Supporting Information

One-step Carbonization Route to Nitrogen-doped Porous Carbon Hollow Spheres with Ultrahigh Nitrogen Content for CO₂ Adsorption

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Experimental Section

Chemicals Melamine was obtained from Tianjin Guangfu Fine Chemical research Institute. Cetyltrimethylammonium bromide (CTAB), Formaldehyde aqueous solution (37~40%) and Ammonium solution(25~28%) were of analytical grade and purchased from Sinopharm Chemical Reagent Co.Ltd. Pluronic F127 was obtained from Sigma–Aldrich. All chemicals were used as received without any further purification. Deionized water was used for all experiment.

Synthesis of MF template

MF spheres was synthesized using a hydrothermal way. 1.4g melamine and 2.0mL Formaldehyde solution was add to 100 mL deonized water and stirred at 50 $^{\circ}$ C for 40 min . After 40 min the clear solution was mixed with solution containing 2.0g of F127 and 200 mL deonized water. The mixture was stirred for 6h and transferred to teflon reactor without stirring and kept at 100 $^{\circ}$ C for 2 days then the obtained white solution was centrifuged and washed with ethanol, the obtained deposit donated as MF.

Synthesis of N-PCHS

Core shell MF@RF spheres was synthesized using a modified method^[1]. Generally the as obtained MF spheres was homogeneously dispersed in a mixture of deionized water (35mL) and ethanol (14mL) by ultrasonication , followed by adding of CTAB(1.15g) ,resorcinol (0.2g) and ammonium solution(0.05mL), then kept stirring at 35 °C. 30 min later 0.6ml formaldehyde solution was added into the dispersion. The mixture was stirred for 6h then cooled to room temperature and aged without stirring for 12h. The product was collected by centrifugation and washed with water for two times and ethanol for once. Then the products was dried at 80°C for at least 6h. The obtained sample was calcined under high-purity argon stream and heated to150 °C at a rate of 10 °C/min and kept in this temperature for 2h , then raised at 1 °C/min to the final temperature and kept for 1h .

Synthesis RF spheres

RF sphere was synthesized using the Liu's method^[2] for comparison. 0.1g resorcinol was added into a mixture containing ammonium solution (0.1mL) ,ethanol (8mL) and 20mL water, after stirred for 30 min, 0.14mL formaldehyde solution was added into the solution, the mixture was stirred for another 24 h, then the obtained RF spheres was collected through centrifugation and washed with water and ethanol then dried at 80°C.

Materials Characterization

SEM was performed on a Hitachi S-5200 electron microscope. TEM images were obtained on an FEI Tecnai G2 F20s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200 kV. Powder XRD patterns were obtained by using a Rigaku 2550 diffractometer with Cu Ka radiation (λ =0.15418 nm). N₂ adsorption-desorption isotherms were obtained at 77K on a Micromeritics ASAP 2020 sorptometer. Samples were degassed at 150 °C for a minimum of 12 h prior to analysis. The BET (Brunauer–Emmett–Teller) surface area (BET) was calculated using the N₂ adsorption isotherm data within the relative pressure ranging from 0.05 to 0.25. Total pore volume was obtained at a relative pressure of 0.995. Micropore volumes were determined according to theV–t plot method The pore size distributions (PSDs) and the ultramicropores volume were obtained from the N₂ adsorption isotherms using the Original Density Functional Theory method. The IR spectra were acquired using a Bruker IFS 66 V/S FTIR spectrometer. The X-ray photoelectron spectroscopy (XPS) spectra were acquired using an ESCALAB250 spectrometer.

Notes and references

[1] B. Guan, X. Wang, Y. Xiao, Y. Liu, Q. Huo, Nanoscale., 2013,5, 2469.

[2] J. Liu, S. Z. Qiao, H. Liu, J. Chen, A. Orpe, D. Zhao, G. Q. Lu, Angew. Chem. Int. Ed., 2011, 50, 5947.



Fig. S1 SEM images of MF, MF@RF and TEM image of MF@RF spheres .



Fig. S2 TG curves of RF(red),MR(black),MF(blue) in nitrogen atmospheres at a heating rate of 10 $^{\circ}$ C from 30 $^{\circ}$ C to 800 $^{\circ}$ C.



Fig. S3 FTIR spectrum of N-PCHS carbonized at 900 $^\circ\!\mathrm{C}$



Fig.S4 X-ray photoelectron spectra(XPS) survey spectrum of N-PCHS carbonized at different temperature: 600 $^{\circ}C(A)$, 700 $^{\circ}C(B)$, 800 $^{\circ}C(C)$, 900 $^{\circ}C(D)$, the insert is the corresponding content of each element .



Fig.S5 X-ray photoelectron spectra(XPS) high-resolution spectra of N1s for N-PCHS carbonized at different temperature: 600 $^{\circ}C(A)$, 700 $^{\circ}C(B)$, 800 $^{\circ}C(C)$, 900 $^{\circ}C(D)$.



Fig.S6 X-ray photoelectron spectra(XPS) high-resolution spectra of C1s for N-PCHS carbonized at different temperature: $600^{\circ}C(A)$, $700^{\circ}C(B)$, $800^{\circ}C(C)$, $900^{\circ}C(D)$.

т(℃)	S/N [a]	C/N [b]	pyridinc-N			pyrrolic-/pyridonic-N			graphitic-type quaternary-N		
			B.E. (eV)	FWHM	%	B.E. (eV)	FWHM	%	B.E. (eV)	FWHM	%
600	71.29	17.54	398.63	1.57	52.18	400.46	1.37	27.57	401.40	2.03	20.25
700	131.82	21.85	398.45	1.40	51.04	400.00	1.08	16.25	401.02	1.29	32.71
800	149.61	23.86	398.33	1.36	34.82	400.00	1.03	9.14	401.00	1.75	56.04
900	303.92	46.40	398.30	1.56	30.87	400.00	1.00	2.75	401.00	1.95	66.38

Table S1. [a], Surface area to N ratio obtained from XPS spectra. [b], carbon to nitrogen ratio . Binding energies and relative surface concentrations of nitrogen species obtained by fitting the N1s core level XPS spectra.



Fig.S7 X-ray diffraction spectra(XRD) of N-PCHS carbonized at different temperature: 600 $^{\circ}C(black)$, 700 $^{\circ}C(green)$, 800 $^{\circ}C(blue)$, 900 $^{\circ}C(red)$.



Fig. S8 (A) SEM image of N-PCHS carbonized at 900 $^{\circ}$ C, (B) EDX spectra show the chemical composition of the areas labeled by the yellow square.

T(° C)	BET	Ms	V _t	V _{mi}	V _{ul}	Elemental analysis (wt%)					surface area/N
	(m ² · g ⁻¹)	(m ² · g ⁻¹)	(cm³/g)	(cm³/g)	(cm³/g)	С	N	Н	O(Calculated)	C/N	
600	365	245	0.43	0.13	0.03	78.40	15.91	1.43	4.26	4.93	22.94
700	551	438	0.38	0.17	0.13	80.26	15.35	0.88	3.51	5.23	35.90
800	579	457	0.70	0.21	0.17	84.72	11.04	0.65	3.59	7.67	52.44
900	775	630	0.87	0.32	0.21	87.77	8.39	0.42	3.42	10.46	92.37
BET, BET surface area; M_{s_i} Micropore Area; V_{t_i} total pore volume; V_{mi} , micropore volume; V_{ul_i} ultramicropore volume(cm ³ /g)											

Table S2. Element analysis results, BET surface area and corresponding Micro pore area of N-PCHS carbonized at different temperature.



Fig.S9 N2 sorption isotherms and corresponding pore size distribution of N-PCHS carbonized at different temperature .



Fig.S10 CO2(red) and N2 (black) adsorption of N-PCHS-900 obtained at different temperature A(273K) ,B(298K).



Fig.S11 Adsorption selectivity of CO2 over N2 for N-PCHS-900 from initial slope calculations isotherms collected at 273K.



Fig.S12 Adsorption selectivity of CO2 over N2 for N-PCHS-900 from initial slope calculations isotherms collected at 273K.

	273K	298K	Ref.
N-PHCS-900	4.42 mmol·g-1 (19.4wt%)	2.96 mmol·g-1 (13wt%)	This work
HEXPOP-3(Porous Polymers)	18wt%		1
C1M3-Al(microporous organic polymers)	18.1wt%		2
N-HCSs(nitrogen-doped hollow carbon)		2.67mmol·g-1	3
NOMC-K(activited carbon)	4.9mmol∙g-1	3.1 mmol∙g-1	4
N-OMCs-0.1(nitrogen-doped ordered mesoporous carbon)		2.43mmol·g-1	5
MCN-1-130s(mesoporous CN based hybrid materials)		1.61mmol·g-1	6
NMgC-2.4(doped Mesoporous Carbon)		2.45 mmol∙g-1	7
MCN-7-130(mesoporous carbon nitride)		1.40mmol·g-1	8
PAF-1-450(carbonized porous aromatic framework)	4.5 mmol g-1		9

Table S3. Comparison of N-PHCS-900 and some recently reported adsorbents for CO2capture at ~1 bar and 273K or 298K.

	273K	298K	Ref.
N-PHCS	35	21	This work
NC-800(Nitrogen-Doped Microporous Carbon)	21.6		10
PC-2(porous carbon)	27.3	18.5	11
NPC-650(polyimine-based carbon)	23.4	12.5	12
CCMs(carbon composite monolith)	32.6	19.8	13
NG7(nitrogen doped graphene/polyaniline material)		17.9	14
N-HCSs (nitrogen-doped hollow carbon)		29	3
PC(Poly(vinylidene chloride)-Based Carbon)		12.59	15

Table S4. comparison of CO2/N2 selectivity of N-PHCS-900 with other materials , based on the initial slopes of N2and CO2adsorption isotherms.

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