Electronic Supplementary Information

N-doped Holey Carbon Materials Derived from Metal-free Macrocycle Cucurbit[6]uril Assembly as Efficient Electrocatalyst for Oxygen Reduction Reaction

Dongshuang Wu,[a,†] Minna Cao,*[a,b] Hanhui You,[a] Chuan Zhao,[b] and Rong Cao *[a]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy Sciences, Fuzhou, 350002, China. E-mail: mncao@fjirsm.ac.cn, rcao@fjirsm.ac.cn.
[b] The University of New South Wales Sydney, New South Wales, 2052, Australia
† Present address: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

Experimental:

Methods:

Chemicals. CB[6] is synthesized according to the literature.[1] All other chemicals are commercially available used without further purification. 5 wt % Nafion aqueous solution was purchased from Sigma-Aldrich; 20 wt % Pt/C is obtained from Alfa Aesar. Other chemicals were commercially available from Shanghai Chemical Reagent Co. Ltd.

Characterization. The morphology of the samples was investigated by using scanning electron microscopy (SEM) (JSM6700-F, 5 kV, Country) and transmission electron microscopy (TEM) (FEI Tecnai F20, 200 kV, USA). X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fischer, Al Kα source) was used to determine the surface chemical components. Specific correction was carried out by employing a C 1s binding energy (BE) of 284.8 eV. X-ray diffraction (XRD) characterization (MiniFlex600, Rigaku, $\lambda = 1.54$ Å, Japan) was employed to confirm the graphitic carbon structure. The Raman spectroscopy (invia-Reflex Micro-Raman Spectroscopy system, Renishaw Co. with 532 nm line of an Ar ion laser at room temperature, country) was conducted to investigated the structure of the NHCs. The specific surface areas were measured through nitrogen-sorption isotherms at 77 K (Micrometitics, ASAS 2020, country) and calculated by Brunauer-Emmett-Teller (BET) equation. The pore size distributions (PSD) were calculated based on Density Function Theory (DFT) model. Infrared spectroscopy (IR) was performed by Lambda900.

Preparation of the N-dope holey Carbon (NHCs) catalysts. A typical preparation of the NHCs is annealing the pre-synthesized CB[6] under different temperature (600, 700, 800, and

900 °C) at a ramp rate of 5 °C/min under N_2 atmosphere for 3 h. The final products without further treatment were used for characterizations and ORR performance tests (denoted as NHCs-temp., ie NHCs-600, NHCs-700, NHCs-800 and NHCs-900).

Electrocatalytic Performance Test. The ORR catalytic performance was tested by using a standard three-electrode system on an electrochemical workstation (Zahner IM6ex, Germany) without returning to open circuit for each test in 0.1 M KOH solution. A glassy carbon rotating disk electrode (RDE) (PINE, 5 nm diameter, 0.196 cm^2, USA) covered by catalyst ink was employed as work electrode. Ag/AgCl (saturated KCl aqueous solution,) and a graphite rod (Φ = 0.6 cm) were employed as reference electrode and counter electrode, respectively. All electrode potentials were recorded with respect to the reversible hydrogen electrode (RHE). A typical ink preparation procedure was prepared by dispersing a certain amount of the NHCs in 1 mL solvent containing 0.96 mL isopropyl alcohol and 0.04 mL 5 wt% Nafion aqueous solution. The catalyst loading on the work electrode was controlled to be 0.2 mg/cm^2. The ORR activity and selectivity were investigated by linear sweep voltammetry (LSV) *via* RDE and rotating ring-disk electrode (RRDE) measurements in O_2-saturated electrolyte at a scan rate of 10 mV/s. LSV in N_2-saturated electrolyte was recorded as reference. LSV of each catalyst were collected at 400, 800, 1000, 1200, and 1600 rpm in the range of 0-1.2 V in O_2-saturated electrolyte. Cyclic voltammograms (CVs) were first performed at 50 mV/s in the range of 0-1.2 V without rotating until reproducible CVs were noted in the oxygen saturated electrolyte. Slow LSVs at 10 mV/s were then collected on the disk again from 1.2 to 0 V to 1.2 V. CVs were also collected in a nitrogen saturated electrolyte serving as a blank.

The kinetic parameters of ORR can be analyzed by the Koutecky – Levich (K – L) equation:

$$\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\omega^{1/2}}+\frac{1}{J_K}$$

$$B=0.62nFC_0(D_0)^{2/3}\nu^{-1/6}$$

Where J is the measured current density, J_K is the kinetic current density, J_L is the diffusion-limited current density, ω is the electrode rotation rate, n is the number of transferred electron per oxygen molecule, F is the Faraday constant (96 485 C/mol), C_0 is the bulk concentration of O_2 (1.2×10^{-3} mol/L for 0.1 M KOH), D_0 is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2/s for 0.1 M KOH), and ν is the kinetic viscosity of the electrolyte (0.01 cm^2/s for 0.1 M KOH).

In the RRDE measurement, the electron transfer number (n) and peroxide yields (HO_2^-%) were calculated according to equation as following:

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

$$HO_2^-\% = 100\frac{(4-n)}{2} = 200\frac{I_R/N}{I_D + I_R/N}$$

Where I_D and I_R are the disk current and ring current, respectively. N is the current collective efficiency of the RRDE, which only is relate to the ring and disk area.

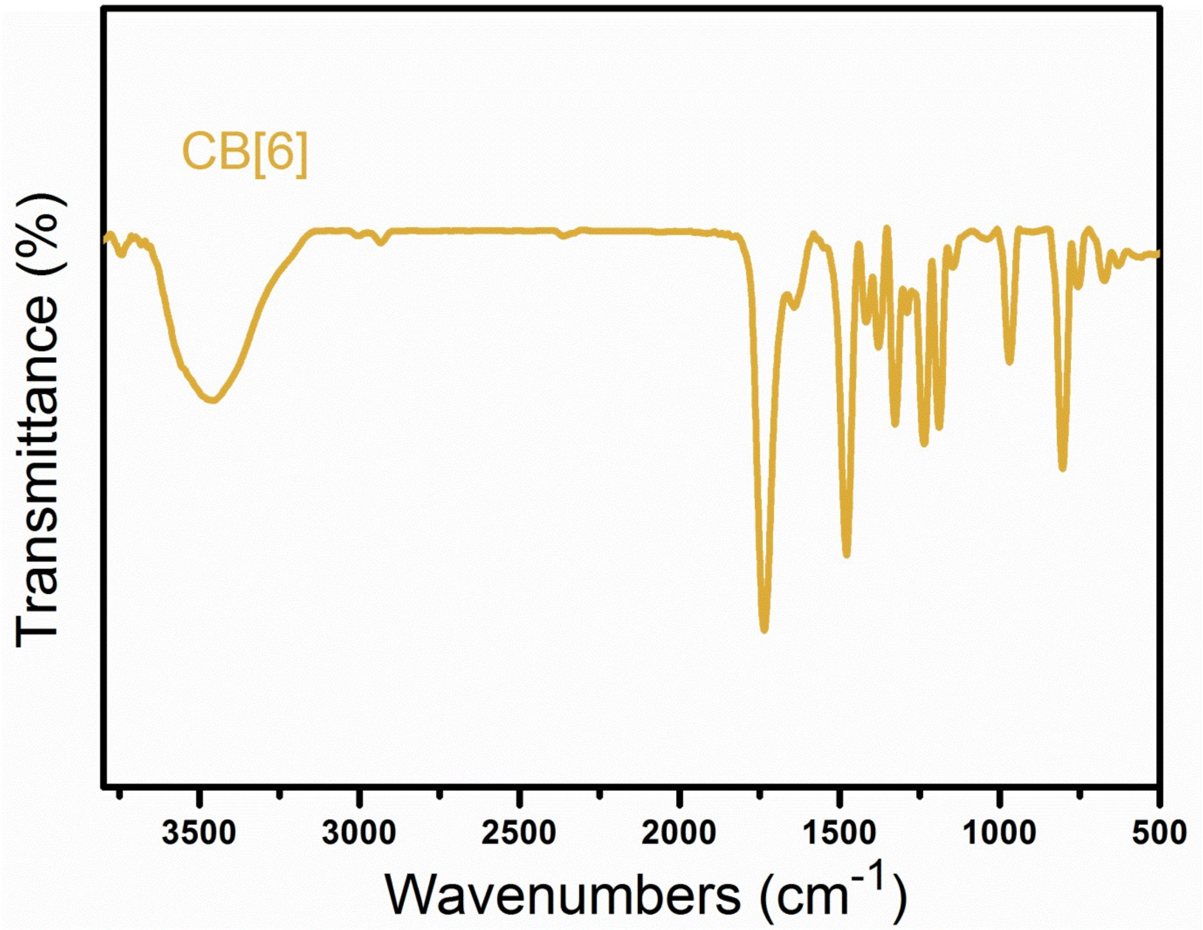

Fig.S1. Fourier-transform infrared spectroscopy (FTIR) spectrum of CB[6] assembly showing the carbonyl at 1735 cm^{-1}.

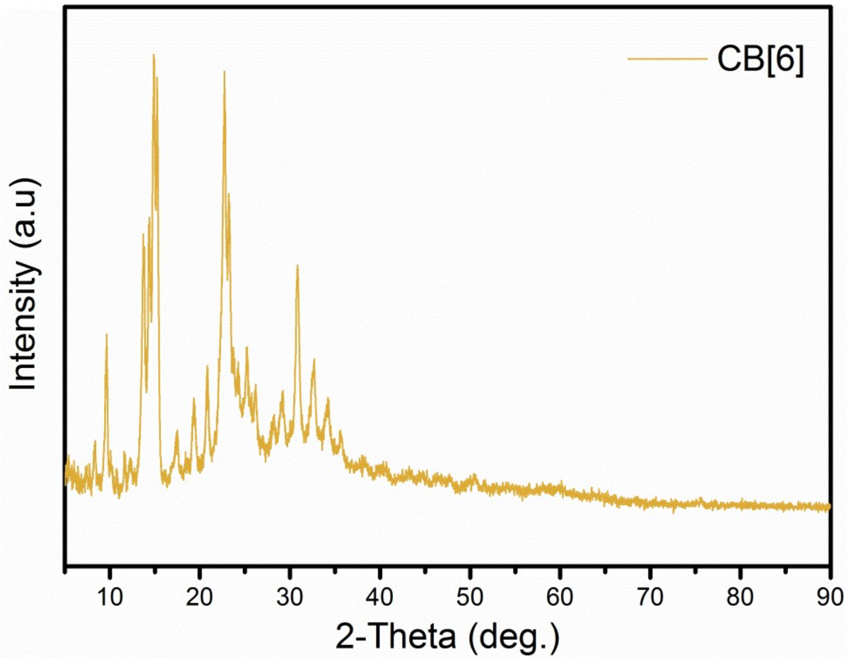

Fig.S2. Powder x-ray diffraction (XRD) pattern of CB[6] assembly.

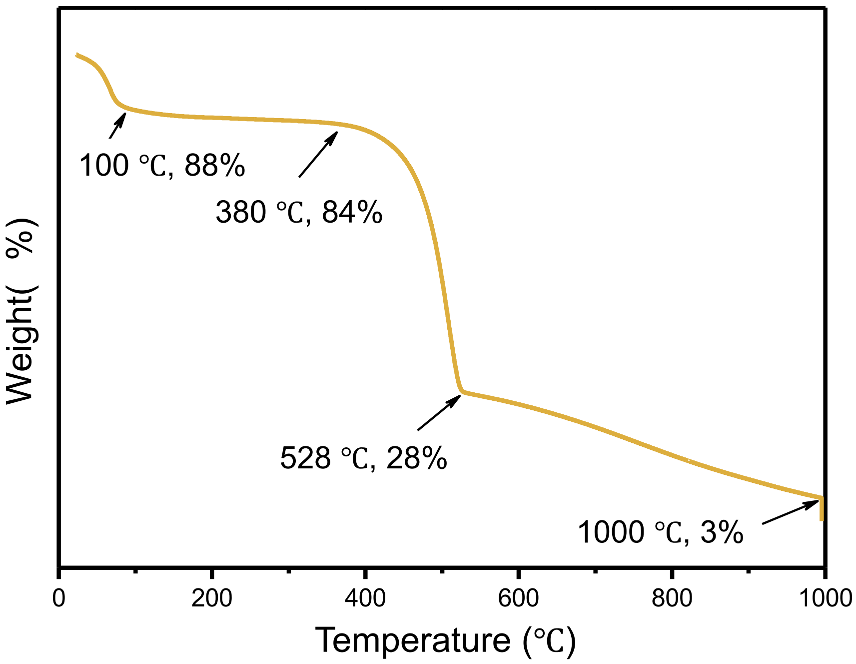

Fig. S3. Thermogravimetric analysis (TGA) of CB[6] assembly. The temperature and remaining weight percentage of the turning points are given along the black arrows.

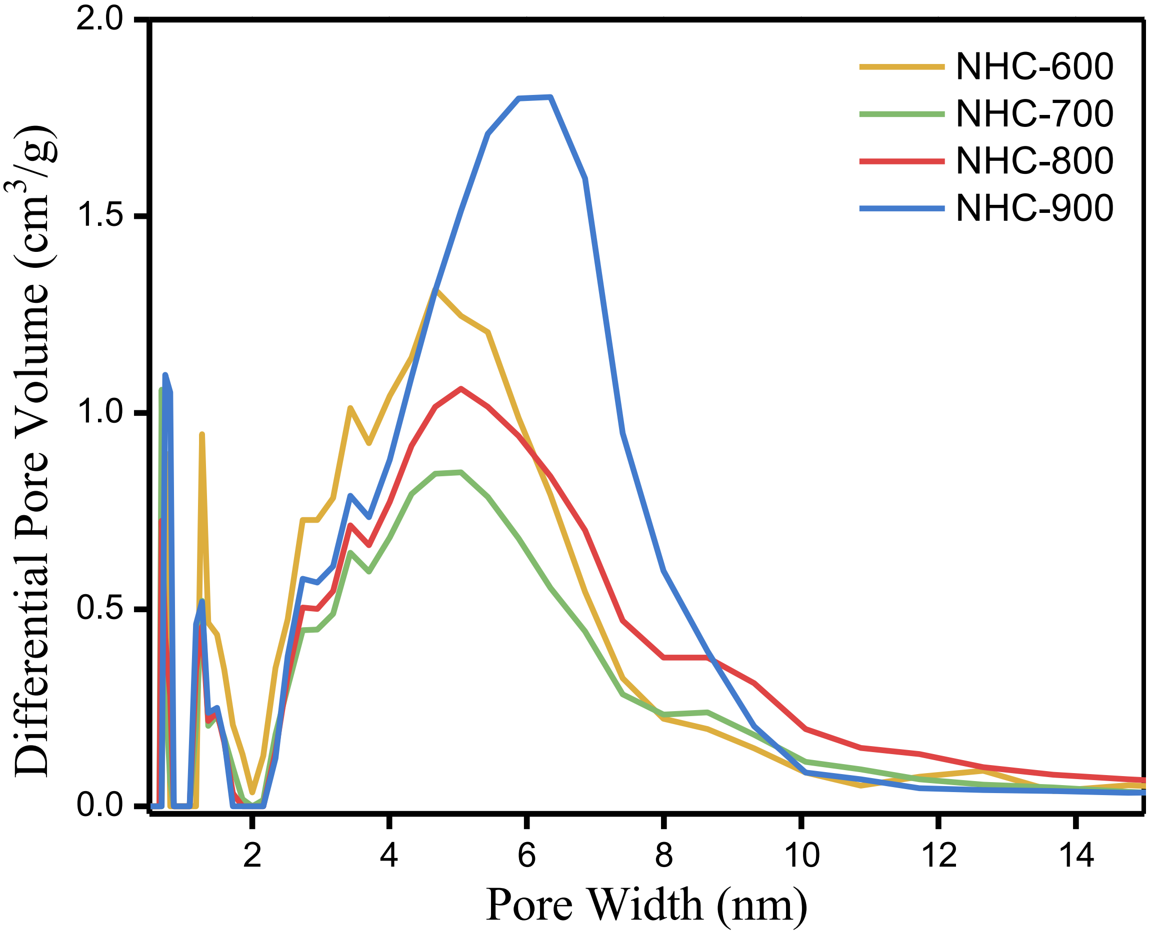

Fig. S4. Pore size distribution of NHCs.

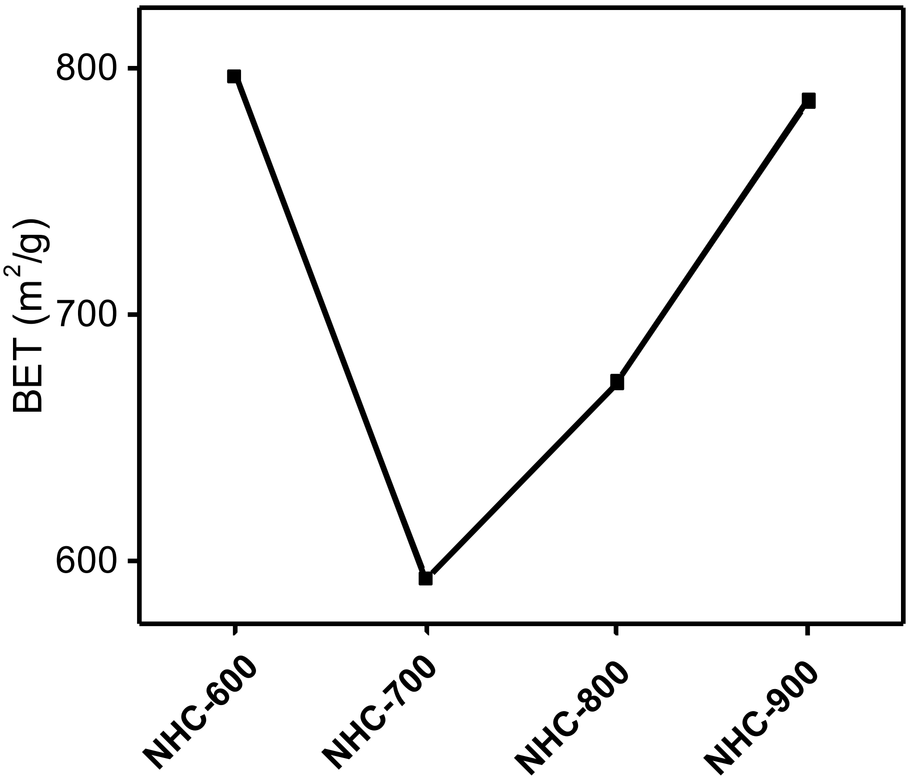

Fig. S5. Calculated BET surface area of NHC.

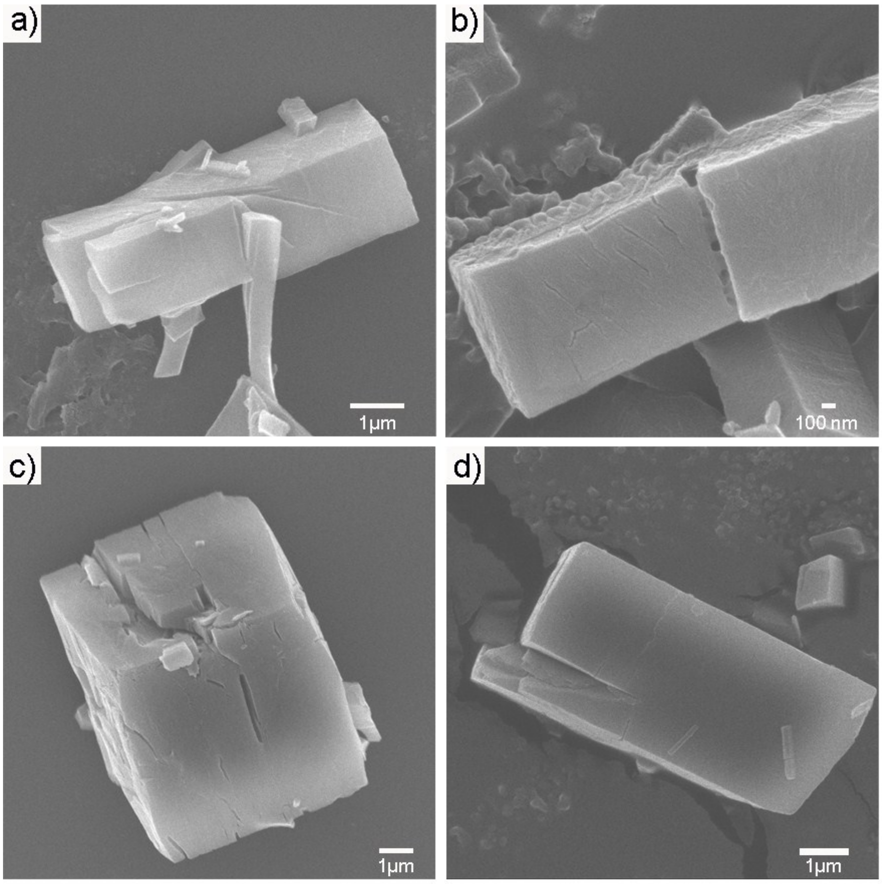

Fig. S6. SEM images of the a) NHC-600, b) NHC-700, c) NHC-800, and d) NHC-900.

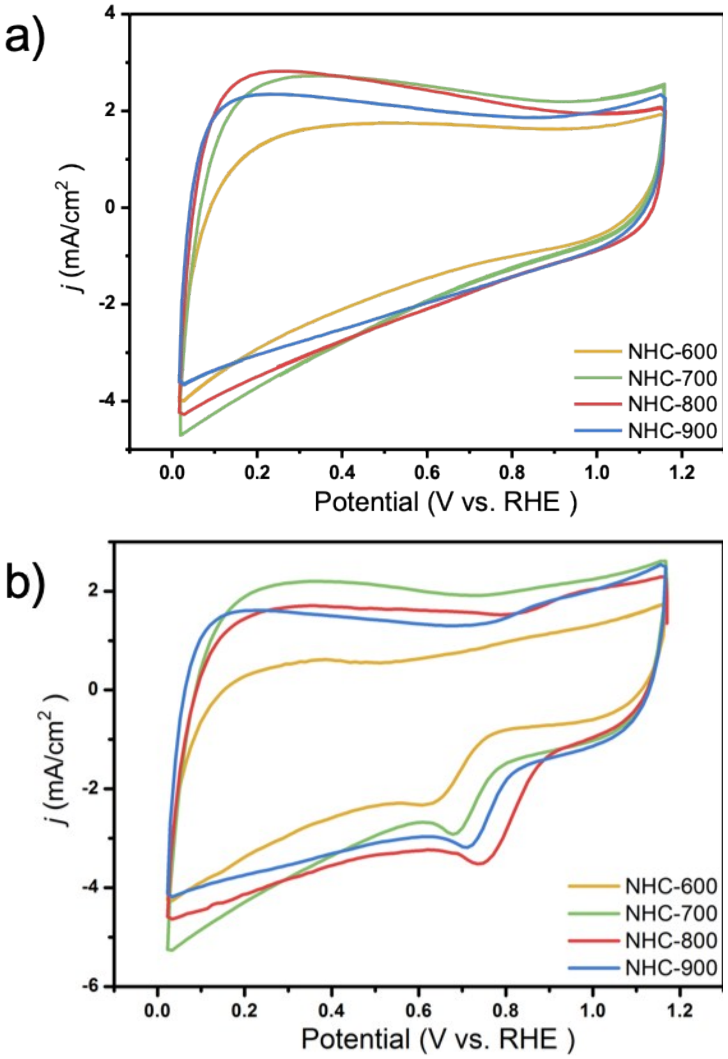

Fig. S7. CV scans of NHCs in (a) N_2-saturated and (b) O_2-saturated 0.1 M KOH electrolyte.

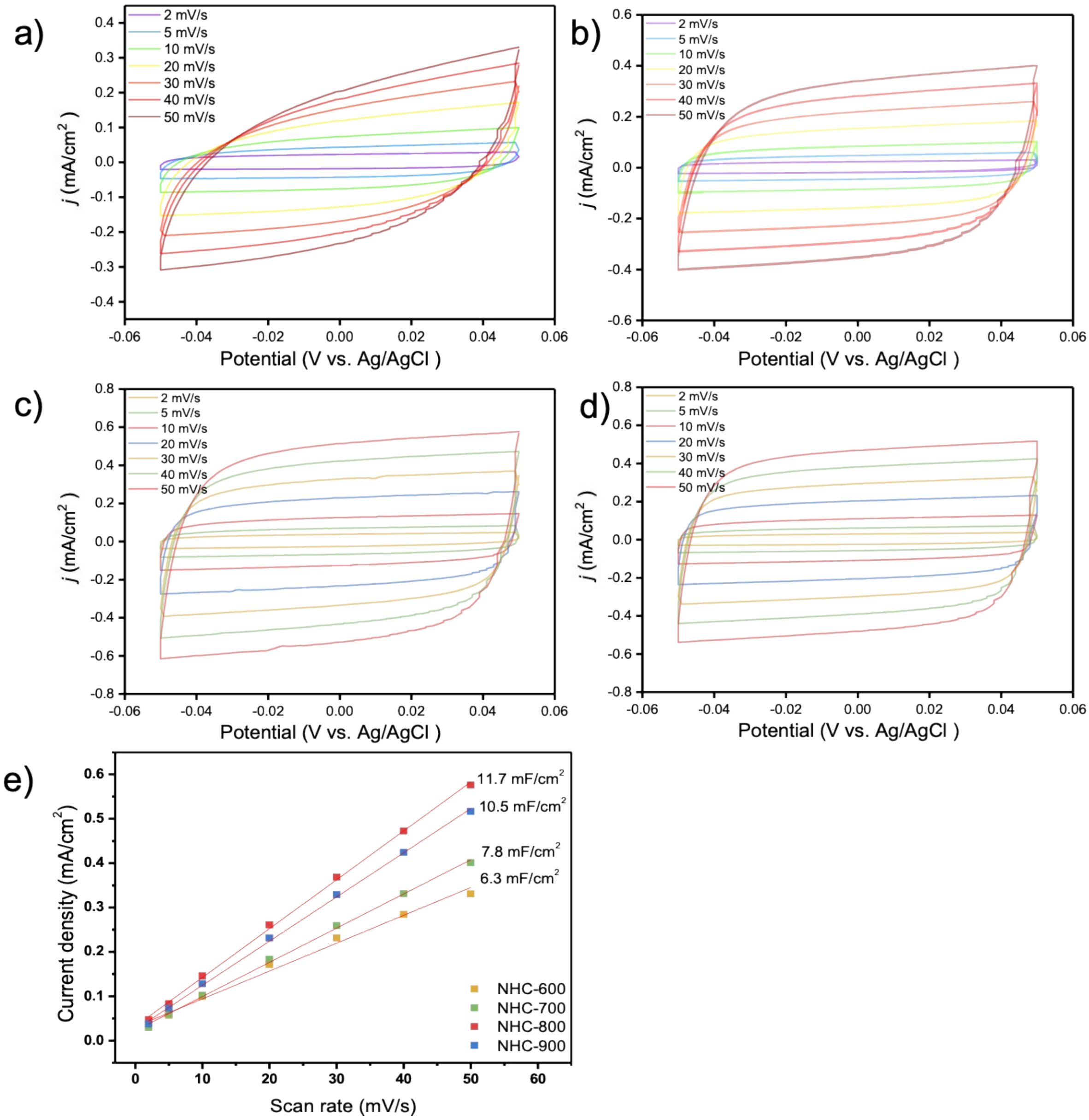

Fig. S8. CV scans at different scan speed of (a) NHC-600, (b)NHC-700, (c)NHC-800 and (d)NHC-900. (e)calculated ECSA of all the NHC from the CV scans by plotting the current density with scan rate.

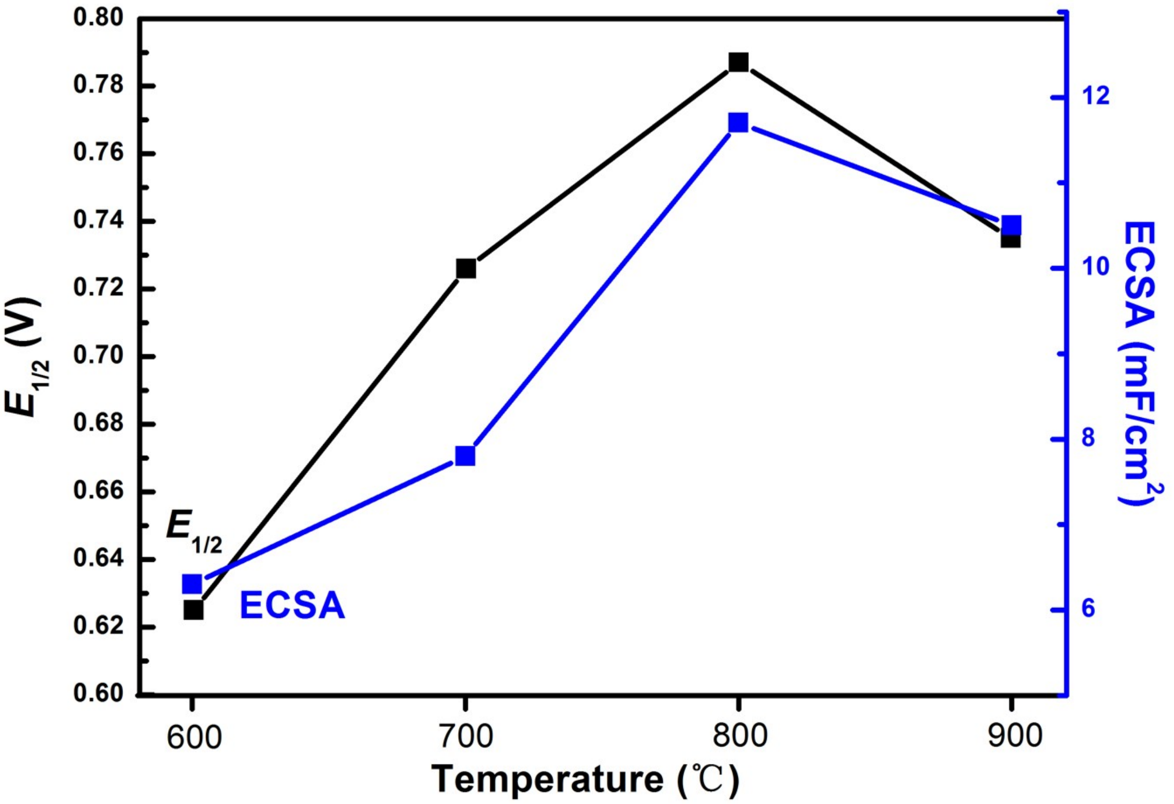

Fig. S9. Correlated the change of half-wave potential E1/2of NHCs at different temperatures as a function of ECSA measured by CV scans.

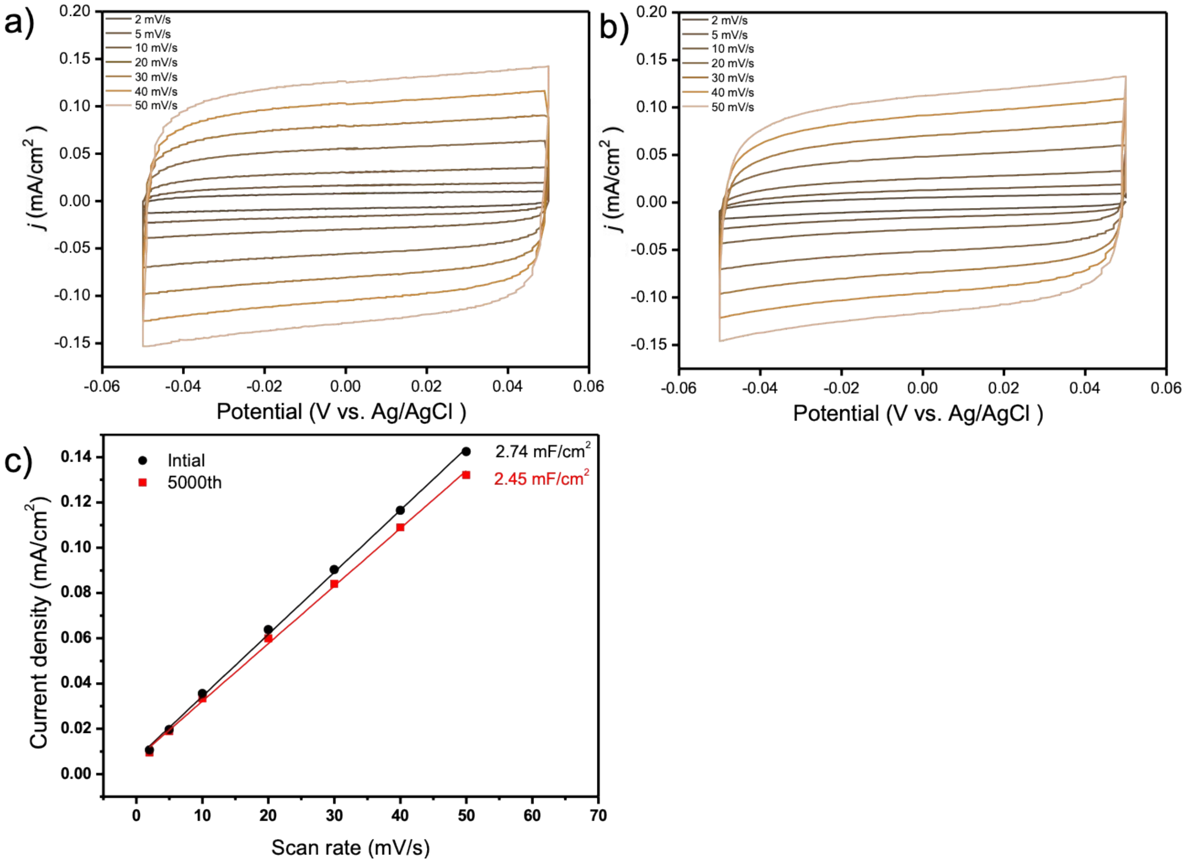

Fig. S10. CV scans at different scan speed of Pt/C (a) before and (b)after 5000th. (c) calculated ECSA of Pt/C before and after 5000th

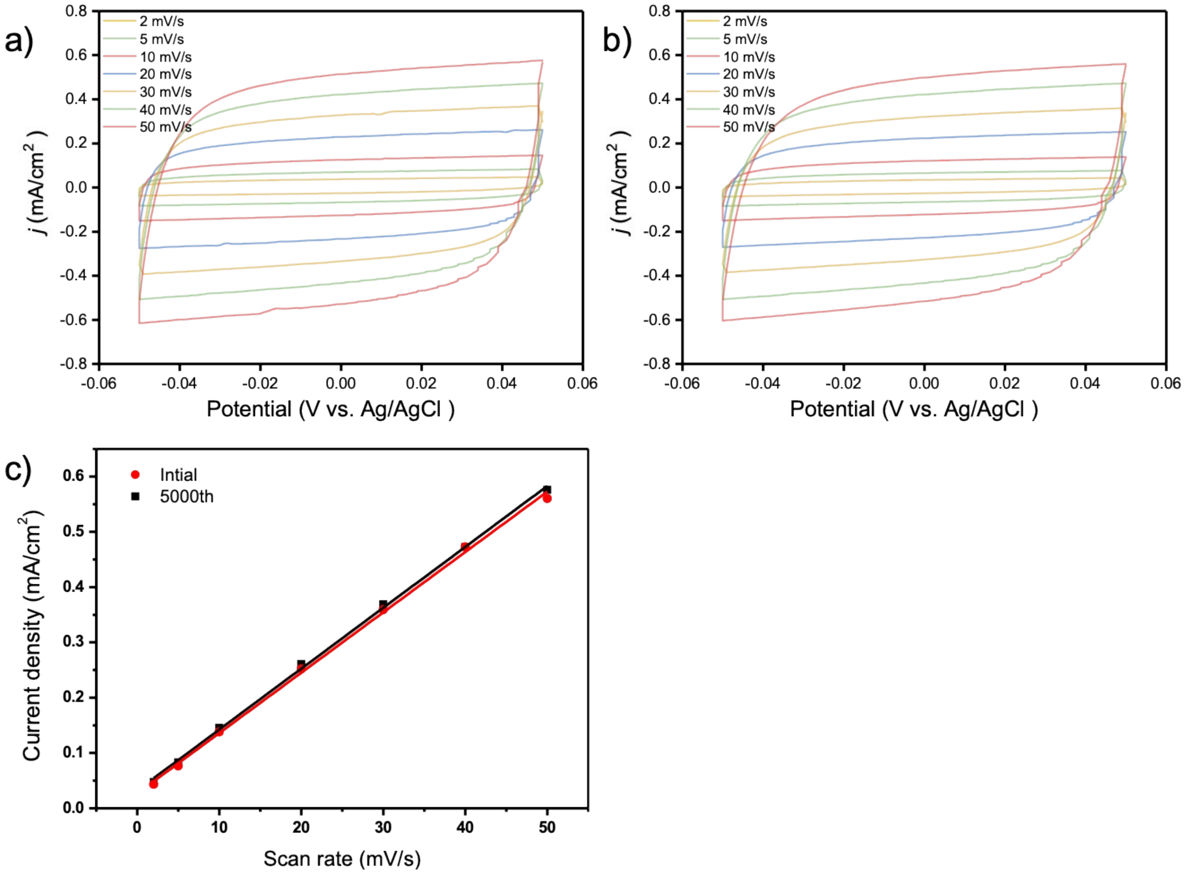

Fig. S11. CV scans at different scan speed of NHC-800 (a) before and (b) after 5000th (c) calculated ECSA of NHC-800 before and after 5000th.

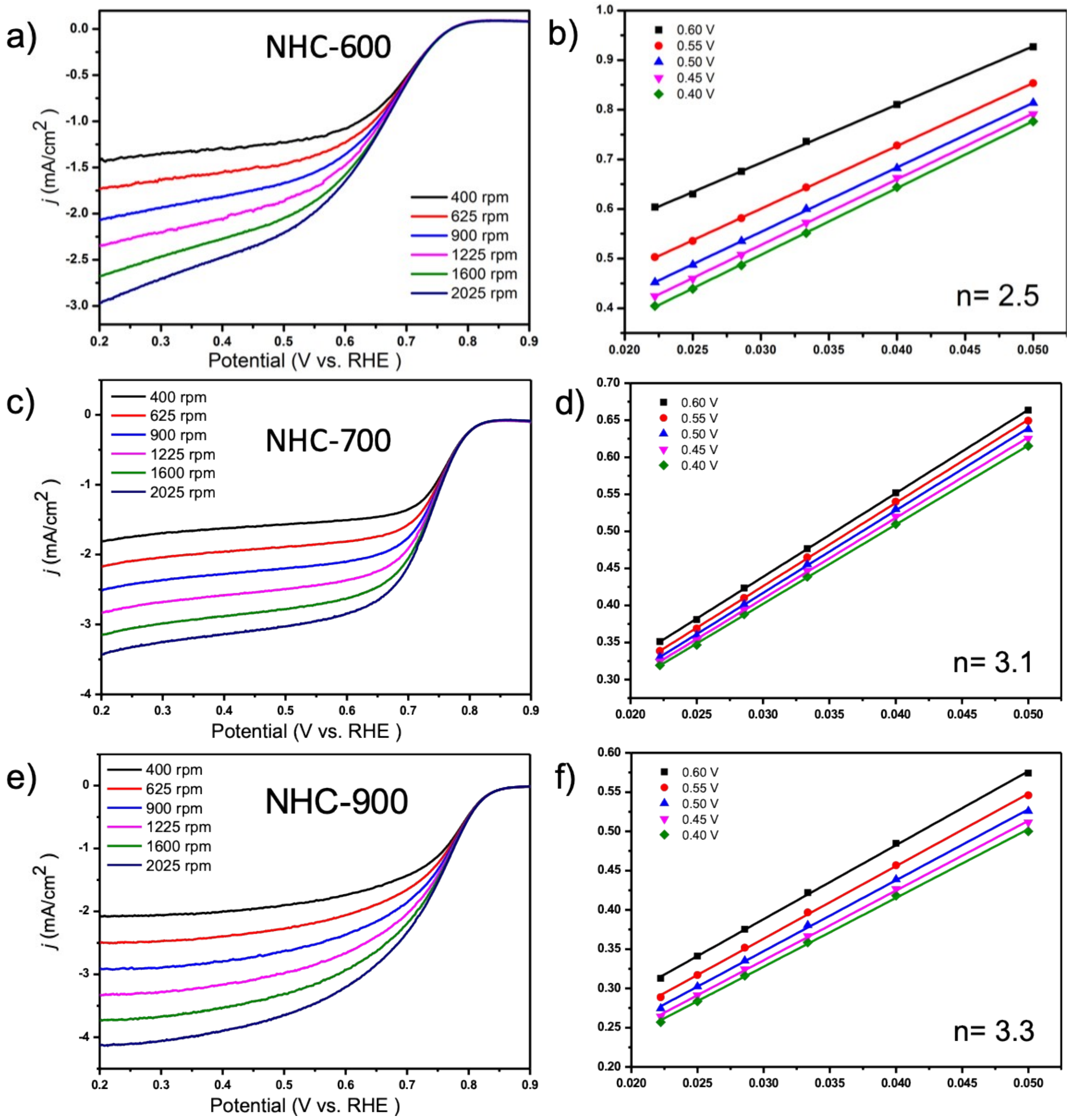

Fig. S12. LSV curves and K-L plots of NHC-600 (a, b), NHC-700 (c, d), and NHC-900 (e, f)

Table S1 The weight percentage of C, N, H, O in NHC and pure CB[6] by elemental analysis.

	C (wt%)	N (wt%)	H (wt%)	O (wt%)
NHC-600	69.24	20.40	2.00	12.71
NHC-700	72.72	16.62	1.58	9.82
NHC-800	79.39	11.55	1.32	10.78
NHC-900	79.94	9.05	1.01	9.90

Table S2 Peak intensities of I_D, I_G, I_{2D} and the related ratios of these values from Raman spectroscopy.

	I_D	I_G	I_{2D}	I_D/I_G	I_G/I_{2D}	I_{2D}/I_G
NHC-600	239.58	258.85	135.53	0.92	1.91	0.52
NHC-700	256.92	263.82	58.32	0.97	4.52	0.22
NHC-800	186.83	190.35	39.34	0.98	4.84	0.21
NHC-900	138.11	143.21	26.89	0.96	5.33	0.19

Table S3 Atomic percentage (at.%) of difference N species in NHCs.

Sample	Pyridinic	Pyrrolic	Graphitic	Oxide
CB600	51.0	20.4	26.0	2.6
CB700	45.7	15.5	34.7	4.1
CB800	38.7	12.3	42.6	6.4
CB900	33.3	11.0	47.6	8.7

Table S4. ORR performance of the NHCs in terms of onset potential, half-wave potential, limited current density and number of electron transfer.

SAMPLE	**ORR PERFORMANCE**			
	E_{onest} (V)	$E_{1/2}$ (V)	j_{L} (mA/cm^2)	N (0.5 V)
CB600	0.716	0.635	2.70	2.5
CB700	0.778	0.726	3.26	3.1
CB800	0.882	0.788	4.64	3.6
CB900	0.801	0.731	3.56	3.3

1 D. Bardelang, K. A. Udachin, D. M. Leek*, et al.*, *CrystEngComm*, 2007, **9**, 973.