

Electronic Supplementary Information

Design and fabrication of energetic metal-organic frameworks

[Cu(ntz)]_n film with high energy-density and stability †

Wei Liu, ‡ Chunpei Yu, ‡ Wenchao Zhang*, Qiang Xie, Yu Gao, Zilong Zheng and
Houhe Chen*

School of Chemical Engineering, Nanjing University of Science and Technology
Xiaolingwei 200, Nanjing, Jiangsu, China.

‡ These authors contributed equally to this work.

E-mail: zhangwenchao@njust.edu.cn (*W. Zhang*); and chhh42792@sina.cn (*H. Chen*).

Table of Contents		
1.	Experimental section	S3
2.	Figure S1 3D microscope images and photographs of samples.	S5
3.	Figure S2 EDS of [Cu(ntz)] _n film.	S6
4.	Figure S3 Elemental mapping images for [Cu(ntz)] _n film.	S7
5.	Figure S4 DSC-TG curves of [Cu(ntz)] _n scraped from CCL substrate.	S8
	References	S9

1. Experimental section

Caution

Although no explosion or hazards were observed during the preparation and handling of materials studied in this work, all compounds investigated are energetic materials and tend to explode under certain conditions. Small-scale preparation are strongly encouraged. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times.

Materials and instruments

All reagents and starting materials were purchased commercially in analytical grade and were used as obtained from the supplier, if not stated otherwise. The decomposition (onset) points were obtained on a differential scanning calorimeter (Mettler Toledo DSC823^e) at a heating rate of 5 °C ·min⁻¹ in closed Al containers with a high-purity nitrogen flow of 50 mL ·min⁻¹. TGA were also performed at a heating rate of 5 °C ·min⁻¹ in flowing high-purity nitrogen on a Mettler Toledo TGA/SDTA851^e instrument. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The morphologies of the sample was measured with FEI field-emission scanning electron microscope (SEM, Quanta 250F) equipped with an energy dispersive X-ray spectrometer (EDS). The ignition performance of the obtained film was investigated by a Nd:YAG laser device. The whole ignition progress was recorded by a high-speed camera (Redlake Motion Xtra HG-100K) running at 25000 frames per second.

Preparation procedures

(1) Electrochemical deposition of cuprous azide transition layer

Prior to the deposition of cuprous azide transition layer, the copper clad laminate (CCL) substrates were cut into square wafers (1.0×1.0 cm²), cleaned by sonicating in acetone and ethanol for 10 min sequentially, and then stored in pure ethanol. Before use, they were taken out and dried in air.

The electrochemical deposition experiment was carried out in a two-electrode electrochemical cell using a 1.0×1.0 cm² CCL substrate as the working electrode, a parallel positioned platinum 1.0×1.0 cm² plate as the counter electrode. The electrolyte

contained 0.05 mmol NaN_3 and 25 mL distilled water. The CCL substrate was submerged and exposed to the deposition bath. By applying a voltage (1.5 V) using a direct current (DC) power source for an optimized deposition time of 15 min, the gray cuprous azide thin layer was then grown on the anode at room temperature. After deposition, the coated CCL substrate was removed from the holder and gently rinsed with water three times to remove the excess NaN_3 .

(2) Solvothermal synthesis of $[\text{Cu}(\text{ntz})]_n$ films

$[\text{Cu}(\text{ntz})]_n$ film was prepared from a solution of Hntz (0.011 g, 0.1 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.0725 g, 0.3 mmol) dissolved in 6.5 ml distilled water. The modified CCL substrate was placed at the bottom of a Teflon-lined autoclave to allow crystal growth at 120 °C for 3 days under autogenous pressure. After crystallization, the red-brown $[\text{Cu}(\text{ntz})]_n$ film was washed with distilled water for three times, and dried at room temperature.

(3) Synthesis of $[\text{Cu}(\text{ntz})]_n$

$[\text{Cu}(\text{ntz})]_n$ was synthesized via a solvothermal process reported by Chen group previously¹. Briefly, a mixture of Hntz (0.1 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.3 mmol) and 0.5 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ were dissolved in 6 ml distilled water. After stirring for 30 min in air, the system was sealed in a 25 ml Teflon-lined stainless autoclave and heated at 90 °C for three days under autogenous pressure and subsequently allowed to cool to room temperature at a rate of 5 °C \cdot h⁻¹. Red-brown block crystals were collected and washed with water and dried in air.

2. 3D microscope images and photographs of samples

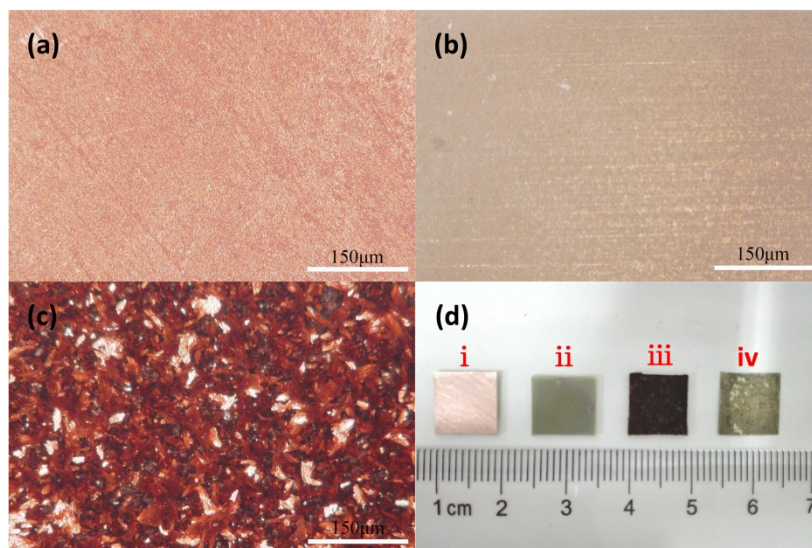


Fig. S1 3D microscope images of (a) CCL substrate; (b) cuprous azide transition layer; (c) [Cu(ntz)]_n film. (d) Photographs of CCL substrate (i), modified CCL substrate (ii), [Cu(ntz)]_n film grown on the modified CCL substrate (iii), and unsuccessfully synthesised [Cu(ntz)]_n film grown on the CCL substrate (iv).

3. EDS of [Cu(ntz)]_n film

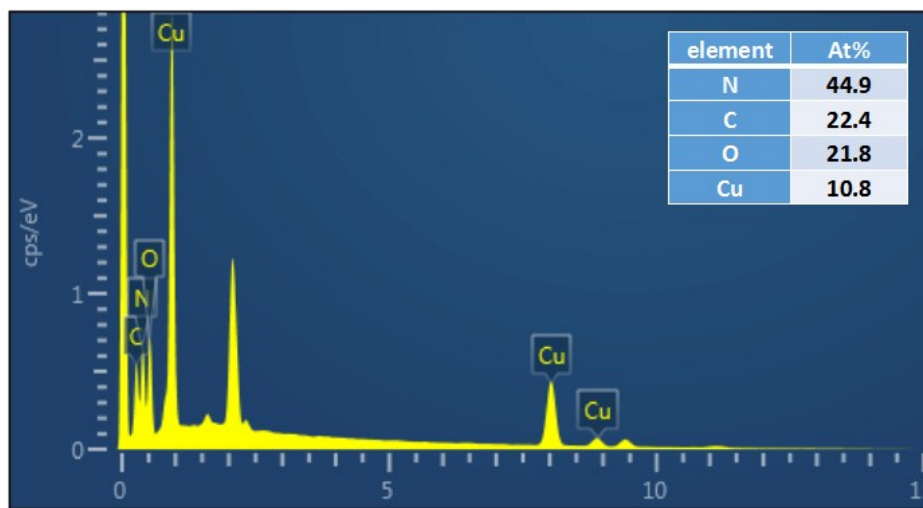


Fig. S2 EDS of [Cu(ntz)]_n film.

4. Elemental mapping images for $[\text{Cu}(\text{ntz})]_n$ film

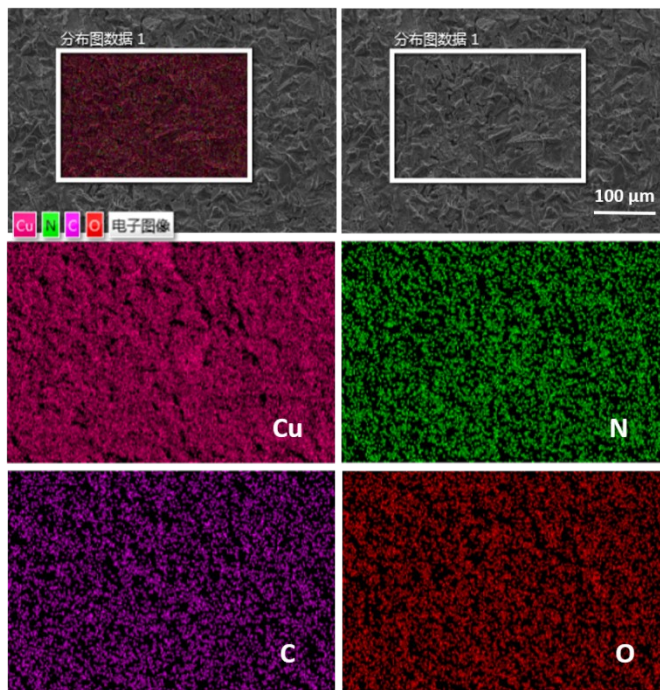


Fig.S3 Elemental mapping images for $[\text{Cu}(\text{ntz})]_n$ film.

5. DSC-TG curves of $[\text{Cu}(\text{ntz})]_n$ scraped from CCL substrate

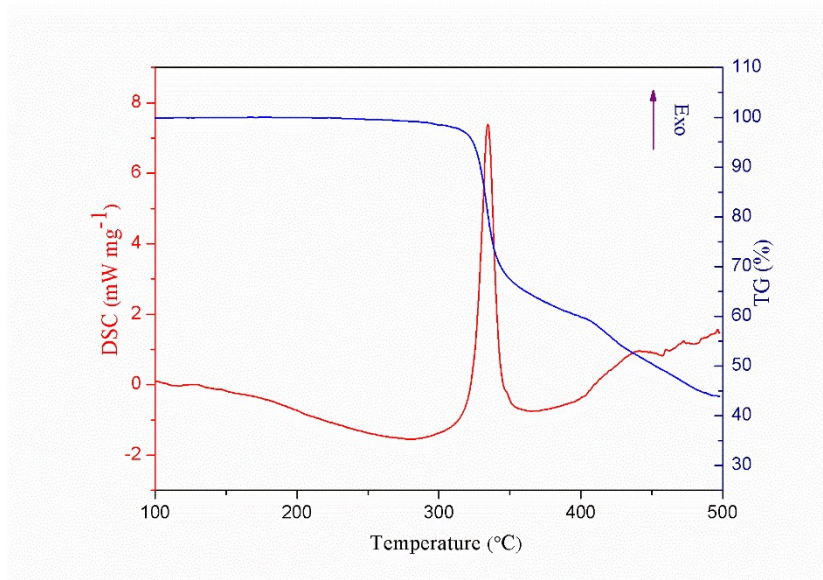


Fig.S4 The DSC-TG curves of $[\text{Cu}(\text{ntz})]_n$ scraped from CCL substrate.

References

- 1 X. Qu, L. Zhai, B. Wang, Q. Wei, G. Xie, S. Chen and S. Gao, Dalton Transactions, 2016, 45, 17304-17311.