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Electronic Supplementary Material

Large-scale synthesis of mesoporous carbon microspheres with controllable structure and nitrogen doping using a spray drying method

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1. Experimental details

1.1 Materials and reagents

Rresorcinol (99.5%, Sinopharm Chemical), formaldehyde (37-40%, Sinopharm Chemical), silica sols (Ludox SM-30, Ludox HS-40, Ludox TM-40, Sigma-Aldrich), sodium hydroxide (96%, Sinopharm Chemical), Vitamin B12 (98%, Sigma-Aldrich), melamine (99%, Sinopharm Chemical) were all used without any further purification.

1.2 Preparation of MCMSs

The resorcinol and formaldehyde were added into the silica sols with continuous magnetic stirring, after which the sol was further diluted with distilled water to the desired content (%w/v). The mole ratio of resorcinol/formaldehyde was fixed at 2 and the weight ratio of resorcinol-formaldehyde/SiO_2 was adjusted to 0.5, 0.75, 1.0, respectively. The mixed sol was stirred for 1 h at 40 °C, and then spray-dried using a spray-dryer (Blon-6000y, Shanghai Bilon Instrument Co., Ltd). The solution was pumped into the nozzle at the rate of 500-1000 ml/h, together with a constant spray air flow. The liquid was atomized into fine droplets at a constant pressure of 0.3 MPa. The inlet temperature was set to 120 °C, generally the outlet temperature was in the range of 58-65 °C. Fine powder was discharged continuously from the drying chamber and then collected using a cyclone separator. The powder was then carbonized in a nitrogen flow at 800 °C for 3 h with a heating rate of 5 °C min^{-1}. Finally, the MCMSs were obtained by the dissolution of silica nanoparticles in 2 M NaOH solution at 80 °C, isolated by filtration, washed with distilled water and ethanol, and dried at 100 °C.

Nitrogen-doped MCMSs were obtained by adding melamine into resorcinol-

formaldehyde solution. Melamine and formaldehyde with the mole ratio of 1:2 were dissolved in 50 ml of distilled water at 80 ^{o}C with consecutive agitation until the solution became clear. The solution was cooled down to 40 ^{o}C, and then resorcinol and formaldehyde were added with continuous magnetic stirring. The above solution was mixed with the silica sol and further diluted with distilled water to the desired content. The mole ratio of melamine/ resorcinol was changed from 0 to 1 and the weight ratio of resorcinol-melamine-formaldehyde/SiO_2 was adjusted to 0.75. The spray conditions and carbonization, silica removal procedures were same with these of MCMSs.

1.3 Characterizations

The morphologies of samples were observed under field emission scanning electron microscopy (SEM, FEI Q-300) and transmission electron microscopy (TEM, JEOL 2100F).

Nitrogen adsorption/desorption isotherms were measured with a Quadrasorb SI analyzer. Before the measurements, the samples were degassed in vacuum at 120 ^{o}C for 12 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore diameters were derived from desorption branch according to Barrett-Joyner-Halenda (BJH) method. The total pore volumes were calculated from the total amount adsorbed at relative pressures near unity.

The surface chemistry of the samples was analyzed using an Axis Ultra DLD X-ray photoelectron spectroscopy. The X-ray source operated at 15 kV and 10 mA. The working pressure was lower than 2× 10−8 Torr (1 Torr = 133.3 Pa). The C1s, N1s

XPS spectra were measured at 0.1 eV step size. The N1s XPS signals were fitted with mixed Lorentzian−Gaussian curves, and a Shirley function was used to subtract the background using a XPS peak processing software.

The volume weighted particle size distribution (PSD) was measured on Mastersizer 2000 by using laser diffraction with an obscuration of 4.73%.

Elemental analysis was carried out using Elemental Vario EL III. The carbon (C), hydrogen (H), and nitrogen (N) contents were determined using the thermal conductivity detector.

The thermogravimetric analysis (TA Instrument Q600 Analyzer) was carried out in a nitrogen flow rate. The samples were heated to 800 °C at a rate of 10 °C min−1.

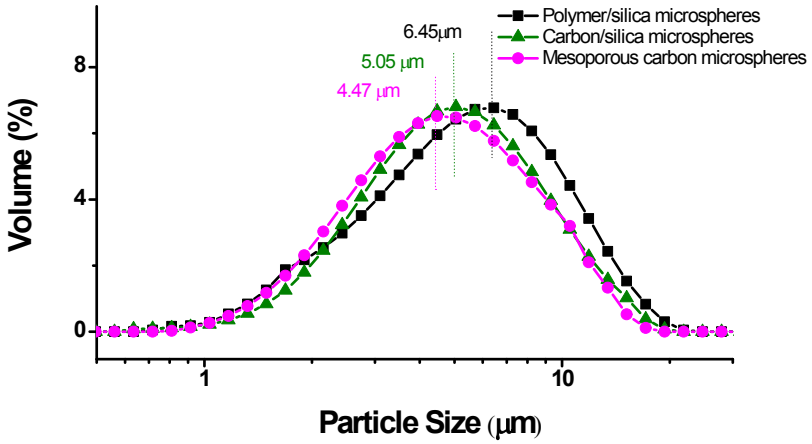

Fig. S1 Particle size distributions of polymer/silica, carbon/silica and mesoporous carbon microspheres. During the pyrolysis process, the average particle size of microspheres experience 21% shrinkage in diameter (from 6.45 μm to 5.05 μm). NaOH etching and drying process result the further shrinkage of 13%.

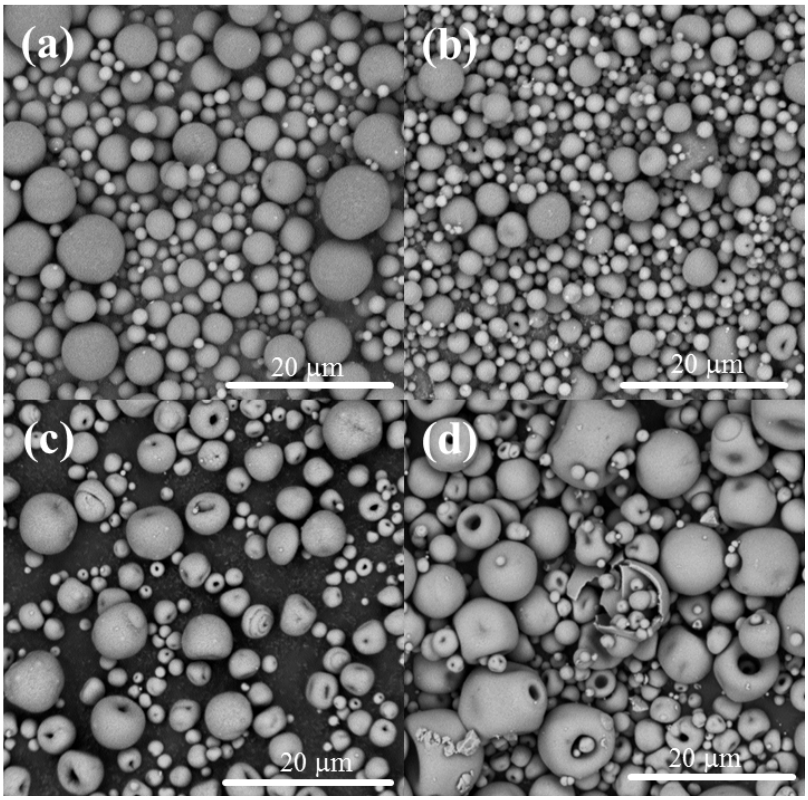

Fig. S2 Polymer/silica microspheres obtained at different inlet temperatures. (a) 120 ^{o}C, (b) 160 ^{o}C, (c) 200 ^{o}C and (d) 240 ^{o}C. Typically, hollow, mushroom-like deformed and crushed particles were formed at inlet temperature of 200 ^{o}C. Integrallty spherical shape, smooth surface, dense structure particles were obtained until temperature decreased to 120 ^{o}C.

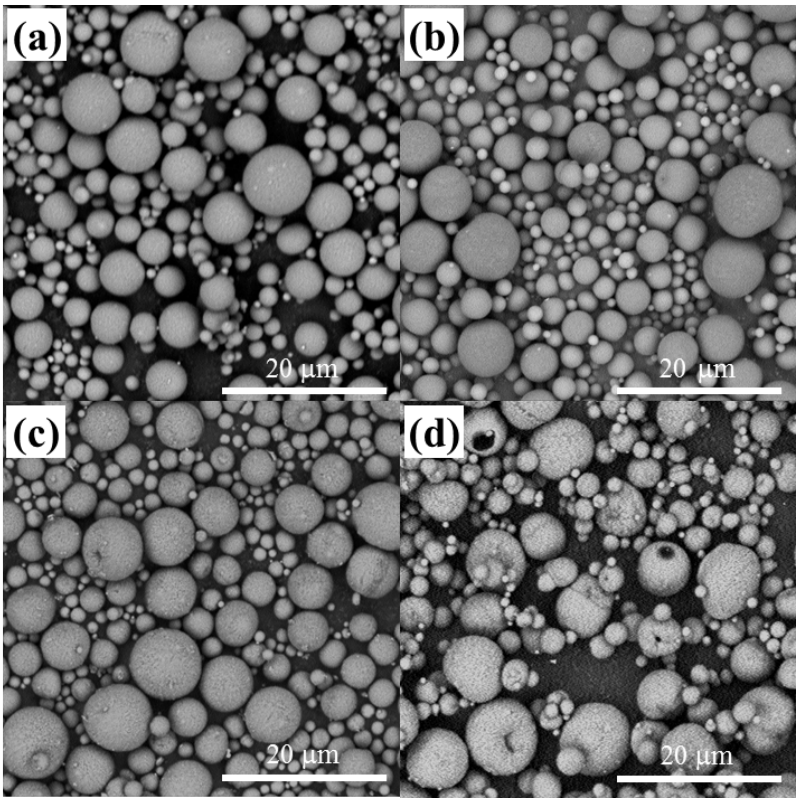

Fig. S3 Polymer/silica microspheres obtained at different precursor (R+F) concentration. (a) 5%w/v, (b) 7.5 %w/v, (c) 10%w/v and (d) 15%w/v. Deformed and crushed particles with some aggregates were formed at a high precursor concentration of 15% w/v.

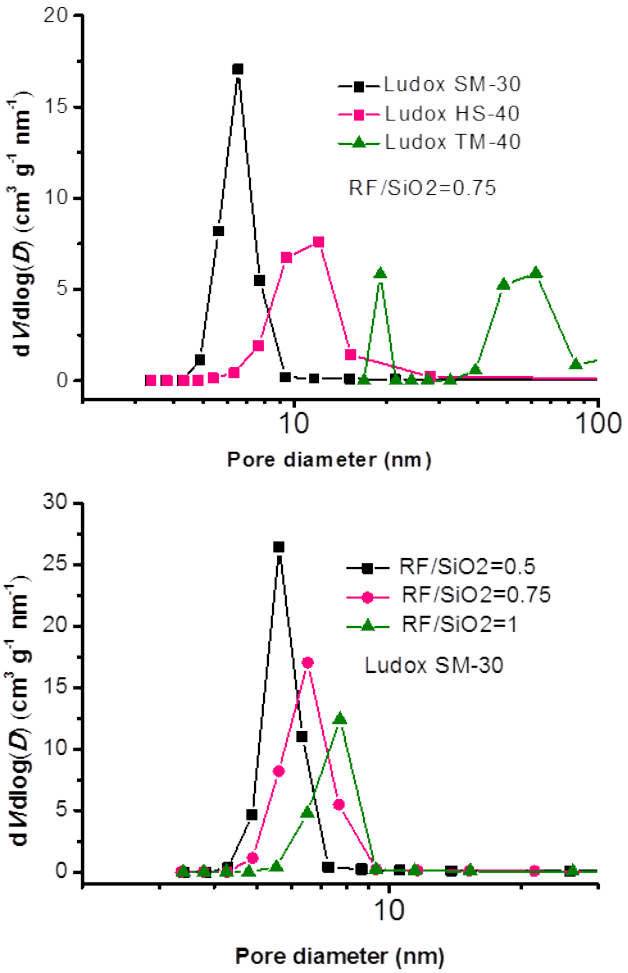

Fig. S4 BJH pore size distributions curves of MCMSs with different mesoporous structures.

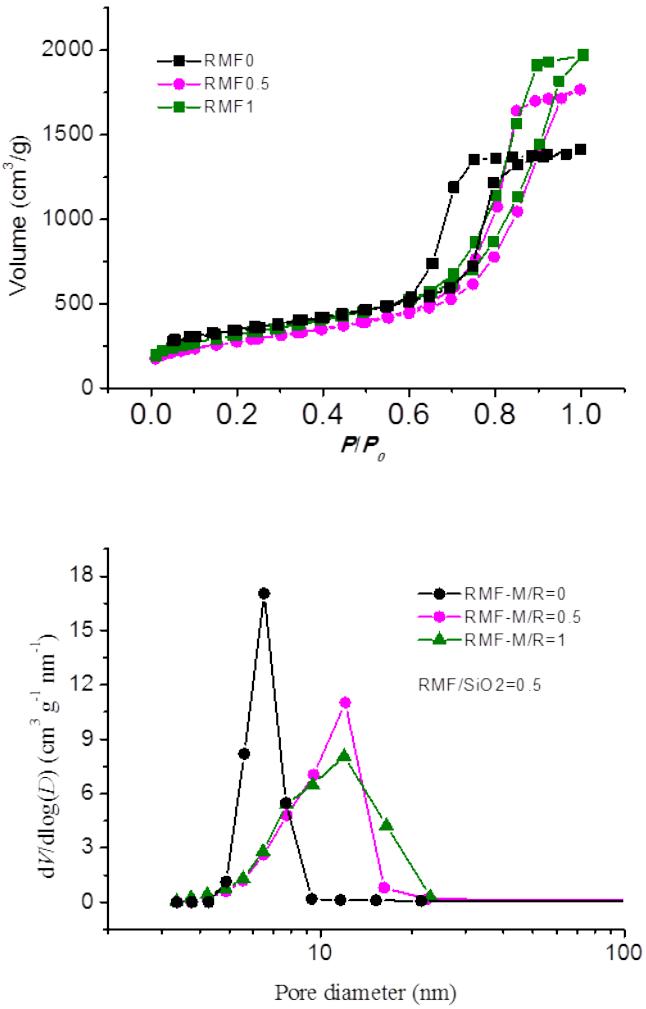

Fig. S5 N_2 adsorption-desorption isotherms and resulting BJH pore size distributions curves of MCMSs with different mesoporous structures. The nitrogen-doped MCMSs have a larger mesopore size compared to the nitrogen-free samples, due to the high-level decomposition of melamine-modified RF framework. Meanwhile, at the same polymer/silica ratio (RF/silica or RMF/silica=0.75), the MCMSs with larger M/R ratio have higher total pore volume due to the decomposition of melamine.

Table S1 The pore structure parameters of the MCMSs

Type of Silica sol	Weight ratio of polymer/silica	M/R	S_{BET} m^2/g	S_{meso} m^2/g	V_{Total} cm^3/g	V_{meso} cm^3/g	Diameter nm
SM-30	0.75	0	1205	905	2.3	2.2	6.5
HS-40	0.75	0	1116	557	2.1	1.9	11.3
TM-40	0.75	0	925	451	2.3	2.2	19.5, 50-80
SM-30	0.5	0	1220	845	2.7	2.5	6.0
SM-30	1	0	928	412	1.5	1.3	7.7
SM-30	0.75	0.5	980	433	2.7	2.5	12.5
SM-30	0.75	1	1138	1025	3.1	3.0	12.5

Table S2 Elemental analysis results of nitrogen-doped MCMSs

Sample	N wt.%	C wt.%	H wt.%	N/C at./at.
M/R=0	0	90.6	1.55	0
M/R=0.5	3.27	87.62	1.39	0.037
M/R=1	6.22	82.60	1.46	0.075

Table S3 XPS results of N-doped MCMSs

Sample	N at.%	Pyridinic N %	Pyrrolic N %	Graphitic N %	Pyridine N-oxide %
M/R=0.5	5.12	37.0	27.5	23.7	11.8
M/R=1	11.5	33.4	26.5	26.2	13.8

VB12 adsorption experiment

Ultrapure water (18 MΩ station Millipore Milli-Q Plus) were used for all adsorption experiments. Before the equilibrium isotherm testing, the adsorption rate of VB12 was tested. The test samples (300 mg) were suspended in 1000 ml of 500 mg/L VB12 aqueous solution at the initial pH value 7.2 (natural solution pH value of VB12). The mixture was continuously shaken in a shaking bath at 150 shake/min and at 25 ◦C. For the VB12 adsorption isotherm determination, 100 mg of different samples was suspended in 100 ml of solutions with concentrations ranging from 25 to 500 mg/L. The resulting mixture was continuously shaken in a shaking bath at 25 ◦C until equilibrium was reached (typically 24 h).

Langmuir equations were used to describe experimental adsorption isotherm data. The Langmuir equation can be written as $\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{bq_m}$, where b is the Langmuir constant, q_m is the monolayer capacity (mg/g), q_e is the equilibrium adsorption capacity (mg/g) and Ce is the equilibrium concentration (mg/L).

Table S4 Isotherm parameters for VB12 adsorption

Adsorbent		Langmuir parameters		
		b	q_m (mg/g)	R^2
RF/SiO2= 0.75	Ludox SM-30	0.095	434.78	0.994
RF/SiO2=0.75	Ludox HS-40	0.094	357.14	0.996
RF/SiO2=0.5	Ludox SM-30	0.134	500.00	0.996

R^2 stands for correlation coefficient of the Langmuir equation