Electronic Supplementary Information (ESI)

for

Advanced fabrication of metal-organic frameworks: template-directed formation of polystyrene@ZIF-8 core-shell and hollow ZIF-8 microspheres

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General Methods

Solvents and all other chemicals were obtained from commercial sources and used as received unless otherwise noted. Carboxylate-terminated polystyrene was purchased from Thermo Scientific (U.S.A.). All scanning electron microscopy (SEM) images were obtained using a Hitachi SU 1510 SEM or JEOL JSM-6701F field-emission SEM, and energy dispersive X-ray (EDX) spectra were obtained using a Hitachi S-4300 field-emission SEM equipped with a Horiba EMAX 6853-H EDS system (Center for Microcrystal Assembly, Sogang University). All transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2011(HC) at 200 kV. The scanning transmission electron microscopy (STEM) image was obtained on a FEI Tecnai G2 F30 ST using dark-field imaging in STEM mode at 300 kV (Korea Basic Science Institute in Seoul). EDX spectrum profile scaning was performed using a STEM attachment. X-ray diffraction studies were conducted using a Rigaku Ultima IV equipped with a graphite-monochromated $Cu_{K\alpha}$ radiation source (40 kV, 40 mA).

Preparation of polystyrene@ZIF-8 core-shell microspheres: A precursor solution was prepared by mixing 2-methylimidazole (HMeIM, 16.6 mg, 0.202 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (6.0 mg, 0.020 mmol) in 0.8 mL of methanol. The carboxylate-terminated polystyrene (3.0 mg) was then added to a precursor solution. The resulting mixture was placed in an oil bath (70 °C) for 10 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 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 isolated amount of the core-shell particles and the nano-sized pure ZIF-8 particles was 3.3 and 2.6 mg, respectively. The second and third ZIF-8 growth cycles were continuously conducted to increase the ZIF-8 shell thickness using a fresh precursor solution.

Preparation of hollow ZIF-8 particles: The polystyrene@ZIF-8 core-shell microspheres were immersed in *N,N'*-dimethylformamide (DMF) to remove polystyrene cores and to induce the formation of hollow ZIF-8 microspheres. The resulting products were collected by centrifugation and were then washed several times with DMF and methanol.

Preparation of ZIF-8 nano-crystals: ZIF-8 nano-crystals were synthesized according to the modified procedure reported in the literature.[1] A precursor solution was prepared by mixing 2-methylimidazole (HMeIM, 16.6 mg, 0.202 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (6.0 mg, 0.020 mmol) in 0.8 mL of methanol. The resulting mixture was placed in an oil bath (70 °C) for 10 min. The products were collected by centrifugation and were then washed several times with methanol (72% yield).

Reference

1 J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2009, **21**, 1410.

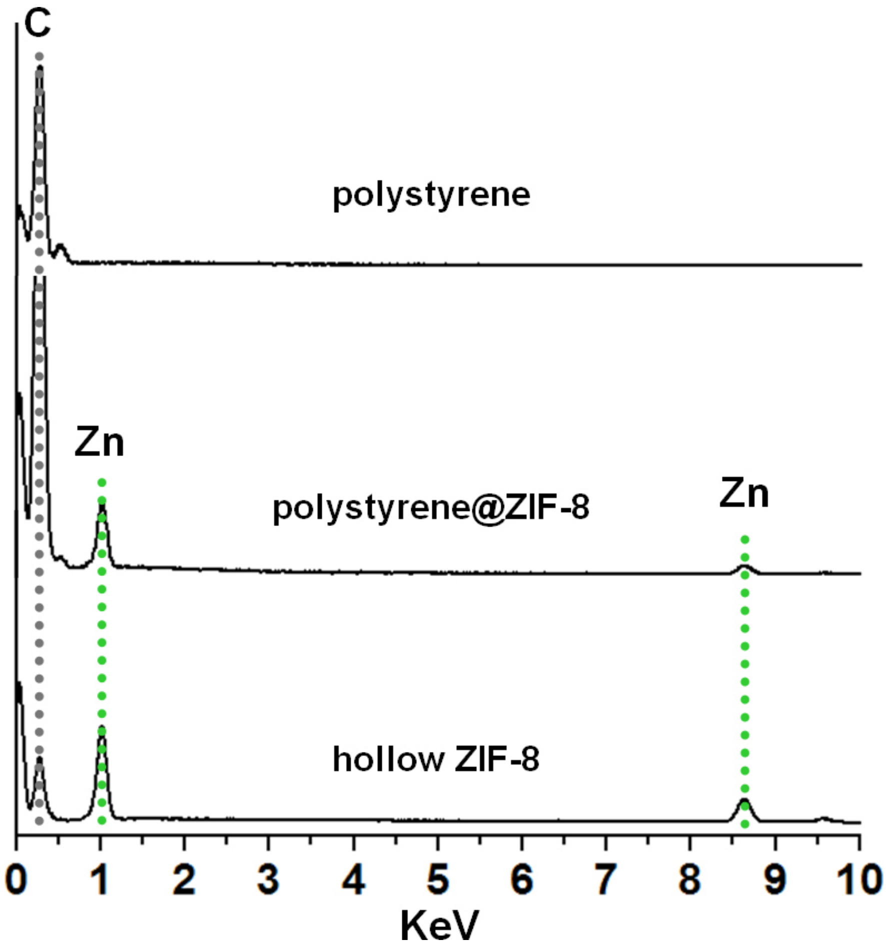

Fig. S1 A series of EDX spectra of initial carboxylate-terminated polystyrene, polystyrene@ZIF-8 core-shell, and hollow ZIF-8 microspheres (top to bottom). Polystyrene@ZIF-8 core-shell and hollow ZIF-8 microspheres were obtained by conducting two cycles of the ZIF-8 growth process.

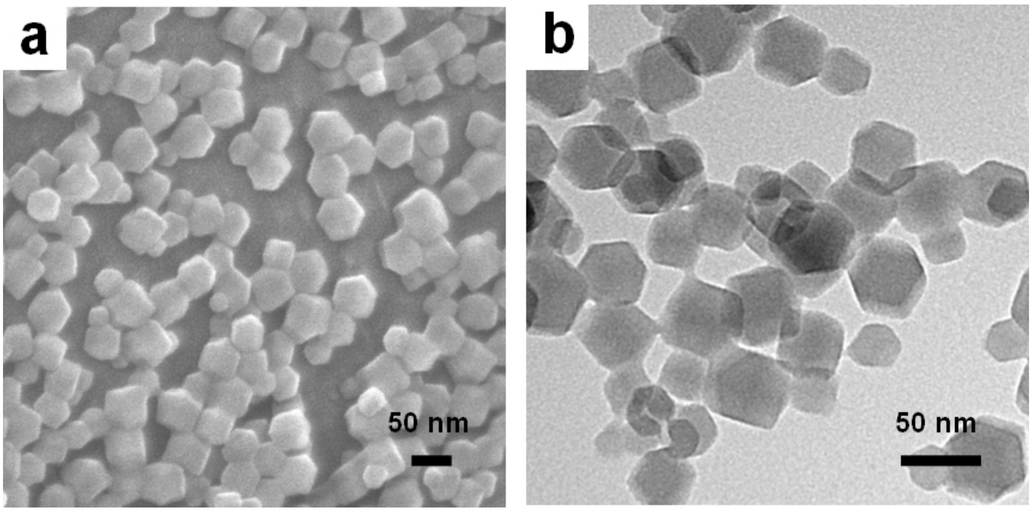

Fig. S2 (a) SEM and (b) TEM images of ZIF-8 nano-crystals.

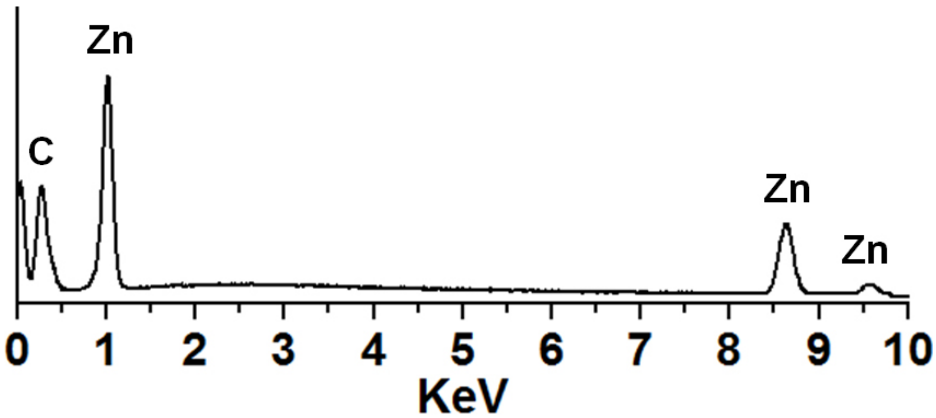

Fig. S3 EDX spectrum of ZIF-8 nano-crystals.

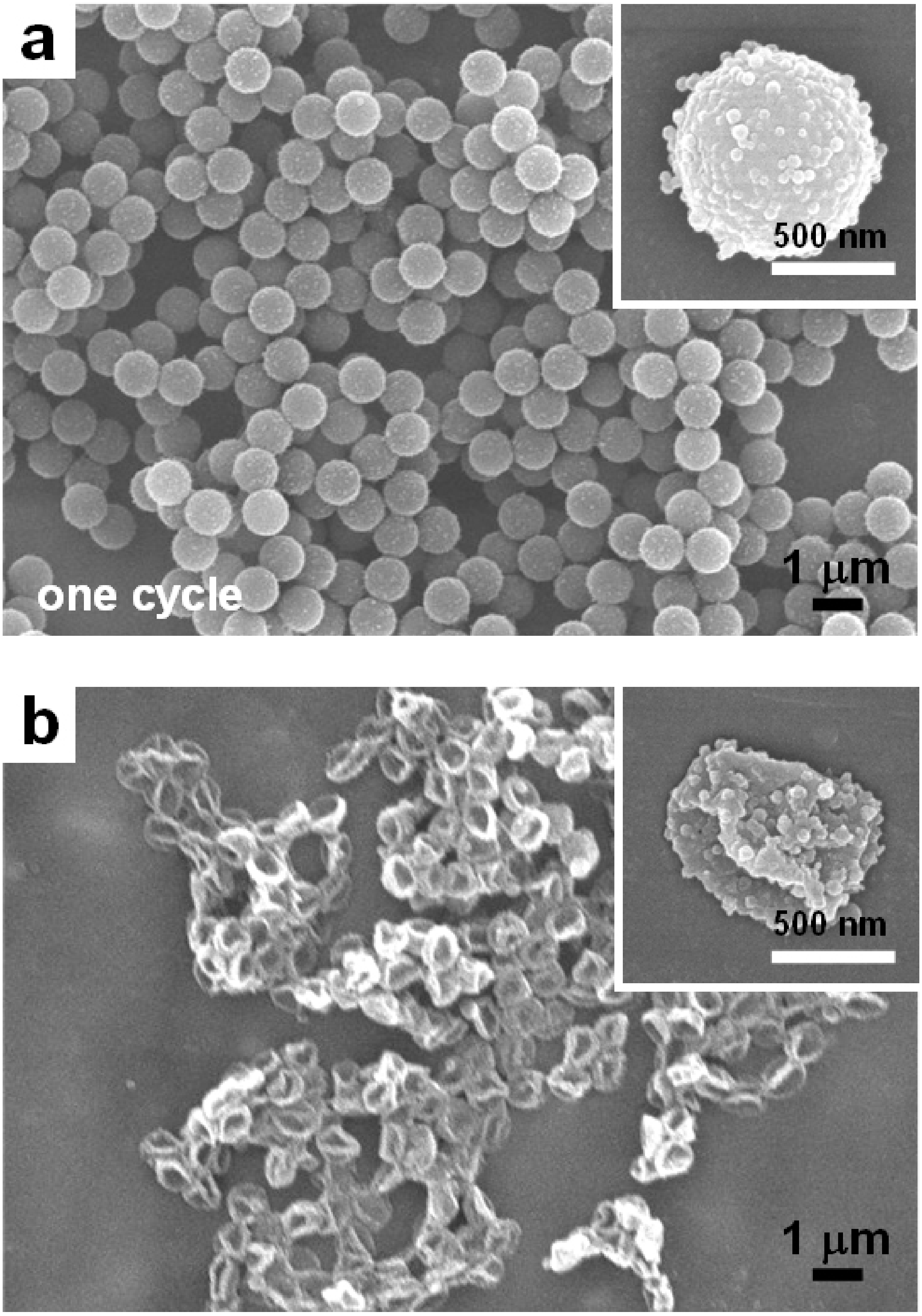

Fig. S4 Broad range SEM images of (a) polystyrene@ZIF-8 core-shell microspheres with an average diameter of 0.90 ± 0.02 μm (s.d., n = 100) obtained by conducting only one ZIF-8 growth cycle and (b) hollow ZIF-8 particles obtained by etching the polystyrene cores of the polystyrene@ZIF-8 core-shell microspheres shown in (a). The insets are high-magnification images.

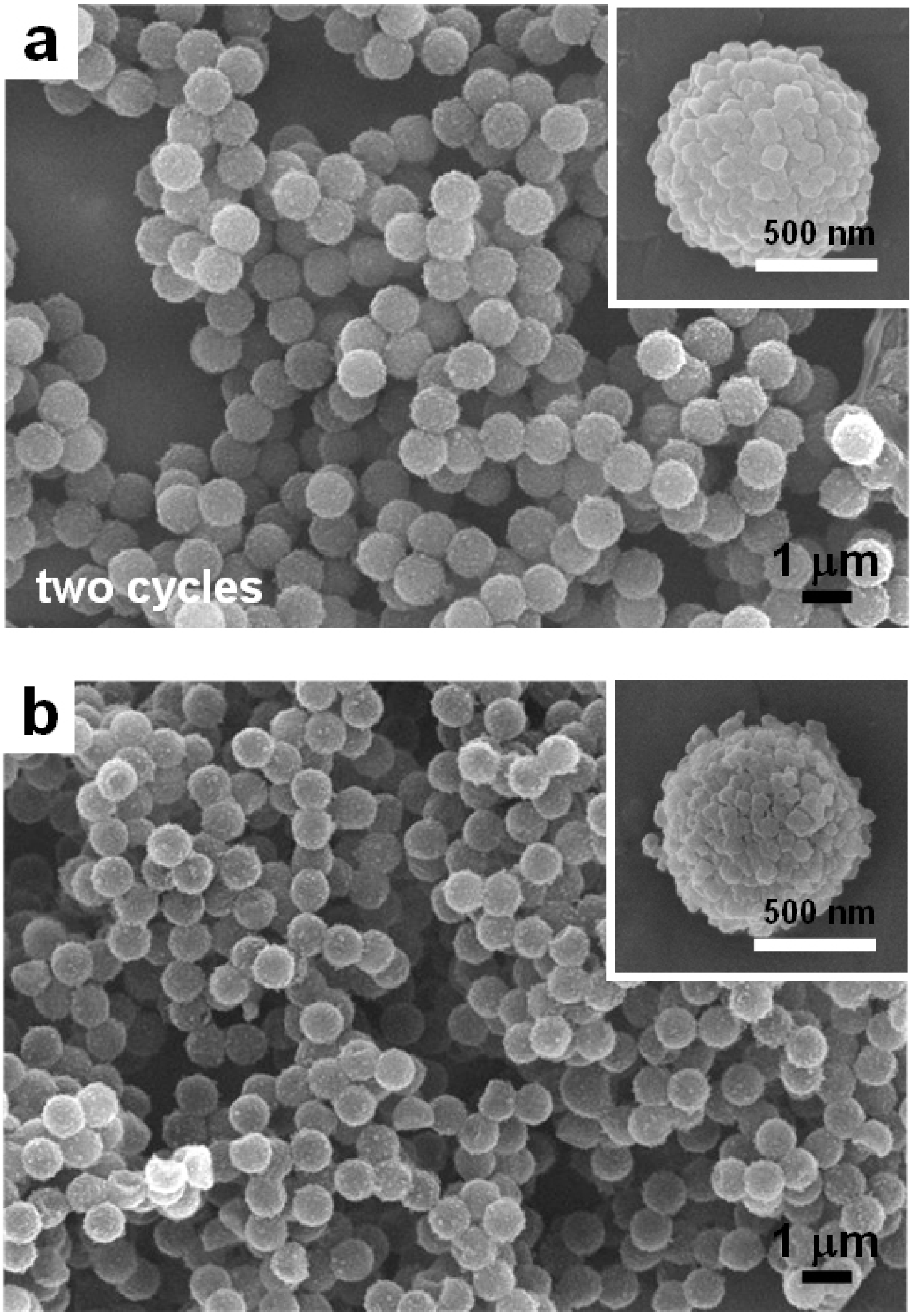

Fig. S5 Broad range SEM images of (a) polystyrene@ZIF-8 core-shell microspheres with an average diameter of 0.97 ± 0.02 μm (s.d., n = 100) obtained by conducting two cycles of the ZIF-8 growth process and (b) hollow ZIF-8 particles obtained by etching the polystyrene cores of the polystyrene@ZIF-8 core-shell microspheres shown in (a). The insets are high-magnification images.

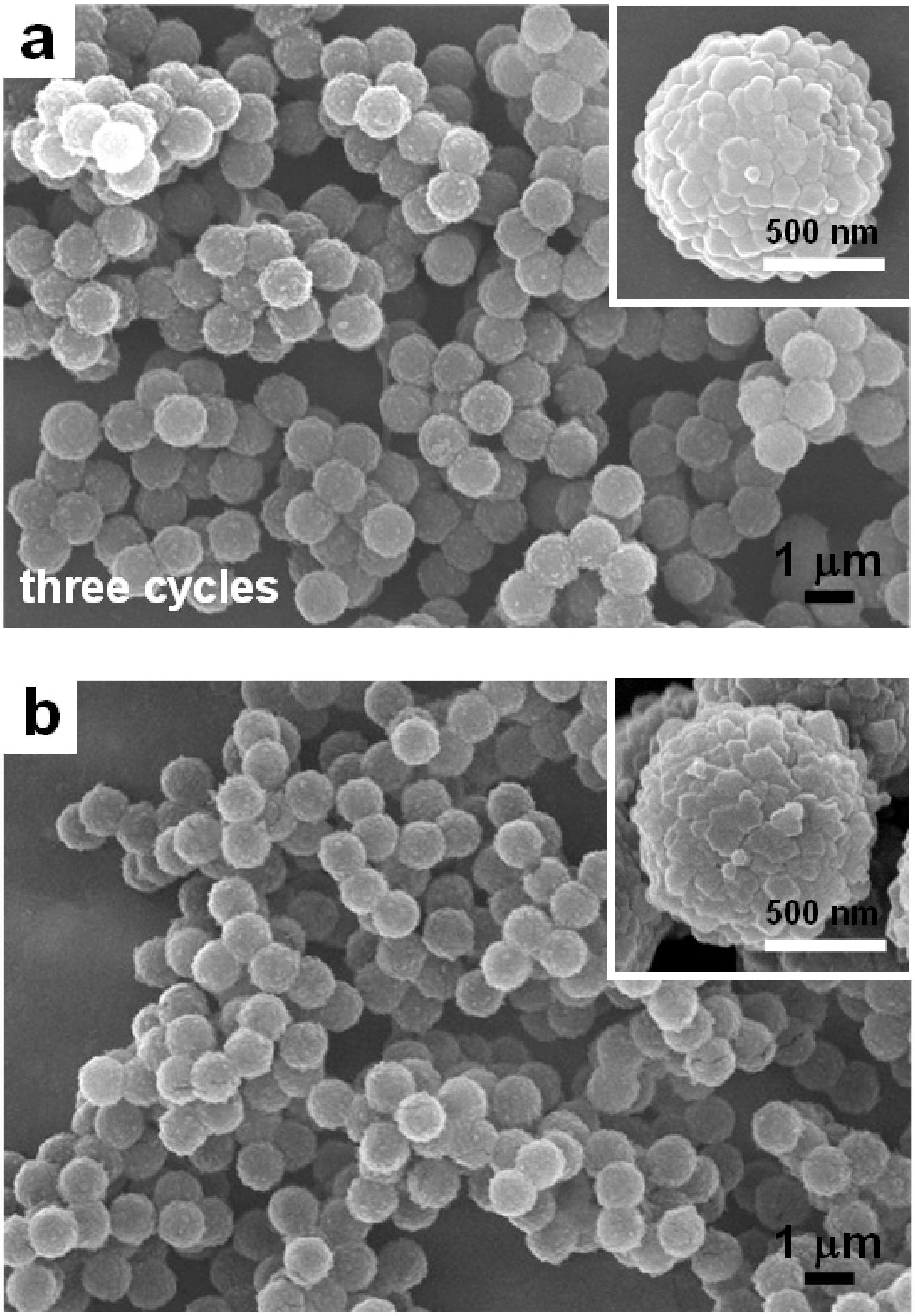

Fig. S6 Broad range SEM images of (a) polystyrene@ZIF-8 core-shell microspheres with an average diameter of 1.06 ± 0.02 μm (s.d., n = 100) obtained by conducting three cycles of the ZIF-8 growth process and (b) hollow ZIF-8 particles obtained by etching the polystyrene cores of the polystyrene@ZIF-8 core-shell microspheres shown in (a). The insets are high-magnification images.

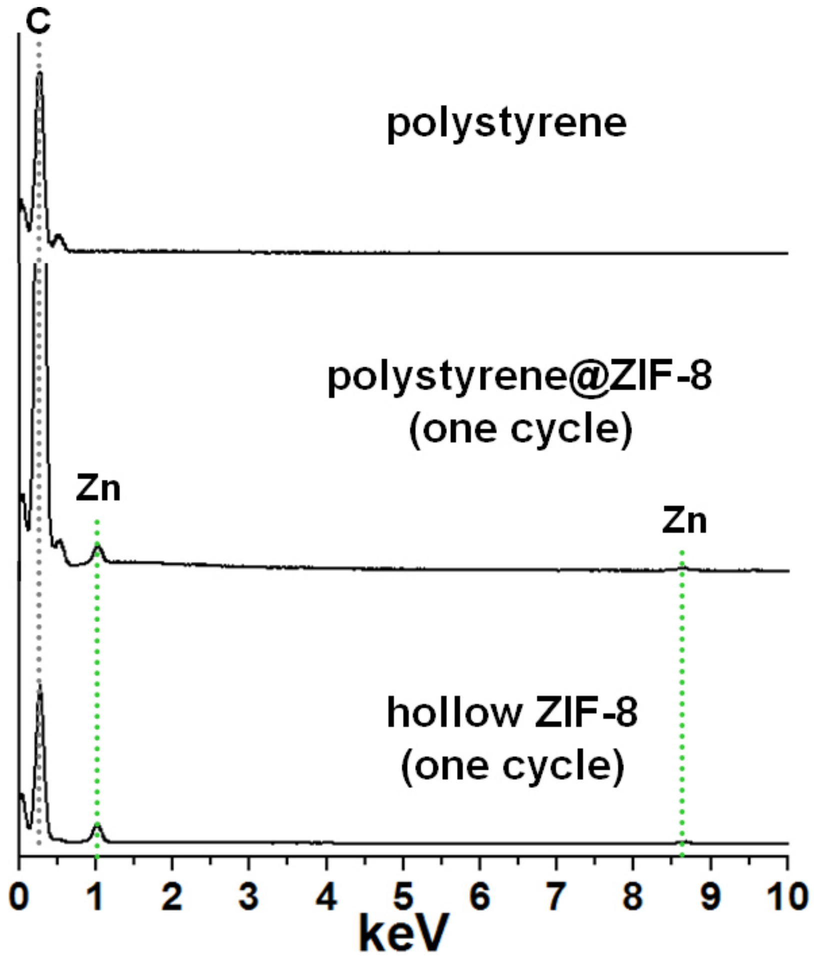

Fig. S7 A series of EDX spectra of initial carboxylate-terminated polystyrene, polystyrene@ZIF-8 core-shell, and hollow ZIF-8 microspheres (top to bottom). Polystyrene@ZIF-8 core-shell and hollow ZIF-8 microspheres were obtained by conducting one cycle of the ZIF-8 growth process.

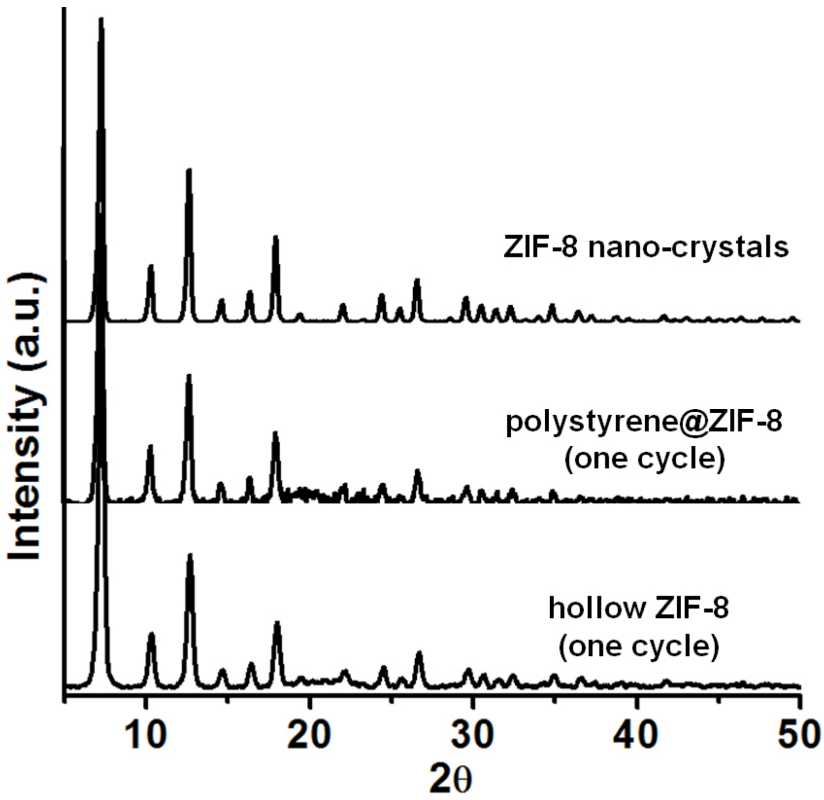

Fig. S8 PXRD patterns for the hollow ZIF-8 microspheres (bottom), polystyrene@ZIF-8 core-shell microspheres (middle), and ZIF-8 nano-crystals (top). Polystyrene@ZIF-8 core-shell and hollow ZIF-8 microspheres were obtained by conducting one cycle of the ZIF-8 growth process. All three PXRD patterns are nearly identical.

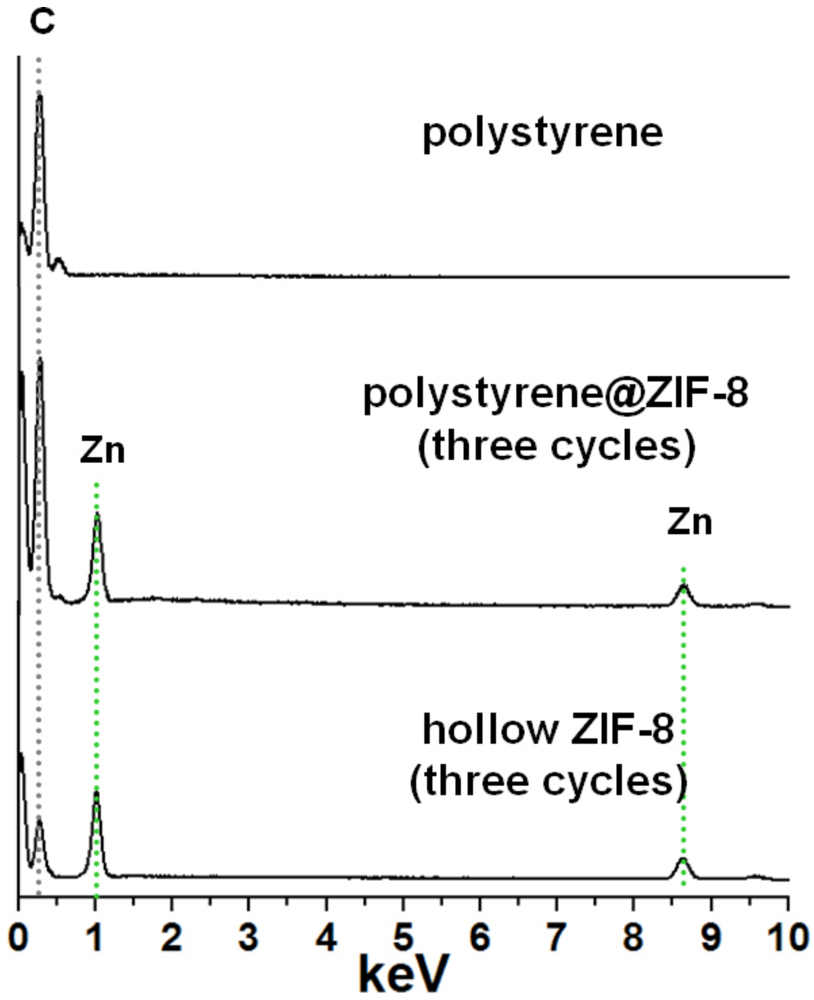

Fig. S9 A series of EDX spectra of initial carboxylate-terminated polystyrene, polystyrene@ZIF-8 core-shell, and hollow ZIF-8 microspheres (top to bottom). Polystyrene@ZIF-8 core-shell and hollow ZIF-8 microspheres were obtained by conducting three cycles of the ZIF-8 growth process.

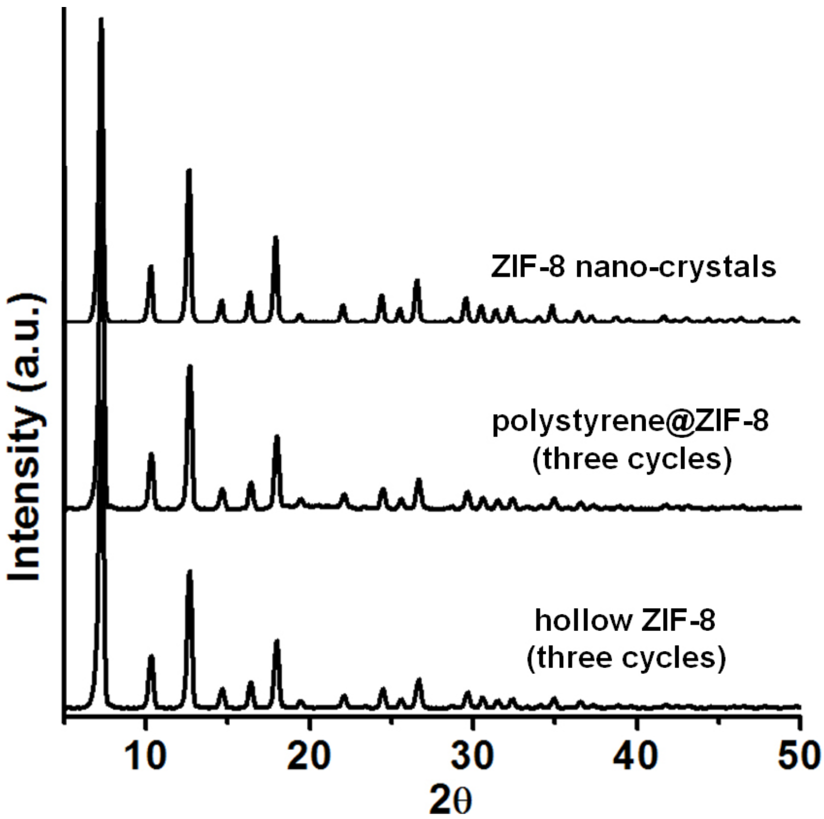

Fig. S10 PXRD patterns for the hollow ZIF-8 microspheres (bottom), polystyrene@ZIF-8 core-shell microspheres (middle), and ZIF-8 nano-crystals (top). Polystyrene@ZIF-8 core-shell and hollow ZIF-8 microspheres were obtained by conducting three cycles of the ZIF-8 growth process. All three PXRD patterns are nearly identical.