Supporting information

MOF catalysis of Fe$^{II}$-to-Fe$^{III}$ reaction for ultrafast and one-step generation of Fe$_2$O$_3$@MOF composite and uranium(VI) reduction by iron(II) at ambient conditions

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Synthesis of Zn-MOF-74. The synthesis of it accords with the reported methods as follows. A mixture of Zn(NO$_3$)$_2$.6H$_2$O (0.0604 g, 0.203 mmol), 2,5-dihydroxy terephthalic acid (0.0191 g, 0.096 mmol), N,N-dimethylformamide (DMF) (2 ml), isopropyl alcohol (0.1 mL) and H$_2$O (2 mL) was placed in a closed 25 ml Teflon reactor and heated at 105°C for 1200 min, in turn cooled to room temperature, produced brown needle-shaped crystals were got and dried in 69 % yield (based on Zn) at room temperature.

Materials and General Methods. Reagents and solvents were commercially available (Alfa) and were used without further purification. X-ray powder diffraction were collected by a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu Ka, (λ=1.5406Å). The simulated powder patterns were calculated by Mercury 1.4. The purity of the bulk products were determined by comparison of the simulated and experimental PXRD patterns. SEM and EDS measurements were carried out using an Oxford X-max microscope. The concentration of Fe(II) and Fe(III) over time is determined by atomic absorption spectroscopy (TAS-990). The uranium concentration is determined by inductively coupled plasma-mass spectroscopy (ICP-MS, NexION 300X). XPS experiments were performed in a Theta probe (Thermo Fisher) using monochromated Al Kα x-rays at $hν=1486.6$ eV. The unit cell of the Zn-MOF-74 crystal is determined by single crystal x-ray diffraction (Bruker smart breeze), giving a=b=26.232(3), c=6.6688(13), trigonal, R-3 space group, which agrees well with the reported values for Zn-MOF-74.

Scheme S1. Schematic description of Zn-MOF-74 shows surface catalysis of inorganic reaction, leading to the one-step generation of Fe$_2$O$_3$@MOF composite and its application in U(VI) reduction by Fe(II). The mechanism of ‘enrichment-oxidation/or redox-nucleation-growth’ is proposed.
Fig. S1 Photograph of the samples and the coloration reaction. a) The as-synthesized Zn-MOF-74 samples dried naturally. b) The solid samples obtained by immersing Zn-MOF-74 in FeSO$_4$ (200 ppm) for 100 minutes. c) The solution of FeSO$_4$ (200 ppm) and phenol (0.01 g) laying for two days. d) Adding one drop H$_2$O$_2$ into the solution of FeSO$_4$ (200 ppm) and phenol (0.01 g) that has been laid for two days. e) The solution of FeSO$_4$ (200 ppm) and phenol (0.01 g) in the present of Zn-MOF-74 for three minutes.

Fig. S2 TEM and HRTEM images of α-Fe$_2$O$_3$@Zn-MOF-74.

Fig. S3 The N$_2$ adsorption at 77 K and its pore distribution for the samples of Fe$_2$O$_3$@Zn-MOF-74.
**Fig. S4** The XPS spectra of Fe(2p) for the sample after reactor I showing the characteristic features of Fe 2p$_{3/2}$ at 711 ev, Fe 2p$_{1/2}$ at 725 ev, and two satellites at 719 ev and 734 ev for α-Fe$_2$O$_3$.

**Fig. S5** SEM image of the sample after reactor I, where the nanoparticle of Fe$_2$O$_3$ and UO$_2$ on MOF surface shows an irregular distribution in the bulk form.
Fig. S6 TEM and HRTEM images of Zn-MOF-74 after reactor I.

Fig. S7 Images of element distribution for Fe, U, and Zn and EDS spectra for the samples after reactor I. The EDS spectra suggests a 10:1 ratio of Fe$_2$O$_3$:U for the resulted samples after reactor I. The images of element distribution for Fe, U, and Zn suggests that the U element is evenly distributed in Fe$_2$O$_3$, where the major is Fe$_2$O$_3$ colored by blue and U, Zn is colored by green and red, respectively.
Fig. S8 The PXRD patterns simulated from single crystal data of Zn-MOF-74, and PXRD patterns of as-synthesizes Zn-MOF-74 samples, the samples after reactor II (denoted as U@Zn-MOF-74), as well as the samples after reactor I, respectively.