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Supporting Information

Microfluidic Synthesis of Uniform Single-Crystalline MOF Microcubes with Hierarchical Porous Structure

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Chemicals:

Styrene, methacrylic acid, copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), 1,3,5-benzenetricarboxylic acid (H_3BTC) were obtained from Alfa Aesar. Toluene, sodium hydroxide, sodium bicarbonate, potassium persulfate, dimethyl sulfoxide (DMSO) and all solvents were supplied by Beijing Chemical Company. All solvents and chemicals are of reagent quality and were used without further purification.

Experimental Section

Synthesis of polystyrene colloidal crystal templates: Non-crosslinked, monodisperse polystyrene spheres with carboxylic acid terminated surface were synthesized using an emulsifier-free emulsion polymerization technique. In a typical synthesis, a three-necked, 200-mL round-bottomed flask was filled with 80 ml of water and heated to 75 °C before 7.0 g of styrene and 0.35 g methacrylic acid were added under intensively stirring. Pure nitrogen was bubbled to deaerate the mixture for 30 min. In a separate 25-mL polyethylene bottle, 0.024 g of sodium hydroxide and 0.024 g sodium carbonate was dissolved to 5 ml water, added to the former solution and reheated to 75°C. 0.03 g potassium persulfate initiator was added to 5 ml water and deaerated for 10 min. After adding the initiator to the total solution, nitrogen was passed through the flask for 10 min. The temperature was kept at 75 °C for 12 h. After alternative centrifugation and dispersion using water several times to expunge residues, the monodisperse COOH-terminated polystyrene particles (330 nm) were obtained.

Preparation of monodisperse HKUST-1 micro-crystals with micro-macro bimodal hierarchical porosity: Firstly, In a typical preparation, 1.22 g $Cu(NO_3)_2 \cdot 3H_2O$ and 0.58 g 1,3,5-benzenetricarboxylate (H_3BTC) were dissolved in 5.0 g DMSO. Then the polystyrene particles were dispersed in above precursor solutions with volume concentration of about 10%.To produce monodisperse precursor solution droplets, we used the microfluidic device which was homemade by glass capillary as shown in Scheme 1. The precursor suspension containing monodisperse polystyrene nanoparticles and silicon oil phases were pumped into the inner and outer capillaries at volumetric flow rates of about 0.8 mL/h and 80 mL/h, respectively. Then, the mother solution droplets were evaporated at 60 °C for 36 hours to induce crystallization. At last, the highly monodisperse micro-sized cubic with hierarchical porosity were obtained after selectively etched the polystyrene template in toluene solution.

Preparation of monodisperse HKUST-1 micro-crystals with micro-meso-macro trimodal hierarchical porosity: 0.244 g $Cu(NO_3)_2 \cdot 3H_2O$, 0.116 g 1,3,5-benzenetricarboxylate (H_3BTC), 0.05 g citric acid and 0.2 g cetyltrimethylammonium bromide were dissolved in 10.0 g DMSO. Then the polystyrene particles were dispersed in above precursor solutions with volume concentration of about 10%. Then, the monodisperse mother solution droplets were evaporated at 60°C for 36 hours to induce crystallization. At last, the highly monodisperse micro-sized cubic with hierarchical porosity were obtained after selectively remove the mesoporous template and macroporous template.

The Friedländer reaction between 2-aminobenzophenones and acetylacetone: A reaction solution was prepared by mixing of 2-aminobenzophenone (3.94 g, 20 mmol) in acetylacetone (10.25 mL, 100 mmol). After adding the HKUST-1 in the reactant mixture, the vessel was placed at 80 ℃. A volume corresponding to 0.2 mL of solution was collected from each bottle after 1, 3, 5, 7, 9, 12, 15, 18, 24, 30 h.

The hydrolysis reaction of ester to assess the acid catalysis of POM@MOFs hybrid materials: Concretely, ethyl acetate hydrolysis were carried out using a 5 wt% of the aqueous (30 ml, 16.90 of mmol ethyl acetate was included) with 0.20 g POM@MOFs catalysts at 333 K under stirring. At given time intervals of reaction, the product and yield were determined by GC/MS analysis. Significantly, the POM@PILs hybrid MOFs materials exhibited excellent catalytic activity and the conversion of ethyl acetate reached a maximum of >90% at ~5 h. After the reaction, the catalyst was recovered by filtration subjected to a recycling experiment after full washing and heated for 6 h under reduced pressure. Besides, the control reactions were made, as a result, no reaction happened in the absence of catalysts or in the presence of only HSCPs (no POMs).

Characterization: XRD measurements were performed on Bruker D8 Advance X-Ray powder diffractometer. TEM images were obtained using JEM 2010 high-resolution transmission electronic microscope at an acceleration voltage of 120 kV. SEM images were obtained using a field emission scanning electron microscopy (ESSEM) on a JEOL JSM-5400 system at an accelerating voltage of 8 kV. Photographs of the monodisperse droplet were taken with an optical microscope (OLYMPUS BXFM) equipped with a CCD camera. N_2 adsorption-desorption isotherm measurements were carried out on a QuadraSorb SI instrument at 77K. Prior to the measurement, the sample was degassed at 100 ^{o}C for 12 h in the vacuum line. The FT-IR spectra measurements were carried out on a Spectrum One FTIR spectrometer (Perkin-Elmer) by the KBr pellet method.

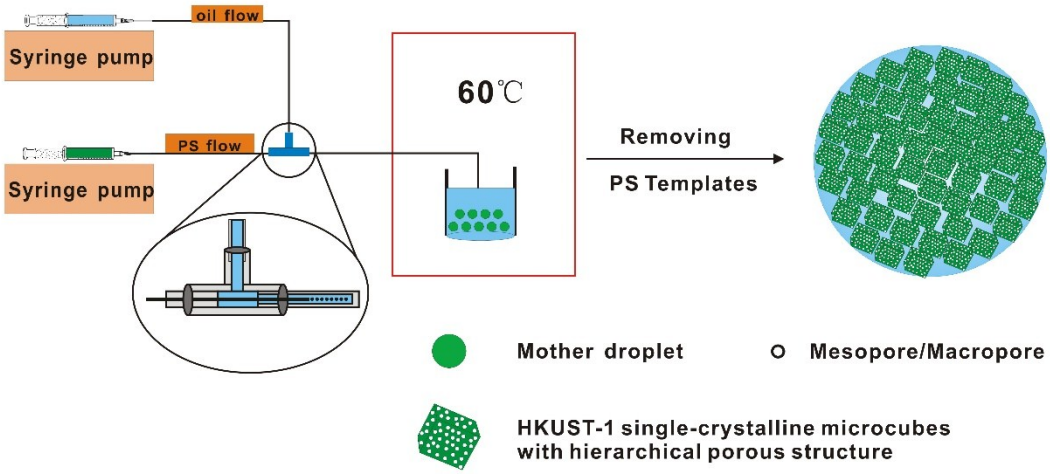

Figure S1. Schematic illustration of the synthesis of uniform HKUST-1 single-crystalline microcubes with hierarchical porous structure.

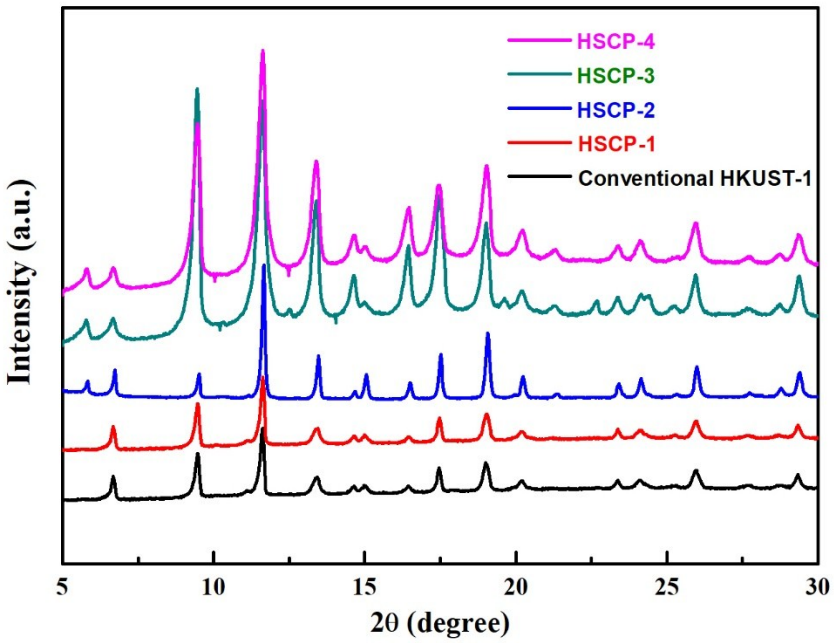

Figure S2. Powder XRD pattern of the conventional HKUST-1 and the HKUST-1 single-crystalline microcubes prepared by using PS template with the diameter of 280 nm (HSCP-1), 400 nm (HSCP-2), 680 nm (HSCP-3) and 2.9 μm (HSCP-4), respectively.

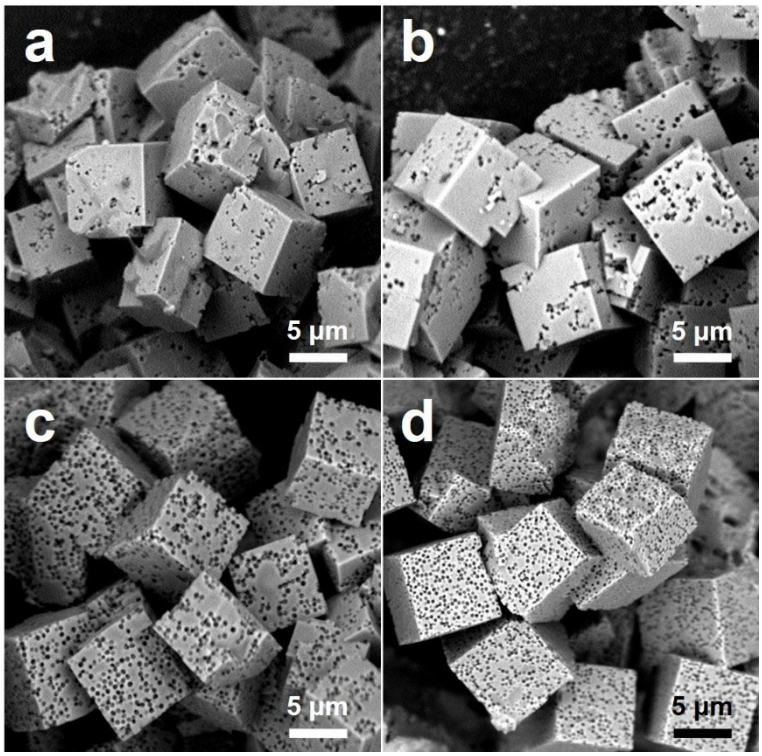

Figure S3. SEM images of uniform hierarchically pore-structured HKUST-1 single crystalline cubes fabricated by using different concentrations of the PS template, a) 5 %, b) 10 %, c) 20 %, d) 25%.

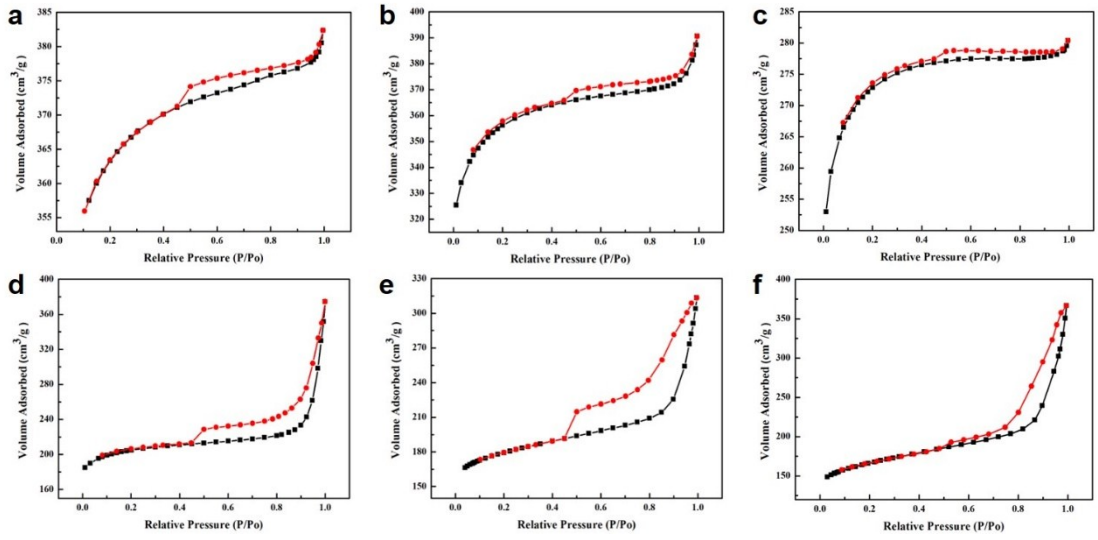

Figure S4. N_2 sorption isotherms of the micro-macro bimodal pore structure (a, b, c) and micro-meso-macro trimodal pore structure (d, e, f) of the HKUST-1 single-crystalline microcubes prepared by using PS template with the diameter of 280 nm (a, d), 400 nm (b, e), 680 nm (c, f), respectively.

Table S1. Surface area data for different hierarchically pore-structured HKUST-1 single crystalline cubes

	a	b	c	d	e	f
BET surface area (m^2/g)	1392.4	1078.1	920.1	822.9	620.9	620.4
Langmuir surface area (m^2/g)	1622.2	1597.0	1211.7	923.3	820.7	784.3

(a, b, c) micro-macro bimodal pore structure and (d, e, f)micro-meso-macro trimodal pore structure of the HKUST-1 single-crystalline microcubes prepared by using PS template with the diameter of 280 nm (a, d), 400 nm (b, e), 680 nm (c, f), respectively.

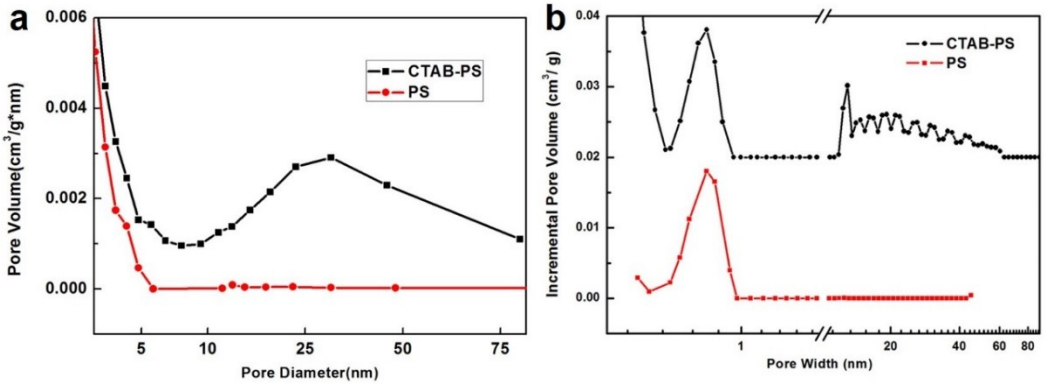

Figure S5. Comparison of pore size distribution of the hierarchical HKUST-1 microcubes with bimodal (micro-macro) and trimodal (micro-meso-macro) porous structure using BJH analysis (a) and NLDFT analysis (b).

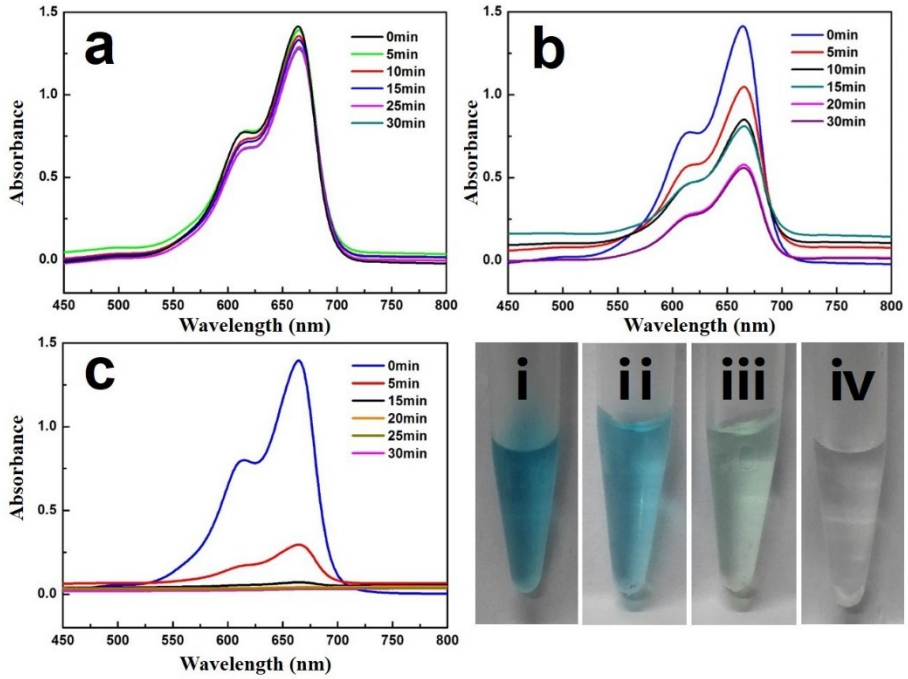

Figure S6. Adsorption of MB in the porous adsorbent. a) UV-vis spectra of the dye solutions before and after it was added to the conventional HKUST-1 particles; b) Bimodal (micro-macro)

hierarchcial porous HKUST-1 single-crystalline microcubes; c) Trimodal(micro-meso-macro) hierarchcial porous HKUST-1 single-crystalline microcubes; Optical images of vials with the initial dye solution (ⅰ), the dye solution with the conventional HKUST-1 particles(ⅱ) , the dye solution with Bimodal (micro-macro) hierarchcial porous HKUST-1 single-crystalline microcubes (ⅲ), and the dye solution with Trimodal(micro-meso-macro) hierarchcial porous HKUST-1 single-crystalline microcubes (ⅳ).

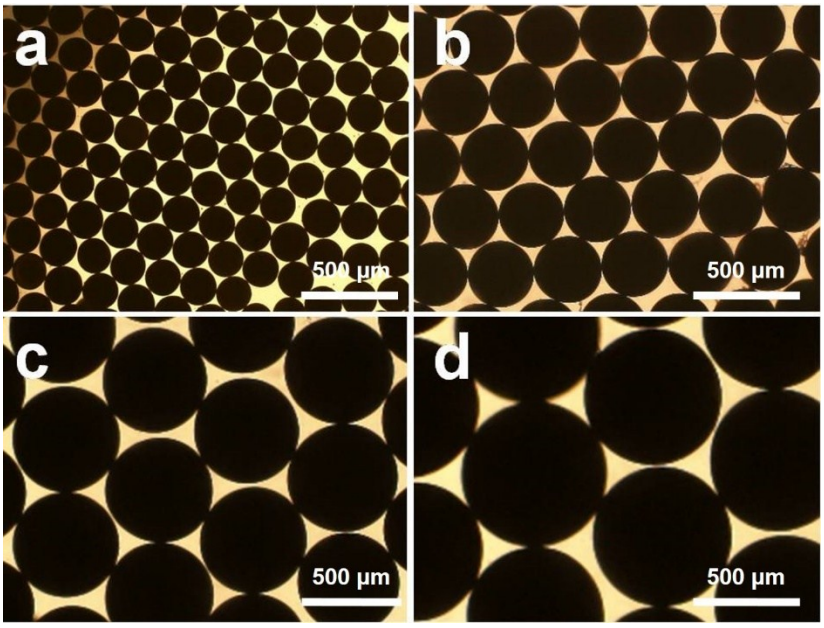

Figure S7. Optical images of the monodisperse droplets of different sizes produced by the used microfluidic system.

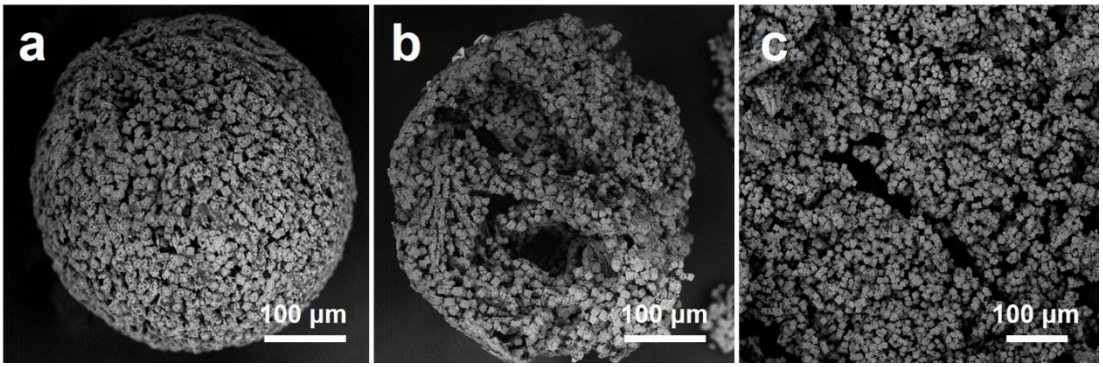

Figure S8. SEM images of the resultant microspheres which contain a large number of uniform single crystalline HKUST-1 microcubes.

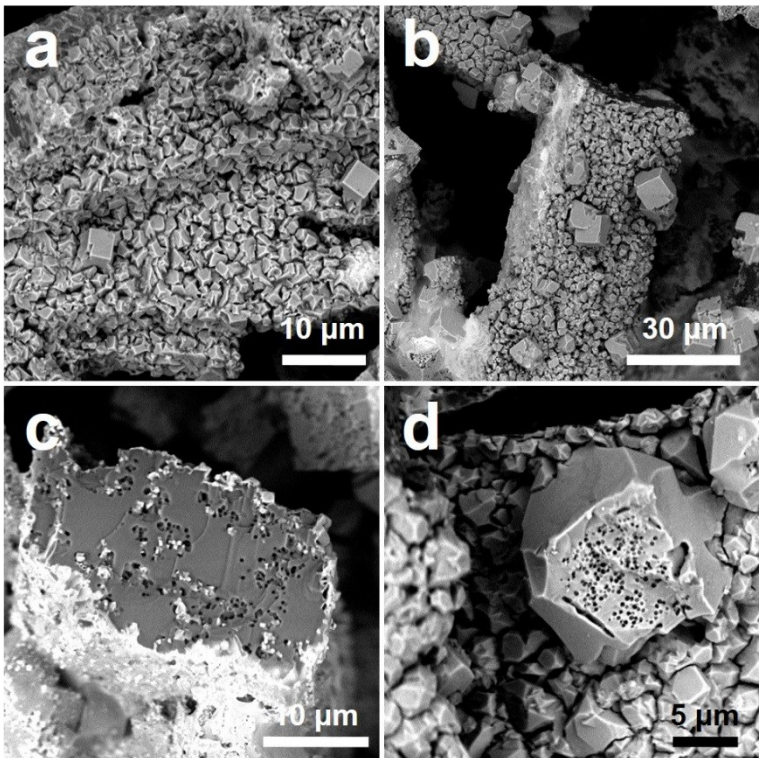

Figure S9. SEM images of the HKUST-1 crystals obtained by conventional synthesis or by unconfined evaporation of precursor solution.

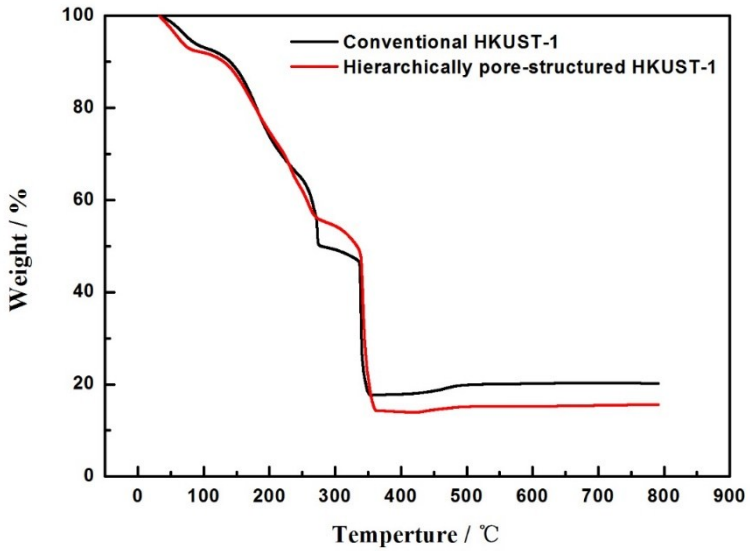

Figure S10. TGA curve of the Conventional HKUST-1 and hierarchically pore-structured HKUST-1 single-crystalline microcubes with a heating rate 5 K/min in a flow of air.

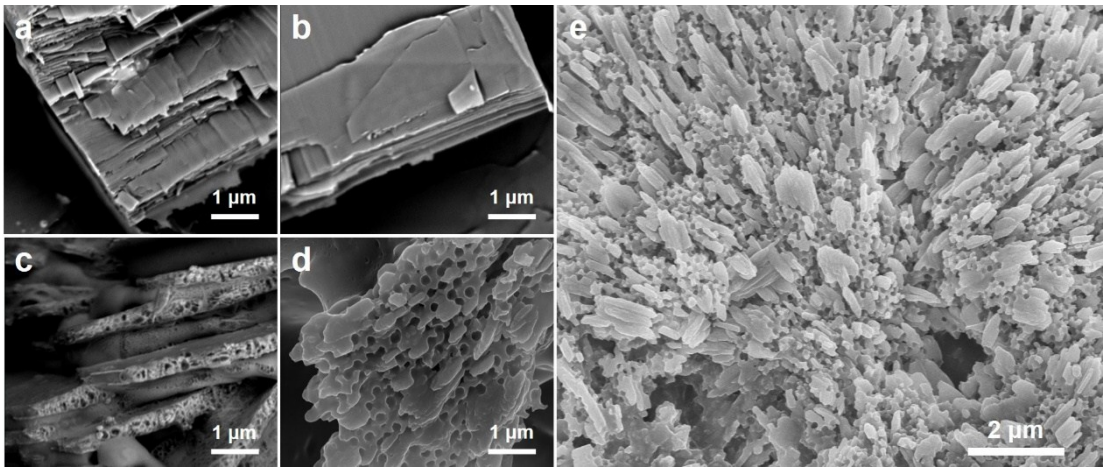

Figure S11. SEM images of the CuBDC crystals obtained by evaporation of precursor solution in microdroplet without using PS nanoparticles as the template (a, b) and the hierarchical porous struxture CuBDC crystals using PS nanoparticles as the template (c, d, e).