

Supplementary information

An environmentally friendly strategy to prepare nitrogen-rich hierarchical porous carbon constructed by nanosheets for high-performance supercapacitors

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Experimental section

Material preparations:

The nitrogen-rich hierarchically porous carbon (NRPC) was prepared by a CaCl_2 -induced green route. In a typical synthesis process: phthalic acid (30 mmol, 4.9839 g) and potassium hydrogen phthalate (30.0 mmol, 6.1266 g) were mixed in 150 mL of deionized water in a round bottom flask and kept for 4 h at 60 °C with a magnetic stirring. After the mixtures were dissolved completely, the solution was cold to 10 °C firstly, and ethylenediamine (30.0 mmol, 5.4090 g) was added into the solution slowly with a magnetic stirring to achieve a clear solution. Then CaCl_2 (15.0 mmol, 1.6650 g) was added into the clear solution in a short time with a fast stirring, after that, the mixture was firstly dried by freeze drying and was then transferred into a copper boat; the mixed precursor was heated to 800 °C with a heating rate of 5 °C min^{-1} and maintained at this temperature for additional 2 h. After cooling down to room temperature naturally, the obtained products were firstly washed by 150 mL of dilute HCl (0.5 mol L^{-1}) one time and then washed by distilled water three times with under continuous stirring. Finally, the as-obtained sample, with a yield of ~15% based on the mass of phthalic acid, was collected by filtration and dried under vacuum at 60 °C overnight to obtain the NRHPC. The elemental analysis of the NRHPC sample as followed: C, 68.8 wt%; N, 7.0 wt% and H, 3.2 wt%.

To further investigate the effect of the addition of CaCl_2 on the composition and structure of the obtained N-doped porous carbons obtained before acid- and water-washing, another material (NDPC) was prepared using the same procedures used for the preparation of NRHPC, except for no the addition of CaCl_2 into the mixed precursor. The elemental analysis of the NDPC sample as followed: C, 71.8 wt%; N, 2.8 wt% and H, 3.8 wt%. The yield is ~14% based on the mass of phthalic acid.

Physical characterizations:

The chemical composition and physical structures of the as-synthesized materials were characterized in detail. The relative information on the used instruments and methods are the same as previously used in the literature.^{1,2}

X-ray powder diffraction (XRD) was performed on a Bruker D8 ADVANCE powder diffractometer using Cu K α radiation at 40 kV and 40 mA at a step of 0.020. The microstructures of all resulting samples were studied with field emission scanning electron microscopy (FE-SEM, Ultra Plus, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100, Japan). The Raman spectra were obtained using a Bio-Rad FTS6000 Raman spectrophotometer with a 532 nm blue laser beam. Nitrogen absorption/desorption measurements were performed at -196 °C using an ASAP 2020 system (Micrometitics). All samples were degassed at 180 °C for 2 h prior to sorption measurements. The elemental microanalysis (C, H, and N) and surface composition were characterized by elemental analyzer (Vario EL) and X-ray photoelectron spectroscopy (XPS, Escalab 210, Germany), respectively.

Electrochemical studies:

The fabrication procedures of the working electrodes in a three-electrode system and a two-electrode system, as well as the formula used to the calculation of the specific capacitance (C, in F g⁻¹) are very similar to those in the previous papers.^{1,2}

In a three-electrode system, a glassy carbon electrode with a diameter of 5 mm was used as a current collector. In a typical working electrode preparation, 4.0 mg of the NRHPC or the NDPC sample was ultrasonically dispersed in 400 μ L Nafion solution (0.25 wt%, DuPont, USA). Afterwards, 16.0 μ L of the above suspension was dropped onto the glassy carbon electrode surface and dried at room temperature and the mass loading is 0.8 mg cm⁻². This mass loading value is closed to that in most of the previously papers. A platinum plate electrode was used as the counter electrode. The reference electrodes are composed of a double salt bridge, with the Hg/HgO electrode in 6 M (mol L⁻¹) KOH electrolyte. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) results

were obtained in a CHI 760 D electrochemical workstation (Cheng-hua Instrument, Shanghai, China). The voltage window which was used in all electrolytes was $-0.971-0.029$ V vs. Hg/HgO .

In a typical two-electrode fabrication: the as-prepared NRHPC sample was mixed with the commercial acetylene black and polyvinylidene fluoride (PVDF) (mass ratio of 8:1:1) in a small quantity of *N*-methyl-2-pyrrolidone (NMP) solvent. The as-obtained muddy mixture was coated on nickel foam and then pressed at 5 MPa followed by drying at 60 °C overnight. A coin-type supercapacitor was assembled with two electrodes with the active material mass loading of (~ 3.5 mg cm⁻²). This mass loading value is usually used to evaluate the electrochemical performance of carbon-based materials for the two-electrode coin cell in most of the previously papers. The two electrodes were separated by a (Whatman filter paper) in 2 M Li₂SO₄ electrolyte. The CV, CGD and results were obtained by a CHI 760 D electrochemical workstation. The specific capacitance (*C*, in F g⁻¹) based on the electrodes' mass of the as-assembled supercapacitor was computed from the GCD curves at different current densities based on the following equation:

$$C = \frac{I \times t}{m \times \Delta U} \quad (1)$$

Herein *I* (A), *t* (s), *m* (g), and ΔU (V) represent the discharging current, the discharging time, the net mass of the active material of both electrodes, and the discharge voltage range, respectively.

The equations (2) and (3) were used to calculate the energy density (*E*, in Wh kg⁻¹) and power density (*P*, in W kg⁻¹) for two-electrode device, respectively.

$$E = \frac{C \times (\Delta U)^2}{2 \times 3.6} \quad (2)$$

$$P = \frac{3600 \times E}{t} \quad (3)$$

C is the specific capacitance of a two-electrode device ($F\ g^{-1}$) measured from the Eq. (1), ΔU is the discharge potential range, and t is the discharge time (s).

1. K.X. Zou, H. Q. Tan, L. M. Wang, Y. X. Qian, Y. F. Deng and G. H. Chen, *J. Colloid Interface Sci.*, 2019, **537**, 475.
2. K. X. Zou, Y. F. Deng, J. P. Chen, Y. X. Qian, Y. W. Yang, Y. W. Li and G. H. Chen, *J. Power Sources* 2018, 378, 579.

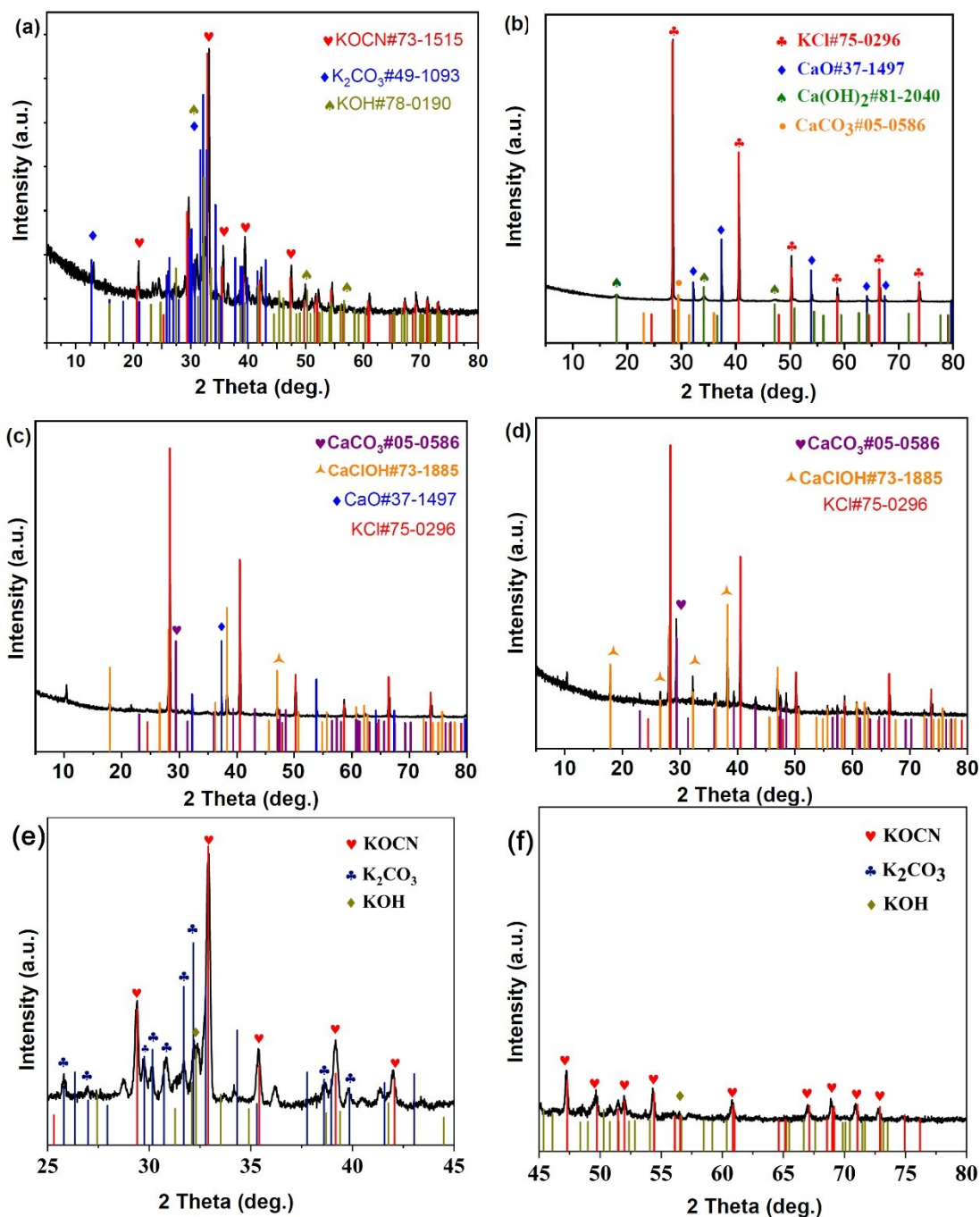


Figure S1. The XRD patterns of the raw products obtained from different ratio of phthalic acid/potassium hydrogen phthalate/ethylenediamine/calcium chloride mixture at 800 °C: (a) 1:1:3:0; (b) 1:1:3:0.5; (c) 1:1:3:1 and (d) 1:1:3:2; (e) and (f) The enlarged XRD patterns located at $2\theta = 25$ to 45 and 45 to 80 degree based on (a), respectively.

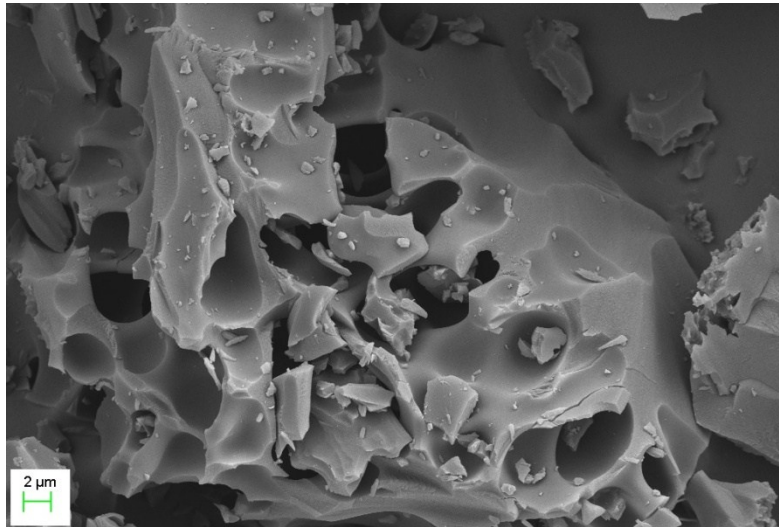


Fig. S2. SEM images of NDPC.

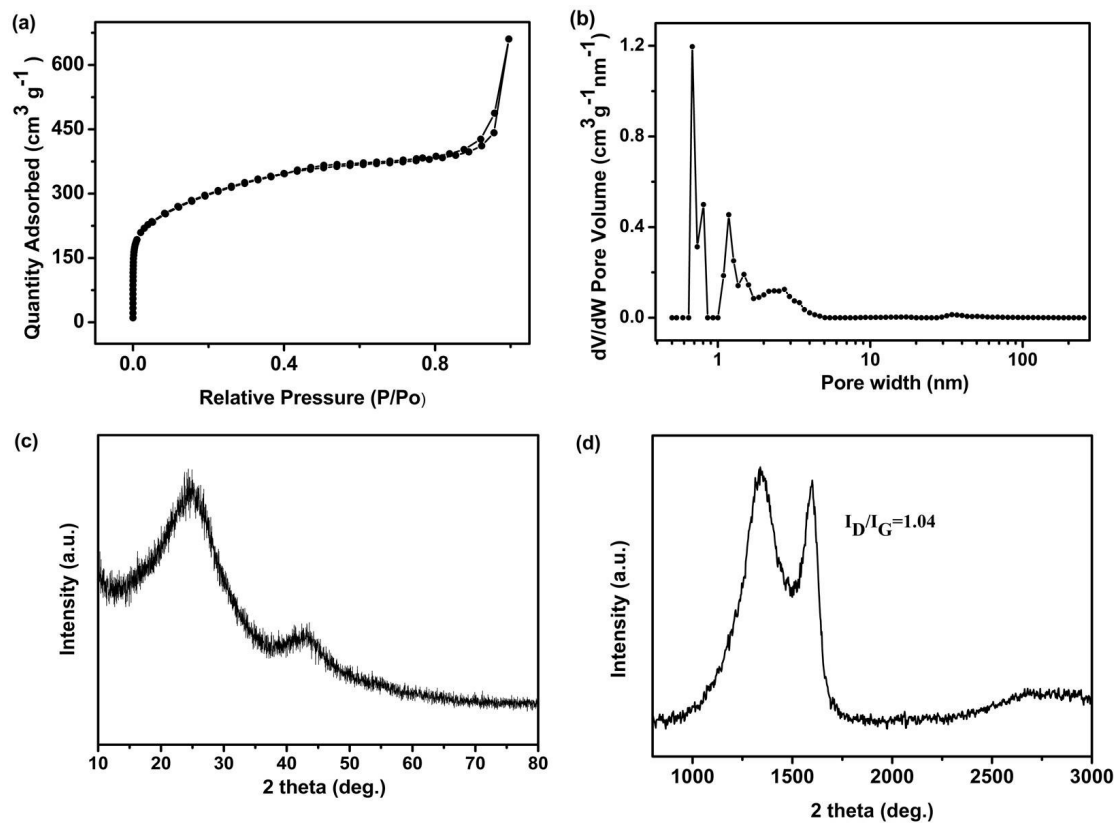


Fig. S3. (a) N₂-adsorption/desorption isotherm, (b) Pore size distribution, (c) XRD and (d) Raman spectrum for NRHPC.

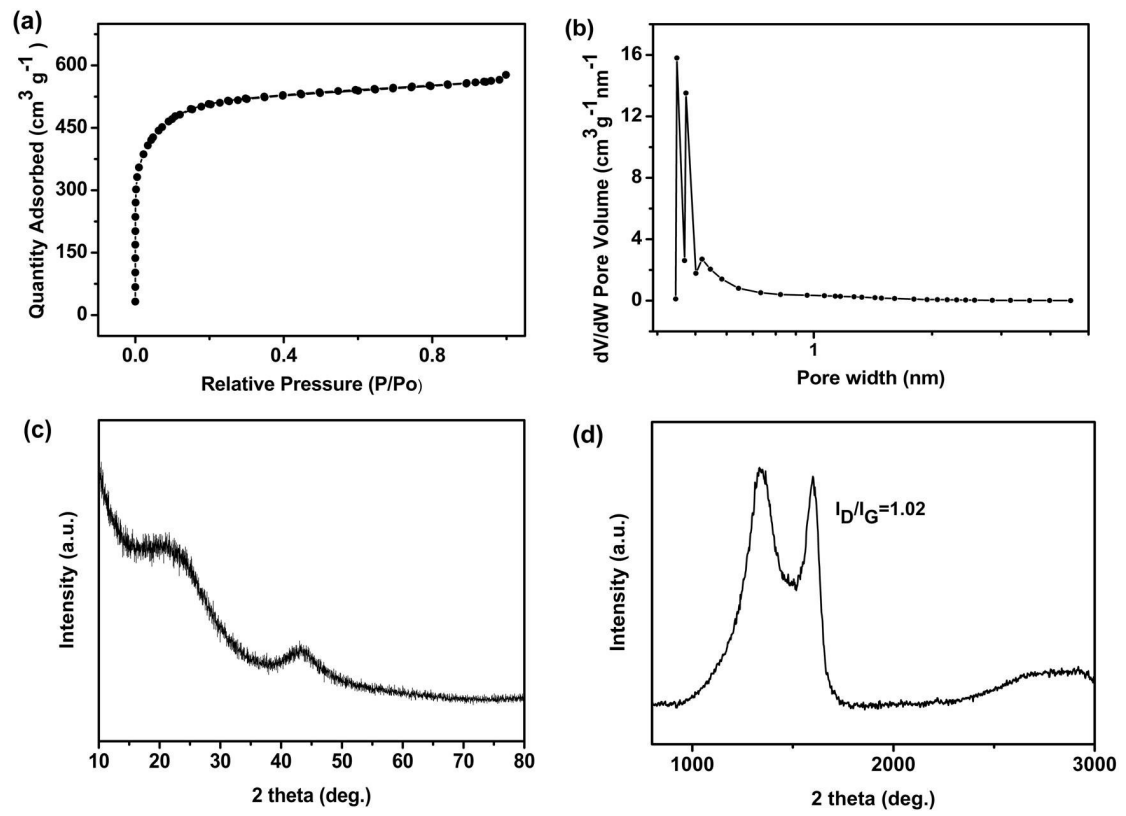


Figure S4. (a) N_2 -adsorption/desorption isotherm, (b) Pore size distribution, (c) XRD and (d) Raman spectrum for NDPC.

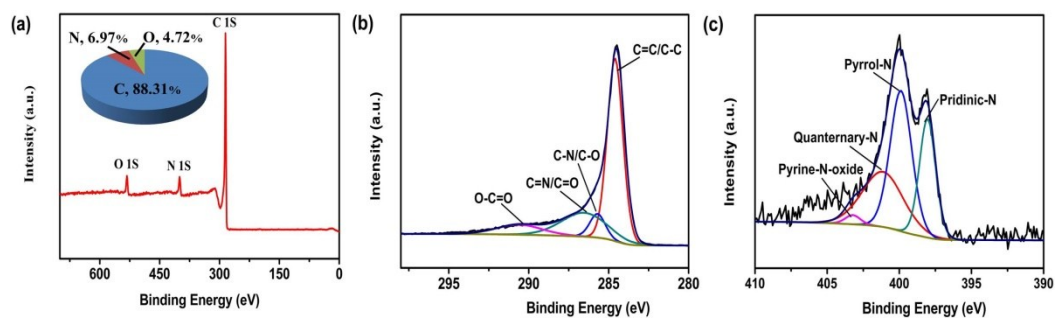


Figure S5. (a) XPS, (b) and (c) high-resolution XPS of C1s and N1s for NRHPC.

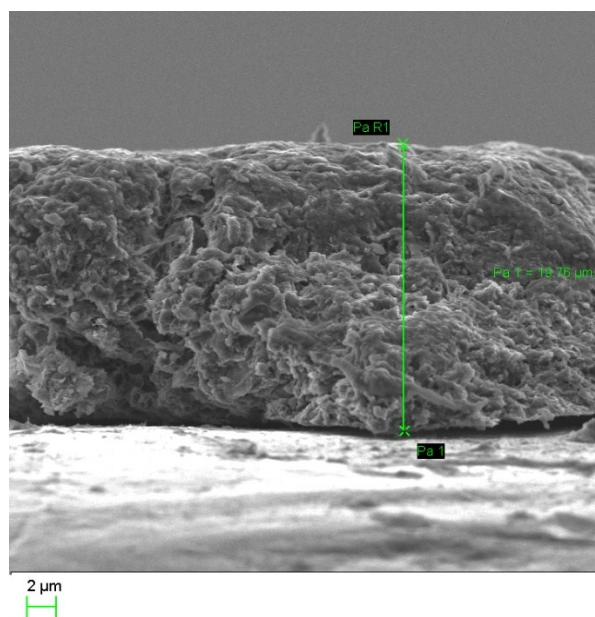


Fig. S6. The cross-section SEM image of a practical electrode (1×1 cm and a mass loading of ~ 1.5 mg) for three-electrode test.

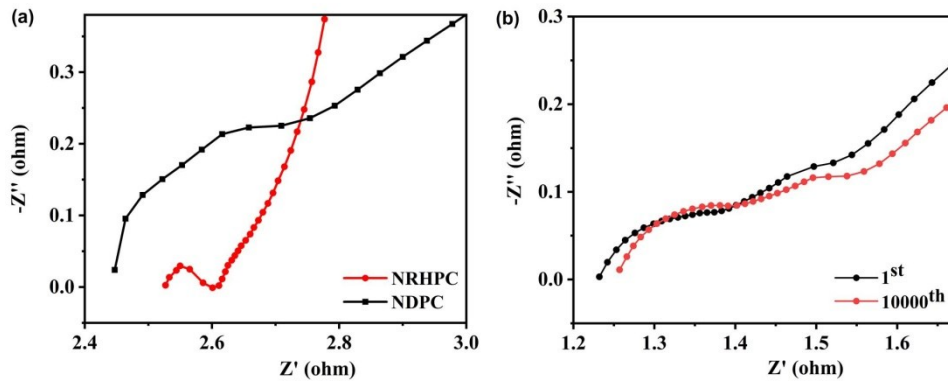


Figure S7. (a) and (b) the enlarged figures to show the semicircles in Fig. 2(e) and Fig. 3(f), respectively.

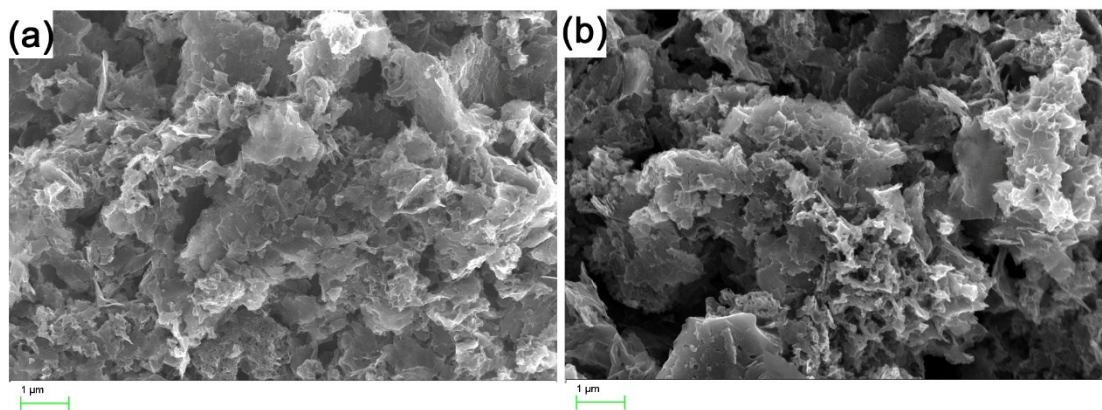


Fig. S8. The SEM images of a practical electrode before and after 5000 cycles for a three-electrode test in 6 M KOH at a current density of 5 A g^{-1} .

Table S1. BET surface areas, pore size parameters, elemental analysis and XPS of NDPC and NRHPC samples.

Sample	$D_{ave}(nm)^a$	$S_{BET}(m^2 g^{-1})$	$V_t(cm^3 g^{-1})$	$V_{mic}(cm^3 g^{-1})$	V_{mic}/V_t (%)	Elemental analysis (wt%)			XPS (at.%)		
						C	H	N	C	N	O
NDPC	2.22	1610.5	0.89	0.74	83.1	71.8	3.8	2.8	/	/	/
NRHPC	3.24	1004.0	0.83	0.50	60.2	68.8	3.2	7.0	88.31	6.97	4.72

^a BJH Adsorption average pore diameter.