Supporting Information

Nanocrystalline MOFs embedded in the crystals of other MOFs and their multifunctional performance for molecular encapsulation and energy-carrier storage

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Details for characterization of materials

Powder X-ray diffraction: The powder X-ray data were collected using a SmartLab θ-2θ diffractometer in reflectance Bragg-Brentano geometry employing Johansson type Ge(111) monochromator filtered Cu Kα1 radiation at 1200W (40 KV, 30 mA) power and equipped with high speed 1D detector(D/teX Ultra). A crushed large single cubic crystal was scanned by 2 °/min scan speed in continuous mode.

Nitrogen sorption for surface area: For measuring the surface area, the nitrogen adsorption analysis was performed on a Quantachrome Autosorb-1 automatic volumetric instrument. A liquid nitrogen bath (77 K) and ultra-high purity trade nitrogen and helium were used through nitrogen adsorption measurements.

Nuclear magnetic resonance (NMR): The solution ^{1}H nuclear magnetic resonance (NMR) has been used to clarify the real existence of the nHKUST-1 linker in the MOF-5 crystals. NMR spectra were collected on the nHKUST-1⊂MOF-5 crystals dissolved in DCl (deuterium chloride)-digested solution. In detail, 8 mg of dried crystals were digested and dissolved with sonication in 1 ml dilute DCL solution (prepared from 200 μl of 35% DCl/D_2O solution (Aldrich) and 10 ml DMSO-d6). The digestion solution was used for the ^{1}H-NMR analysis (500 Hz, Korea Research Institute of Chemical Technology).

Scanning electron microscopy (SEM): In the SEM (JEOL, JSM-7600F) measurement, we used a mild electron beam, 0.5 KeV acceleration voltages in the gentle beam mode to avoid structural damage. We observed the surface and interior of the nHKUST-1⊂MOF-5 crystals to prove the existance of nHKUST-1 in MOF-5.

Transmission electron microscopy (TEM) and Dispersive X-ray spectrometer (EDS): The TEM images were collected by JEOL (JEM-ARM200F) Cs-corrected scanning transmission electron microscopy. EDS images were observed by using a BRUKER QUANTAX EDS.

Confocal microscopy measurement: The confocal microscopy data were collected using a Carl Zeiss confocal microscope (LSM510META NLO) after inserting a small amount ($<10^{-4}$ mole %) of molecular dye (Rhodamine) inside the crystal. Rhodamine 6G was purchased from Sigma Aldrich. Before preparing Rhodamine⊂nHKUST-1, 0.146 M of the Rhodamine stock solution was made with DMF and Rhodamine 6G. 1 ml of the Rhodamine stock solution was added to the initial solution of the nHKUST-1 and the synthesized nHKUST-1. After making Rhodamine⊂nHKUST-1, the crystals were washed 8 times with DMF to remove the Rhodamine remaining on the surface of the crystals. After the washing process, we confirmed with the UV-Vis measurement that there was no Rhodamine left in the washing solvent. To see if Rhodamine was not coming out of nHKUST-1 in the synthesis of MOF-5, the Rhodamine⊂nHKUST-1 samples were dispersed in DEF and placed in an oven at 110 ºC for the same period of time as the reaction of nHKUST-1⊂MOF-5. After removing Rhodamine⊂nHKUST-1 using a centrifuge, the remaining solvent was measured with UV-Vis and there was no absorbance of Rhodamine found, thus indicating that no dye was coming out from Rhodamine⊂nHKUST-1.

High pressure adsorption of methane: The high-pressure gases adsorption of methane (CH_4) was measured by a gravimetric method, MSB (Magnetic Suspension Balances, Rubotherm, Germany). The MSB was equipped with a micro-balance and electromagnet to precisely measure the amount of gas adsorption. To obtain the adsorption isotherm, data points were corrected for two independent buoyancies: buoyancy from the empty vessel components of the gravimetric measuring system and buoyancy from the adsorbent material.

Pore size distribution of nHKUST-1⊂MOF-5:

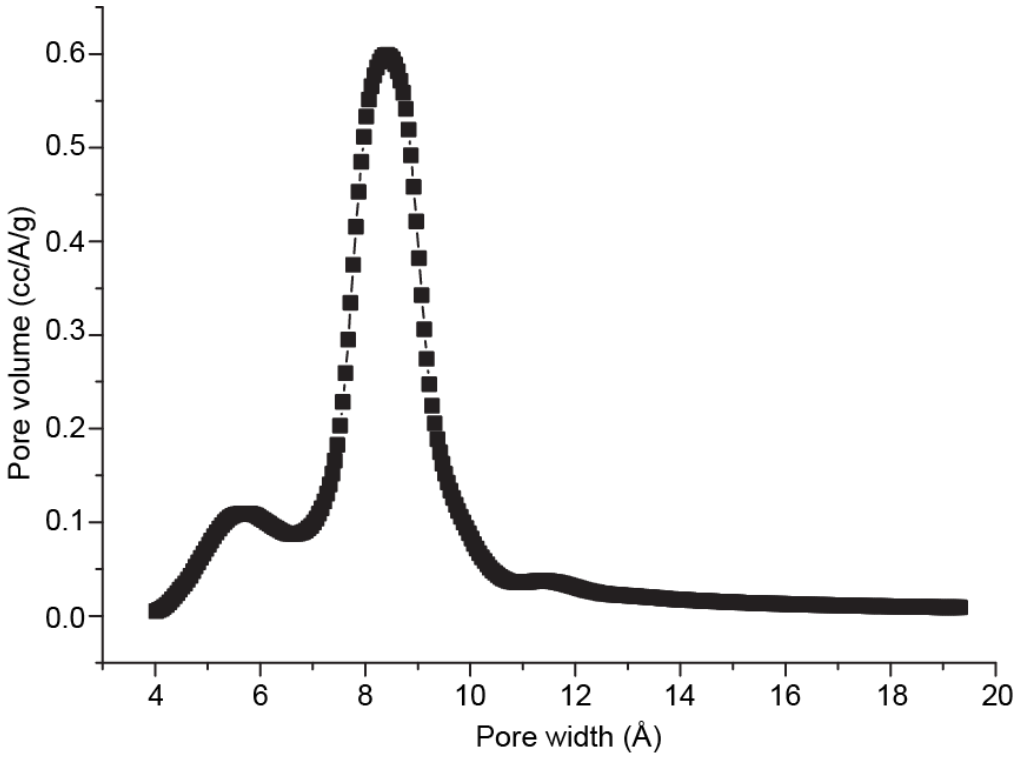

Figure S1. Pore-size distribution of nHKUST-1⊂MOF-5.

Thermogravimetric data of nHKUST-1⊂MOF-5 and MOF-5

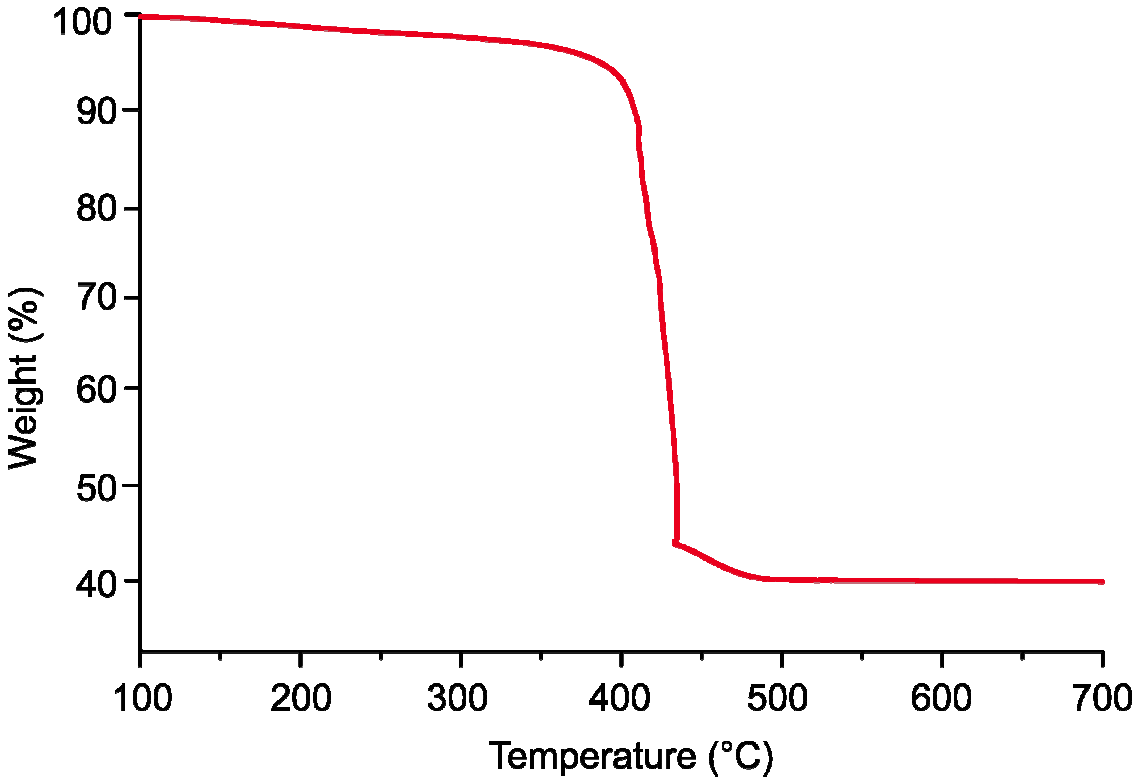

Figure S2. Thermogravimetric data of nHKUST-1⊂MOF-5.

SEM Images for MOF-5 and nHKUST-1⊂MOF-5

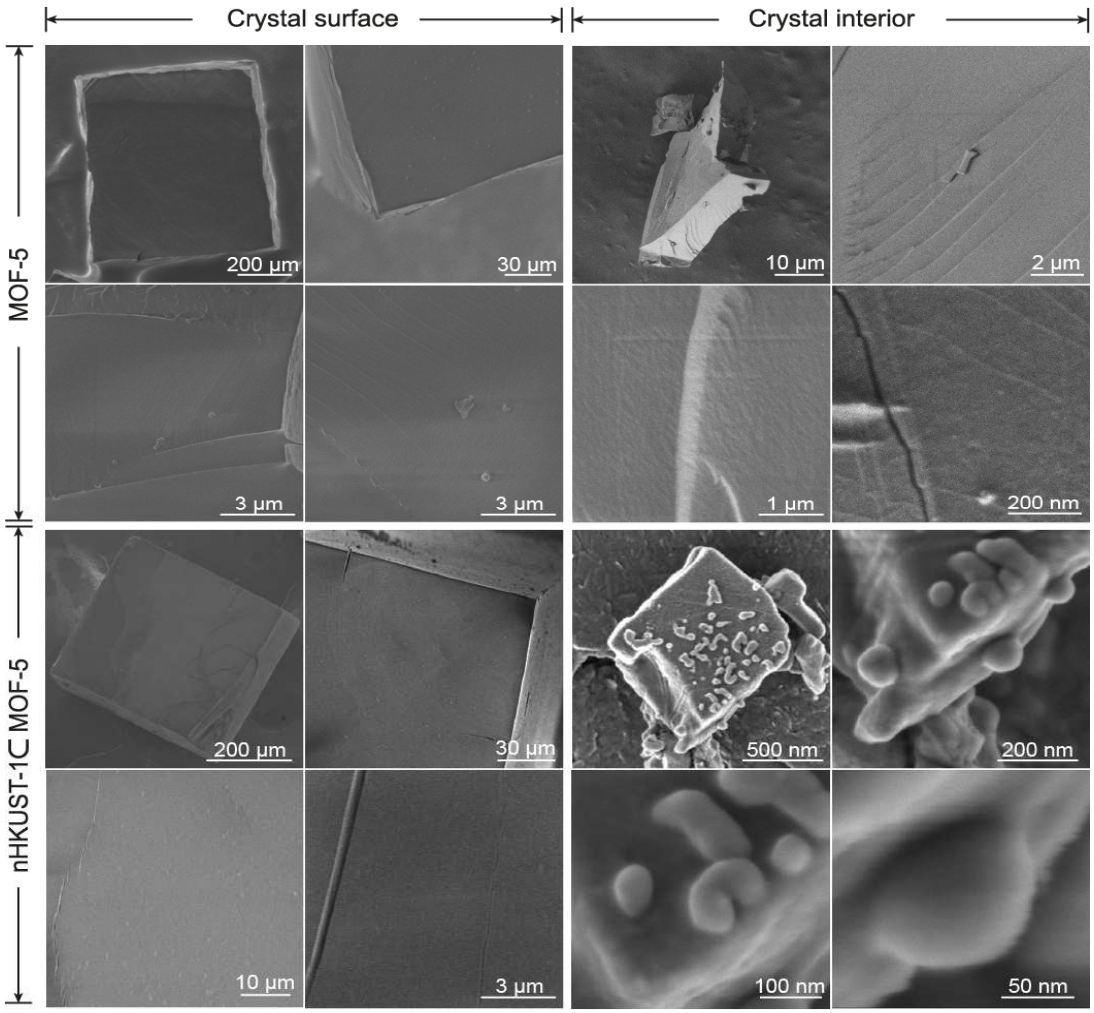

Figure S3. SEM images of MOF-5 and nHKUST-1⊂MOF-5 samples showing their surfaces and interior crystals.

HRTEM and HAADF STEM images for the interface of nHKUST-1⊂MOF-5

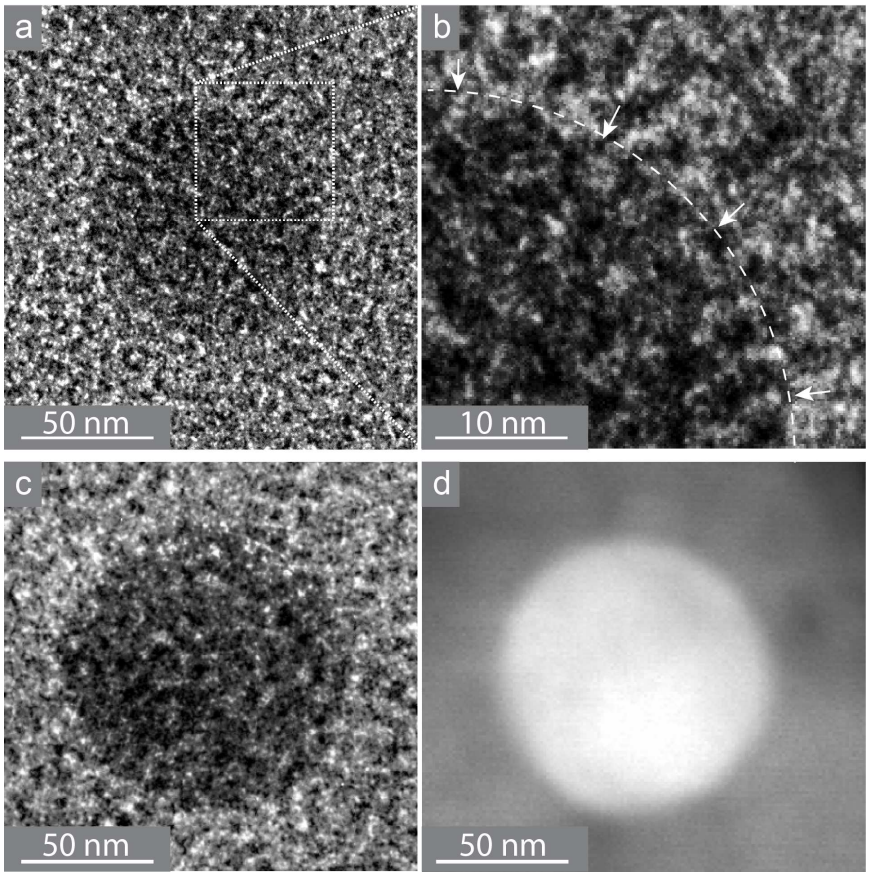

Figure S4. Observation for the interface of nHKUST-1 and MOF-5. a and c) HRTEM images of randomly selected two spots in the nHKUST-1⊂MOF-5 sample. b) high-magnification image of Figure S4a. d) HAADF STEM image of Figure S4c.

CH_4 uptake capacities with different amount of nHKUST-1⊂MOF-5

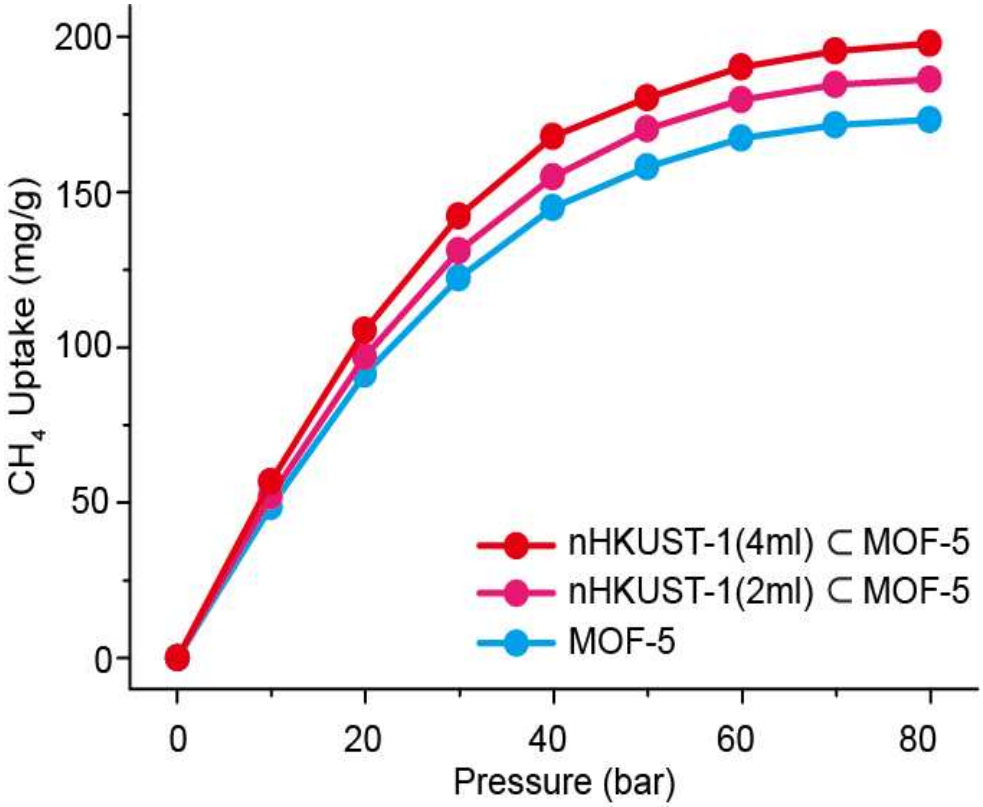

Figure S5. The CH_4 uptake capacities of nHKUST-1⊂MOF-5 samples embedding different loading amounts of nHKUST-1 crystals.