

Supplementary Material

**Preparation and Characterization of an Edible Metal-
Organic Framework/Rice Wine Residue Composite**

Teer Ba, Chenyang Shen, Xiaoshan Zhang, Chang-jun Liu*

Collaborative Innovation Center of Chemical Science & Engineering, School of
Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

E-mail address: cjL@tju.edu.cn

Experimental Section

Materials

γ -cyclodextrin (γ -CD) was purchased from Energy Chemical (Shanghai, China), while KOH, NaOH, isopropanol (*i*PrOH), CTAB, H₃BTC, 2-methylimidazole, MeOH, Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O, and FeCl₂·4H₂O were all obtained from Shanghai Aladdin Biochemical Technology Co. Ltd., China. Rice wine residue was made in Hubei Mipopo Biotechnology Co. Ltd., China. All the materials aforementioned were used without any further purification.

Synthesis of γ -CD-MOF Powder

γ -CD-MOF was synthesized based on a slight modification of the method previously reported by Liu *et al*^{S1}. γ -CD (162 mg, 0.125 mmol) and KOH (56 mg, 1 mmol) were dissolved into a 5 mL aqueous solution, then the mixed solution was filtered through a 0.45 μ m organic filter membrane into a beaker with the pre-addition of 0.5 mL MeOH. The vapor diffusion of MeOH at 50 °C for 24 h was followed. After that, the supernatant was then transferred into another beaker. CTAB (8 mg·mL⁻¹) was then added to it in order to induce the rapid precipitation of crystalline MOFs. The suspension was incubated at room temperature overnight. Finally, the precipitate was washed three times with *i*PrOH and dried by vacuum freeze-drying for 12 h.

Synthesis of HKUST-1

HKUST-1 was synthesized at room temperature according to the method previously reported in the literature^{S2}. 7.7 mmol (1.82 g) Cu(NO₃)₂·3H₂O and 4.2 mmol (0.875 g) H₃BTC were dissolved in 50 mL MeOH, respectively. They were mixed followed by vigorous stirring for 10 seconds and placed at room temperature for 2 h without any disturbance. The consequent bright blue precipitate was obtained by centrifugation and washed with MeOH three times. The obtained sample was then dried overnight at 60 °C under vacuum.

Synthesis of ZIF-67

ZIF-67 was synthesized at room temperature via the method previously reported in the literature.^{S3} $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3 g, 1 mmol) and 2-methylimidazole (0.66 g, 8 mmol) were dissolved in 15 mL MeOH, respectively. They were mixed and stirred at 600 rpm for 1 h. The consequent purple precipitate was obtained by centrifugation and washed by MeOH three times. The sample was then dried at 80 °C for 12 h.

Synthesis of MIL-100(Fe)

Based on the previously reported method^{S4}, two solutions should be prepared firstly. Solution 1 was 23.72 g of 1 M NaOH (22.8 mmol) aqueous solution containing 7.6 mmol (1.676 g) H_3BTC . Then 11.4 mmol (2.26 g) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 97 mL of deionized water to form Solution 2. Solution 1 was added dropwise into Solution 2. After the mixture of these two solutions became clear, the obtained solution was stirred for 24 h at room temperature. The precipitate was obtained by centrifugation and washed with water and MeOH three times, respectively. The sample was then dried at room temperature.

Synthesis of MOF-based Rice Wine Residue Composites

Rice wine residue was soaked in deionized water for 12 h. It was then washed with deionized water three times before being vacuum freezing-dried. Some certain amounts of the aforementioned dry rice wine residue were soaked in the precursor solution that contained metal ions. The obtained sample was then mixed with the organic ligand solution as described in the synthesis of the respective MOFs.

Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku D/MAX-2500 with $\text{Cu K}\alpha$ ($\lambda=1.54056 \text{ \AA}$) radiation. The diffraction data were collected with a scanning rate of $4^\circ/\text{min}$ at the 2θ angle from 5° to 40° .

Thermogravimetry analyses (TGA) were carried out on a Netzsch STA 449 F3 under the flow of air with 100 mL min^{-1} . The samples were heated from room temperature to $800 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$.

Nitrogen adsorption/desorption isotherms were measured on a Quantachrome, AUTOSORB-1-C at 77 K to explore the specific surface area and pore distributions of the samples.

Scanning electron microscopy (SEM) was used to characterize the morphology of the samples using a scanning electron microscope (S-4800). All the samples were immobilized via double-sided, conductive adhesive tape and sprayed with gold before being observed.

Fourier-transform infrared (FT-IR) spectra were conducted on a Tensor 27 spectrometer (Bruker, German) with a scanning range of 4000-400 cm^{-1} .

Elemental analysis (EA) was conducted by a LECO-TC500 elemental analyzer to investigate the atomic ratio (C, H, N) of the rice wine residue.



Fig. S1. Digital images of HKUST-1/RWR composite, ZIF-67/RWR composite and MIL-100(Fe)/RWR composite

Table S1. Elemental analysis of pure rice wine residue

Content (atom%)		
C	H	N
49.34	6.62	8.19

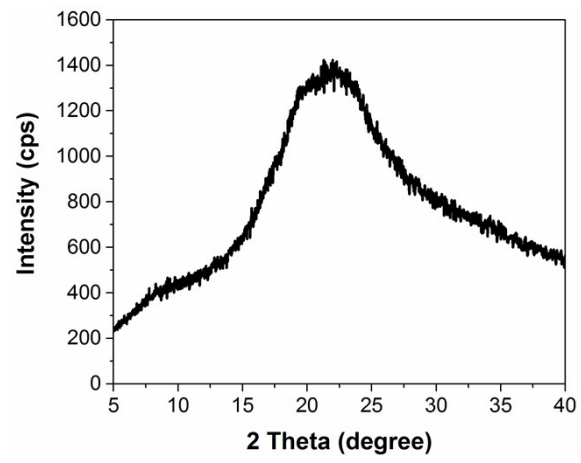


Fig. S2. XRD pattern of pure rice wine residue

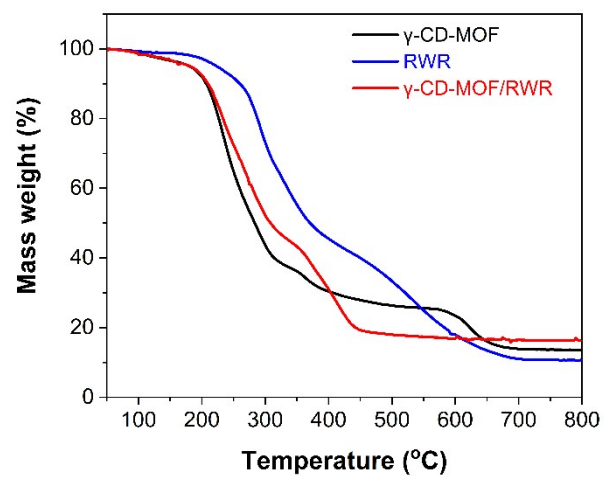


Fig. S3. Thermogravimetric analysis of γ -CD-MOF/RWR composite

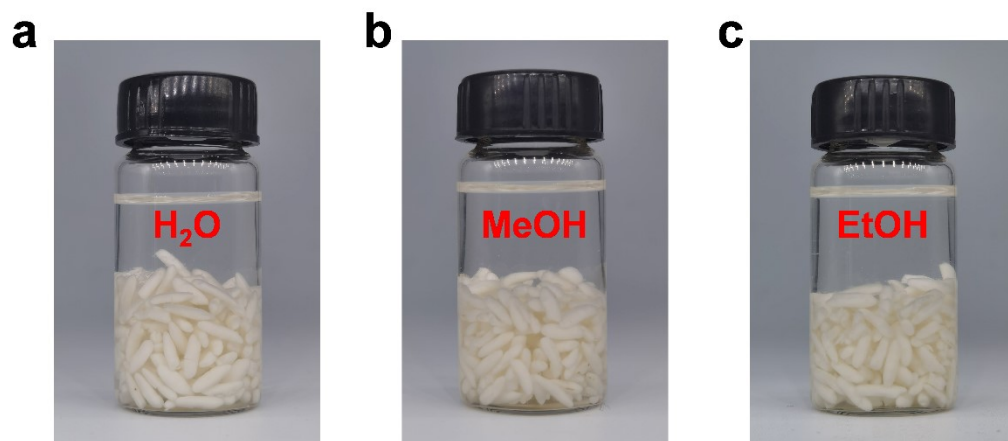


Fig. S4. Digital photos of γ -CD-MOF/RWR composite soaked in a) water; b) methanol and c) ethanol. The samples remain stable for more than a year tested.

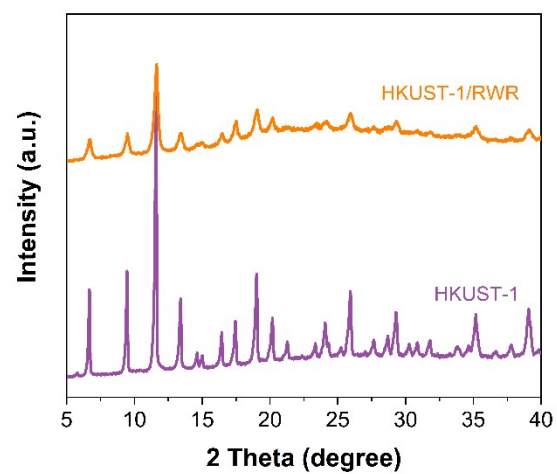


Fig. S5. XRD patterns of HKUST-1 and the corresponding composite

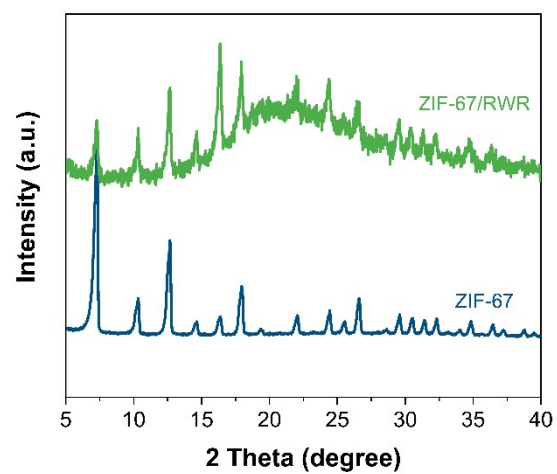


Fig. S6. XRD patterns of ZIF-67 and the corresponding composite

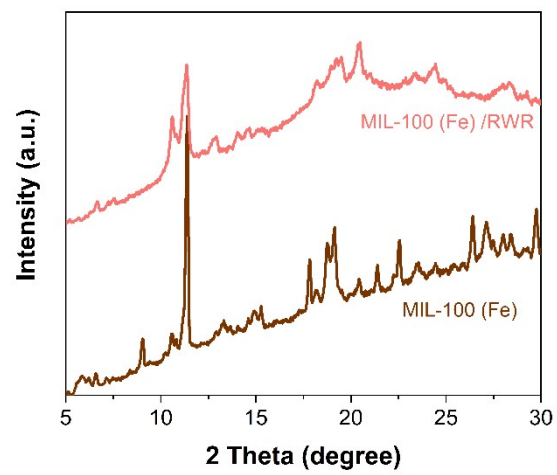


Fig. S7. XRD patterns of MIL-100(Fe) and the corresponding composite

References

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