Supporting information

Solvent-free Vacuum Growth of Oriented HKUST-1 Thin Films

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Figure S1. The O1s XPS spectra for 5 cycled HKUST-1 thin films grown with (a) 0.5 ML Cu , (b) 1.0 ML Cu, and (c) 1.5 ML Cu depositions in each cycle. There is no component for copper oxides in all spectra, which is supposed to be shown at 530.5 - 529.5 eV.



Figure S2. (a) XRD patterns for the 5 layers of unannealed H_3BTC (blue, 5 layers mean 5 times of H_3BTC deposition for 3 minutes in each), the 5 cycles of HKUST-1 films (gray), and the 5 layers of annealed H_3BTC at 343 K for 15 mins (red). (b) The Cu2p XPS spectra for 5 layers of unannealed (red) and annealed (black) H_3BTC



Figure S3. Photographs of blank $SiO_2/Si(100)$ substrate, 5 layers of annealed H₃BTC, and 5 layers of unannealed H₃BTC.



Figure S4. The O1s XPS spectra for 5 cycled HKUST-1 thin films (1.0 ML Cu deposited in each cycle) grown with back-filled O_2 at (a) 2.5 x 10⁻⁵ Torr and (b) 5.0 x 10⁻⁵ Torr. There is no component for copper oxides in both spectra, which is typically located at 530.5 ~ 529.5 eV.



Figure S5. Photographs of 2, 5, and 10 cycles of HKUST-1 films



2θ (degrees) **Figure S6.** XRD of 2, 5, and 10 cycles of HKUST-1 films.

(a) 2 cycles of HKUST-1



Figure S7. AFM images of (a) 2 cycles, (b) 5 cycles, and (c) 10 cycles of HKUST-1 thin films. (I) and (II) show profiles for thickness, and III and IV describe top and lateral views of each sample respectively.



Figure S8. Temperature programmed desorption (TPD) of H_2O (m/z⁺= 18) adsorbed on the 5 cycled HKUST-1 film at 120 K (red) and 200 K (blue) by 2.0 x 10⁻⁶ Torr of H_2O for 30 mins. We also conducted the H_2O -TPD tests for the tantalum (Ta) sample holder with the same amount of H_2O exposures at 120 K (black) and 200 K (gray).



Figure S9. XRD patterns of before (black) and after (red) H_2O adsorption & desorption tests on the 5 cycled HKUST-1 thin film.