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Supplementary Information

Controllable Synthesis of Hollow Mesoporous Silica Particles by a Facile One-Pot Sol-Gel Method

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Experimental Section:

Chemicals. Formaldehyde (37 wt %) and hexadecyltrimethylammoniumchloride (CTAC) were purchased from Aladdin Industrial Corporation (Shanghai, China). 3-Aminophenol was purchased from Xiya Reagent (Chengdu, China). Ammonia aqueous solution (25%) and ethanol were purchased from Beijing Chemical works (Guangdong, China). All chemicals were used as received. Distilled water was used throughout the work.

Preparation of hollow mesoporous silica particles. The hollow mesoporous silica particles were prepared via a one-pot sol-gel method in the present of phenolic resin and tetraethylorthosilicate (TEOS). Typically, 0.83 ml of hexadecyltrimethylammonium chloride (CTAC) (25 wt% in water) was dissolved in the solution containing water (19 ml) and ethanol (4-10 ml). The mixture was stirred for 30 min at 30 °C. Following, some amount of 3-aminophenol (0.05-0.20 g) was added under stirring. After stirring for 30 min at 30 °C, TEOS (0.36-1.44 ml) was added into the system, followed by the quick injection of (0.07-0.28 ml) formaldehyde. The particle size was tuned by varying the concentration of TEOS or 3-aminophenol and the volume ratio of ethanol/water. The detailed synthesis parameters are given in Table S1. The product was washed with water for three times and was collected by centrifugation at 10000 rpm for 15min. To gain hollow mesoporous silica particles, the as-made resin/silica nanocomposite particles were calcinated in air from room temperature to 550 °C for 6 h at a rate of 1 °C/min.

Loading of NaCl Microcrystals. NaCl-loaded hollow mesoporous silica particles were prepared according to the literature procedure with modifications.[1] Briefly, 1.5 mg dried hollow mesoporous silica particles were redispersed in 0.9 ml water which were used as a stock solution. Then the prepared stock solution (0.3 ml) was mixed with ethanol (0.3 ml) and a NaCl solution (0.3 ml, 5.1mM). The mixture was treated with a vacuum for 10 min, stirred for another 2h. Afterwards, 5ml of the resultant NaCl-loaded hollow mesoporous silica particles suspension was dropped onto a carbon-coated copper and dried at 100 °C for 3 min to remove all water inside mesoporous silica particles prior to TEM characterization.

Characterization. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2010 microscope (JEOL, Japan) operated at 100 kV. Field emission scanning electron microscopy (FE-SEM) images were recorded on a FEI XL30 ESEM FEG electron microscopy operating at 25 kV. Diffuse reflectance Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 spectrometer. The nitrogen adsorption measurement was conducted on a Micromeritics Tristar 3000 system with micropore analysis at 77 K. Surface area was calculated using the Brunauer–Emmett–Teller (BET) method from nitrogen adsorption–desorption isotherms. The total pore volume was estimated from the adsorbed amounts at a relative pressure (P/P_0) of 0.99. Before measurements, samples were degassed in a vacuum for 6h at 180°C.

Table S1. Synthesis parameters of hollow mesoporous silica particles and the corresponding size, shell thickness and adsorption parameters.

Sample	3-Aminophenol (g)	Formaldehyde (ml)	TEOS (ml)	Ethanol (ml)	NH_3H_2O (mL)	Water (ml)	CTAC solution (ml)	Mean Diameter (nm)	Shell Thickness (nm)	Surface Area (m^2/g)	Pore Volume (cm^3/g)
1	0.20	0.28	0.36	8	0.1	19	0.83	420	36	626	1.08
2	0.20	0.28	0.72	8	0.1	19	0.83	440	60	644	0.82
3	0.20	0.28	1.08	8	0.1	19	0.83	655	103	761	0.81
4	0.20	0.28	1.44	8	0.1	19	0.83	690	112	723	0.86
5	0.05	0.07	0.72	8	0.1	19	0.83	149	----	1156	1.70
6	0.10	0.14	0.72	8	0.1	19	0.83	270	95	1146	1.11
7	0.20	0.28	0.72	4	0.1	19	0.83	85	14	718	1.64
8	0.20	0.28	0.72	6	0.1	19	0.83	170	22	724	1.90
9	0.20	0.28	0.72	10	0.1	19	0.83	890	197	790	0.87

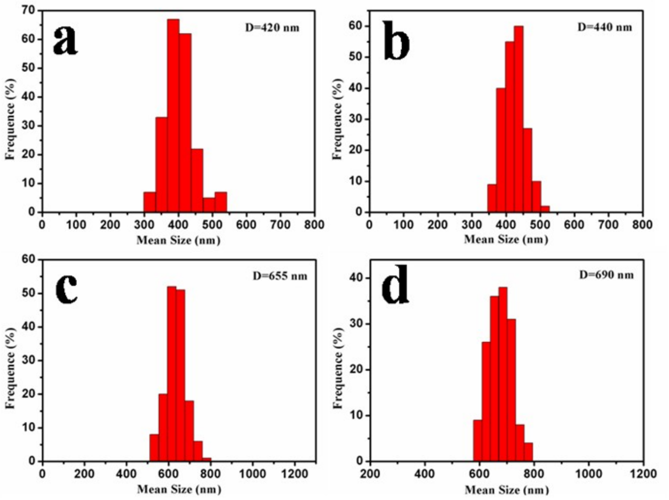

Fig. S1 The hollow silica particle size distribution of a) sample 1, b) sample 2,c) sample 3 and d) sample 4, obtained from more than 200 particles in the FE-SEM images.

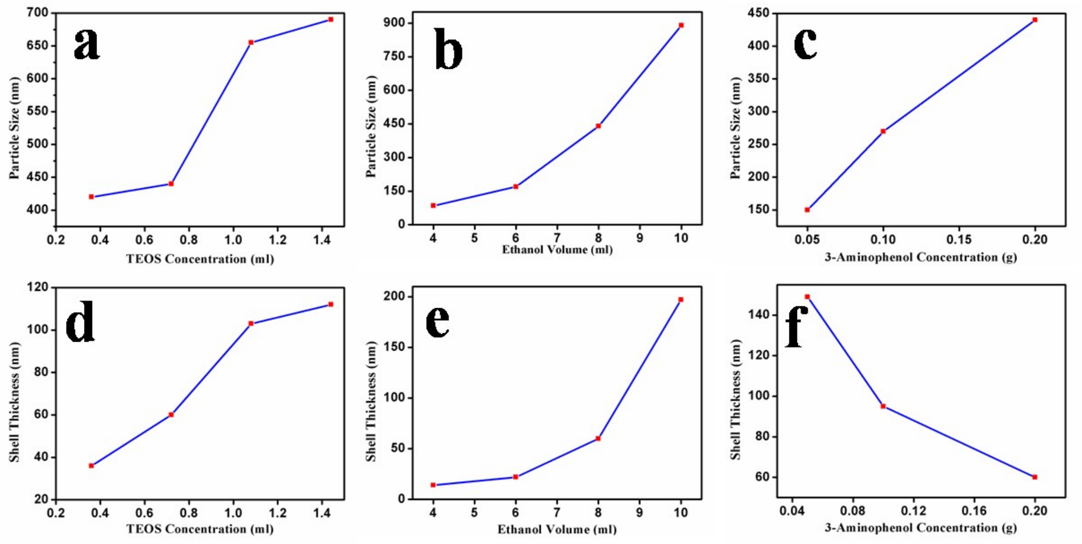

Fig. S2 The hollow silica particle size and shell thickness as the function of TEOS concentration, ethanol volume and 3-aminophenol concentration. The detailed conditions can be seen in Table S1: (a and d) sample 1-4, (b and e) sample 2, 7, 8 and 9, (c and f) sample 2, 5 and 6.

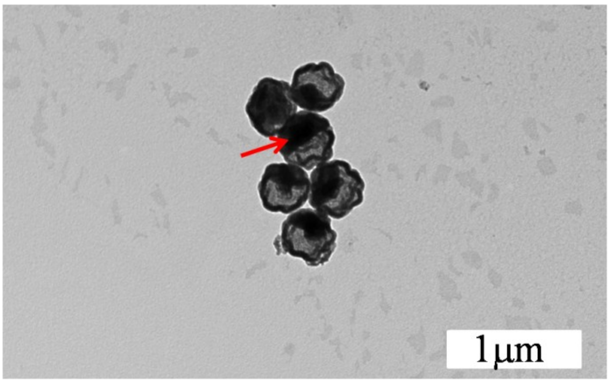

Fig. S3 TEM image of NaCl-encapsulated hollow mesoporous silica particles. The red arrow shows the NaCl microcrystal located in the hollow particle.

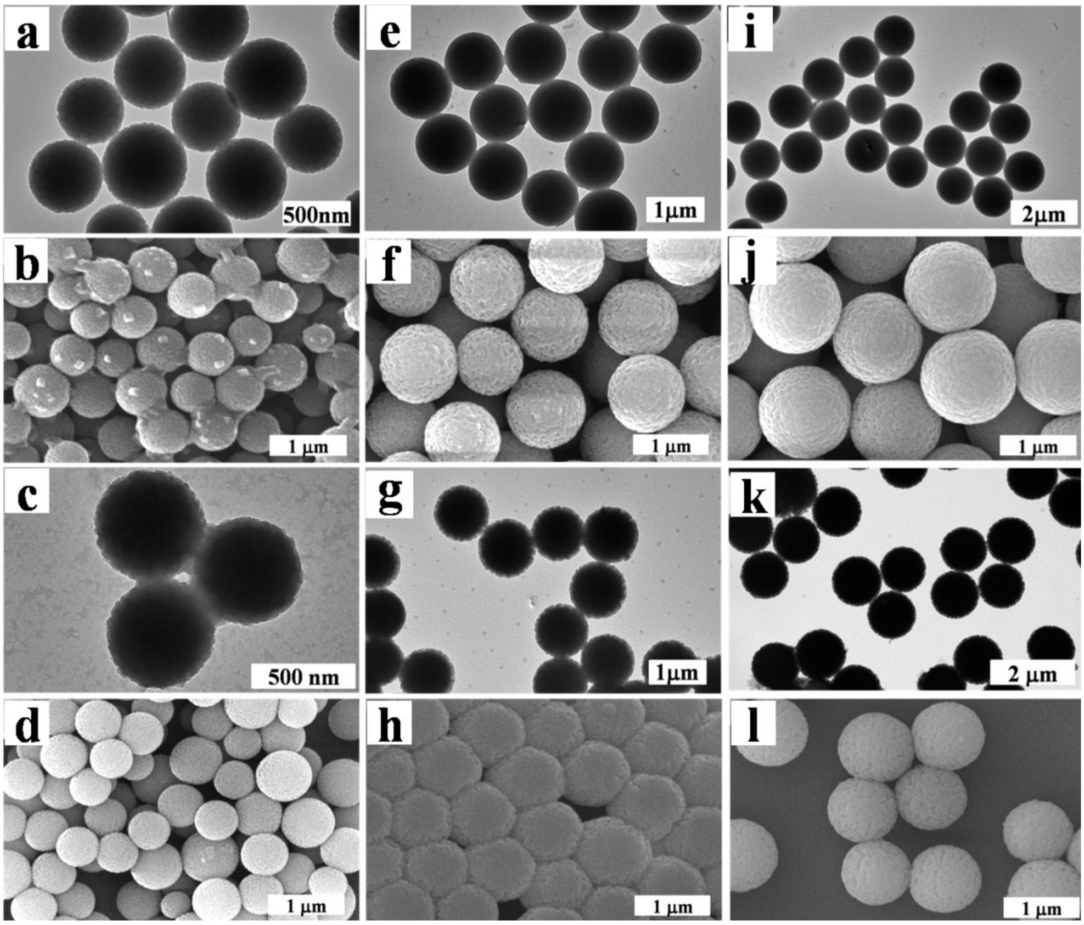

Fig. S4 a, e and i) TEM images and b, f and j) FE-SEM images of resin/silica nanocomposites synthesized at 0.36 ml, 1.08 ml and 1.44 ml of TEOS, respectively. c, g and k) TEM images and d, h and l) FE-SEM images of the obtained resin particles after etching silica in the corresponding nanocomposite particles.

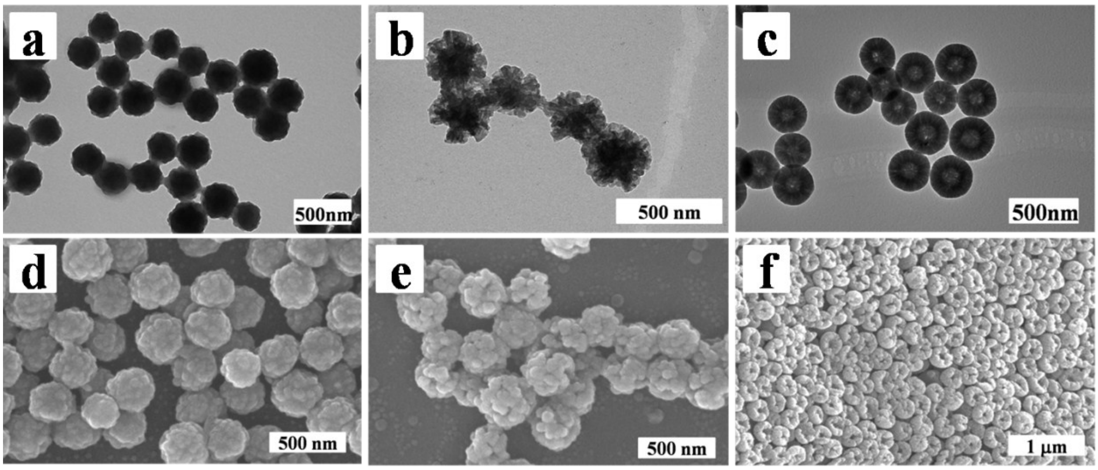

Fig. S5 TEM images and FE-SEM images of resin/silica nanocomposites particles. Resin particles are obtained after etching silica and the resulted hollow silica particles are synthesized at 0.1 g of 3-aminophenol. a) TEM image and d) FE-SEM image of resin/silica nanocomposites particles. b) TEM image and e) FE-SEM image of resin particles after etching silica. c) TEM image and f) FE-SEM image of the resulted hollow silica particles.

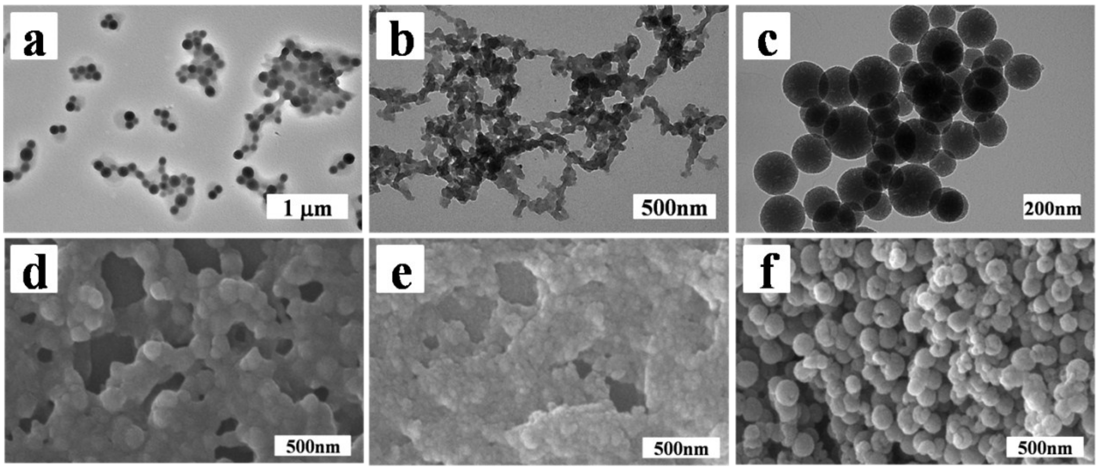

Fig. S6 TEM images and FE-SEM images of resin/silica nanocomposites particles. Resin particles are obtained after etching silica and the resulted hollow silica particles are synthesized at 0.05 g of 3-aminophenol. a) TEM image and d) FE-SEM image of resin/silica nanocomposites particles. b) TEM image and e) FE-SEM image of resin particles after etching silica. c) TEM image and f) FE-SEM image of the resulted hollow silica particles.

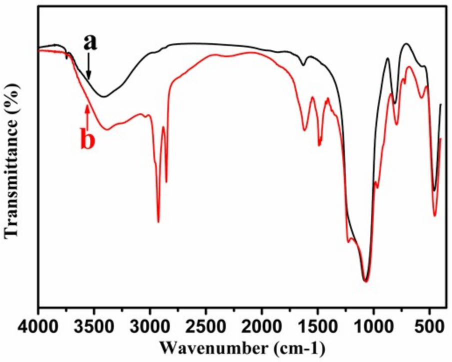

Fig. S7 FT-IR spectra of a) the obtained particles after calcinating and b) as-synthesized resin/silica nanocomposites particles of sample 5. The characteristic peaks of aliphatics at 2850-2950 cm^{-1} in resin disappear after calcinating(a), confirming the complete removal of resin. [23]

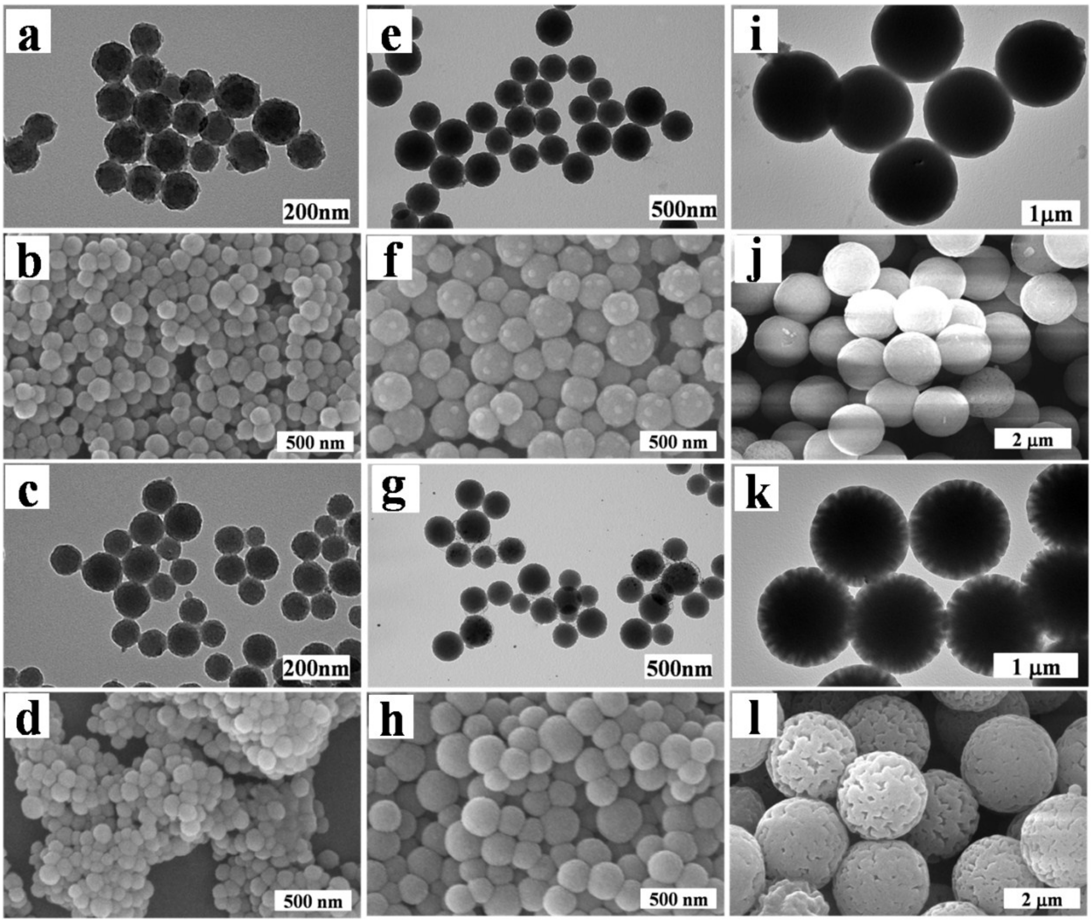

Fig. S8 a, e and i) TEM images and b, f and j) FE-SEM images of resin/silica nanocomposites synthesized at 4 ml, 6 ml and 10 ml of ethanol, respectively. c, g and k) TEM images and d, h and l) FE-SEM images of the obtained resin particles after etching silica in the corresponding nanocomposite particles.

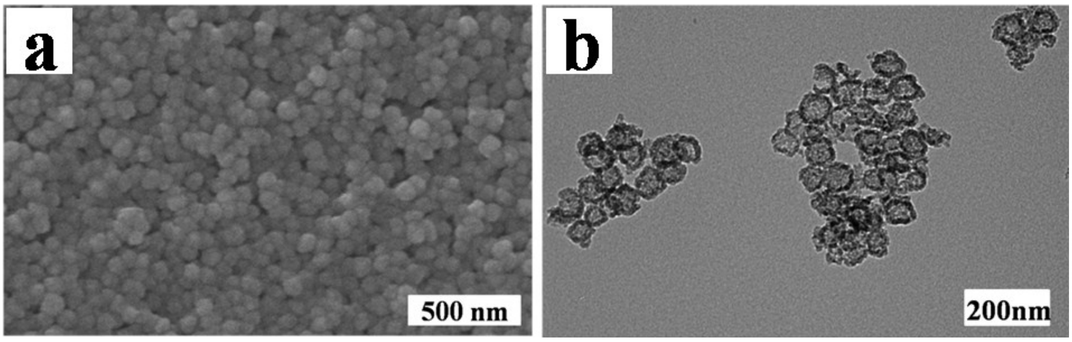

Fig. S9 FE-SEM images (a) and TEM images (b) of hollow silica particles prepared at 4ml of ethanol.

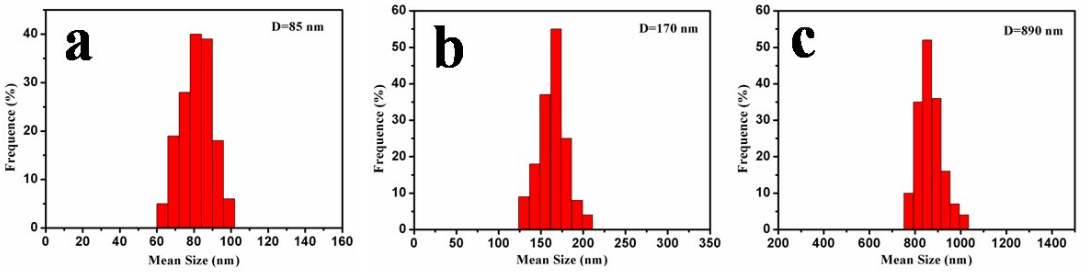

Fig. S10 The size distribution of hollow silica particle obtained from more than 200 particles in the FE-SEM images. a) sample 7, b) sample 8,c) sample 9.

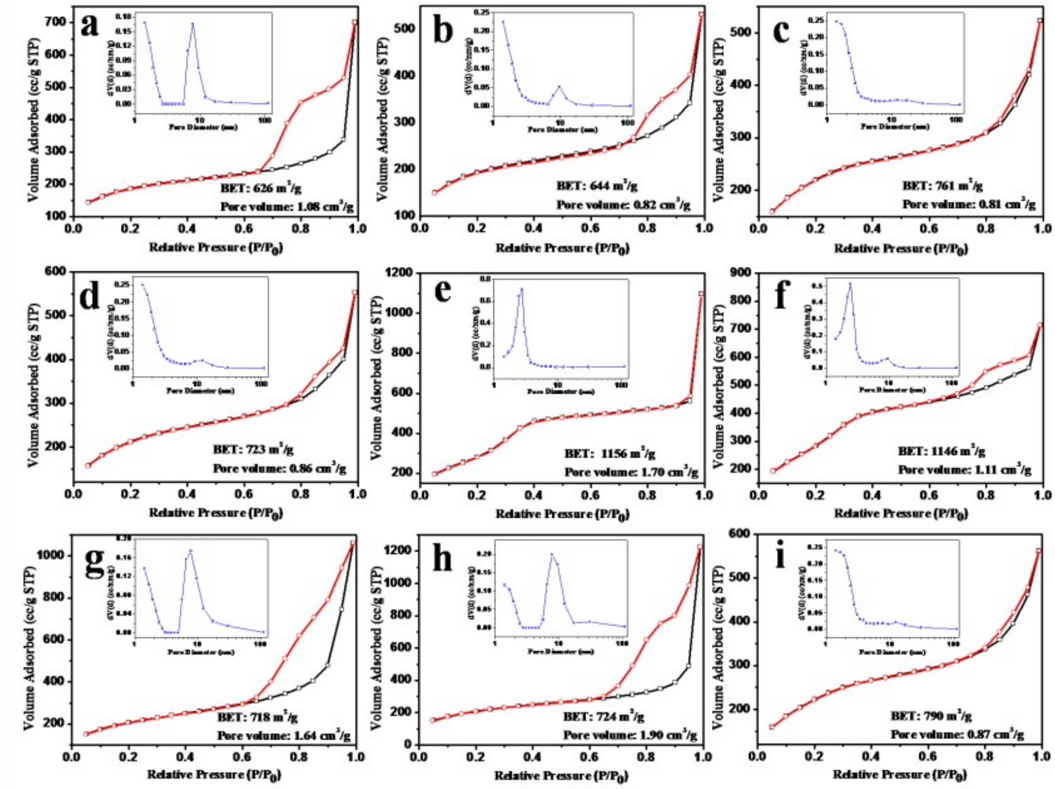

Fig. S11 Nitrogen adsorption–desorption isotherms of a)-i) samples 1-9, respectively. The insets correspond to the pore size distribution curves.

Reference:

[1] M. Bai, C. Moran, L. Zhang, C. Liu, Y. Zhang, L. V. Wang and Y. Xia, Adv. Funct. Mater., 2012, 22, 764.