

Supporting Information for

Facile Growth of Single-Crystal Pattern: A Case Study of HKUST-1

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Materials and Methods

1. Materials

Methanol (99.9%), Ethanol (99.9%), Dimethyl sulfoxide (DMSO, 99.9%) and Dimethylformamide (DMF, anhydrous, 99.8%), 16-mercaptohexadecanoic acid (MHA, 90%), 11-mercapto-1-undecanol (MUA, 97%), 1H,1H,2H,2H-perfluorodecanethiol (97%), 1,3,5-benzenetricarboxylate (H_3btc , 97%), Copper(II) nitrate hemi(pentahydrate) (ACS reagent 98%) were all purchased from Sigma-aldrich and used as received. Sylgard 184 Polydimethylsiloxane(PDMS) was purchased from Dow Corning Chemicals.

2. Patterned Self-assembled Monolayers (SAMs) on gold substrate

Substrates were prepared by evaporating Au (50 nm) on a Si (100) wafer primed with 5 nm of Ti as an adhesion layer. Gold substrates were cut into 1x1cm pieces and cleaned in a piranha (3:1 ratio of H_2SO_4 and 30% H_2O_2) solution for 5 minutes, washed with deionized water, and dried with N_2 . The gold substrates with patterned SAMs were fabricated by first micro-contacted printing (μ CP) using PDMS stamps inked with desired solution in methanol followed by soaked faced-down in corresponding SAM solutions for at least 10 hours and no more than 24 hours. Substrates were washed in the respective SAM-prepared solvent, rinsed with ethanol, and dried with nitrogen.

3. Formation of seeds pattern on gold substrate

A $COOH/CF_3$ -terminated or OH/CF_3 -termianted SAMs selectively patterned on gold substrate was immersed in a fresh prepared mixture of $Cu(NO_3)_2 \cdot 2.5H_2O$ (100 mM, in EtOH) and H_3btc (50 mM, in EtOH) for 10 seconds. The sample was taken out and dried with N_2 , then washed with ethanol and dried with N_2 again. The precipitates in ethanolic solution were collect after 2 h and washed with ethanol and dried in oven at 80 °C for overnight.

4. Solution growth of HKUST-1 crystal pattern

The seeded substrate was then placed downside up in a glass bottle with solution obtained by mixing of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.468 g) and H_3btc (0.232 g) in pure dimethyl sulfoxide (DMSO, 2 g). 20 mL absolutely pure ethanol was added slowly on the top of the DMSO solution. The bottle was capped and hold for 12 to 48 h before the substrate was taken out, washed by ethanol and dried with N_2 for further characterizations. The precipitates were collected and washed with ethanol and dried in oven at 80°C for overnight.

5. Investigation of the seeds formation mechanism

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and H_3btc were dissolved in methanol, DMF and DMSO separately to form desire concentrated solution ($\text{Cu}(\text{NO}_3)_2$ 100mM and H_3btc 50 mM). The patterned gold substrate was immersed in a fresh prepared mixture of $\text{Cu}(\text{NO}_3)_2$ and H_3btc solution for 10 seconds. The sample was taken out and dried with N_2 , then washed with ethanol and dried with N_2 again.

For the seeds formed in ethanol/ H_2O mixture, $\text{Cu}(\text{NO}_3)_2$ was dissolved in DI water to form 100 mM solution. H_3btc was dissolved in ethanol to form 50 mM solution. The patterned gold substrate was immersed in a fresh prepared mixture of $\text{Cu}(\text{NO}_3)_2$ and H_3btc solution for 10 seconds. The sample was taken out and dried with N_2 , then washed with ethanol and dried with N_2 again.

6. Synthesis HKUST-1 films on SAMs gold surface

In a typical procedure, 5 mL $\text{Cu}(\text{NO}_3)_2$ (100mM, in ethanol) and 5 mL H_3btc (50mM, in ethanol) was mixed and the SAM-functionalized gold substrate was placed inside. The substrate was taken out after 1 h and washed with ethanol, then dried with N_2 for further characterizations.

7. Solution growth of ZIF-8 crystal patterns

The $-\text{COOH}/\text{CF}_3$ patterned substrate was immersed in a fresh prepared mixture of 2-methylimidazole (50 mM, in EtOH) and $\text{Zn}(\text{Ac})_2$ (25 mM, in EtOH) for 10 seconds. The sample was taken out and dried with N_2 , then washed with ethanol and dried with N_2 again. The seeded substrate was placed downside up in a glass bottle with 30 mL 2-methylimidazole solution (30 mM in H_2O). 1 mL $\text{Zn}(\text{Ac})_2$ solution (50 mM in ethanol) was added slowly on the top of the aqueous solution. The bottle was capped and hold for 12 h before the substrate was taken out, washed by ethanol and dried with N_2 for further characterizations.

8. Characterizations

The optical characterizations were carried out using Nikon 3100 optical microscope. The sample morphologies were characterized by using JSM 6360 scanning electron microscope and JSM 6340F field emission scanning electron microscope equipped with oxford EDS system. X-ray diffraction (XRD) measurements of powders and patterns were performed using a Schmaz Thin film ($\text{Cu-K}\alpha 1 = 1.5406 \text{ \AA}$; $\text{Cu-K}\alpha 2 = 1.5444 \text{ \AA}$) in $\theta/2\theta$ geometry. The samples were measured between 5° and 35° , with a step-size of 0.02° and a scan-speed of $0.3^\circ/\text{min}$.

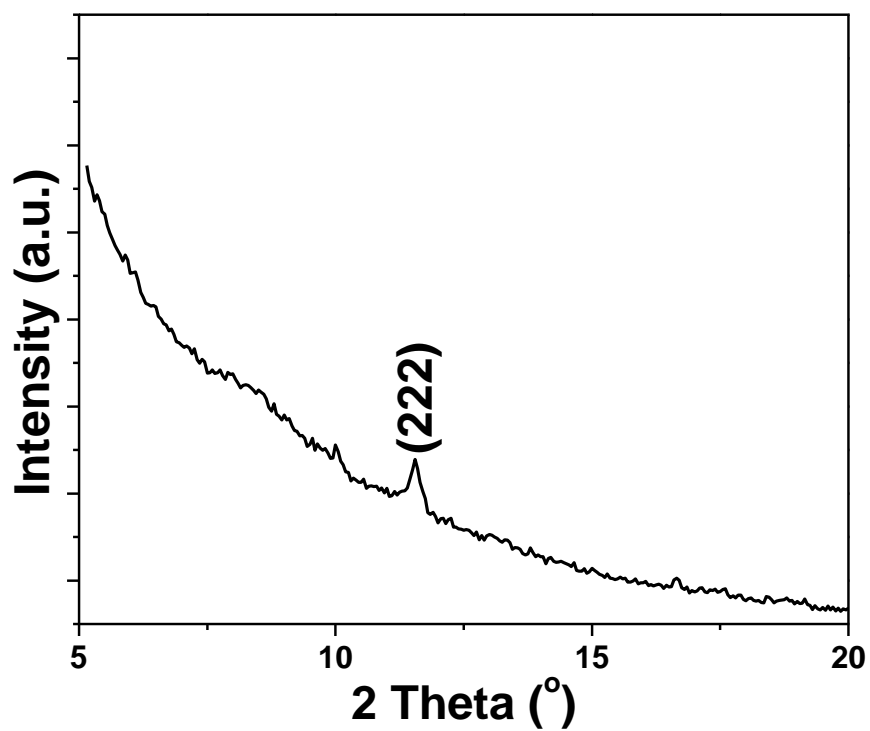


Figure S1. XRD pattern of the HKUST-1 seeds formed on SAM surface by vaporizing of the ethanolic solvent. It shows that the seeds are highly [111] oriented.

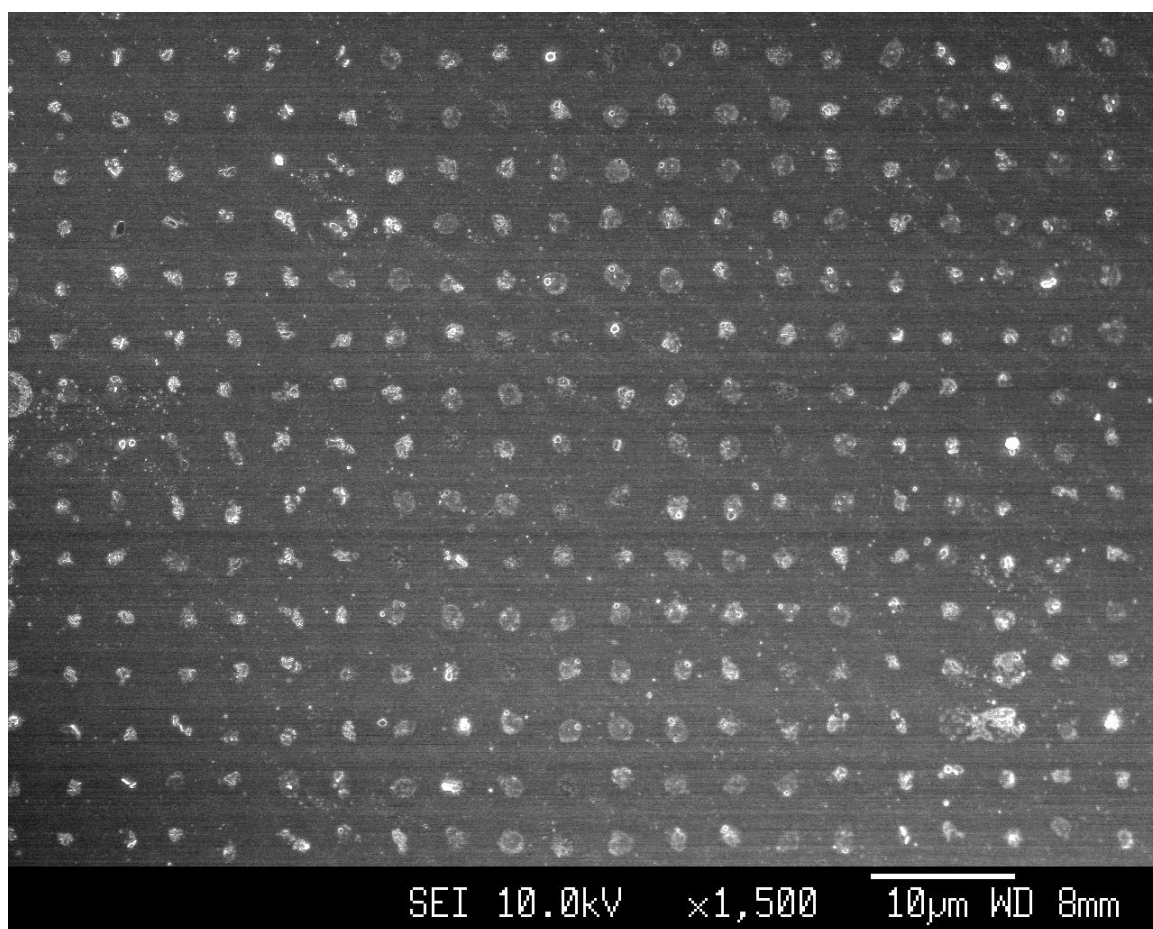


Figure S2. SEM image of the multi-seeds formed on SAM-functionalized gold surface by vaporizing DMF solvent.

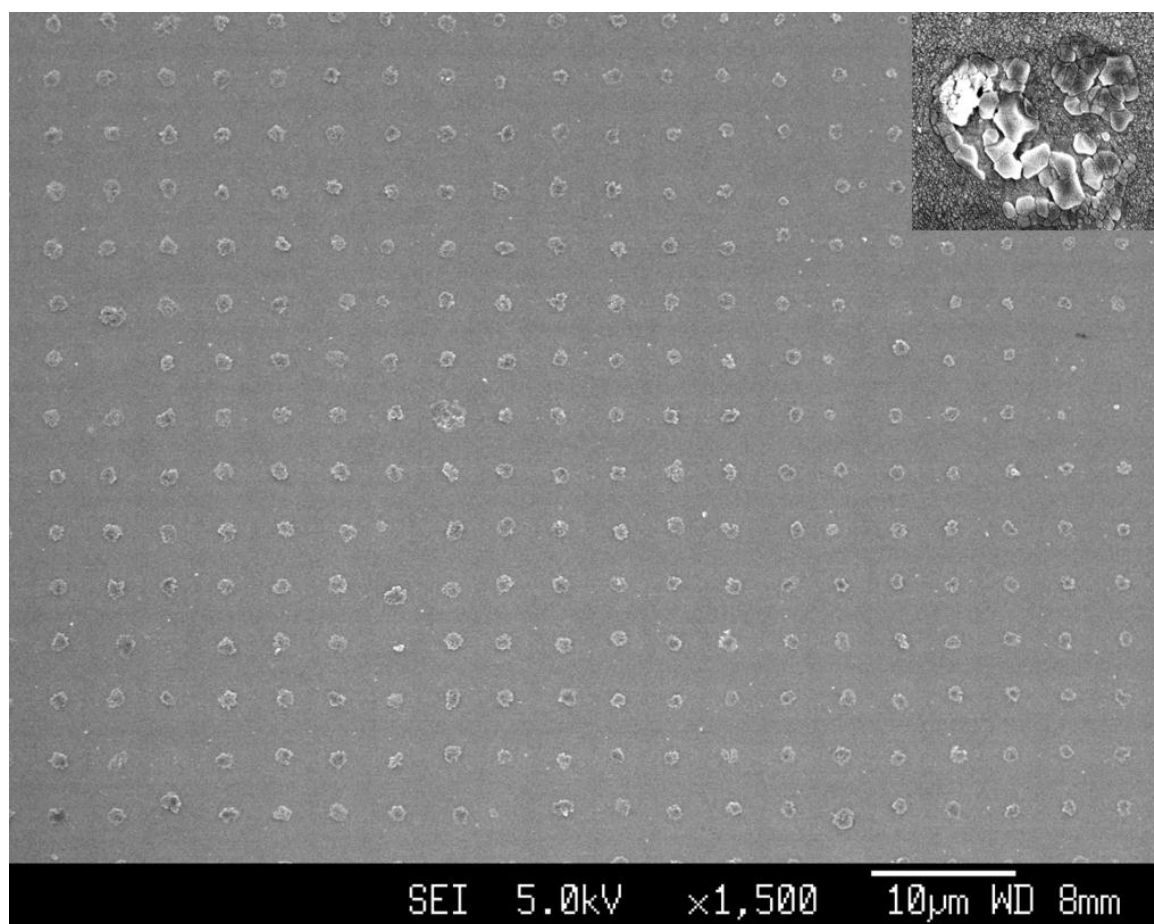


Figure S3. SEM image of the HKUST-1 pattern formed on SAM-functionalized gold substrate by directly immersing the sample into ethanolic precursor. The inset shows the polycrystalline HKUST-1 dot pattern.

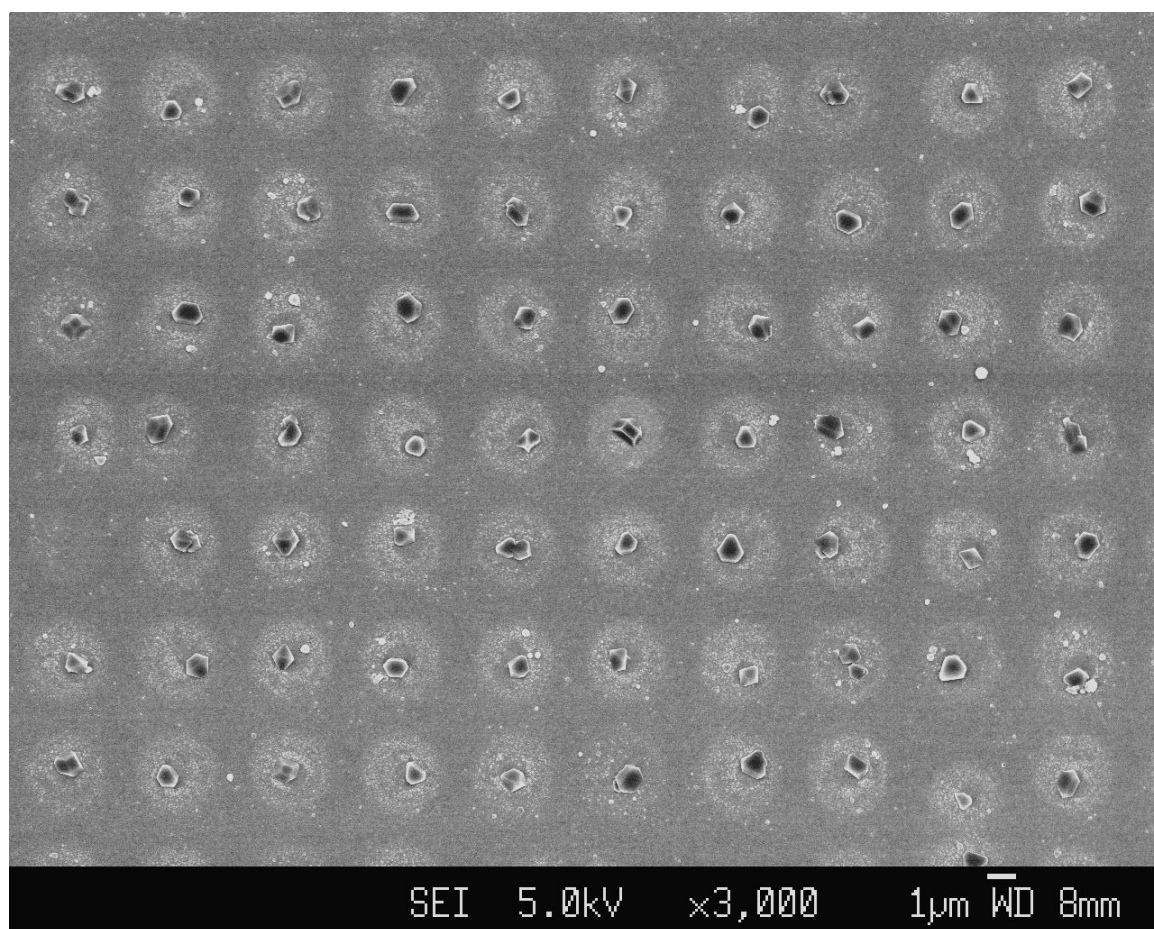


Figure S4. SEM image of the HKUST-1 pattern grew for 48 h. Besides the large crystals ($\sim 1\ \mu\text{m}$), small crystals were start to grown on the pattern surface.

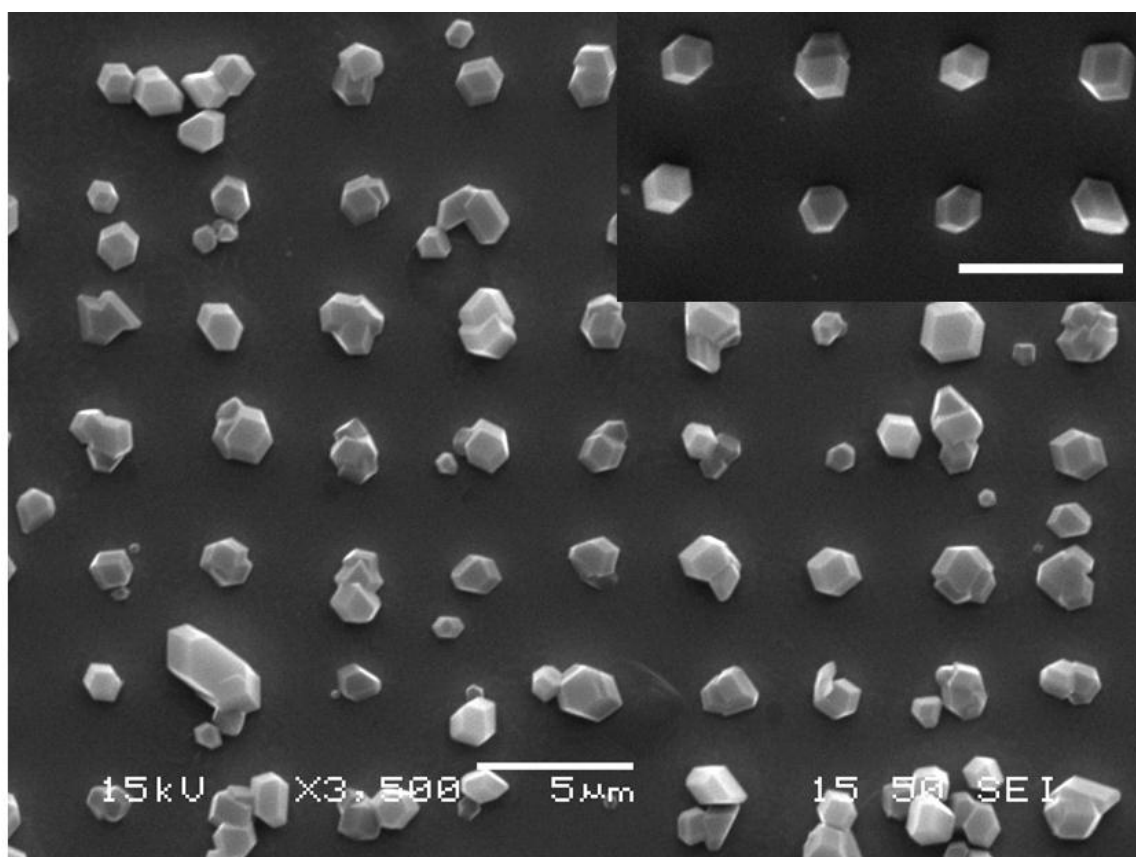


Figure S5. The crystal pattern of ZIF-8 crystals grown on -COOH/CF₃ functionalized gold substrate. Single-crystal pattern of ZIF-8 were obtained in some regions as shown in the inset. The scale bar in inset image is 5 μm.