

Supporting Information for

“Synthesis and Water Sorption Properties of a Series of Exfoliated Graphene/MIL-100(Fe) Composites”

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Section S1 **Raw materials**

1,3,5-Benzenetricarboxylic acid (H₃-BTC, $\geq 98\%$ purity), ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O, $\geq 99\%$ purity), ammonium fluoride (NH₄F, 99.99% purity), and nitric acid (HNO₃, 70% v/v) were purchased from Sigma Aldrich Chemical Co. Graphene nanoplatelets (GNPs) were obtained from XG Sciences Inc. Both ethanol (99.999%) and deionized water were of highest purity available and used without further purification. All chemicals were used without further purification.

Section S2 **Characterization methods**

Elemental analysis (EA) was performed using high temperature combustion with a Perkin Elmer CHNS/O Series II 2400 Elemental Analyser. Powder X-ray diffraction (PXRD) analyses were performed using a Rigaku UltimaIV Multipurpose diffractometer equipped with Ni-filtered Cu K α radiation. Samples were packed densely in a 0.5 mm deep well on a zero-background holder. Programmable divergence slits were used to illuminate a constant length of the samples (8 mm), thus preserving the constant volume assumption. The operating power of the diffractometer was set at 45 kV and 40 mA, and the diffraction data were collected between $2\theta = 3\text{-}50^\circ$ with a total scan time of 3 h. PXRD patterns for the residues recovered after thermogravimetric analysis, as well as the MOF samples subjected to cyclic water ad-/desorption tests, were obtained on a Bruker D8 Advance Multipurpose diffractometer equipped with a Ni-filtered Cu K α radiation. The operating power of the diffractometer was set at 35 kV and 25 mA, and the diffraction data were collected between $2\theta = 10\text{-}60^\circ$ with a step-size of 0.02046° and 0.25 s per step.

Low-pressure nitrogen physisorption measurements were conducted using a Quantachrome Autosorb iQ volumetric gas sorption analyser. Ultrapure N₂ and He (99.999%) were used for all adsorption measurements. A liquid N₂ bath (77 K) was used in all N₂ isotherm measurements. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method in the P/P_0 range of 0.06-0.2. The total pore volume was taken by a single-point method at $P/P_0 = 0.9$. Fourier transform infrared (FTIR)

spectra were recorded with KBr pellets on a Thermo Fisher Scientific Nicolet 6700 FTIR spectrometer. Output absorption bands are described as: s, strong; m, medium; w, weak; and br, broad.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed on a TESCAN LYRA3 FEG microscope. SEM samples were prepared by placing drops of the as-synthesized MOF suspended in acetone on Cu tapes. The solvent was allowed to evaporate before the images were obtained at an accelerating voltage of 5 kV and a working distance of 5-6 mm with a standard secondary electron detector. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100F/HR microscope. TEM samples were prepared by placing drops of the as-synthesized MOF, suspended in ethanol on carbon-coated 200 mesh Cu grids. Images were collected using an accelerating voltage of 120 kV. Thermogravimetric analysis (TGA) was carried out on a TA Q500 thermal analyser under air flow with a heating rate of 5°Cmin⁻¹. Powdered samples were heated overnight at 120°C to remove moisture prior to performing TGA measurements.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer.

Water adsorption isotherms and cycling ad-/desorption measurements were recorded on a Dynamic Vapor Sorption Analyzer (DVS Vacuum, Surface Measurement Systems Ltd., London, U.K.). The samples were degassed under vacuum at 120 °C for 15 h prior to commencing the appropriate experiments. For the cycling tests, samples were subjected to 21 successive ad-/desorption cycles between 40 °C and 140 °C at 5 h per cycle and a constant water vapour pressure of 5.6 kPa. The heating profile used for the test is as follows: heating from 40 °C to 140 °C at 5 °C min⁻¹, followed by an isothermal step for 90 min allowing complete desorption, and finally cooling back to 40 °C at 5 °C min⁻¹ to begin water adsorption.

Section S3 Synthesis methods

Acid-treatment of GNPs

The acid-treatment of GNPs was carried out according to the already published literature [S1]. Typically, GNPs (3 g) were first dispersed in 70% HNO₃ (300 mL) using sonication. The mixture was then transferred to a 500 mL round bottom flask equipped with a condenser and was refluxed at 60 °C for 2 h. After cooling to room temperature, the mixture was diluted with 500 mL deionized water and then washed repeatedly with deionized water *via* centrifugation until the pH of the decanted solvent reached ~5.5. The resulting exfoliated graphene nanoplatelets (Ex-GNPs) suspension was dried at 80 °C in air for 2 d and ground for further use.

Synthesis of MIL-100(Fe)

The synthesis and activation of MIL-100(Fe) was carried out according to a previously reported procedure [S2]. Briefly, Fe(NO₃)₃·9H₂O (4.04 g, 0.01 mol) was first dissolved in de-ionized water (50.2 mL, 2.8 mol) and the mixture was completely transferred to a 125 ml Teflon-liner containing BTC (1.4097 g, 0.00671 mol). The Teflon-liner was then sealed inside a stainless steel autoclave and kept at 160 °C for 14 h. After slow cooling of the autoclave to room temperature, the as-synthesized dark orange solid was recovered using centrifugation. For activation in order to remove the unreacted BTC, the dried solid (1 g) was first immersed in deionized water (60 mL) and the resulting suspension was stirred at 70 °C for 5 h. The suspension was again centrifuged and the procedure was repeated using ethanol (60 mL) at 65 °C for 3 h. This two-step purification was continued until the decanted solvent following centrifugation became completely colourless, after which the dried solid was immersed in a 38 mM aqueous NH₄F solution and stirred at 70 °C for 5 h. The suspension was again centrifuged, after which the solid was washed 5 times with deionized water at 60 °C, and finally dried in air at 75 °C for 2 d followed by 95 °C for 2 d.

Synthesis of Ex-GNP/MIL-100(Fe) composites

Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 4.04 g, 0.01 mol) and a pre-determined amount of Ex-GNPs (70, 180 and 300 mg for MIL-G1, MIL-G2 and MIL-G3 respectively) were mixed thoroughly in solid-state until a uniform colour of the mixture was achieved. Next, deionized water (5 mL) was added periodically to the mixture and the resulting paste was sonicated until the water inside the mixture evaporated completely. The dry paste, along with BTC (1.4097 g, 0.00671 mol) and deionized water (50.2 mL, 2.8 mol), were then transferred completely to a 125 ml Teflon-lined autoclave, which was kept at 160 °C for 14 h. The recovery of the as-synthesized solid and the post-synthesis activation procedure are exactly the same as followed for pristine MIL-100(Fe).

Section S4 Synthesis scheme for Ex-GNP/MIL-100(Fe) composites

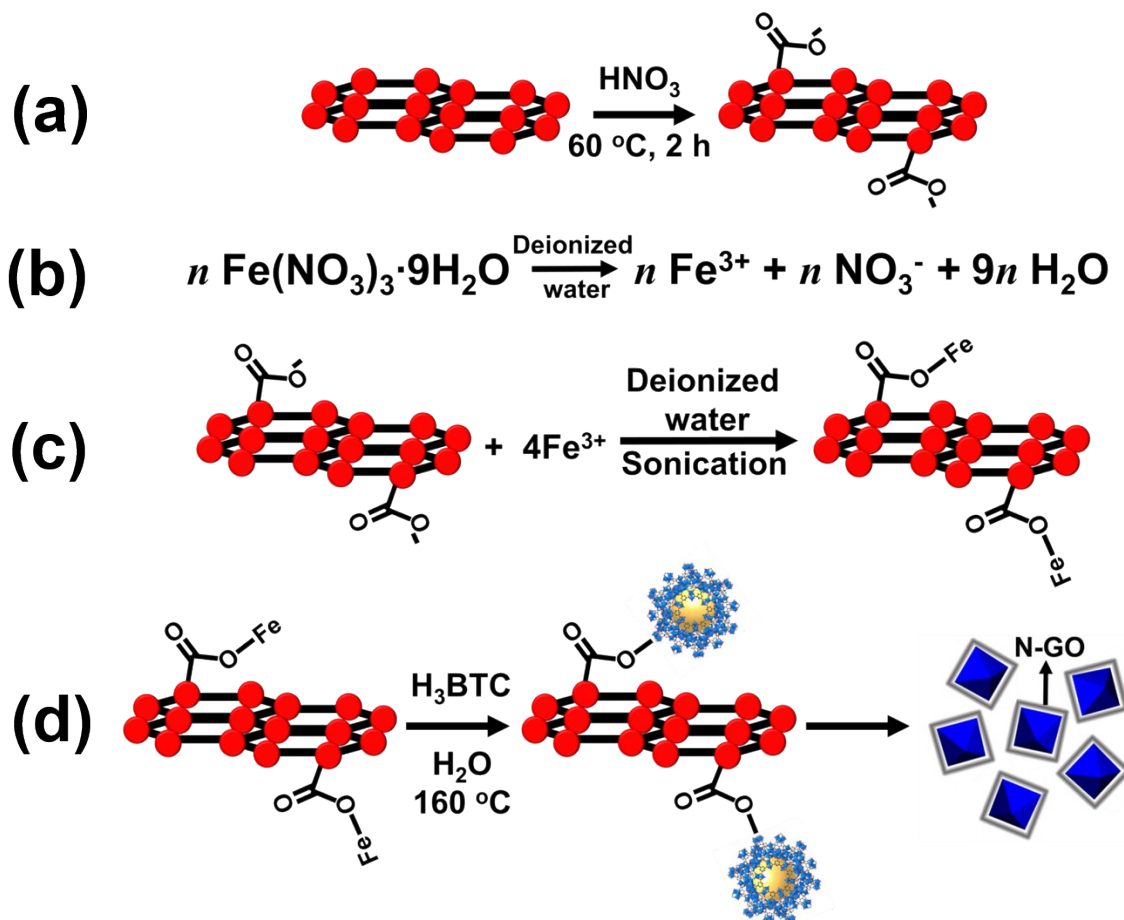


Fig. S1 *In-situ* synthesis of Ex-GNP/MIL-100(Fe) composite: (a) GNP functionalization, (b) Dissociation of hydrated Fe-salt in deionized water, (c) Molecular-level interaction of negatively charged carboxyl groups on Ex-GNPs and Fe^{3+} ions in aqueous solution, (d) Hydrothermal synthesis resulting in Ex-GNP/MIL-100(Fe) composites with Ex-GNPs wrapped around the MIL-100(Fe) crystals.

Section S5 Chemical formulation of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites using EA data

MIL-100(Fe) (Activated):

Calculated (wt%): C: 18.05; H: 5.98; N: 0.12.

Found (wt%): C: 18.14; H: 5.70; N: 0.15.

Fitted formula unit: $\text{Fe}_3\text{O}(\text{H}_2\text{O})_2(\text{OH})(\text{NO}_3)_{0.1}[\text{C}_6\text{H}_3(\text{CO}_2)_3]_2 \cdot 30\text{H}_2\text{O}$.

MIL-G1 (Activated):

Calculated (wt%): C: 20.03; H: 5.32; N: 0.30.

Found (wt%): C: 20.02; H: 5.60; N: 0.31.

Fitted formula unit: $\text{Fe}_3\text{O}(\text{H}_2\text{O})_2(\text{OH})(\text{NO}_3)_{0.23}[\text{C}_6\text{H}_3(\text{CO}_2)_3]_2 \cdot 23\text{H}_2\text{O}$.

Wt% Ex-GNPs = wt% C (MIL-G1) – wt% C (MIL-100(Fe)) = 1.88 wt%.

MIL-G2 (Activated):

Calculated (wt%): C: 23.22; H: 4.44; N: 0.24.

Found (wt%): C: 23.70; H: 4.24; N: 0.25.

Fitted formula unit: $\text{Fe}_3\text{O}(\text{H}_2\text{O})_2(\text{OH})(\text{NO}_3)_{0.16}[\text{C}_6\text{H}_3(\text{CO}_2)_3]_2 \cdot 15\text{H}_2\text{O}$.

Wt% Ex-GNPs = wt% C (MIL-G2) – wt% C (MIL-100(Fe)) = 5.56 wt%.

MIL-G3 (Activated):

Calculated (wt%): C: 32.91; H: 1.69; N: 0.21.

Found (wt%): C: 33.24; H: 1.5; N: 0.26.

Fitted formula unit: $\text{Fe}_3\text{O}(\text{H}_2\text{O})_2(\text{OH})(\text{NO}_3)_{0.1}[\text{C}_6\text{H}_3(\text{CO}_2)_3]_2$.

Wt% Ex-GNPs = wt% C (MIL-G3) – wt% C (MIL-100(Fe)) = 15.10 wt%.

Section S6 Determination of Ex-GNP content in Ex-GNP/MIL-100(Fe) composites using TGA data

The content of Ex-GNPs in the Ex-GNP /MIL-100(Fe) composites can be calculated using the TGA data using Eq. (S1):

$$\text{Ex - GNPs (wt. \%)} = \left[\text{W.L.}_{T_{\text{GO-O}_2} \rightarrow 700^\circ\text{C}}^{\text{comp}} - \text{W.L.}_{353^\circ\text{C} \rightarrow 700^\circ\text{C}}^{\text{MIL-100(Fe)}} \right] + 2.73$$

(S1)

where $T_{\text{GO-O}_2}$ is the temperature at which linker decomposition ends or GNP oxidation begins during TGA, $\text{W.L.}_{T_{\text{GO-O}_2} \rightarrow 700^\circ\text{C}}^{\text{comp}} = \text{W}_{T_{\text{GO-O}_2}}^{\text{comp}} - \text{W}_{700^\circ\text{C}}^{\text{comp}}$ stands for the weight loss between $T_{\text{GO-O}_2}$ and 700°C expressed as a percentage of the initial weight, and the superscript "comp" denotes Ex-GNP/MIL-100(Fe) composite. The weight loss for MIL-100(Fe) between 353 and 700°C was measured to be equal to 1.8148 wt%, i.e. $\text{W.L.}_{353^\circ\text{C} \rightarrow 700^\circ\text{C}}^{\text{MIL-100(Fe)}} = 1.8148\%$. The residual Ex-GNPs at the end of TGA amounts to 2.73 wt%.

The corresponding percentages of Ex-GNPs in the composites are calculated to be 6.54, 12.93 and 16.16, respectively (Table S1). The synthesized Ex-GNP/MIL- 100(Fe) composites are referred to as MIL-G n with n from 1 to 3 corresponding to the amount of added Ex-GNPs (70 mg, 180 mg and 300 mg respectively).

Table S1 – Calculation of Ex-GNP contents in Ex-GNP/MIL-100(Fe) composites using TGA data.

Sample ID	$T_{\text{GO-O}_2}$ ($^\circ\text{C}$)	$\text{W}_{T_{\text{GO-O}_2}}^{\text{comp}}$ (%)	$\text{W}_{700^\circ\text{C}}^{\text{comp}}$ (%)	$\text{W.L.}_{T_{\text{GO-O}_2} \rightarrow 700^\circ\text{C}}^{\text{comp}}$	Ex-GNPs (wt%)
MIL-G1	341	60.2562	54.6326	5.6236	6.5396
MIL-G2	343	67.0191	55.0041	12.0150	12.9310
MIL-G3	349	52.5967	37.3552	15.2415	16.1575

Section S7 PXRD profiles of Ex-GNPs, MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites

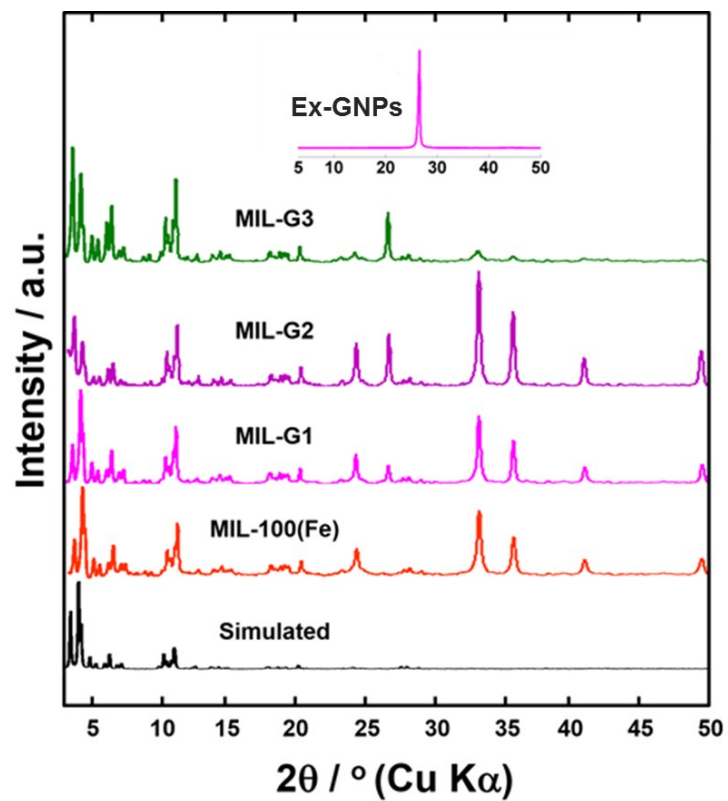


Fig. S2 PXRD patterns of Ex-GNPs, MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites.

Section S8 FT-IR spectra of pristine and acid-treated (functionalized) Graphene Nanoplatelets (Ex-GNPs)

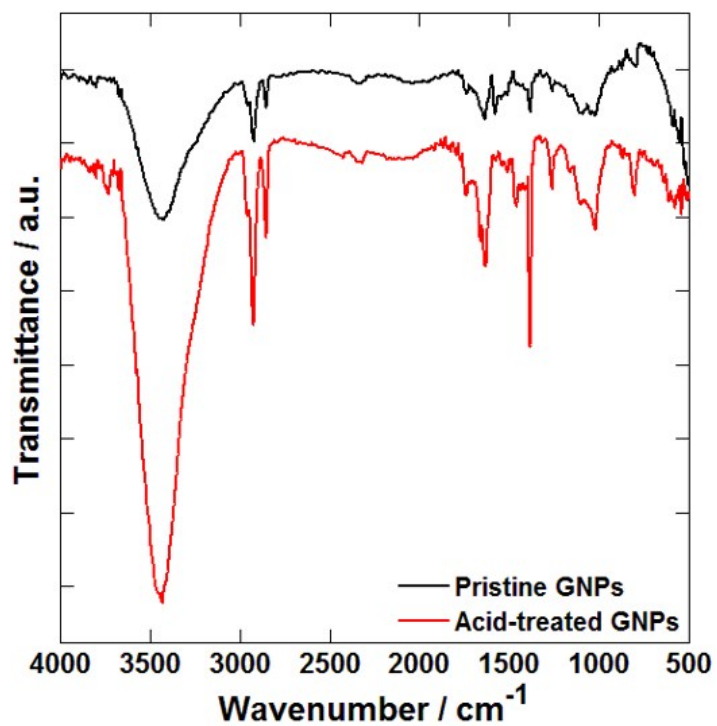


Fig. S3 FT-IR spectra of pristine and acid-treated GNPs (Ex-GNPs).

Section S9 **PXRD pattern of pristine and acid-treated (functionalized) Graphene Nanoplatelets (Ex-GNPs)**

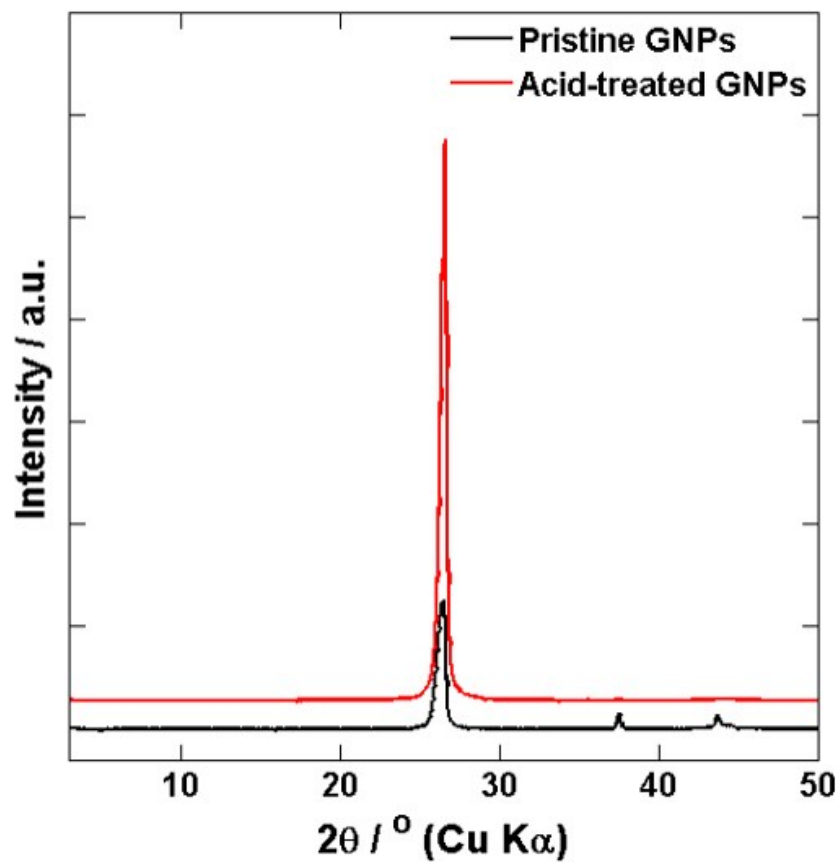


Fig. S4 PXRD patterns of pristine and acid-treated GNPs (Ex-GNPs).

Section S10 N₂ adsorption-desorption isotherms at 77 K of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites

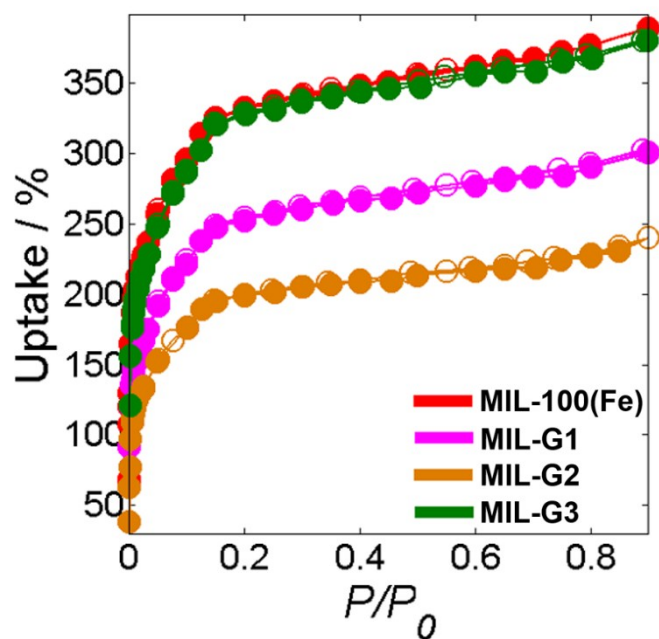


Fig. S5 N₂ adsorption-desorption isotherms of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites at 77 K (open circles: desorption, closed circles: adsorption).

Table S2 – BET surface area ($P/P_0 = 0.06-0.2$) and pore volume ($P/P_0 = 0.9$) data for MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites

Material	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
MIL-100(Fe)	1360	0.832
MIL-G1	1104	0.675
MIL-G2	890	0.544
MIL-G3	1390	0.850

Section S11 SEM micrographs of pristine and acid-treated GNPs (Ex-GNPs).

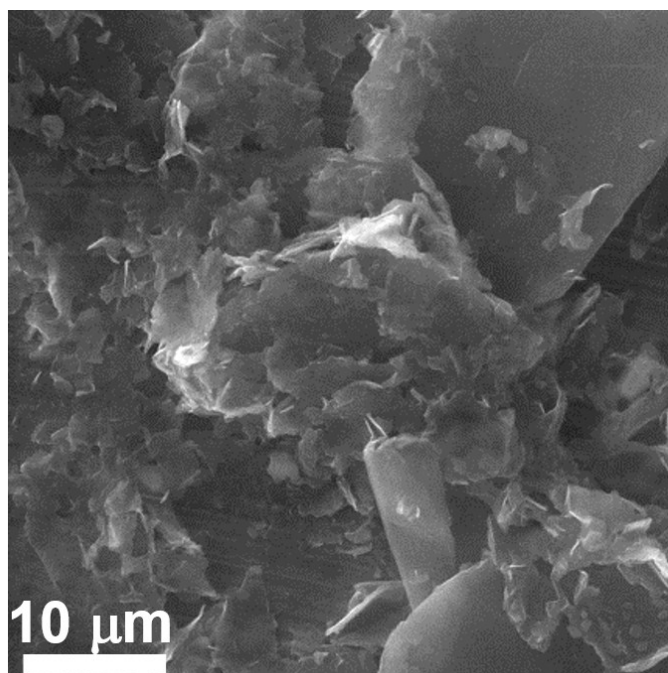


Fig. S6 SEM micrograph of pristine GNPs.

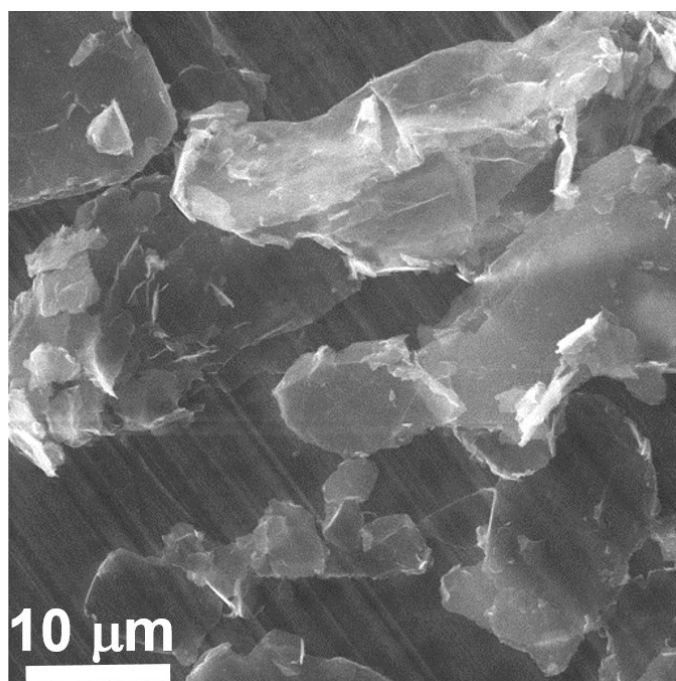


Fig. S7 SEM micrograph of acid-treated GNPs (Ex-GNPs).

Section S12 SEM images of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites

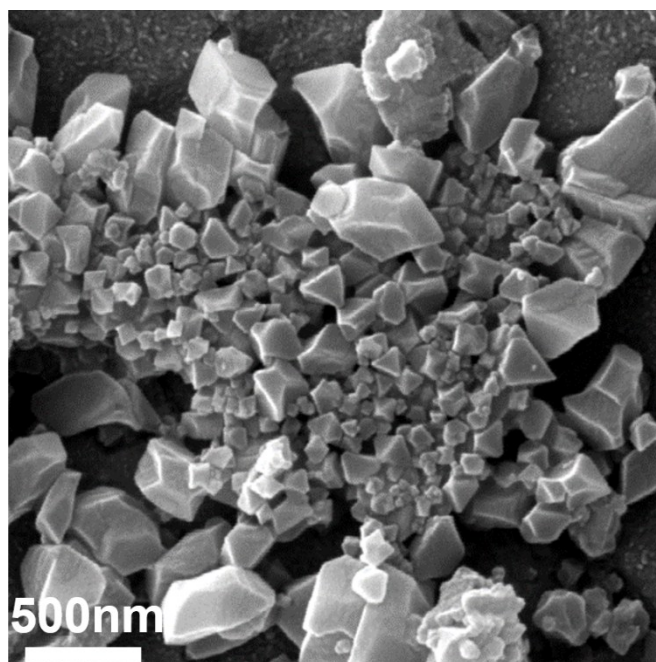


Fig. S8 SEM micrograph of MIL-100(Fe).

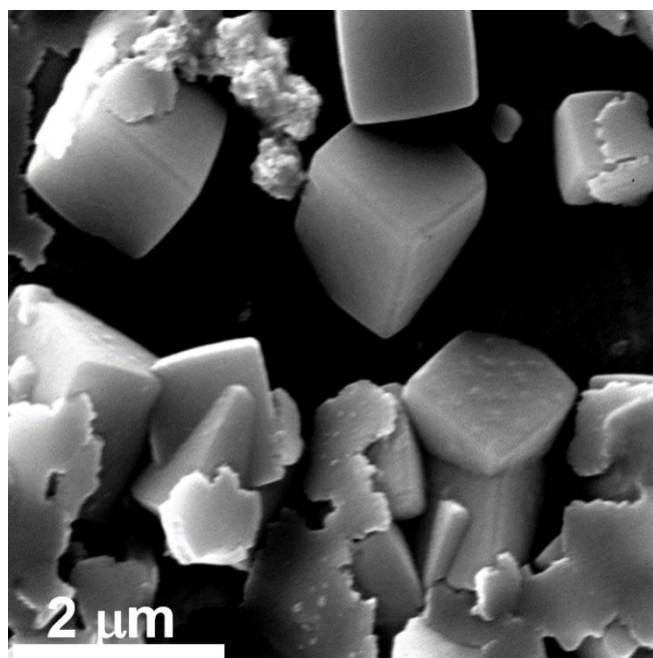


Fig. S9 SEM micrograph of MIL-G1.

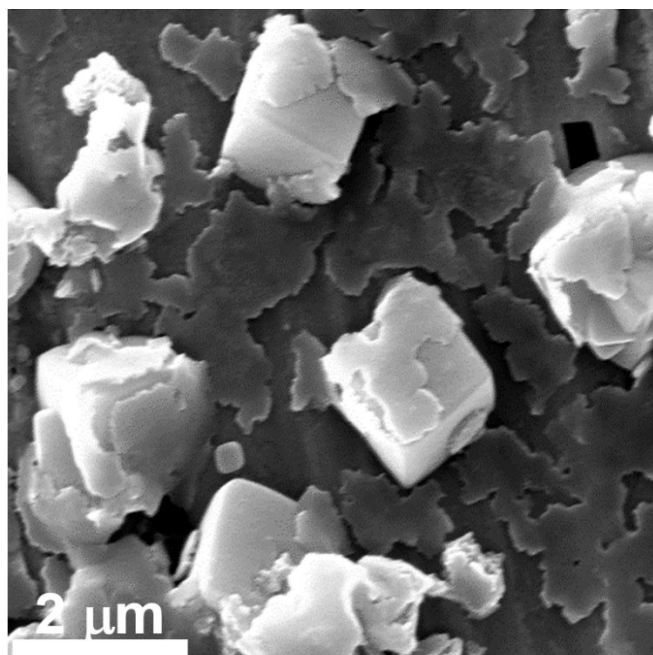


Fig. S10 SEM micrograph of MIL-G2.

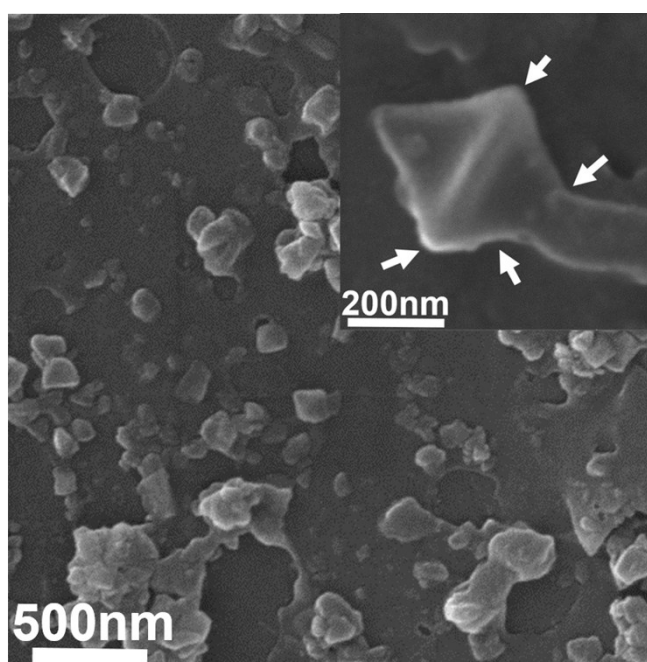


Fig. S11 SEM micrograph of MIL-G3 (white arrows indicate wrappings of Ex-GNPs around MIL-100(Fe) crystals).

Section S13 TEM images of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites

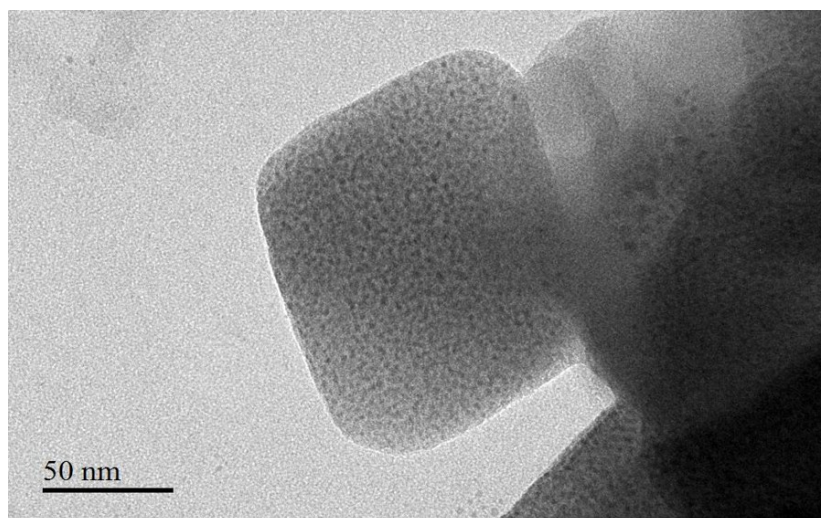


Fig. S12 TEM micrograph of MIL-100(Fe).

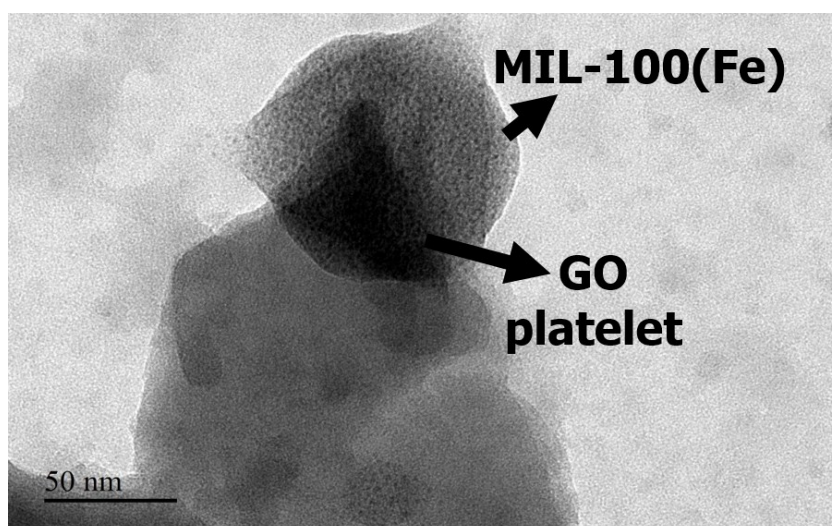


Fig. S13 TEM micrograph of MIL-G1.

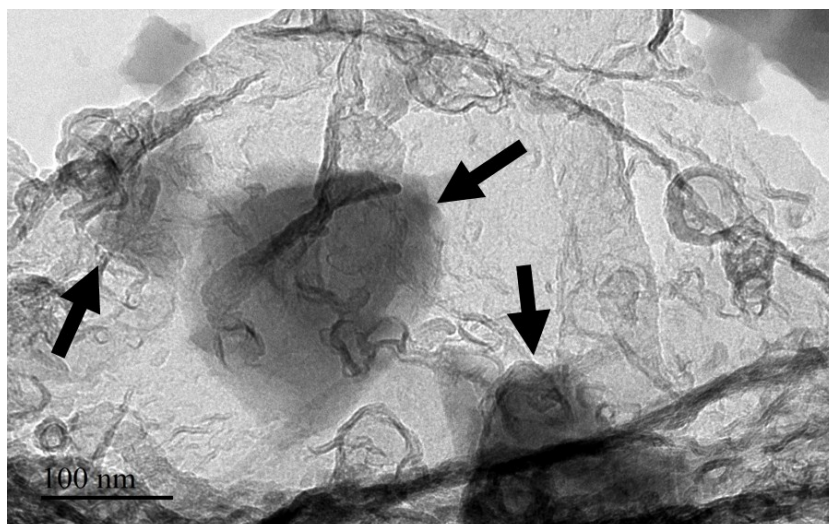


Fig. S14 TEM micrograph of MIL-G2.

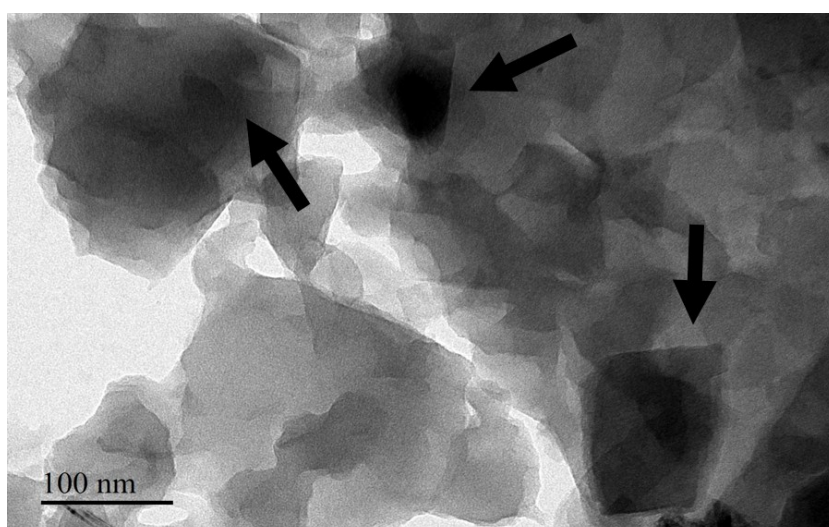


Fig. S15 TEM micrograph of MIL-G3 (black arrows indicate shadows of MIL-100(Fe) crystals behind Ex-GNPs).

Section S14 FT-IR spectra of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites

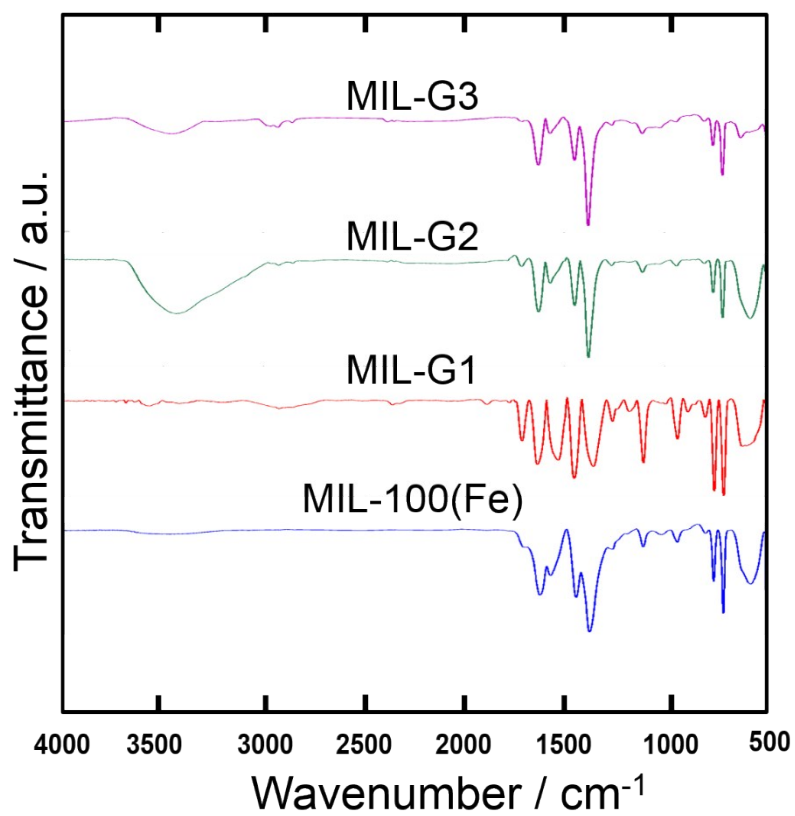


Fig. S16 FTIR spectra of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites.

Section S15 Absorption band classification in FT-IR spectra of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites

MIL-100(Fe):

FT-IR (KBr, 4000-400 cm^{-1}): 3494(br), 2892(w), 1700(w), 1624(s), 1589(m), 1490(s), 1443(m), 1383(s), 1205(w), 1107(m), 1021(w), 937(m), 787(w), 757(s), 740(s), 708(s), 673(s), 575(s).

MIL-G1:

FT-IR (KBr, 4000-400 cm^{-1}): 3579.7(w), 3507.2(w), 3427.5(w), 3331.9(w), 3210.1(w), 2930.4(br), 2376.8(w), 1908.7(w), 1865.2(w), 1798.6(w), 1778.3(w), 1736.2(m), 1700(m), 1659.4(m), 1614.5(m), 1562.3(m), 1513(m), 1479.7(s), 1439.1(m), 1384.1(m), 1318.8(w), 1289.9(w), 1237.7(w), 1207.2(w), 1171(w), 1137.7(m), 1089.9(w), 1030.4(w), 1004.3(w), 968.16(m), 939.13(w), 918.84(w), 891.30(w), 860.87(w), 831.88(w), 811.59(w), 786.96(s), 768.12(s), 742.03(s), 707.25(m), 653.62(m), 640.58(w), 540.58(m).

MIL-G2:

FT-IR (KBr, 4000-400 cm^{-1}): 3426.9(br), 2981(w), 2924(w), 2880(w), 2853.8(w), 2829(w), 2384.5(w), 2364(w), 2345(w), 1748.5(w), 1712(w), 1678.4(w), 1628.7(m), 1595(m), 1573(m), 1488.3(m), 1448.8(m), 1419.6(m), 1380(s), 1298.2(w), 1263.2(w), 1146.2(w), 1111(w), 1055.6(w), 1022(w), 973.68(w), 938.6(w), 872.81(w), 845(w), 831.87(w), 802.63(w), 783.63(w), 755.85(m), 732.46(m), 709.06(m), 675.44(m), 573(m), **502.92(m)**.

MIL-G3:

FT-IR (KBr, 4000-400 cm^{-1}): 3451.8(br), 2962(w), 2943(w), 2925.4(w), 2880(w), 2852.3(w), 2380(w), 2359.6(w), 2342(w), 2329(w), 1710.5(w), 1687(w), 1628.7(m), 1590.6(m), 1567.3(m), 1504.4(m), 1448.8(m), 1424(m), 1378.7(s), 1292.4(w), 1260.2(w), 1165.2(w), 1111(w), 1022(w), 969.3(w), 944.4(w), 847.95(w), 801.17(w), 780.7(w), 738.3(w), 712(m), 669.59(m), 622.81(w), 590.64(w), 574.56(w), **513.16(w)**.

Note: Absorption bands marked in red indicate C–O–Fe stretching in Ex-GNP/MIL-100(Fe) composites [S5].

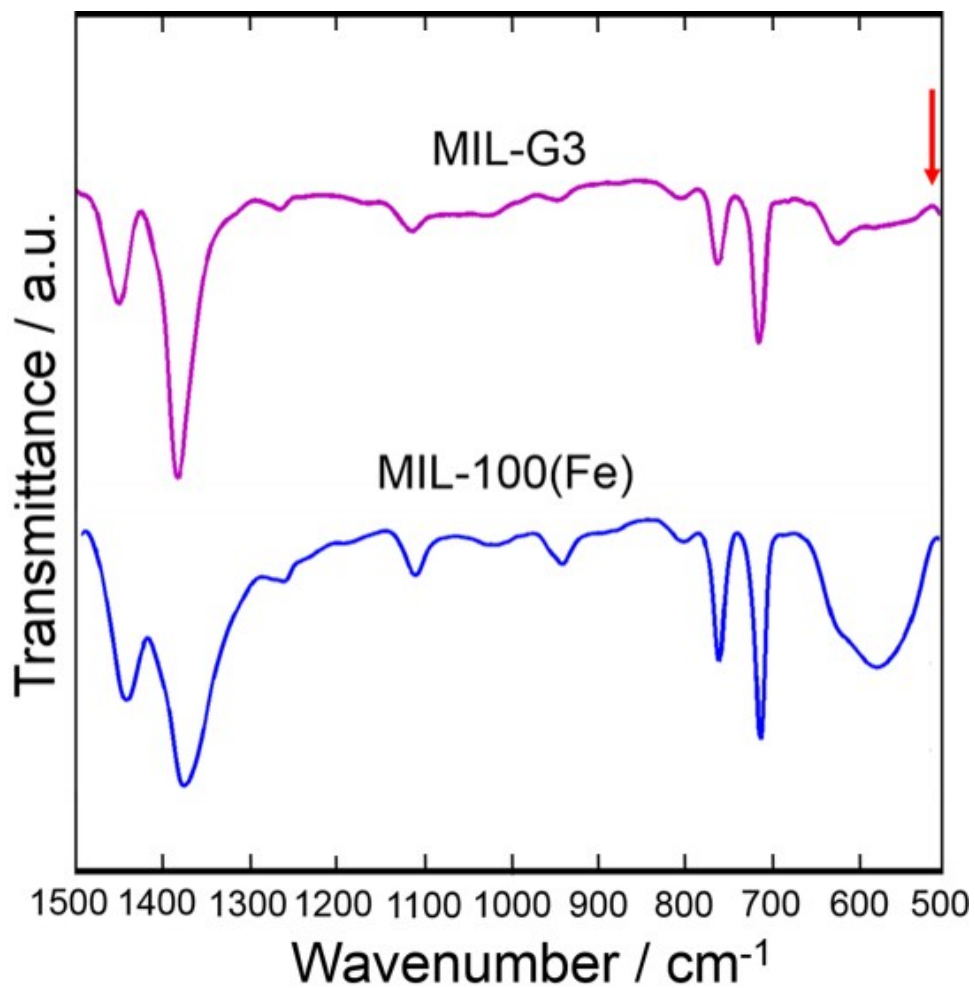
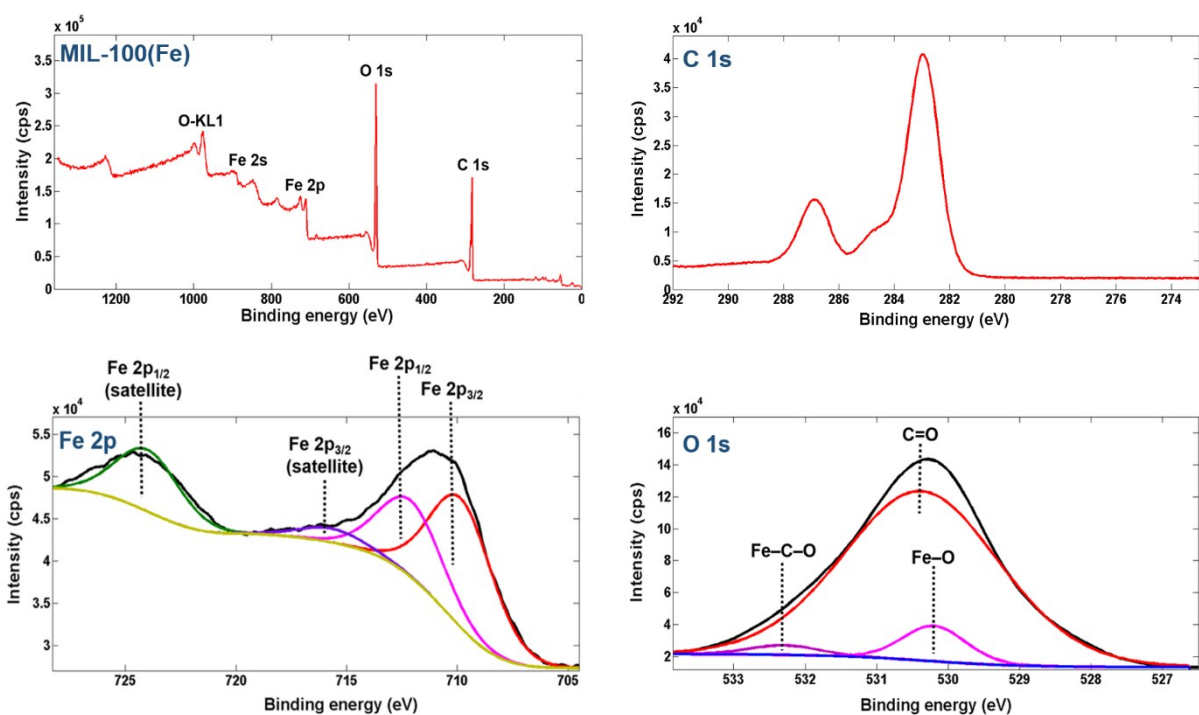
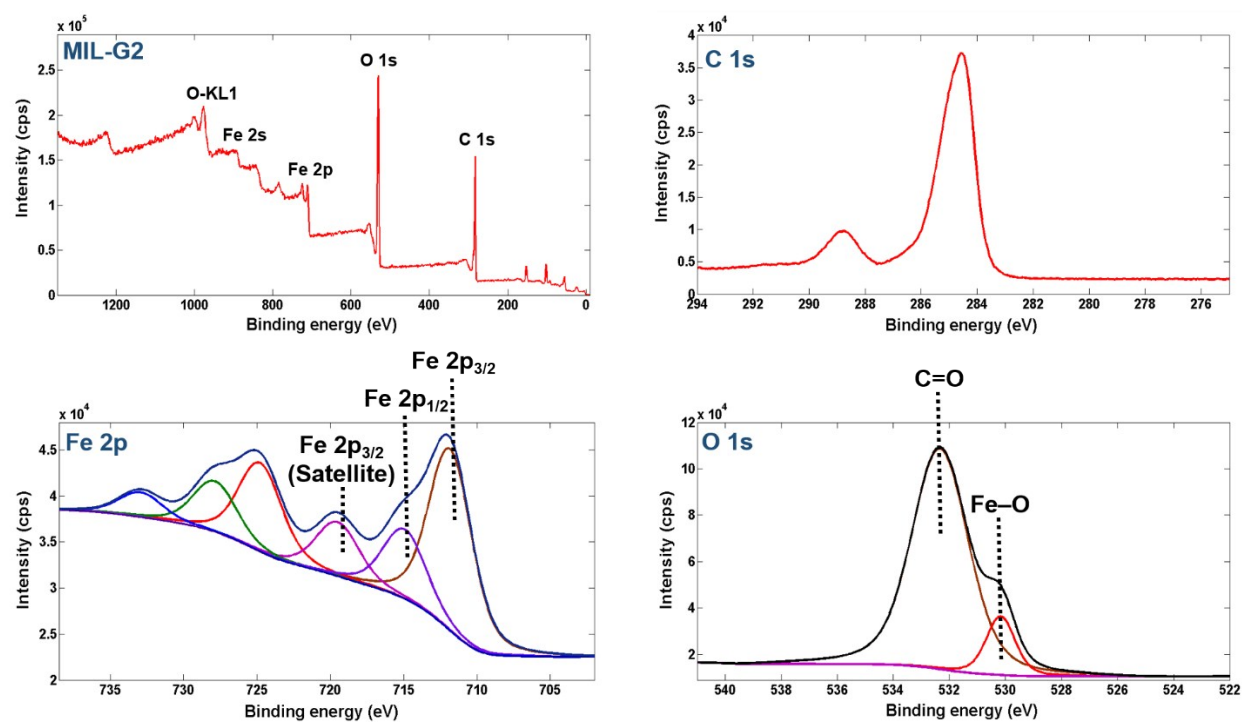


Fig. S17 Magnified FTIR spectra of MIL-100(Fe) and MIL-G3 (Red arrow indicates C–O–Fe stretching which is absent in case of MIL-100(Fe)).

Section S16 XPS analysis of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites



(a)



(b)

Fig. S18 XPS profiles of (a) MIL-100(Fe) and (b) MIL-G2.

Table S3. Peak position and intensity data for XPS spectra of MIL-100(Fe) and MIL-G2.

Peak	MIL-100(Fe)		MIL-G2	
	Position (ev)	Intensity (at.%)	Position (ev)	Intensity (at.%)
O1s-A	532.29	0.96	530.17	10.47
O1s-B	530.20	3.22	532.34	76.17
Fe2p-A	709.83	1.38	711.82	5.14
Fe2p-B	724.01	0.66	724.79	2.55
Fe2p-C	712.12	0.81	732.95	0.70
Fe2p-D	715.72	0.15	719.51	1.55
Fe2p-E	NA	NA	727.87	1.46
Fe2p-F	NA	NA	714.95	1.98

Note: Higher intensity of O1s-A in MIL-G2 as compared to MIL-100(Fe) and lower intensity of Fe2p-C indicate existence of Fe-C-O bonding between Ex-GNPs and MIL-100(Fe) in MIL-G2.

Section S17 TGA profiles of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites and PXRD profiles of post-TGA residues

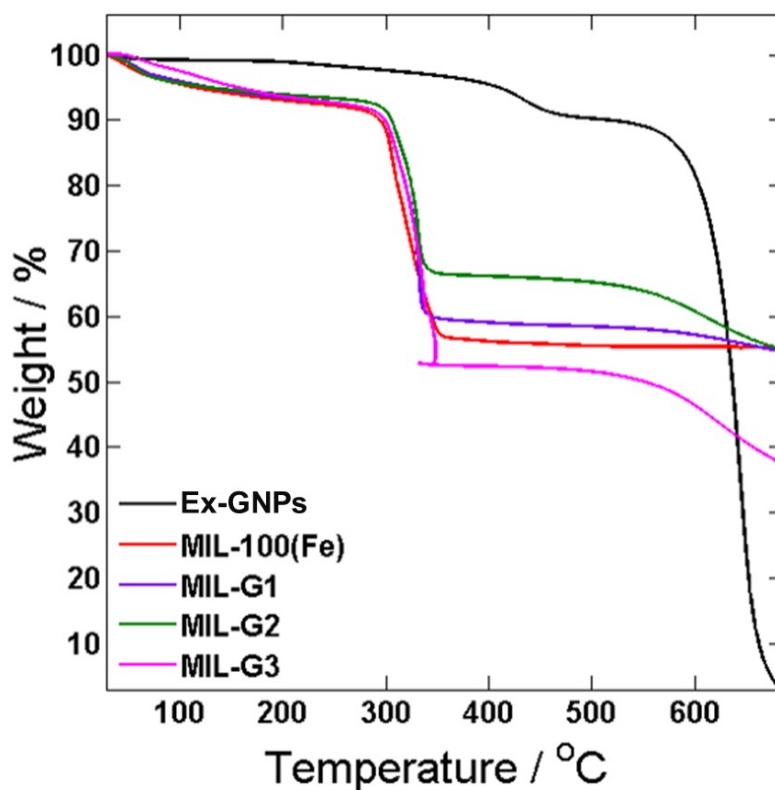


Fig. S19 TGA profiles of Ex-GNPs, MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites.

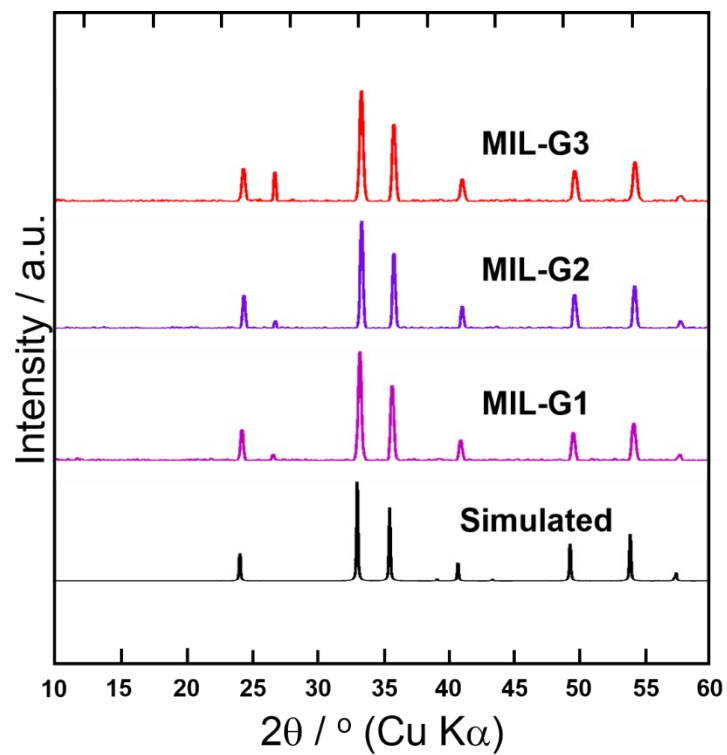


Fig. S20 PXRD profiles of Ex-GNP/MIL-100(Fe) composites after TGA showing the existence of $\alpha\text{-Fe}_2\text{O}_3$.

Section S18 Water sorption isotherms of MIL-100(Fe), Ex-GNPs and Ex-GNP/MIL-100(Fe) composites at 298 K

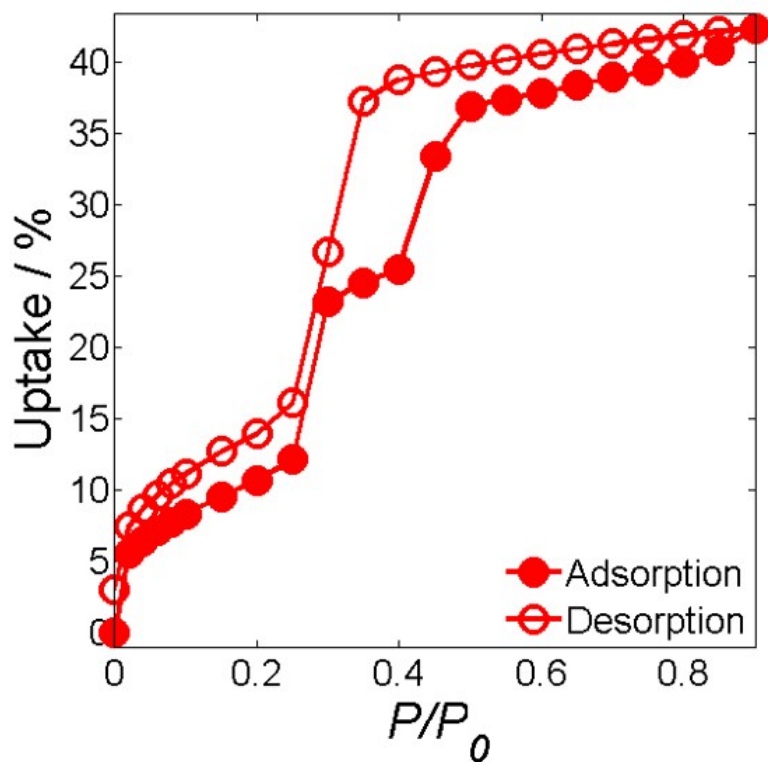


Fig. S21 Water adsorption-desorption isotherms of MIL-100(Fe) measured at 298 K.

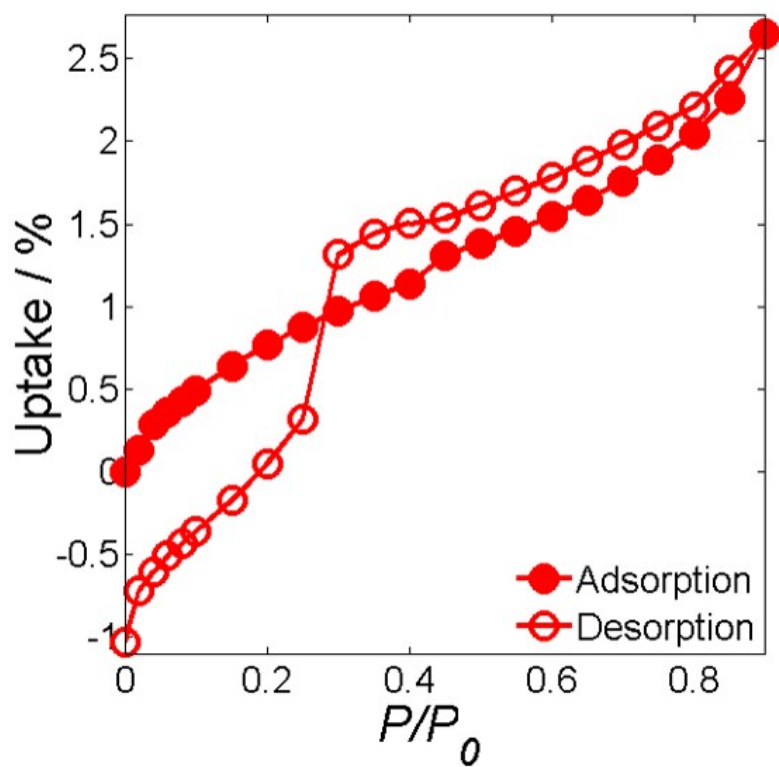


Fig. S22 Water adsorption-desorption isotherms of Ex-GNPs measured at 298 K.

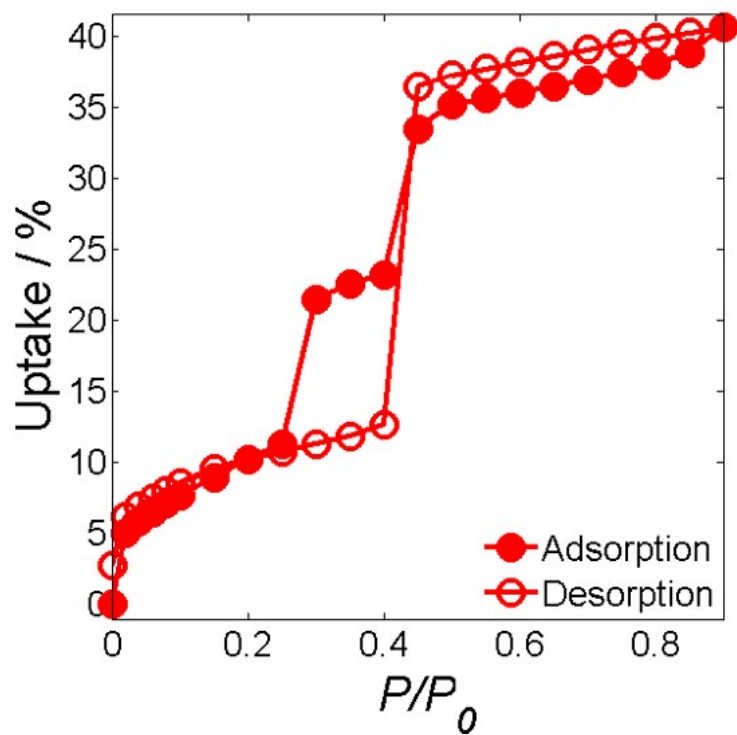


Fig. S23 Water adsorption-desorption isotherms of MIL-G1 measured at 298 K.

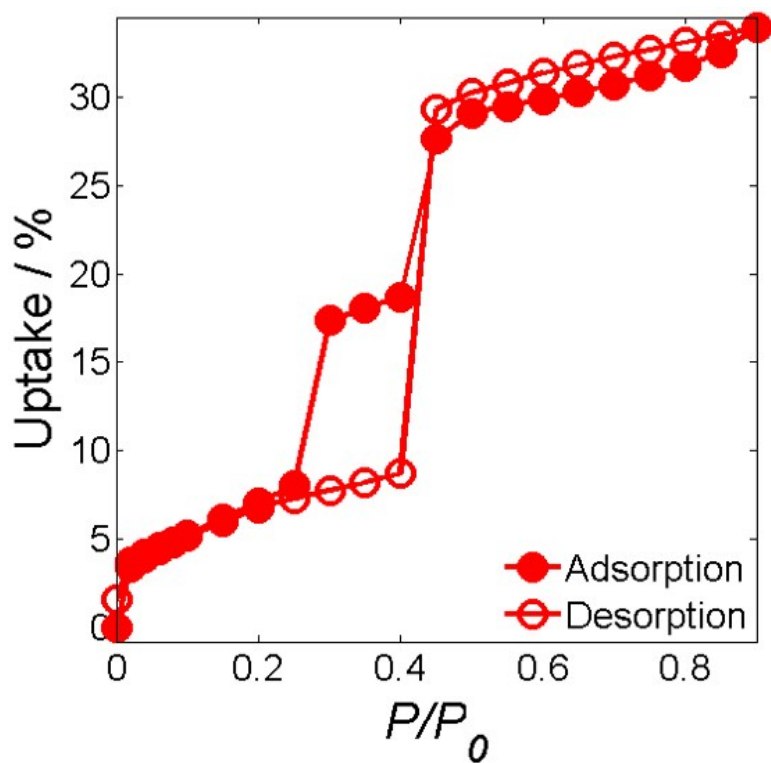


Fig. S24 Water adsorption-desorption isotherms of MIL-G2 measured at 298 K.

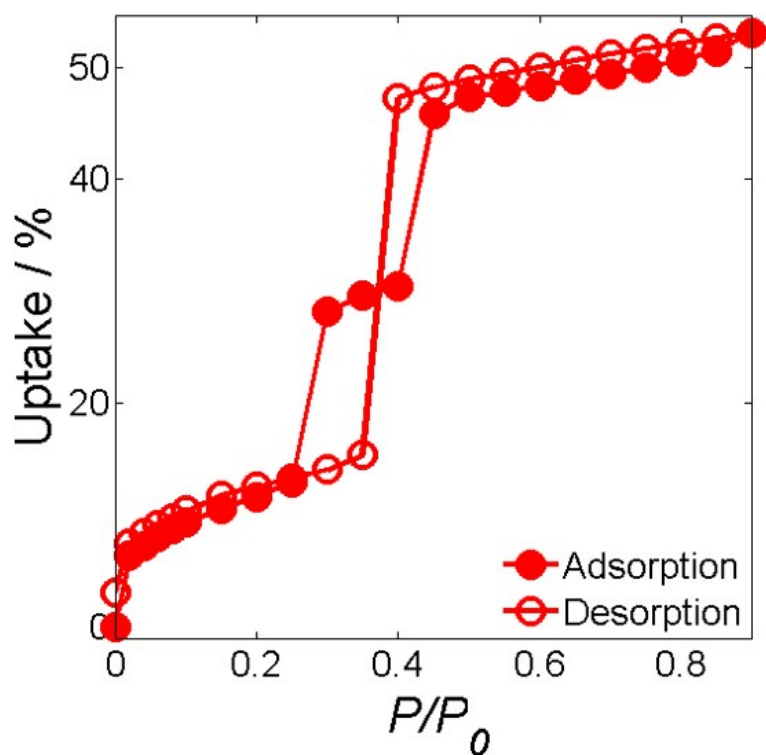


Fig. S25 Water adsorption-desorption isotherms of MIL-G3 measured at 298 K.

Section S19 Calculation of hysteresis in water sorption isotherms measured at 298 K

The cumulative hysteresis between the adsorption and desorption branches can be expressed as [S3]:

$$\mathbf{H} = \left| \frac{1}{q_{high} - q_{low}} \int_{q_{low}}^{q_{high}} H_{diff}(q) dq \right| \quad (\text{S2})$$

where q_{low} and q_{high} denote the lower and upper limits of instantaneous water uptake respectively, while the differential hysteresis H_{diff} can be expressed as [S4]:

$$H_{diff}(q) = \ln \left[\frac{P_A(q)}{P_D(q)} \right] \quad (\text{S3})$$

where P_A and P_D are the adsorption and desorption pressures corresponding to the instantaneous uptake q .

Table S4 – Important parameters related to water sorption kinetics measured for MIL-100(Fe) and Ex-GnP/MIL-100(Fe) composites.

Sample ID	α^*	Water uptake at 298 K (%)	Hysteresis	Retained uptake at end of desorption (%)	Loss of uptake b/w first and last cycles (%)
MIL-100(Fe)	0.2902	42.45	0.4235	3.02	48.20
MIL-G1	0.2947	40.62	0.0086	2.77	27.57
MIL-G2	0.2966	33.92	0.0831	1.57	48.24
MIL-G3	0.2936	53.05	0.1041	3.12	29.00

* Relative pressure P/P_0 at which adsorbed amount at 298 K is half of the adsorbed amount at $P/P_0 = 0.9$

Section S20 SEM and PXRD analyses of samples after cyclic adsorption-desorption test

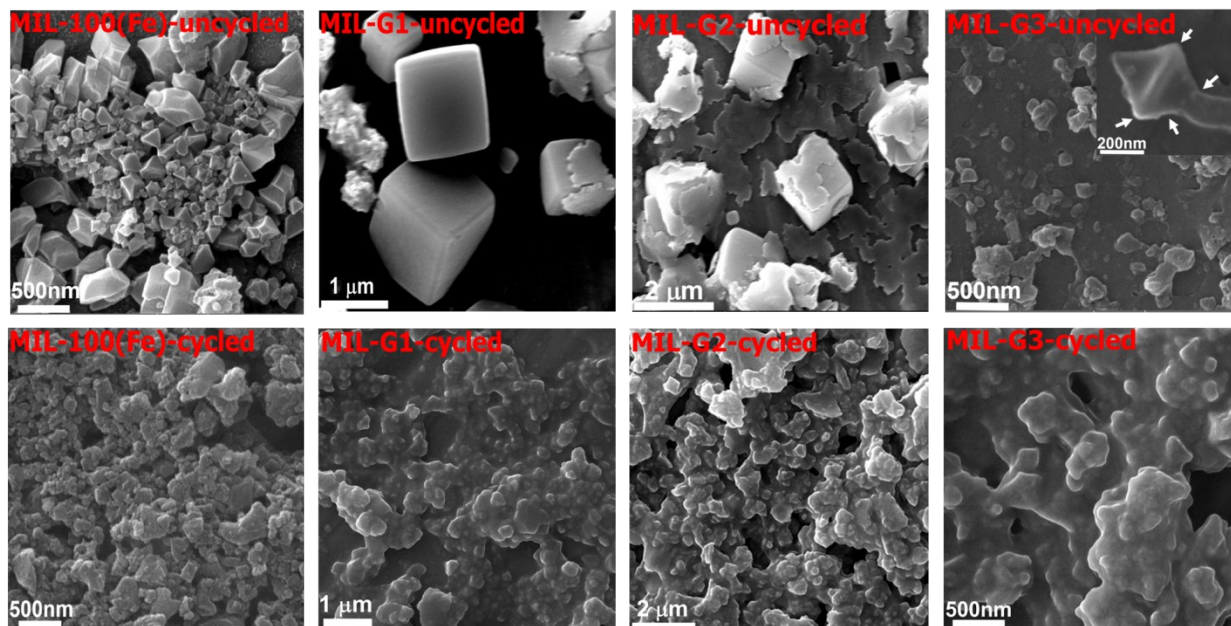


Fig. S26 SEM micrographs of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites before and after cyclic adsorption-desorption test (white arrows in inset of MIL-G3 indicate wrappings of Ex-GNPs around MIL-100(Fe) crystals).

Figure Explanation:

A comparison of the SEM micrographs of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites before and after the cyclic adsorption/desorption test are not exactly similar but at least reveal that the octahedral morphology of the crystals is preserved after the test. However, a continuous cyclic water adsorption/desorption process has resulted in partial disintegration of the intrinsic lattice structure of the MIL-100(Fe) framework which makes the crystallites appear relatively

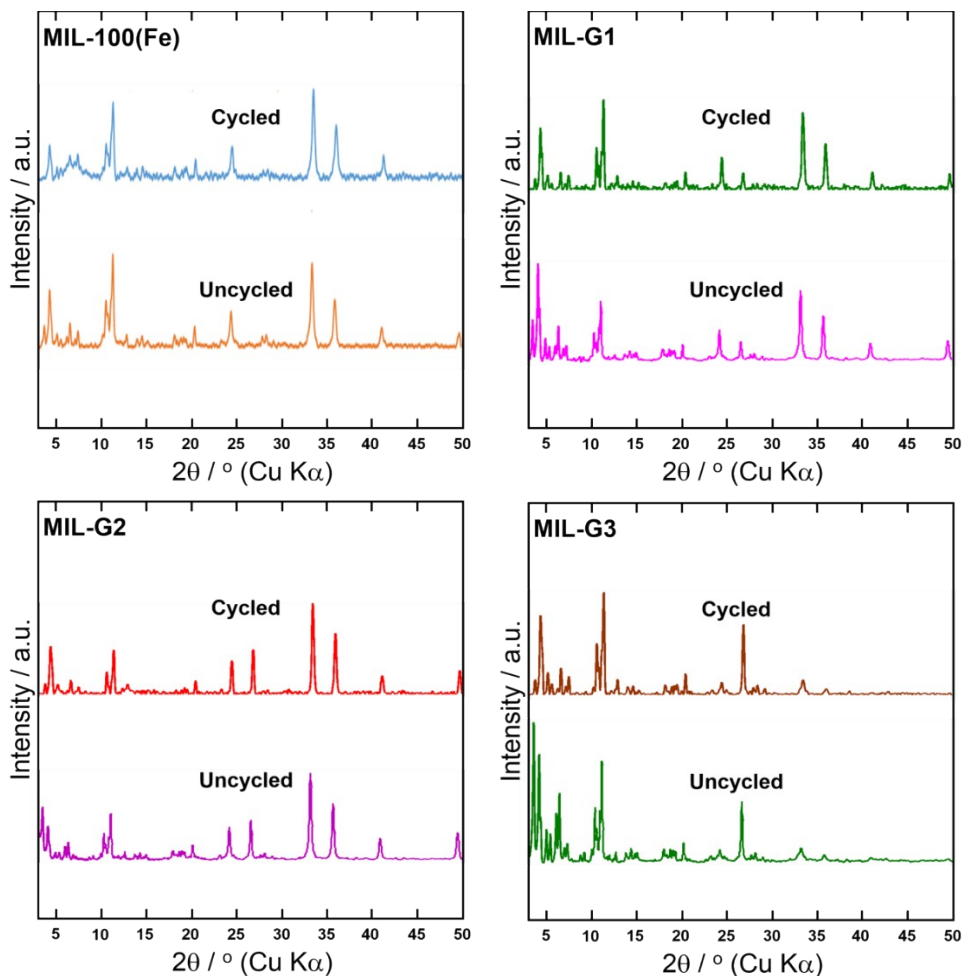


Fig. S27 PXRD profiles of MIL-100(Fe) and Ex-GNP/MIL-100(Fe) composites before and after cyclic adsorption-desorption test.

smaller in size as compared to the crystals before the test as exhibited in Figure S26. More importantly, the crystallinity of the structure is maintained after the cyclic test without any noticeable shifts in characteristic peak positions or individual peak intensities as shown by the comparison of the PXRD profiles of each of the four types of materials displayed in Figure S27.

Supporting Information References

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