Supporting Information

Synthesis of nitrogen-doped hollow carbon nanospheres for CO_2 capture

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Experimental Section

Chemicals. Tetraethyl orthosilicate (TEOS), resorcinol, formaldehyde solution (37 wt%), melamine, methanol, ethanol and concentrated ammonia solution (28 wt%), were of analytical grade and purchased from Shanghai Chemical Corp. Deonized water was used for all experiment.

Synthesis of core-shell SiO_2@resorcinol-formaldehyde nanospheres (SiO_2@RF). Monodisperse core-shell SiO_2@RF spheres were prepared by a modified Stöber coating method. Generally, 0.85 mL of TEOS mixed with 15 mL of ethanol was added to a solution containing ethanol (10 mL), deionized water (3 mL) and ammonia aqueous solution (2 mL) under stirring. After 1 h, 0.2 g of resorcinol and 0.28 mL of formaldehyde solution were added, respectively. The solution was stirred for 24 h at room temperature, then transferred to a 40-mL Teflon-lined stainless steel autoclave, and hydrothermally treated for 24 h at 373 K. After cooling down, the solid product was obtained by washed and air-dried at 60 °C for several hours.

Synthesis of nitrogen-doped hollow carbon spheres (N-HCSs). The nitrogen doped hollow carbon spheres were prepared according to the literature method.[1] Typically, 0.3 g of melamine was dispersed in 4 mL of methanol; and 0.5 g of the core-shell SiO_2@RF spheres obtained above were added with stirring at room temperature until methanol was full evaporated. The as-loaded methanol/SiO_2@RF powder samples were calcined under high-purity nitrogen stream at 600 °C for 1 h with a temperature ramp of 3 °C min^{-1}, denoted as SiO_2@N-CSs. After the composites immersed in 10 wt% HF solutions for 24 h, the SiO_2 colloidal cores were removed and N-HCSs were obtained.

Materials Characterization.

Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100 F microscope (Japan) operated at 200 kV. The samples for the TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Field-emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4800 microscope. The dried samples were directly used for the observation without any treatment. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 180 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas.

Elemental analyses were done on an Elementar Vario EL III microanalyzer. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV) or Al Kα radiation ($h\nu$ = 1486.6 eV). Binding energies were calibrated by using the containment carbon (C_{1s} = 284.6 eV). The CO_2 adsorption isotherms were measured in a temperature-controlled water bath on IGA gravitometer adsorption apparatus. The samples were degassed at 200 °C for 8 h (increasing rate: 10 $°C \cdot min^{-1}$, outgas rate: 50 $mbar \cdot min^{-1}$).

Reference

1. Z. Wu, P. A. Webley and D. Y. Zhao. *J. Mater. Chem.* 2012, **22**, 11379.

Table S1. Element analysis results of the N-doped hollow carbon nanospheres (N-HCSs).

Sample	C (%)	H (%)	N (%)	O (Calculated**)** (%)
N-HCSs	66.73	4.04	14.77	14.46

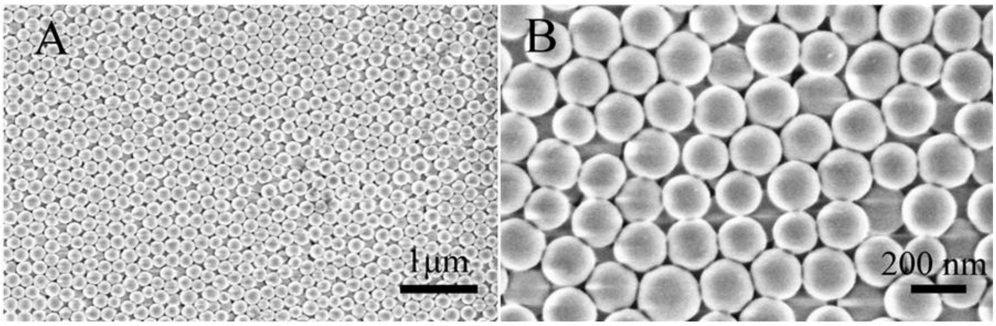


Fig. S1 SEM images (A and B) with different magnification of the colloidal SiO_2 spheres prepared via classical the Stöber method.

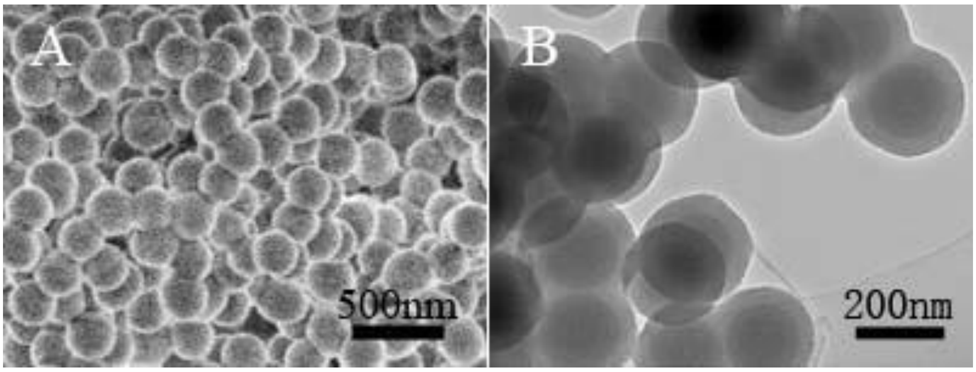


Fig. S2 FESEM (A) and TEM (B) images of the core-shell SiO_2@RF nanospheres prepared via a modified Stöber coating method.

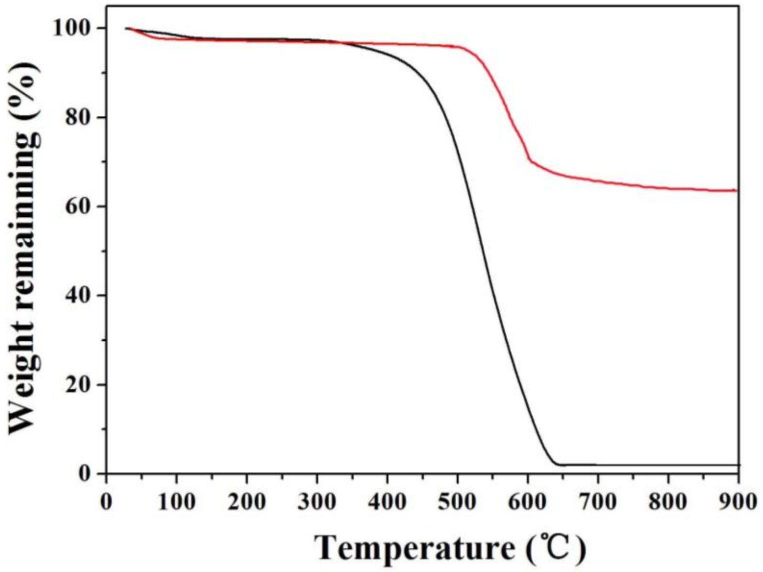


Fig. S3 TG curve of the N-HCS in air (black) and N_2 (red) atmospheres with a heating rate of 5 °C /min from 25 to 700 °C.

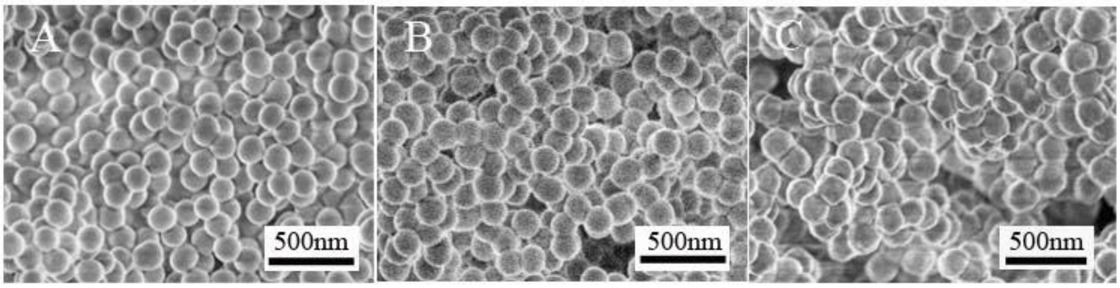


Fig. S4 FESEM images of the core-shell SiO_2@N-CS spheres synthesized with different resorcinol concentrations: (A) 0.0885; (B) 0.118; (C) 0.236 mol/L.

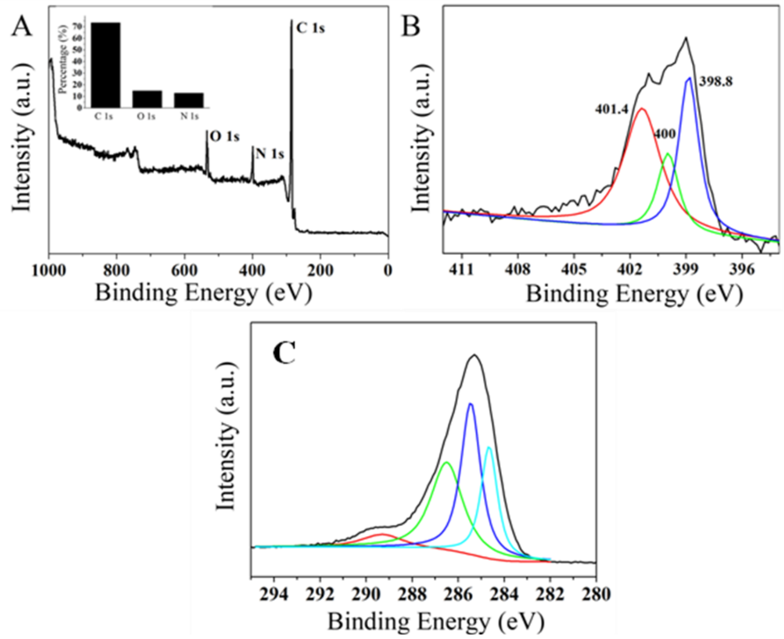
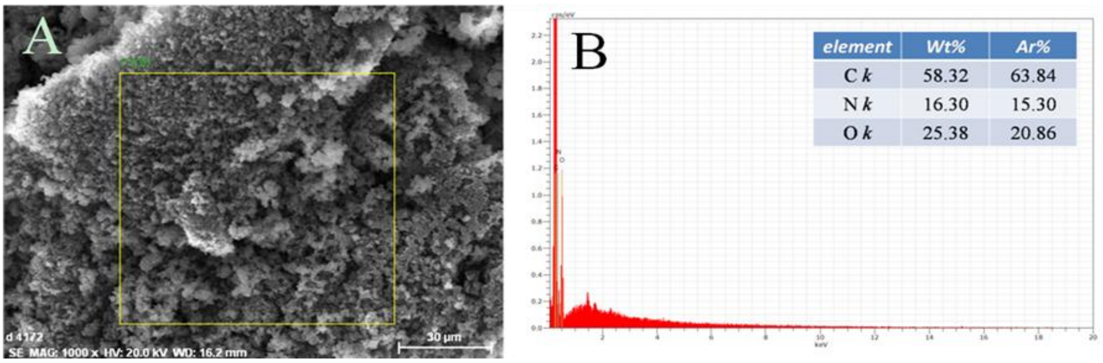


Fig. S5 X-ray photoelectron spectra (XPS) of the N-HCS spheres prepared via a two-step Stöber method followed by the carbonization with melamine and the removal of cores: A) the survey spectrum; B) N_{1s} and C) high-resolution spectra of C_{1s}. The insert in A is the corresponding content of each element.



element	Wt%	Ar%
C *k*	58.32	63.84
N *k*	16.30	15.30
O *k*	25.38	20.86

Fig. S6 (A) Typical SEM image of N-HCSs via a two-step Stöber method followed by the carbonization with melamine and the removal of the silica cores and (B) EDX spectra show the chemical composition of the areas labeled by the yellow square.

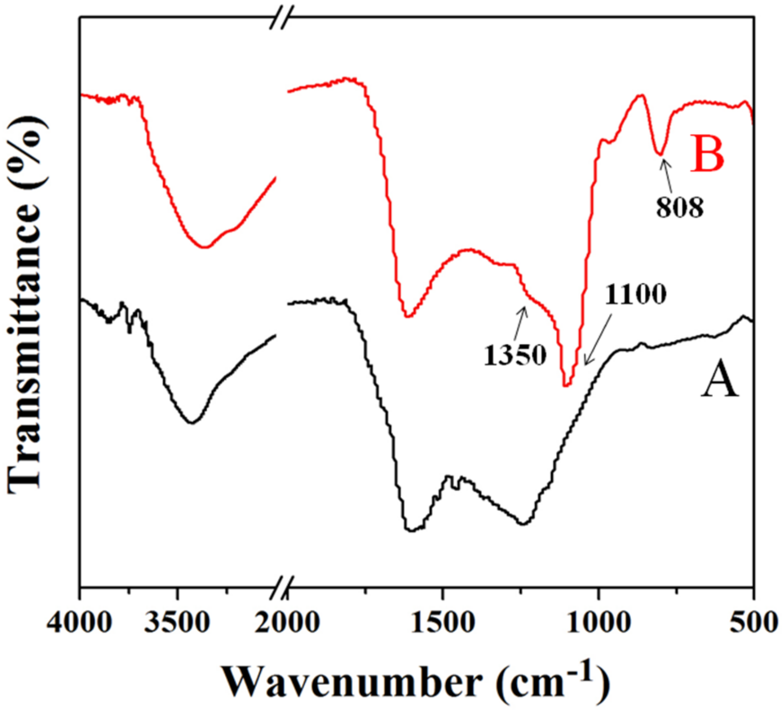


Fig. S7 FTIR spectrum of the hollow carbon nanspheres with(B) and without (A) nitrogen doping.

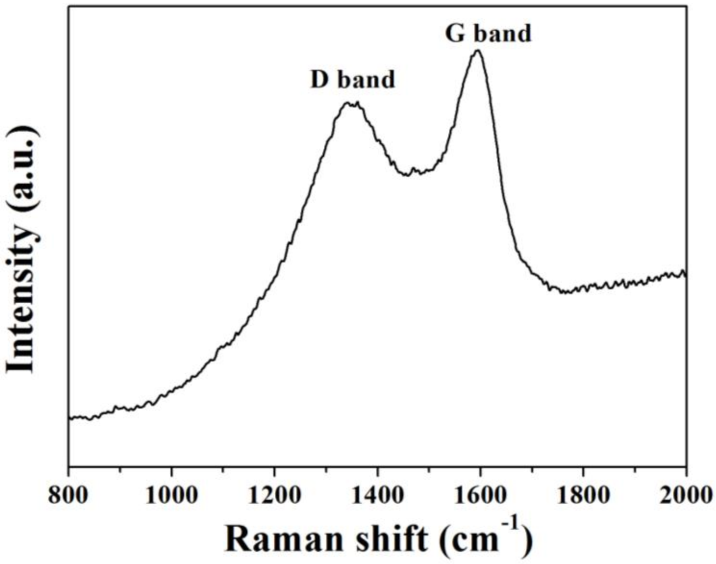


Fig S8 Raman spectra of the nitrogen-doped hollow carbon nanospheres. The ratio of peak intensity (I_D/I_G) is 0.96.

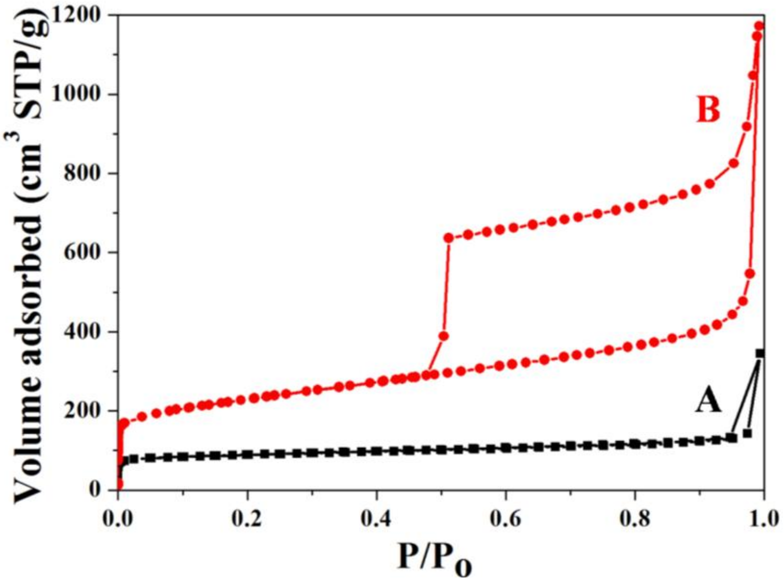


Fig. S9 N_2 sorption isotherms of the core-shell SiO_2@nitrogen-doped carbon nanospheres (SiO_2@N-CSs) (A) and N-doped hollow carbon spheres (N-HCSs) (B).

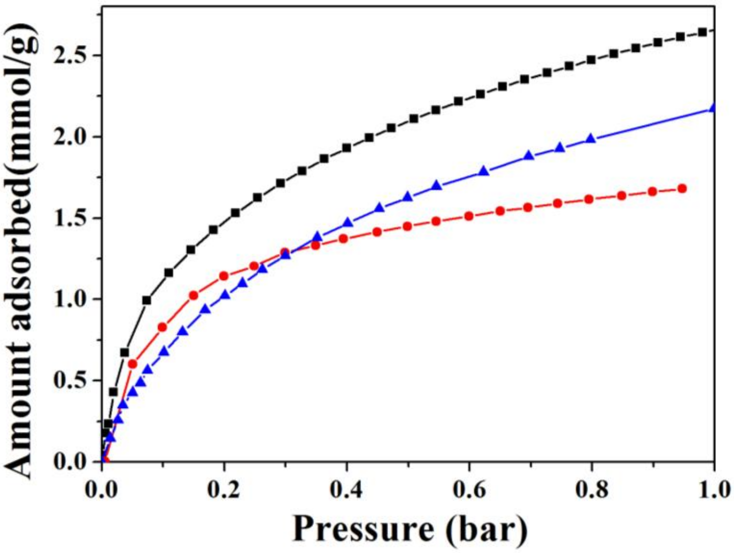


Fig S10 CO_2 adsorption isotherms of the N-HCSs with different N content: 3.1 wt% (red), 6.7 wt% (blue), and 14.8 wt% (black) at 298 K and 1.0 bar.