Electronic Supplementary Information (ESI)

From metal-organic framework to hierarchical high surface-area hollow octahedral carbon cages

Arshad Aijaz, Jian-Ke Sun, Pradip Pachfule, Takeyuki Uchida and Qiang Xu*

National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan

E-mail: ***q.xu@aist.go.jp***

1. Materials and instrumentation

All chemicals were commercial and used without further purification: trimethyl-1,3,5-trimesate ($C_{12}H_{12}O_6$, TCI, >98 %), aluminum nitrate ($Al(NO_3)_3.9H_2O$, Sigma-Aldrich, ≥98 %), nitric acid (HNO_3, 67 %, TCI), Methylene Blue (Kishida Chemical Co. Ltd) and hydrofluoric acid (HF, 46%, Kishida Chemical Co. Ltd). Ultrapure water was used for sample preparations and washing processes. Powder X-ray diffraction (XRD) was performed on a Rigaku Ultima IV X-ray diffractometer with Cu Kα source (40 kV, 40 mA). The sorption isotherms of nitrogen and other gases were measured by using automatic volumetric adsorption equipments BELSORP max and BELSORP mini II, respectively, and the surface areas were calculated using nitrogen sorption data in the relative pressure range of 0.05-0.20. The gas sorption measurements for all these carbon materials were performed after pre-activation at 120-150 ^oC overnight. The pore-size distributions were calculated by non-localized density functional theory (NLDFT) using nitrogen adsorption isotherms at 77 K. The UV-vis absorption measurements were performed using a UV-2550 spectrophotometer (SHIMADZU). Thermogravimetric analysis (TGA) was carried out at a ramp rate of 5 °C/min from 25 to 1000 °C under argon atmosphere on a Rigaku Thermo plus EVO2/TG-DTA analyzer. The aluminum content in h-C800 (before acid wash) was analyzed using ICP-OES on Thermo Scientific iCAP6300. Scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM) images and energy-dispersive X-ray (EDX) spectra were recorded on Tecnai G2 F20 (FEI) with operating voltages of 200 kV quipped with energy-dispersive X-ray detector. Tomographic experiments were performed on TECNAI G^2 F20 equipped with a −59.6° to +59.6° tomography tilt stage and holder operated at 200 kV to minimize the beam damage with punctual resolution 0.27 nm. Images for tomographic reconstruction were taken using a 2° interval over the largest possible angle (preferably 100°). A reference image taken at 0° tilt was taken before and after image acquisition to ensure no changes in the sample structure due to beam damage during acquisition. Tomographic reconstruction was performed using the INSPECT 3D software package.

2. Synthesis of MIL-100 (Al)

Crystals of aluminum-based MOF MIL-100(Al) was synthesized following the procedure reported in the literature.[1] A mixture of $Al(NO_3)_3 \cdot 9H_2O$ (230 mg), $(CH_3O)_3C_6H_3$ (denoted as $btcMe_3$) (104 mg), HNO_3 (1M) (0.77 mL) and deionized water (2.8 mL) were placed in a 10 mL Teflon-liner autoclave and heated at 210 °C for 3.5 h. After very slow cooling to room temperature within 12 h, the resulting yellow powder was filtered off, washed with distilled water several times, and then further purified by solvothermal and hydrothermal treatments with DMF at 150 ^oC (6 h) and with water at 110 ^oC (24 h), respectively. The resulting white solid was carefully filtered, washed with hot water several times, and finally dried overnight at 200 °C under vacuum for further use.

3. Synthesis of hollow h-C800

The as-synthesised microcrystals of MIL-100(Al) (250 mg) were directly transferred into a ceramic boat and placed in a furnace under Ar flow. The samples were preheated at 200 ^oC for 24 h, and subsequently carbonized at 800 ^oC for 7h. After cooling, the resulting black powders were directly immersed into HF solutions (20 %) without stirring the solution. The black solid was continuously immersed with changing the fresh HF solutions three times over a period of 1 week. Finally the black solid was separated and washed by decantation technique with continuous washing with ultrapure distilled water for several times. After drying under vacuum at 120 ^oC for overnight, the resulting samples were labeled as h-C800.

4. Synthesis of h-C600 and h-C1000

h-C600 and h-C1000 were prepared under similar experimental conditions as described above for h-C800 except the carbonization temperature (600 ^oC for h-C600 and 1000 ^oC for h-C1000).

5. Adsorption of Methylene Blue (MB) by h-C800

In a typical adsorption experiment, 2 mg h-C800 powder was added into a glass bottle containing 20 mL MB solution (20 mg L^{-1}) under vigorous shaking for time-dependent

measurements. After a certain given period, 3 mL of mixture solution was took out and the h-C800 powder was separated from the solution via centrifugation (rotation speed: 15000 rpm). The concentration of residual MB in the supernatant solution was analyzed using a UV-vis spectrophotometer.

Reference:

1) C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas and F. Taulelle, *Chem. Mater.*, 2009, **21**, 5695.

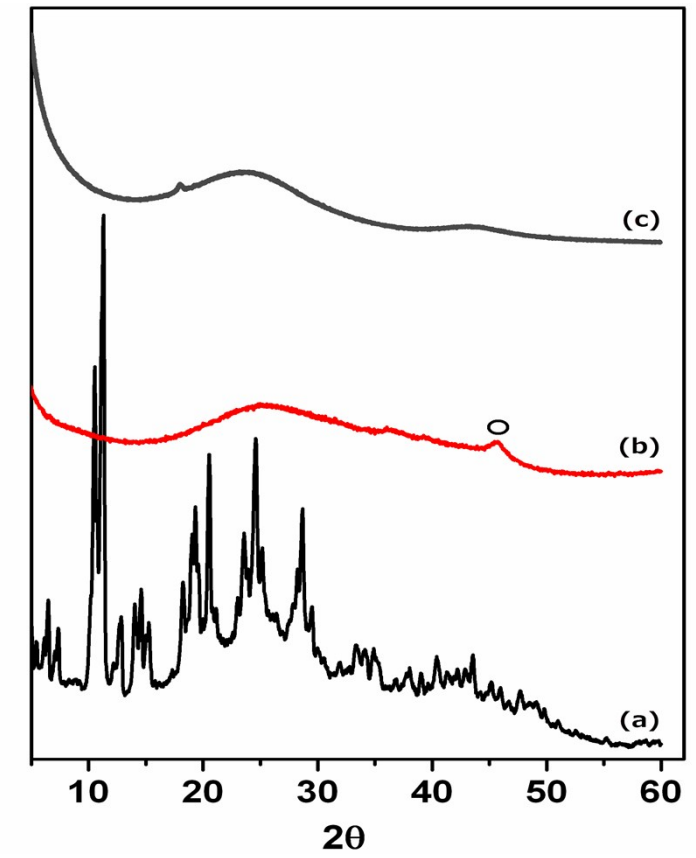

Figure S1. Powder XRD patterns of (a) MIL-100(Al) and h-C800 (b) before and (c) after washing with HF acid (the small peak marked by sphere in (b) corresponds to aluminum oxide).

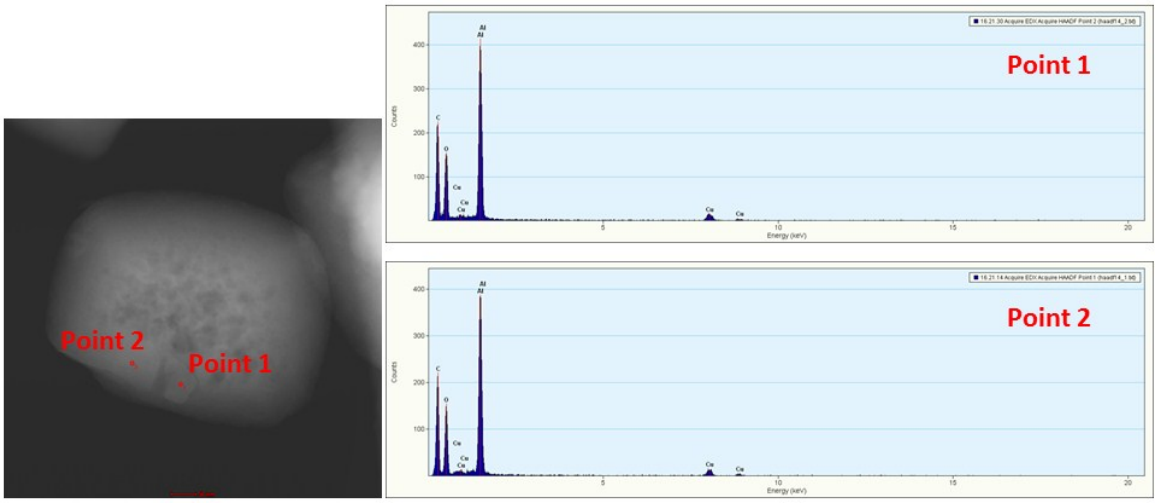

Figure S2. (left) HAADF-STEM image of h-C800 (before HF wash), and (right) the corresponding EDX spectra for selected points 1 and 2, respectively. The copper peaks arise from the TEM grid.

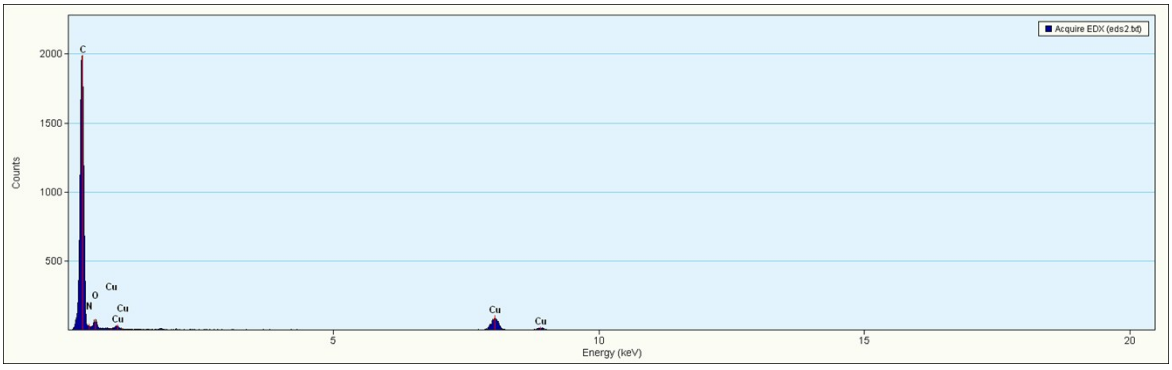

Figure S3. Bulk EDX spectrum of hollow h-C800. The copper peaks arise from the TEM grid.

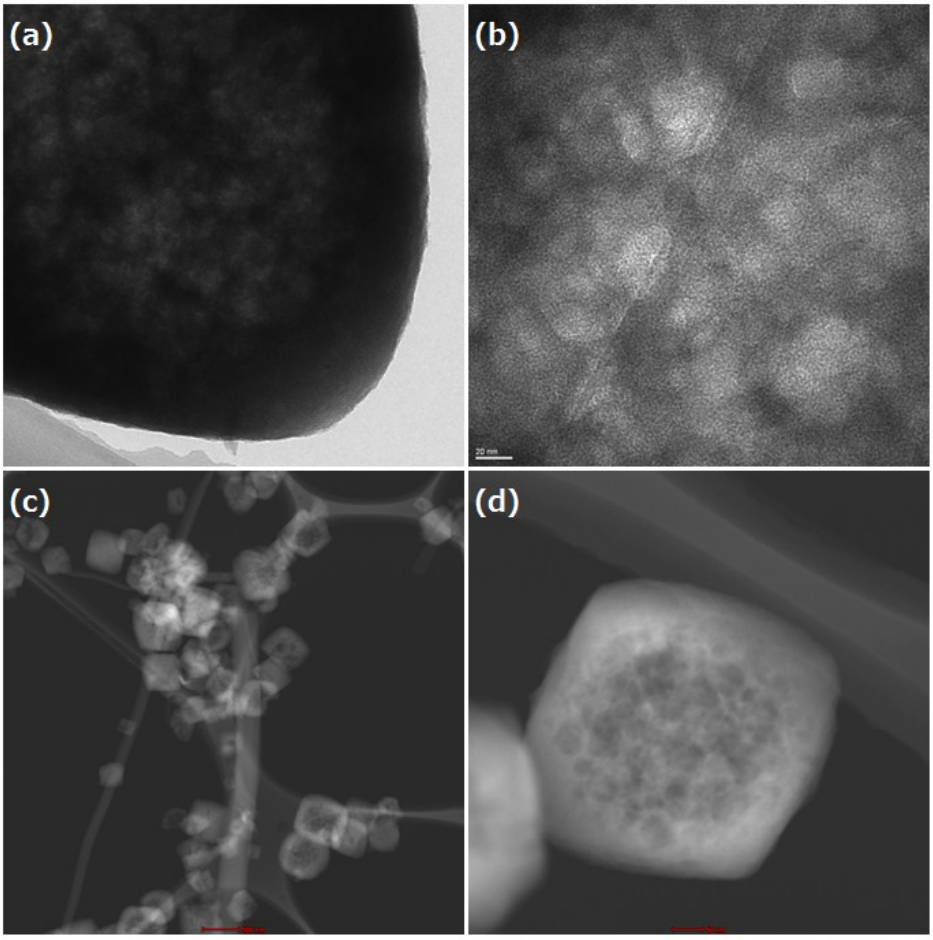

Figure S4. (More images of h-C800) TEM images of (a) vertex and (b) middle of a single octahedral cage and HAADF-STEM images of (c) bulk sample and (d) octahedral single cage.

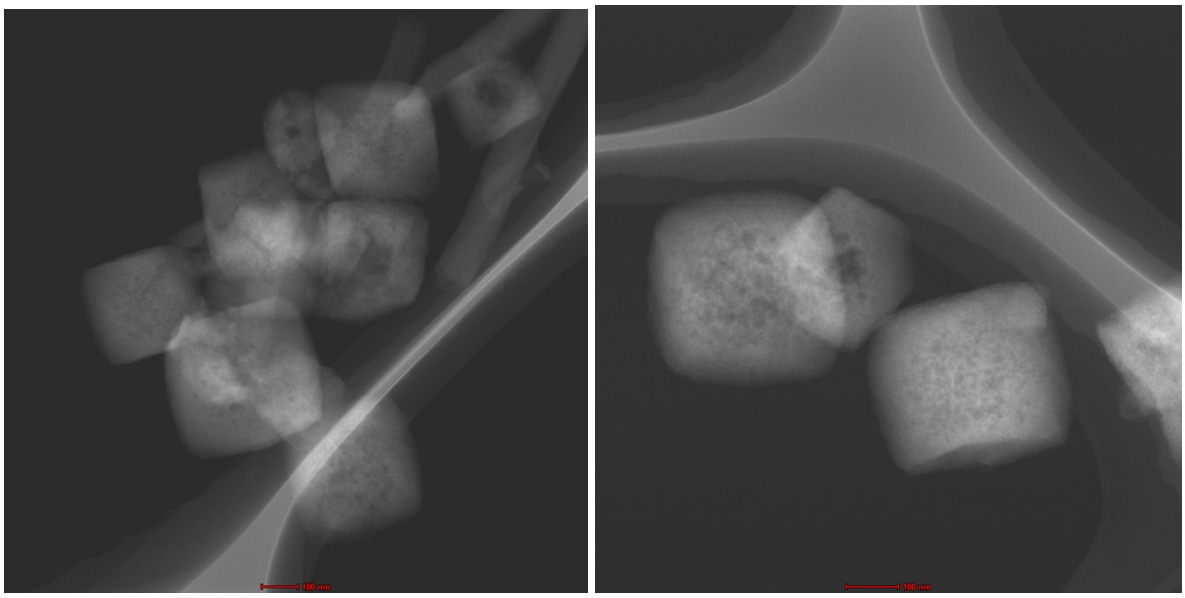

Figure S5. HAADF-STEM images of h-C600.

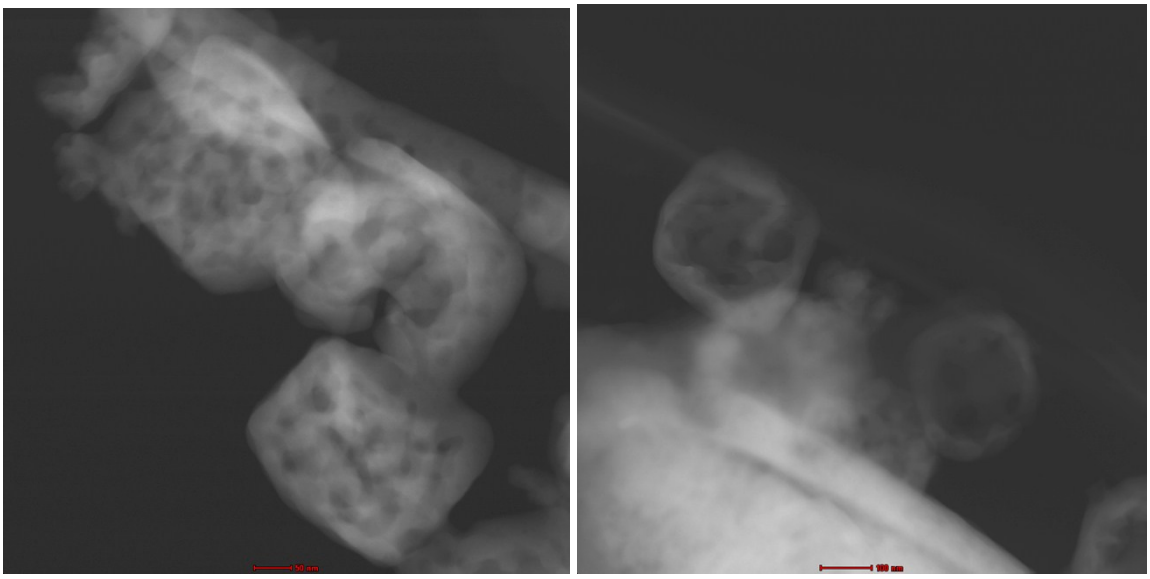

Figure S6. HAADF-STEM images of h-C1000.

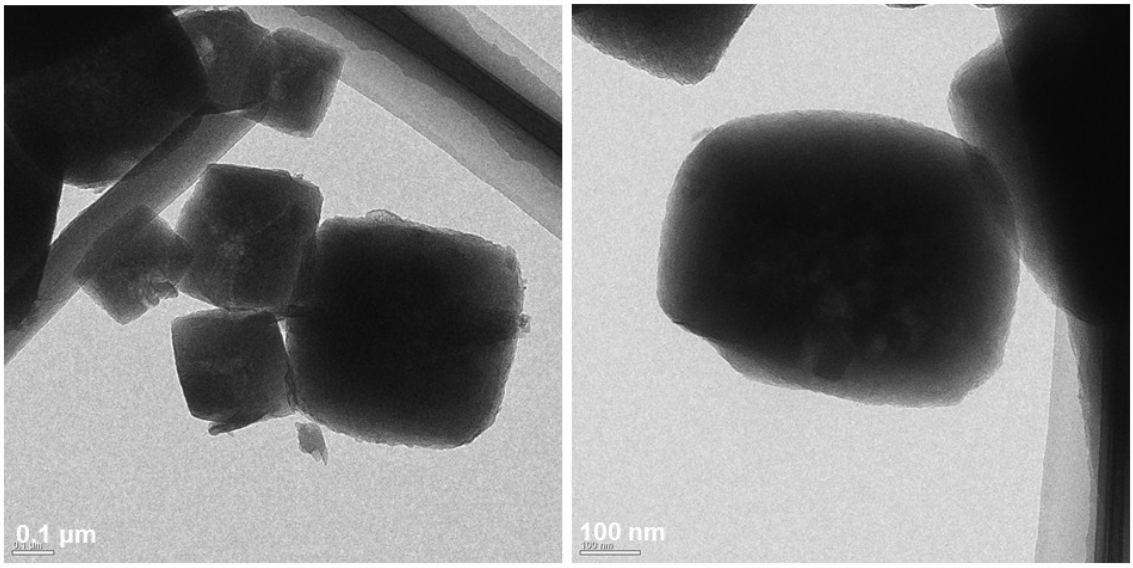

Figure S7. TEM images of h-C800 (before HF wash).

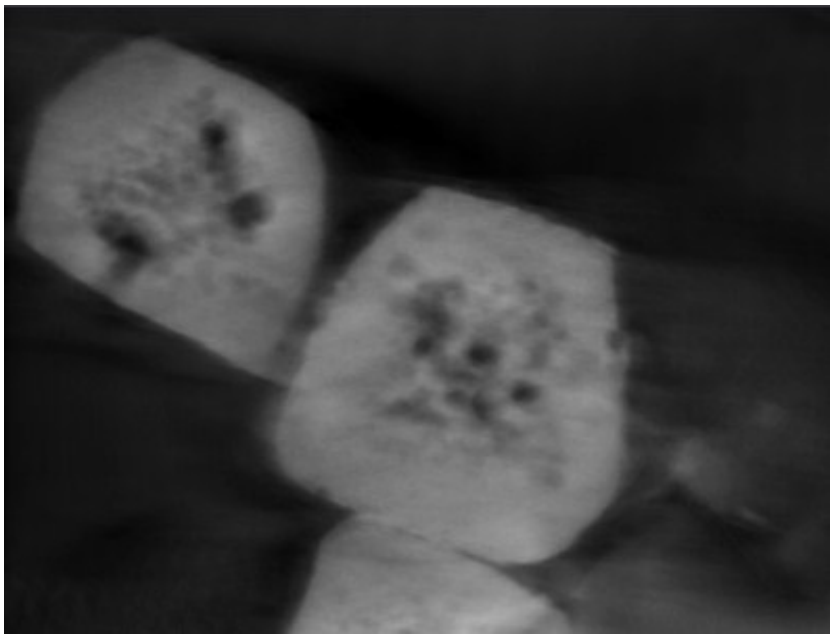

Figure S8. Tomographic cross section of octahedral cages of h-C800 (before HF wash).

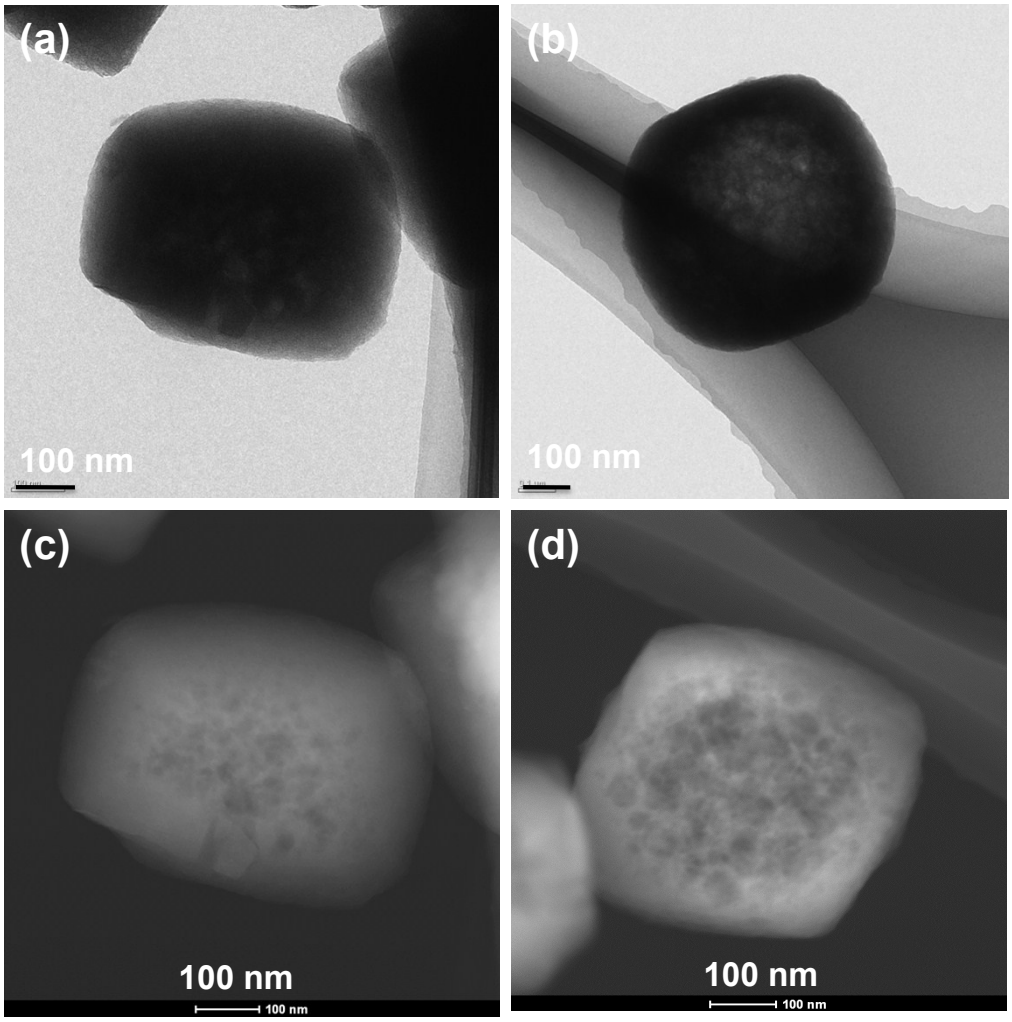

Figure S9. (For clear comparison) TEM images of single octahedral cage of (a) h-C800 (before HF wash) and (b) h-C800 (after HF wash); HAADF-STEM images of single octahedral cage of (c) h-C800 (before HF wash) and (d) h-C800 (after HF wash).

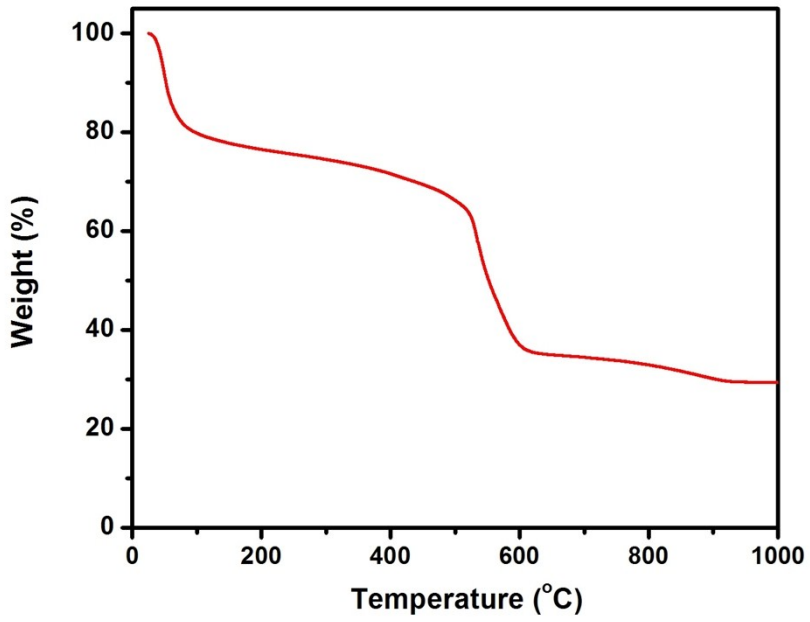

Figure S10. TGA of as-synthesized MIL-100(Al) under argon atmosphere.

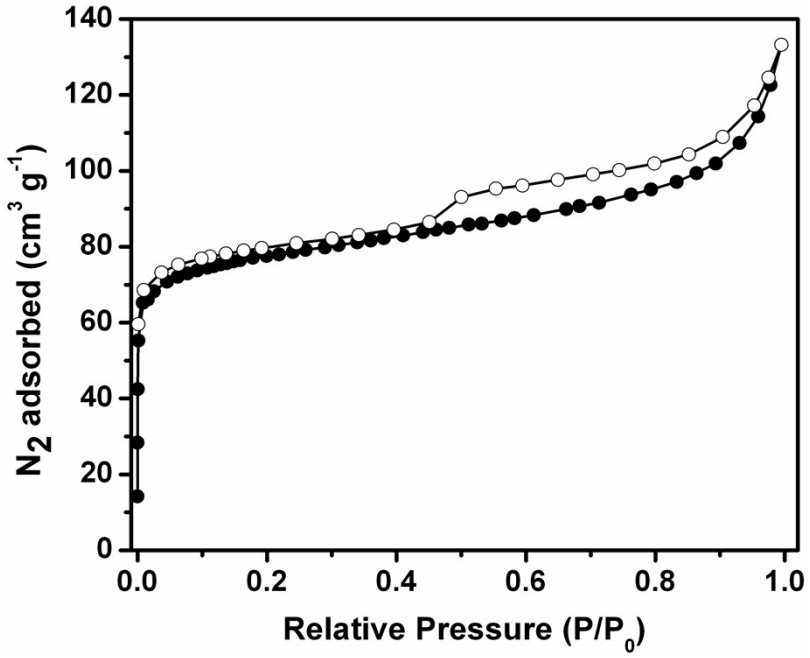

Figure S11. N_2 sorption isotherms of h-C800 (before HF wash)

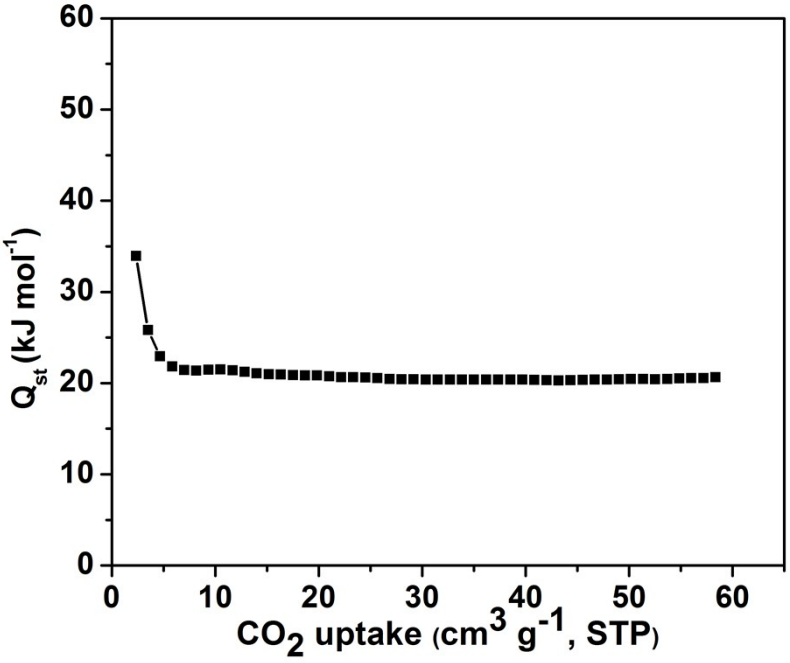

Figure S12. Isosteric heats of adsorption (Q_{st}) of h-C800 calculated using the CO_2 sorption isotherms measured at 273 and 298 K.