Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Controlled Growth of Dense and Ordered Metal-Organic Frameworks Nanoparticles on Graphene Oxide

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Experimental Section

Chemicals

All chemicals were purchased from commercial sources and used without further purification. All solvents were analytical grade and distilled prior to use.

Synthesis of MOF-253

MOF-253 was prepared from solvothermal reaction of $AlCl_3 \cdot 6H_2O$ (151 mg, 0.625 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol), and 10 mL N,N'-dimethylformamide (DMF) at 130 °C for 24 h. The resulting white powder was filtered and washed with DMF thoroughly. The solid was washed with methanol via soxhlet extraction for 24 h, and then was collected by filtration and finally dried at 150 °C under vacuum for 12 h.

Synthesis of MOF-253/GO (MG) hybrids

MOF-253/GO was prepared by using two different methods.

Method A: 15.2 mg GO was added into 10 mL N,N'-dimethylformamide (DMF) under ultrasound for 8 h, afterwards, $AlCl_3 \cdot 6H_2O$ (151 mg, 0.625 mmol) and 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) were added. After solvothermal reaction at 130 °C for 24 h, the obtained light gray powder was filtered and washed with DMF thoroughly. The solid was washed with methanol via soxhlet extraction for 24 h, and then was collected by filtration and finally dried at 100 °C under vacuum for 12 h. The obtained material was denoted as MG-A.

Method B: 15.2 mg GO and $AlCl_3 \cdot 6H_2O$ (151 mg, 0.625 mmol) were added into 10 mL DMF under ultrasound for 8 h, afterwards, 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) was added. After solvothermal reaction at 130 °C for 24 h, the resulting dark gray powder was filtered and washed with DMF thoroughly. The solid was washed with methanol via soxhlet extraction for 24 h, and then was collected by filtration and finally dried at 100 °C under vacuum for 12 h. The obtained mateial was denoted as MG-B.

Synthesis of MIL-101

$Cr(NO_3)_3 \cdot 9H_2O$ (2.00 g, 5 mmol), HF (48 wt%, 5 mmol), and terephthalic acid (0.823 g, 5 mmol) were added into 24 mL deionized water. After heating at 220 °C for 8 h, the mixture was cooled first to 150 °C in 1 h, and then slowly to room temperature in 12 h. The green MIL-101 powder was isolated from the solution and washed with deionized water and ethanol, and then soaked in ethanol (95% EtOH with 5% water) at 80 °C for 24 h. The obtained solid was finally dried overnight at 150 °C under vacuum.

Synthesis of MIL-101/GO (LG) hybrids

GO (80 mg) was added into 24 mL deionized water under ultrasound for 4 h. Afterwards, $Cr(NO_3)_3 \cdot 9H_2O$ (2.00 g, 5 mmol), HF (48 wt %, 5 mmol), and terephthalic acid (0.823 g, 5 mmol) were added. Then, a similar process was followed as that for synthesis of MIL-101. The obtained solid was finally dried overnight at 100 °C under vacuum. The obtained material was denoted as LG-A.

GO (80 mg) and $Cr(NO_3)_3 \cdot 9H_2O$ (2.00 g, 5 mmol) were added into 24 mL deionized water under ultrasound for 4 h. Afterwards, HF (48 wt%, 5 mmol) and terephthalic acid (0.823 g, 5 mmol) were added. Then, a similar process was followed as that for synthesis of MIL-101. The obtained material was finally dried overnight at 100 °C under vacuum. The obtained material was denoted as LG-B.

Ethylbenzene oxidation reaction

Typically, ethylbenzene (1 mmol), TBHP (1 mL, 70% in H2O), anisole (0.3 mmol, as internal standard for GC-MS analysis), and catalyst (10 mg) were added to acetonitrile (2 mL). The reaction mixture was stirred at the desired temperature for fixed time. After cooling to room temperature, the catalyst was isolated from the solution by filtration and washed with ethyl acetate. The crude was quantified by GC-MS analysis (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column).

Materials characterization

BET surface area measurements were performed with N2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020M instrument. Prior to analysis, the samples were degassed at 100 °C for 12 h. Powder X-ray diffraction patterns of the samples were recorded on a Rigaku diffractormeter (D/MAX-IIIA, 3 kW) using Cu Kα radiation (40 kV, 30 mA, 0.1543 nm). The sizes and morphologies of materials were studied by high-resolution scanning electron microscopy (HR-SEM, S-3700N of HITACHI) and transmission electron microscopy (TEM, CM300 of Philips). TGA curves were obtained on a NETZSCH STA449C under N2 atmosphere. Elemental analysis was performed on an Elementar Vario EL III equipment. The aluminum contents in the samples were measured quantitatively by ICP-AES on a LEEAN-LABS Prodigy Instrument. The chromium contents in the samples were measured quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument. The chromium contents in the samples were measured quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument.

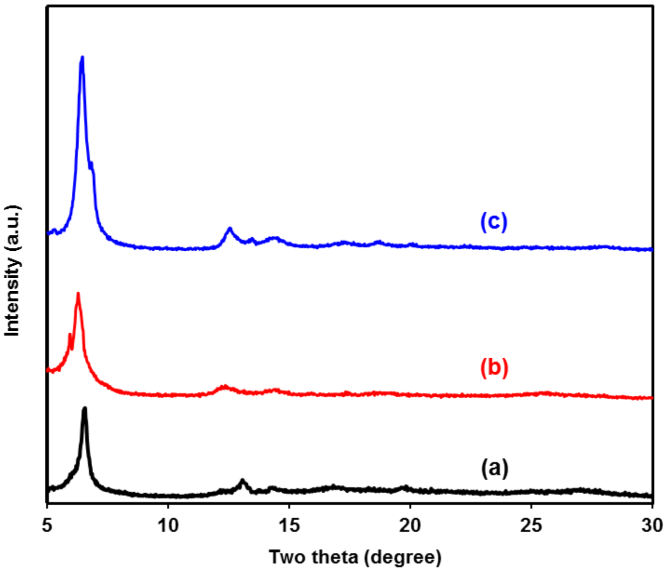

Figure S1. Powder XRD patterns of MOF-253 (a), MG-A (b), and MG-B (c).

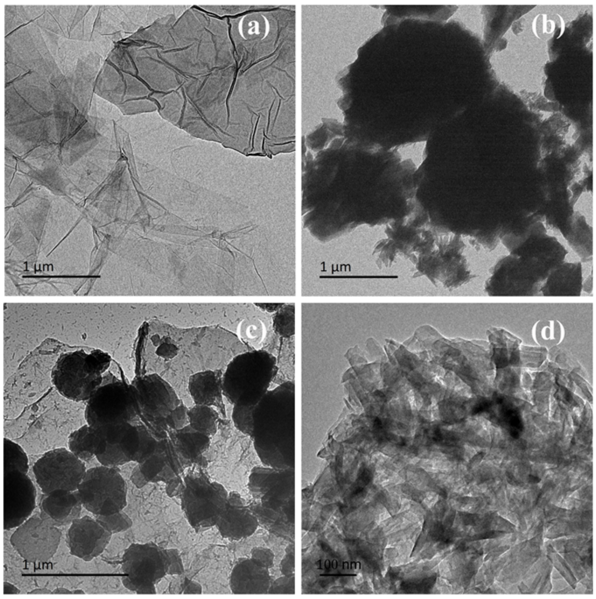

Figure S2. TEM images of (a) graphene oxide (GO), (b) MOF-253, (c) MG-A, and (d) MG-B.

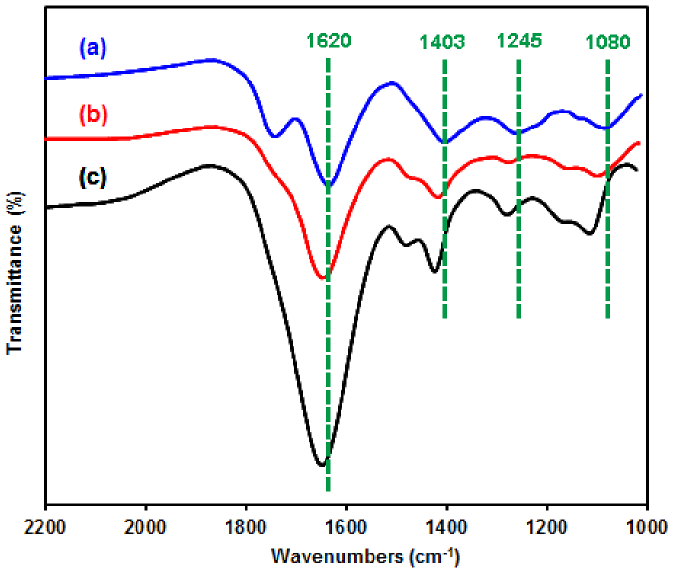

Figure. S3 FT-IR spectra for GO (a), GO + $AlCl_3$ tested immediately (b), and GO + $AlCl_3$ mixed for 8 h.

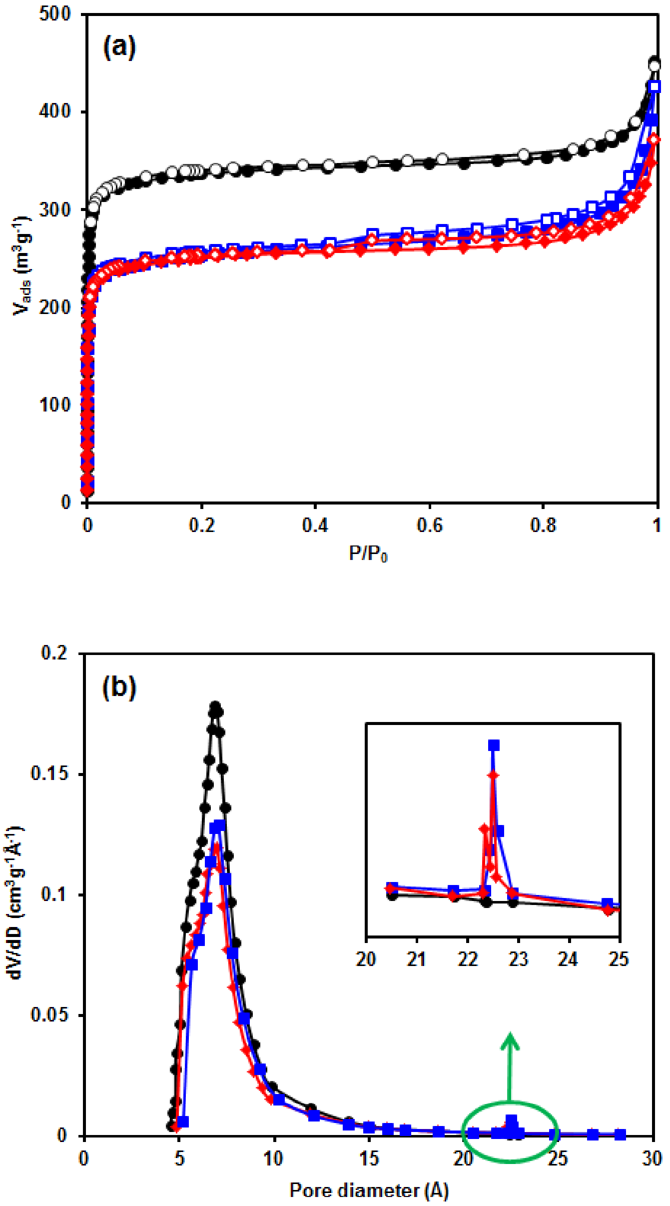

Figure S4. Nitrogen adsorption/desorption isotherms at 77 K (a) and pore size distribution (b). Symbols: MOF-253 (●), MG-A (◆), and MG-B (■).

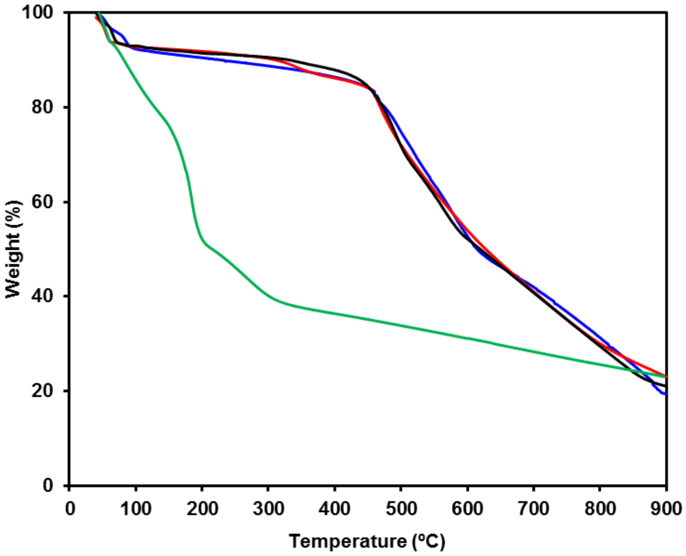

Figure. S5 TGA curves for GO (green), MOF-253 (black), MG-A (red), and MG-B (blue) under N2.

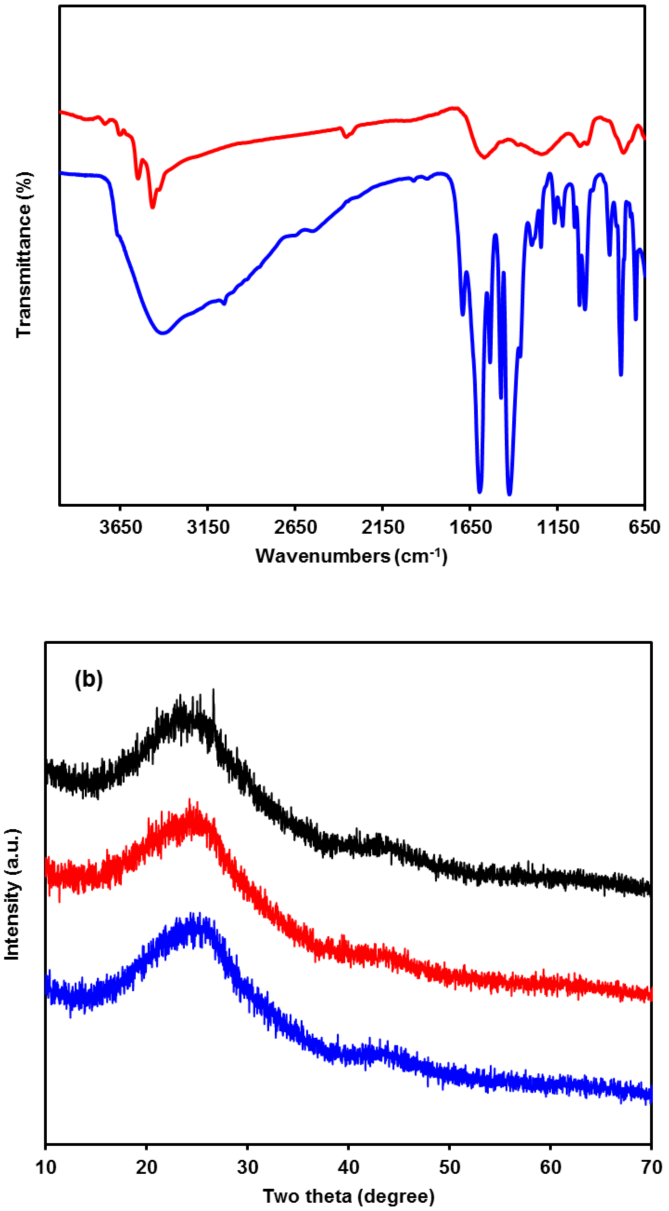

Figure S6. a) FT-IR spectra for MOF-253(blue) and MOF-253-900 (red); b) Powder XRD patterns for MOF-253-900 (black), MG-A-900 (red), and MG-B-900 (blue)

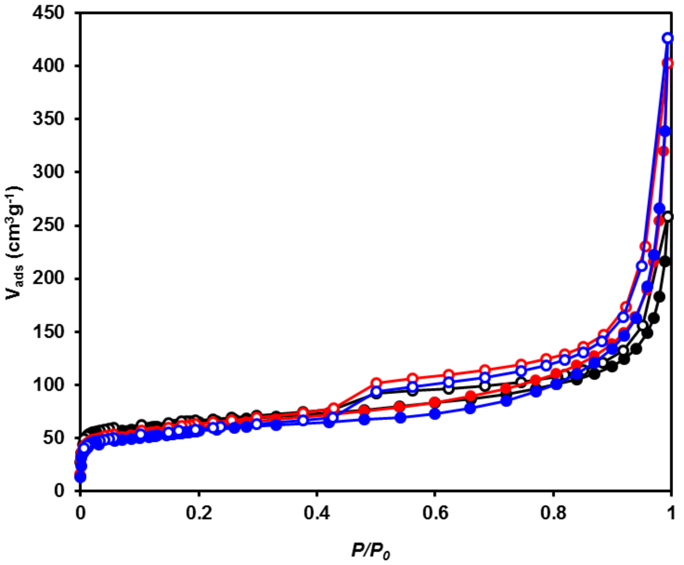

Figure S7. Nitrogen adsorption/desorption isotherms for MOF-253-900 (black), MG-A-900 (red), and MG-B-900 at 77 K (blue). Filled symbols: adsorption branch; open symbols: desorption branch.

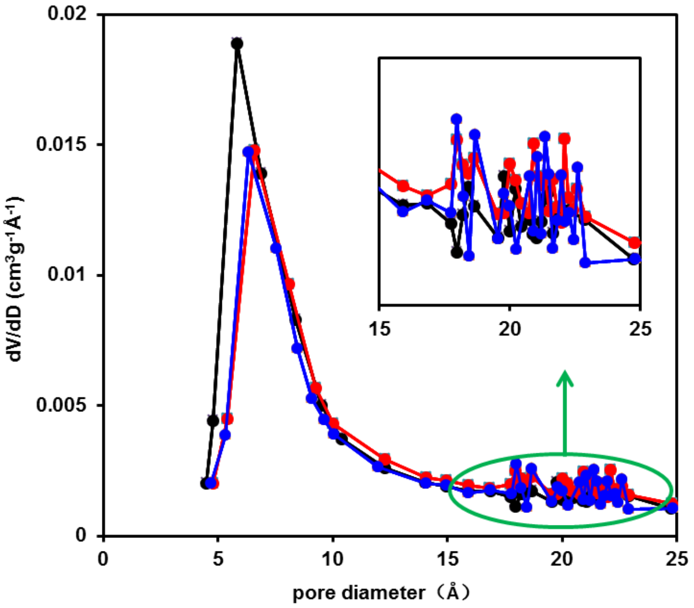

Figure S8. Pore distribution curves for MOF-253-900 (black), MG-A-900 (red), and MG-B-900 (blue).

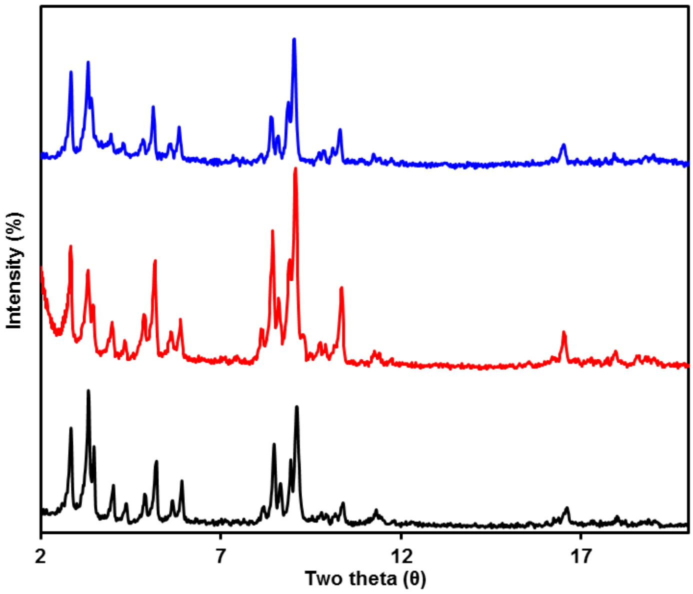

Figure S9. Powder XRD patterns for MIL-101 (black), LG-A (red), and LG-B (blue).

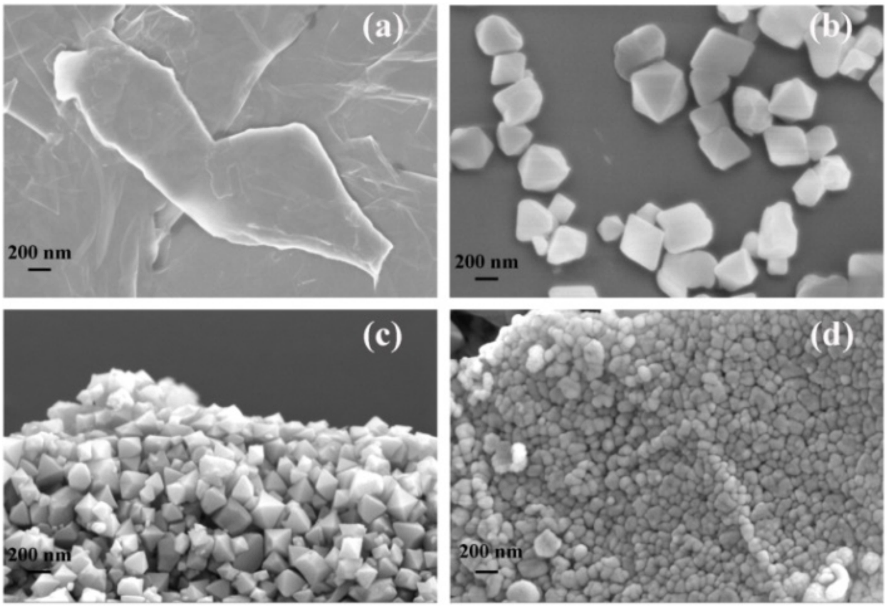

Figure. S10 SEM images of (a) GO, (b) MIL-101, (c) LG-A, and (d) LG-B.

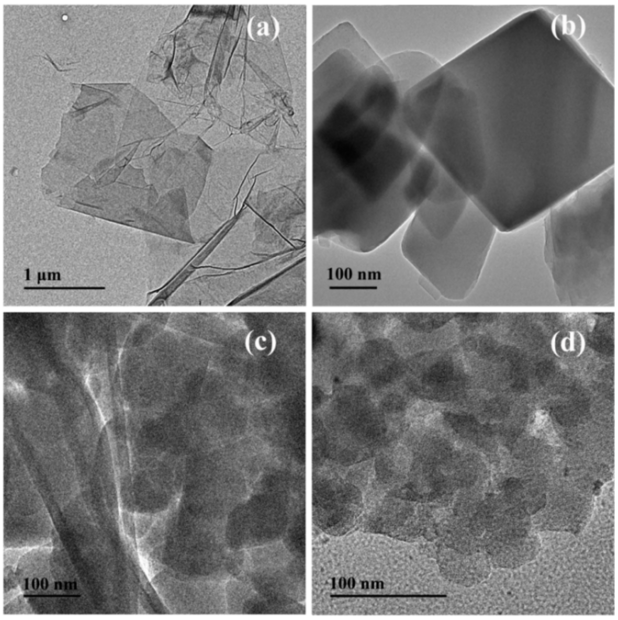

Figure. S11 TEM images of (a) graphene oxide (GO), (b) MIL-101, (c) LG-A, and (d) LG-B.

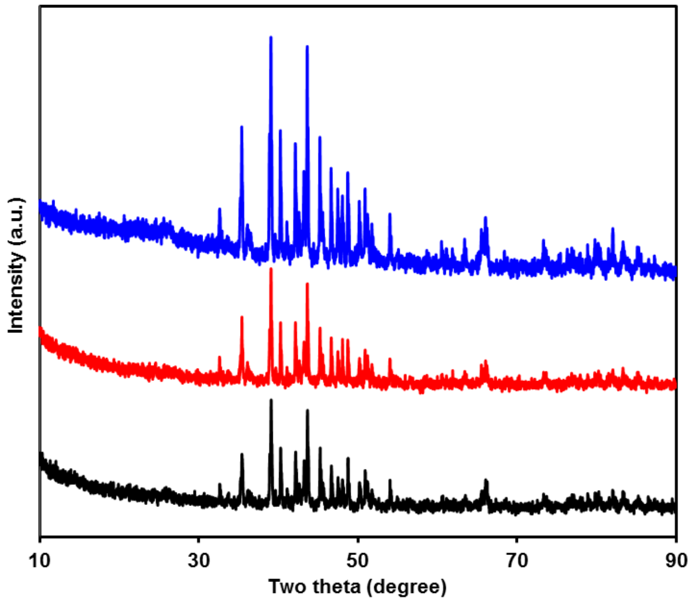

Figure S12. Powder XRD patterns for MIL-101-900 (black), LG-A-900 (red), and LG-B-900 (blue).

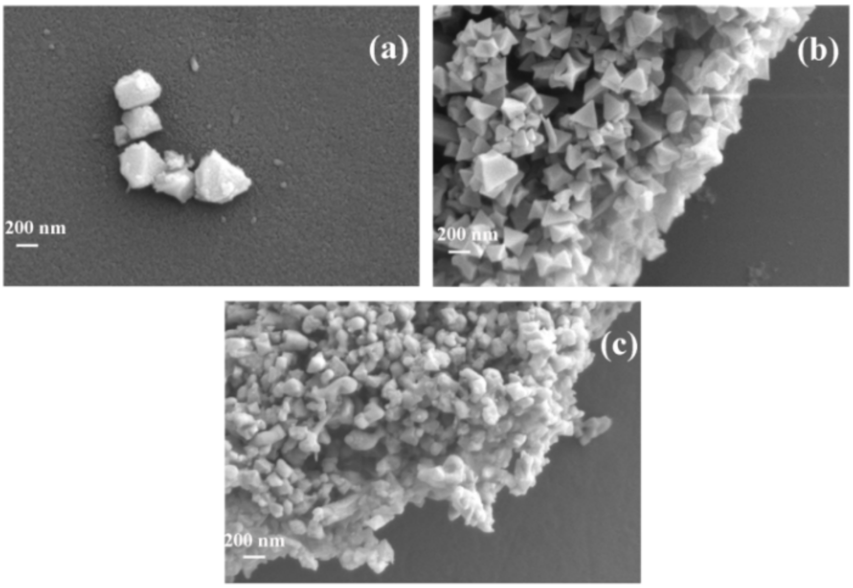

Figure. S13 SEM images of (a) MIL-101-900, (b) LG-A-900, and (c) LG-B-900.

Table S1. Surface areas and porosities of the materials.

Sample	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (Å)
MOF-253	1102	0.67	6.8
MG-A	966	0.64	6.8 and 22.5
MG-B	973	0.66	6.8 and 22.5
MOF-253-900	221	0.40	5.8
MG-A-900	209	0.62	6.6 and 22.0
MG-B-900	194	0.66	6.4 and 21.0

Table S2. Elemental content of the materials.

Sample	N content (wt%)[a]	C content (wt%)[a]	H content (wt%)[a]	Al content (wt%)[b]
MOF-253-900	8.1	47.5	2.4	22.7
MG-A-900	8.9	54.9	2.1	17.6
MG-B-900	8.8	56.2	2.3	16.1

[a] Measured by elemental analysis.

[b] Measured by ICP-AES.