Electronic Supplementary Information for

Fe_3O_4@MOF core–shell magnetic microspheres with a designable metal–organic framework shell

Fei Ke,[a] Ling-Guang Qiu,*[a] Yu-Peng Yuan,[a] Xia Jiang[a] and Jun-Fa Zhu[b]

[a] *Laboratory of Advanced Porous Materials, School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039 (P.R. China)*

Fax: (+86)551-5108212; E-mail: lgqiu@ahu.edu.cn

[b] *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029 (P.R. China)*

Experimental

Instruments

The powder X-ray diffraction (PXRD) patterns of the samples were collected using an X-ray diffractometer with Cu target (36 kV, 25 mA) from 5 to 65°. Analyses of the morphology and chemical composition of the samples were conducted by a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) and a JEOL JEM 2100 transmission electron microscope at 200 kV, respectively. Nitrogen sorption-desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2020M+C analyzer. Elemental analysis of C, H and N was carried out on a Vario ELIII, and the Cu and Fe contents were determined by atomic absorption spectrometry using a Thermo Elemental, USA M6 spectrometer. The magnetization curves were measured at room temperature under a varying magnetic field from -10000 to 10000 Oe on a BHV-55 vibrationg sample magnetometer (VSM).

Synthesis of core–shell magnetic Fe_3O_4@MOF microspheres

Fe_3O_4 nanoparticles were synthesized by a solvothermal method as reported previously.[2a] Mercaptoacetic acid (MAA)-functionalized Fe_3O_4 nanoparticles were prepared according to the following process. In a typical procedure, 0.05 g Fe_3O_4 was added to 10 mL of ethanol solution of mercaptoacetic acid (0.29 mM) under shaking for 24 h. The product was recovered by an external magnetic field and washed several times with distilled water and ethanol, then re-dispersed in ethanol. 0.05 g MAA-functionalized Fe_3O_4 core synthesized as described above was dispersed in 4 mL of $Cu(CH_3COO)_2 \cdot H_2O$ (for Fe_3O_4@[$Cu_3(btc)_2$] microspheres, or $FeCl_3 \cdot 6H_2O$ for Fe_3O_4@MIL-100(Fe) microspheres) ethanol solution (10 mM) for 15 minutes and then in 4 mL of benzenetricarboxylic acid (H_3btc) ethanol solution (10 mM) for 30 minutes at 25 °C or 70 °C. Between each step the microspheres were separated by magnetic decantation and washed with ethanol. After a given number of cycles the samples were washed with ethanol, and dried under vacuum at 150 °C.

Table S1.

Porosity properties, Fe_3O_4 contents, saturation magnetization values of Fe_3O_4@[$Cu_3(btc)_2$] **A1** (25 °C, 25 cycles), **A2** (25 °C, 50 cycles), **A3** (70 °C, 50 cycles) and Fe_3O_4@MIL-100(Fe) **B1** (25 °C, 50 cycles) core–shell magnetic microspheres.

	A1	**A2**	**A3**	**B1**
Fe_3O_4 Content [wt%]	46.1	30.0	16.1	33.17
S_{BET} [m^2 g^{-1}]	230.79	550.93	668.15	523.32
V [m^3 g^{-1}]	0.14	0.32	0.49	0.31
M_s [emu g^{-1}]	36.51	24.42	14.23	38.63

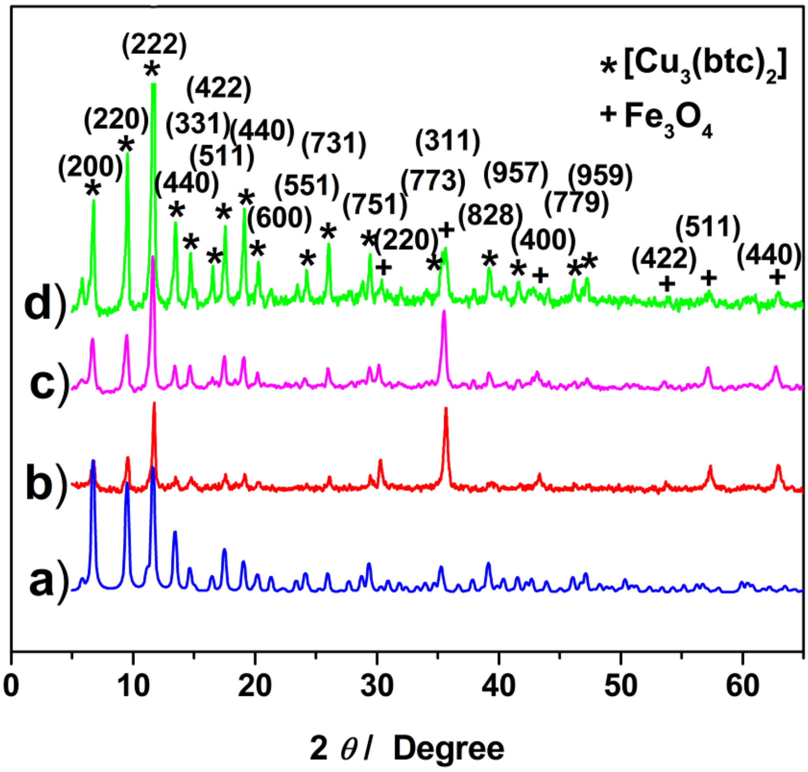

Fig. S1 PXRD patterns simulated from the crystallographic data of (a) HKUST-1 and Fe_3O_4@[Cu_3(btc)$_2$] core–shell microspheres (b) **A1** (25 °C, 25 cycles), (c) **A2** (25 °C, 50 cycles) and (d) **A3** (70 °C, 50 cycles).

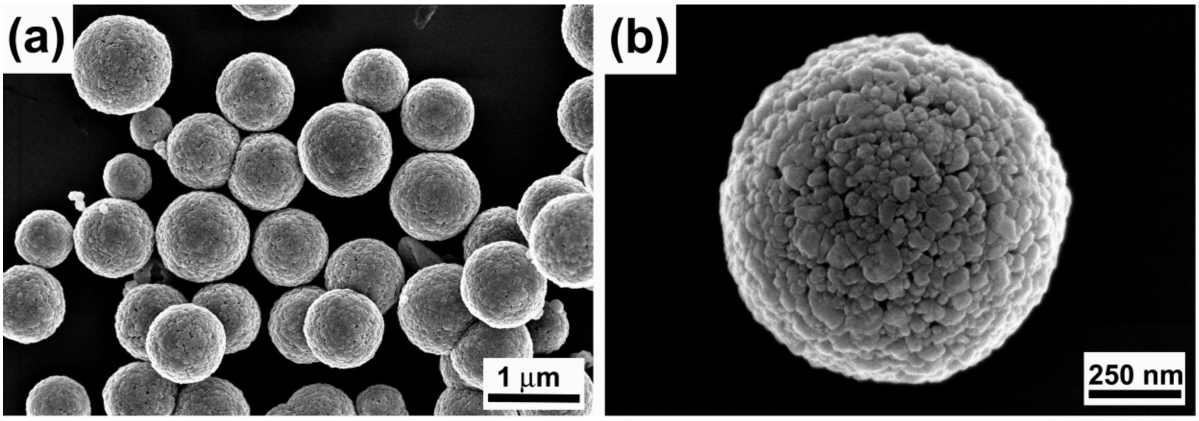

Fig. S2 SEM images of the initial Fe_3O_4 nanospheres (a) at low magnification, and (b) at high magnification.

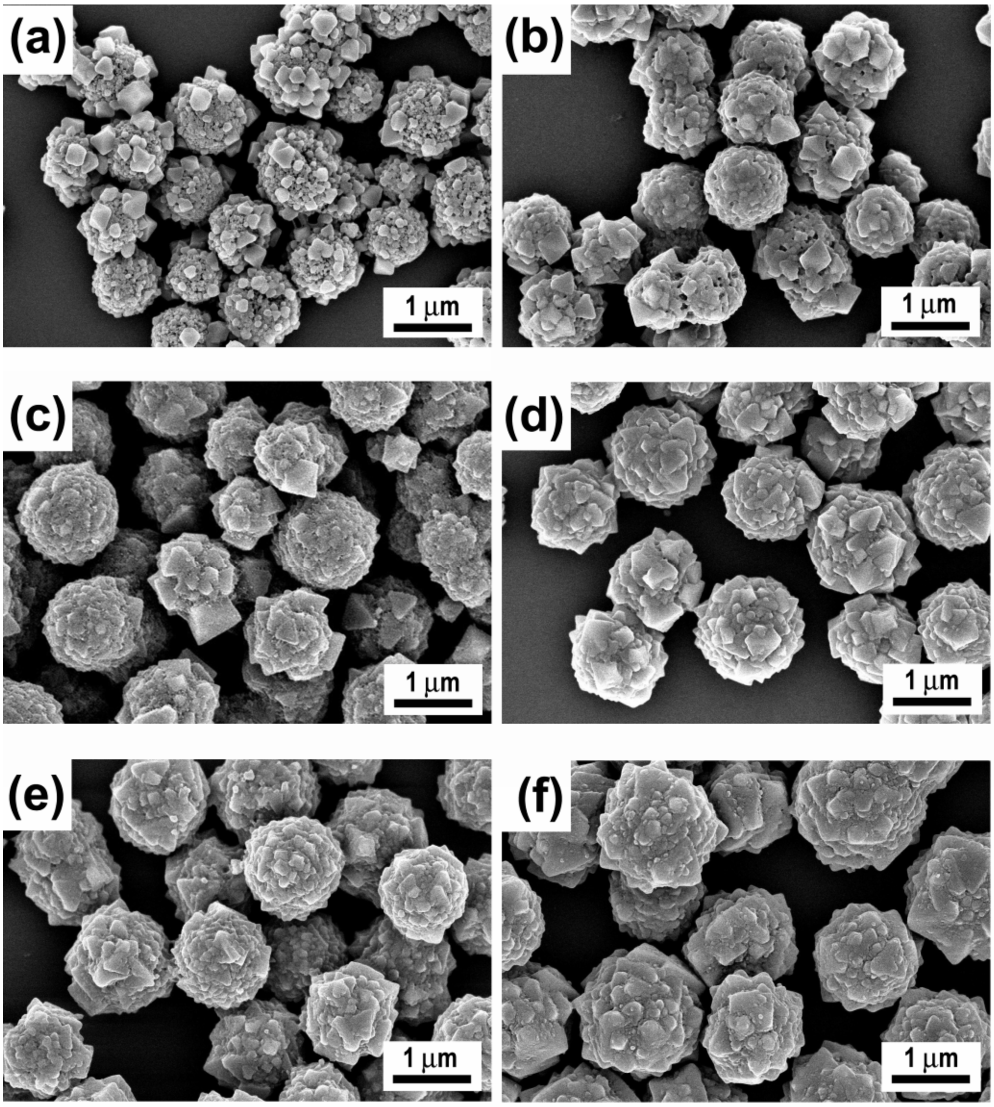

Fig. S3 SEM images of Fe_3O_4@[$Cu_3(btc)_2$] core–shell magnetic microspheres after (a) 10, (b) 20, (c) 25, (d) 30, (e) 40, and (f) 50 assembly cycles at 25 °C.

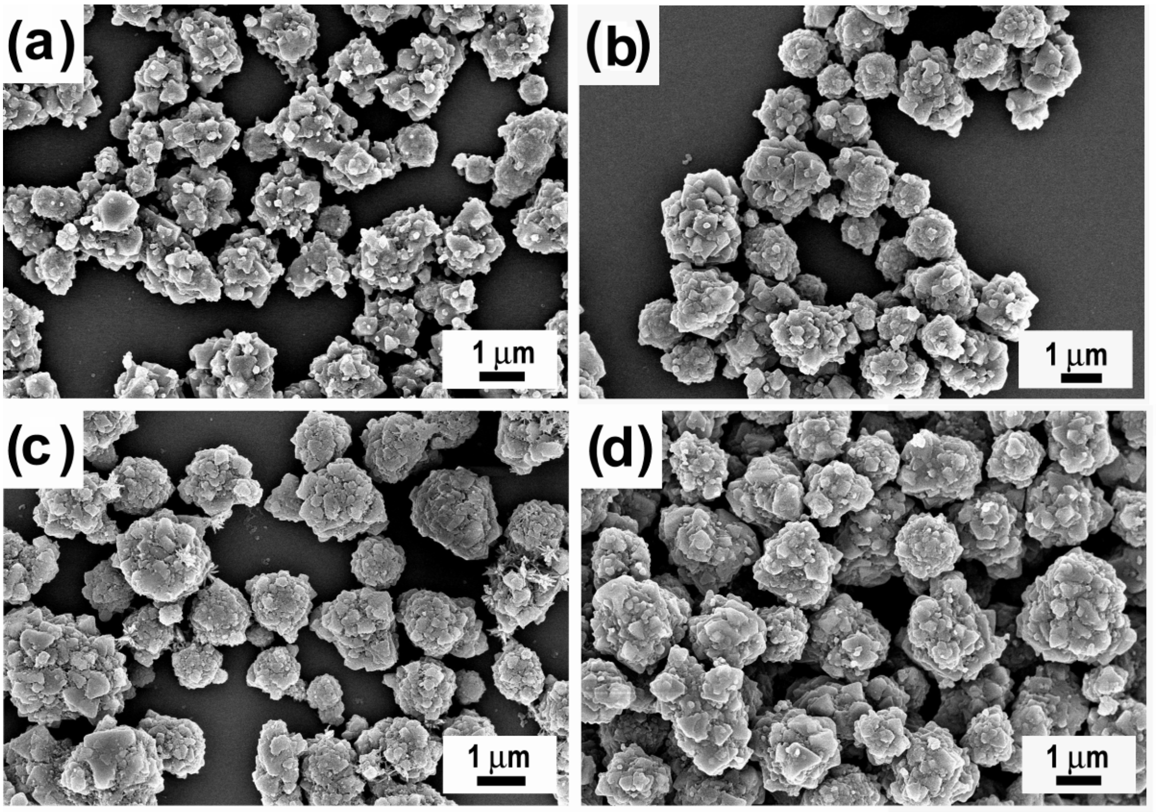

Fig. S4 SEM images of Fe_3O_4@$[Cu_3(btc)_2]$ core–shell magnetic microspheres prepared at 70 °C after (a) 20, (b) 30, (c) 40 and (d) 50 assembly cycles.

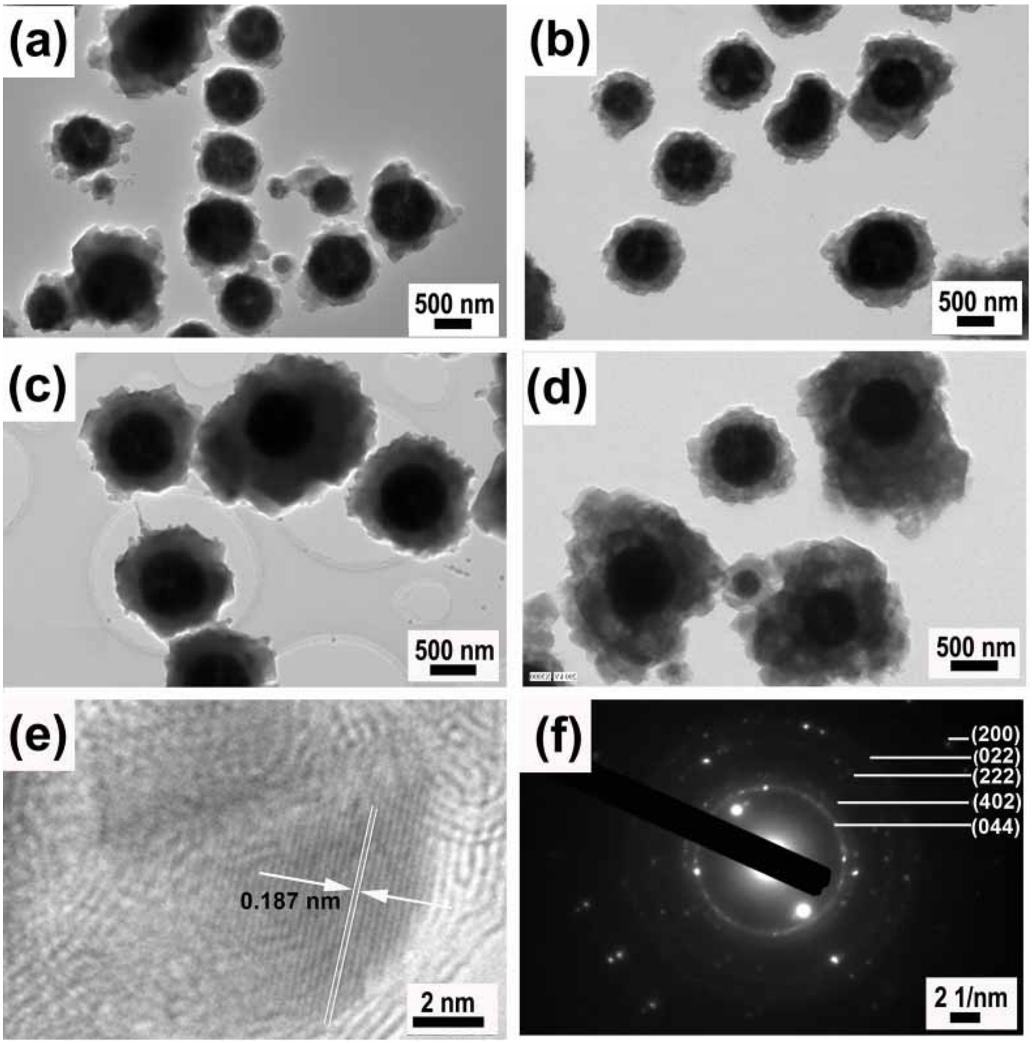

Fig. S5 TEM images of Fe_3O_4@[$Cu_3(btc)_2$] core–shell microsphere after (a) 20, (b) 30, (c) 40, and (d) 50 assembly cycles at 70 °C, (e) HRTEM image of the MOF shell, and (f) the selected area electron diffraction pattern.

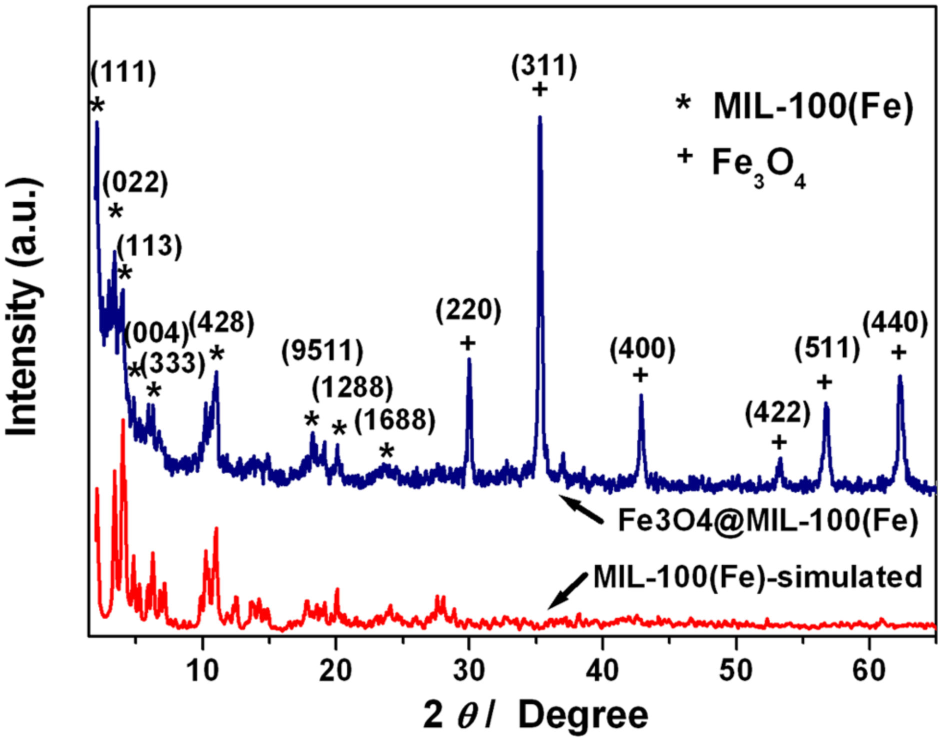

Fig. S6 PXRD patterns of simulated from the crystallographic data of MIL-100(Fe) and Fe_3O_4@MIL-100(Fe) core–shell magnetic microspheres after 50 assembly cycles at 25 °C.

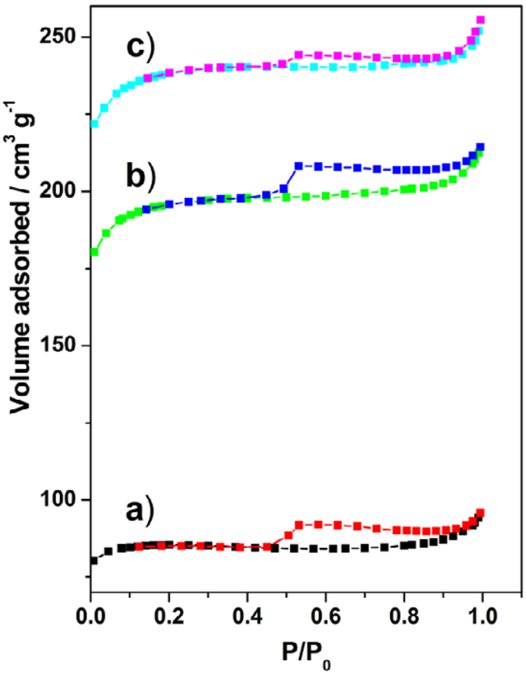

Fig. S7 Nitrogen sorption-desorption isotherms of Fe_3O_4@[$Cu_3(btc)_2$] microspheres (a) **A1** (25 °C, 25 cycles), (b) **A2** (25 °C, 50 cycles) and (c) **A3** (70 °C, 50 cycles) measured at 77 K.

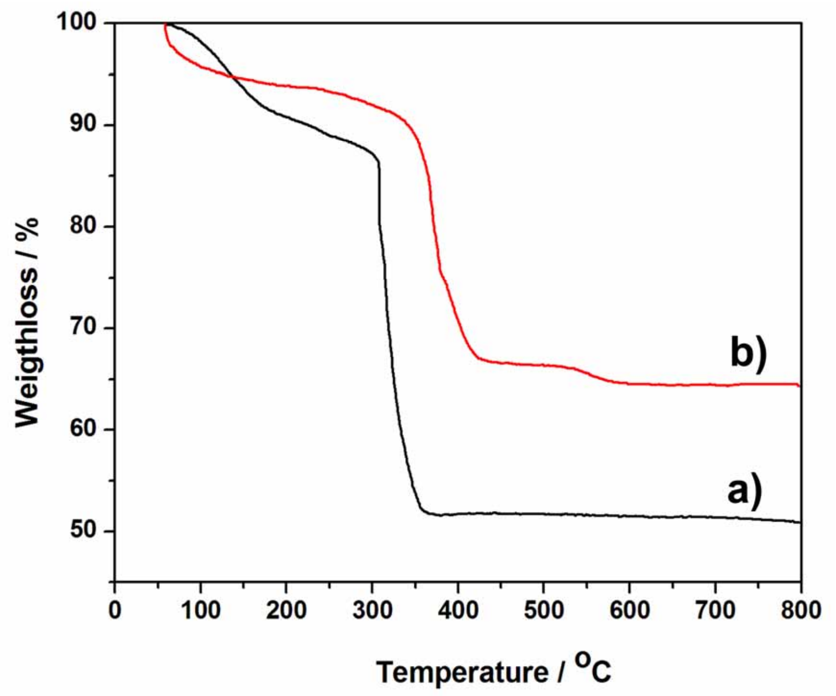

Fig. S8 TGA under air of (a) Fe_3O_4@[$Cu_3(btc)_2$] microspheres A3 (70 °C, 50 cycles) and (b) Fe_3O_4@MIL-100(Fe) B1 (25 °C, 50 cycles).