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Electronic Supplementary Information

Designable magnetic MOF composite and facile coordination-based post-synthetic strategy for enhanced removal of Hg^{2+} from water

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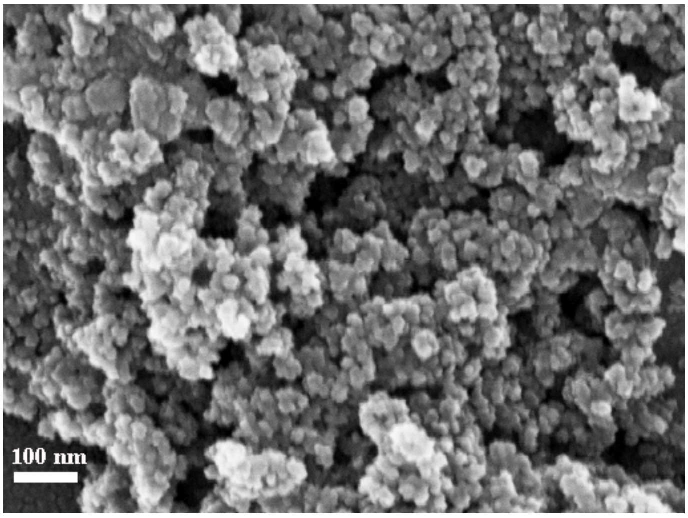

Fig. S1. SEM image of $Fe_3O_4@SiO_2@$HKUST-1 (Note: $Fe_3O_4@SiO_2$ NPs had a uniform size of about 20 nm.)

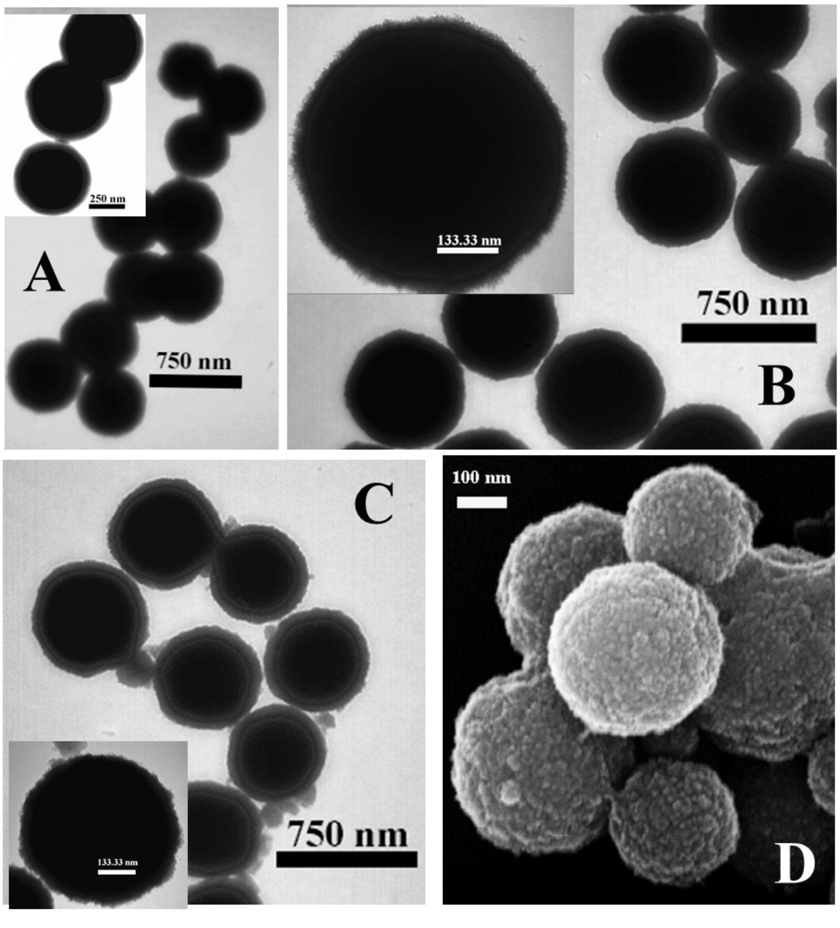

Fig. S2. TEM and SEM images of prepared magnetic micro-composites
(a) $Fe_3O_4@SiO_2$, (b) $Fe_3O_4@SiO_2@Cu(OH)_2$, (c) $Fe_3O_4@SiO_2@$HKUST-1 (The insets show the enlarge images), (d) SEM image of $Fe_3O_4@SiO_2@$HKUST-1

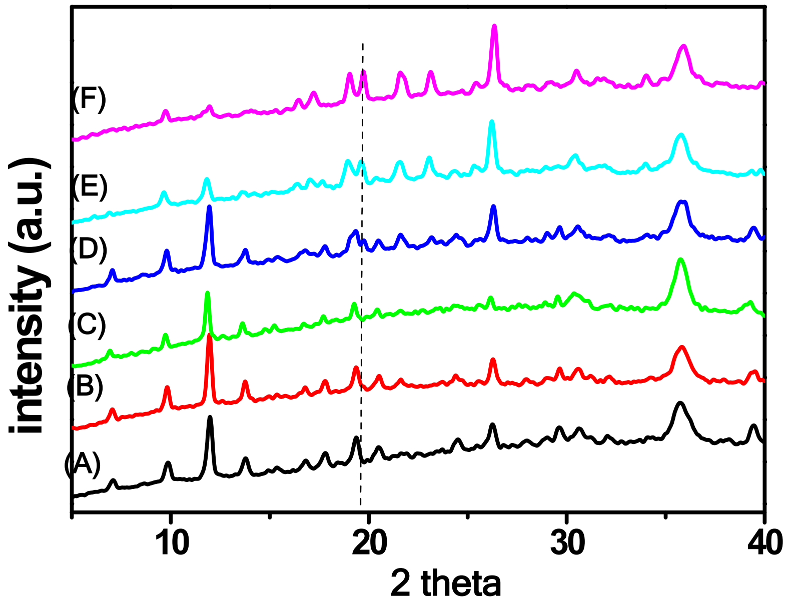

Fig. S3 XRD patterns of the prepared Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 before spiking into aqueous solution (A); dispersed in 10 mg L^{-1} Hg^{2+} solution at pH 3 for 10 min (B); 20 min (C); 30 min (D); 45 min (E); and 60 min (F).

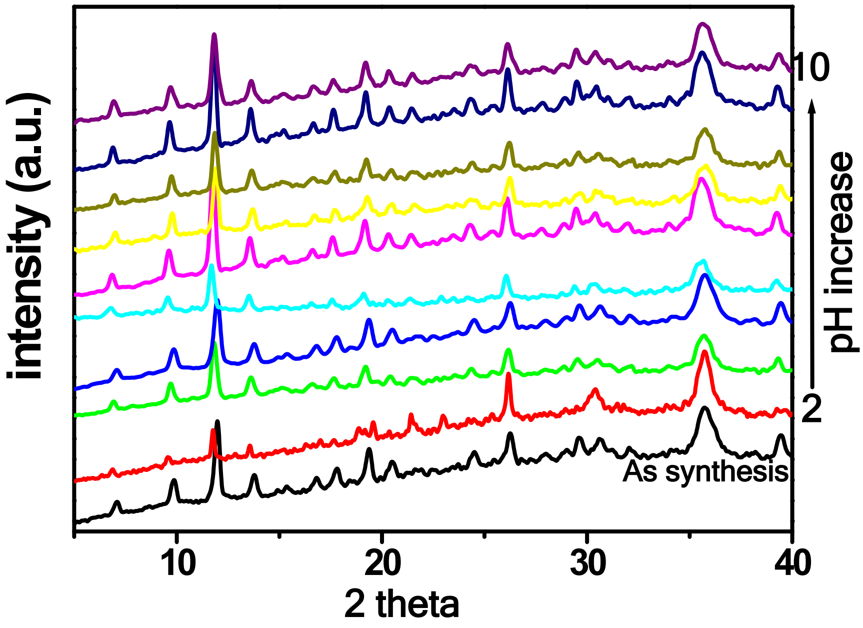

Fig. S4 XRD patterns of the prepared Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 before and after mercury adsorption at different pH (Hg^{2+} concentration: 10 mg L^{-1}, exposure time: 20 min).

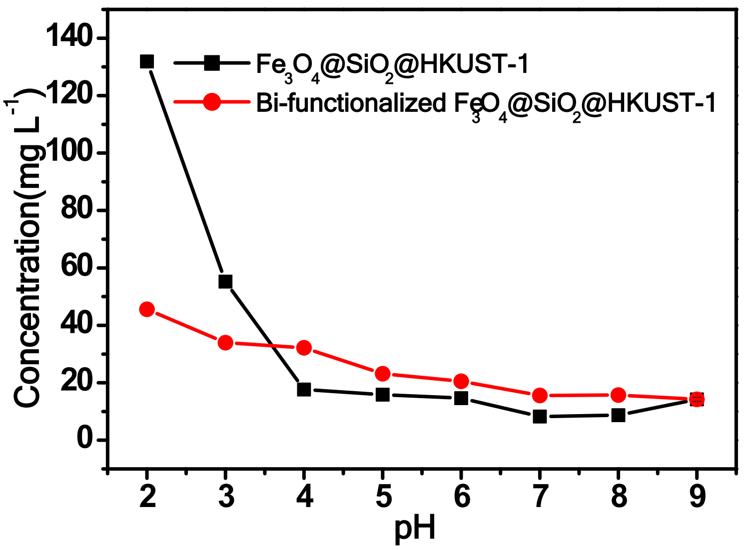

Fig. S5 The effect of pH on the concentration of Cu^{2+} in the solution after MSPE process with the prepared Fe_3O_4@SiO_2@HKUST-1 and Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 (Hg^{2+} concentration: 10 mg L^{-1}, exposure time: 20 min).

Preparation of 400 nm Fe_3O_4 micro-spheres:

Superparamagnetic Fe_3O_4 nano/micro-spheres with tunable average sizes were synthesized according to a hydrothermal method[1]. Typically, $FeCl_3 \cdot 6H_2O$ (0.65 g, 4.0 mmol) and trisodium citrate (0.20 g, 0.68 mmol) were first dissolved in ethylene glycol (20 mL), afterward, NaAc (1.20 g) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated at 200 °C and maintained for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deioned water for several times and then dispersed in water (16 mL).

Synthesis of Fe_3O_4@SiO_2 Microspheres with Core/shell Nanostructure:

The obtained Fe_3O_4 microspheres were coated by a layer of SiO_2 shell. In particular, an aqueous solution (8 mL) of Fe_3O_4 was diluted with water (8 mL) and ethanol (40 mL). The mixture was homogenized by ultrasonication for 30 min, prior to the addition of ammonia solution (1 mL). After 15 min, a solution of TEOS (200 μL) in ethanol (4 mL) was added dropwise into the solution. The reaction was performed for 12 h and that the product was collected by the help of a magnet and washed with ethanol and water for several times. Finally, the product of Fe_3O_4@SiO_2 microspheres with core/shell nanostructure was dispersed in water (10 mL).

Preparation of Fe_3O_4@SiO_2@$Cu(OH)_2$:

The Fe_3O_4@SiO_2@$Cu(OH)_2$ microspheres were prepared by the conventional co-precipitation method. 5 mL aqueous solution of Fe_3O_4@SiO_2 was diluted with high purity water (200 mL), followed by the addition of 200 mg $CuCl_2 \cdot H_2O$. The mixture was ultrasounded for 20 min, and then adjusted pH to 9.0~10.0 by 1.0 mol L^{-1} NaOH aqueous solution under vigorously stirring. The mixture was kept at 85 ^{o}C for 3 h. After cooling to room temperature the product was washed with water and ethanol sequentially for several times, and finally dried at 50 ^{o}C under vacuum overnight.

Preparation of Fe_3O_4@SiO_2@HKUST- 1:

Fe_3O_4@SiO_2@HKUST-1 composite was prepared according to Report[2] with minor modifications. 80 mg as-synthesized Fe_3O_4@SiO_2@$Cu(OH)_2$ was dispersed in 1 mL high purity water, followed by the addition of 2 mL ethanol solution containing 126 mg H_3BTC for transforming $Cu(OH)_2$ into HKUST-1. The mixture solution was then stirred for 12 h at room temperature. The products were washed several times with water and ethanol, then dried overnight at 150 °C under air atmosphere.

Reference

1. Deng, Y.; Deng, C.; Qi, D.; Liu, C.; Liu, J.; Zhang, X.; Zhao, D., Synthesis of core/shell colloidal magnetic zeolite microspheres for the immobilization of trypsin. *Adv. Mater.*, 2009, **21**, 1377-1382.
2. Majano, G.; Perez-Ramirez, J., Scalable room-temperature conversion of copper(II) hydroxide into HKUST-1 (Cu3(btc)2). *Adv. Mater.*, 2013, **25**, 1052-1057.