Successful implementation of the stepwise layer-by-layer growth of MOF thin films on confined surfaces: Mesoporous silica foam as a first case study

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Experimental Procedures

Synthesis of the Mesoporous Silica Foam

The mesoporous silica foam with ultra large pores was synthesized according to our previously reported method. In a typical synthesis, 3.0 g of neutral triblock co-polymer surfactant, Pluronic 123, was dissolved in a mixture of acetic acid (3.0 g), deionized (DI) water (52 g), and ammonium fluoride (0.3 g) at 40 °C. After stirring for 2 h, a solution of sodium silicate (2.35 g) in water (40 g) was added and the resultant mixture was reacted under vigorous stirring for 5 min. Then, the mixture was kept under static condition for 24 h at 40 °C followed by aging at 70 °C overnight. The solid products were washed with DI water and collected by filtration and air-dried. The obtained white mixture was then calcined at 560°C for 6h to remove the surfactant template.

MOF Formation in the Presence of the Mesoporous Silica Foam

a- MOF formation using conventional solvothermal method

The silica foam (50 mg) was added to the reactant mixture as follows: 1,3,5-benzenetricarboxylic acid (H_3btc) (2.38 mmol) was mixed in 6 mL of a 1:1:1 mixture of DMF/EtOH/H_2O, $Cu(OAc)_2.5H_2O$ (4.31 mmol) was mixed with 12 mL of the same solvent, and the mixtures were combined with stirring. Triethylamine (0.5 mL) was added to the reaction mixture and stirred for 23 h.[1] The product was collected by filtration and washed twice with 25 mL of DMF and dried. In the case of ZIF-8, the foam was mixed in a freshly prepared methanolic solution of 2-methylimidazole (25 mM) and $Zn(NO_3)_2.6H_2O$ (25 mM) at room temperature for 30 minutes, then centrifuged and washed with methanol twice. This process was repeated 10 times in order to increase the thickness of the thin film following the same procedure used by Hupp, et al.[2]

b- MOF thin film using stepwise layer-by-layer (LBL) method

The reactants for the MOF synthesis were used as diluted ethanolic solutions of copper acetate pentahydrate ($Cu(OAc)_2.5H_2O$) (1 mM) and H_3btc (0.1 mM). The MOF thin films were fabricated by suspending the mesoporous silica foam first in 5 ml of the $Cu(OAc)_2$ ethanolic solution for 3 min. The foam was then separated through magnetic stirring, and then the silica foam was washed twice with pure absolute ethanol before suspending it in 5 ml of the H_3btc ethanolic solution for 5 min. The cycle was completed by washing the silica foam with pure absolute ethanol twice, as shown schematically in Figure S1. The thickness of the MOF thin film was controlled by the number of cycles used. In the case of the ZIF-8, the same growth procedure was used except that methanol was the solvent, $Zn(NO_3)_2$ (5 mM) was used as the metal ion source, and 2-methylimidazole (5 mM) was used as ligand.

Characterization

- Powder X-ray diffraction (PXRD) patterns of the silica foam and all obtained MOF thin films were recorded on a Panalytical X'pert PRO MPD X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm, 45 kV, 40 mA).

- Fourier transform infrared (FT-IR) spectra were collected in the solid state on a Nicolet 6700 FT-IR spectrometer with 8 cm^{-1} resolution at room temperature.

- Ultraviolet-visible spectra were collected using a PerkinElmer Lambda 950 UV/vis spectrometer.

- TEM analysis was conducted by a FEI Titan 300 transmission electron microscope, operated at 120kV. TEM samples were prepared by placing a droplet of ethanol-diluted carbon foam dispersion on a carbon coated microscope grid and dried in air.

- SEM was performed using an FEI Quanta 600 field emission scanning electron microscope (accelerating voltage: 30 kV). Low pressure gas sorption studies: Gas sorption measurements were performed on a fully automated micropore gas analyser, Autosorb-1C (Quantachrome Instruments), at relative pressures up to 1 atm. The cryogenic temperatures were controlled using a liquid nitrogen bath at 77 K. The apparent surface areas of silica foam and MOF-coated silica foam were determined from the nitrogen adsorption isotherms by applying the Brunauer-Emmett-Teller (BET) model using adsorption points in the relative pressure (P/P_0) range of 0.015 to 0.046. Pore size analyses were performed using a cylindrical NLDFT pore model system by assuming an oxidic (zeolitic) surface. High pressure gas sorption studies: Adsorption equilibrium measurements of CO_2 and C_3H_6 were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flowmeters and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere, and is able to perform adsorption measurements across a wide pressure range, i.e., from 0 to 20 MPa. The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied. The evacuated adsorbent is then exposed to a continuous gas flow (typically 50 ml/min) at a constant temperature. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount (Ω). Correction for the buoyancy effect is required to determine the excess adsorbed amount using equation 1, where $V_{adsorbent}$ and V_{ss} refer to the volume of the adsorbent and the volume of the suspension system, respectively. These volumes are determined using the helium isotherm method by assuming that helium penetrates in all open pores of the materials without being adsorbed. The density of the gas is determined experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. Simultaneous measurement of adsorption capacity and gas phase density, as a function of pressure and temperature, is therefore possible. The excess uptake is the only experimentally accessible quantity and there is no reliable experimental method to determine the absolute uptake. For this reason, only the excess amounts are considered in this work.

$$\Omega = m_{excess} - \rho_{gas}(V_{adsorbent} + V_{ss}) \tag{1}$$

The pressure is measured using two Drucks high-pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to each adsorption experiment, about 100 mg to 300 mg of sample is outgassed at 423 K at a residual pressure 10-6 mbar. The temperature during adsorption measurements is held constant by using a circulating bath.

References

[1] D. J. Tranchemontagne, J. R. Hunt, O. M. Yaghi, *Tetrahedron* **2008**, 64, 8553-8557.

[2] G. Lu, J. T. Hupp, *J. Am. Chem. Soc.* **2010**, 132, 7832-7833.

Fig. S1 Schematic representation of the stepwise LBL method used to grow MOF thin films on the mesoporous silica foam. The metal solution was added to the silica foam (1) and mixed for 3 minutes (2). The silica foam is then separated using a centrifuge (3), where the excess solvent is removed and the foam is washed with the pure solvent two times. The ligand solution is then added (4), mixed with the foam for 5 minutes (5), and the foam is separated using a centrifuge (6) to remove the excess solvent, and the foam is washed with the pure solvent two times to complete the cycle.

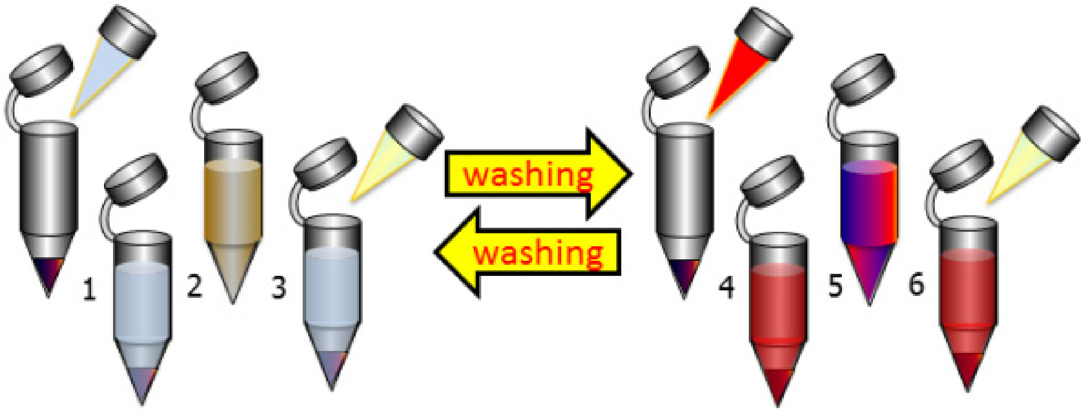

Fig. S2 PXRD pattern of HKUST-1 grown using the solvothermal method on mesoporous silica foam.

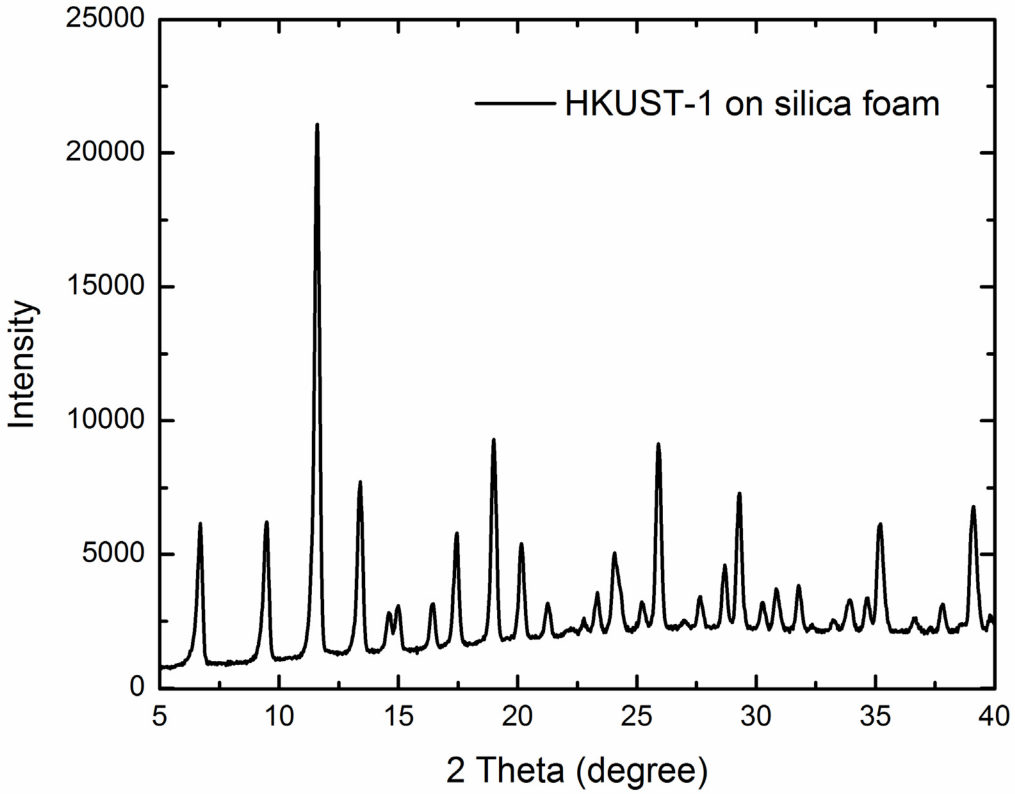

Fig. S3 PXRD pattern of the ZIF-8 grown using solvothermal process on mesoporous silica foam.

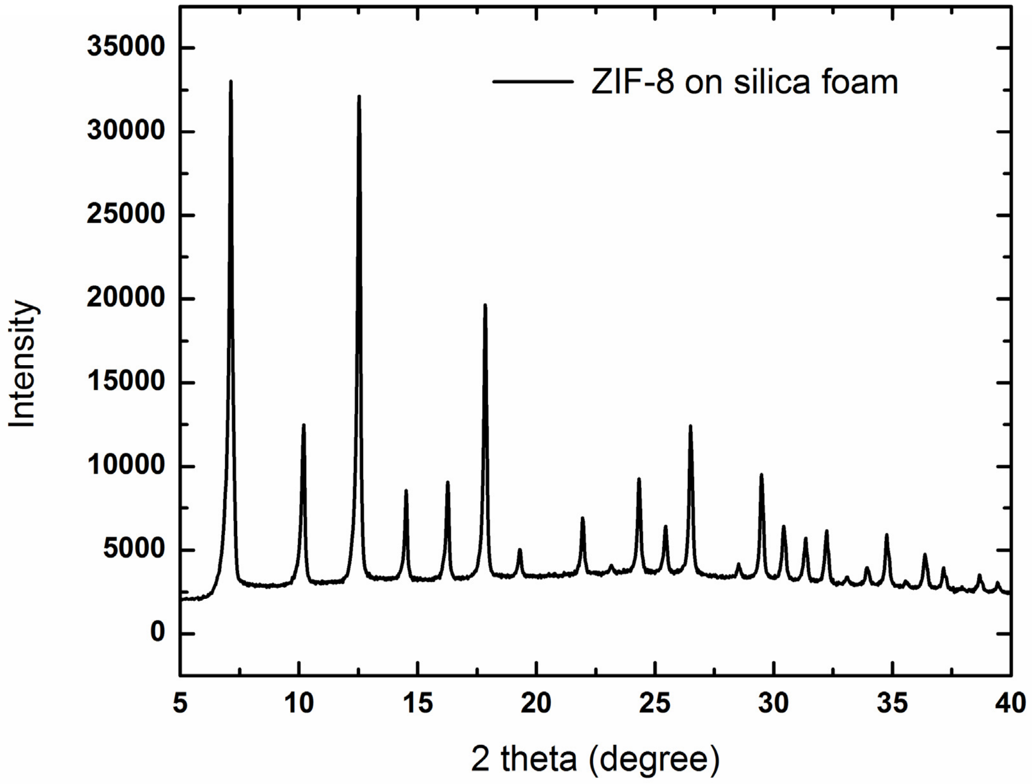

Fig. S4 Absorption spectra of silica foam (black) and HKUST-1 on silica foam after 15 deposition cycles using the LBL technique (red).

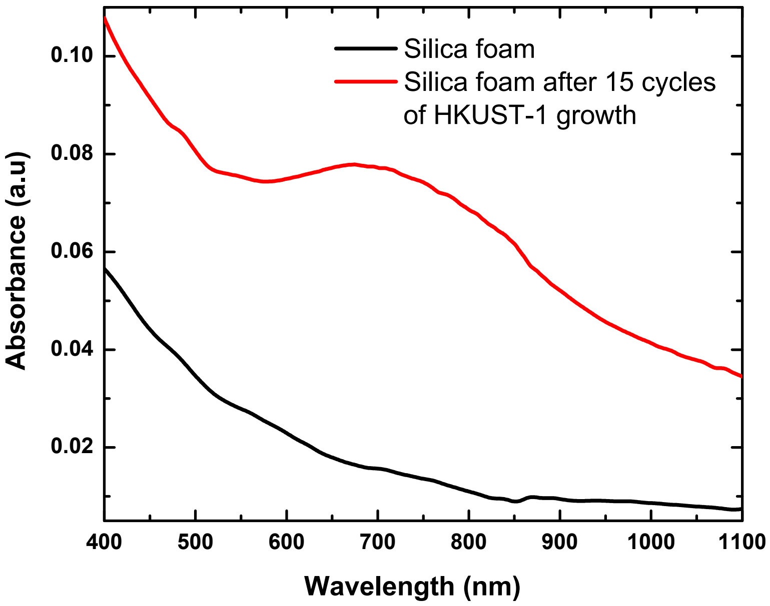

Fig. S5 Optical images of the silica foam in ethanol solution before and after the growth of the HKUST-1 MOF thin film after 30 cycles using the LBL method.

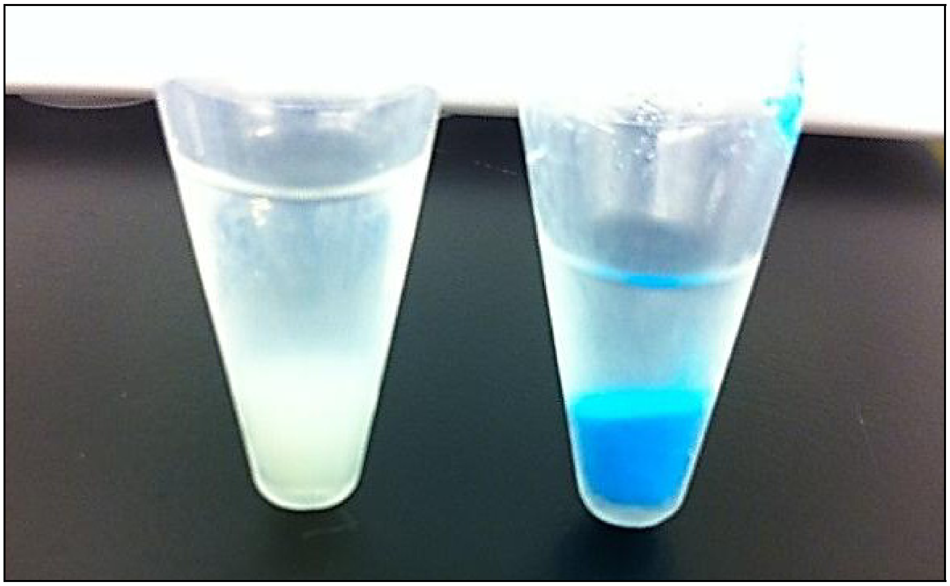

Fig. S6. FT-IR of silica foam bulk sample and after 30 cycles of HKUST-1 thin film growth using the LBL method.

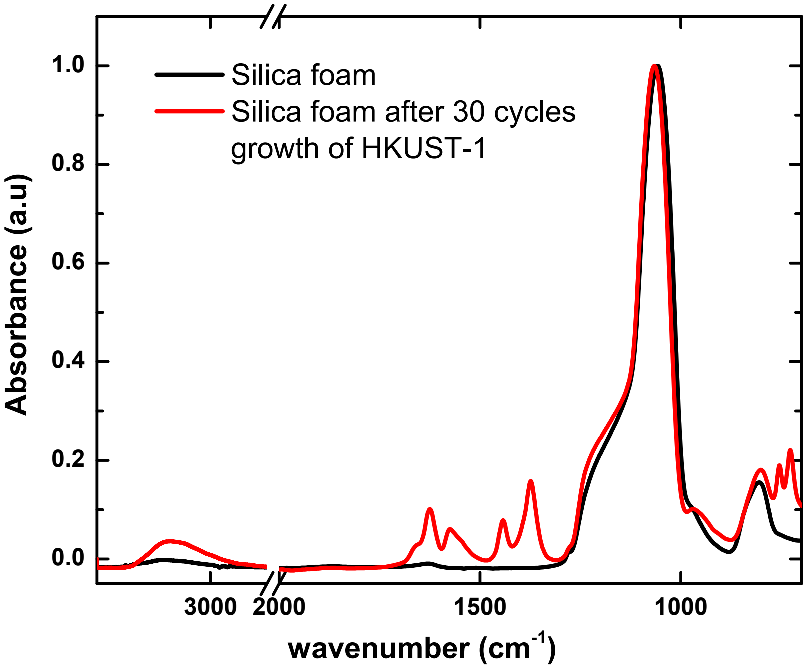

Fig. S7 TEM images of silica foam after growth of HKUST-1 MOF using the LBL method after (a) 5 cycles, (b) 10 cycles and (c) 15 cycles.

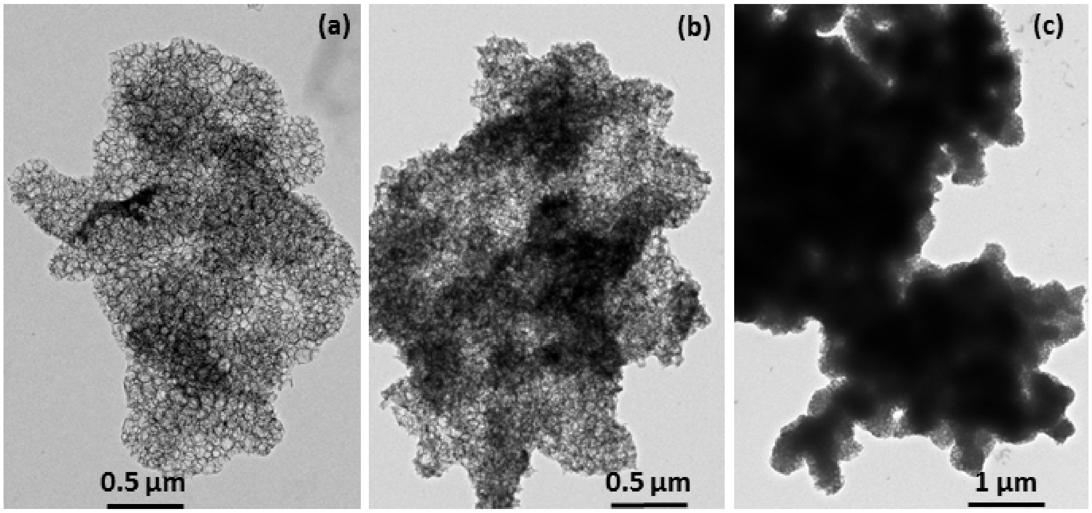

Fig. S8 FT-IR of silica foam bulk sample and after 5 cycles of growth of ZIF-8 thin film using the LBL method.

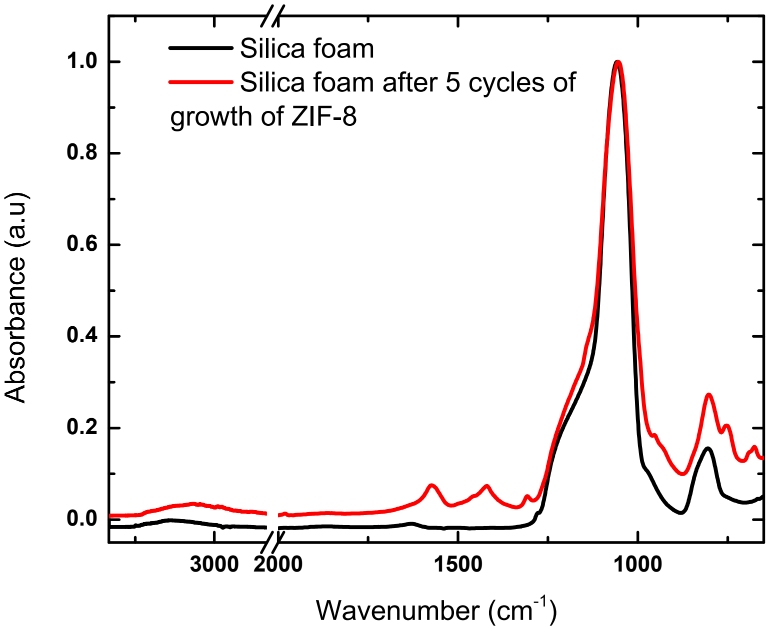

Fig. S9 N_2 sorption isotherms at 77 K for silica foam and HKUST-1 MOF grown on silica foam using the LBL method.

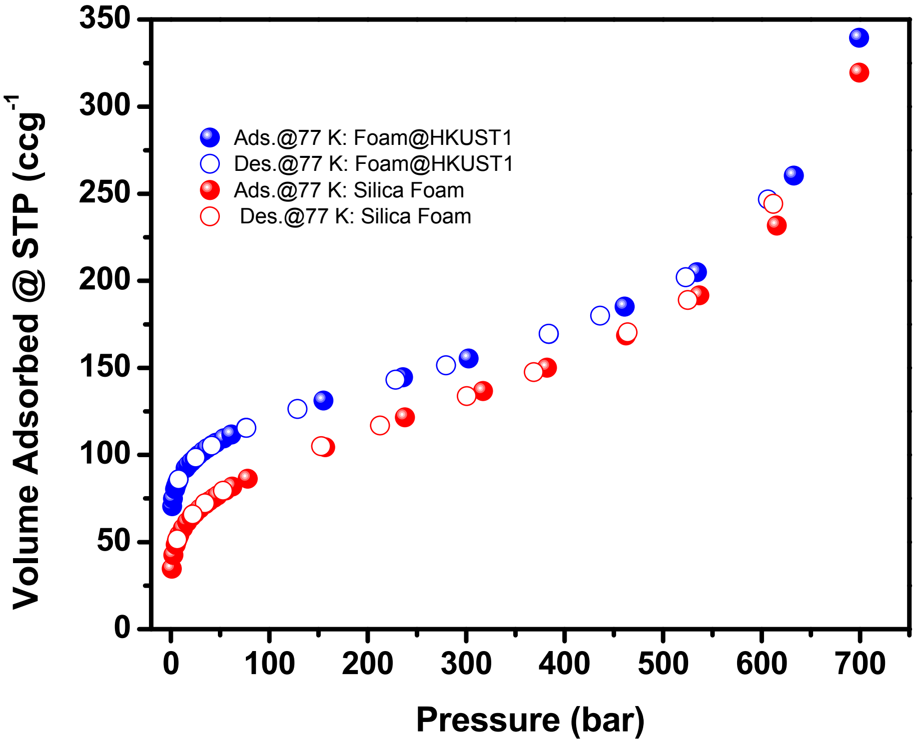

Fig. S10 Pore size distribution from N_2 sorption isotherms at 77 K for silica foam (right) and HKUST-1 MOF thin film grown on silica foam using the LBL method (left).

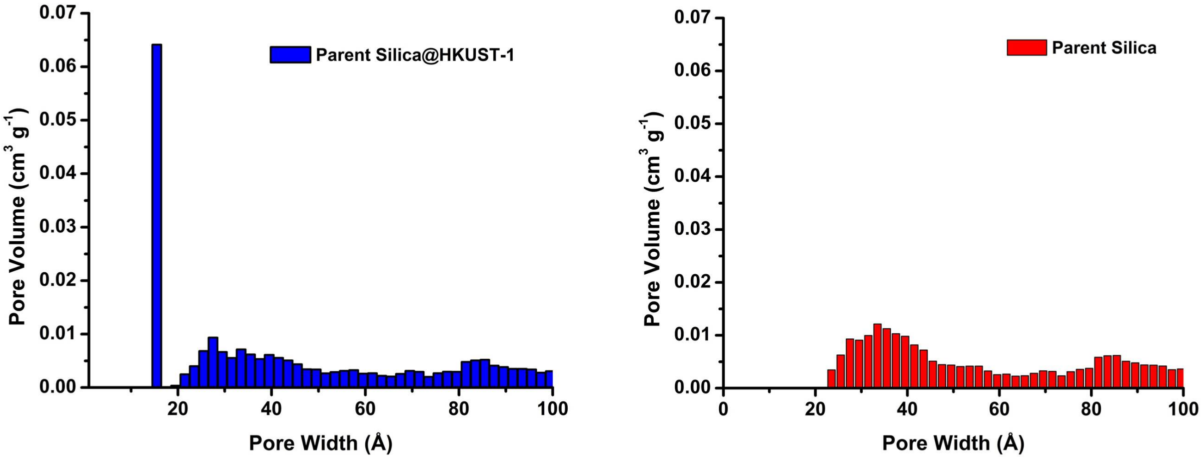

Fig. S11 C_3H_6 high pressure isotherms of silica foam and HKUST-1 MOF grown on silica foam using the LBL method.