Electronic Supplementary Information for

Mechanically stable, hierarchically porous $Cu_3(btc)_2$ (HKUST-1) monoliths via direct conversion of copper(II) hydroxide-based monoliths

Nirmalya Moitra,[a] Shotaro Fukumoto,[a] Julien Reboul,[b] Kenji Sumida,[b] Yang Zhu,[a] Kazuki Nakanishi,[a] Shuhei Furukawa,[b] Susumu Kitagawa,[b] and Kazuyoshi Kanamori*[a]

[a] Department of Chemistry, Graduate School of Science, Kyoto University, Japan

[b] Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Japan

*kanamori@kuchem.kyoto-u.ac.jp

Experimental

General procedure for synthesis of $Cu(OH)_2$ monolith: 1.53 g of $CuCl_2•2H_2O$ was added to a solution containing 1.10 mL of water, 0.30 mL of ethanol, and 2.40 mL of glycerol, and the solution was vigorously stirred under an ambient condition. After dissolution of $CuCl_2•2H_2O$, a desired amount of PAAm was slowly added, and the whole mixture was stirred overnight under an ambient condition. To this homogeneous solution was added 1.47 mL of propylene oxide. The whole mixture was stirred at room temperature for 5 min, and then transferred to an oven operating at 30 °C for gelation. The gel formation occurred after 30 min, followed by isothermal aging for 2 d. The resultant wet gel was washed several times with 2-propanol and dried at room temperature for 3 d.

Coordination replication of Cu-06 to $Cu_3(btc)_2$ monolith: 200 mg of Cu-06 was soaked in a 5 mL of 0.5 M H_3btc solution in DMF/EtOH (1:1 vol). The resulting monolith was then taken out at different time intervals and washed several times with ethanol, and dried at an ambient condition.

Characterizations: Microstructures of the fractured surface of the samples were observed under a scanning electron microscope (SEM, JSM-6060s, JEOL Ltd. (Japan)). Meso- and micropores present in the material were analyzed by nitrogen adsorption-desorption measurements (BELSORP-mini II, BEL Japan, Inc. (Japan)). The samples were degassed at 60 °C overnight before each measurement. Thermogravimetry-differential thermal analysis (TG-DTA) has been performed on Thermo plus EVO II (Rigaku Corp. (Japan)) at a heating rate of 10 °C min^{-1} under an air flow. The X-ray diffraction (XRD) was recorded by a powder X-ray diffractometer (RINT Ultima III, Rigaku Corp. (Japan)) using Cu Kα (λ = 0.154 nm) as an incident beam. Mechanical properties were evaluated by the uniaxial compression test using a material tester (EZGraph, Shimadzu Corp. (Japan)). The crosshead speed was 1.0 mm min^{-1}.

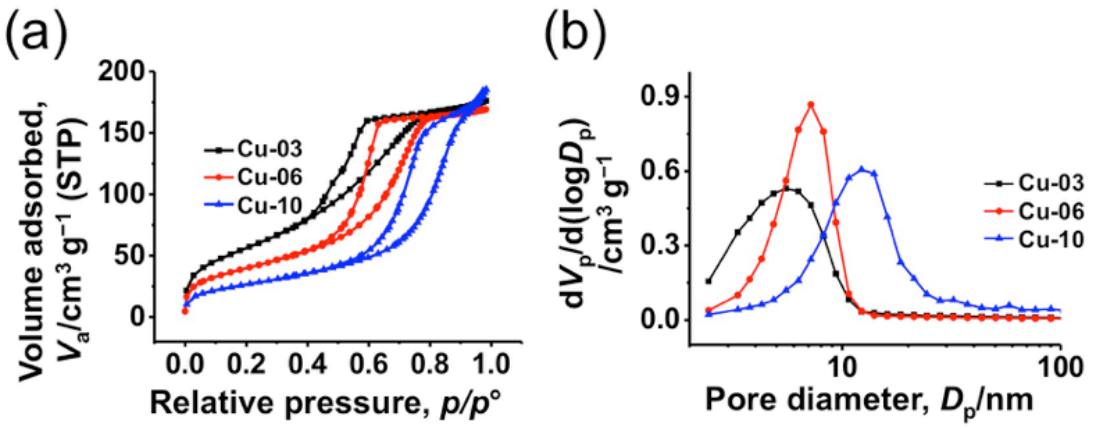

Figure S1 (a) Nitrogen adsorption-desorption isotherms and BJH pore size distributions (from adsorption branch) of the $Cu(OH)_2$-based samples.

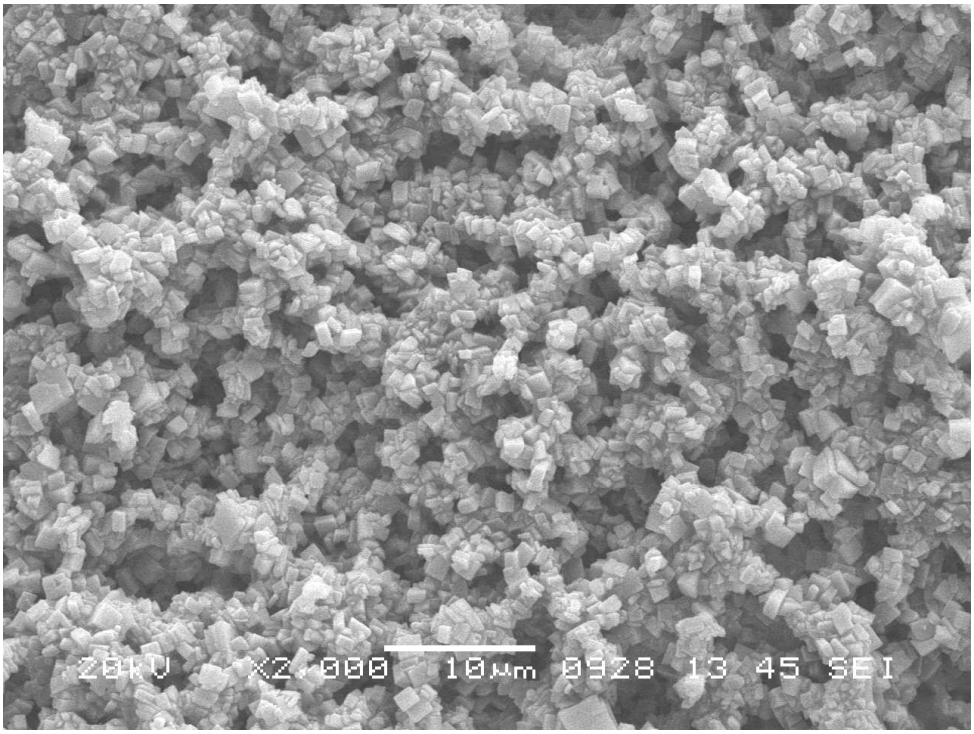

Figure S2 SEM image after the complete replication, showing the macroporous monolithic architecture of $Cu_3(btc)_2$ crystallites.

Table S1 BET specific surface area of the $Cu_3(btc)_2$ monoliths at different conversion time.

Time/min	$a_{BET}/m^2\ g^{-1}$	Time/min	$a_{BET}/m^2\ g^{-1}$
1	127	4	724
2	227	5	1046
3	536	6	1350

Acknowledgement

This work has been performed under the financial support from Advanced Low Carbon Technology Research and Development Program (ALCA) administrated by Japan Science and Technology Agency (JST).