Synthesis of Metal-Organic-Framework Related Core-Shell Heterostructures and

Application to Ions Enrichment in Aqueous Circumstance

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Supplementary Information

Part S1. Detailed experimental section

Chemicals

All chemicals used in this study were of analytic grade. SiO_2 microspheres with a diameter of about 0.4 μm were purchased from Alfa Aesar Company.

Synthesis of SiO₂@HKUST-1 core-shell microspheres

The synthetic procedure of SiO_2@HKUST-1 core-shell microspheres included three stages (shown in Scheme 1): the first stage is O_2 plasma activation of raw SiO_2 microspheres; the second stage is chemical carboxylation of SiO_2 microspheres; the third stage is growth of HKUST-1 MOFs shells.

1) *O_2 plasma activation of raw SiO_2 microspheres*

The apparatus for O_2 plasma oxidation has been depicted in our previous paper.[1] A plasma generator induced by a radio frequency (RF) inductively coupled plasma (ICP) was used in this study. Prior to ignition of the O_2 plasma, the pressure in the reactor was evacuated to 2.0 Pa. Pure O_2 gas was then introduced into the reactor via a needle valve. Plasma ignition occurred at 5 Pa with a frequency of 13.56 MHz and supplied power of 80 W. SiO_2 microspheres were oxidized by O_2 plasma for 20 minutes under continuous stirring.

2) *Chemical carboxylation of activated SiO_2 microspheres*

In this study, a new method of SiO_2 surface carboxylation was developed. In the typical experimental process, 0.5 g O_2 plasma activated SiO_2 microspheres and 0.5 g

terephthalic acid were added to 20 mL dimethyl formamide (DMF) in a 50 mL flask and sonicated for 20 min. 0.5 g Na_2CO_3 was added into the above solution. The mixture was refluxed at the temperature of 120 °C for 2 hours with stirring in an oil bath. After cooling to room temperature, the product was collected by centrifuged and washed by ethanol and water for several times, and then dried at the temperature of 60 °C under vacuum. The carboxylate-terminated SiO_2 microspheres were obtained.

3) *Growth of HKUST-1 MOFs shells on the carboxylate-terminated SiO_2 microspheres*

In this stage, HKUST-1 shell was grown using a layer-by-layer method according to the literature.[2] In a typical process, a certain amount carboxylate-terminated SiO_2 microspheres were immersed in 1 mM of $Cu(CH_3COO)_2•H_2O$ ($Cu(Ac)_2$) ethanol solution for 30 minutes with stirring, and then collected by centrifuged and washed by ethanol. Following that, the collected sample was immersed in 1 mM of benzenetricarboxylic acid (H_3BTC) ethanol solution for 1 hour with stirring at room temperature, and then collected by centrifuged and washed by ethanol. After repeating the immersion of $Cu(Ac)_2$ solution and H_3BTC solution in turn for several cycles, the final products with light blue color were obtained.

Synthesis of Fe_3O_4@HKUST-1 core-shell nanospheres

According to the literature,[3] Fe_3O_4 nanospheres were prepared by a solvothermal method. Briefly, 2.70 g of $FeCl_3•6H_2O$ and 7.20 g of NaAc were dissolved in 100 mL ethylene glycol. The mixture was sealed in a Teflon-lined stainless-steel autoclave to heat at the temperature of 200 °C for 8 hours. The obtained black particles were

washed with ethanol for several times, and then dried in vacuum at 60 ^{o}C for 12 h.

By the same synthetic process as the fabrication of SiO$_2$@HKUST-1 core-shell microspheres, the Fe$_3$O$_4$@HKUST-1 core-shell nanospheres were fabricated. TEM images of the as-prepared sample were shown in the Figure S3.

Synthesis of SiO$_2$@ Cr-BTC core-shell nanospheres

By the same synthetic process as the fabrication of SiO$_2$@HKUST-1 core-shell microspheres, the SiO$_2$@Cr-BTC core-shell nanospheres were fabricated. TEM images of the as-prepared sample were shown in the Figure S4.

Characterization

The scanning electron microscopy (SEM) images were taken by using a field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F, 10 kV). The transmission electron microscopy (TEM) investigations were carried out in a JEOL JEM-2000EX operating at 100 keV. The nitrogen adsorption and desorption isotherms at 77 K were measured with a Micromeritics ASAP 2020 analyzer. Horvath-Kawazoe method was employed to analyze the successive pore size distribution (PSD) curves. X-Ray photoelectron spectroscopy (XPS) analyses of the samples were conducted on a VG ESCALAB MKII spectrometer using an Mg Kα X-ray source (1253.6 eV, 120 W) at a constant analyzer. Infrared spectroscopy (IR) analyses of the samples were conducted on a VERTEX 80. UV-vis absorption spectra was recorded on a double beam UV-vis spectrophotometer (UV-2550, SHIMADZU).

Adsorption and desorption experiments

Adsorption and desorption experiments were carried out at 293 K and in

polyethylene centrifuge tubes by using the bath technique. Stock solutions of 1000 mg/L fluorinion were prepared from NaF in deionized water. The stock solution was further diluted with deionized water to the required concentration in the adsorption experiments. The pH values were adjusted with negligible amount of 0.1 M HCl or NaOH. The adsorption experiments were carried in polyethylene centifuge tubes containing 40 mg adsorbents and 10 mL F⁻ solution with initial concentration of 103.3 mg/L at pH 4.0. The tubes were sealed and placed on a shaker for stirring 24 hours. Through separation by centrifugation, the supernatant was collected to analyze the final F⁻ concentrations remaining in the solution. And the sediment was collected and dried for desorption experiment. In desorption experiment, the sediment was added to 10 mL deionized water at pH 8.0 and shaken for 24 hours. And the supernatant was collected by centrifugation to measure the F⁻ concentration of the solution. The sediment was collected and dried for next adsorption experiment. The F⁻ concentrations of the solutions were analyzed by ion chromatograph (Dionex ICS-3000).

Methodology

All DFT simulations were performed with Gaussian03 package. Their geometries are optimized via unrestricted density functional theory (UB3LYP) combined with split valence basis sets 6-31+G. The vibrational frequencies were analyzed on the basis of optimized geometry in order to ensure that no imaginary frequencies were obtained and local minima on the potential energy surface were located.

Reference List for Supplementary Information

1 X. Y. Yu, T. Luo, Y. X. Zhang, Y. Jia, B. J. Zhu, X. C. Fu, J. H. Liu and X. J. Huang, *ACS Appl. Mat. Interfaces*, **2011**, 3, 2585.

2 O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer and C. Wöll, *J. Am. Chem. Soc.*, **2007**, 129, 15118.

3 H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen and Y. D. Li, *Angew. Chem. Int. Ed.*, **2005**, 44, 2782.
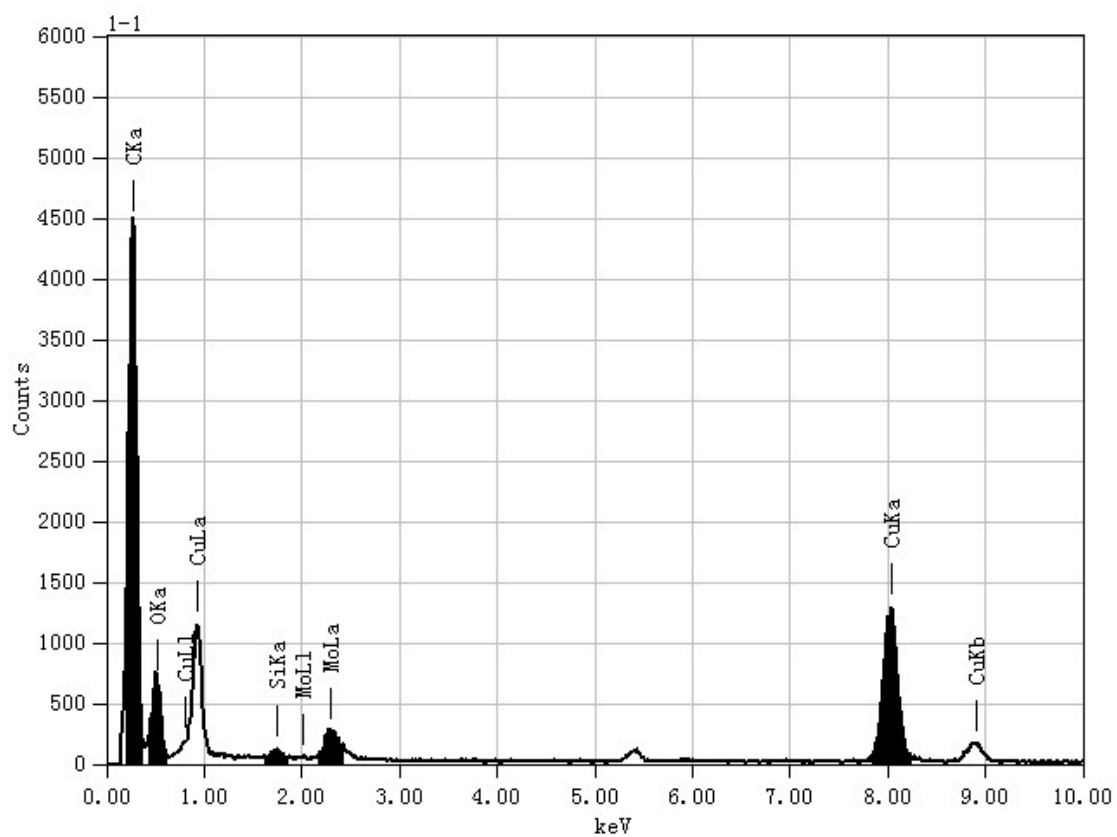
Part S2. Additional experimental data

Figure S1. EDS characterization of the shell layer of the as-prepared SiO_2@HKUST-1 core-shell heterostructure.
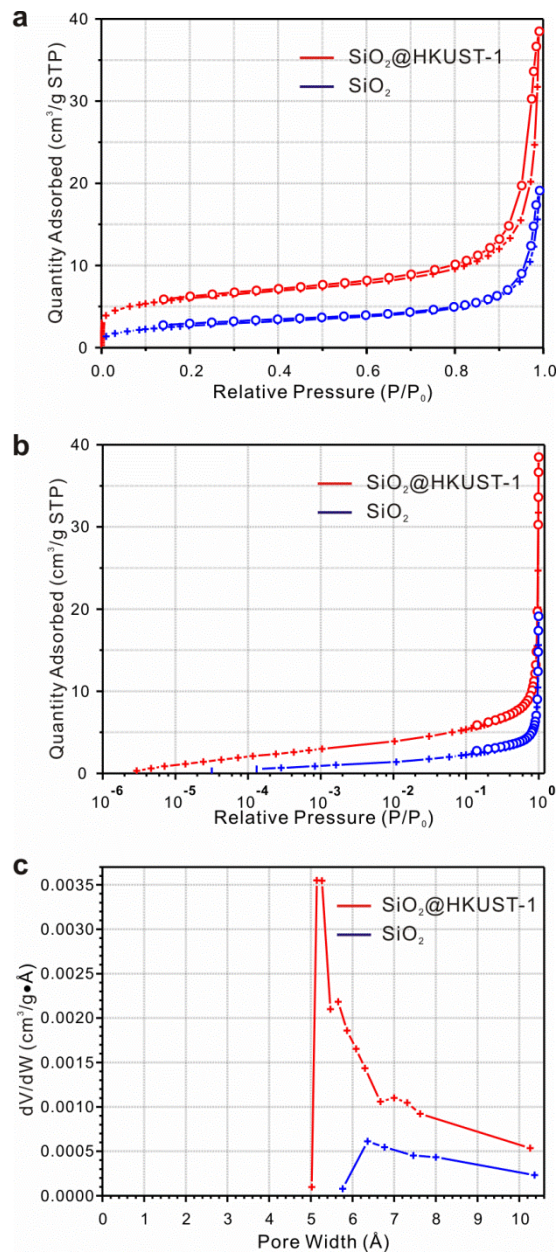
Figure S2. BET N$_2$ Adsorption isotherms and pore size distribution of the raw SiO$_2$ and SiO$_2$@HKUST-1 MOFs. **a**, Isotherm Linear Plot. **b**, Isotherm log Plot. **c**, Horvath-Kawazoe Differential Pore Volume Plot.
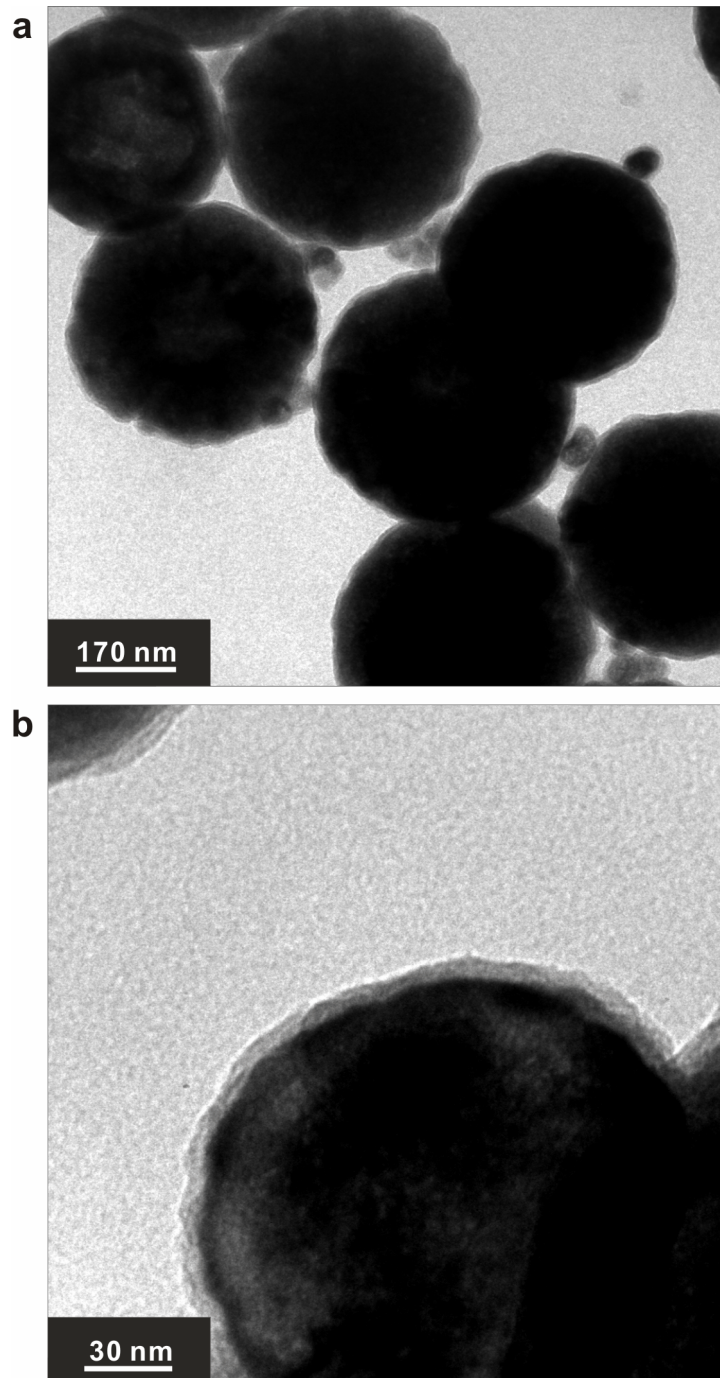
Figure S3. TEM images of Fe$_3$O$_4$@HKUST-1 synthesized by the as-proposed step-by-step synthetic strategy: a) low magnification; b) high magnification.
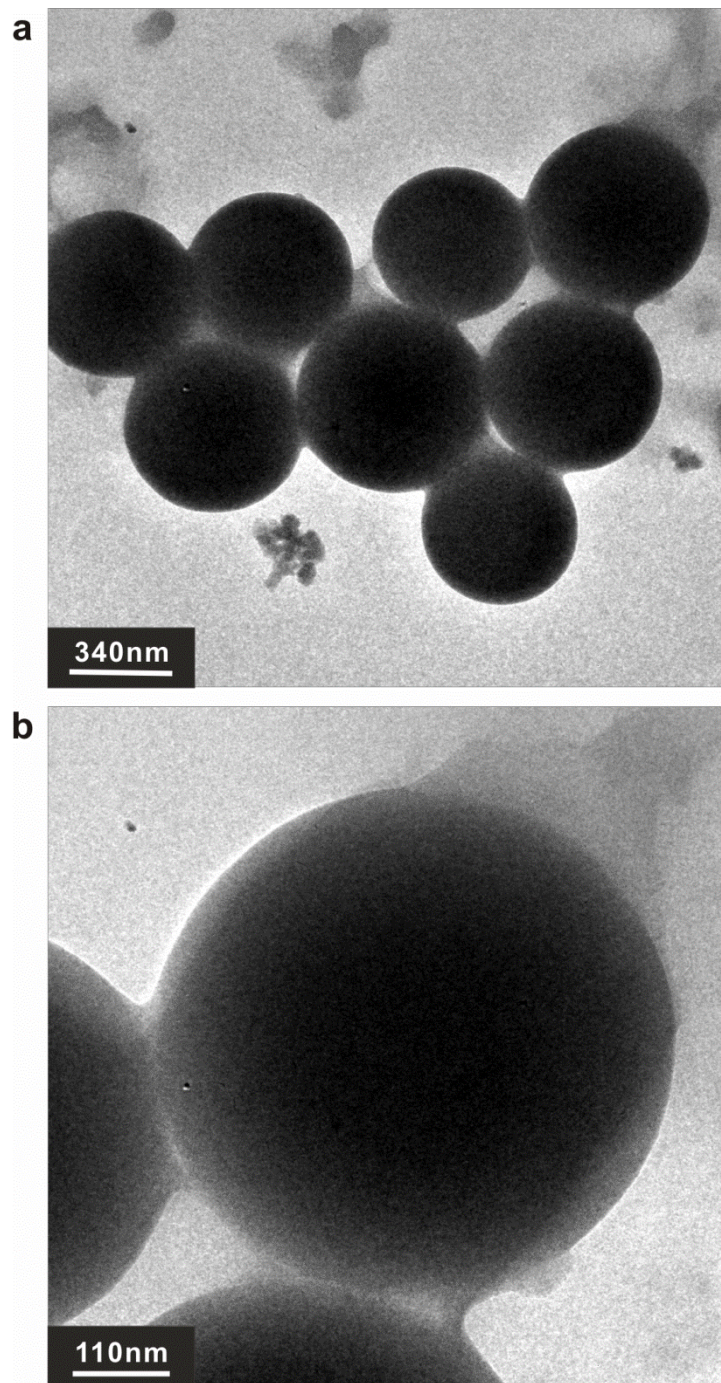
Figure S4. TEM images of SiO$_2$@Cr-BTC synthesized by the as-proposed step-by-step synthetic strategy: a) low magnification; b) high magnification.
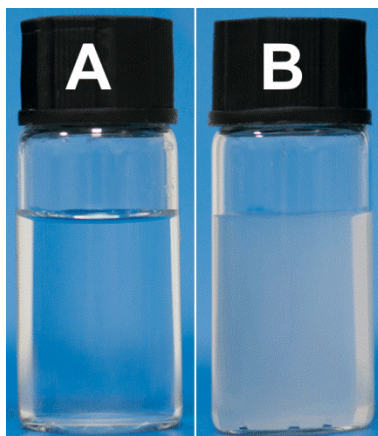
Figure S5. Optical photo of the fluoride solutions: A) the supernatant after adsorption of fluoride onto SiO_2 microspheres at pH 4; B) the supernatant at pH 8. (Combining with the fluoride concentration data listed in **Table S1**, it can be found that only a little amount of fluoride adsorbed on the SiO_2 microspheres, large amount of fluoride reacted with SiO_2 to form SiF_6^{2-} existing in the supernatant after sorption at pH 4. So, the supernatant at pH 4 was a clear solution. When the pH of the supernatant was adjusted to 8, SiF_6^{2-} reacted with OH^- to form SiO_2 precipitate. The supernatant became turbid.)

Table S1 The concentration of fluoride in the solutions in the test of the sorption/desorption behaviors of fluoride onto SiO_2 microshperes and SiO_2@HKUST-1 heterostructure.

Sample		Original solution	Supernatant after sorption	Supernatant after desorption
Concentration of Fluoride (ppm)	By SiO_2	103.3	2.3	5.4
	By SiO_2@HKUST-1	103.3	1.3	101.9

Table S2 The simulated structure parameters of $F^-(H_2O)$ and $SiF_6^{2-}(H_2O)_3$ clusters.

Cluster	$F^-(H_2O)$			$SiF_6^{2-}(H_2O)_3$					
Distance				O8-O11	O8-H12	O8-H13			
	F1-O3	F1-H4	O3-H4	O8-O14	O11-H15	O11-H16	O8-F5	O11-F3	O14-F2
							O8-F7	O11-F4	O14-F6
				O11-O14	O14-H9	O14-H10			
Length(Å)	2.49	2.89	0.98	6.52	6.29	5.83	5.15	5.15	5.15