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Supporting Information

In situ Polydopamine Coating-Directed Synthesis of Nitrogen-Doped Ordered Nanoporous Carbons with Superior Performance in Supercapacitors

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Experimental

1. Sample preparation

Synthesis of SBA-15. SBA-15 was prepared according to the method described in the reference[1]. Briefly, 1 g of P123, 18.2 ml of H_2O, and 0.46 ml of HCl (37 wt%) were mixed and stirred until complete homogenization. Subsequently, 1.73 ml of TEOS was added and continuously stirred at 35 °C for 24 h. After that, the mixture was heated at 100 °C for 24 h. The product was filtered, dried and then calcined at 550 °C for 6 h, leading to formation of SBA-15.

Synthesis of nitrogen-doped ordered nanoporous carbon. In a typical synthesis, 1 g of SBA-15 powder was added to 150 mL of Tris-buffer (pH 8.5). Subsequently, 2.5 g of dopamine was added into the mixture under string for 24 h at room temperature. The obtained polydopamine/silica nanocomposite was carbonized for 3 h at 800 °C in N_2 flow. The heating rate was 1 °C/min below 600 °C and then was increased to 5 °C/min above 600 °C. After that,

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the resulting carbon/silica nanocomposite was treated using 40 wt% HF to remove silica, washed, filtrated and then dried, producing nitrogen-doped ordered nanoporous carbon.

Synthesis of nitrogen-free ordered nanoporous carbon from phenolic resin. For the synthesis of the phenolic resin raw material, 0.61 g of phenol was melted in a flask and mixed with 0.13 mL of 5 mol/L NaOH aqueous solution under stirring. 1.05 g of 37 wt% formaldehyde solution was then added. Subsequently, the clear mixture was reacted at 70 ^{o}C for 1 h under stirring and then was cooled to room temperature. The pH was adjusted to ~7.0 by 5 mol/L HCl aqueous solution. The product was dissolved in ethanol to obtain a 10 mL of resol resin solution. After that, 1 g of SBA-15 powder was added to the obtained resol resin solution and stirred for about 18 h at room temperature, followed by heating for 24 h at 100 ^{o}C. The phenolic resin/silica nanocomposite was carbonized for 3 h at 800 ^{o}C in N_2 flow. The heating rate was 1 ^{o}C/min below 600 ^{o}C and then was increased to 5 ^{o}C/min above 600 ^{o}C. After that, the resulting carbon/silica nanocomposite was treated using 40 wt% HF to remove silica, washed, filtrated and then dried, leading to nitrogen-free ordered nanoporous carbon.

2. Characterization

The microstructure of the samples was investigated by a JSM-6330F scanning electron microscope (SEM) and JEM-2010HR transmission electron microscope (TEM). XRD patterns were recorded on a D-MAX 2200 VPC diffractometer using Cu Kα radiation (40 kV, 30 mA). N_2 adsorption measurements were carried out using a Micromeritics ASAP 2010 analyzer at 77 K. The BET surface area (S_{BET}) was analyzed by Brunauer-Emmett-Teller (BET) theory. The external surface area (S_{ext}) was determined by t-plot method, and then the micropore surface area (S_{mic}) was obtained by subtracting the S_{ext} from the S_{BET}. The pore size distribution was obtained by performing analysis of the N_2 adsorption isotherms based on Barret-Joyner-Halenda (BJH) method. The total pore volume (V_t) was calculated according to the amount adsorbed at a relative pressure P/P_0 of about 0.99. Raman measurement was carried out with inVia-Reflex Renishaw Raman system. The elemental analysis was performed on an Elementar Analysensysteme GmbH Vario EL analyzer. XPS measurements were carried out with an ESCALAB250 instrument. The contact angle of the water on the surface of samples was measured using a drop shape analysis system (Krüss, DSA100).

The carbon electrodes in the form of round sheet were obtained by pressing a mixture film of 92 wt% carbon sample and 8 wt% polytetrafluorethylene into a nickel foam current collector. The mass of carbon sample for each electrode was controlled at 3±1 mg. Cyclic voltammetry (CV) was carried out using an IM6e electrochemical workstation with a typical three-electrode configuration in 6 mol/L KOH aqueous solution. Hg/HgO was chosen as a reference electrode. The galvanostatic charge-discharge behavior was characterized with the assembled two-electrode coin-type supercapacitor by using BT2000 (ARBIN Instruments). In the CV measurement, the specific capacitance (C_m) was calculated according to the equation $C_m = \frac{I}{v \cdot m}$, where I is the current at the middle voltage of the potential window, v the sweep rate and m the mass of the carbon materials[2, 3]. In the galvanostatic charge-discharge measurement, the C_m was calculated according to the equation $C_m = \frac{I \cdot \Delta t}{\Delta V} \cdot \frac{m_1 + m_2}{m_1 \cdot m_2}$, where I is the discharge current, Δt the discharge time, ΔV the potential window, m_1 and m_2 the mass of carbon samples in the two electrodes[4, 5].

Table S1 Pore structure parameters of NONC and ONC.

Sample	S_{BET} (m^2/g)	S_{ext} (m^2/g)	S_{mic} (m^2/g)	V_t (cm^3/g)	D_{mes} (nm)
NONC	1013	850	163	1.14	3.8
ONC	1030	813	217	0.94	4.3

Table S2 Elemental composition information of the NONC and ONC.

Sample	Carbon source	Elemental analysis				XPS			
		C (wt%)	N (wt%)	H (wt%)	N/C [a)]	C (at%)	N (at%)	O (at%)	N/C [b)]
NONC	Dopanmine	70.1	4.5	2.0	0.064	82.5	5.1	7.6	0.062
ONC	Phenolic resin	77.2	0.0	2.5	0.0	89.8	0.0	9.2	0.0

[a)] Atomic ratio from combustion elemental analysis; [b)] Atomic ratio from XPS.

Table S3 Approximate distribution of nitrogen functional groups for NONC.

Sample	N-Q (at%)	N-5 (at%)	N-6 (at%)	N-X (at%)
NONC	40.6	8.3	14.7	36.4

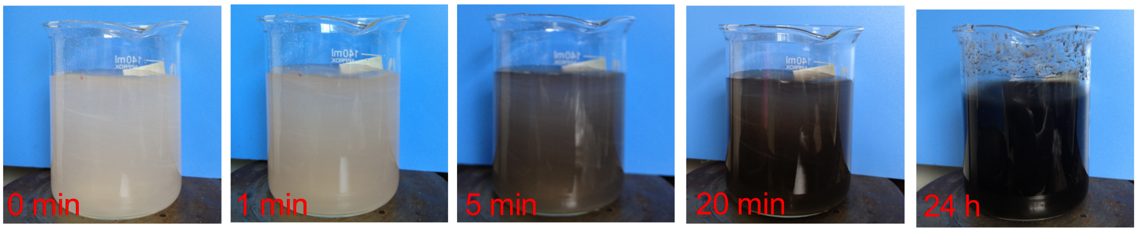

Fig. S1 Photographs of the SBA-15/dopamine reaction system at room temperature showing its change with the reaction time.

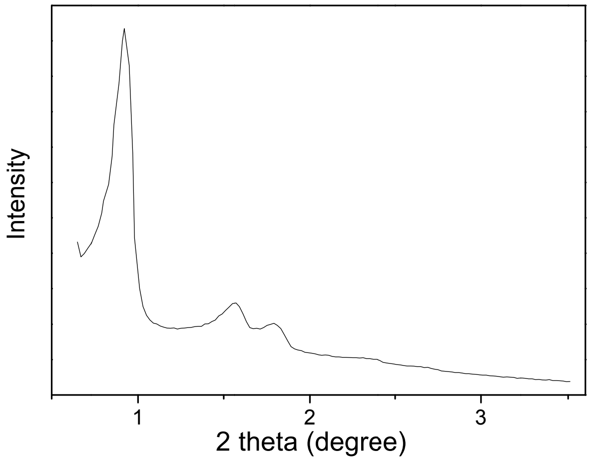

Fig. S2 Low-angle XRD pattern of SBA-15.

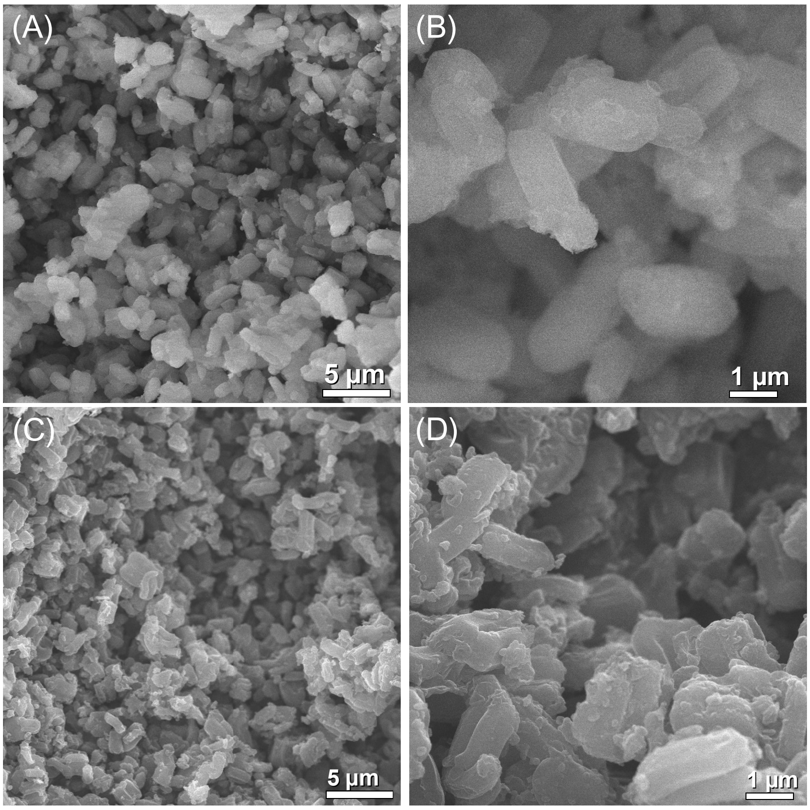

Fig. S3 SEM images of A, B) SBA-15 and C, D) NONC.

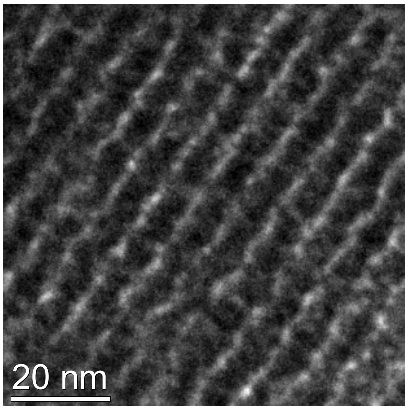

Fig. S4 TEM image of NONC.

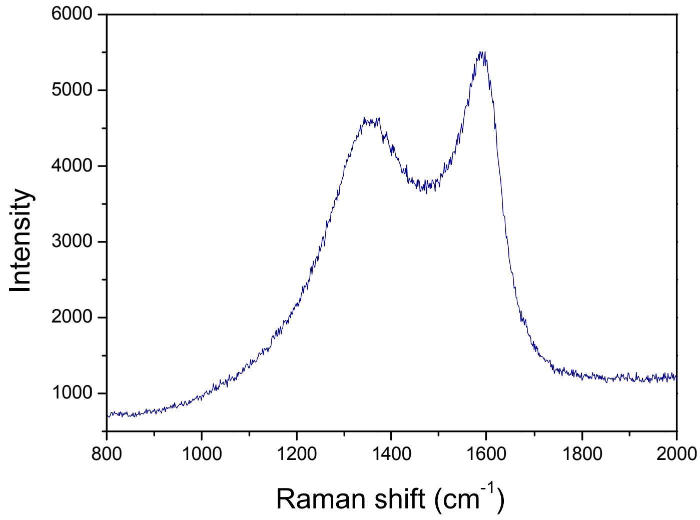

Fig. S5 Raman spectrum of NONC.

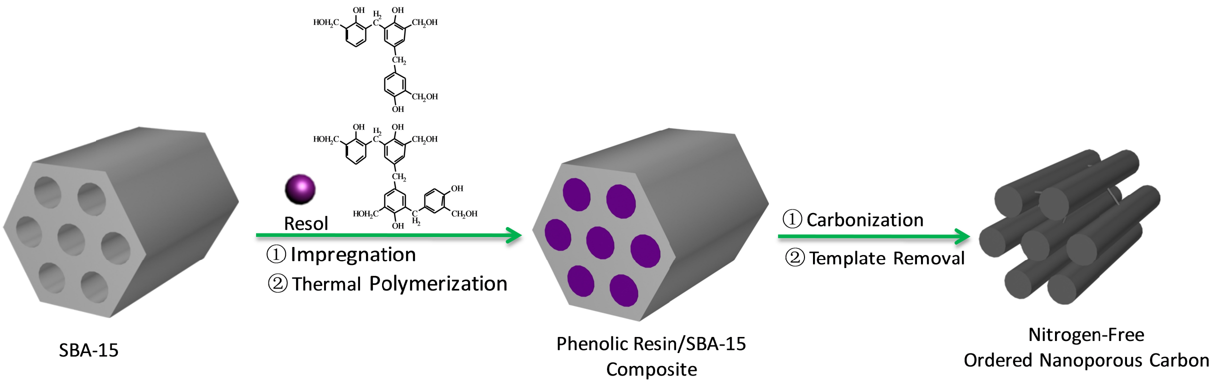

Fig. S6 Schematic representation of the preparation procedure of nitrogen-free ONC by using phenolic resin and SBA-15 as carbon source and template, respectively. Detailed preparation course can be found in the experimental section.

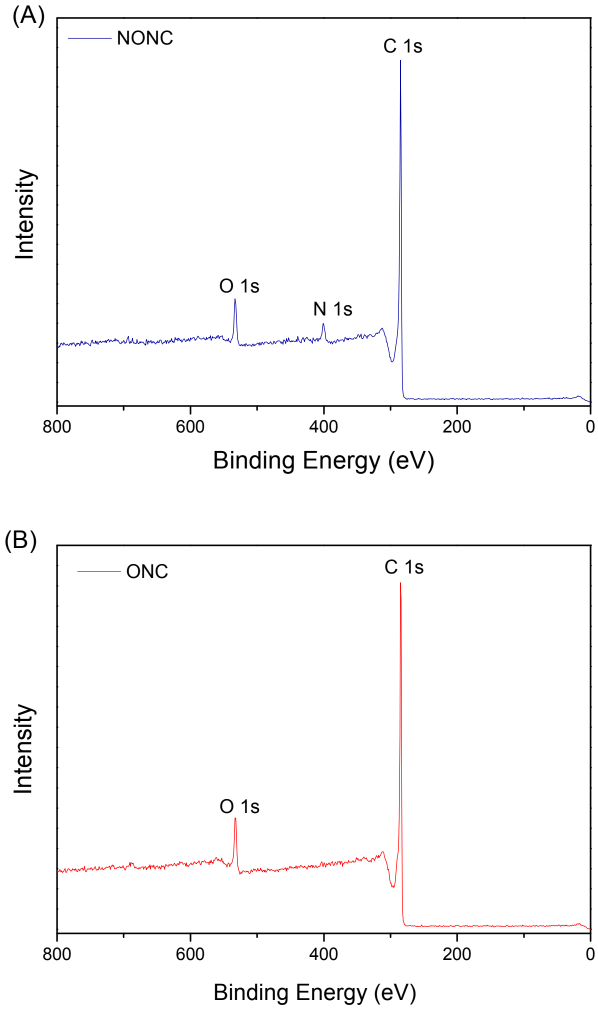

Fig. S7 XPS spectrums of (A) NONC and (B) ONC.

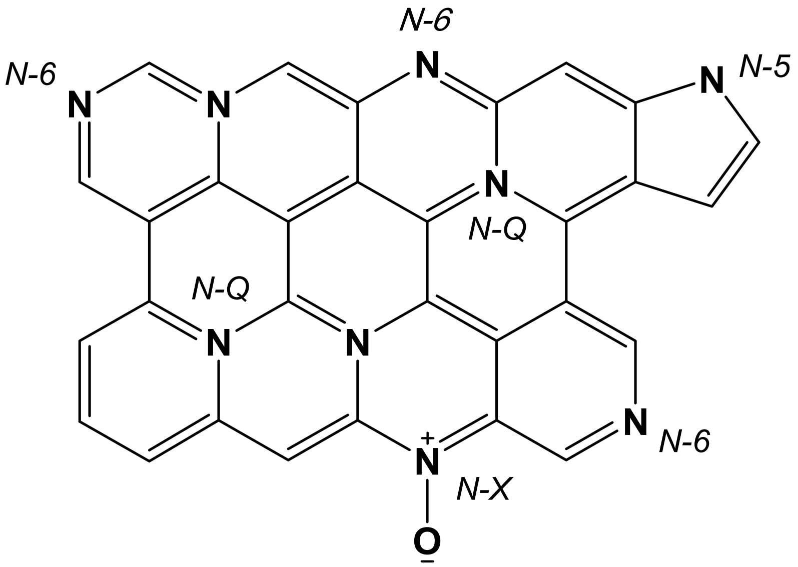

Fig. S8 Schematic model of nitrogen-containing surface functional groups on carbon.

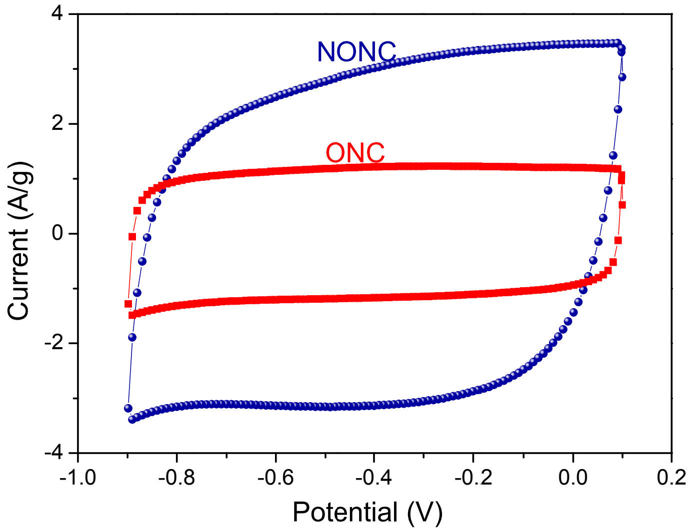

Fig. S9 Cyclic voltammograms for NONC and ONC at a sweep rate of 25 mV/s.

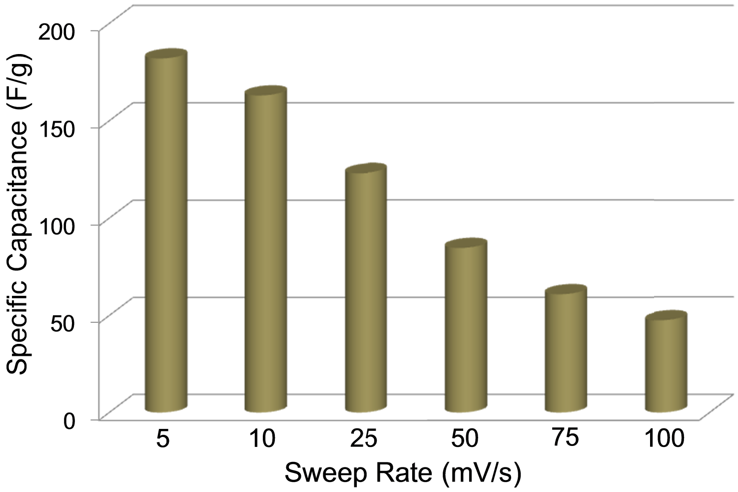

Fig. S10 Mass specific capacitances of activated carbon YP-50 at various sweep rates.

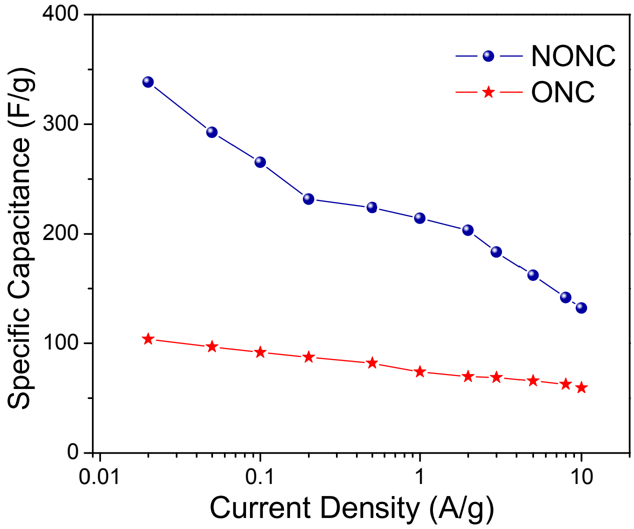

Fig. S11 Mass specific capacitances of NONC and ONC calculated from the galvanostatic charge-discharge measurement.

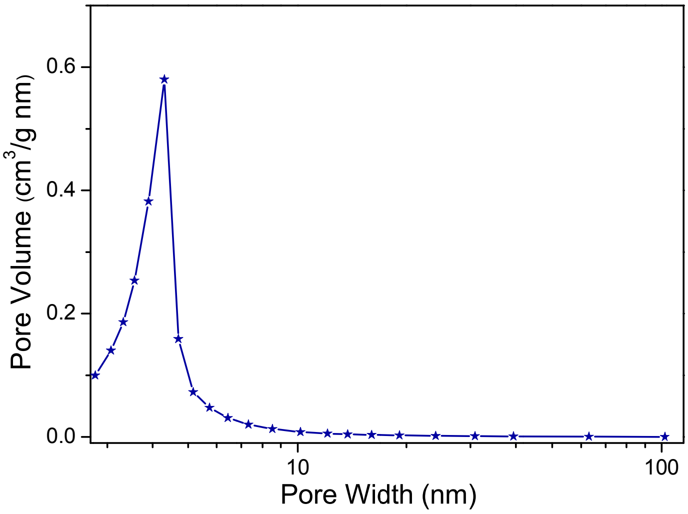

Fig. S12 BJH pore size distribution of nitrogen-free ONC.

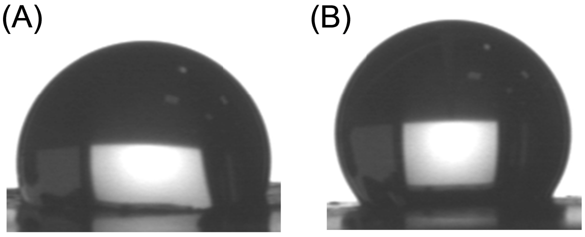

Fig. S13 Optical micrographs of the water droplets on (A) NONC and (B) ONC.

References

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