Support information

Experimental part

Chemicals

Potassium hydroxide (KOH) and hydrochloride acid (HCl) in this work were purchased from Shanghai Chemical Corp. All the reagents were of analytical grade and used as received without further purification. Ultra-pure water was used throughout the experiment.

Synthesis of nitrogen-doped carbon aerogels with hierarchically porous architectures (NHCAs)

To obtain NHCAs, a cubic piece of cantaloupe (6 g) and deionized water (30 mL) were first put in a 100 mL Telfon-lined stainless-steel autoclave, which was then thermally treated at 180 ^{o}C for 12 h. The obtained carbonaceous hydrogel monolith was immersed in water for several times to remove the soluble impurities. After freeze-drying, the resulting carbonaceous aerogel was immersed in the aqueous solution of KOH (2 M) overnight, dried at 80 ^{o}C and then thermally treated (at 600, 700 and 800 ^{o}C) for 2h under N_2 atmosphere. After that, the obtained samples were washed with HCl solution (1 M), water and ethanol for several times, and then dried at 80 ^{o}C for 24 h to produce NHCAs. According to the temperature of the activation process, the NHCAs were denoted as NHCA-600, NHCA-700 and NHCA-800, respectively.

In controlled experiments, the carbonaceous aerogels were thermally treated (at 600, 700 and 800 ^{o}C) for 2h under N_2 atmosphere without the presence of KOH to evaluate the effect of the activation process. And the corresponding products were named as NCA-600, NCA-700 and NCA-800, respectively.

Structural characterization

Scanning electron microscopy (SEM) measurements were performed on a JSM-6700F scanning electron microscope. Transmission electron microscopy (TEM)

measurements were acquired by using JEM-2010F at operating voltage of 200 kV. The sample was dispersed in ultrapure water and the suspension dropped on carbon-coated copper grid by evaporation in air. X-ray diffraction (XRD) patterns were carried out on a 3KW D/MAX2200V X-ray diffraction using Cu Kα radiation (40 kV, 40 mA). Raman spectra were recorded using a continuous-wave linearly polarized laser (514.5 nm wavelength, 2.41 eV, 16 mW power). Nitrogen physisorption measurements were taken with ASAP 2010 M+C apparatus.

Electrochemical measurement

Supercapacitor electrodes

All the electrochemical measurements were taken using a CHI 660E electrochemical workstation under ambient conditions. In a three-electrode system, KOH (6 M) was used as the aqueous electrolyte, a platinum plate as the counter electrode, a Hg/HgO electrode as the reference electrode and cut a piece of the samples (NHCAs or NCAs) from the aerogel as a working electrode between two pieces of nickel foam and pressed under 15 MPa face to face for 5 minutes. In this process, no binder is needed. The electrochemical performance based electrode was examined by cyclic voltammetry (CV) and galvanostatic charge-discharge measurement. The single electrode capacitance was calculated from cyclic voltammetry according to the following equation:

$$C = \frac{\int IdV}{2mS\Delta U}$$

where I is the response current density (A), S is the scan rate (V s^{-1}), ΔU is the absolute value of potential window (V), and m is the total mass of the active material (g). The areal mass loading of the active material on nickel form is about 2 mg cm^{-2}.

Electrocatalyst for oxygen reduction reaction

The oxygen reduction reaction (ORR) measurements were carried out via PINE

electrochemical workstation (Pine Research Instrumentation, USA) at room temperature. The catalyst (NHCAs or 20 wt % Pt/C from Alfa Aesar, 1 mg)) was dissolved in 1mL Nafion and ethanol (V: V ratio=1: 9), then ultrasonicated for at least 40 min to form a homogeneous suspension. The catalyst ink (50 μL) was dropped onto a glassy carbon rotating ring-disk electrode (disk area=0.2471cm^2, ring area=0.1858 cm^2). Ag/AgCl, KCl (Saturated) and a Pt electrode were used as reference and counter electrode. The electrochemical experiments were measured in 0.1 M KOH aqueous solution as electrolyte for ORR after purging O_2 for at least 30 min. The sample were circularly scanned by sweeping the potential from -1.2 to -0.2 V at a scan rate of 100 mV s^{-1} for 10 times cycle until steady state CV curves were obtained. The rotating ring disk electrode (RRDE) measurements were carried out with a sweep rate of 10 mV s^{-1} at a rotating speed of 1600 rpm. On the basis of ring current and disk current, the electron transfer number (n) and the four-electron selectivity of catalysts based on the H_2O_2 yield were calculated from the following equations:

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

in which n, I_D, I_R and N represent electrons transfer numbers, disk current, Pt ring current and collection efficiency (N=0.37), respectively.

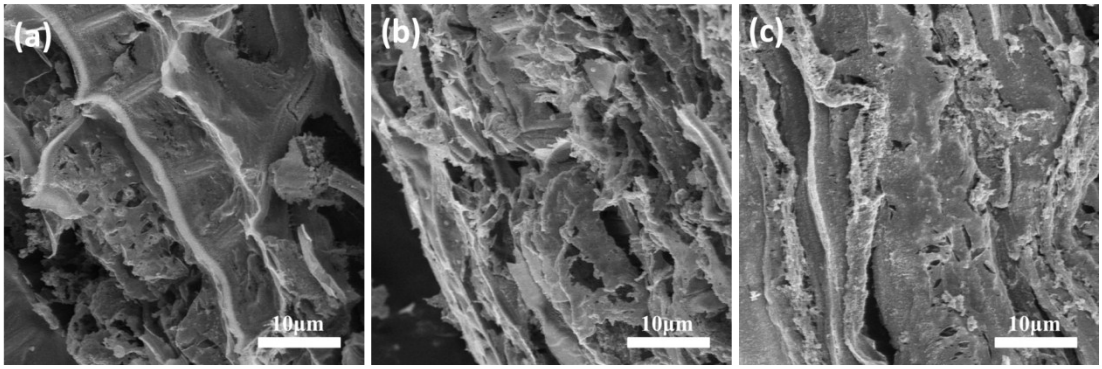

Figure S1. SEM images of (a) NCA-600, (b) NCA-700, and (c) NCA-800.

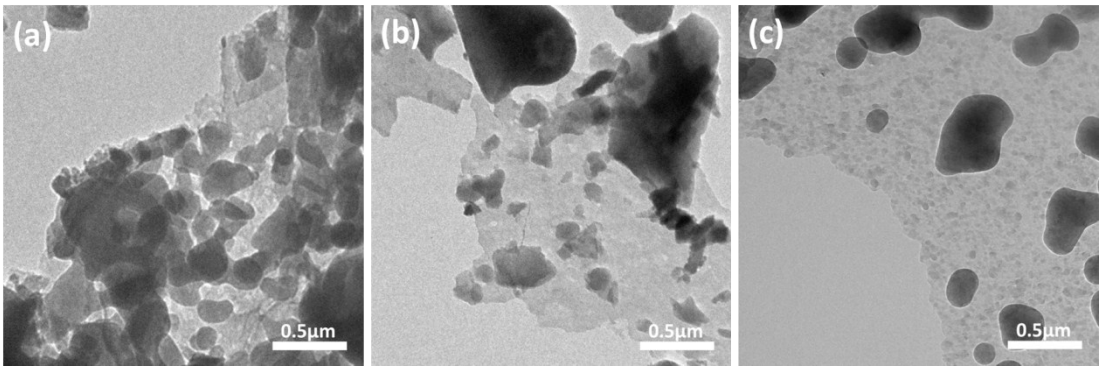

Figure S2. TEM images of (a) NCA-600, (b) NCA-700, and (c) NCA-800.

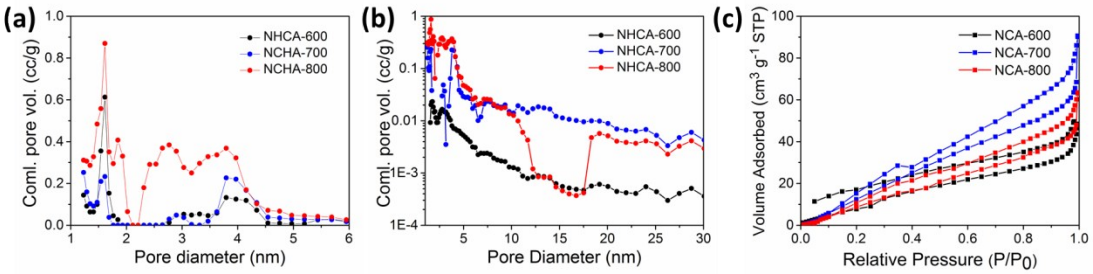

Figure S3. (a) The DFT pore size distribution in the range of 1 – 6 nm of NHCA-600, NHCA-700 and NHCA-800, (b) the log scale plot of pore size distribution of NHCA-600, NHCA-700 and NHCA-800, and (b) N_2 adsorption-desorption isotherms of NCA-600, NCA-700 and NCA-800.

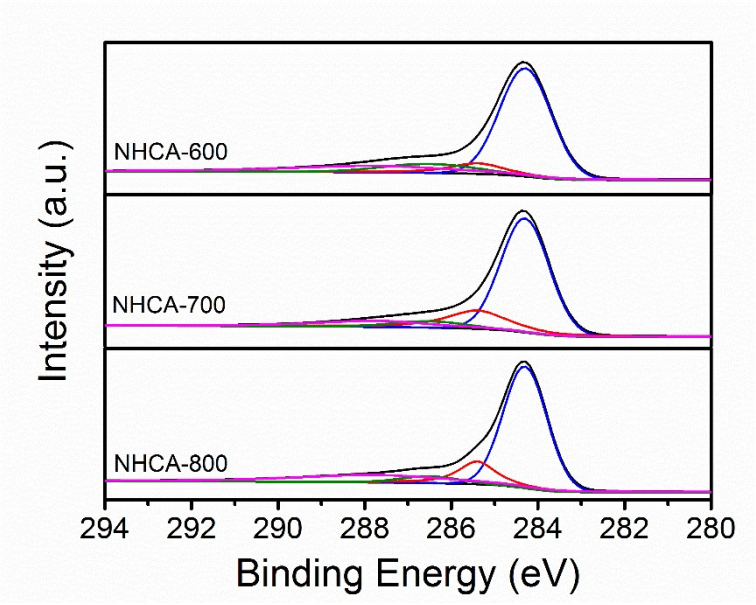

Figure S4. High-resolution C 1s spectra of NHCA-600, NHCA-700, and NCHA-800.

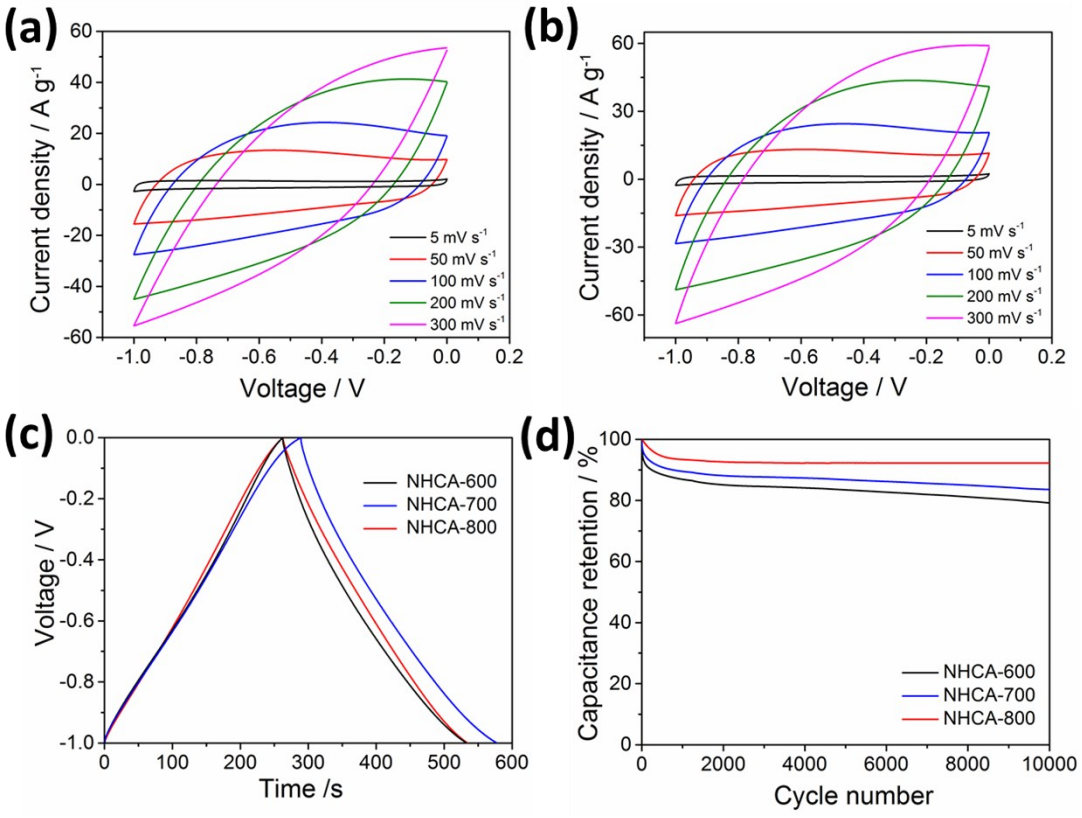

Figure S5. CV curves of (a) NHCA-600, (b) NHCA-700 at different scan rates from 5 to 300 mV s^{-1}; (c) the galvanostatic charge–discharge curves of NHCAs obtained at 1 A g^{-1}; (d) the cycling stability of NHCA-600, NHCA-700, and NHCA-800.

Table S1. Specific surface areas, chemical compositions, N distribution and electrochemical performances of NHCAs.

	NHCA-600	**NHCA-700**	**NHCA-800**
S_{BET} (m^2 g^{-1})	530	787	1778
Vp (cm^3 g^{-1})	0.52	0.72	1.31
C (wt %)	70.17	85.88	87.93
N (wt %)	1.46	2.14	2.01
O (wt %)	28.36	11.98	10.06
Pyridinic N (%)	22.8	33.8	39.8
Pyrrolic N (%)	39.7	38.6	24.8
Graphitic N (%)	13.6	7.5	19.3
Oxidized N (%)	23.9	20.1	16.1
Capacitance (F g^{-1} at 1A g^{-1})	270	288	272
Capacitance (F g^{-1} at 5 A g^{-1})	225	238	240
Capacitance (F g^{-1} at 20A g^{-1})	180	192	221
Capacitance (F g^{-1} at 50A g^{-1})	104	128	200
Capacitance (F g^{-1} at 80A g^{-1})	50	90	179
Capacitance (F g^{-1} at 100A g^{-1})	-	75	176