Electronic Supplementary Information

Rapid Collection and Re-dispersion of MOF Particles by a Simple and Versatile Method Using Thermo-Responsive Polymer

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Experimental

Materials.: Cobalt nitrate hexahydrate (≥98%), 2-methylimidazole (99%), aluminium chloride hexahydrate (≥99%), 2-aminoterephthalic acid (99%), iron trichloride hexahydrate (≥98%), trimethyl 1,3,5-benzenetricarboxylate (98%), titanium isopropoxide (≥97%), 2-amino-1,4-benzenedicarboxylic acid (97%), zirconium tetrachloride (99.5%), 1,4-benzendicarboxylic acid (99%), N,N-dimethylformamide (DMF, >99.9%), anhydrous methanol, and methylene blue were all purchased from Sigma-Aldrich and used as received. Poly(N-isopropyl acrylamide) (molecular weight: 39000, polydispersity index: 1.45) was purchased from Polymer Source Inc. and used as received. All water used was purified Type I water with a resistivity of 18.2 MΩ•cm (Barnstead NANO pure DIamond system, Thermo Scientific, Asheville, NC).

Characterization: Powder X-ray diffraction (PXRD) data were collected at an ambient temperature using Cu SMART6000 rotating anode diffractometer. MOF particles were characterized by JEOL JSM 7000 Scanning Electron Microscopy (SEM). UV-visible spectra were recorded on a DU 800 UV/vis spectrophotometer. Concentration of cobalt in water was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Synthesis of MOFs: All MOF particles were prepared according to the published literatures. The procedures are briefly described as follows for readers' convenience.

ZIF-67: Cobalt nitrate hexahydrate (0.249 g, 1 mmol) and 2-methylimidazole (0.328g, 4 mmol) was respectively dissolved in 25 ml methanol. The 2-methylimidazole solution was then poured into the former solution under vigorous stirring. The mixture was allowed to stand still at room temperature for 24h. A purple powder was obtained by centrifugation. The product was washed with methanol for three times and dried in vacuum at room temperature.

MIL-53-NH$_2$(Al): Aluminum chloride hexahydrate (1.97 g, 8.2 mmol) and 2-aminoterephthalic acid (1.5 g, 8.3 mmol) were dissolved in deionized water (18 ml) and DMF (2 ml). The mixture was heated at 150 °C for 5 h in an oven to form a pale yellow powder. The resulted product was centrifuged and washed with acetone, and it was then consecutively re-dispersed in DMF and methanol at 150 °C and 70 °C overnight, respectively. Finally, the product was centrifuged and washed with acetone for three times, and dried at 120 °C overnight.

MIL-100(Fe): FeCl$_3$·6H$_2$O (0.65 g, 4 mmol) and trimethyl 1,3,5-benzenetricarboxylate (0.55 g, 2.64 mmol) were mixed in deionized water (20 ml). The mixture was heated at 130 °C for three days. The obtained orange powder was then centrifuged, washed with acetone for three times, and dried under room temperature.

MIL-125-NH2(Ti): 2-Amino-1,4-benzenedicarboxylic acid (0.56 g, 3.1 mmol) was dissolved in a mixture solvent ($V_{DMF}/V_{Methanol}$ = 9:1). Titanium isopropoxide (0.6 mL,

2.0 mmol) was added into the former solution under stirring. The mixture was heated at 150 °C for 24 hours. The resulting yellow powder was washed with DMF (three times) and methanol (three times), then centrifuged. The product was re-dispersed in DMF at 150 °C overnight and isolated by centrifugation. Vigorous washing with acetone was required to remove the DMF. The product was finally centrifuged and dried in vacuum at room temperature.

UiO-66: $ZrCl_4$ (81.3 mg, 0.35 mmol), 1,4-benzendicarboxylic acid (57.3 mg, 0.35 mmol) and acetic acid (0.6 mL) were dissolved in 20 ml DMF. The mixture was capped and heated at 120 °C for 24 h. The obtained white solid was centrifuged and washed with DMF for three times, it was then dispersed in methanol at 60 °C for three days to exchange DMF. The product was finally centrifuged and dried in vacuum at room temperature.

Reversible Dispersion and Collection of ZIF-67: ZIF-67 (2 mg) was added into 4 ml PNIPAM solution (0.06 mg/ml) as in Sample 1-4. The mixture was well dispersed in an ultrasound generator for 1 minute. The suspension was heated to 40 °C for 2 minutes and precipitation occurred spontaneously. The precipitate could be easily re-dispersed by cooling down temperature with stirring. This procedure of collection and re-dispersion was repeated for two cycles. All the other MOF samples were tested with the same procedure except for the concentration of PNIPAM. The PNIPAM concentration effect will be discussed in the Results and Discussion.

UV Degradation of Methylene Blue (MB) by MIL-100(Fe): MIL-100(Fe) (2mg) and H_2O_2 (6 mg) were added into 4ml MB (200 ppm) solution, which contained certain amount PNIPAM (0.04 mg/g) in a beaker. The beaker was placed under a 100 W mercury spot lamp for 1 h and the distance between the beaker and the light source was fixed at 10 cm. After decolorization, the mixture was heated to 40 °C for 2 minutes to collect MIL-100(Fe). The supernatant was then decanted and fresh MB solution and H_2O_2 were added for another cycle of the decolorization reaction.

Table S1. Concentration of cobalt of sample 1-2 before (Sample 1) and after (Sample 2) collection by heating by ICP-OES.

Sample	Element	PPM
1	Co	91.421
2[a]	Co	0.7538

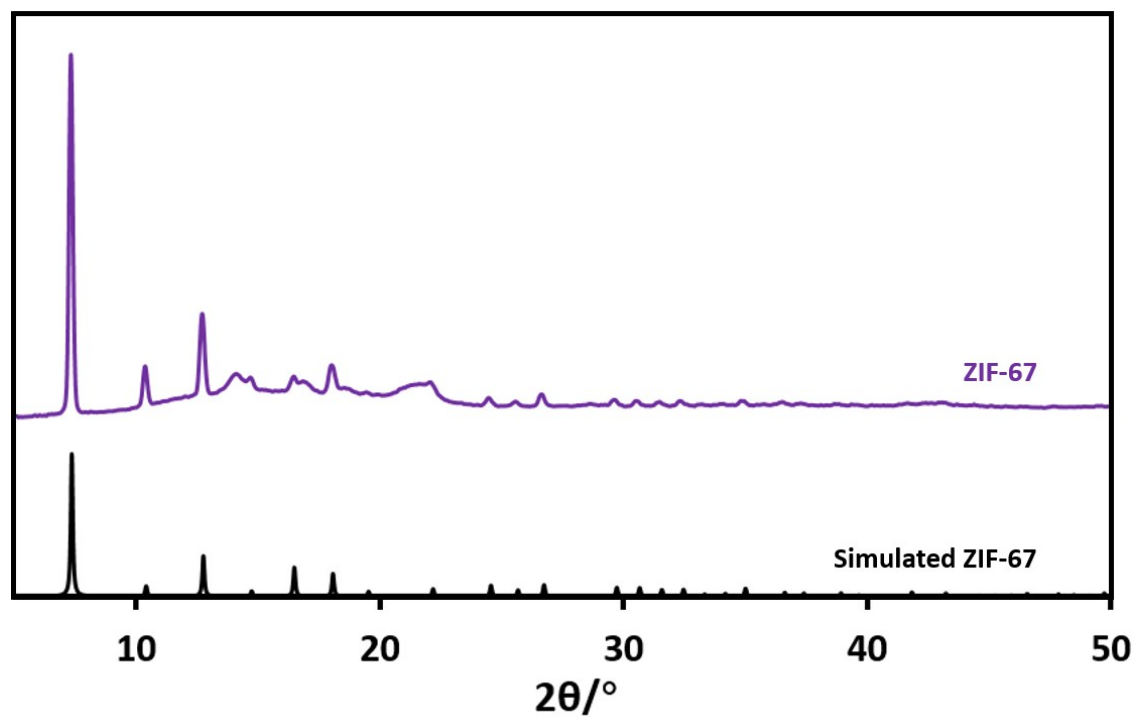[a]The supernatant was taken out carefully from sample 1-2 after 1 h after heating.

Figure S1. Powder X-ray diffraction (PXRD) patterns comparing the simulated ZIF-67 pattern (black) to the diffractograms of ZIF-67 (purple) collected by PNIPAM.
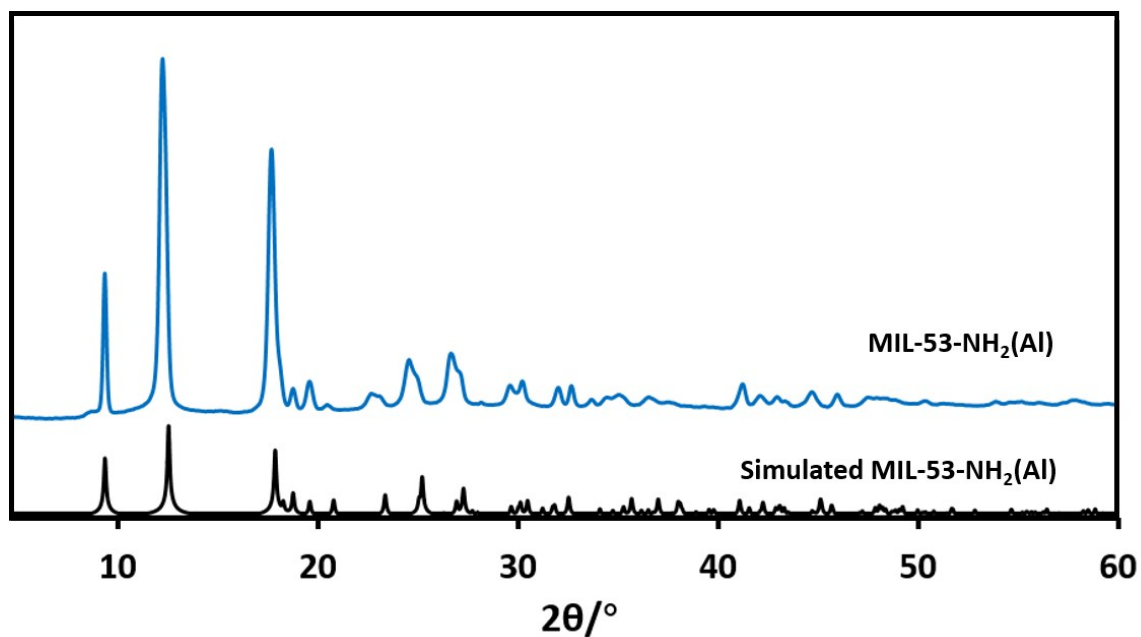
Figure S2. Powder X-ray diffraction (PXRD) patterns comparing the simulated MIL-53-NH$_2$(Al) pattern (black) to the diffractograms of MIL-53-NH$_2$(Al) (blue) collected by PNIPAM.
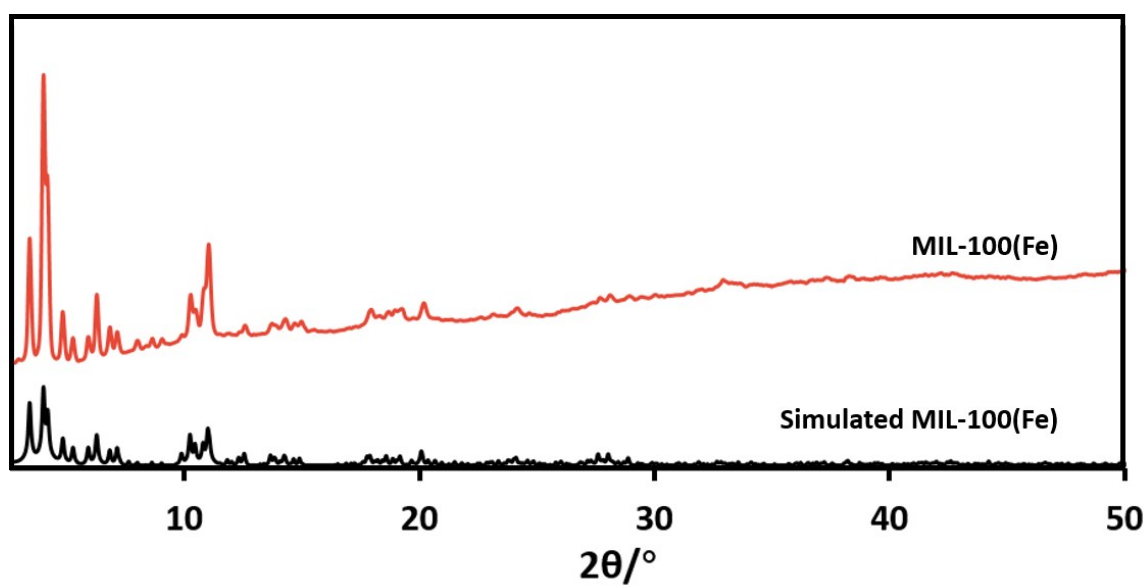

Figure S3. Powder X-ray diffraction (PXRD) patterns comparing the simulated MIL-100(Fe) pattern (black) to the diffractograms of MIL-100(Fe) (orange) collected by PNIPAM.
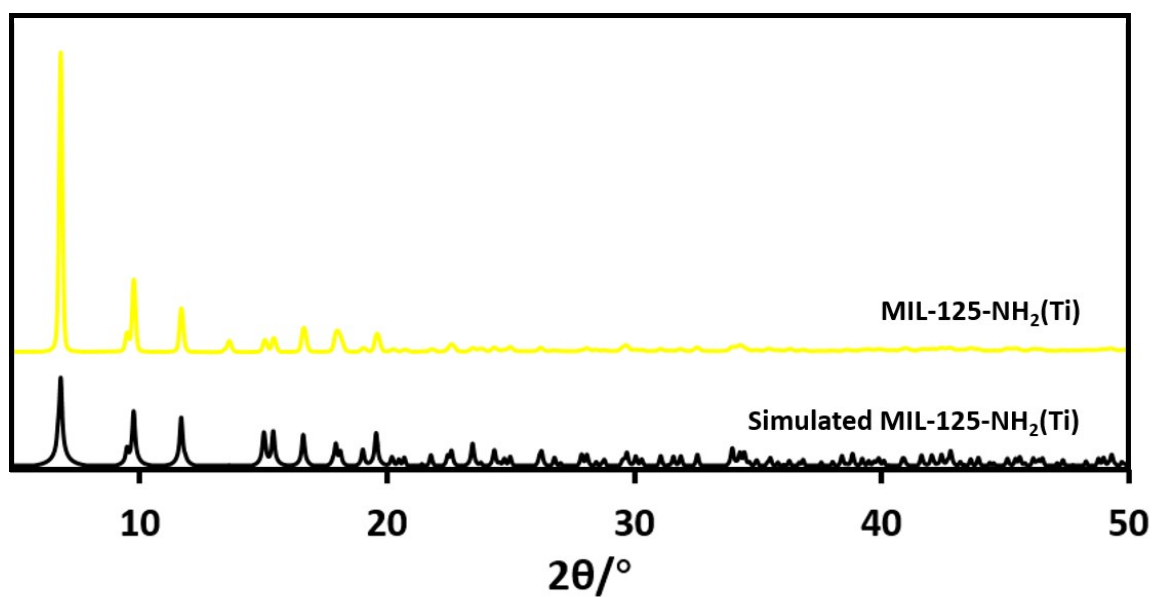
Figure S4. Powder X-ray diffraction (PXRD) patterns comparing the simulated MIL-125-NH$_2$(Ti) pattern (black) to the diffractograms of MIL-125-NH$_2$(Al) (yellow) collected by PNIPAM.
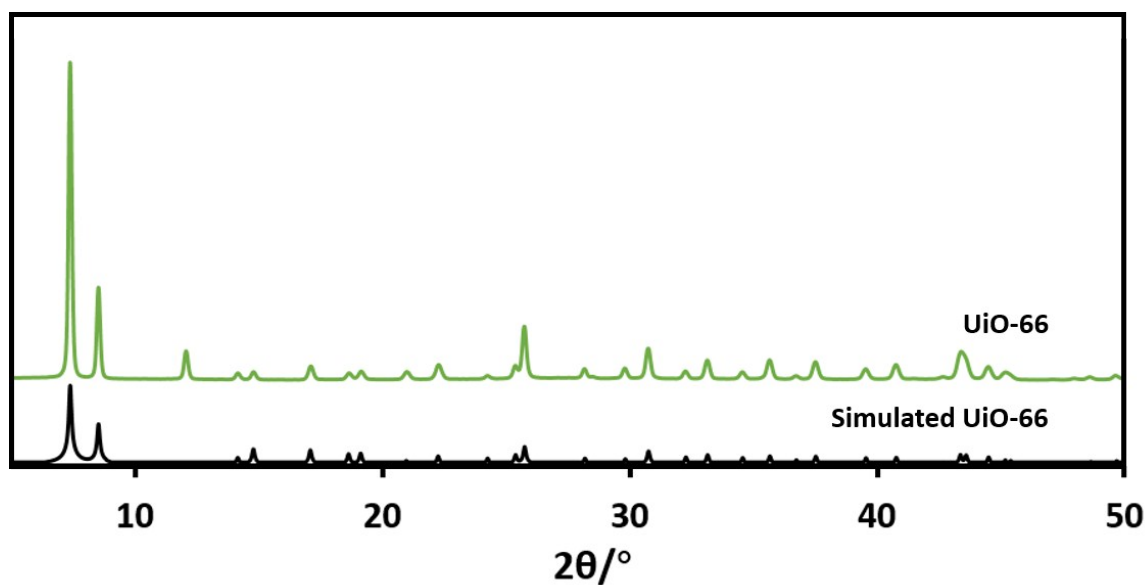

Figure S5. Powder X-ray diffraction (PXRD) patterns comparing the simulated UiO-66 pattern (black) to the diffractograms of UiO-66 (green) collected by PNIPAM.
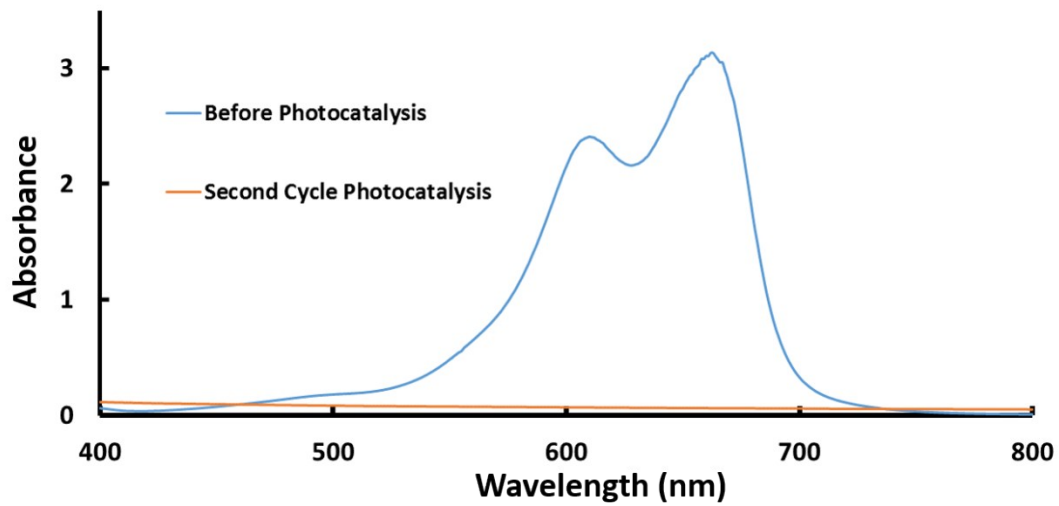
Fig S6. The UV-vis absorption spectrum of MB in water before and after second cycle photocatalysis by MIL-100(Fe).
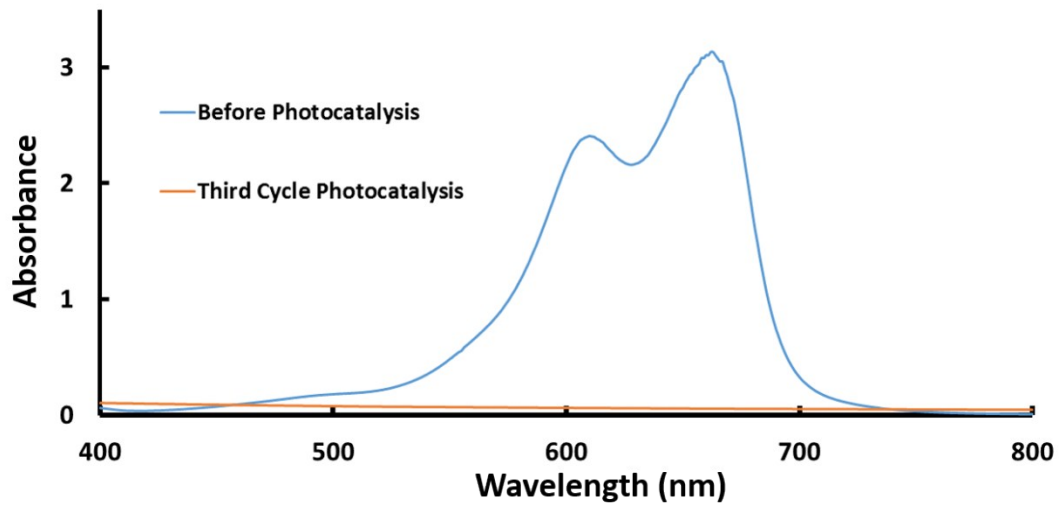

Fig S7. The UV-vis absorption spectrum of MB in water before and after third cycle photocatalysis by MIL-100(Fe).