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Graphene oxide templated preferential growth of continuous MOF thin films

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Electronic Supporting Information (ESI)

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1. Materials and Experimental methods

Materials and Methods: Copper(II) nitrate trihydrate (Sigma-Aldrich) and Trimesic acid (TMA, Aldrich) were purchased and used without further purification. Anionic alumina oxide (AAO) film with 200 nm pore size and 48 mm diameter was supplied from Whatman (Anodisc Inorganic membrane). Powder X-ray diffraction (PXRD) analysis was carried out using XRD (D/MAX, Rigaku) with CuK radiation (λ=1.5406Å) at a generator voltage of 40 kV and a generator current of 100 mA; XRD measurement was performed with 1ºC/min of scan speed in the 2Θ range from 5 to 30 degree. For the scanning electron microscopy (SEM) analysis, all the samples were attached on carbon tapes and then coated with osmiums. After the procedure, SEM images were obtained using Nova230 of FEI Company; specific measurement conditions are as follows; Landing E: 5 keV and working distance: 5.6 mm. Fourier transform infrared spectroscopy (FT-IR) data was obtained using Bruker Alpha with 64 scan-times and 4 cm^{-1} of resolution. X-ray photoelectron spectroscopy (XPS) analysis was performed with a multi-purpose XPS (Sigma Probe, Thermo VG Scientific, X-ray Source: monochromatic Al K(alpha)).

Synthesis of Graphene oxide (GO): GO was synthesized through a modified Hummers method.[S1] Graphite (1 g) was mixed with concentrated sulfuric acid (98%, 150 mL). After oxidation of graphite for 2 h at 35°C, distilled H_2O and H_2O_2 were added sequentially into the reacting solution in an ice bath. After filtering the oxidized product, it was washed with hydrochloric acid (10 v/v%) and subsequently with distilled H_2O to remove the remaining reactants and acid. As-prepared product was then freeze-dried to yield 1.5 g of GO as brown powder.

Exfoliation of graphene oxide layers in water: In order to disperse and exfoliate GO layers into single sheets, as prepared bulk GO were immersed in 100 mL of DI water, and then the resulting mixture was sonicated for 5 h using a 100 W sonicator. Unreacted graphite flakes and GO sheets were removed by centrifuging the sonicated solution at 6000 rpm for 60 min.

Fabrication of GO film on AAO: For the fabrication of a GO film with a few nanometer thickness on AAO substrate, the dispersed GO solution (1.5 mL, 0.025 mg ml^{-1}) was slowly vacuum-filtered using a porous AAO film.

HKUST-1 film growth: Thermal seeding and secondary growth of the HKUST-1 film was conducted by the methods reported in the literature.[20] For the preparation of seed solution, $Cu(NO_3)_2.3H_2O$ (2.63 g, 10.9 mmol) and TMA (1.26 g, 6 mmol) were dissolved in 35 mL of DI water and EtOH, respectively. After mixing them under vigorous stirring for 15 min at room temperature, the solution temperature was raised to 120ºC and kept for 6 h. As prepared seed solution was dropped on a pre-heated GO/AAO substrate at 200ºC. The seeded substrate was sonicated for 1 min in EtOH to remove any physisorbed MOF crystals. For the secondary growth, $Cu(NO_3)_2.3H_2O$ (3.50 g, 14.5 mmol) and TMA (1.68 g, 8 mmol) were dissolved in 95 mL of water and EtOH, respectively and mixed while stirring for 10 min. The seeded substrate and solution were placed in a reactor and kept at 120ºC for 6 h. After the completion of the reaction, the reactor was slowly cooled down to the room temperature and the membrane was collected. The as-synthesized membrane was washed with EtOH (50 mL) and dried in 80ºC oven for 12 h.

2. Characterization

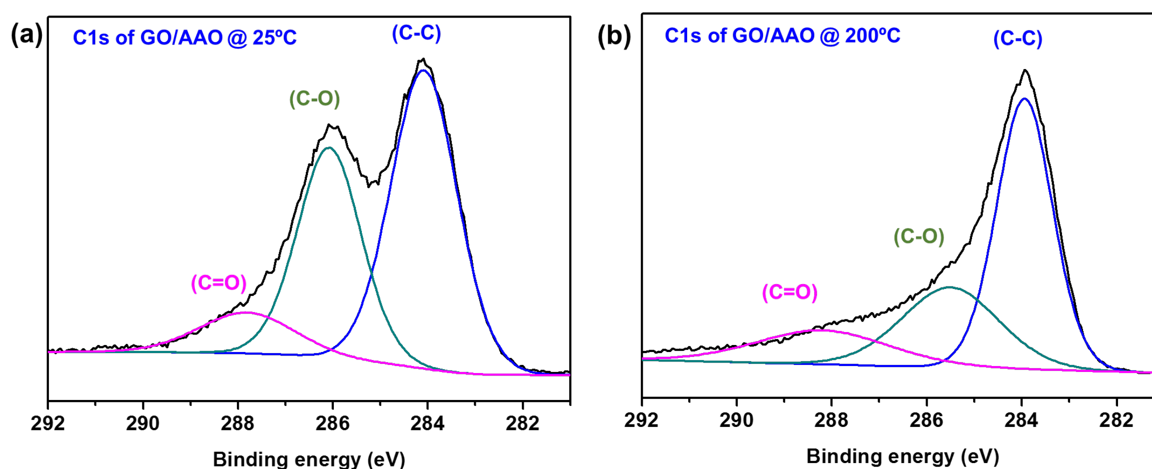

Figure S1. C1s X-ray photoelectron spectra of GO/AAO substrate (a) before and (b) after heating at 200ºC.

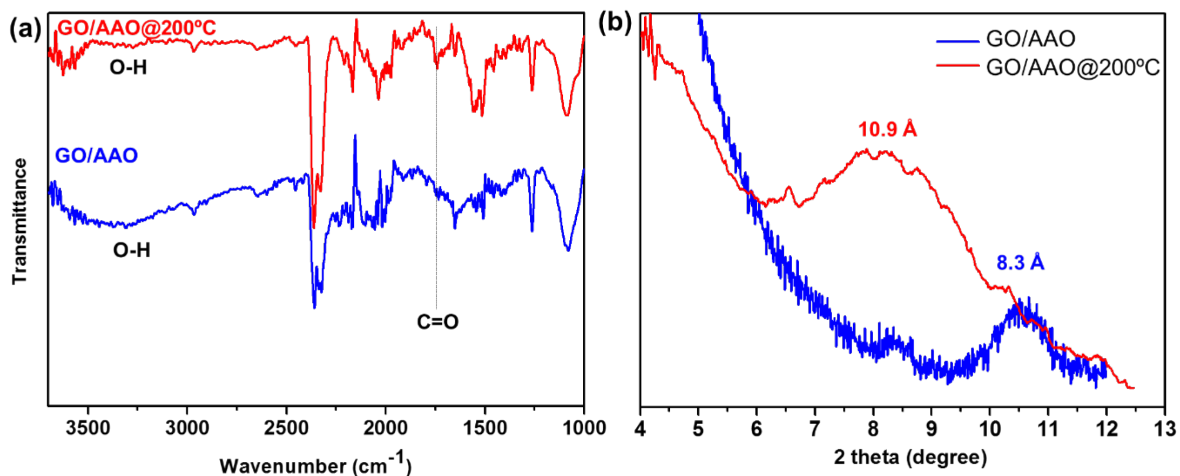

Figure S2. (a) FT-IR and (b) XRD spectra of GO/AAO substrate before (blue) and after heating at 200ºC (red).

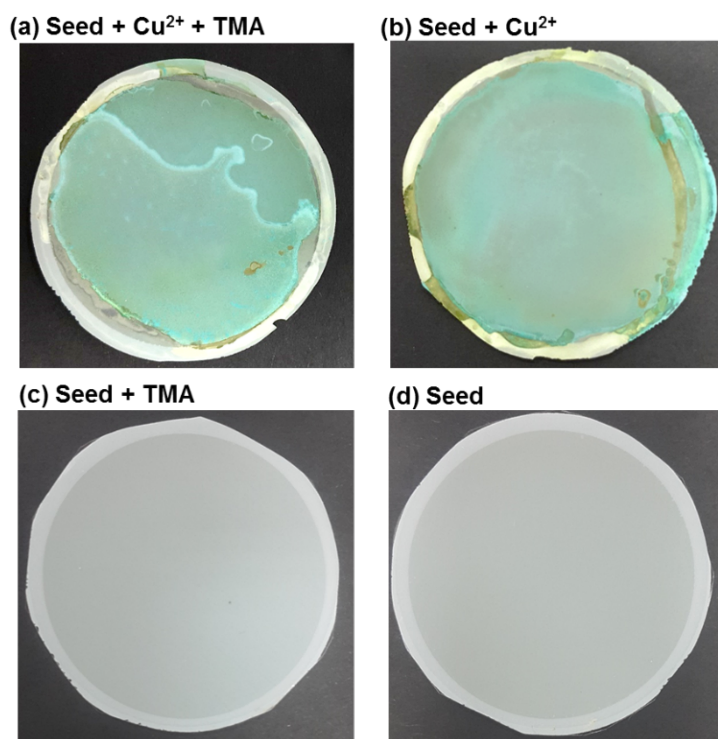

Figure S3. Digital images of GO/AAO substrate seeded with the mixture of EtOH and water containing (a) seed crystal + Cu^{2+}+ TMA, (b) seed crystal + Cu^{2+}, (c) seed crystal + TMA and (d) seed crystal only.

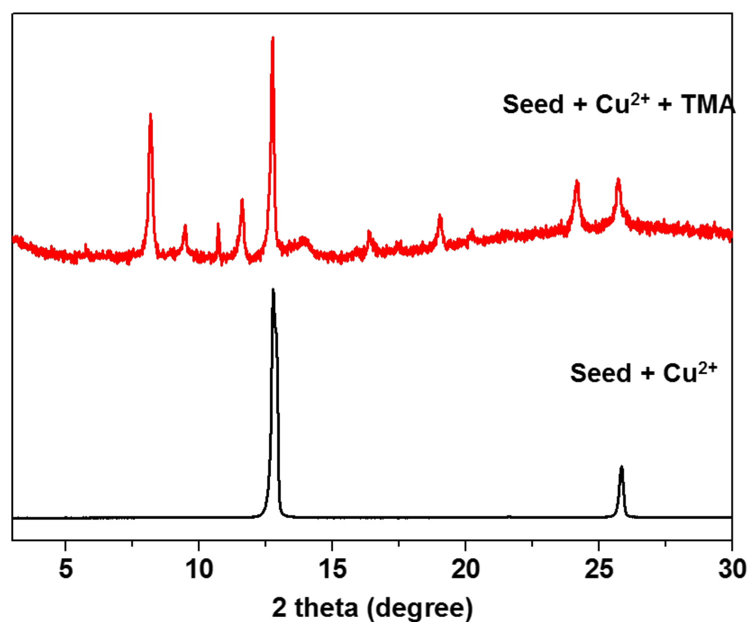

Figure S4. XRD patterns of GO/AAO substrate seeded with seed crystal + Cu^{2+} + TMA (red) and seed crystal + Cu^{2+} (black) in a mixture of ethanol and water.

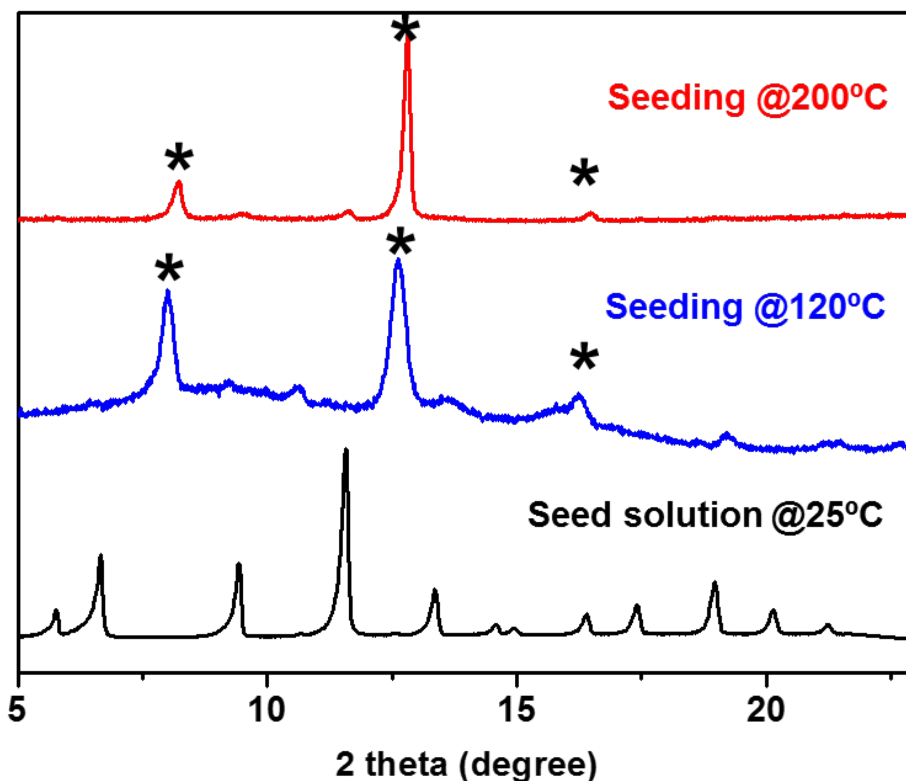

Figure S5. XRD analysis of seed crystals filtered from the seed solution (black), GO/AAO after seeding at 120 (blue) and 200 °C (red), respectively. Asterisks indicate diffraction peaks from the new rod-like crystalline phase.

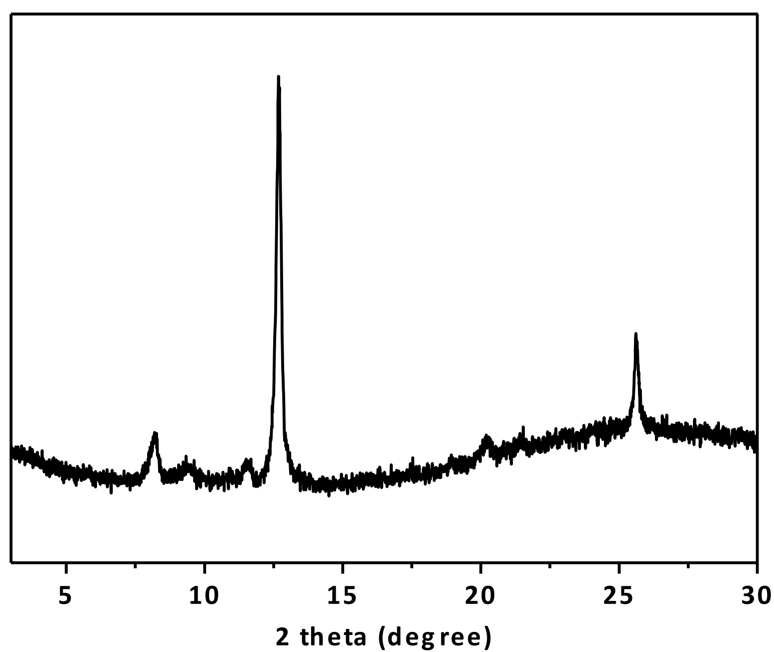

Figure S6. XRD analysis for GO/AAO after seeding with mixture of HKUST-1 precursors at 200ºC.

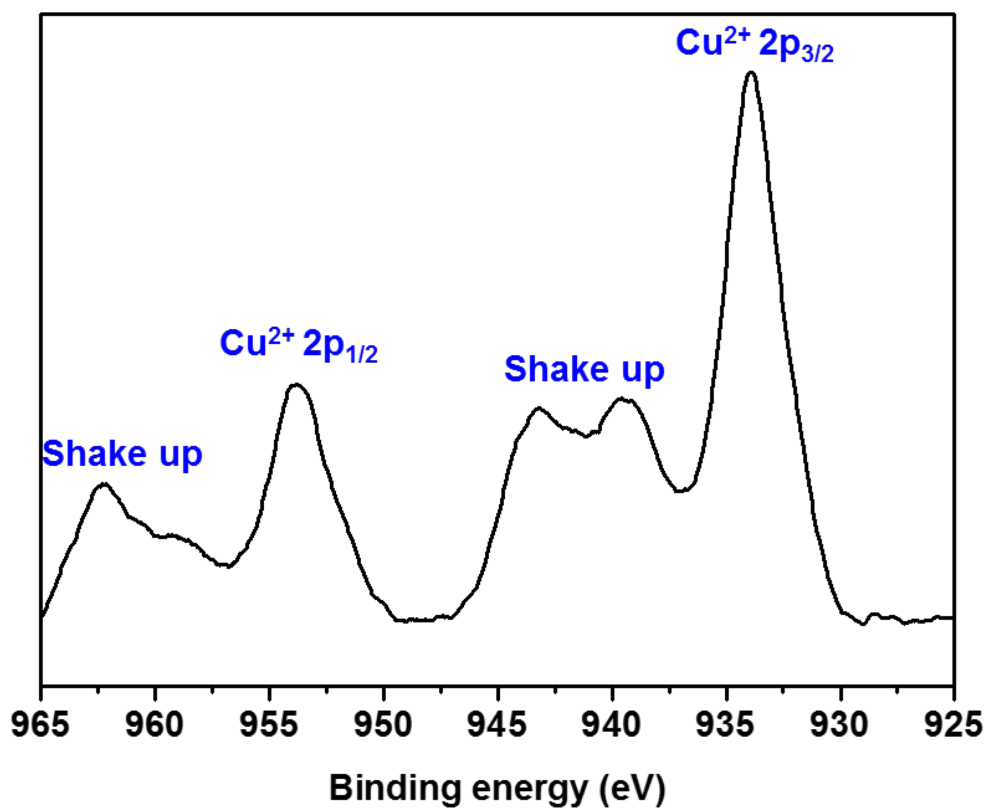

Figure S7. Cu 2p XPS spectrum of seeded GO/AAO.

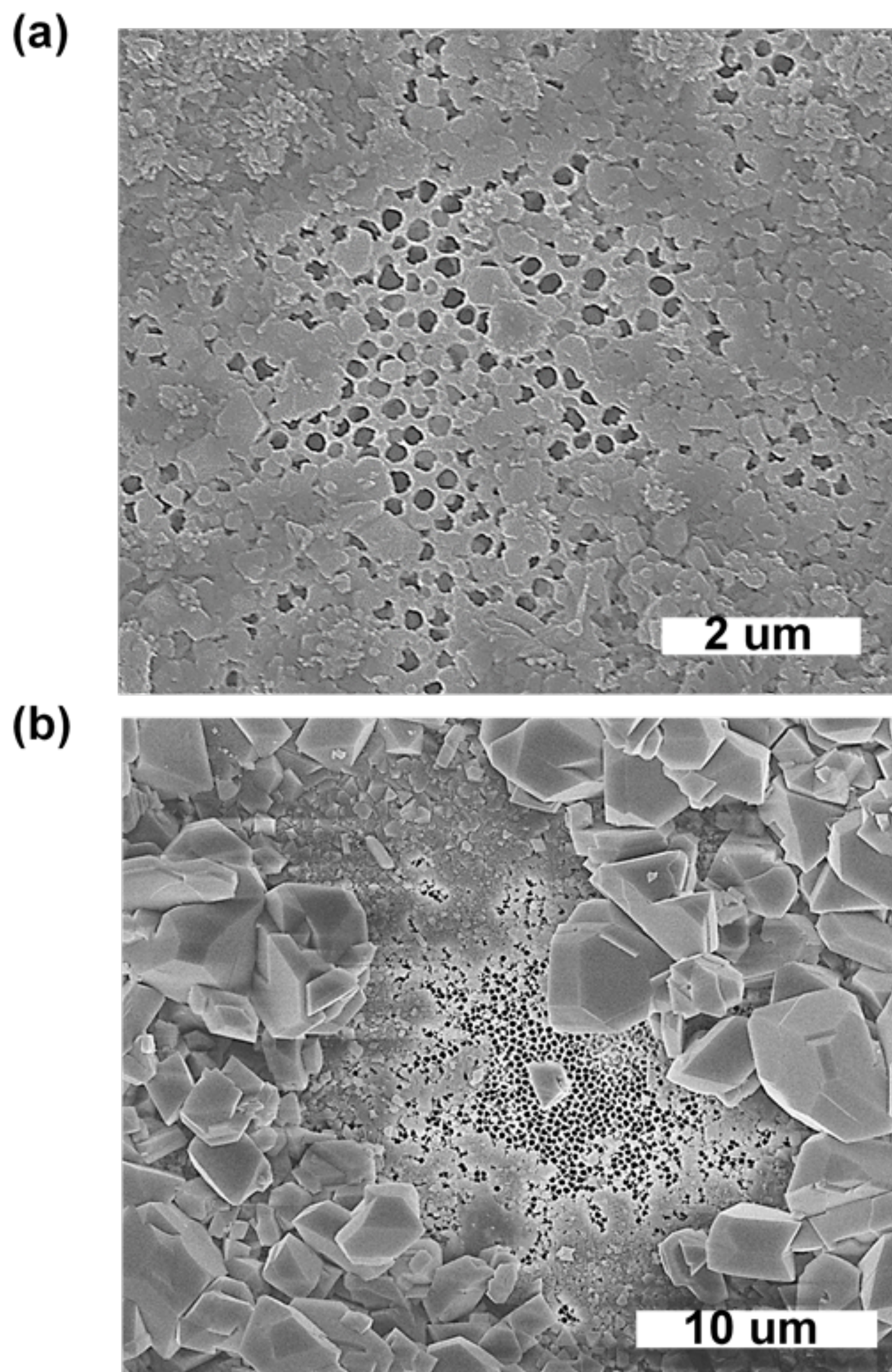

Figure S8. Digital images of (a) seeded GO/AAO substrate with a GO-free region and (b) after hydrothermal reaction. Black-colored holes are the pores of AAO film.

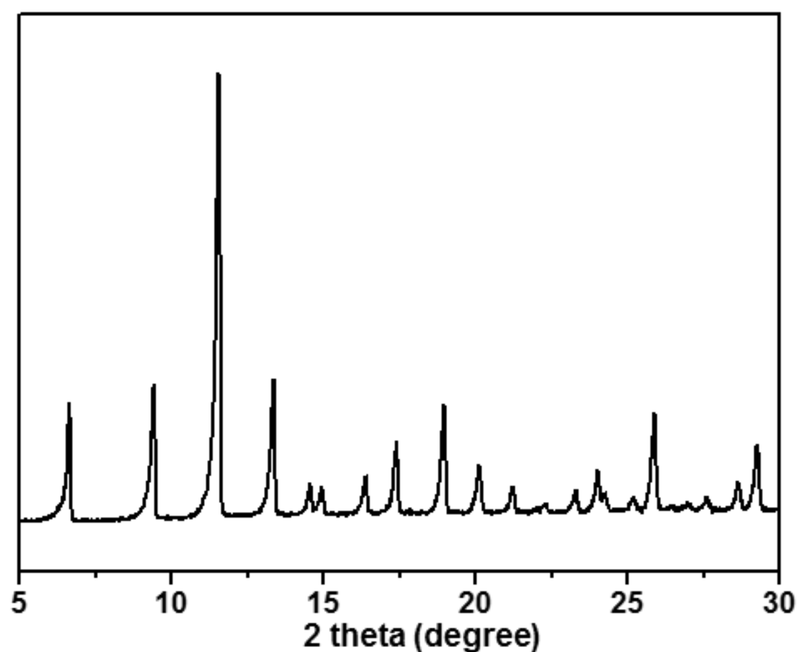

Figure S9. XRD spectrum of HKUST-1 as a bulk powder.

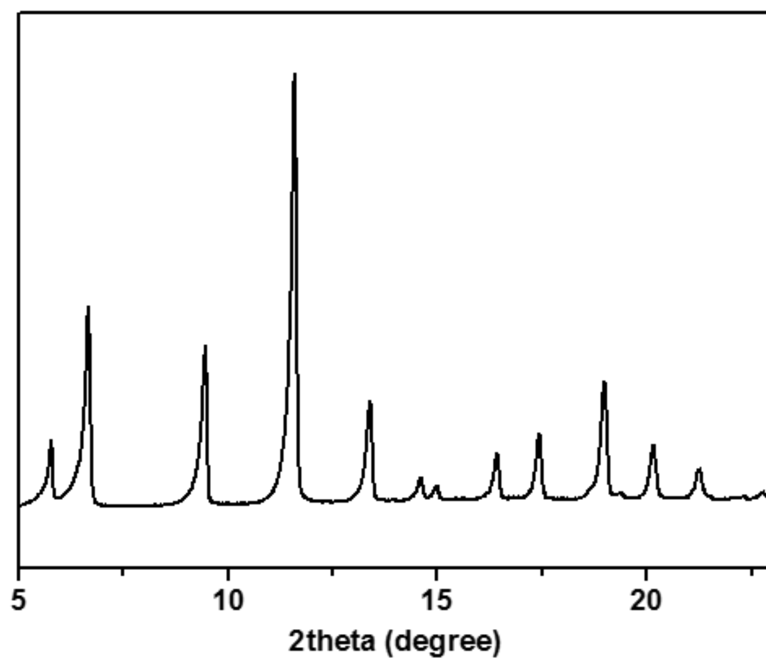

Figure S10. XRD spectrum of HKUST-1 powder precipitated in the reactor during hydrothermal reaction of GO/AAO.

3. References

[S1] W. Hummers, R. offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.