

ARTICLE

Increased proton conductivity of Metal–Organic Framework micro-film prepared by a facile salt-free approach

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Experimental details

Materials.

1,3,5-benzenetricarboxylic acid (BTC, Trimesic acid, 95%, Alfa Aesar), anhydrous ethanol (EtOH, AR) and N,N-dimethylformamid (DMF, 99.8%, AR) were commercially available and used without further purification, and the water was double-distilled and deionized.

Method

X-ray diffraction (XRD) data were taken with a Bruker D8 ADVANCE powder X-ray diffractometer with (Cu K_α). Scanning electron micrographs (SEM) were taken with a JSM-6330F microscope. The high-resolution transmission electron microscope (HRTEM) image was taken with a FEI Tecnai G2 F30 transmission electron microscope (Holland), using an accelerating voltage of 300 kV. X-ray photoelectron spectrometer (XPS) was taken with an ESCALab250 spectrometer. Thermogravimetric analysis (TGA) was performed on a Netzsch TG-209 F1 Thermogravimetric Analyzer at a heating rate of 10°C min⁻¹ under a nitrogen gas flow of 20 mL·min⁻¹. Relative humidity was controlled by sealing the HKUST-1 microfilm in a quartz cell which contained various saturated salt solutions at room temperature (25°C)^{1,2}, kept for 1day to 3days in the cell.

The conductivity of the sample was calculated from the impedance value using the following equation.

$$\sigma = \frac{L}{Z \cdot A}$$

where σ is the conductivity (S cm⁻¹), L is the measured sample thickness (cm), A is the electrode area (cm²) and Z is the impedance (Ω).

The electrical properties were measured by solarton 1260 Impedance/Gain-Phase analyzer. The AC impedance was carried out with solarton 1260 Impedance/Gain-Phase analyzer, in the frequency range 0.1Hz-10MHz with inputting voltage amplitude of 300mV. The DC polarization experiments were carried out with solarton 1260 Impedance/Gain-Phase analyzer and 1287 electrochemical interface, using Potentiostatic mode. The conductivity of the microfilm was calculated by the method in reference 22. Two platinum wires were attached on the same side of the HKUST-1 microfilm with silver paste (purchased from the Alfa Aesar). The distance between two electrodes is 6.5 mm (L). The thickness of the microfilm investigated by SEM was about 20 μ m (Figure S1), the width is 8.5 mm (A = 20 \times 10⁻⁴ cm \times 0.85 cm). The disk-shaped pellet of the HKUST-1 powder was prepared under the press (4MPa), the size of the disk-shaped pellets are 10.98 mm in diameter (A=0.25 \times π \times 1.098² cm²) and 3.01mm (L) in thickness. Both sides of the pellet were attached to platinum wires with silver paste.

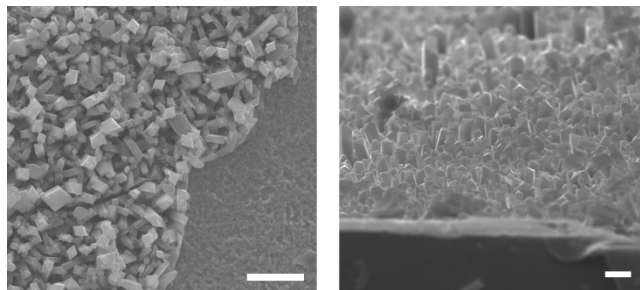


Figure S1 The cross-section of microfilm prepared for 19h. Scale bar is 20 μm .

Figure S1 showed that the thickness of microfilm was about 20 μm .

Figure S2 showed the film with size of 10 cm \times 10 cm. We believed that the film can be bigger since the reaction is mild and effective.



Figure S2 The photo of film with size of 10 cm \times 10 cm.

Figure S3 showed the SEM images with low magnification of HKUST-1 microfilm prepared for different time (2h-19h), from which one can see the film is very uniform.

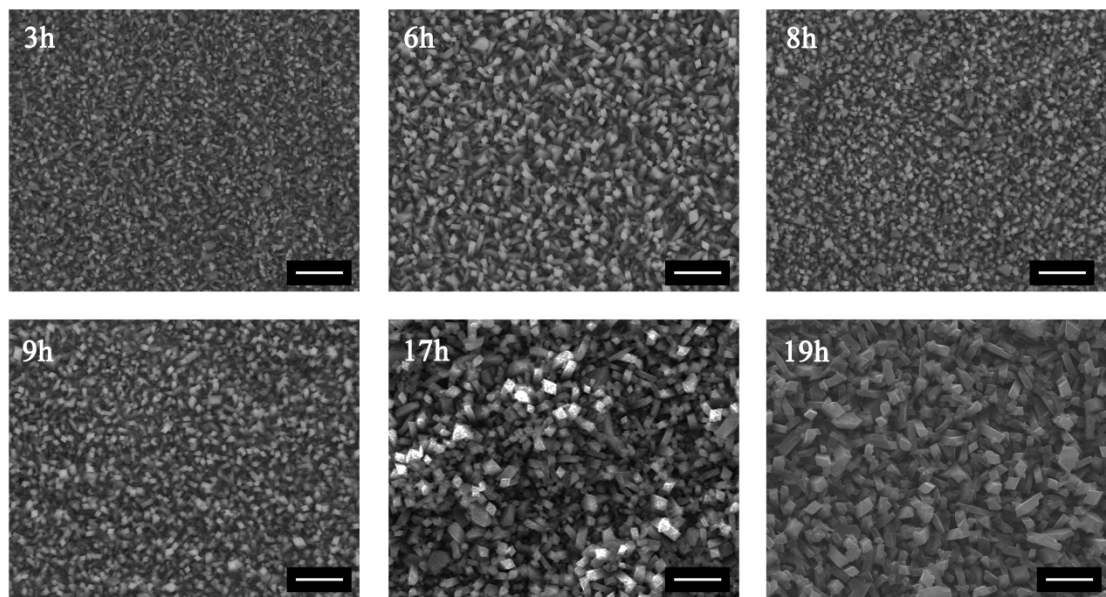


Figure S3 The low magnification SEM images of HKUST-1 microfilm prepared for different time (2h-19h). Scale bar is 10 μm .

The SEM images of samples prepared under hydrothermal condition were shown in Figure S4. These are uncovered copper foil after 12 h and 24 h. The substrate was “fully covered” till 72 h. Part of crystals on copper foil were removed by scraping the film carefully. From the cross-section image of 72 h sample one can see vacancies inside the film.

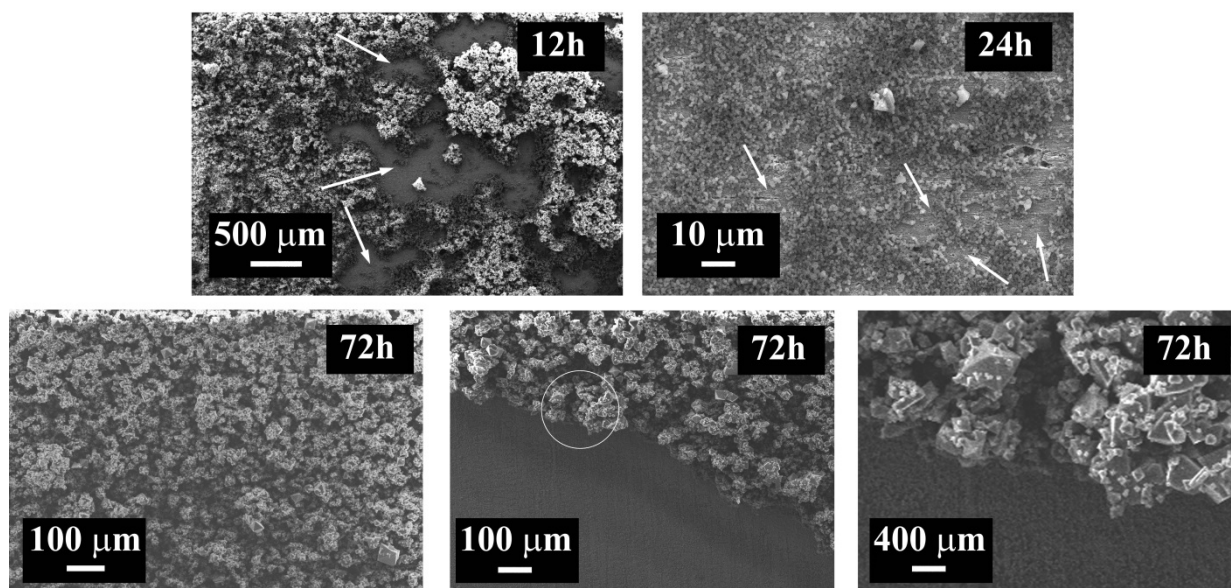


Figure S4 The SEM images of samples obtained under solvothermal condition.

XPS was used to characterize the oxidation number of copper in the film, as shown in Figure S5. There were typical Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks with the measured binding energies of 935.1 and 955.4 eV, respectively, and their concomitant shake-up lines at (940.9 eV, 944.3 eV) and (960.5 eV, 964.2 eV), indicating the chemical state of Cu^{2+} (Figure S5 b).³

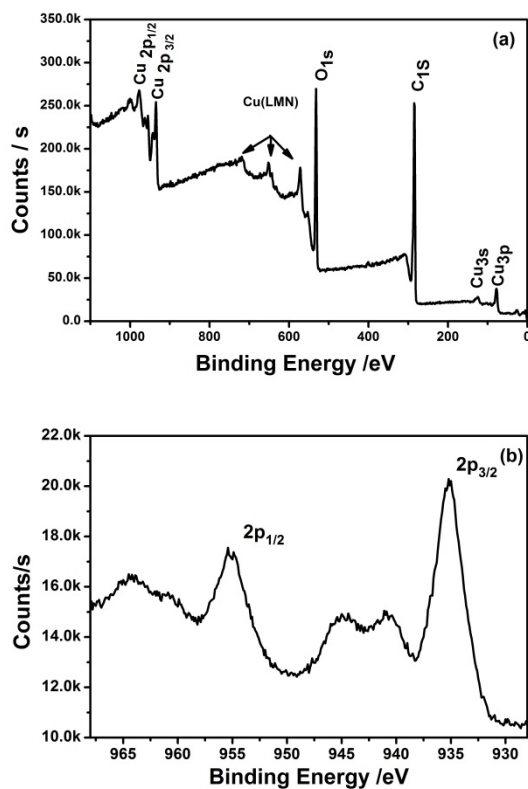


Figure S5. X-ray photoelectron spectrum of the as-prepared HKUST-1 microfilm on copper foil, (a) the survey (b) the Cu scan.

Figure S6 showed the thermogravimetric curve of the as-prepared HKUST-1 (reaction time:19h) kept under varying relative humidity, i.e. 63%, 75%, 85% and 98% RH at room temperature for 1day to 3days. The ramp rate is $10^{\circ}\text{C min}^{-1}$. TGA for HKUST-1 confirm that the amount of adsorbed guest water molecules increased significantly with the humidity and time.

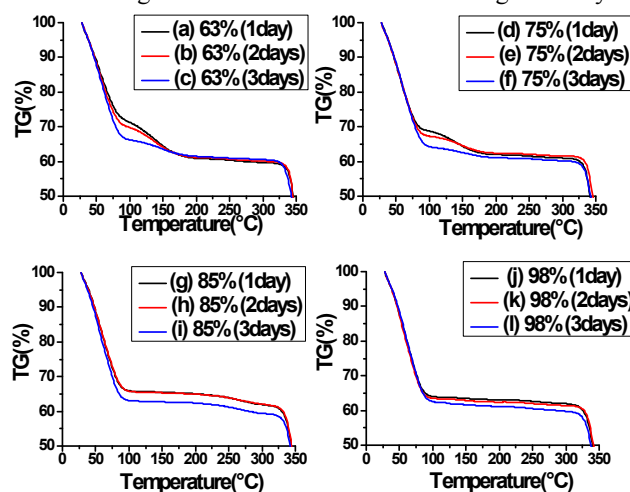


Figure S6. Thermogravimetric analysis curve for the as-prepared HKUST-1 (reaction time:19h) kept under different relative humidity, i.e. 63%, 75%, 85% and 98% RH at room temperature for 1day to 3days. The ramp rate is $10^{\circ}\text{C min}^{-1}$.

Figure S7 showed the XRD of as-prepared HKUST-1 microfilm kept under different RH for 1day to 3 days after impedance analysis. The phase of the HKUST-1 microfilm does not change under humidity.

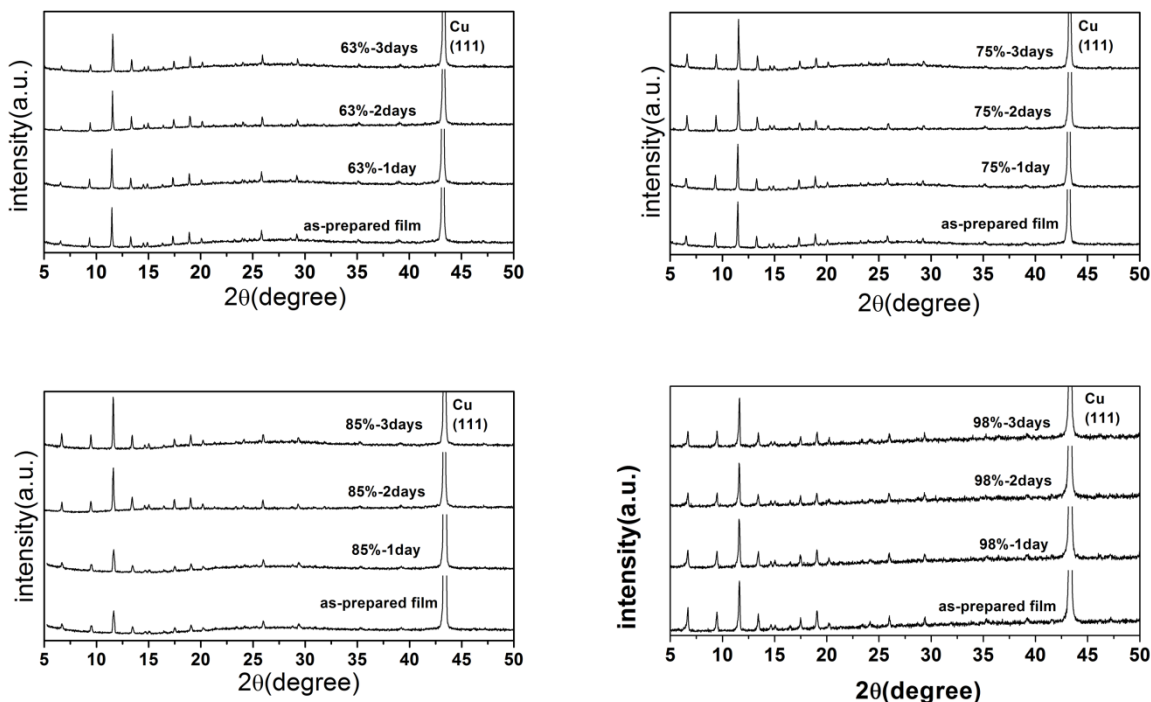


Figure S7. XRD for the as-prepared HKUST-1 microfilm (reaction time:19h) kept under different relative humidity, i.e. 63%, 75%, 85% and 98% RH at room temperature for 1day to 3days after impedance analysis.

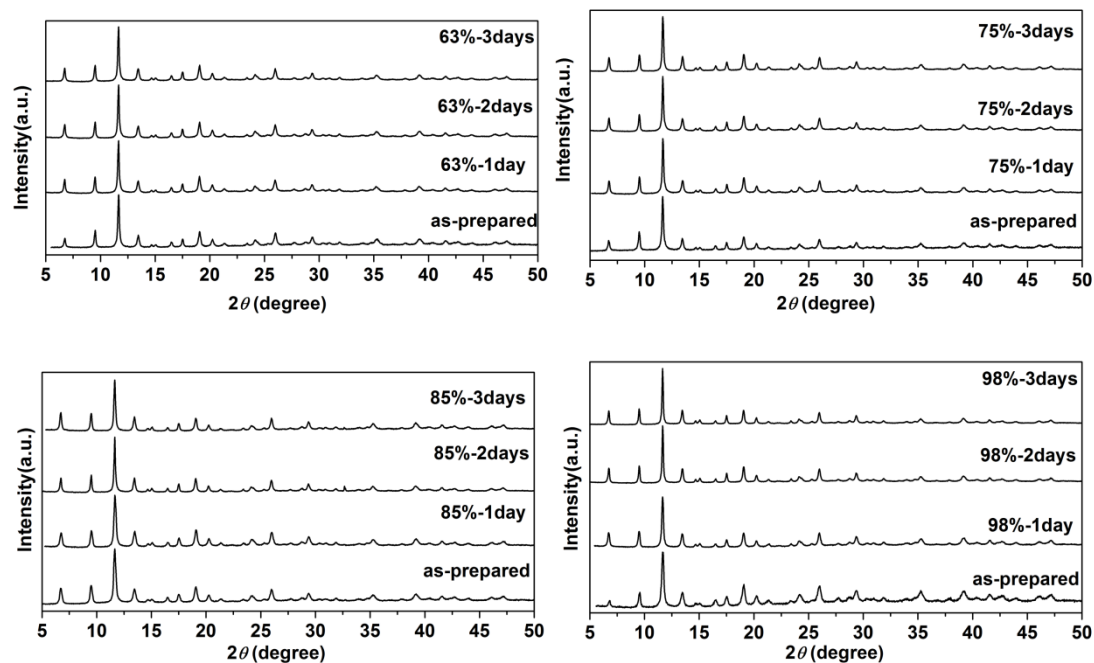


Figure S8. XRD for the as-prepared disk-shaped pellet of HKUST-1 powder kept under different relative humidity, i.e. 63%, 75%, 85% and 98% RH at room temperature for 1day to 3days after impedance analysis.

Figure S8 showed the XRD of as-prepared HKUST-1 microfilm kept under different RH for 1day to 3 days after impedance analysis. The phase of the HKUST-1 microfilm does not change under humidity.

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