

Supporting Information

Magnetic induction framework synthesis: a general route to the controlled growth of metal-organic frameworks

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Experimental

Synthesis of carboxylic acid groups decorated magnetic nanoparticles (MNPs): MgFe_2O_4

MNPs were firstly synthesized in a one-pot protocol mediated by hyperbranched polyglycerol (HBP, MW: 3000 g mol^{-1}) [S1, S2]. In a typical process, 0.86 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.9 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added into a flask containing 100 mL of HBP aqueous solution (5 mg mL^{-1}). The reaction was performed at 80 °C for 3 hours under N_2 atmosphere. The resultant HBP passivated MNPs were thoroughly rinsed with deionised (DI) water and redispersed in 20 mL of succinic anhydride solution in pyridine (0.4 g mL^{-1}). Upon heating at 70 °C for 7 hour, HBP passivation layer of MNPs was tailored with succinic acid moieties, producing carboxylic acid decorated MNPs. After thoroughly washed with DI water, the purified MNPs was recollected with a magnet and redispersed in DMF (20 mg mL^{-1}) for the further use.

Magnetic induction framework synthesis (MIFS) to synthesize magnetic framework

composites (MFCs): To synthesize magnetic Mg-MOF-74 composite through MIFS, 0.472 g of 2,5-dioxido- 1,4-benzenedicarboxylate (DOBDC) and 1.96 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ were dissolved in 200 mL of a 14:1:1 (v/v/v) mixture of dimethylformamide (DMF)-ethanol- H_2O . 10 mL of the resulting solution was then transferred to a scintillation vial containing 1 mL of MNP suspension. After exposing the reaction system to an alternating magnetic field generated with an EasyHeat frequency generator equipped with eight-turn coil (Ambrell, 350 kHz) for a certain of time of period, the reaction mixture was cooled down to room temperature. The mother liquor was decanted and replaced with methanol. The methanol was then decanted and replenished four times over two days. The resultant mMOFs were collected with magnet and naturally dried in a glove bag. Following the same procedures, control over the reaction time, MNPs concentration, and the applied magnetic field strength resulted in a series of mMOFs with controlled yield and size. Control experiments were performed by heating the same reaction mixture in the presence and in the absence of MNPs

with a traditional hotplate heating at 115 °C. All the resulting materials were activated under vacuum at 250 °C over 5 h. According to the weight of the activated samples, the yield of the MOF component in mMOFs was calculated based on DOBDC ligand.

Following the similar synthetic protocol, magnetic Co-MOF-74, magnetic PCN-250, magnetic HKUST, and magnetic ZIF-8 were also synthesized by exposing 10 mL of the corresponding MOF mother liquors containing 20 mg of MNPs. The procedures for synthesizing magnetic PCN-250, magnetic HKUST, and magnetic ZIF-8 were based on the previous reports [S3-S5].

Characterisations: The microstructures of MOF samples were analysed using a Zeiss Merlin FESEM equipped with an EDX unit. Dry samples were mounted on a silicon substrate followed by an Iridium coating. Powder X-ray diffraction of MOFs was measured at Bruker D8 Advanced X-ray Diffractometer operating under CuK α radiation (40 kV, 40 mA) equipped with a LynxEye detector. The diffraction pattern was collected in the 2 θ range of 3.5-80° with a step size of 0.02° and a count time of 3.2 s step⁻¹.

Magnetic measurements: Magnetic measurements were performed using a vibrating sample magnetometer by Quantum Design (Physical Property Measurement System with VSM option) at room temperature. The powdered samples were filled into gelatine capsules and sealed with two-component adhesive. The sealed capsules were fixed in a small plastic tube and mounted onto the instruments sample holder. Magnetic heating experiments were carried out on an EasyHeat frequency generator equipped with eight-turn coil (Ambrell, 350 kHz). In a typical process, a scintillation vial containing a certain concentration of MNP solution in MOF mother liquor was exposed to a magnetic field with desired magnetic field strength. The temperature change of the solution was monitored with an infrared camera (FLIR system) with resolution of 0.1 °C.

Low-pressure gas adsorption measurements. For gas-adsorption isotherms, high-purity grade (99.999%) helium, nitrogen, and CO₂ were used throughout the adsorption experiments. Low-pressure volumetric nitrogen isotherms up to 1 bar were measured using a Micromeritics ASAP 2420 gas sorption analyzer. BET and Langmuir surface areas and pore size were determined by measuring N₂ adsorption isotherms at 77 K in a liquid-nitrogen bath and calculated using Micromeritics software. Static and dynamic CO₂ adsorption isotherms up to 1 bar were measured using a Micromeritics Tristar II instrument. Static CO₂ adsorption isotherms were collected at 273 and 298 K. Dynamic CO₂ adsorption experiments were performed on Micromeritics Tristar II instrument equipped with EasyHeat frequency generator (Ambrell). Dynamic CO₂ adsorption profiles were obtained by intermittently exposing MFCs to a magnetic field during the adsorption experiments at 298 K.

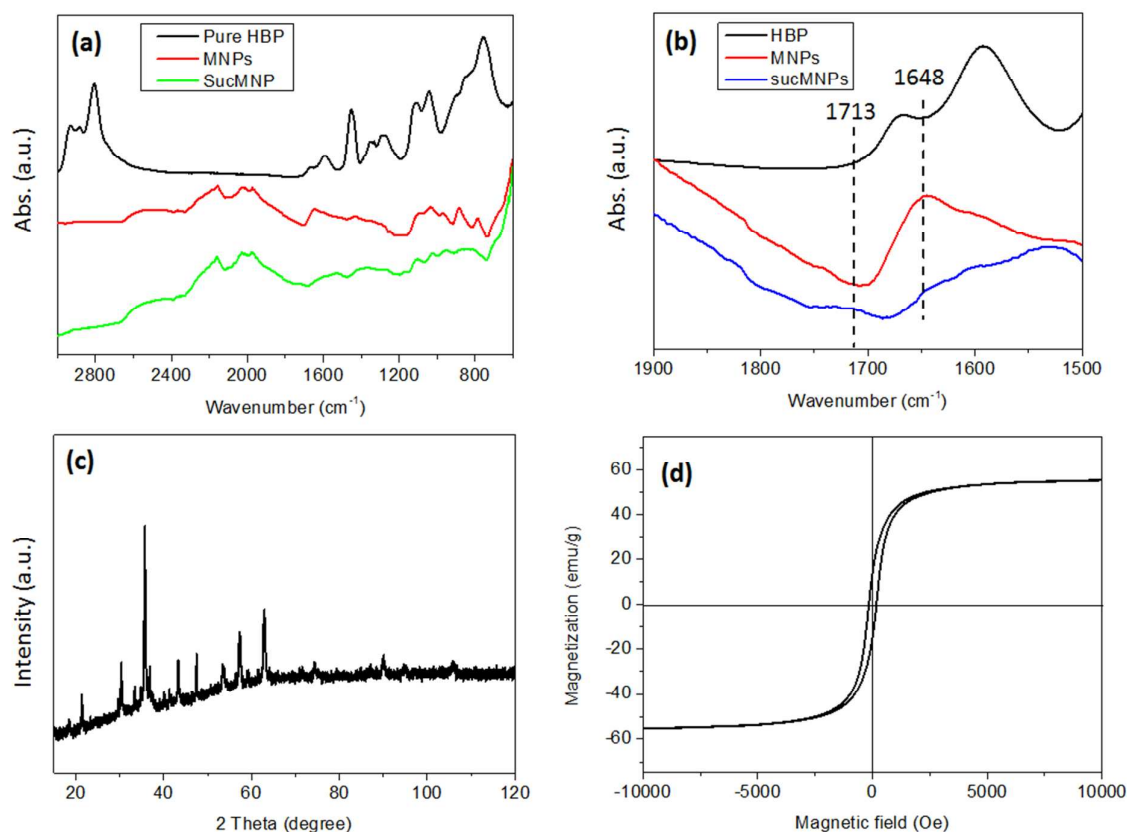


Figure S1. FTIR spectra of pure HBP, MNPs before and after surface modification with succinic acid (a) and (b). In (b), the appearance of a broad band centred at 1713 cm^{-1} confirms successful introduction of carboxylic acid groups on MNP surface. Powder XRD pattern (c) and magnetic hysteresis loop of carboxylic acid decorated MNPs (d).

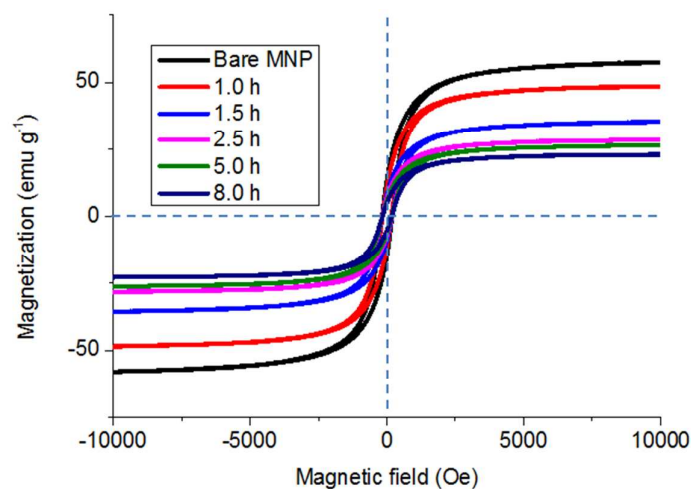


Figure S2. Magnetic hysteresis loops of bare MNPs and magnetic Mg-MOF-74 obtained by exposing 2.0 mg mL^{-1} of MNPs solution in Mg-MOF-74 mother liquor to an alternating magnetic field of 94.8 mT for different time of period.

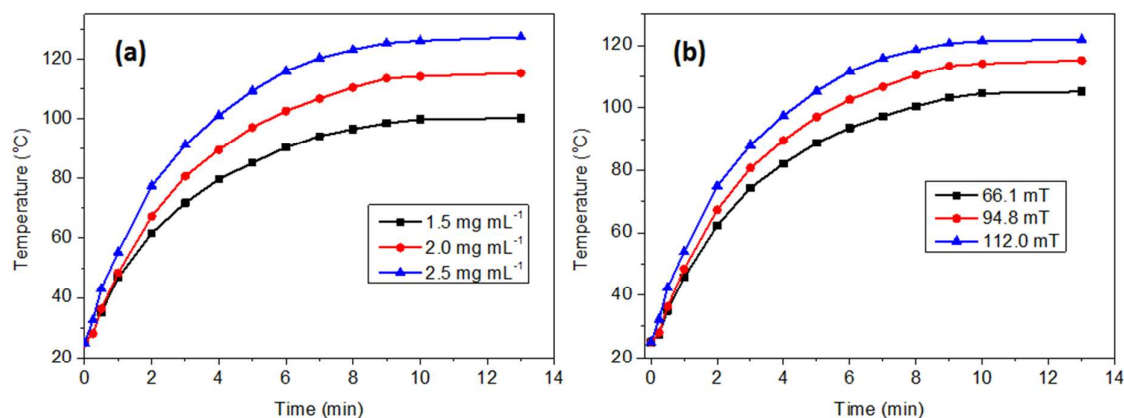


Figure S3. Magnetic induction heating profiles of Mg-MOF-74 mother liquor containing different concentration of MNPs after exposing them to an alternating magnetic field of 94.8 mT (a); Magnetic induction heating profiles of Mg-MOF-74 mother liquor containing 2.0 mg mL⁻¹ of MNPs upon exposure to an alternating magnetic field with different magnetic field strength (b).

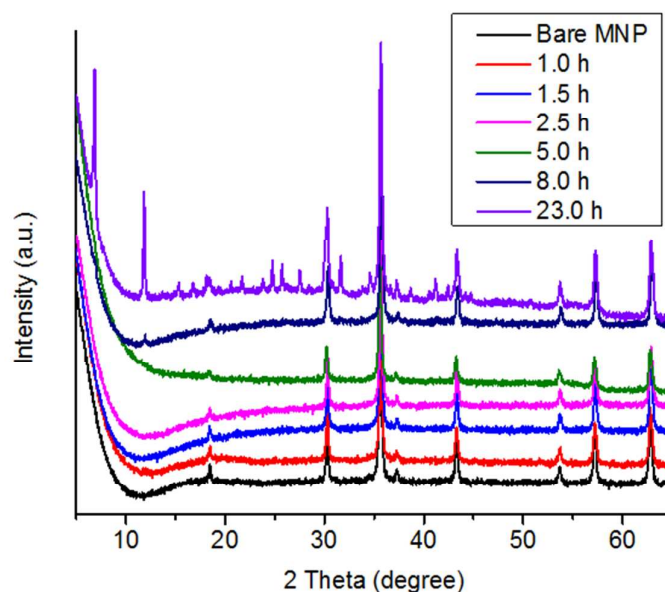


Figure S4. Powder XRD patterns of the materials obtained by heating 2.0 mg mL⁻¹ of MNP solution in Mg-MOF-74 mother liquor with a hotplate at 115 °C for different time of period.

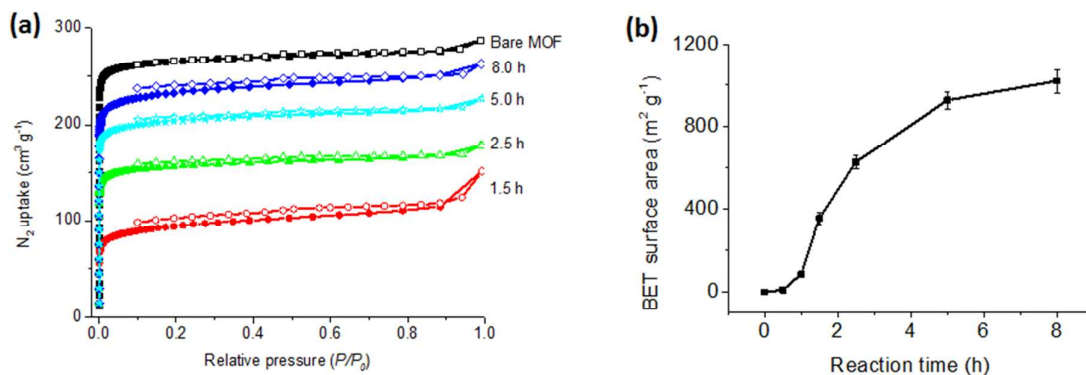


Figure S5. Nitrogen gas adsorption isotherms (a) and BET surface areas (b) of bare Mg-MOF-74 and magnetic Mg-MOF-74 obtained by exposing 2.0 mg mL^{-1} of MNPs solution in Mg-MOF-74 mother liquor to an alternating magnetic field of 94.8 mT for different time of periods. The isotherms were recorded at 77 K.

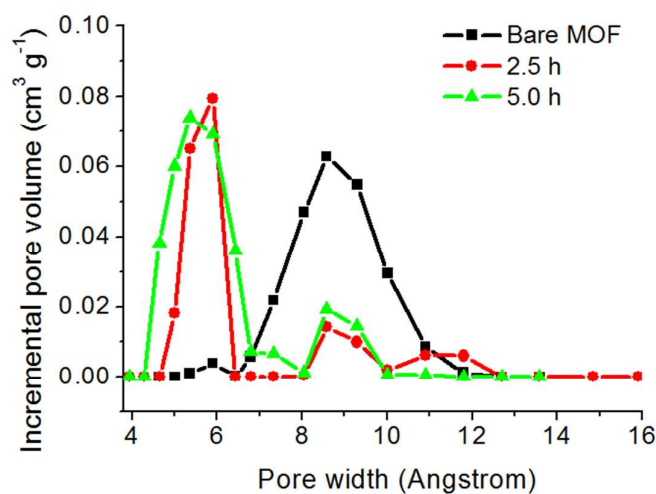


Figure S6. Pore size distribution of bare Mg-MOF-74 and magnetic Mg-MOF-74 composites obtained by exposing 2.0 mg mL^{-1} of MNPs solution in Mg-MOF-74 mother liquor to an alternating magnetic field of 94.8 mT for 2.5 h and 5.0 h.

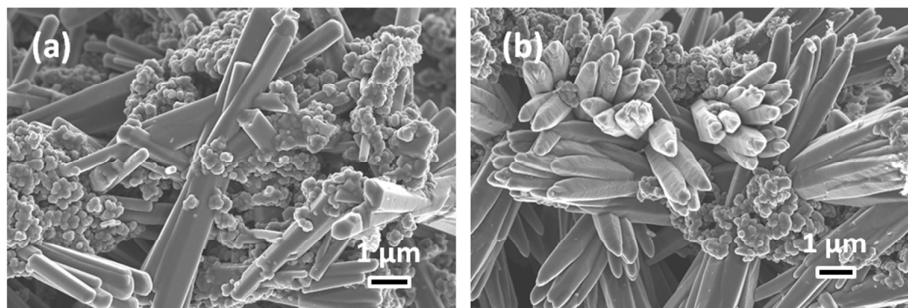


Figure S7. SEM images of mMOF composite obtained by heating 2.0 mg mL⁻¹ of MNP solution in Mg-MOF-74 mother liquor at 115 °C for 8 h (a) and 23 h (b).

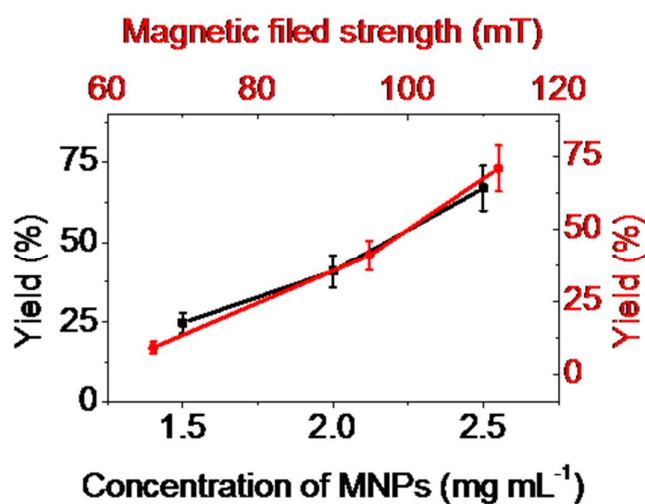


Figure S8. Yield of MOF component in mMOFs (a) and particle size of mMOFs (b) as a function of NNP concentration (black line) and magnetic field strength (red line). Inset of (b) is the particle size of mMOFs obtained by different reaction time.

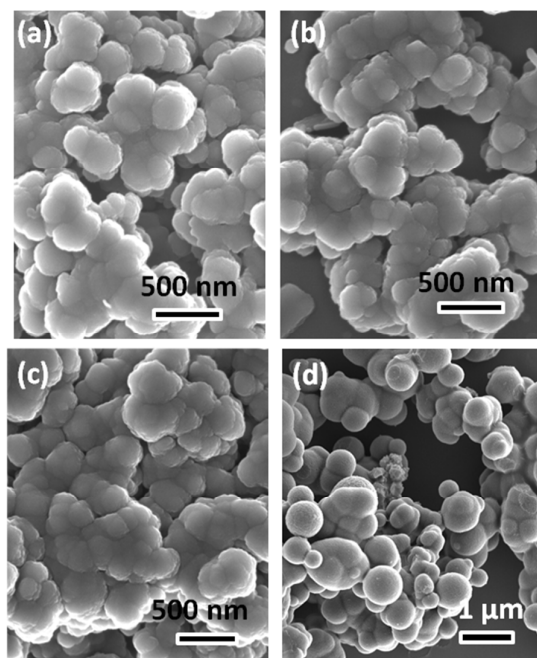


Figure S9. SEM images of magnetic Mg-MOF-74 obtained by exposure of 1.5 mg mL^{-1} (a) and 2.5 mg mL^{-1} (b) of MNP solution in Mg-MOF-74 mother liquor to an alternating magnetic field of 94.8 mT for 1.5 h. SEM images of magnetic Mg-MOF-74 obtained by exposure of 2.0 mg mL^{-1} of MNP solution in Mg-MOF-74 mother liquor to an alternating magnetic field of 66.1 mT (c) and 122 mT (d) for 1.5 h.

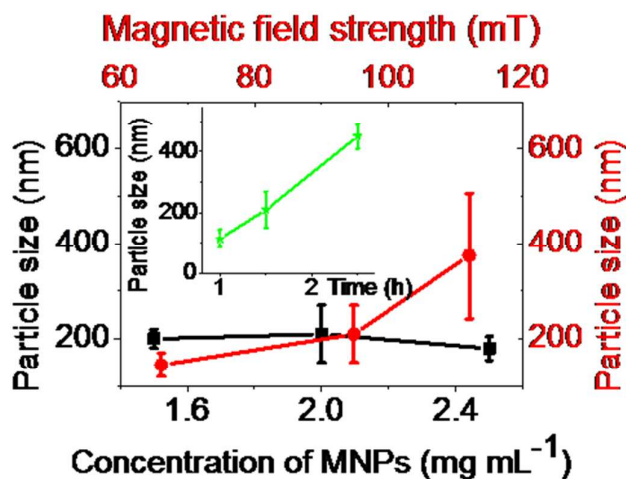


Figure S10. The yield of Mg-MOF-74 components in the resulting mMOFs (a) and the particle size of mMOFs (b) depending on the utilized MNP concentration in the reaction systems (magnetic field strength in 94.8 mT) and the applied magnetic field strength (MNP concentration is 2.0 mg mL^{-1}) (a). Inset of (b) is the changes in particle size of mMOFs depending on reaction time (94.8 mT of magnetic field strength and 2.0 mg mL^{-1} of MNP concentration).

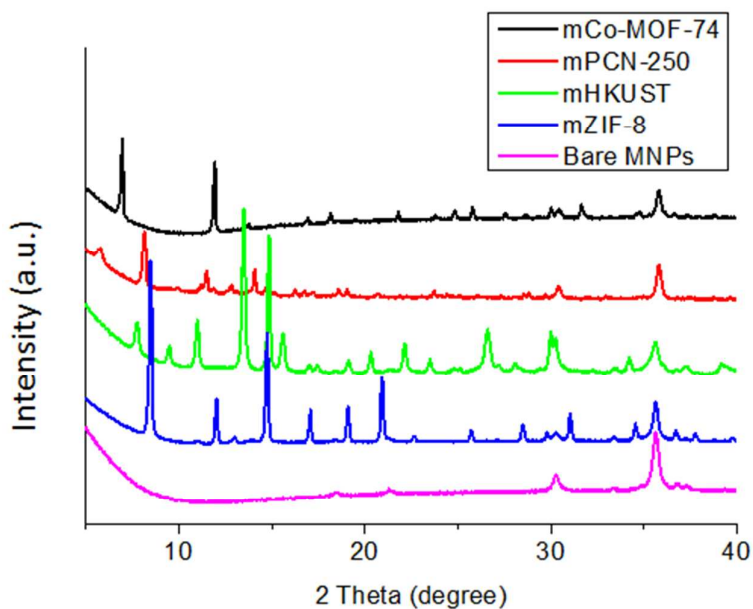


Figure S11. Powder XRD patterns of the magnetic MOF composites: mCo-MOF-74, mixed solvent DMF:Ethanol:H₂O = 1:1:1, 2.0 mg mL^{-1} of MNPs; mPCN-250, solvent DMF, 2.0 mg mL^{-1} of MNPs; mZIF-8, solvent H₂O, 2.0 mg mL^{-1} of MNP; mHKUST, solvent Ethanol, 1.0 mg mL^{-1} of MNP. All the reactions were performed in the presence of 94.8 mT of magnetic field for 1.5 h.

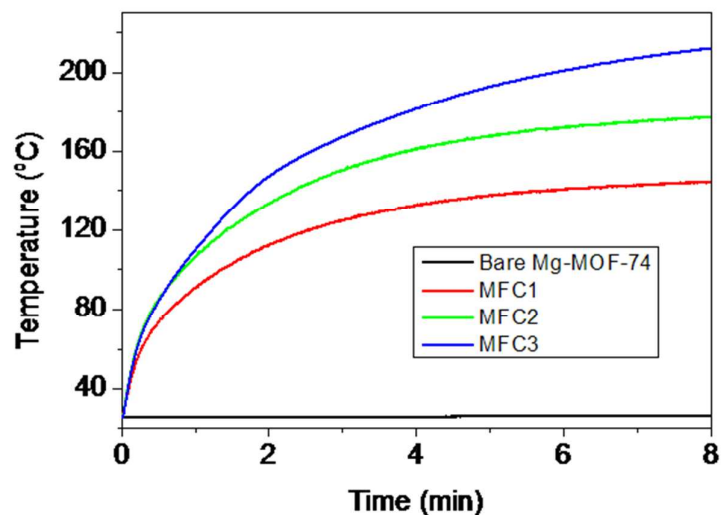


Figure S12. Magnetic induction heating profiles of bare magnetic Mg-MOF-74 and magnetic Mg-MOF-74 composites with 39.8% (MFC1), 50.6% (MFC2), and 62.4% of MNP content (MFC3) obtained through MIFS method. The applied magnetic field strength is 39 mT.

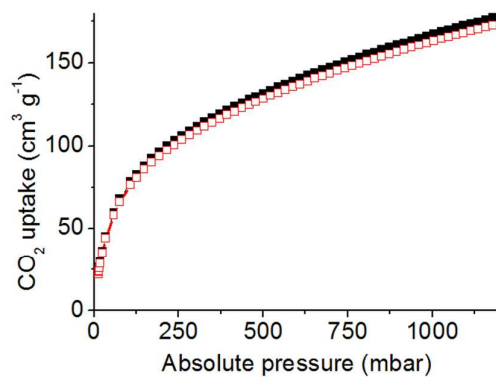


Figure S13. CO₂ uptake isotherms of bare Mg-MOF-74 with (red line) and without application of magnetic field (black line).

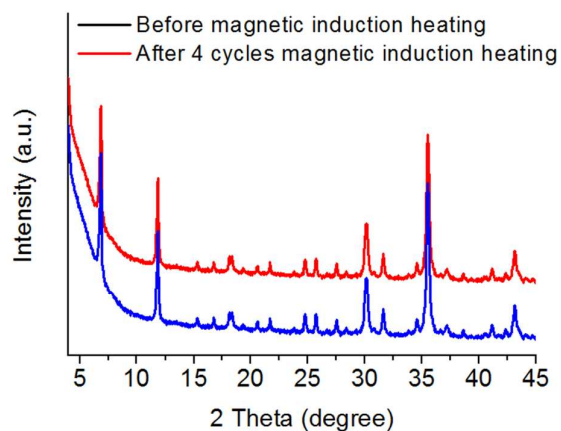


Figure S14. Powder XRD patterns of magnetic Mg-MOF-74 (MFC2) before and after magnetic induction heating treatment for 4 cycles. In each cycle, the sample was exposed to 39 mT of magnetic field for 8 min.

References:

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