Electronic Supplementary Information (ESI)

for

Well-dispersible hollow porous carbon spheres synthesized by direct pyrolysis of core-shell type metal-organic framework and their sorption properties

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General Methods

All chemicals and solvents were obtained from commercial sources and were used as received. All transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G2 F30 ST at 300 kV (Korea Basic Science Institute, Seoul, Korea). EDX spectrum profile scanning was conducted using a STEM attachment. All scanning electron microscopy (SEM) images were acquired using a JEOL JSM-7001F field-emission SEM. Energy dispersive X-ray (EDX) spectra were obtained using a Hitachi SU 1510 SEM equipped with a Horiba EMAX Energy E-250 EDS system. Raman spectroscopy data were collected using a HORIBA Jobin Yvon LabRAM ARAMIS confocal Raman microscope at room temperature with a 0.5 mW YAG laser at 532 nm. X-ray diffraction studies were carried out using a Rigaku Ultima IV equipped with a graphite-monochromated $Cu_{k\alpha}$ radiation source (40 kV, 40 mA). TGA measurements were conducted using a Shimadzu TGA-50 in a nitrogen atmosphere at a heating rate of 5 °C min^{-1}. The adsorption isotherms of N_2 (77 K) and CO_2 (195 K and 298 K) were measured in the gaseous state using a BELSORP Max volumetric adsorption equipment. All gas-adsorption isotherms were measured after pretreatment under a dynamic vacuum at 150 °C. UV-vis absorption spectra were acquired using a Shimadzu UV-1650PC spectrophotometer by using quartz cells (10 x 4 mm light path). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha KA1066 spectrometer using a monochromatic Al Kα X-ray source (hv = 1486.6 eV).

Preparation of polystyrene@ZIF-8 core-shell microspheres

A ZIF-8 precursor solution was prepared by mixing 2-methylimidazole (664 mg, 8.1 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (240 mg, 0.81 mmol) in 32 mL of methanol. Carboxylic acid-terminated polystyrene (120 mg) was then added to the precursor solution. The resulting mixture was placed in an oil bath (70 °C) in the presence of an ultrasonic dispersion for 15 min. Polystyrene@ZIF-8 core-shell microspheres generated during this time were isolated by cooling the reaction mixture to room

temperature, collecting the precipitate by centrifugation, and washing the precipitate several times with methanol. During the centrifugation process, the desired micro-sized core-shell particles were easily separated from the nano-sized pure ZIF-8 particles due to their density difference. The second, third and fourth ZIF-8 growth cycles were continuously conducted to increase the ZIF-8 shell thickness using a fresh precursor solution.

*Preparation of hollow porous carbon (HPC) spheres (**HPC-2** ~ **HPC-4**)*

Thickness-controlled polystyrene@ZIF-8 core-shell microspheres were placed in a tube furnace and calcined up to 1000 °C for 5 hrs under a nitrogen gas flow at a heating rate of 5 °C min^{-1}. After reaching the targeted temperature, the resulting hollow porous carbon spheres were cooled to room temperature.

*Adsorption of methylene blue (MB) from aqueous solution using **HPC-3** and **PC-1***

HPC-3 (5 mg) or **PC-1** (5 mg) was added to 30 mL of MB aqueous solution (10 mg L^{-1}) and was stirred to form the dispersed solution. UV-Vis spectra were measured at various time points after removing the MB-adsorbed **HPC-3**.

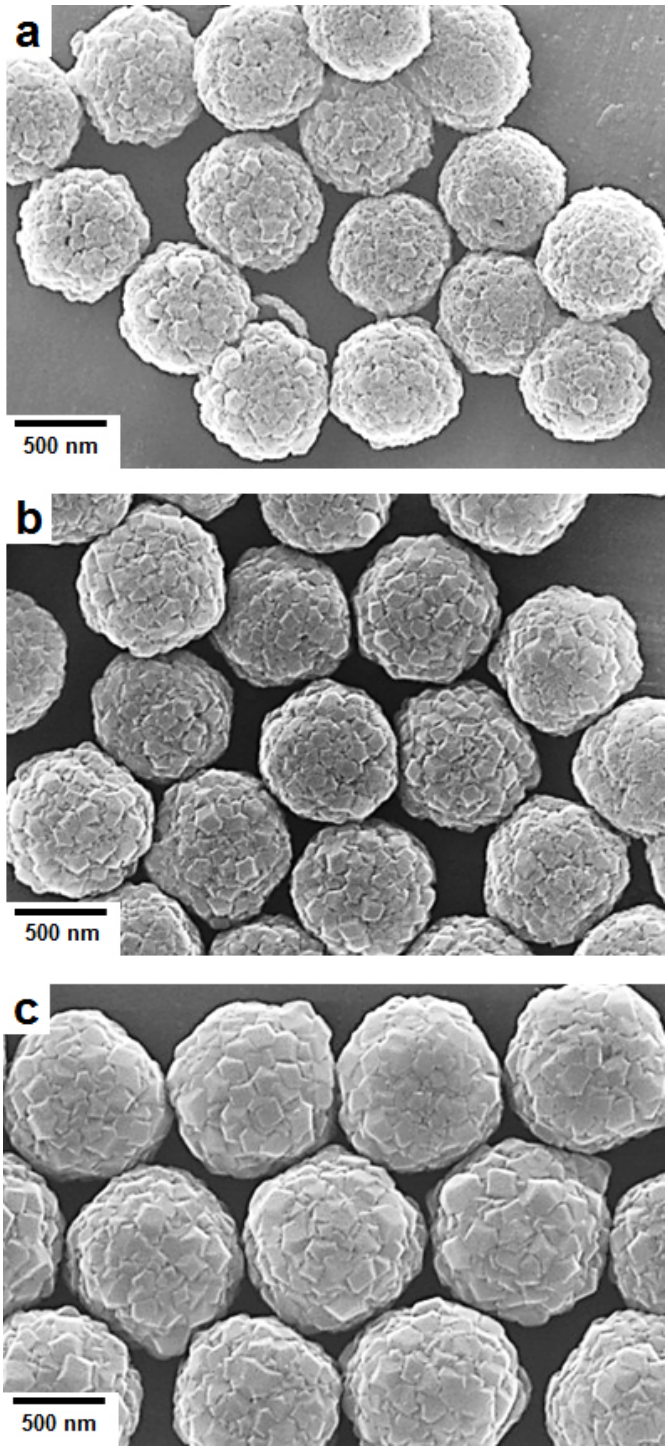

Fig. S1 High magnification SEM images of (a) **HPC-2**, (b) **HPC-3** and (c) **HPC-4**.

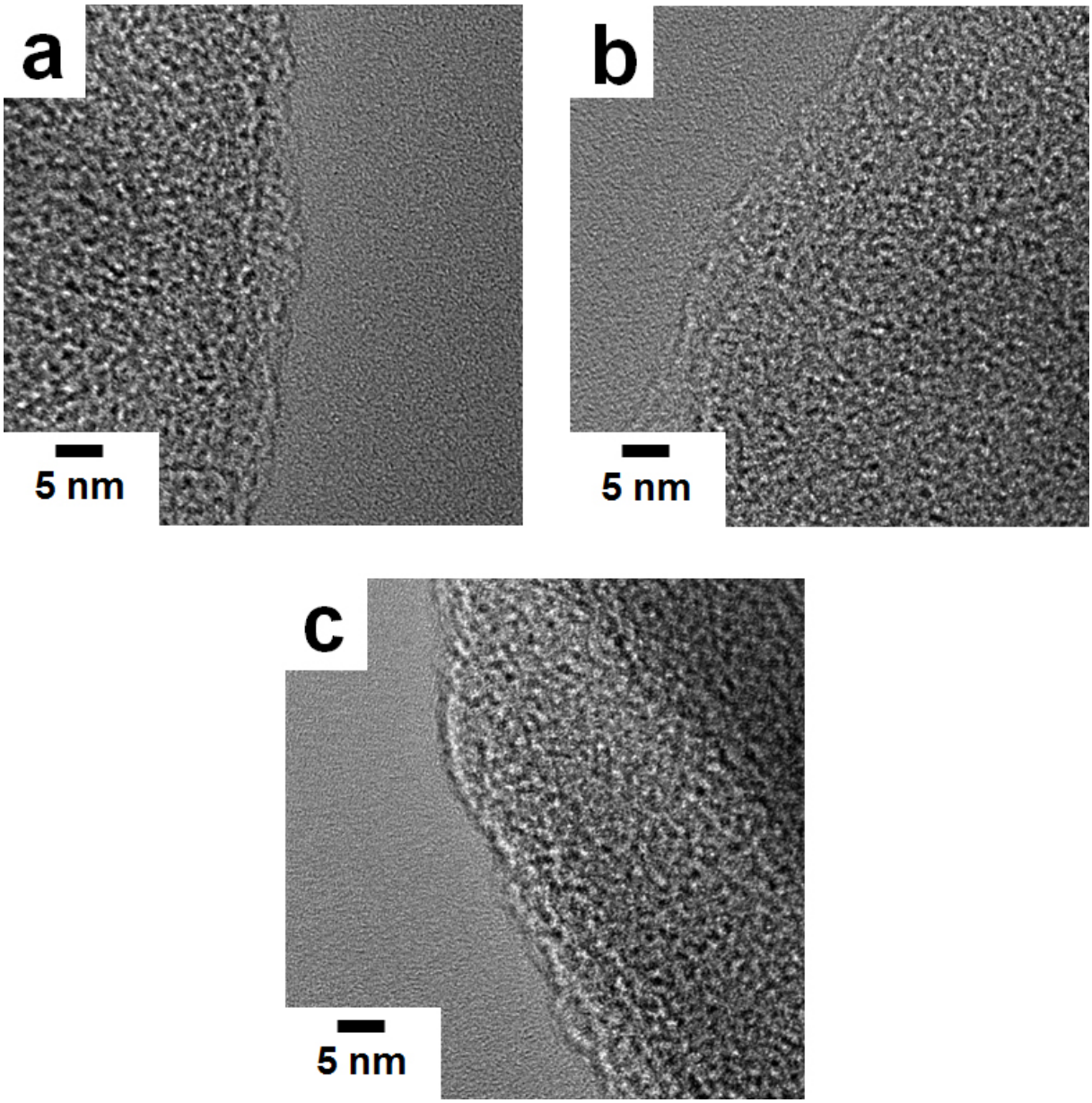

Fig. S2 High resolution TEM (HRTEM) images of (a) **HPC-2**, (b) **HPC-3** and (c) **HPC-4**.

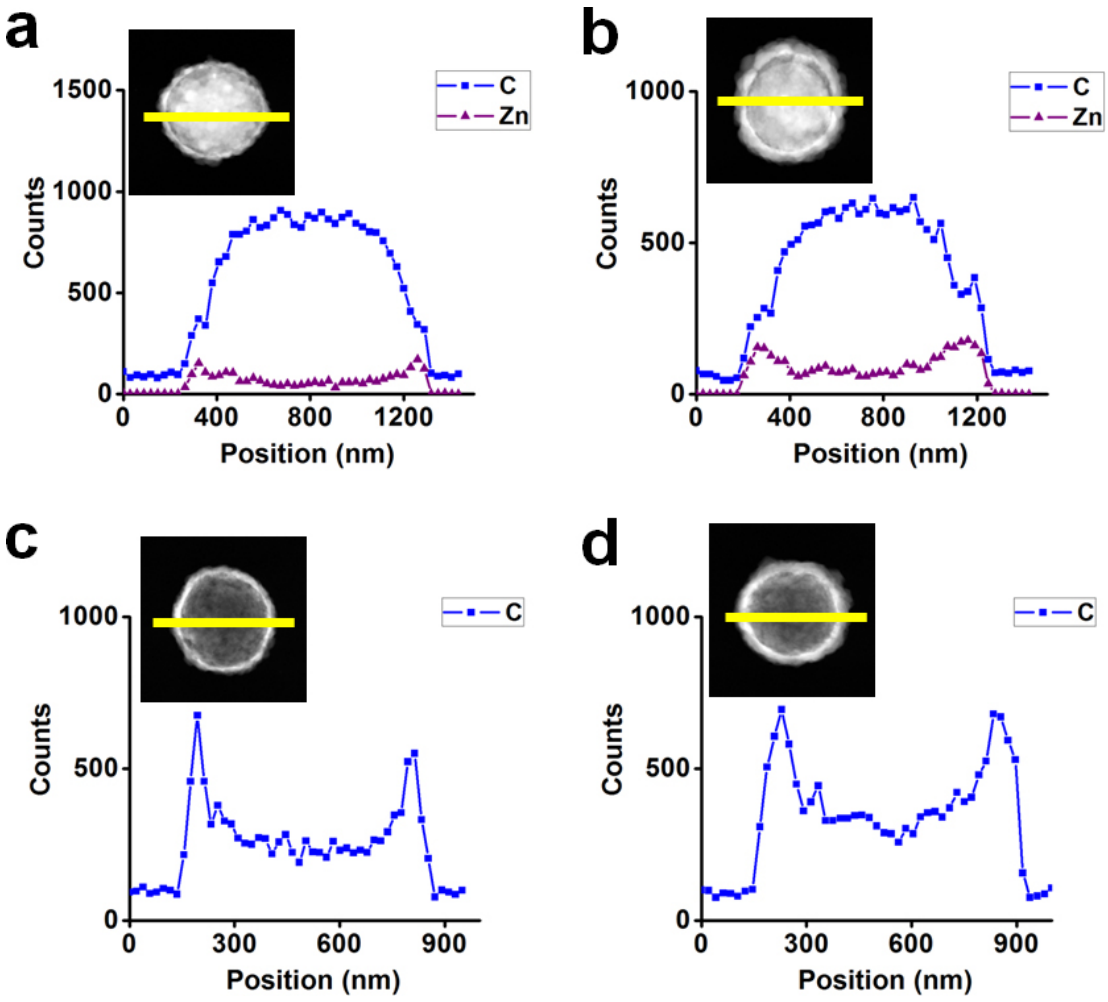

Fig. S3 EDX spectrum profile scanning data of (a,b) polystyrene@ZIF-8 core-shell precursors, (c) **HPC-2** and (d) **HPC-3**. EDX spectrum profile scanning data were obtained by performing the scan shown in the STEM images.

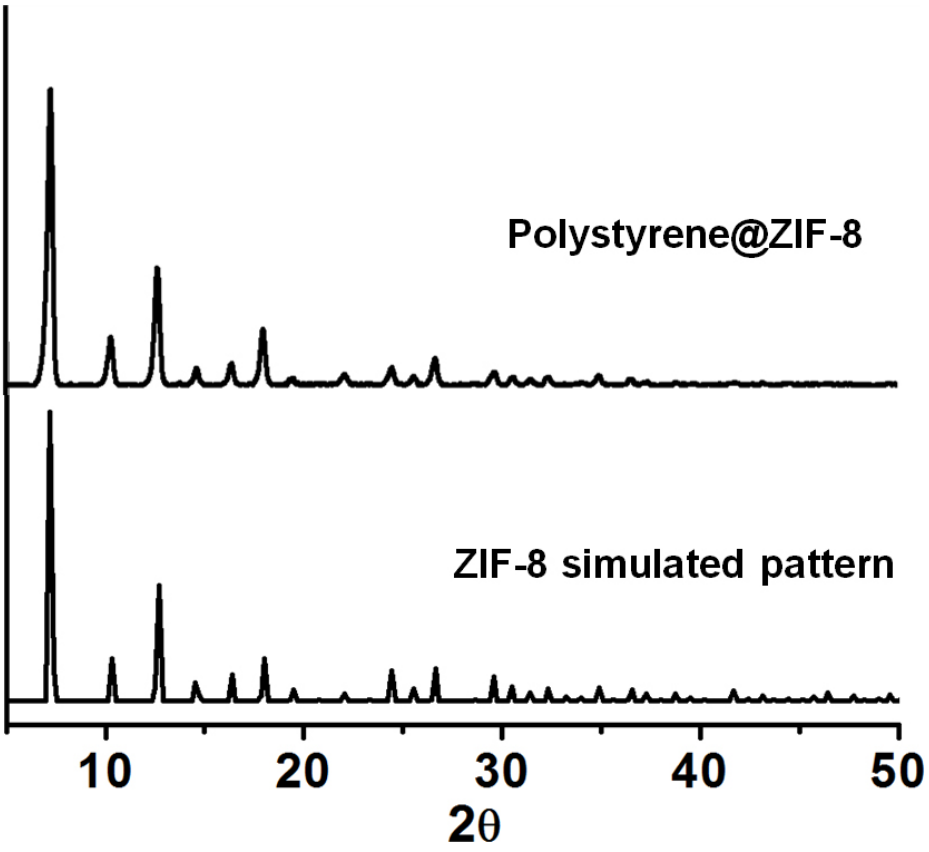

Fig. S4 PXRD patterns of polystyrene@ZIF-8 core-shell microspheres (up) and the simulated pattern of ZIF-8 (down).

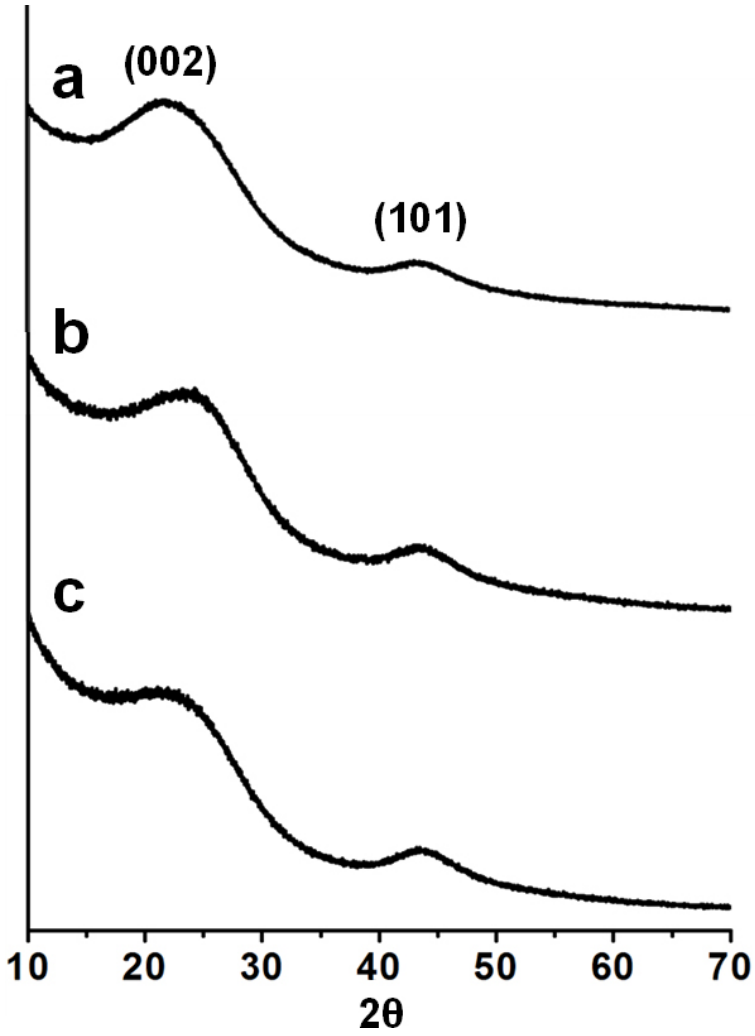

Fig. S5 PXRD patterns of (a) **HPC-2**, (b) **HPC-3** and (c) **HPC-4**.

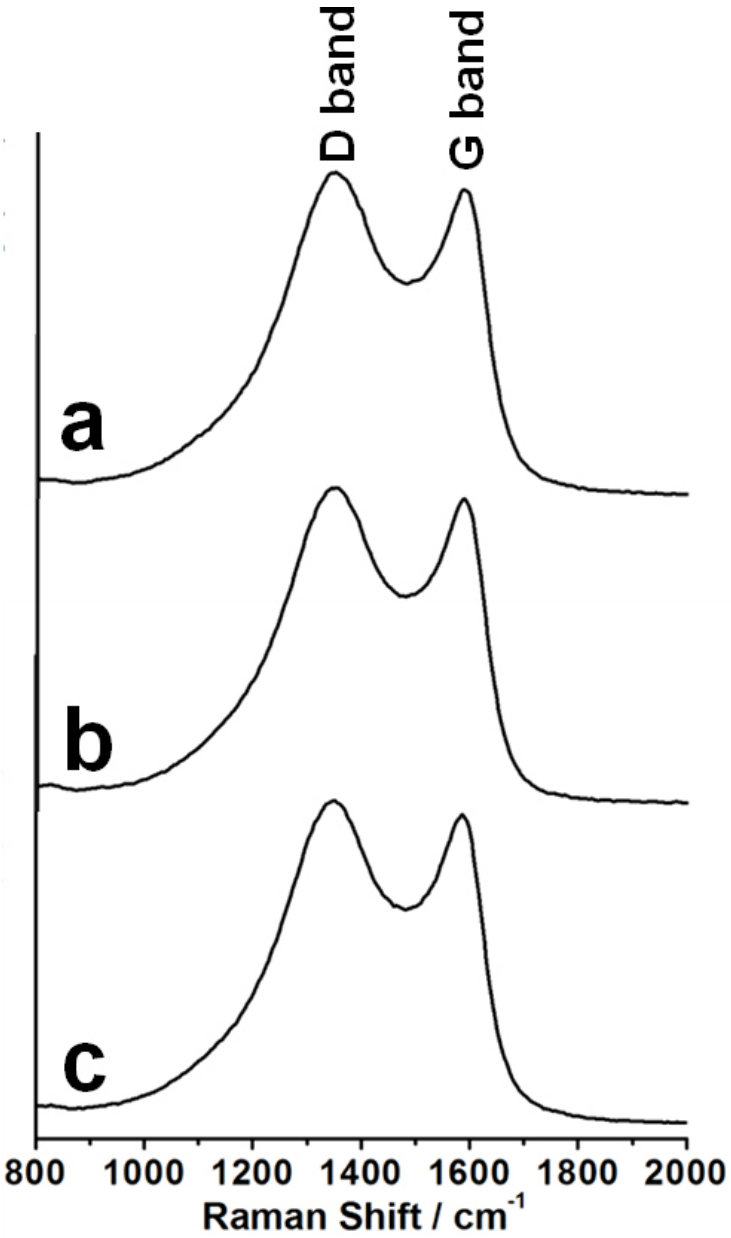

Fig. S6 Raman spectra of (a) **HPC-2**, (b) **HPC-3** and (c) **HPC-4**.

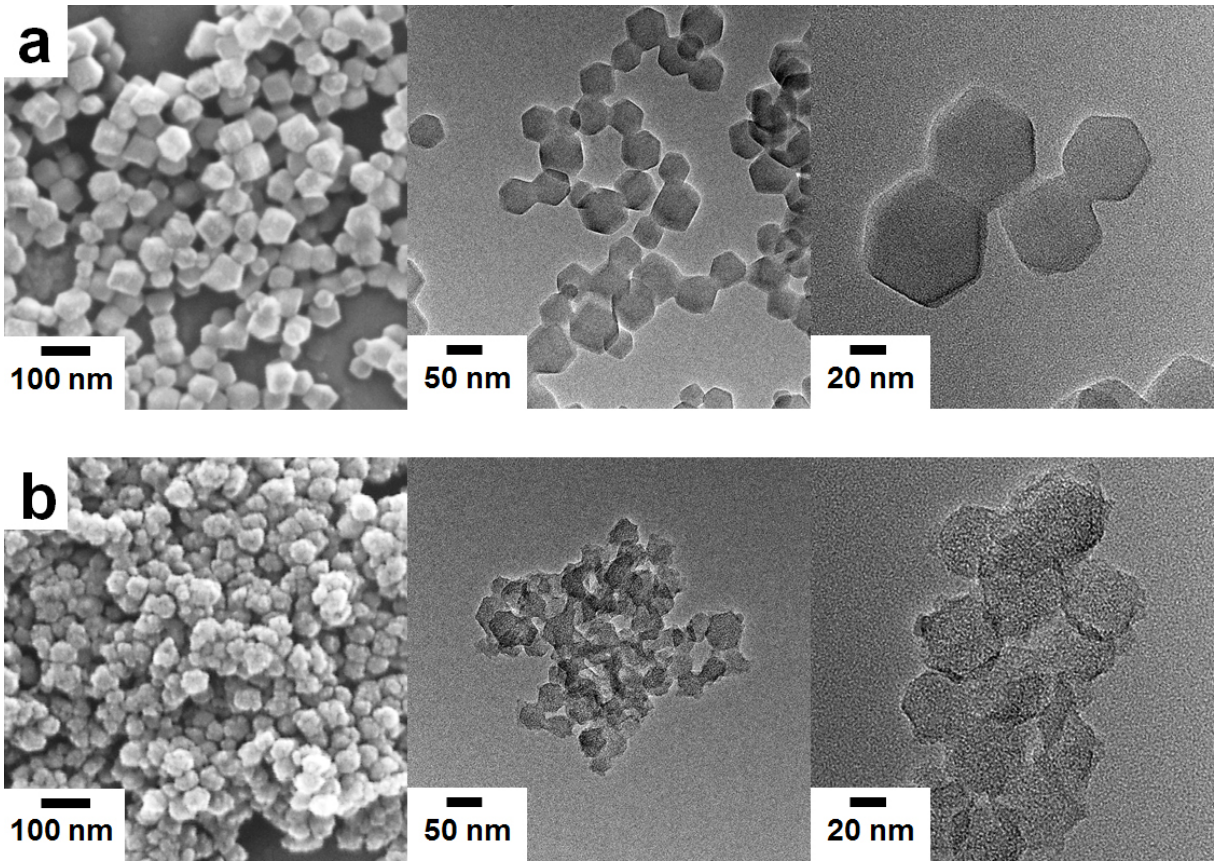

Fig. S7 SEM and TEM images of (a) nano-sized ZIF-8 particles and (b) **PC-1** obtained from the pyrolysis of nano-sized ZIF-8 particles.

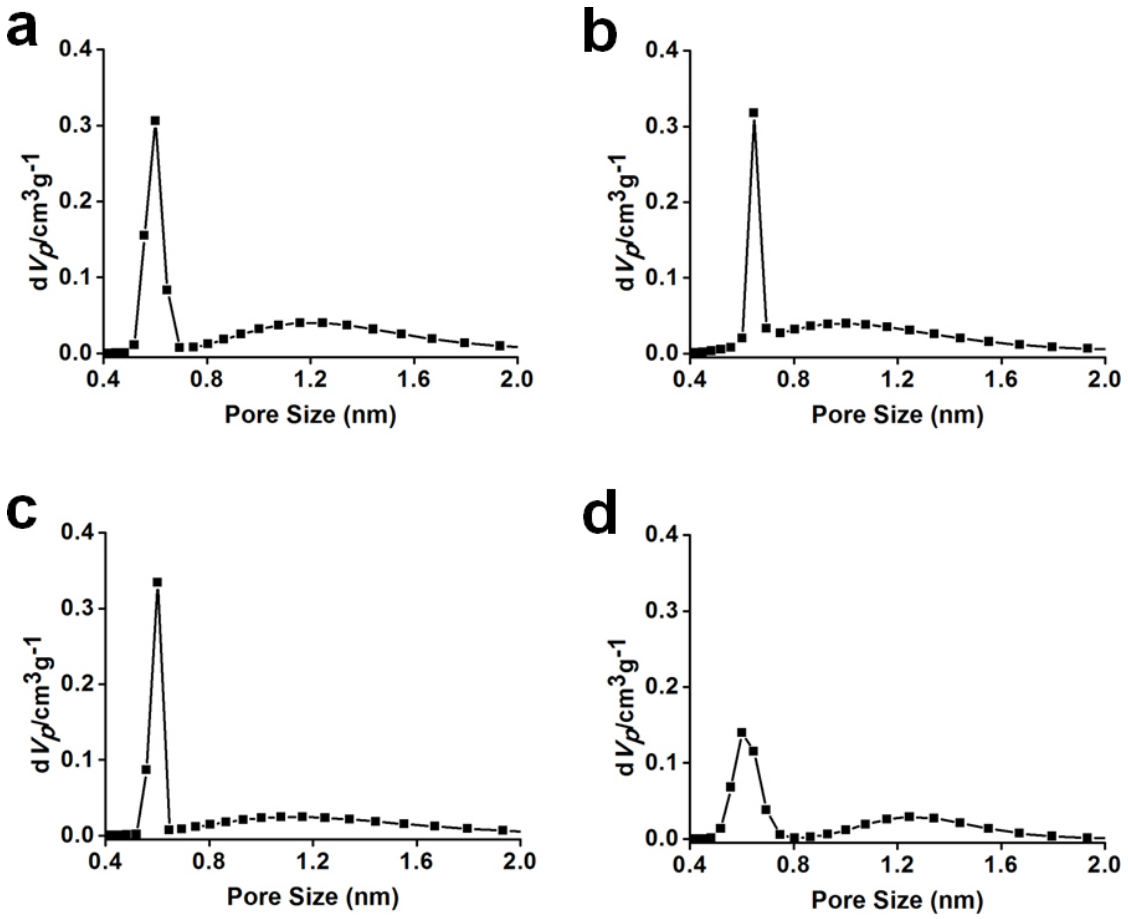

Fig. S8 Pore size distributions of (a) **HPC-2**, (b) **HPC-3**, (c) **HPC-4** and (d) **PC-1** calculated from the NLDFT (non local density function theory) method.

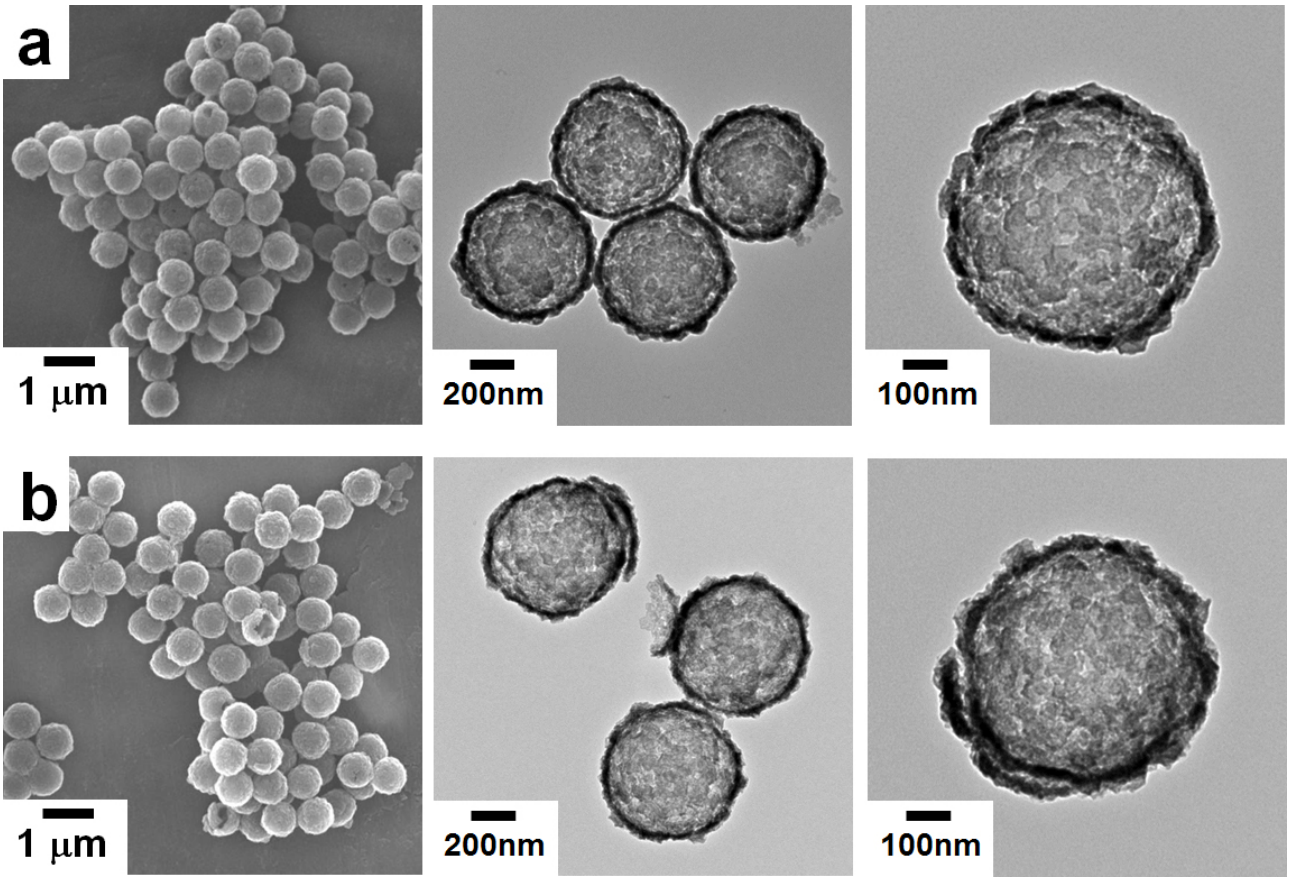

Fig. S9 SEM and TEM images of hollow porous carbons obtained a pyrolysis at (a) 800 °C and (b) 900 °C.

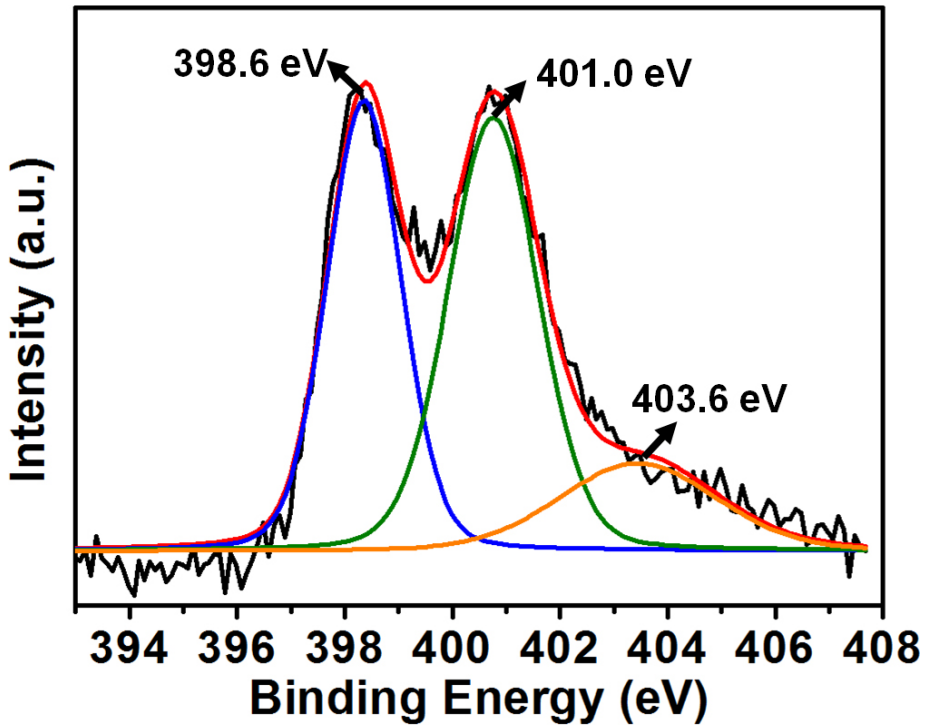

Fig. S10 XPS spectrum of **HPC-3**.

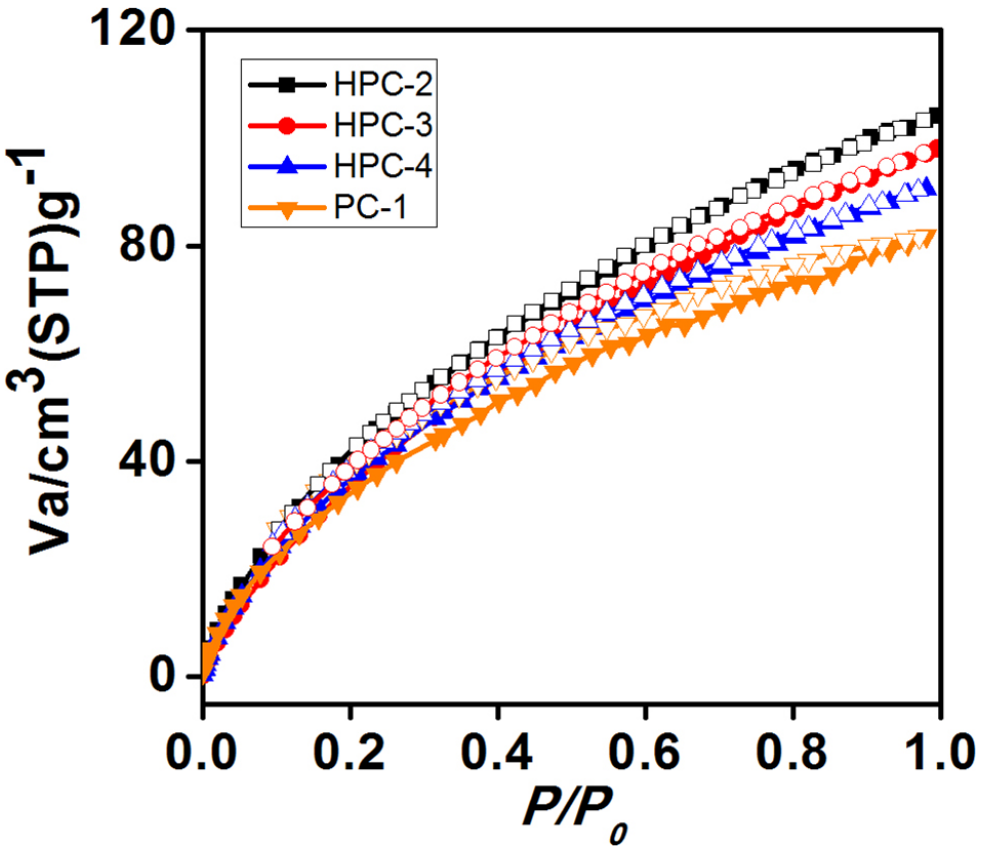

Fig. S11 CO_2 sorption isotherms measured at 298 K. Solid symbols denote adsorption and open symbols denote desorption.