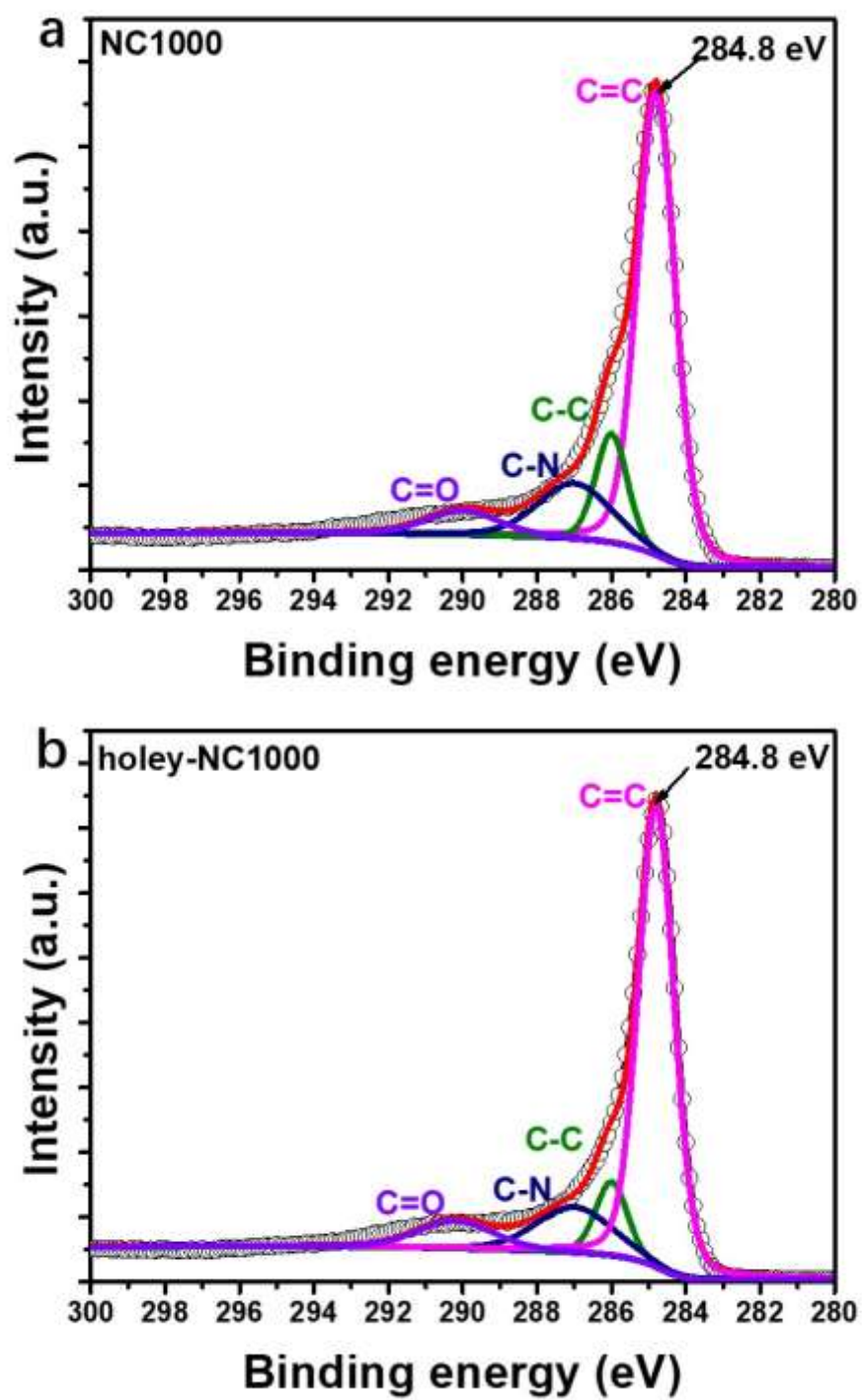


Figure S4. C_{1s} XPS of (a) NC1000 and (b) holey-NC1000.

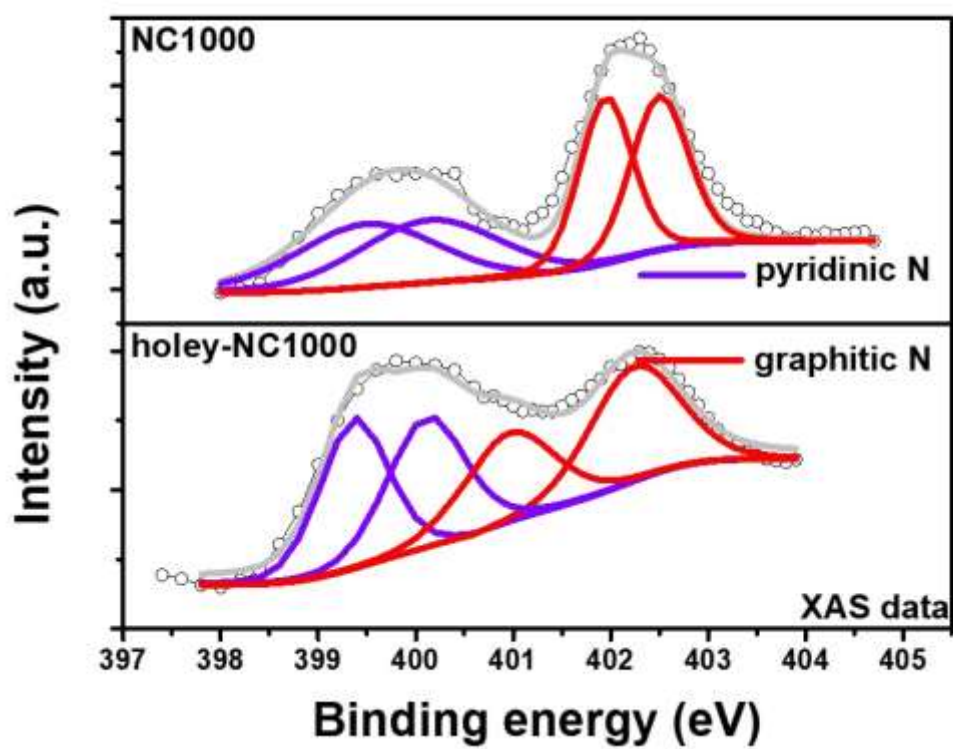


Figure S5. The high-resolution N K-edge XAS of NC1000 and holey-NC1000.

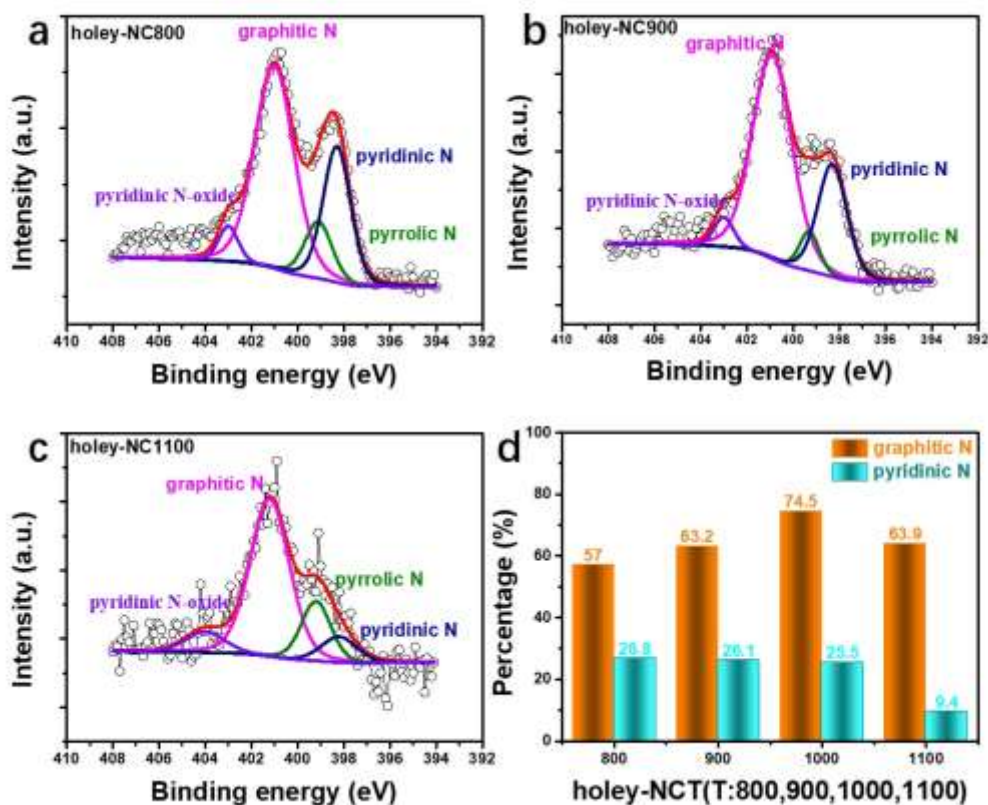


Figure S6. N 1s XPS of (a) holey-NC800, (b) holey-NC900 and (c) holey-NC1100; (d) the comparison of pyridinic N and graphitic N of holey-NCT (T: 800, 900, 1000, 1100).

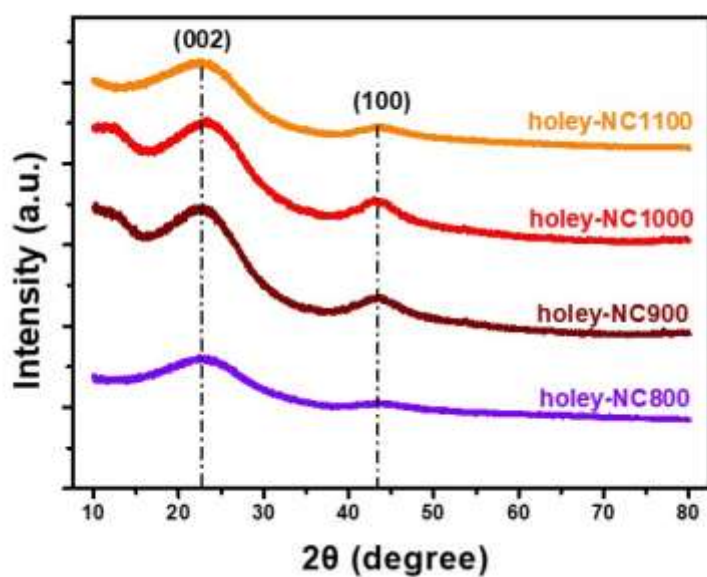


Figure S7. The XRD spectra of holey-NCT (T: 800, 900, 1000, 1100).

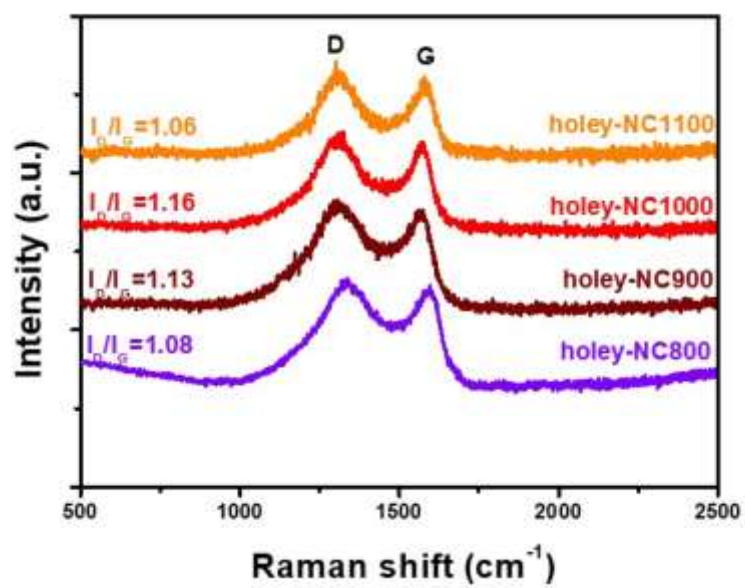


Figure S8. The Raman spectra of holey-NCT (T: 800, 900, 1000, 1100).

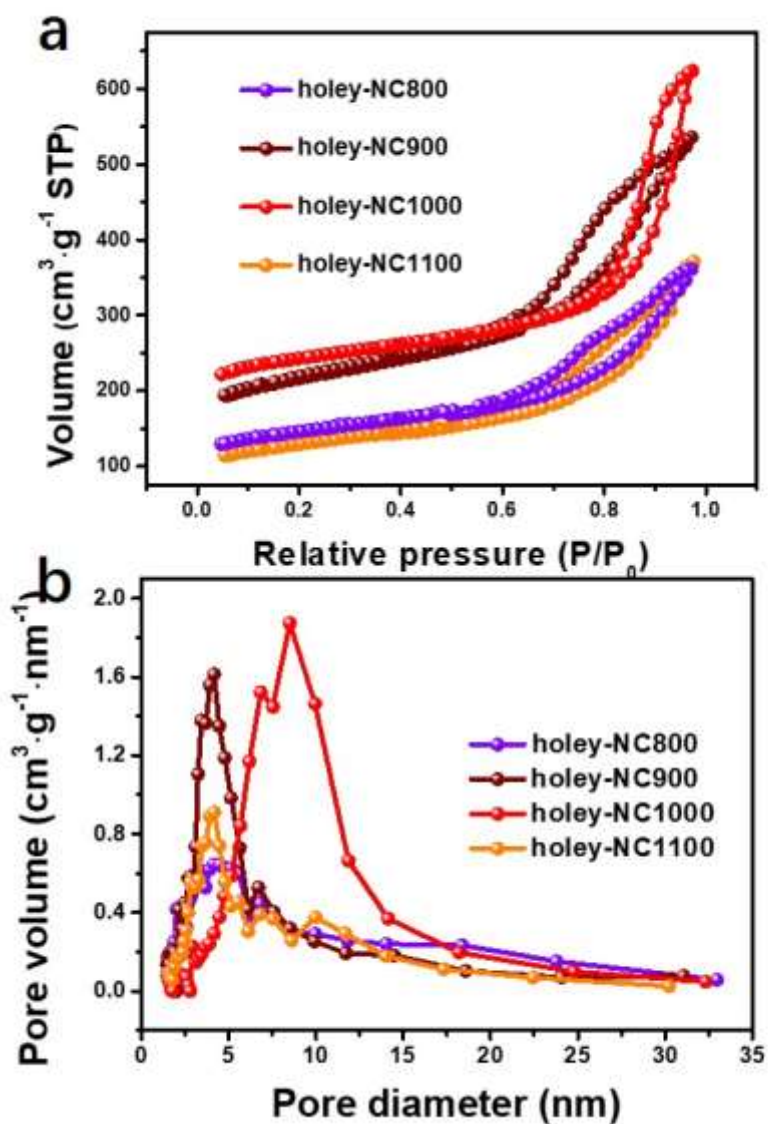


Figure S9. (a) N_2 adsorption-desorption isotherm and (b) the pore size distribution curves of holey-NCT (T: 800, 900, 1000, 1100).

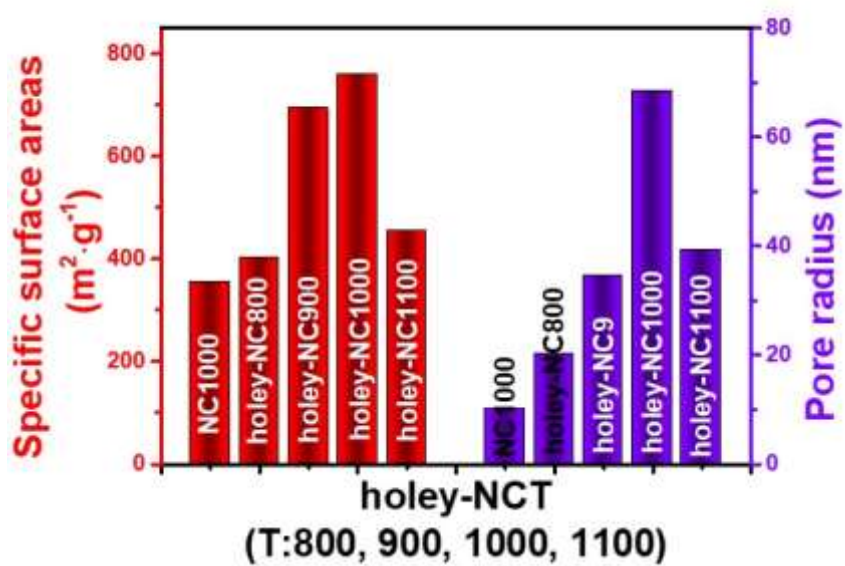


Figure S10. Specific surface areas and Pore radius of NC1000, holey-NC800, holey-NC900, holey-NC1000, and holey-NC1100.

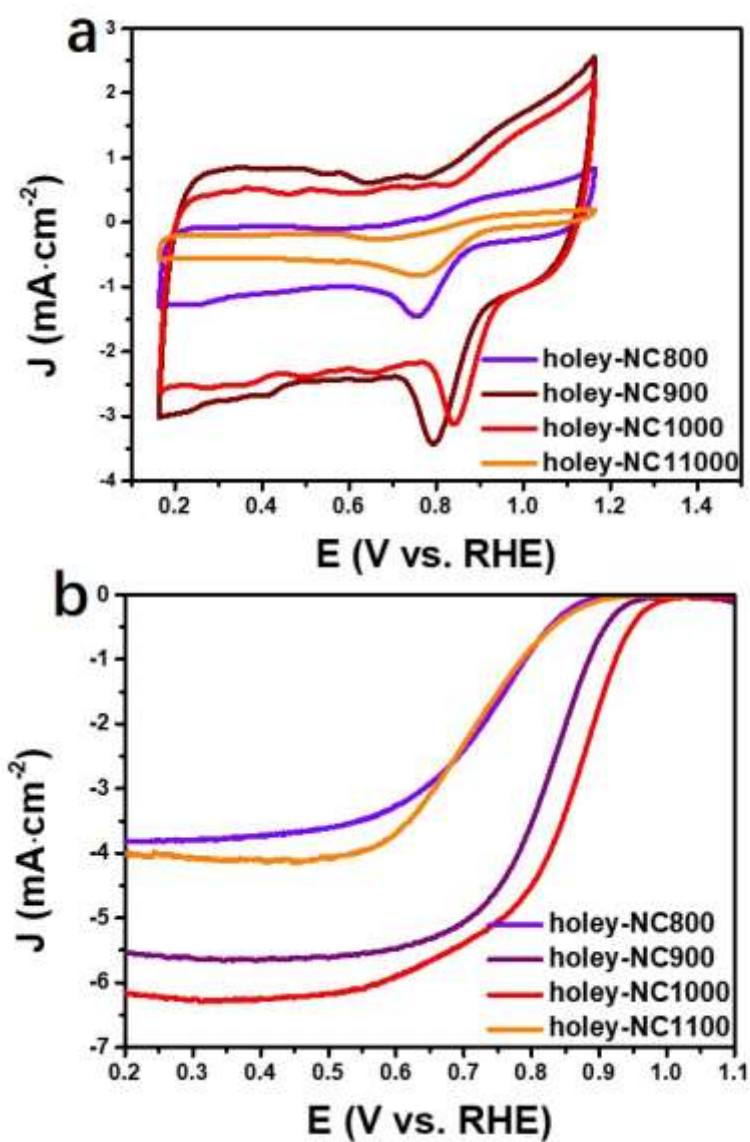


Figure S11. (a) CV curves and LSV curves at 1600 rpm of holey-NC800, holey-NC900, holey-NC1000, and holey-NC1100.

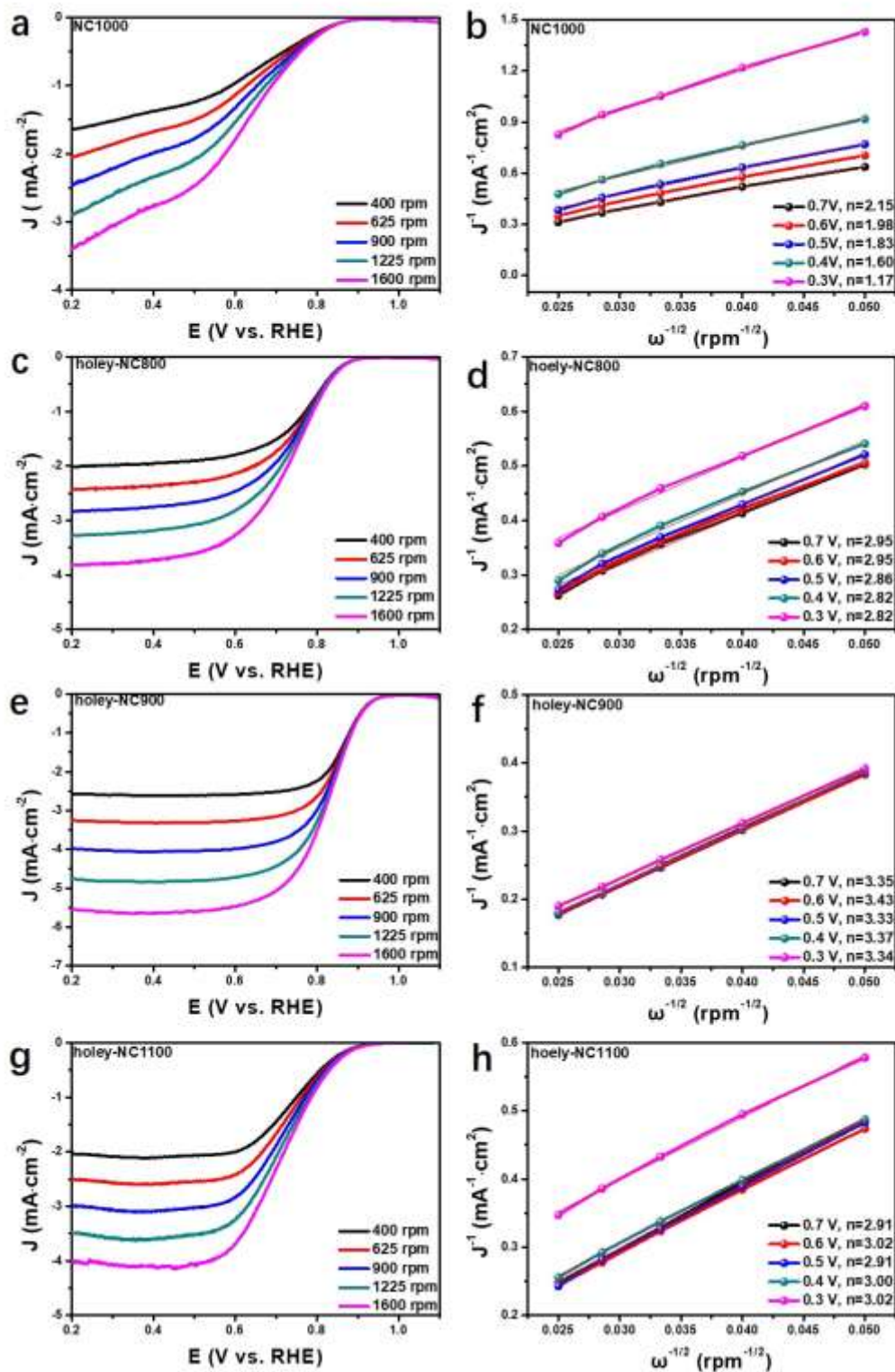


Figure S12. The LSV curves of NC1000, hoely-NC800, hoely-NC900, and hoely-NC1100 at different rotate speed range from 400 rpm to 1600

rpm, and the corresponding K-L curves.

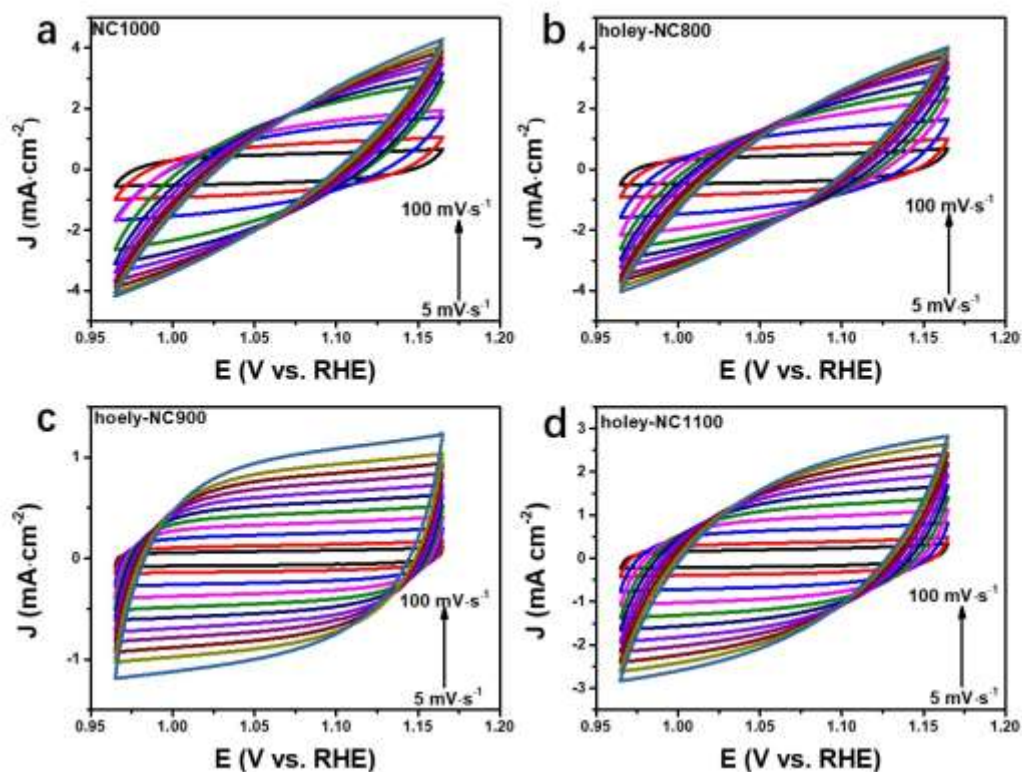


Figure S13. CV curves taken at 0.96-1.16 V without faradaic processes of NC1000, holey-NC800, holey-NC900, and holey-NC1100.

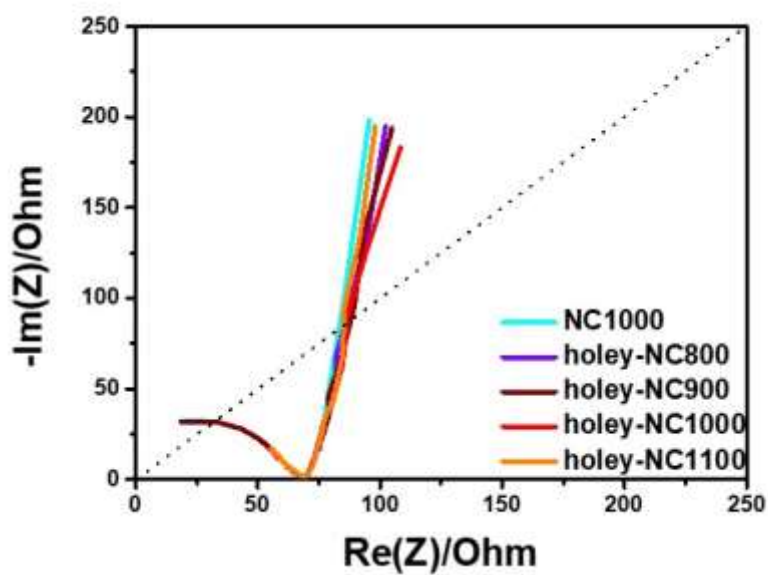


Figure S14. Nyquist plots of the above catalysts at 0.85 V.

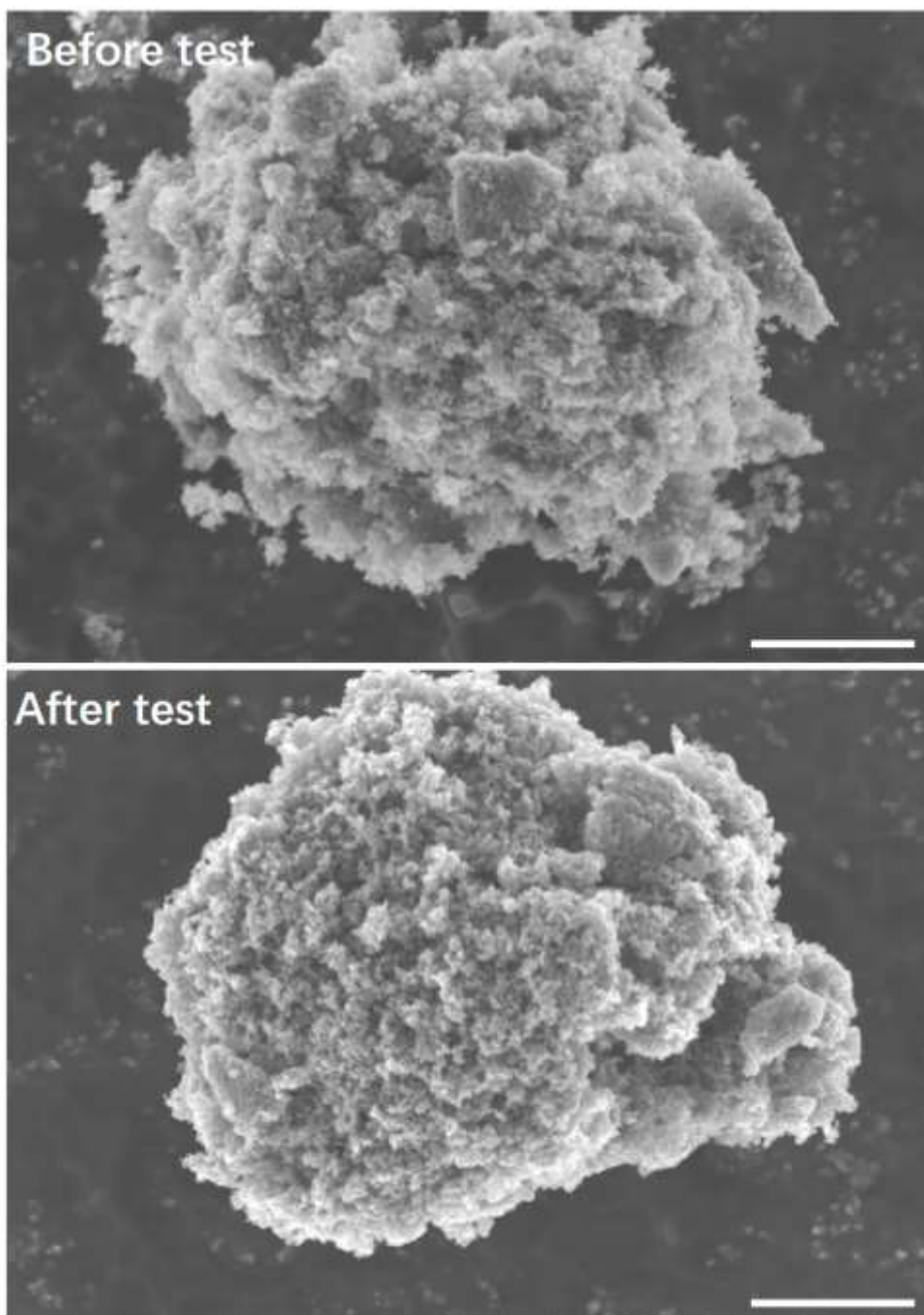


Figure S15. The structural stability of the holey-NC1000.

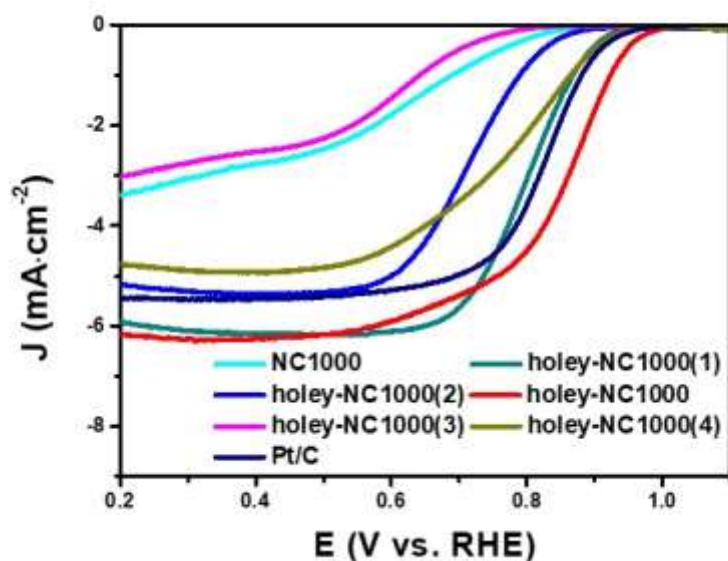


Figure S16. The LSV curves of holey-NC with different ratio for melamine and bisphenol AF under 1000 ° C of pyrolysis temperature. The specific meaning of each catalyst is shown in Table S3.

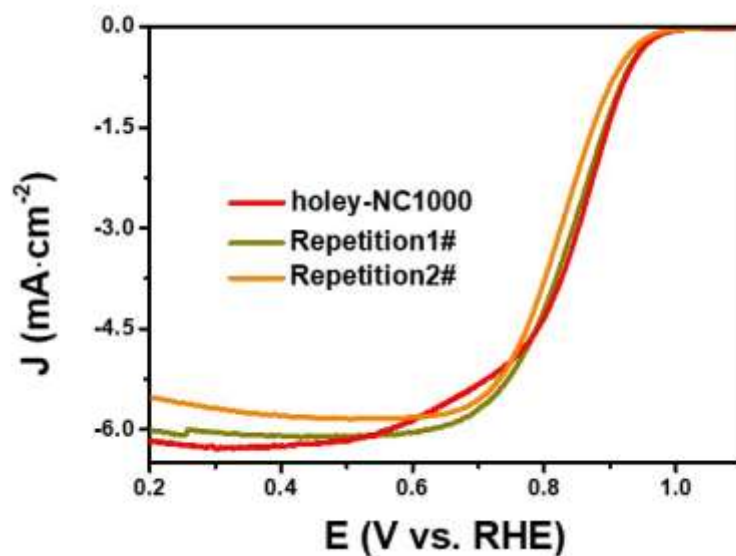


Figure S17. The LSV curves of three repetitions. Repeatability test is a performance test based on the same conditions for different batches of holey-NC1000 catalysts.

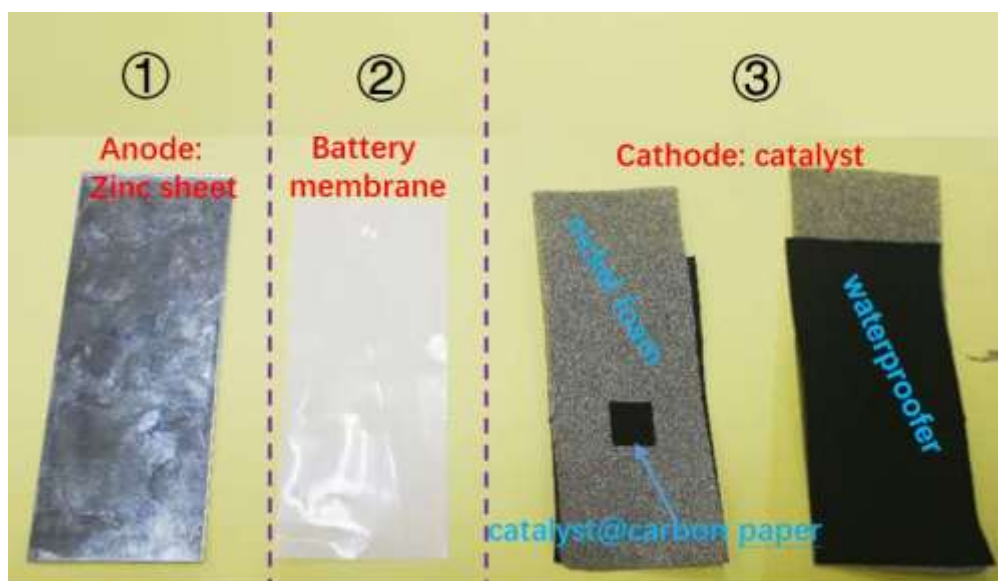


Figure S18. The key components (anode, cathode, membrane, and catalyst layer, current collector) of Zinc-air battery assembly.

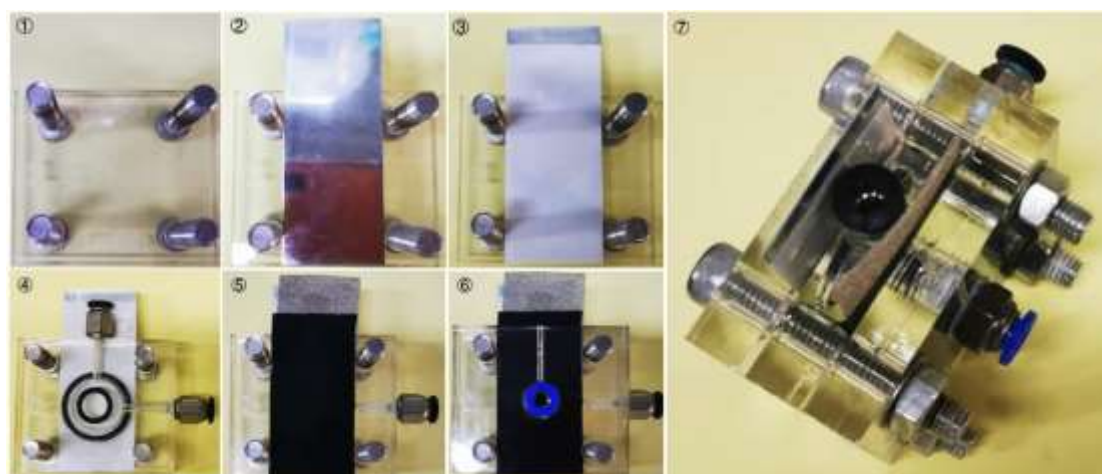


Figure S19. Photographs of the assembly processes for the fabrication of a rechargeable zinc-air battery.

Table S1. Specific surface areas and Pore Radius of NC1000, holey-NC800, holey-NC900, holey-NC1000, and holey-NC1100.

Samples	Specific surface areas /m ² g ⁻¹	Pore Radius/ nm
NC1000	353.01	10.03
holey-NC800	400.62	20.02
holey-NC900	693.14	34.32

holey-NC1000	759.43	68.42
holey-NC1100	453.34	39.17

Table S2. The $J_k@0.85$ V and $E_{1/2}$ of NC1000, holey-NC800, holey-NC900, holey-NC1000, and holey-NC1100.

Samples	$J_k@0.85$ V/ mA cm ⁻²	$E_{1/2}$ / V
NC1000	0	0.64
holey-NC800	-0.3	0.73
holey-NC900	-1.9	0.82
holey-NC1000	-3.4	0.86
holey-NC1100	-0.3	0.72

Table S3. The naming rules for catalysts.

Name	Melamine (mol)	Bisphenol AF (mol)	Molar ratio	Pyrolysis temperature(°C)
NC	0.6	0	-	1000
holey-NC800	0.6	0.64	2.5:1	800
holey-NC900	0.6	0.64	2.5:1	900
holey-NC1000	0.6	0.64	2.5:1	1000
holey-NC1100	0.6	0.64	2.5:1	1100
holey-NC1000(1)	0.23	0.64	1:1	1000
holey-NC1000(2)	0.48	0.64	2:1	1000
holey-NC1000(3)	0.72	0.64	3:1	1000
holey-NC1000(4)	0.96	0.64	4:1	1000

Table S4. Comparison of ORR performances of our holey-NC1000 catalyst with the recently reported highly active metal-free carbon.

Catalyst	Onset potential (V vs. RHE)	Tafel slope (mV dec ⁻¹)	$E_{1/2}$ (V vs. RHE)	Reference
holey-NC1000	1.02	79	0.86	This work
N-GRW	0.92	50	0.84	Science Advances 2, e1501122 (2016)
N-graphene/CNT	0.88	-	0.7	Small 10, 2251-2259 (2014)
P-C ₃ N ₄	0.90	52	0.81	Angew. Chem. Int.

P-T/rGO	0.94	70.4	0.79	Ed. 54,4646-4650 (2015) Angew.Chem. Int.Ed. 58,11369 -11373 (2019)
B, N-carbon	0.98	-	0.84	Advanced Science 5, 1800036 (2018)
HNCSs	0.92	65.7	0.82	Carbon 146, 248-256 (2019)
NGM	0.89	-	0.77	Advanced Materials 28, 6845-6851 (2016)
