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Surface wettability switching of metal-organic framework mesh for oil-water separation

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ABSTRACT

The surface wettability switching of JUC-150 Metal-Organic Framework (MOF) mesh from hydrophilicity to hydrophobicity was achieved by a facial polydimethylsiloxane (PDMS) modification method. The PDMS modified JUC-150 mesh (JUC-150@PDMS mesh) exhibited high oil-water separation efficiency and flux attributed to the porous structure of the nickel mesh substrate. The passing phase (water or oil) through the MOF mesh can be determined according to the demand, which is of vital importance for industrial applications. Furthermore, this method is universal for other MOF meshes, films and membranes that will be applied in the field of water purification and gas mixture separation with steam.

1. Introduction

Metal-organic frameworks (MOFs), benefited from their crystallinity and tenability, have emerged as novel candidates in gas storage and separation [1,2]. Nowadays, turning MOFs into membrane materials [3] and exploring their performances for applications in separation and purification have attracted great interests of researchers working in the fields of chemistry, chemical engineering, materials science, etc. [4–7].

At present oil leakage and oil-contaminated water need to be addressed urgently since it has become a worldwide issue [8–11]. Developing new functional materials for efficient treatment of oily water is therefore imperative. Currently, the research of “smart” surface with reversible wettability has aroused great interests [12–15], especially the wettability switching between hydrophobicity and hydrophilicity drived by external stimuli, such as light, temperature, electricity, solvent, etc. However, the transitions of surface wettability triggered by the aforementioned approaches generally require a long period of time, even several weeks, which restricts their large-scaled uses. Additionally, these approaches need either complex steps or special equipment to be carried out. Hence, it would be highly demanded to manipulate the wettability transition with a time saving and convenient method.

In this work, we will suggest a facial PDMS modification method to realize the surface wettability switching of MOF mesh. A hydrophilic and stable MOF (JUC-150) we previously synthesized was chosen to grow on the nickel mesh substrate [16]. After a simple in-situ growth step, the nickel mesh substrate was coated with intergrown JUC-150 crystals. Then, the hydrophilic surface of the MOF mesh could be turned into hydrophobic by 1 h PDMS modification. The JUC-150@PDMS mesh showed outstanding hydrophobic behavior. It allowed the oil phase to permeate through quickly, whereas the aqueous phase was effectively retained. The separation methodology was solely based on gravity, the results of which proved the JUC-150@PDMS mesh to be an energy-efficient oil-water filter (Fig. 1). Our work shows the great potential of the JUC-150@PDMS mesh for future practical applications in oil-water related separations. More importantly, this modification method is universal and can be extended to various MOF meshes, films and membranes, especially when they are applied in humid conditions.

2. Results and discussion

2.1. JUC-150@PDMS mesh

The JUC-150 MOF mesh was prepared by in-situ growth method on the nickel mesh substrate and the easy-operation PDMS modification was carried out at 220 °C for one hour. The powder X-ray diffraction (PXRD) patterns collected from the as-synthesized JUC-150 MOF mesh and JUC-150@PDMS mesh are shown in Fig. 2a. As can be seen, the PXRD patterns of the pristine and the modified JUC-150 meshes are in accordance with the simulated one of JUC-150. It suggests that high crystalline MOF crystals were grown on the substrate surface and their crystal characteristics were well preserved after the thermal PDMS modification step at high temperature,

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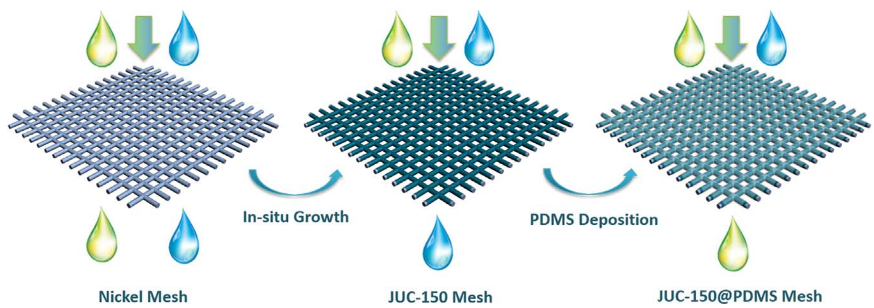

Fig. 1. Schematic illustration of the surface wettability switching of JUC-150 MOF mesh.

confirming the desired thermal stability of JUC-150 material.

Different magnification SEM pictures of the pristine JUC-150 mesh and JUC-150@PDMS mesh are shown in Figs. 2b and 2c. As seen in these pictures, JUC-150 crystals homogeneously covered the substrate surface, forming a continuous MOF layer with a roughness comparable to the size of the individual MOF crystals. After modification with PDMS, the outlines of the JUC-150 crystals could still be clearly distinguished (Figs. 2e and 2f), which means the MOF crystallinity was maintained well. This is consistent with the XRD results. The JUC-150@PDMS mesh exhibited smoother surface with a water contact-angle of 143.6° (Fig. 2d), suggesting the successful switching of the mesh surface wettability from hydrophilicity to hydrophobicity.

To investigate the interaction between JUC-150 and PDMS in JUC-150@PDMS mesh, XPS spectra were recorded and shown in the supporting information. As can be seen in Fig. S1b, the peak of Si 2p only appeared for JUC-150@PDMS, suggesting the successful modification of JUC-150 mesh with PDMS. We also noticed that the binding energy of Ni 2p shifted a little bit (Fig. S1c), which revealed the possible bond formed between the Ni centers of JUC-150 and O atoms from the PDMS [17].

We also extended this method to another MOF [Ni_2(L-asp)$_2$Bipy, L-asp= L-aspartic acid, Bipy =4'4-bipyridine] mesh and membrane [18]. The structure and morphology characterizations of Ni_2(L-asp)$_2$Bipy mesh and membrane before and after PDMS modification can be found in supporting information (Fig. S2 and S3). The PDMS modification method shows potential in turning MOF membrane materials to suitable candidates for gas separation in humid conditions, such as reforming gas purification.

2.2. Water-oil separation

The pristine JUC-150 mesh is hydrophilic with a water contact angle close to 0°, compared with 143 ± 2^{o} after PDMS modification. From the Wenzel equation [19], it can be observed that the apparent water contact angle is determined by the combined effect of surface morphology and the surface chemical composition. Since the surface chemical composition is fixed for a solid, the roughness can magnify the wettability levels of the solid surface to its extreme. In this case, the rough multi crystal surface raises either the hydrophilicity or hydrophobicity of MOF meshes before and after the modification.

Given the fact that the pristine JUC-150 and JUC-150@PDMS meshes exhibit hydrophilic and hydrophobic character respectively, the separation tests of gasoline-water were carried out on these meshes and the nickel mesh substrate (Fig. 3). When a mixture of water (dyed by acid red 18) and gasoline was poured into the filter with a nickel mesh substrate, both components passed through and fell into the baker. After the nickel mesh substrate was coated with the hydrophilic JUC-150 MOF layer, a water film was formatted on the pre-wetted

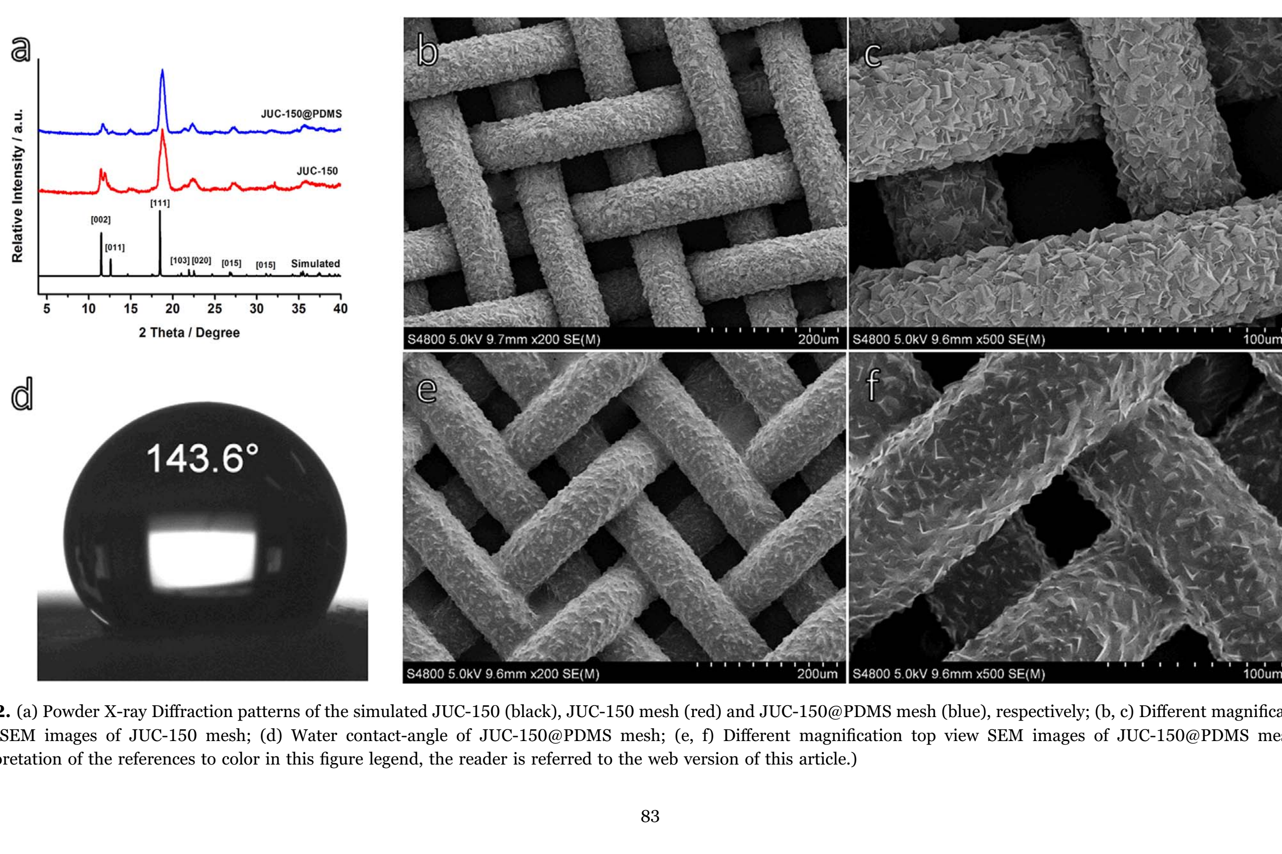

Fig. 2. (a) Powder X-ray Diffraction patterns of the simulated JUC-150 (black), JUC-150 mesh (red) and JUC-150@PDMS mesh (blue), respectively; (b, c) Different magnification top view SEM images of JUC-150 mesh; (d) Water contact-angle of JUC-150@PDMS mesh; (e, f) Different magnification top view SEM images of JUC-150@PDMS mesh. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

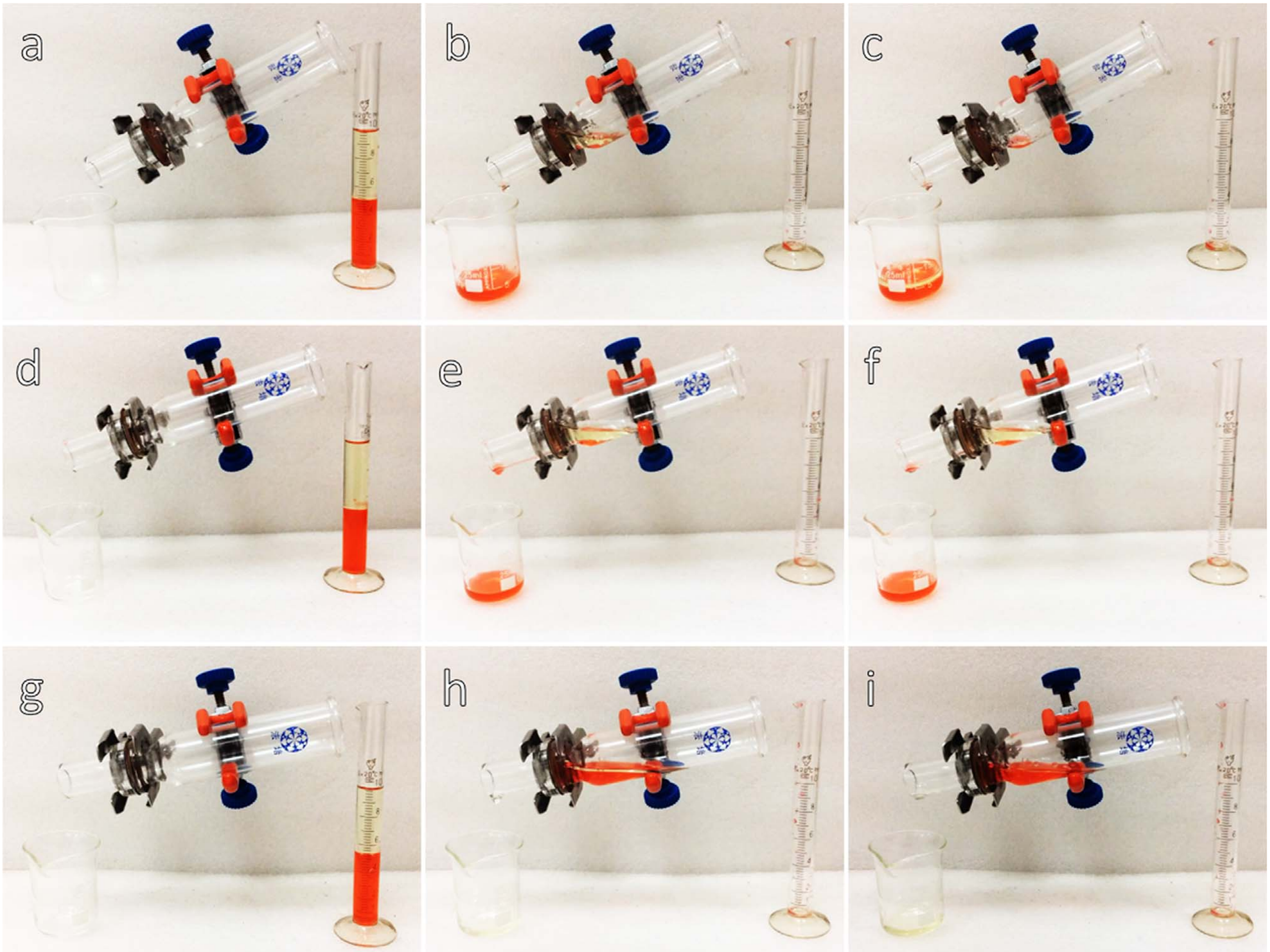

Fig. 3. Snapshots of the water-oil separation tests using (a-c) the nickel mesh substrate, (d-f) JUC-150 mesh and (g-i) JUC-150@PDMS mesh: (a, d, g) the mixture of water-gasoline before separation tests; (b, e, h) different components passing through the meshes during separation tests; (c, f, i) different components collected in the backer after the separation tests. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

JUC-150 mesh surface during the test, which became highly oil-repulsive. Water permeated through the JUC-150 mesh quickly, and no visible gasoline was observed in the collected water. However, when the JUC-150@PDMS mesh was placed into the filter, the red aqueous phase was hindered by the hydrophobic surface and the oil phase with lower density went through easily. Similarly, no visible colored water phase was found in the collected gasoline. Furthermore, it only took a few minutes to complete all these separation tests, indicating the high separation efficiency of our JUC-150 and JUC-150@PDMS meshes.

To further confirm the performance of JUC-150@PDMS mesh on the water-oil separation, the separation efficiency was calculated using the oil rejection coefficient (R (%)) [20] according to:

$$R(\%) = \left(1 - \frac{C_r}{C_0}\right) \tag{1}$$

where C_0 and C_r are the oil concentration of the original water-oil mixture and the retentate after the first separation, respectively. Based on the equation, the separation efficiency of JUC-150@PDMS mesh for a series of tested objects was above 99.0%, as shown in Table S1. Recyclability of the JUC-150@PDMS mesh was further investigated by repeated separation tests (Table S2). The oil rejection coefficient could be retained after 5 uses, showing the stable performance of JUC-150@ PDMS mesh on water-oil separation.

3. Conclusion

In summary, the controllable surface wettability switching of MOF JUC-150 mesh was achieved by a facial PDMS modification method. The surface of JUC-150 mesh was transformed from hydrophilic to hydrophobic after the deposition of PDMS. As a result, the separation process was reversed for the same water-oil mixture system. For the as-prepared JUC-150 mesh, water phase selectively passed through the mesh and the oil phase was rejected. However, after the JUC-150 mesh was modified with PDMS, the oil phase could pass through the mesh and the water phase was held. This modification method is also suitable for other MOF meshes, films and membranes that will be applied in the field of water purification and gas separation with steam.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.matlet.2016.11.088.

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