Supplementary Material (ESI) for Chemical Communications

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for

Coordination polymer nanorods of Fe-MIL-88B and their utilization for selective preparation of hematite and magnetite nanorods

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General Methods

Solvents and all other chemicals were obtained from commercial sources and used as received unless otherwise noted. Infrared spectrum of solid sample (as a KBr pellet) was obtained on a Bruker Vertex 70 FT-IR spectrometer. Elemental analysis was performed at the Organic Chemistry Reaction center, Sogang University. All scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were obtained using either a Hitachi S-4300 field-emission SEM equipped with a Horiba EMAX 6853-H EDS system (Center for Microcrystal Assembly, Sogang University) or a JEOL JSM-6500F field-emission SEM equipped with a JEOL EX-23000 BU EDS system (Yonsei Nanomedical National Core Research Center). All transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were obtained using a FEI Tecnai G2 F30 ST (Korea Basic Science Institute in Seoul). X-ray diffraction studies were conducted using a Rigaku Miniflex equipped with a graphite-monochromated Cu Kα radiation source (30 kV, 15 mA). TGA measurements were carried out using a Shimadzu TGA-50 in a nitrogen atmosphere at a heating rate of 10 °C/min in the temperature range of 25-900 °C. Magnetization measurments were obtained using a Quantum Desing MPMSXL at 300K. X-ray photoelectron spectroscopy measurement was performed on a VG ESCALAB 220i-XL using Mg Kα X-ray source.

Preparation of rod-shaped CPP-15 having the hexagonal 3D structure of Fe-MIL-88B: A precursor solution was prepared by mixing 1,4-benzenedicarboxylic acid (3.0 mg, 0.018 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (8.0 mg, 0.020 mmol) in 0.4 mL of DMF, and added to 0.4 mL of CH_3CN. The resulting mixture was placed in an oil bath (120 °C) for 40 min. The rod-shaped CPP-15 generated in this time were isolated by cooling the reaction mixture to room temperature. Particle products were isolated and subsequently washed with DMF and methanol via centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh methanol. IR for CPP-15 (KBr pellet, cm^{-1}): 1692m, 1596s, 1505s, 1389s, 1321w, 1300w, 1160m, 1111w, 1017m, 886w, 824m, 749m, 622m, 555m, 463w. Anal. Calcd for $Fe_3O(BDC)_3NO_3$: C, 39.07; N, 1.90; H, 1.64. Found: C, 39.02; N, 1.82; H, 1.70.

Preparation of hematite (α–Fe_2O_3): CPP-15 was placed in a furnace and calcined at 380 °C in air. After 50 min holding at 380 °C, the generated hematite was cooled to room temperature. The EA data revealed that the resulting hematite contained a trace amount of carbon (0.34 weight %) and no nitrogen (0.00 weight %) and hydrogen (0.00 weight %).

Preparation of magnetite (Fe_3O_4): CPP-15 was placed in a furnace and calcinated at 300 °C for 50 min in air. Subsequently, the generated nanorods were transferred into a tube furnace and calcined up to 700 °C under nitrogen atmosphere at a heating rate of 5 °C/min and held at 700 °C for 10 min. The generated magnetite was cooled to room temperature. The EA data revealed that the resulting magnetite contained 0.54, 0.00 and 0.00 weight % of carbon, nitrogen and hydrogen, respectively.

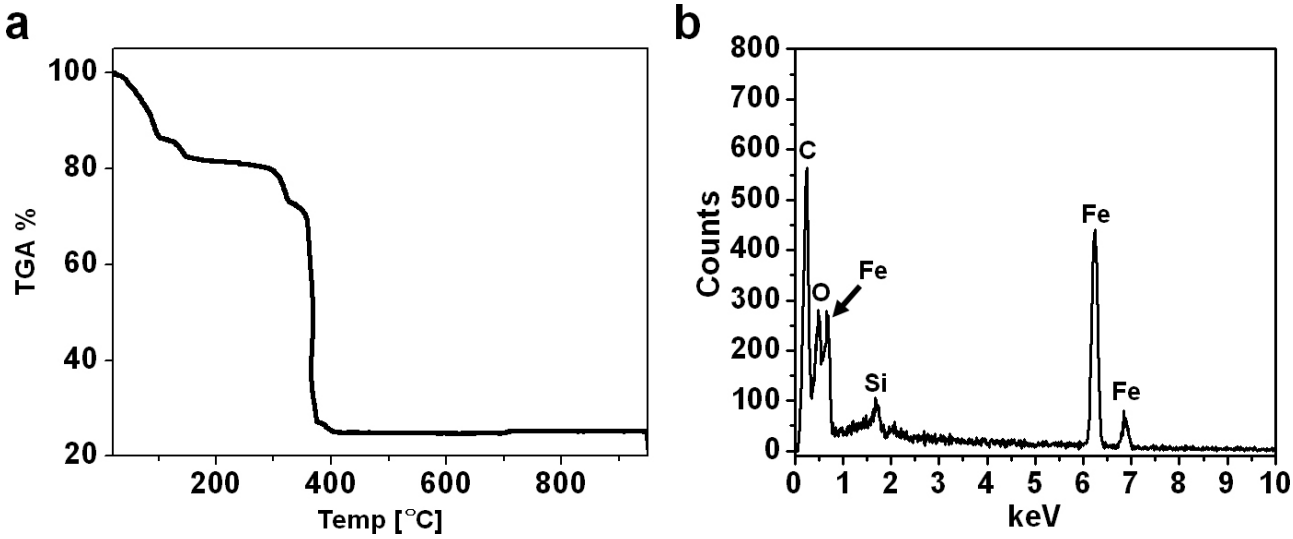

Fig. S1 (a) TGA curve and (b) EDX spectrum of coordination polymer nanorods (CPP-15).

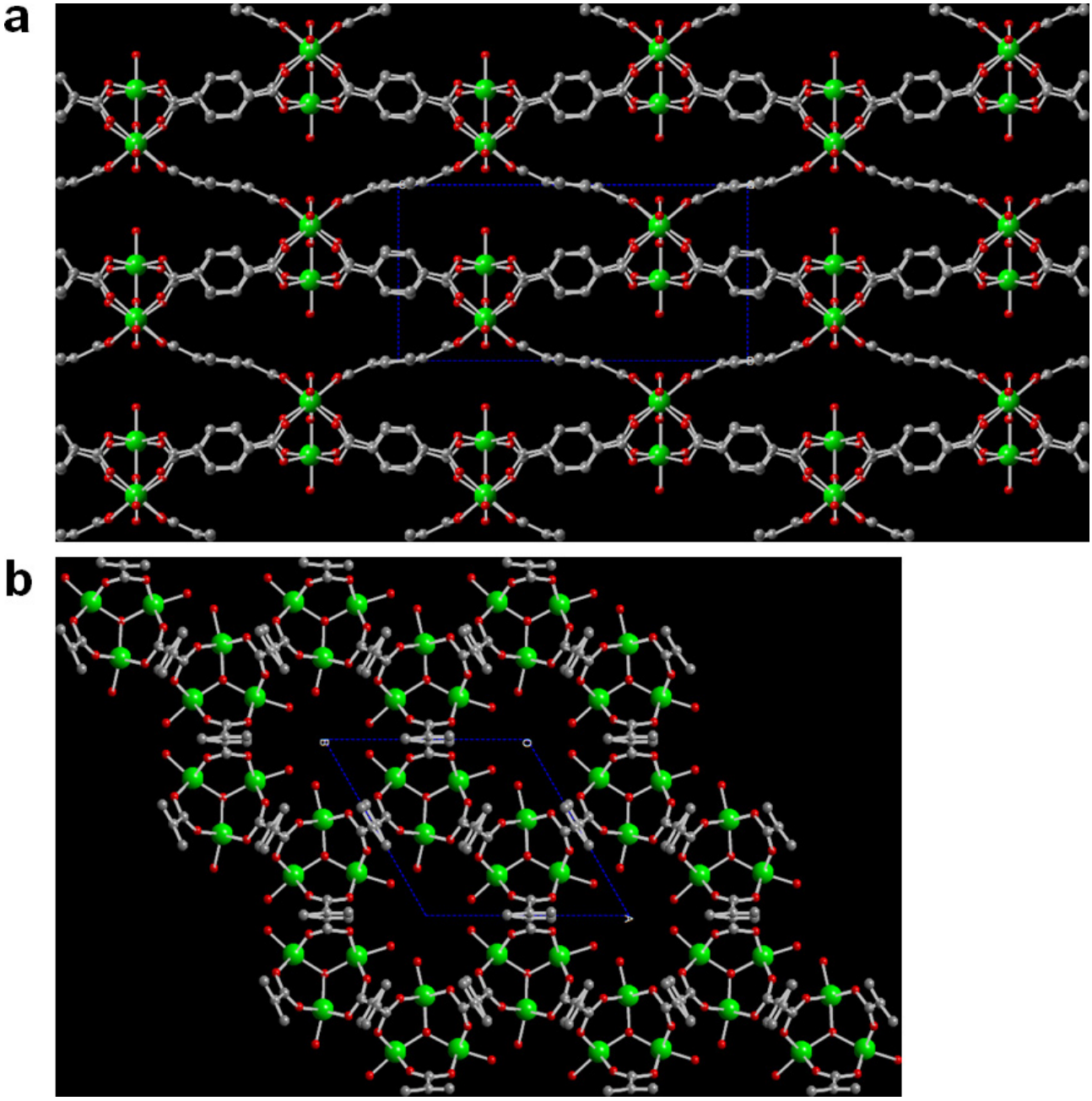

Fig. S2 Ball-and-stick representations of MIL-88B.[12] (a) A view of the *bc* plane. (b) A view of the *ab* plane. Gary, red, and green represent C, O, and Cr, respectively. Hydrogen atoms and guest molecules are omitted for clarify.

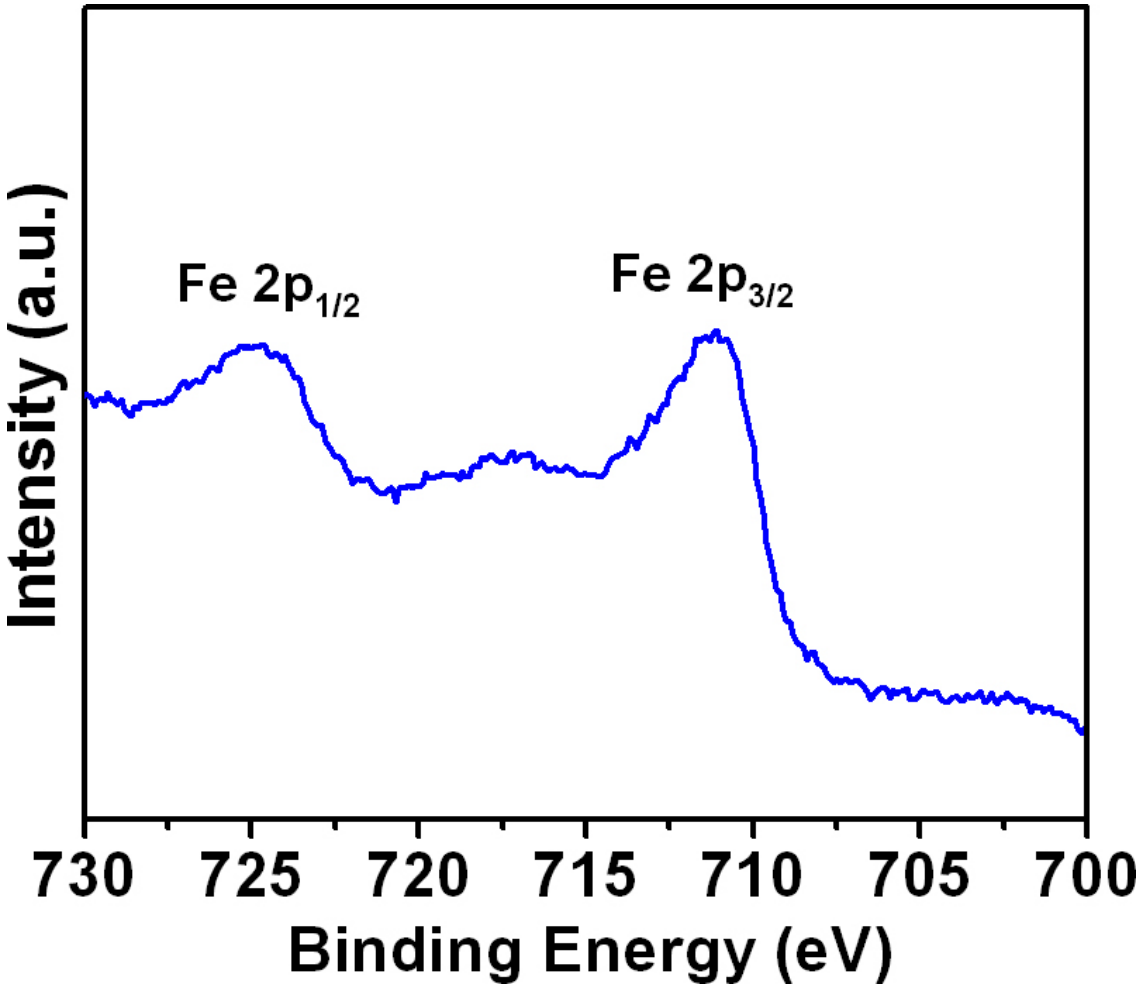

Fig. S3 XPS data of CPP-15. The binding energies of $Fe2p_{3/2}$ (711.1 eV) and $Fe2p_{1/2}$ (724.6 eV) are close to the reported values observed for Fe(III) compounds.

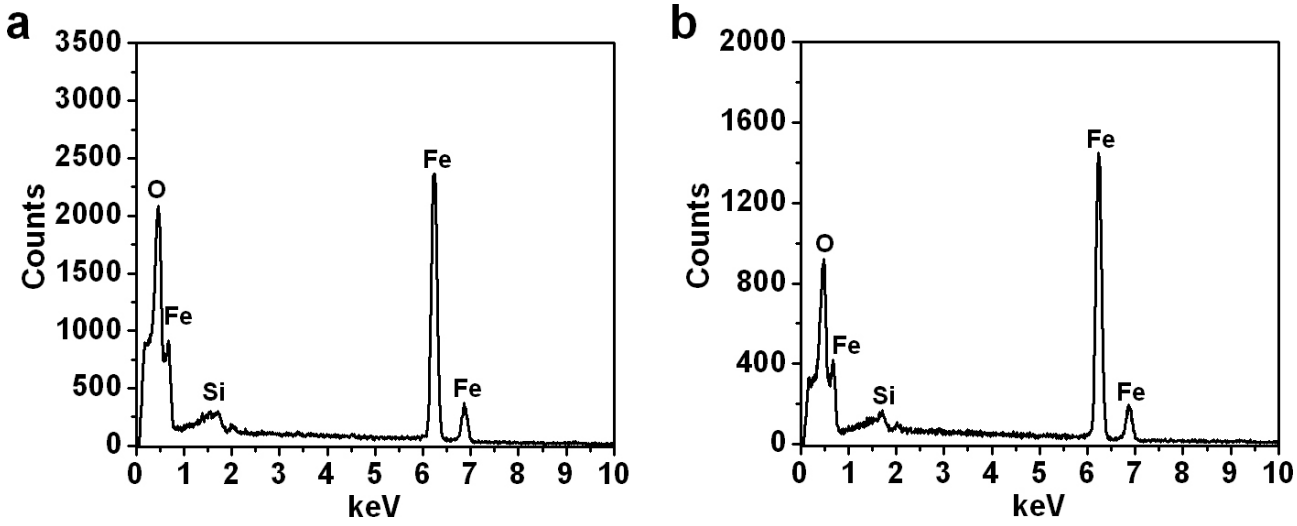

Fig. S4 EDX spectra of (a) hematite (α–Fe_2O_3) nanorods and (b) magnetite (Fe_3O_4) nanorods.

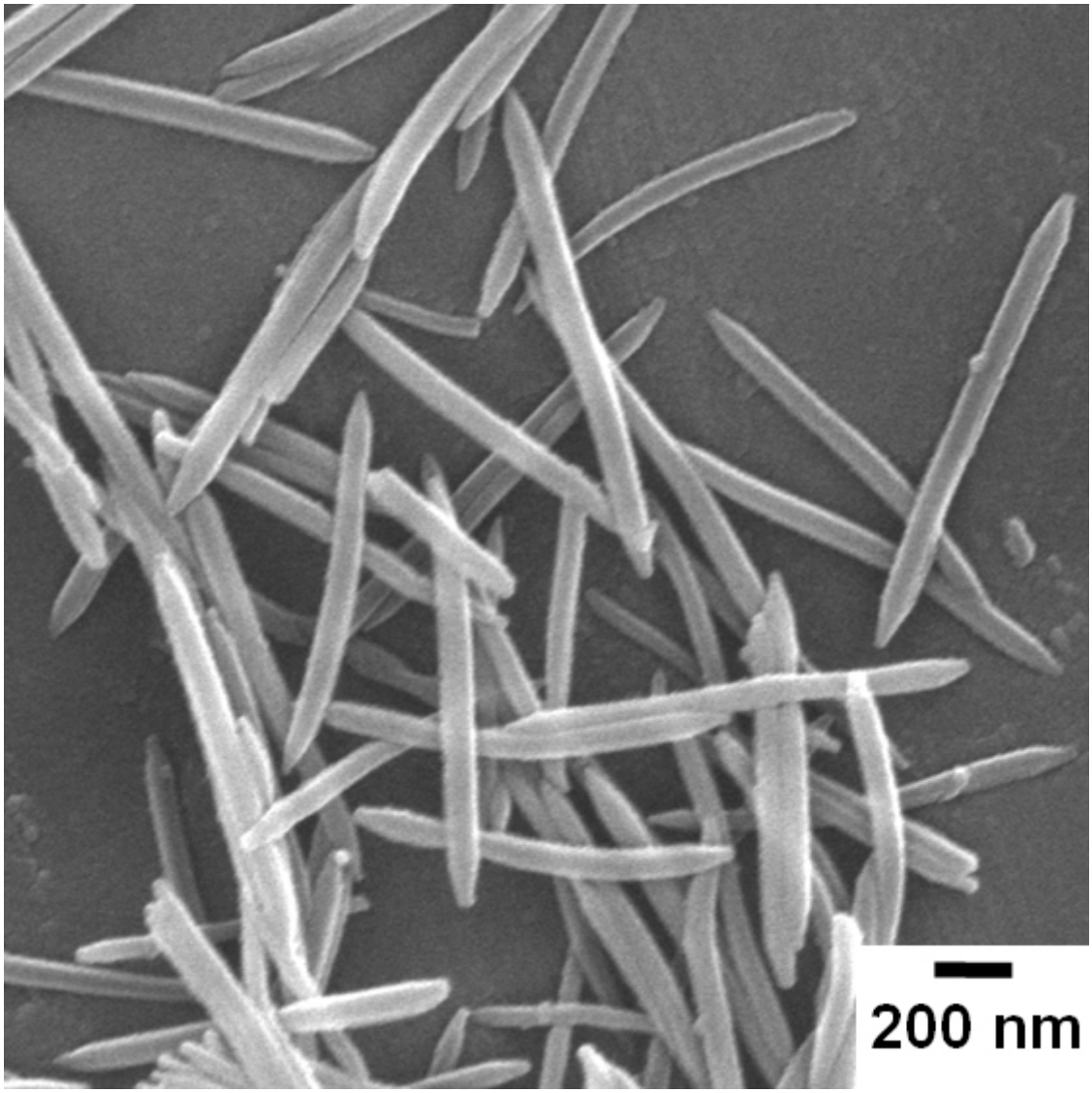

Fig. S5 SEM image of hematite nanorods containing the organic residues prepared by incomplete calcination at 300 °C in air for 50 min.

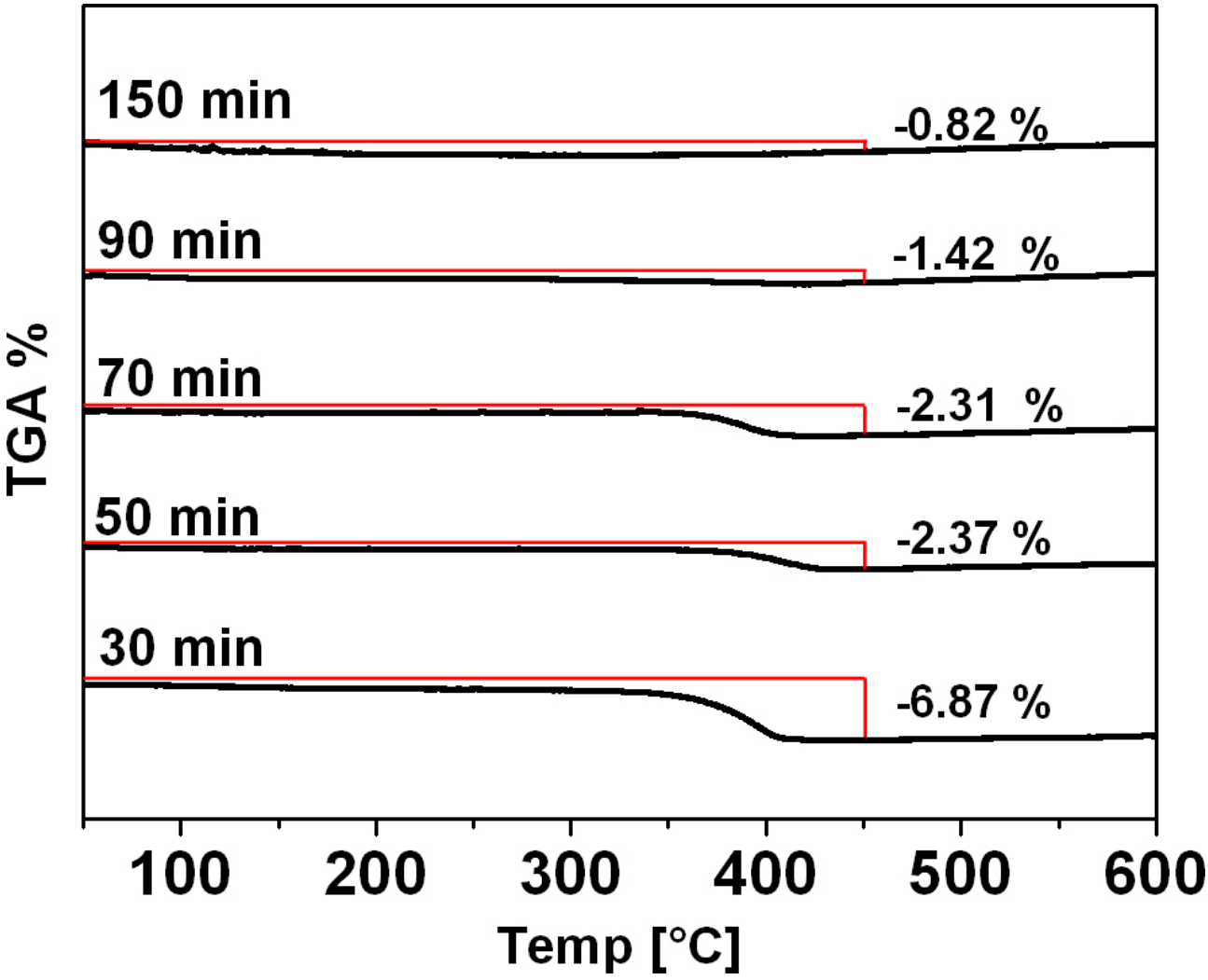

Fig. S6 TGA curves of hematite nanorods containing the organic residues prepared by incomplete calcination at 300 °C in air for 30, 50, 70, 90 and 150 min. These show the approximate amount of organic residues within the incompletely calcined particles.

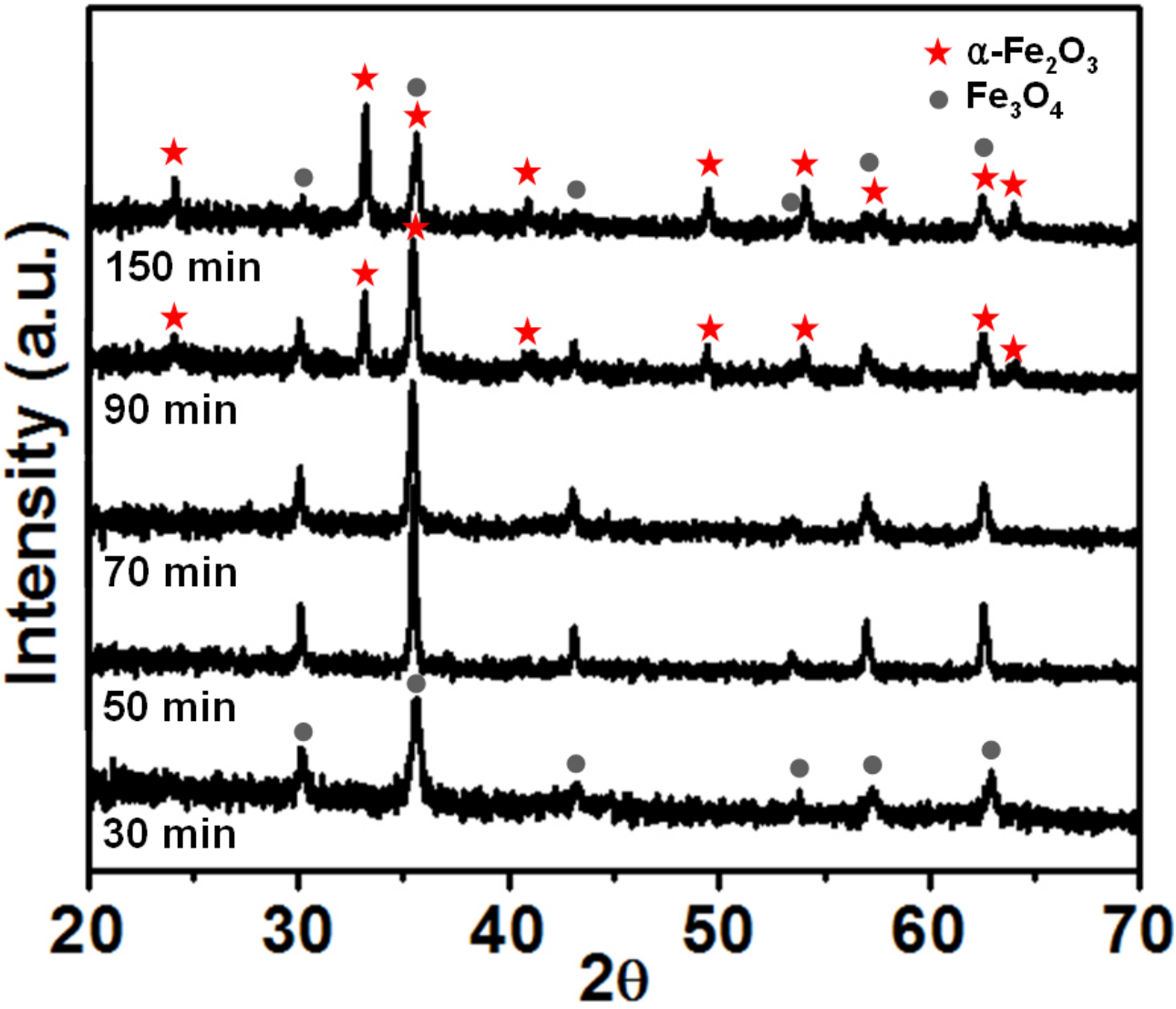

Fig. S7 PXRD patterns of final products after the second thermal treatment at 700 °C under N_2 atmosphere on a series of the incompletely calcined particles containing the organic residues prepared by incomplete calcination at 300 °C in air for 30, 50, 70, 90 and 150 min. There was no complete phase transformation in the samples containing small amount of organic residues as a result of long holding time (90 and 150 min) during the first thermal treatment.

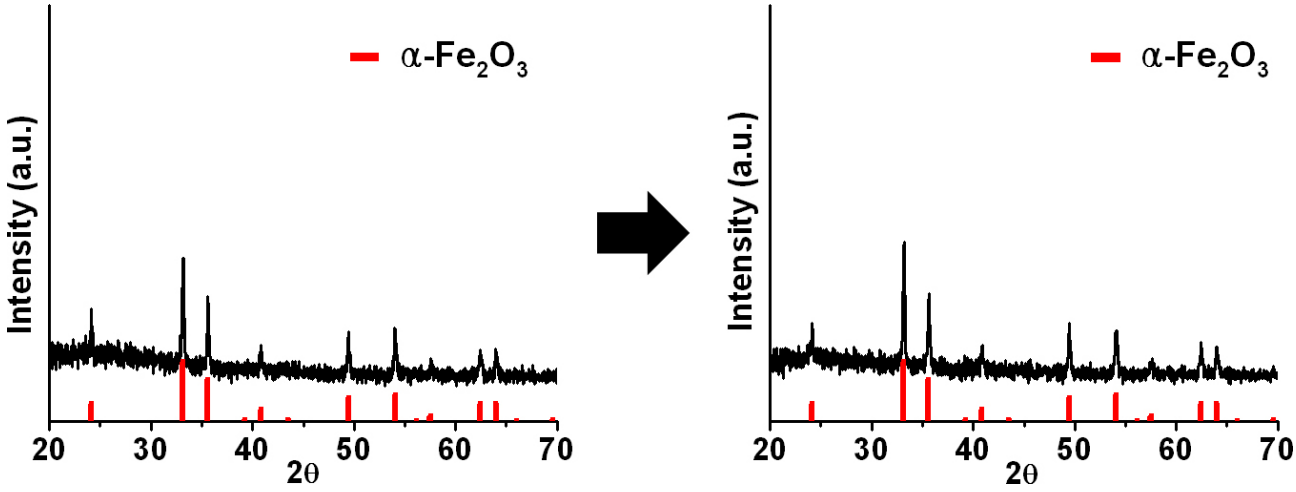

Fig. S8 PXRD patterns of the sample after the first thermal treatment at 700 °C in air for 50 min (left), and the sample after the second thermal treatment at 700 °C under N_2 atmosphere for 10 min (right). Because the sample after the first thermal treatment at 700 °C in air for 50 min did not contain the significant organic residues, there was no reduction of hematite (α–Fe_2O_3) to magnetite (Fe_3O_4) during the second thermal treatment under N_2 atmosphere.