# Supporting Information

## Confined Crystallization of HKUST-1 Metal-Organic Framework within Mesostructured Silica for Enhanced Structural Resistance Toward Water

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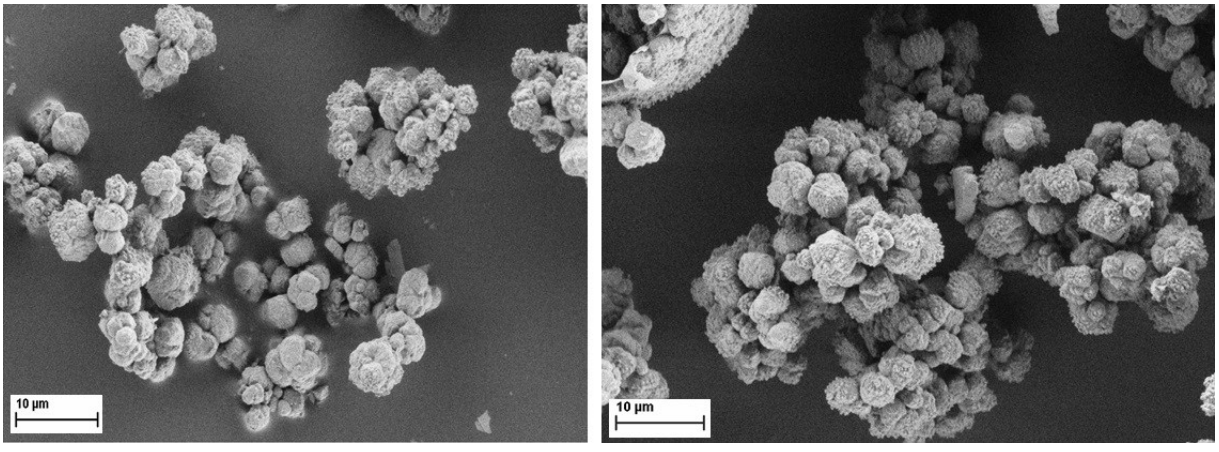


**Figure S1:** Typical SEM micrographs of $NH_2$-FDU-12 matrix (left) and FDU-12/HKUST-1 composite (right). Crystallization of HKUST-1 within FDU-12 does not cause any significant morphological changes on the matrix and there are no individual crystals of HKUST-1 visible as a separate phase.

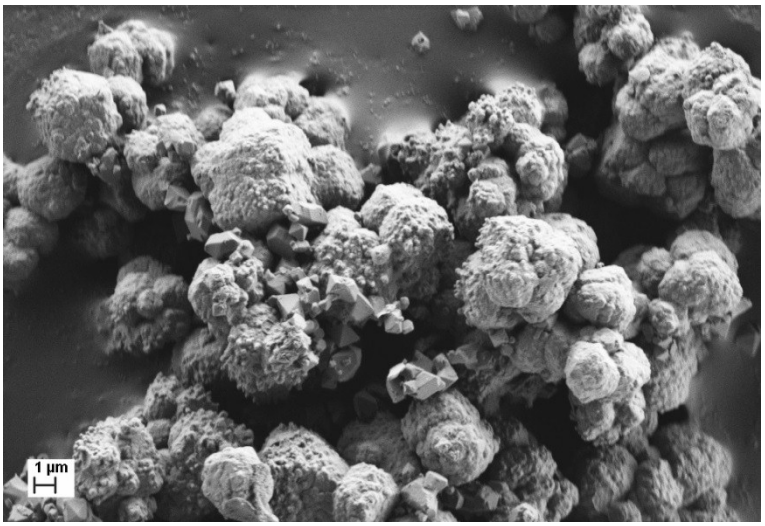


**Figure S2**: SEM micrograph of HKUST1-FDU12 with separate octahedral crystals of HKUST-1 with the size of approximately 1 μm crystallizing after the grafting with the 0.1 M $Cu^{2+}$ solution.

**Calculations of HKUST-1 occupancy within $NH_2$-FDU-12 matrix**

The occupancy of the mesopores with HKUST-1 material can be expressed as

$$\frac{W_1}{W_2},$$

where $W_1$ represents measured contribution of HKUST-1 within the FDU-12 matrix, whereas $W_2$ defines the theoretical content of HKUST-1 at fully occupied FDU-12 mesopores with MOF material. $W_1$ is further determined by

$$\frac{W_{Cu-exp}}{W_{Cu-HKUST1}},$$

where $W_{Cu\text{-}exp}$ represents Cu weight content in the composite determined by EDS analysis and $W_{Cu\text{-}HKUST1}$ theoretical Cu weight content within the bulk HKUST-1, considering the chemical formula $Cu_3(BTC)_2.3H_2O$. On the other hand $W_2$ is defined by the expression

$$\frac{\rho_{HKUST1}.V_{mes}}{1+\ \rho_{HKUST1}.V_{mes}}.$$

$\rho_{HKUST1}$ is calculated crystal density of the bulk HKUST-1(1.367 g/cm$^3$) whereas $V_{me}$ represents the mesopore volume of $NH_2$-FDU-12 matrix determined from $N_2$ sorption isotherm analysis using BJH method (described later in the manuscript). Considering the above explained expressions, the occupancy of the mesopores with HKUST-1 material can be calculated using formula

$$\frac{W_{Cu-exp}.Mr_{HKUST1}.(1+\rho_{HKUST1}.V_{mes})}{3Mr_{Cu}.\rho_{HKUST1}.V_{mes}}.$$

If we assume that all HKUST-1 crystallizes within the mesopores, the occupancy of the mesopores with MOF phase would be 53 % or with other words the composite contains 19 wt.% of HKUST-1 phase occupying approximately 1/2 of the total available mesopores.

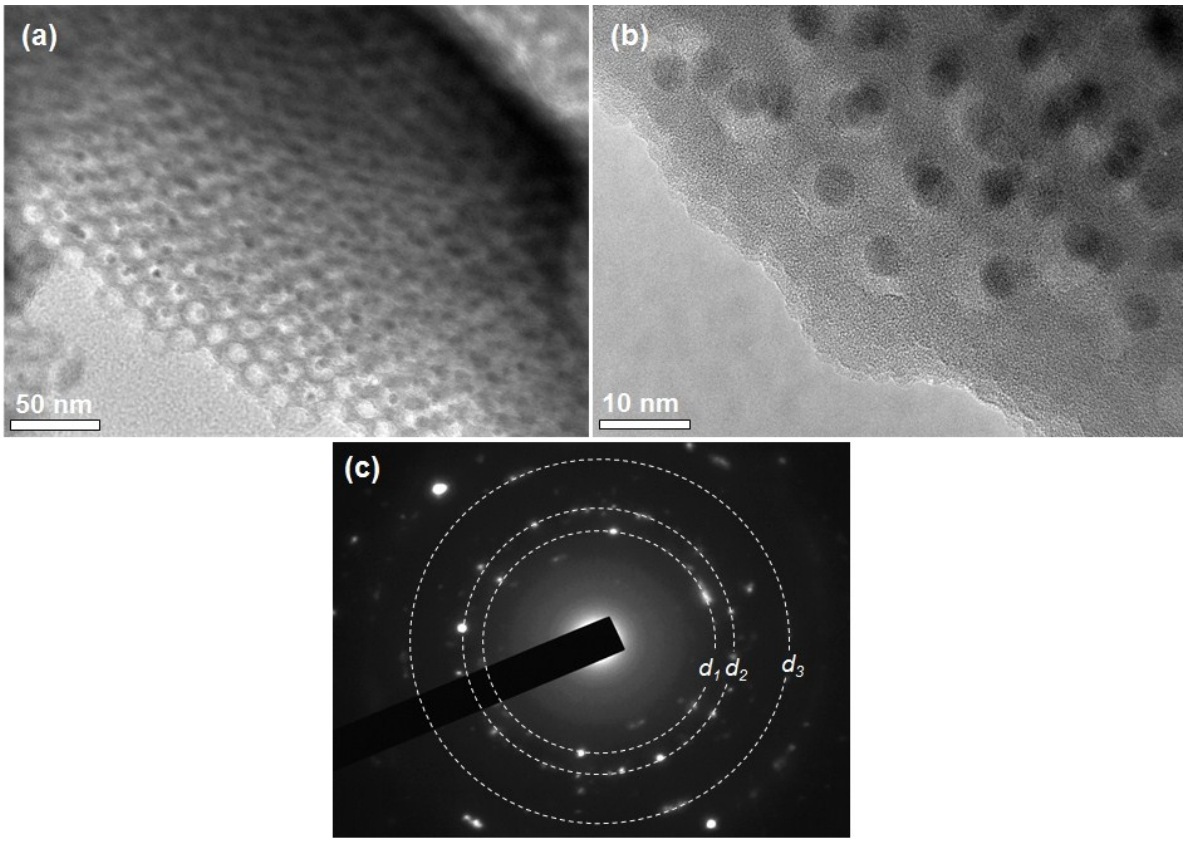

**Figure S3**: HRTEM micrographs of HKUST1-FDU12 at lower magnification (a) and higher magnifications (b). (c) Selected area electron diffraction (SAED) of the corresponding region shown in (a).

**Table S1: Comparison of measured and referenced d values of corresponding crystal planes extracted from SAED analysis.**

| | $d_1$ | $d_2$ | $d_3$ |
|---|---|---|---|
| crystallographic plane | [110] | [002] | [202] |
| measured [nm] | 2.79 | 2.56 | 1.60 |
| PDF (#01-080-1917) | 2.75 | 2.52 | 1.58 |

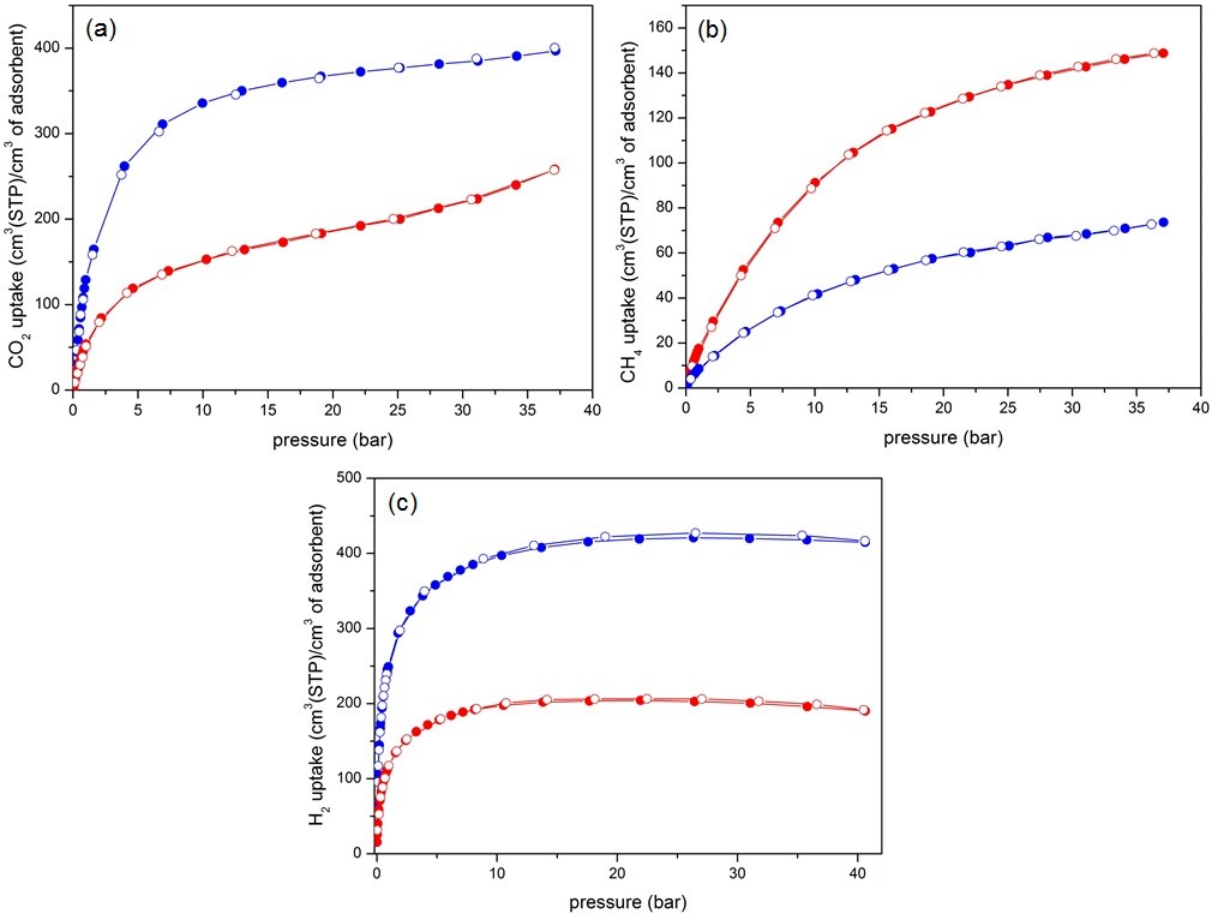


**Figure S4**: Gas sorption isotherms of bulk HKUST-1 (blue) and HKUST1-FDU12 composite (red) for (a) $CO_2$ measured at 25 °C, (b) $CH_4$ and (c) $H_2$ measured at -196 °C, respectively. Full circles - adsorption points, empty circles – desorption points.

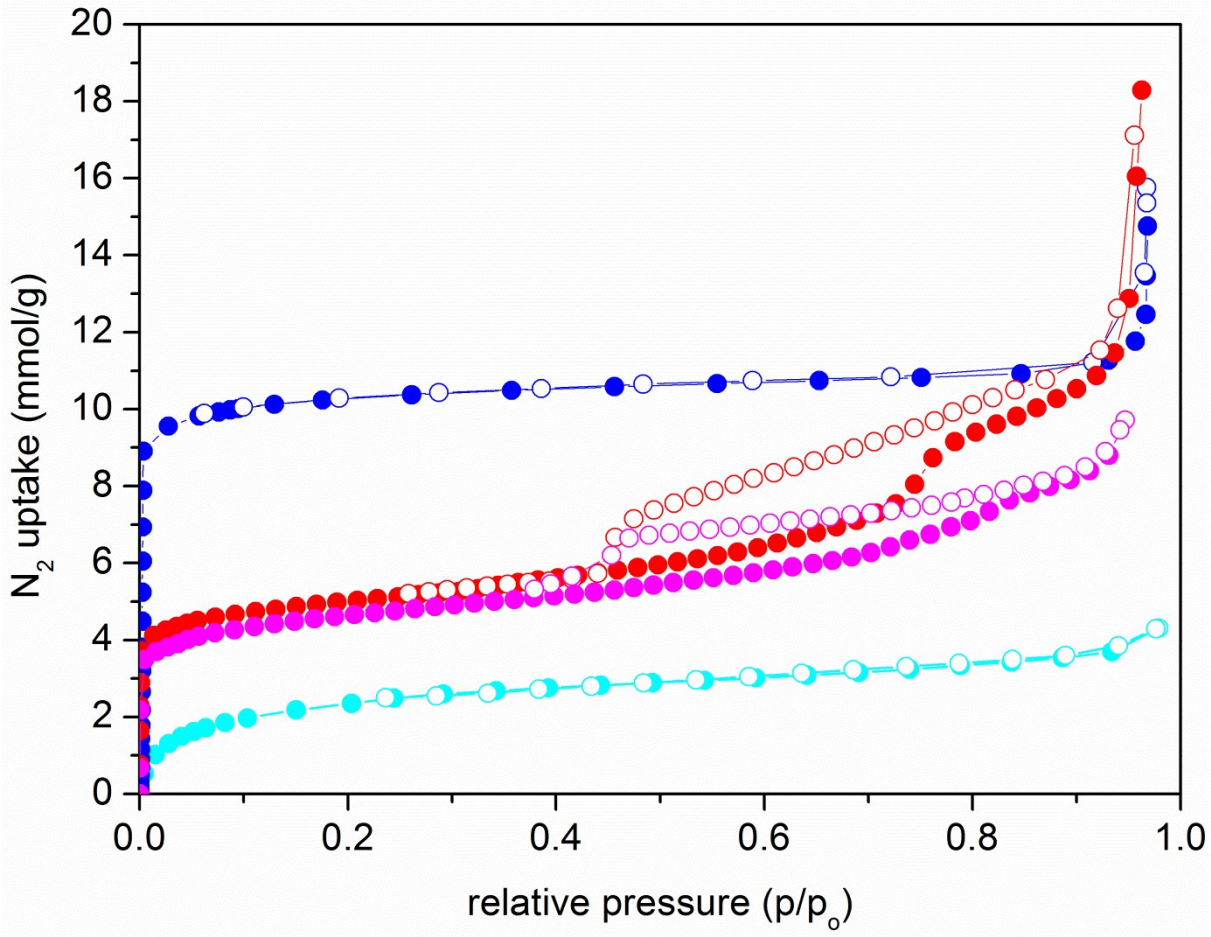


**Figure S5**: The comparison of $N_2$ sorption isotherms of HKUST-1 and HKUST1-FDU12 before and after stirring in water at 25°C overnight. Dark blue – bulk HKUST-1 before water treatment, light blue - bulk HKUST-1 after water treatment, red - HKUST1-FDU12 before water treatment, pink - HKUST1-FDU12 after water treatment. Full circles - adsorption points, empty circles – desorption points.

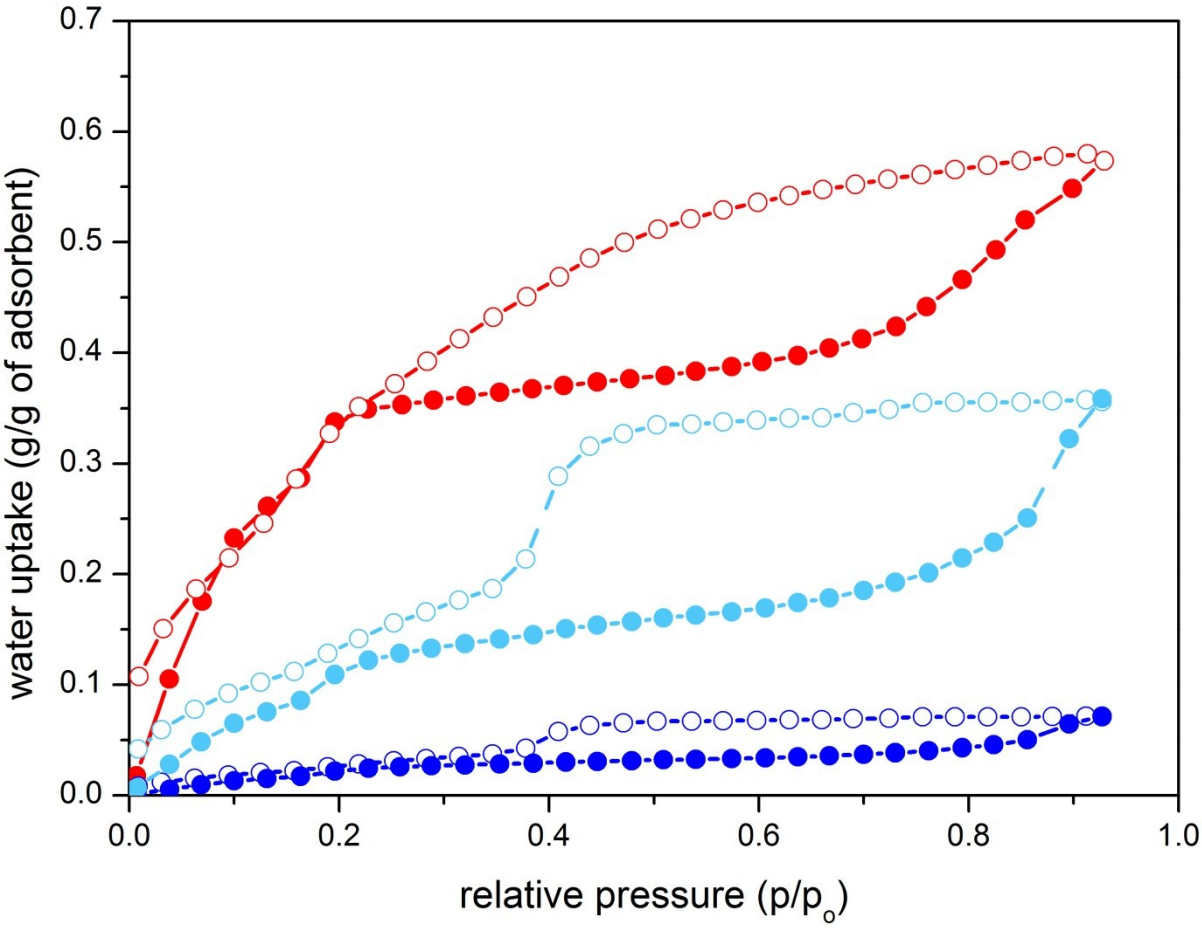


**Figure S6**: Water isotherms of bulk HKUST-1 (red) and HKUST1-FDU12 composite (blue) measured at 25 °C. Light blue circles connected with dashed lines represent the water isotherm with the normalized uptakes to MOF content within the composite. Full circles - adsorption points, empty circles – desorption points.