Surfactant-assisted synthesis of large Cu-BTC MOFs single crystals and the potential utilization as photodetectors

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Experimental

1. Materials

   Pluronic F-127 (PF-127) and 1, 3, 5-Benzenetricarboxylic acid ($C_6H_3(COOH)_3$, H_3BTC), from aldrich, copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) and ethanol from Wako Chemical were used without further purification. All solvents were prepared by using Milli-Q water.

2. Characterization

Powder X-ray diffraction data were collected on a Rigaku (D/MAX-2500/PC) diffractometer using Cu-Kα radiation (λ= 1.54056 Å) at room temperature.To prepare the samples for field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3), the HKUST-1 powders were re-dispersed in the DI water, dropped onto carbon tape, and finally dried at 40 °C in the oven. Diffuse reflectance spectra were obtained using a PerkinElmer Lamda 750 spectrometer with an integrating sphere detector in the wavelength range from 2500 to 220 nm. UV-vis absorption spectroscopy (Lambda 750 UV-vis spectrometer, PerkinElmer 220 nm ~ 2500 nm), Fourier Transformation-infrared Spectrometer (FTIR, Bruker Tesnor 27), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB250Xi) and equipped Ultraviolet photoelectron spectroscopy (UPS) were carried out for both HKUST-1 and Cu-BTC dense MOFs (*Cu-s*) at room temperature. All samples were ground well before measurements. For UV-vis, all powder samples were diluted to 10 wt% with dry $BaSO_4$ and the diffuse reflectance spectra were converted into Kubelka–Munk (K–M) functions with the concentration corrections. For FTIR measurements, all powder samples were diluted to 10 wt% with KBr. The I-V electrical measurements (I-V curves) in dark and under illumination were carried out by two point measurement through I-V Probe station (NANORian Technologies) equipped with Keithley 2400 sourcemeter. It was able to fabricate the simple devices for I-V electrical measurements thanks to the large size of single crystal (Figure S1). Briefly, Ag paste was first coated at the two ends of *Cu-s*, then the *Cu-s* crystal was put on a slice of glass, and finally more Ag paste was used to fix the *Cu-s* firmly on the glass.

Scheme S1: Illustration of fabrication of a simple device for I-V electrical measurements on a glass slide.

Single-crystal X-ray structural analysis

X-ray diffraction measurement was conducted using a Rigaku XtaLAB-Synergy diffractometer with a HyPix-6000 area detector and a multilayer mirror-monochromated Cu Kα radiation (λ = 1.54184 Å) at 150 K. The crystal was mounted on a MicroMount with paratone-N oil. Diffraction data were collected and processed using *CrysAlisPro* software.[R1] The structure was solved by the direct methods using *SHELXT*.[R2] Structural refinements were conducted by the full-matrix least-squares method using *olex2.refine*.[R3] Non-H atoms were refined anisotropically, and H atoms were refined using the riding model. All calculations were performed using *Olex2*.[R4] The crystallographic data are summarized in Table S1 together with the reported data.

Computational methods

The DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP) within the projector augmented wave (PAW) formalism in conjunction with the PBE parameterization of the generalized gradient approximation to the exchange correlation functional. We adopted the parameters Gu. Et at.al [R5] and used an on-site Coulomb interaction of U = 5 together with a spin-polarized, anti-ferromagnetic setting yielding the lowest energy. A plane wave basis set with a cutoff energy of 520 eV was used, together with a $2 \times 2 \times 2$ k-points mesh. The atomic and cell degrees of freedom were relaxed till the forces acting on the atoms were less than 0.01 eV/atom and the stress was less than 1 kbar.
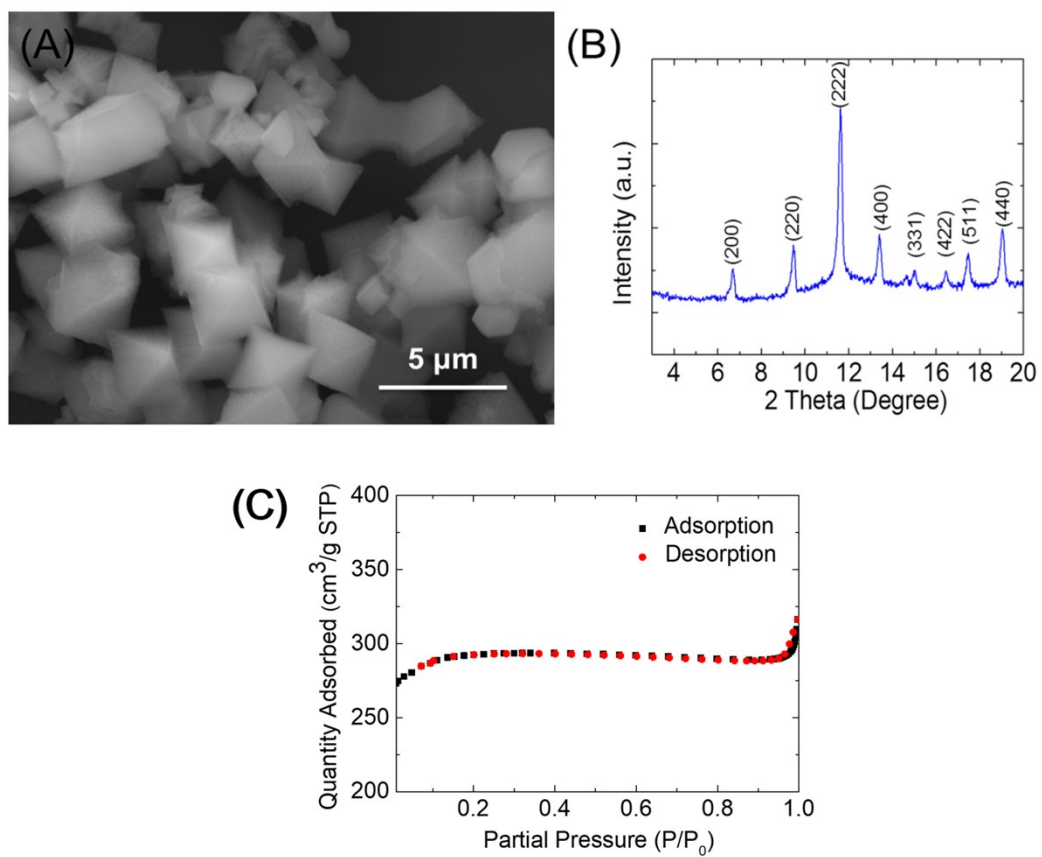
Figure S1 (A) SEM image, (B) P-XRD pattern, and (C) N_2 Adsorption-desorption isotherms of powder-like precipitants synthesized in our work. (The powder-like precipitant was proved to be HKUST-1).
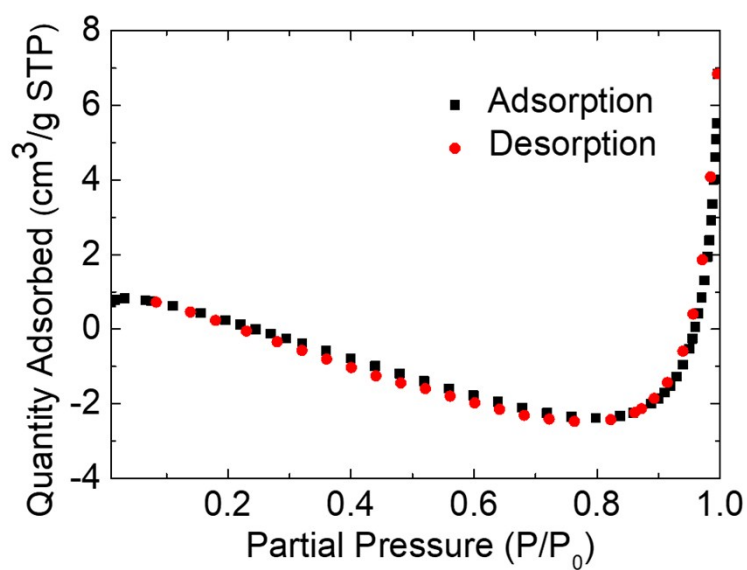

Figure S2: N_2 Adsorption-desorption isotherms of crystal-like precipitants (*Cu-s*).

	This data	Previous report[R6]
formula	$C_9 H_{10} Cu O_9$	$C_9 H_{10} Cu O_9$
fw	325.72	325.71
crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a / Å	6.7741(1)	6.7778(7)
b / Å	18.8491(3)	18.8206(18)
c / Å	8.5298(1)	8.5384(8)
β / deg	92.503(1)	92.471(4)
V, Å^3	1088.09(3)	1088.09(3)
Z	4	4
d_{calc} / g cm^{-3}	1.9882	1.988
T / K	150	143
radiation / Å	1.54184 (Cu Kα)	0.71073 (Mo Kα)
index ranges	-8 < h< 8, -23 < k < 23, -10 < l < 7	-8 ≤ h ≤ 8, -24 ≤ k ≤ 24, -11 ≤ l ≤ 11
reflections collected	13526	37602
unique reflections	2290	2488
data/restraints/params	2290 / 4 / 182	2488 / 0 / 173
completeness	0.9858	0.997
R_{int}	0.0310	0.0170
R_1 ($I > 2\sigma(I)$)	0.0656	0.0194
wR_2 (all data)	0.1968	0.0526
GOF on F^2	1.0442	1.112

Table S1: Summary of structure determination of ***Cu-s*** and comparison with the previous reported structure of Cu(BTC)•3H$_2$O (CCDC: 99209).
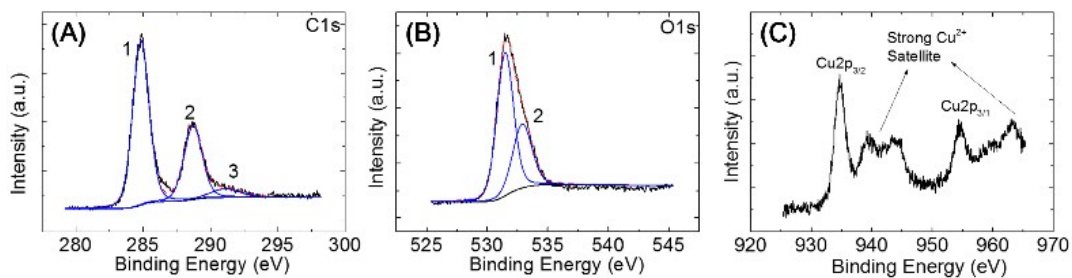
Figure S3: XPS data of *Cu-s*: (A) C 1s spectra fitted by three peaks; (B) Cu 2p spectra; (C) O1s spectra fitted by two peaks.
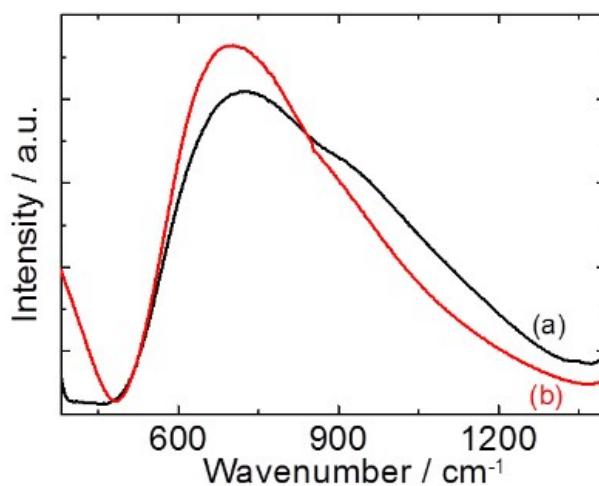

Figure S4: UV-vis spectra of (a) porous Cu-BTC MOFs (HKUST-1) and (b) dense Cu-BTC MOFs (*Cu-s*).

Reference

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