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Facile fabrication of concave cubic nitrogen-rich metal-organic framework nanocrystals for gas uptake

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1. Experimental details

1.1 Preparation of concave cubic N-MOF nanocrystals

In a typical synthesis, $Cu(NO_3)_2 \cdot 3H_2O$ (0.024 g, 0.1 mmol) was added into a mixture of ET/DMF (4.5 mL / 4.5 mL) to form the solution 1. 1-Methylimidazole (0.057 g, 0.7 mmol) was added to the same mixture of ET/DMF (4.5 mL / 4.5 mL) to form the solution 2. Then, solution 2 was added into the solution 1, and the mixture solution was stirred at room temperature for 10 min. Compound $H_{6\text{-}1}$ (0.02 g) was dissolved in the mixture of ET/DMF (9 mL / 9 mL) to form the solution 3. The solution 3 was added into the above mixture solution. The mixture was stirred at 90 °C for 6 h. After reaction, the products were collected by high-speed centrifugation and washed several times with ethanol. The concave cuboctahedron and octahedron products were synthesized in a similar way except that 0.2 and 1.5 g benzimidazole were used instead of 1-methylimidazole, respectively.

1.2 Characterizations

The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) patterns using a Panalytical X-pert diffractometer with Cu Kα radiation.

The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (SEM, S4800), and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai-F30) with an acceleration voltage of 300 kV. All TEM samples were prepared by depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid.

1.3 Gas sorption

Before gas sorption measurement, the samples were immersed in CH_2Cl_2 for one day, and the CH_2Cl_2 was replaced three times within one day. Then, the samples were dried under vacuum at 60 °C for 12 h and using the "outgasser" function of the autosorp-IQ instrument at 120 °C for 5 h. The brunauer-emmett-teller (BET) surface area and pore size distribution were calculated from the N_2 sorption isotherms at 77 K. The pore size distribution was calculated based on the non-local density functional theory (NL-DFT, a zeolite/silica model containing spherical/cylindrical pores) model in the Quantachrome AsiQwin 2.01 software package. The isosteric heats of adsorption (Q_{st}) for CO_2, defined as

$$Q_{st} = RT^2\left(\frac{\partial \ln p}{\partial T}\right)_q \quad \text{(Clausius-Clapeyron equation)}$$

were determined by using the CO_2 adsorption isotherms at 273 and 298 K, respectively.

2. Experimental results

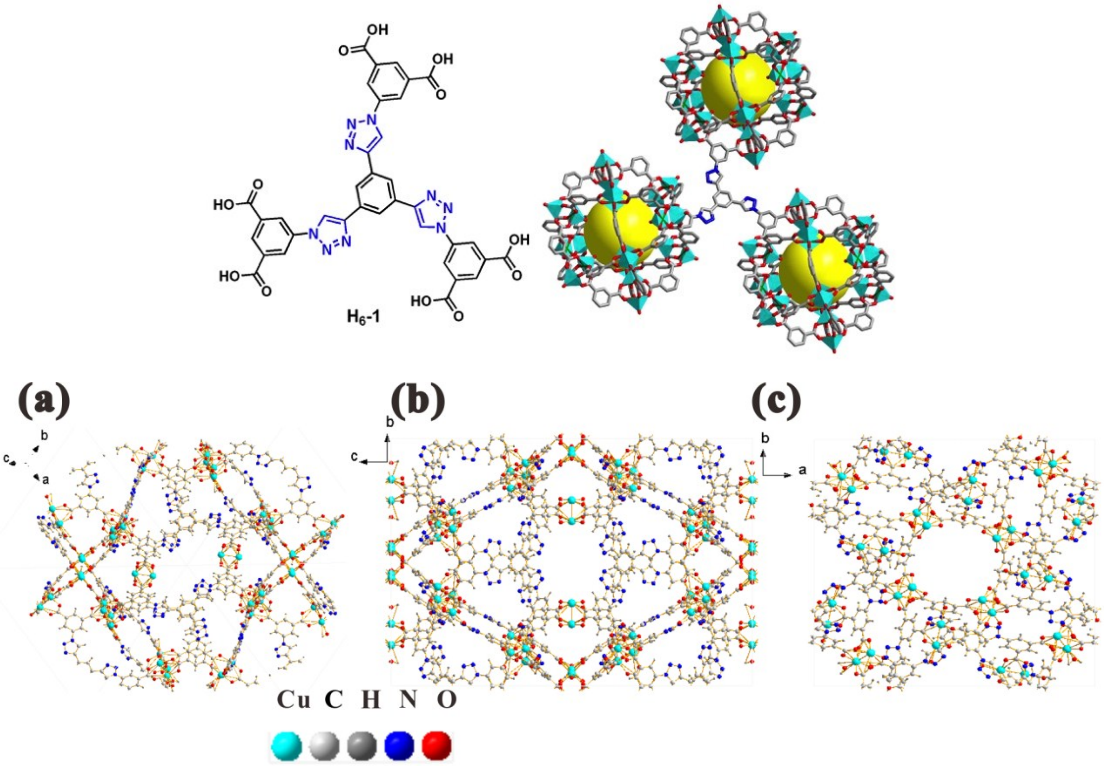

Fig. S1 Chemical structure of organic ligand H_6-1, and crystallographic structures of N-MOF crystal projected from different directions: (a) [111] direction, (b) [100] direction, and (c) [001] direction.

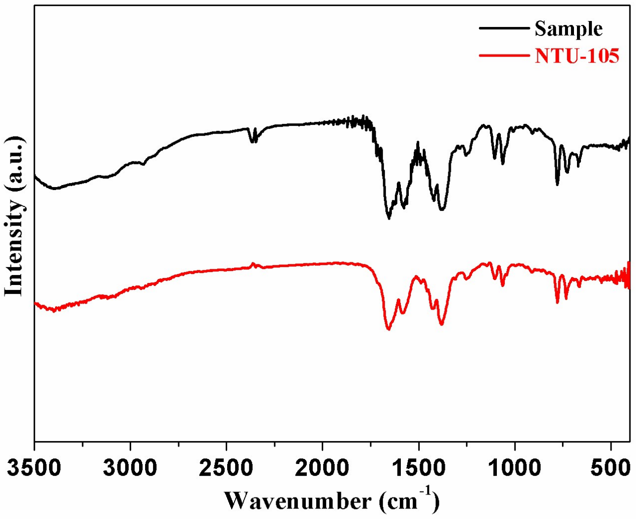

Fig. S2 FT-IR spectra of concave cubic N-MOF nanocrystal (Sample) and single crystal (NTU-105).

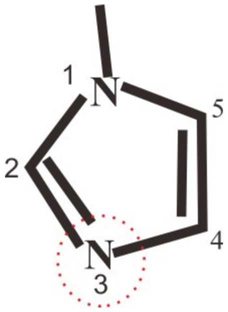

Fig. S3 Molecular structure of 1-methylimidazole.

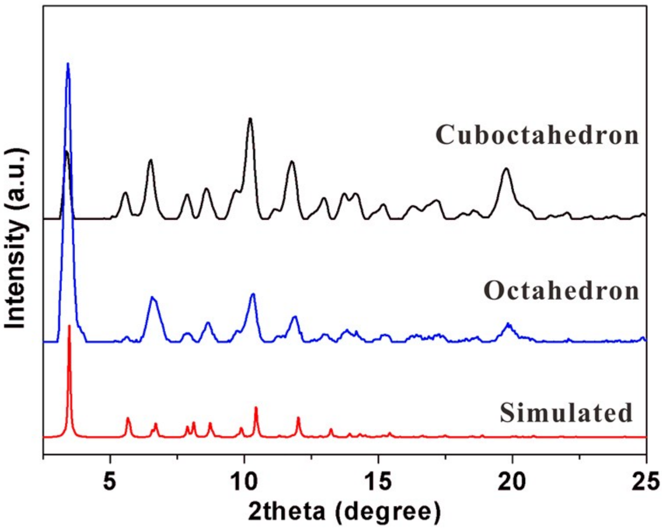

Fig. S4 Powder XRD patterns of octahedron and cuboctahedron nanocrystals. It can be seen that the synthesized octahedron and cuboctahedron are the pure phase of the NTU-105 MOF.

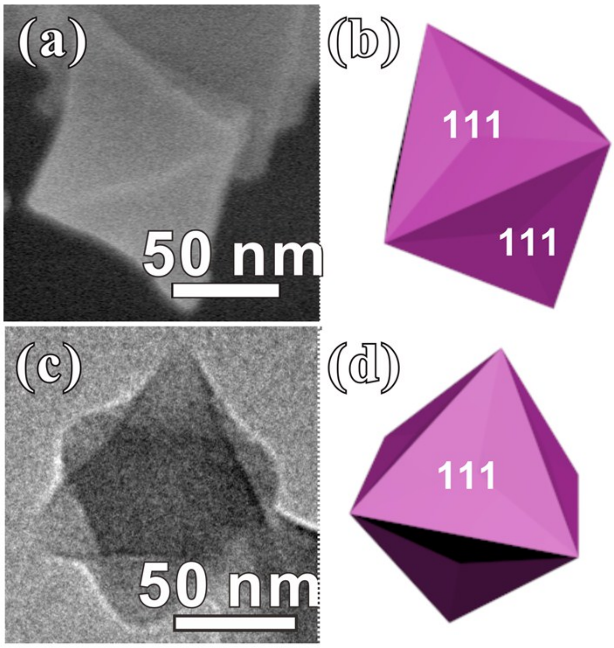

Fig. S5 (a,c) SEM and TEM images of single concave octahedral nanocrystal with different orientations, and (b,d) corresponding ideal geometrical models.

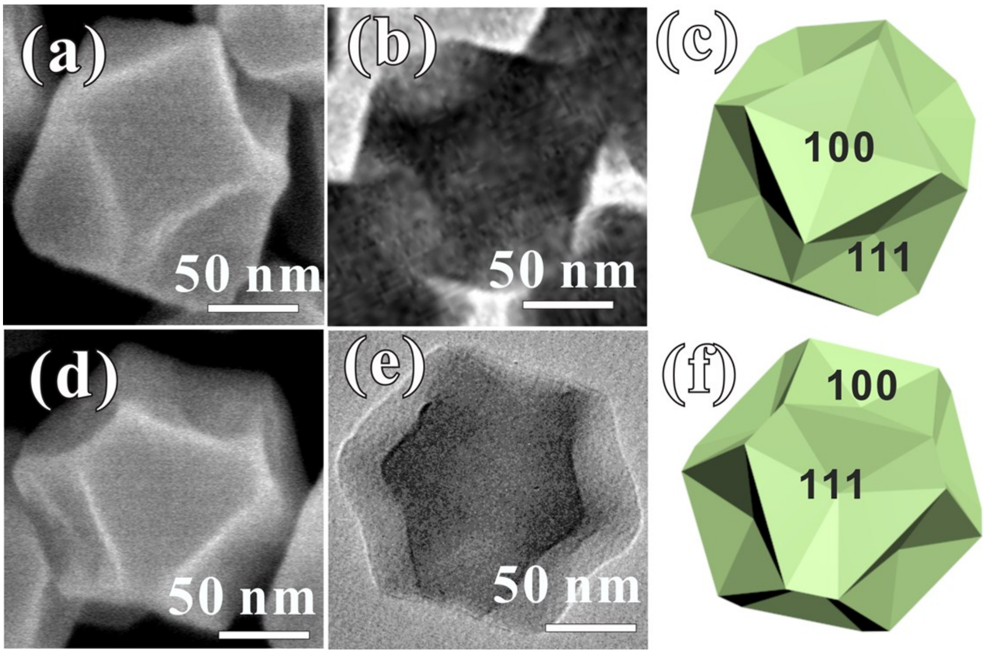

Fig. S6 (a,b) and (d,e) SEM and TEM images of single concave cuboctahedral nanocrystal with different orientations, and (c,f) corresponding ideal geometrical models.

According to the crystal data of the N-MOF (NTU-105), we built corresponding models exposed with [010], [001], and [100] direction surfaces, *i.e.*, Fig. S5b,d corresponds to concave octahedron with [111] direction surface, and Fig. S6c,f is for concave cuboctahedron with exposed [111] and [100] direction surfaces. The models match well with the SEM and TEM images of nanocrystals (Fig. S5 and S6), indicating that the cube of N-MOF nanocrystals was exposed with more percentages of [001] and [100] direction surfaces than that of octahedron and cuboctahedron morphologies.

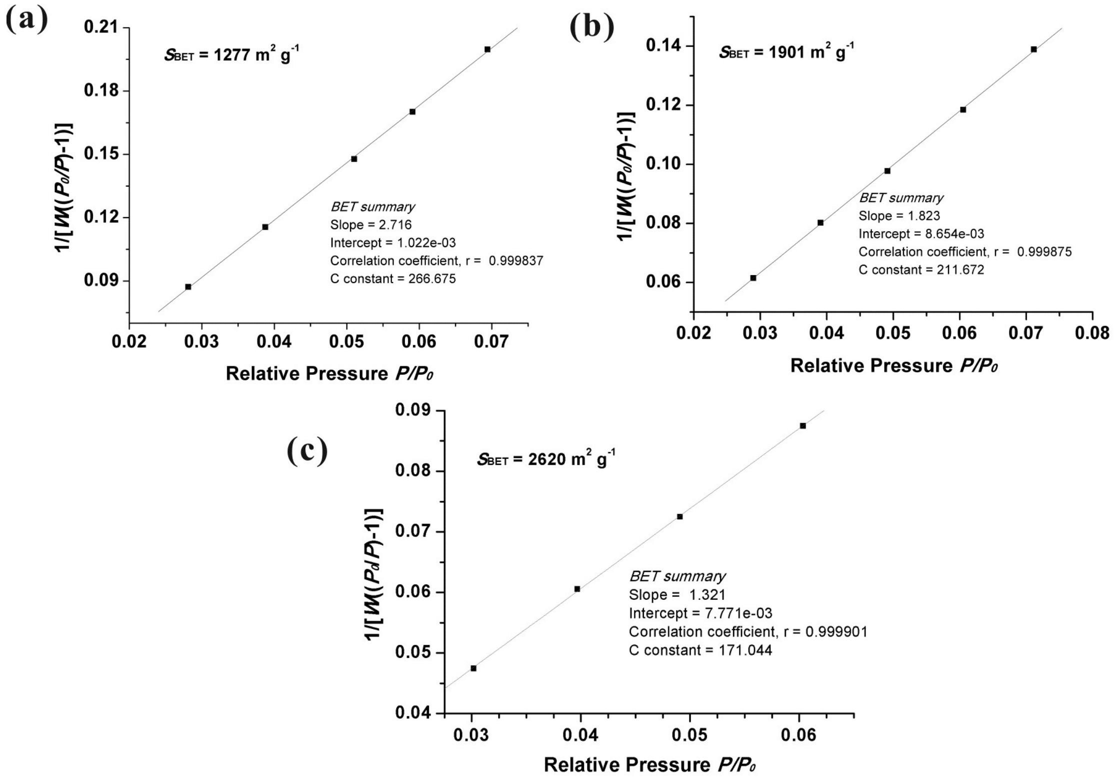

Fig. S7 BET linear plots for three samples: (a) Sample 3 (octahedron), (b) Sample 2 (truncated octahedron), and (c) Sample 1 (cuboctahedron).

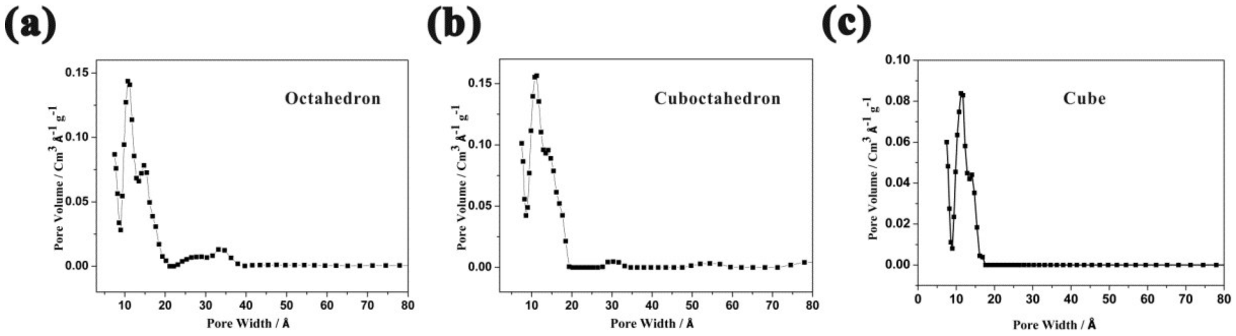

Fig. S8 Pore size distribution plots of (a) octahedron, (b) cuboctahedron, and (c) cube nanocrystals.

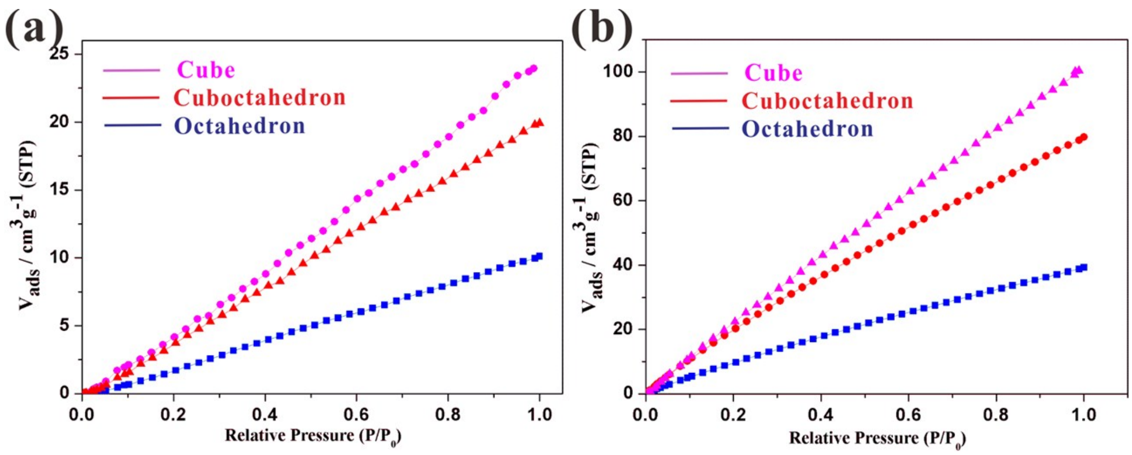

Fig. S9 (a) CH_4 adsorption isotherms at 298 K, and (b) CO_2 adsorption isotherms at 298 K.

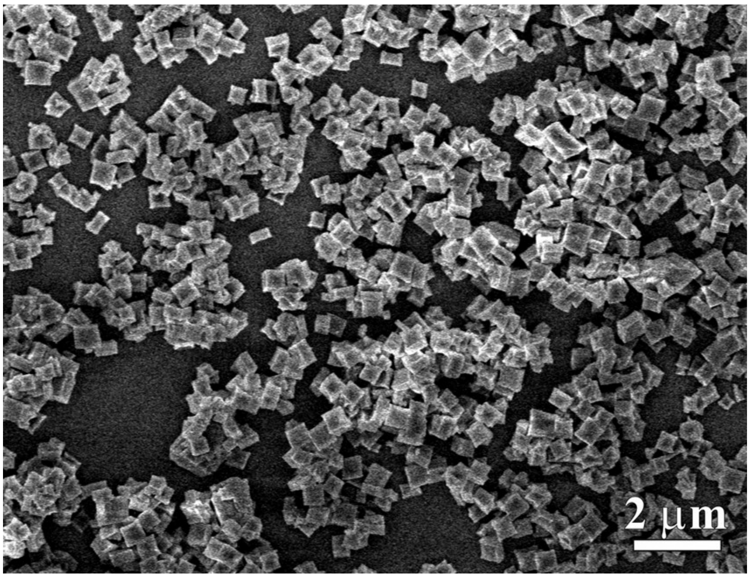

Fig. S10 SEM image of cubes after gas uptake.

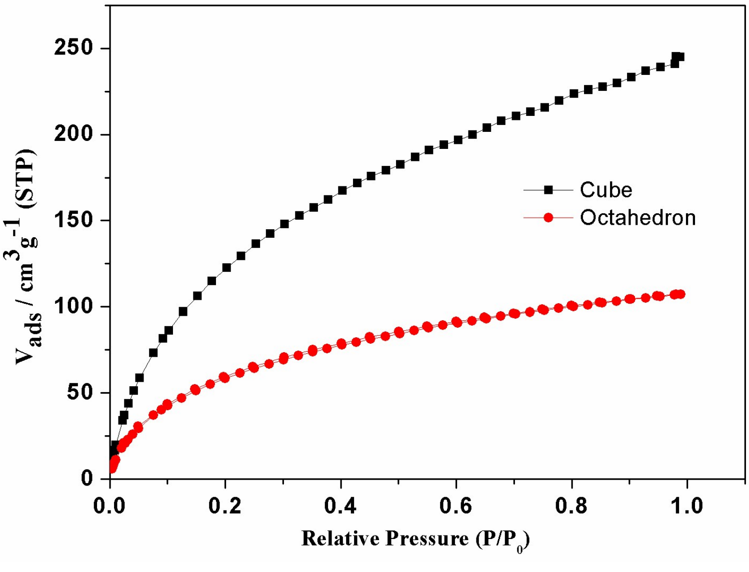

Fig. S11. H_2 adsorption isotherms of cube and octahedron at 77K. The results show that the cubes possess higher H_2 uptake capability than that of octahedrons.