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Supplementary Information

A Template-Catalyzed *in-situ* Polymerization and Co-assembly Strategy for Rich Nitrogen-Doped Mesoporous Carbon

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Experimental Section

Chemicals.

N,N,N',N",N"-pentamethyldiethylenetriamine (98%) was purchased from J&K China Chemical Ltd. CuBr (CP), urea (AR), formaldehyde solution (37 wt%), styrene (CP), tetrahydrofuran (AR), alcohol (AR), dichloromethane (AR), acetic acid (AR), 1,4-dioxane (AR), hydrochloric acid (37 wt%), petroleum ether (60-90 °C), and neutral alumina (FCP, 200-300 mesh) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethyl α-bromoisobutyrate (98 %) and *tert*-butyl acrylate (99 %) were purchased from Aladdin-Reagent Co., Ltd. Monomer (styrene or *tert*-butyl acrylate) was purified by neutral alumina column to remove the polymerization inhibitor before use. CuBr was washed with acetic acid and alcohol for three times, respectively, and then dried under vacuum. Other chemicals were used as received without any further treatment. Millipore water was used in all experiments.

Synthesis of PS-Br.

Polystyrene with a bromic terminal group (PS-Br) was synthesized by an atom transfer radical polymerization (ATRP) method. Typically, ethyl α-bromoisobutyrate (130 μL) and N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA, 580 μL) were mixed with styrene (60 mL) in a three-necked bottle with stirring. Then the reaction solution in the sealed bottle was bubbled with argon for 30 min before CuBr (200 mg) was added under argon atmosphere quickly. After stirring for another 30 min, the resealed bottle was placed in an oil bath at 90 °C for polymerization under stirring. After 3 h, the viscous solution was quickly taken out from the oil bath, cooled down to room temperature, diluted with dichloromethane and exposed to air with stirring before it was filtered through a neutral alumina column to remove the copper complex using dichloromethane as an eluent. After the filtrate was concentrated, PS_{138}-Br was precipitated in alcohol, and dried under vacuum. Similarly, PS_{230}-Br was prepared through the same procedure, and the reaction time was changed to 5 h.

Synthesis of PS-*b*-PtBA.

Polystyrene-*block*-poly(*tert*-butyl acrylate) with a bromic terminal group (PS-*b*-PtBA) was prepared and purified as a similar procedure as that of PS_{138}-Br. Typically, with PS_{138}-Br as macroinitiator, PS_{138}-*b*-$PtBA_{171}$ was prepared by using 5.0 g of PS_{138}-Br, 100 mg of CuBr, 30 mL of *tert*-butyl acrylate, 290 μL of PMDETA, and 15 mL of 1,4-dioxane at 70 °C for 18 h, and precipitated in a mixed solution of alcohol and water (7/1, v/v) after purification. Similarly, PS_{230}-*b*-$PtBA_{156}$ was prepared through the same process, and the amount of macroinitiator PS_{230}-Br used was changed to 7.9 g.

Synthesis of PS-*b*-PAA.

Polystyrene-*block*-poly(acrylic acid) with a hydroxyl terminal group (PS-*b*-PAA) was obtained through hydrolyzation of PS-*b*-PtBA with concentrated hydrochloric acid according to the previous report.[1] Typically, PS_{138}-*b*-$PtBA_{171}$ (6.0 g) was dissolved in 1,4-dioxane (120 mL), then concentrated hydrochloric acid (24 mL, 37 wt%) was added to the above solution. The mixture was refluxed at 90 °C in an oil bath for 24 h, then cooled down to room temperature, and poured into petroleum ether to precipitate the block copolymer PS_{138}-*b*-PAA_{171}. The product was collected by filtration, and dried under vacuum. Similarly, PS_{230}-*b*-PAA_{156} was prepared through the same process, and the amount of PS_{230}-*b*-$PtBA_{156}$ used was 6.0 g.

Characterization.

The nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal reference. Fourier-transform infrared (FT−IR) spectra were recorded on a Nicolet 5700 or Nicolet iS10 Fourier Transform Infrared Spectrometer. The molecular weight distributions of polymers were estimated by an Agilent 1100 gel permeation chromatography (GPC) system using THF as the eluent against polystyrene standards with a RID detector. Wide-angle X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Advance X-ray diffractometer using a CuKα radiation source (λ = 1.5406 Å). Raman spectra were recorded on a Renishaw inVia Reflex spectrometer. Thermogravimetric analysis (TGA) experiments were conducted on a PerkinElmer TGA 4000 analyzer with a heating rate of 5 °C/min from 25 to 600 °C in nitrogen atmosphere.

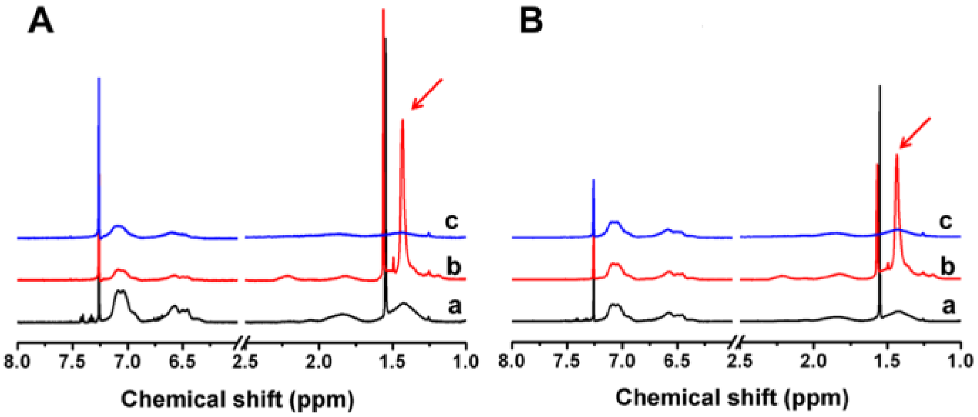

Fig. S1 (A) ^{1}H nuclear magnetic resonance (NMR) spectra (400 MHz, $CDCl_3$) of (a) PS_{138}-Br, (b) PS_{138}-*b*-$PtBA_{171}$ and (c) PS_{138}-*b*-PAA_{171}. (B) ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (a) PS_{230}-Br, (b) PS_{230}-*b*-$PtBA_{156}$ and (c) PS_{230}-*b*-PAA_{156}. The bands at 1.43 ppm (marked by red arrows) in part A and part B disappear after hydrolyzation, respectively, indicating the successful departure of *tert*-butyl groups.

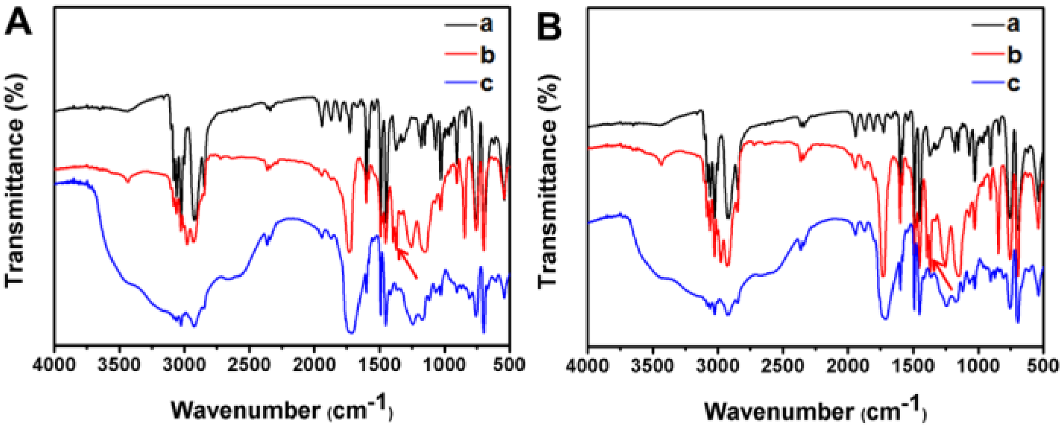

Fig. S2 (A) Fourier-transform infrared (FTIR) spectra of (a) PS_{138}-Br, (b) PS_{138}-*b*-$PtBA_{171}$ and (c) PS_{138}-*b*-PAA_{171}. (B) FTIR spectra of (a) PS_{230}-Br, (b) PS_{230}-*b*-$PtBA_{156}$ and (c) PS_{230}-*b*-PAA_{156}. The split double peaks at around 1380 cm^{-1} (marked by red arrows) in part A and part B are the characteristic absorption peaks of *tert*-butyl groups, respectively. After hydrolyzation, both the disappearance of the characteristic absorption peaks and the appearance of broad peaks at around 3000 cm^{-1} reflect the emerging of carboxyl groups after the departure of *tert*-butyl groups.

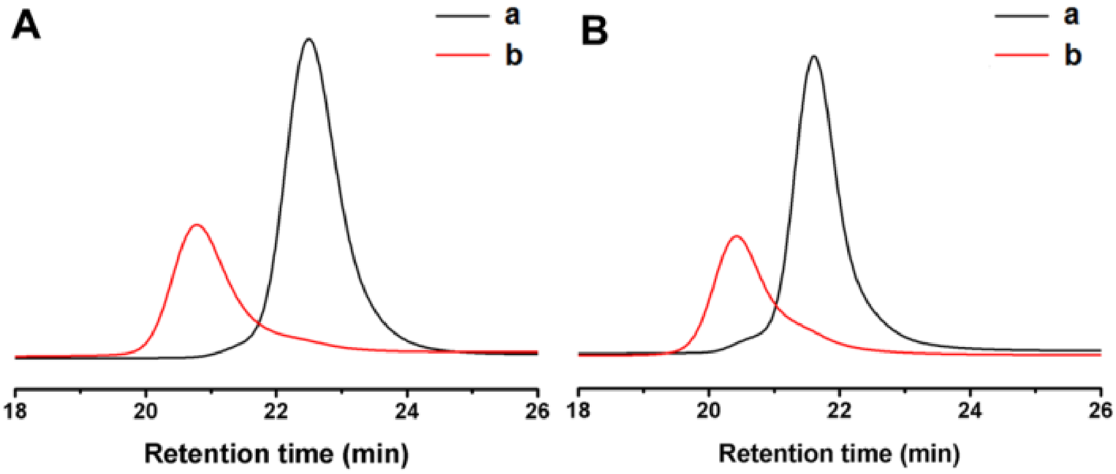

Fig. S3 (A) Gel permeation chromatography (GPC) plots of (a) PS_{138}-Br and (b) PS_{138}-*b*-$PtBA_{171}$. (B) GPC plots of (a) PS_{230}-Br and (b) PS_{230}-*b*-$PtBA_{156}$. The weight-average molecular weights (Mw, g/mol) of polymer PS_{138}-Br, PS_{138}-*b*-$PtBA_{171}$, PS_{230}-Br and PS_{230}-*b*-$PtBA_{156}$ are 14539, 36496, 24158 and 44209, respectively. The average numbers of the styrene unit and the *tert*-butyl acrylate unit in one polymer are calculated based on the weight-average molecular weight. The polydispersity indices (PDI) of polymer PS_{138}-Br, PS_{138}-*b*-$PtBA_{171}$, PS_{230}-Br and PS_{230}-*b*-$PtBA_{156}$ are 1.11, 1.12, 1.09 and 1.15, respectively.

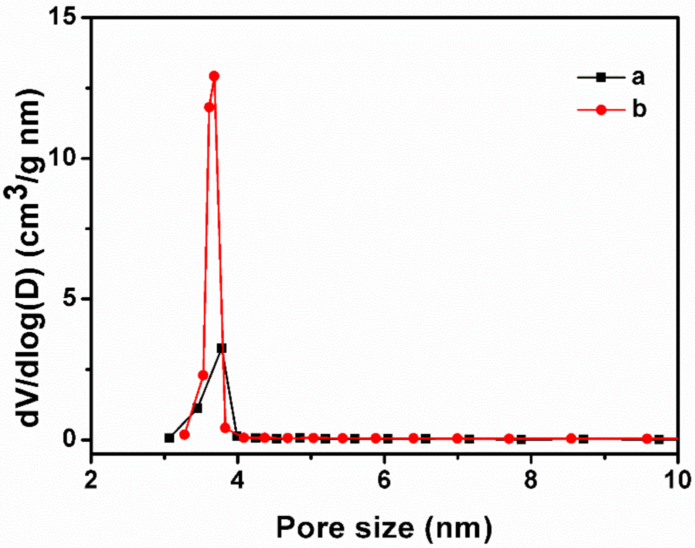

Fig. S4 Pore size distributions derived from the desorption branch for N-doped mesoporous carbons prepared using (a) PS_{138}-*b*-PAA_{171} or (b) PS_{230}-*b*-PAA_{156} as a template, respectively.

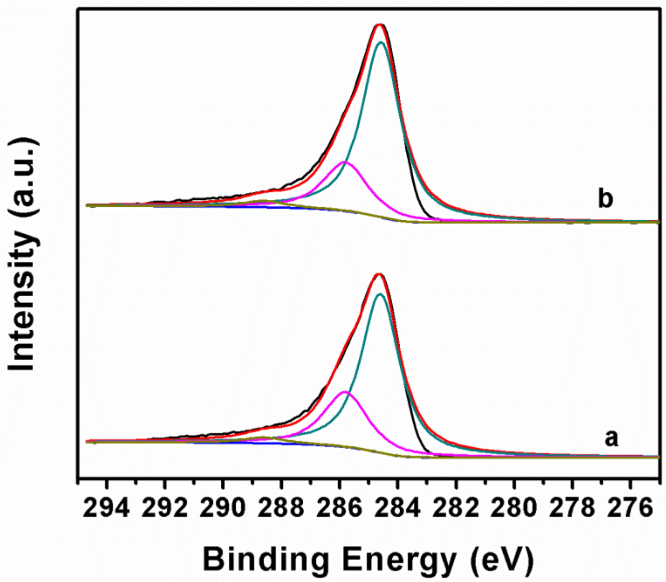

Fig. S5 C_{1s} XPS spectra of N-doped mesoporous carbons prepared with (a) PS_{138}-*b*-PAA_{171} (C-PS_{138}-*b*-PAA_{171}) or (b) PS_{230}-*b*-PAA_{156} (C-PS_{230}-*b*-PAA_{156}) as a template.

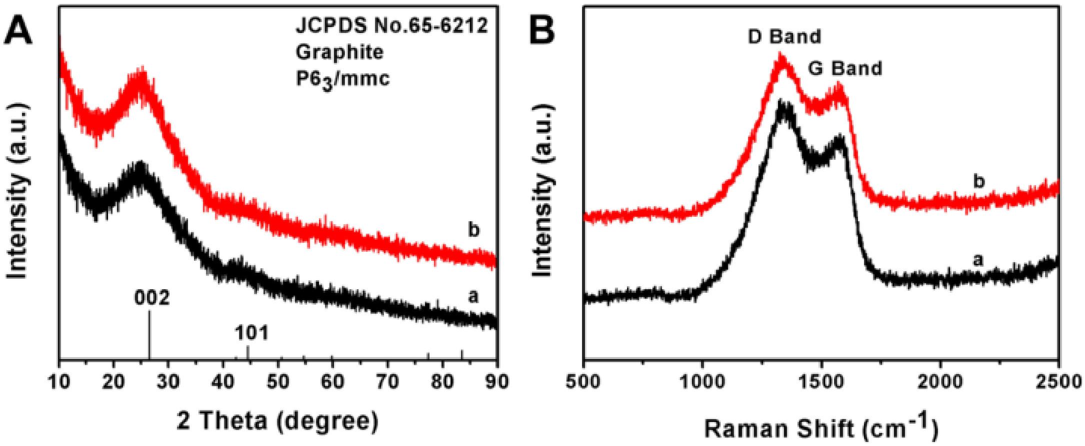

Fig. S6 (A) Wide-angle X-ray diffraction (XRD) patterns and (B) Raman spectra of N-doped mesoporous carbons prepared with (a) PS_{138}-*b*-PAA_{171} or (b) PS_{230}-*b*-PAA_{156} as a template, respectively.

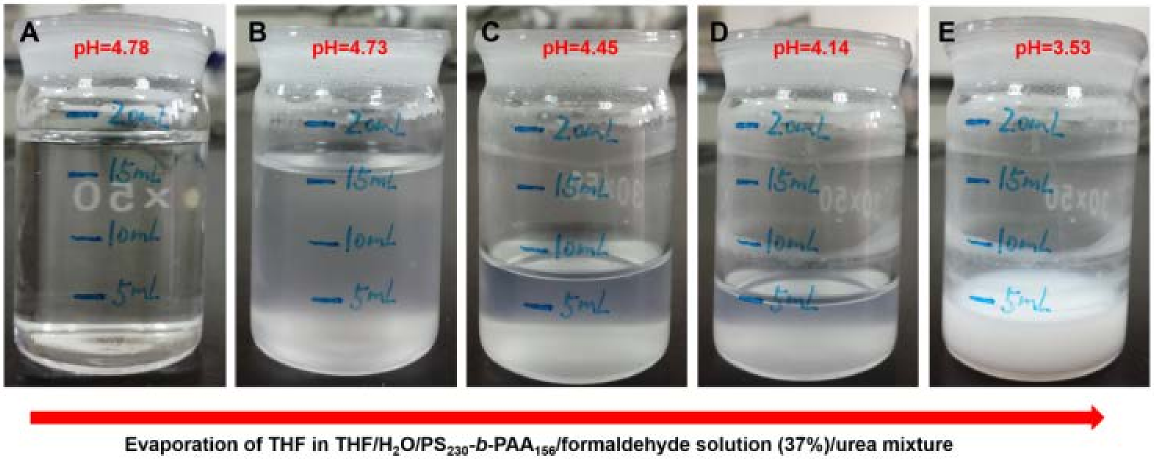

Fig. S7 Optical photographs of the reaction solution as the evaporation of THF. The pH values of the solution are shown inset. In order to monitor the reaction and meter the pH value during evaporation of THF, the reaction solution is left in the reaction bottle instead of the petri dish.

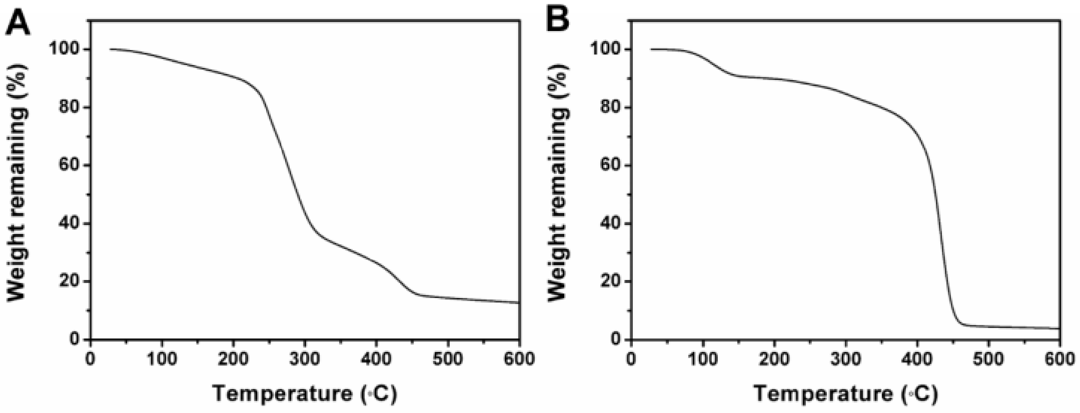

Fig. S8 Thermogravimetric analysis (TGA) curves of (A) the as-made UF resin/PS$_{230}$-*b*-PAA$_{156}$ composites and (B) the block copolymer PS$_{230}$-*b*-PAA$_{156}$ with a heating rate of 5 °C /min from 25 to 600 °C in nitrogen atmosphere.

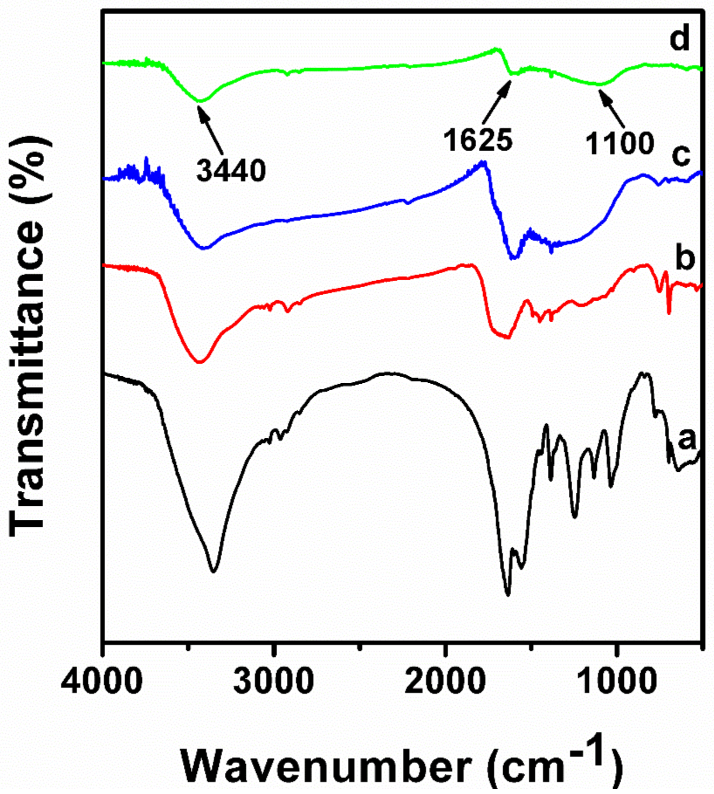

Fig. S9 FTIR spectra of (a) the as-made UF resin/PS$_{230}$-*b*-PAA$_{156}$ composites, (b) the intermediate product at 300 °C, (c) intermediate product at 450 °C and (d) N-doped mesoporous carbon at 600 °C after pyrolysis of the composites in nitrogen atmosphere.

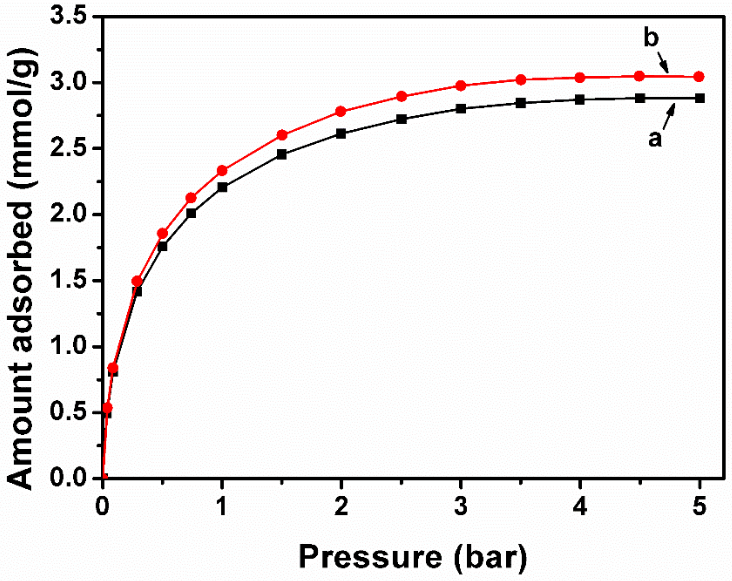

Fig. S10 High pressure adsorption isotherms of the N-doped mesoporous carbons with (a) PS_{138}-*b*-PAA_{171} or (b) PS_{230}-*b*-PAA_{156} as a template for CO_2 at 298 K.

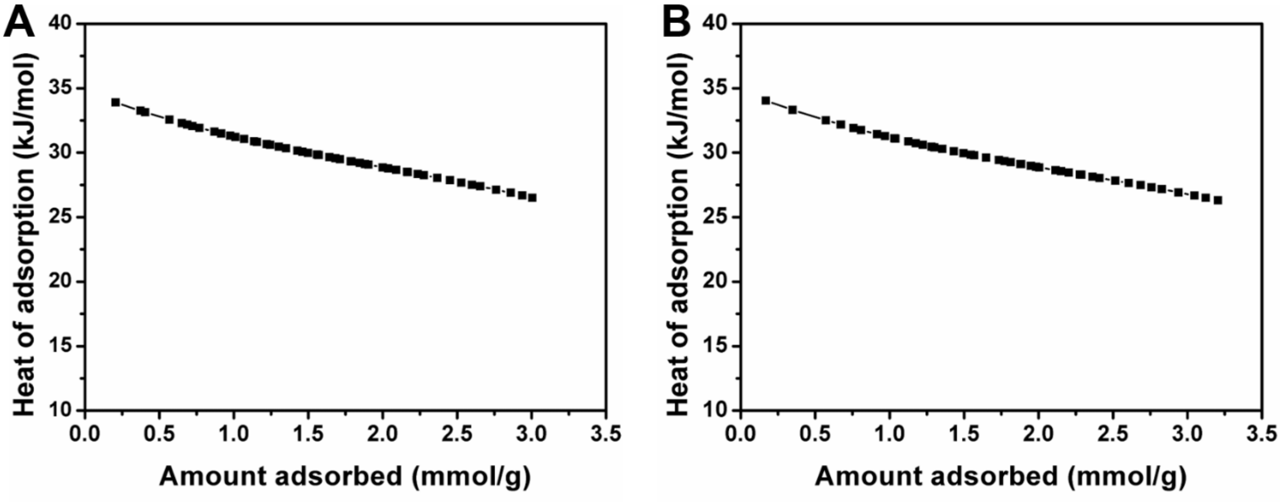

Fig. S11 Plots of isosteric heat of adsorption with CO_2 loading on N-doped mesoporous carbons prepared with (A) PS_{138}-*b*-PAA_{171} or (B) PS_{230}-*b*-PAA_{156} as a template.

Table S1 The C_{1s} XPS core level peak analyses of N-doped mesoporous carbons prepared with (a) PS_{138}-*b*-PAA_{171} (C-PS_{138}-*b*-PAA_{171}) or (b) PS_{230}-*b*-PAA_{156} (C-PS_{230}-*b*-PAA_{156}) as a template.[a]

sample	C-1 (%)	C-2 (%)	C-3 (%)
C-PS_{138}-*b*-PAA_{171}	69.8	27.3	2.9
C-PS_{230}-*b*-PAA_{156}	73.7	23.2	3.1

[a] Each peak corresponds to a specific type of C species: C-1 (284.6 eV): sp^2 hybridized carbon; C-2 (285.8 eV): C=N bond; C-3 (288.6 eV): C-O bond.

Table S2 Summary of CO_2 uptake performance of N-doped mesoporous carbon materials prepared by using PS_{138}-*b*-PAA_{171} or PS_{230}-*b*-PAA_{156} as a template in comparison to reported N-doped carbons with the high capacity or the excellent selectivity.

sample	N content (wt%)	S_{BET} (m^2/g)	CO_2 uptake capacity[a] (mmol/g)	normalized capacity[b] ($\mu mol/m^2$)	IAST selectivity[c] CO_2/N_2	ref
HCM-DAH-1	-	670	2.6	3.88	-	[2]
MCN-7-130	-	901.1	1.40	1.55	-	[3]
SU-MAC-500	5.8	941	4.50	4.78	39:1	[4]
nCN2600	5.9	979	2.8	2.9	-	[5]
Py2600	12.4	976	3.4	3.5	49:1[d]	[5]
nZDC700-cln	-	950	3.51	3.70	79:1[d]	[6]
NPC-650	4.11	1561	3.10	1.99	-	[7]
N-HCSs	14.8	767	2.67	3.48	-	[8]
NDAB3-500	5.4	1863	2.1	1.13	-	[9]
KNC-A-K	10.5	614	4.04	6.6	48:1	[10]
KNC-A-HCl	12.9	1004	4.03	4.0	26:1	[10]
SBA-NC	17.4	726	2.34	3.2	31:1	[10]
C-PS_{138}-*b*-PAA_{171}	18.95	476	2.24	4.71	60:1	this work
C-PS_{230}-*b*-PAA_{156}	18.88	458	2.36	5.15	67:1	this work

[a] CO_2 uptake capacity at 298 K and 1 bar. [b] normalized CO_2 capacity at 298 K and 1 bar. [c] IAST selectivity for the mixture of 0.1/0.9 CO_2/N_2 at 298 K and 1 bar. [d] IAST selectivity for the mixture of 0.15/0.85 CO_2/N_2 at 298 K and 1 bar.

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