A stable ZIF-8-coated mesh membrane with micro-/nano architectures produced by a facile fabrication method for high-efficiency oil-water separation

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ABSTRACT With the possibility of large-area processing, the ZIF-8-coated mesh membranes with rough micro-/nanostructures and underwater superoleophobic properties were successfully fabricated at ambient temperature and pressure. These membranes exhibited excellent separation efficiency over 99.99% for various oil-water mixtures with the residual oil content in the collected water less than 4 ppm, and high water flux of $10.2 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$. Furthermore, the ZIF-8-coated mesh membrane displayed outstanding stability towards high temperature and various organic solvents immersion. More importantly, based on its facile fabrication method, this kind of ZIF-8-coated mesh membrane can be easily enlarged, which is critical for the practical oil-water separation applications.

Keywords: membrane, metal-organic frameworks, underwater superoleophobicity, oil-water separation

INTRODUCTION

The separation of oil and water has become an urgent global challenge owing to water pollution caused by frequent oil spillage events, and it is also necessary to remove oil or fat from the water system for many industrial processes [1–3]. Currently implemented oil-water separation technologies include centrifugation, filtration, dissolved air flotation, distillation, oil skimmers, adsorption, and electrochemical methods, etc. [4–6]. Such technologies are low efficiency and consume a lot of energy during complex separation processes [7]. And some adsorption materials also have the drawbacks of the oleophilic materials and absorbed oil waste, and the secondary pollution during the post-treatment process.

Therefore, due to the pressure of economic development and more stringent environmental control, application of cost-effective and high efficient processes for oil and water separation becomes more important [8].

Recently, membrane technologies have attracted increasing interest in the separation application as a promising and economical approach [9–11]. Mesh membrane for separating oil-water mixture driven by capillarity has been recognized as an effective way to achieve high flux and separation efficiency [12–16]. Some polymers, such as polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS) and poly(stearylmethacrylate) (PStMA) have been successfully applied on mesh membranes [17,18], however, owing to their oleophilic property, the surface of these membranes is easily polluted or even blocked up by oil [19]. It is well known that the wetting behavior of the solid surfaces is mainly affected by the geometrical structure and chemical composition [20,21]. We often use the contact angle (CA) given by Young's equation to assess the wettability of the solid surface [22]. The Young's equation is applicable to both liquid droplets on solid surfaces in the air and liquid droplets on solid surfaces under second liquid [23]. Particularly, the Cassie state can be realized under solid/water/oil three-phase existing simultaneously, when rough structure is introduced into the solid surface [24]. Water molecules are imbibed in the rough solid surface to form a barrier layer, which provides a strong repulsive force to the oil droplet, so solid surface can show the underwater superoleophobic property [25]. In recent years, the underwater superoleophobic materials and fundamental mechanisms have been developed [26–28],

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which present a new opportunity and promise to solve high efficiency oil-water separation [29,30], and some inorganic and polymer materials have been prepared on the mesh membrane, but the idea superoleophobic membranes with a strong separation ability, high separation efficiency, extensibility of the preparation process and long-term durability are still rather sparse and highly required.

Metal organic frameworks (MOFs) are new porous crystalline materials composed of inorganic metal centers coordinated to organic linkers and thus possess the properties of both inorganic and organic materials, which are promising candidates for various applications, including gas storage, catalysis, sensors and water harvesting, etc. [31–39]. Particularly, zeolite imidazole frameworks (ZIFs) as a subfamily of MOFs, exhibit various topologies, diverse morphologies, robust chemical and thermal stabilities [40,41]. Nowadays, MOFs and ZIFs membrane have exhibited excellent performances for applications in gas and liquid separation [42,43], and attracted much attention of researchers working in the fields of materials science, chemistry and chemical engineering [44–52]. Several studies have shown that MOF materials can be prepared onto the mesh by *in-situ* growth, such as JUC-150-coated and HKUST-1-coated mesh membranes previously reported by our group, which exhibited excellent gas separation properties [53,54]. As known, ZIF-8 is one of the most popular MOFs, which has the advantages of outstanding chemical stability, thermal stability, the readily available and cheap raw materials and straightforward synthesis. In the present work, we developed a stable ZIF-8-coated mesh membrane with micro-/nano architecture by a facile strategy for high-efficiency oil-water separation. Compared to most of inorganic materials coated membranes, which usually have been fabricated by the chemical vapor deposition or hydrothermal synthesis, we successfully constructed a ZIF-8-coated mesh membrane with excellent oil-water separation performance by simply immersing mesh in precursor solution under room temperature and atmospheric pressure (Fig. S1). The ZIF-8-coated mesh membrane showed underwater superoleophobic properties, leading to high oil-water separation efficiency over 99.99% and high water flux of $10.2 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$, which can efficiently separate different oil and water mixtures driven by gravity. In addition, these membranes exhibited excellent thermal and chemical stabilities. It is worth noting that this ZIF-8-coated mesh membrane can realize large area fabrication and provides potential applications in various oil-water se-

paration fields.

EXPERIMENTAL SECTION

2-Methylimidazole (Hmim, 98%, Aladdin), zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 99%, Aladdin), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Sigma-Aldrich), cyclohexane (AR, West Long Chemical Co., Ltd.), soybean oil, diesel and pump oil were commercially available. The stainless steel mesh (400 mesh/38 μm , 500 mesh/28 μm , 800 mesh/10 μm , 540 Equipment Co., Xinxiang City, China. When the thickness of the ZIF-8 layer reached 700 nm, the pore size of the mesh decreased only about 1.4 μm) were cleaned with deionized water and ethanol under ultrasonic.

ZIF-8 crystal seeds were fabricated as follows: 1.50 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 20 g of Hmim were added into 90 mL of deionized water. The solutions were mixed and stirred for about 30 min at room temperature. The product was washed with ethanol by repeated centrifugation, and then dried in the oven at 80°C for 24 h. A seeds solution (1 wt%) was fabricated by dispersing the ZIF-8 seeds into the deionized water. The seed mesh was prepared by immersing the pre-cleaned stainless steel mesh in the seed solution for 5–10 min under the ultrasonic condition, and then seed mesh was dried in the oven at 120°C for 2 h. For secondary growth, the seeded mesh was immersed in a precursor solution consisting of deionized water, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, and Hmim under ambient temperature and pressure for 24 h. The molar ratio of the solution was $\text{Zn}^{2+}:\text{Hmim}:\text{H}_2\text{O} = 1:28:2222$. The process of secondary growth was repeated two times, and the ZIF-8-coated mesh membrane was obtained. In this work, 500 mesh stainless steel mesh was used as the main substrate to study the performance of oil-water separation. The layered mixture of water and oil (50%, *v/v*) is slowly poured onto the prewetted membrane that was fixed between two glass tubes. The separation was carried out by the gravity of liquids. Then the permeated liquid was collected in the glass bottle.

The X-ray diffraction (XRD) data were recorded on a PANalytical B.V. diffractometer using a Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM, EDXS) images were measured using JEOS JSM-6510. Oil and water contact angles were recorded at ambient temperature with the OCA20 machine (Data-Physics, Germany). The concentrations of oil in filtered water for different kinds of oils were measured with the infrared spectrophotometer oil content analyzer (OIL-460, China). The roughness was measured by Cypher S Atomic Force Microscopy (AFM). The adhesion force was re-

Scheme 1 Schematic diagram of the preparation route of ZIF-8-coated mesh membrane with underwater superoleophobicity.

corded *via* a high-sensitivity micro-electromechanical balance system (Data-physics DCAT21, Germany).

RESULTS AND DISCUSSION

Synthesis of ZIF-8-coated mesh membrane

ZIF-8-coated mesh membrane was prepared by a simple secondary growth method at ambient temperature and pressure, which could be readily scaled up (Scheme 1). XRD pattern of the ZIF-8-coated mesh membrane was in consistent with the ZIF-8 simulated pattern, indicating that the highly crystalline ZIF-8 crystals could be grown on the stainless steel mesh (Fig. S2). In addition, we found that the Zn and N elements were uniformly distributed on the as-synthesized membrane by elemental mapping analysis (Fig. S4).

Compared with the smooth bare stainless steel mesh, the layer of ZIF-8 nano-seeds was obviously formed on the mesh by van der Waals interaction (Fig. 1a, b). SEM images of the ZIF-8-coated mesh membrane demonstrated the smooth mesh surface was completely covered by rough ZIF-8 coatings after the secondary growth (Fig. 1c, d). The higher magnification SEM image exhibited that the surface of ZIF-8-coated mesh membrane was composed of continuous intergrown polyhedral nanocrystals with a dense, homogeneous and corrugated geometrical structure (Fig. 1e). From the cross-sectional view, it can be seen that the ZIF-8 crystal layer was about 700 nm thickness and there were no pinholes inside the membrane, and the ZIF-8 nanocrystals were exceedingly compact and tightly attached to the substrate (Fig. 1f). These characteristics demonstrated the ZIF-8 was successfully fabricated on the stainless steel mesh through a simple method at ambient temperature and pressure. And the growth of nanostructured ZIF-8 crystals led to the formation of rich micro-/nano hierarchical surface, which greatly promoted the surface roughness of membrane. Similarly, ZIF-8 crystals completely covered the supports with 400 and 800 mesh, showing the micro and nano hierarchical rough surface and there were no visible defects on membrane surface (Fig. S5).

In order to further research the surface properties of the

Figure 1 SEM images of ZIF-8-coated mesh membrane prepared on stainless steel mesh (500 mesh) by seeding and secondary growth process. (a) The bare stainless steel mesh and (b) the seeded stainless steel mesh with uniform ZIF-8 seeds. (c) The ZIF-8-coated mesh membrane and (d) a single ZIF-8-coated wire after secondary growth. (e) The magnified image of ZIF-8-coated membrane surface, in which the homogeneous intergrown polyhedral nanocrystals can be clearly observed. (f) The cross-sectional view of ZIF-8-coated mesh membrane.

ZIF-8-coated mesh membrane, surface roughness of membrane was analyzed by AFM for a scanned area of $2\ \mu\text{m} \times 2\ \mu\text{m}$ on the thread of stainless steel mesh. The root-mean-square (RMS) roughness was very accurate, which was often used to characterize the roughness. The RMS roughness (R_{rms}) is calculated by the Equation (1):

$$R_{\text{rms}} = \sqrt{\frac{1}{L} \int_0^L |Z^2(x)| dx}, \quad (1)$$

where L is the evaluation length, $Z(x)$ is the function of sample height (Z) and sample position (x), which is used to describe the surface profile. Obviously different surface structures of bare stainless steel mesh and ZIF-8-coated mesh membrane can be observed in AFM images. While

Figure 2 3D and 2D AFM images of the bare thread of stainless steel mesh (a₁, a₂) and after coated with ZIF-8 (b₁, b₂).

the surface of bare stainless steel mesh exhibited smooth morphology with a RMS roughness of about 8.66 nm (Fig. 2a), the surface of the ZIF-8-coated mesh membrane showed a micro and nano hierarchical rough structures, and RMS roughness was about 68.67 nm (Fig. 2b). The result indicated that ZIF-8 crystals covered the stainless steel mesh resulting in a high surface roughness, which was conducive to ZIF-8-coated mesh membrane to achieve underwater superoleophobicity.

Wettability study of the ZIF-8-coated mesh membrane

A ZIF-8-coated mesh membrane was immersed into the water, showing superoleophobic performance (Fig. 3a), which was attributed to the micro and nanostructure on the surface of the ZIF-8-coated membrane. When underwater oil contact angle (OCA) of a bare stainless steel mesh was about 85° (Fig. S6), the ZIF-8-coated mesh membrane showed outstanding underwater superoleophobic behaviours with a high oil contact angle of 150° (Fig. 3b) and an oil sliding angle around 8° (Fig. S7). The oil adhesion force was only about 13 μN, which indicated the membrane was not easily fouled by oil (Fig. S8). Through theoretical calculations, for solid/water/oil three phase system that possesses the rough surface, the CA can be exhibited using Cassie model, which is shown in Equation [19,24]: $\cos\theta' = f\cos\theta + f - 1$ (2), where θ is the underwater OCA on a smooth surface, θ' is the underwater OCA on a rough surface, and f represents the area fraction of solid. When the area fraction becomes smaller, the contact chance decreases between oil droplet and solid surface, resulting in the larger OCA underwater.

Figure 3 Special wettability of ZIF-8-coated mesh membrane under water. (a) The photograph of several oil droplets on the ZIF-8-coated mesh membrane; (b) a contact angle image of an oil droplet on the ZIF-8-coated mesh membrane underwater; (c, d) schematic illustrations of an oil droplet on a rough micro and nano architecture surface of ZIF-8-coated mesh membrane (dichloroethane dyed with Sudan III).

As schematically shown in Fig. 3c, d, owing to the sharp polyhedral nanocrystals, our ZIF-8-coated mesh membrane has a rather rough surface, which means a very small area fraction as well as a larger OCA.

Due to the special wettability of ZIF-8-coated mesh membrane, a series of experiments on separation of oil and water mixtures were performed. As an underwater superoleophobic material, these mesh membranes had been pre-wetted with water before the oil-water separation. The cyclohexane and water (50%, v/v) mixture was slowly poured onto the pre-wetted stainless steel membranes. The bare stainless steel mesh was used for oil and water separation, which exhibited both water and oil permeated through the bare stainless steel mesh completely (Fig. S11a, b and Video S1). In other words, the bare stainless steel mesh has no ability of oil-water separation. Compared with the bare mesh, the water permeated through the ZIF-8-coated mesh membrane with high flux, but the oil phase was rejected above the membrane (Fig. 4a, b and Video S2). Our ZIF-8-coated mesh membranes exhibit the “water-removing” performance. The mechanism is the water pre-wetted ZIF-8-coated mesh membranes preferentially attracted water molecules into the ZIF-8 micro and nanostructures and reduced the overall interfacial energy of the solid/water/oil three phase system, implying a very small area fraction of solid and exhibiting underwater oleophobic phenomenon. The formed water barrier layer on a very rough surface allows water to permeate through the membrane efficiently by gravity without any external force, whereas

Figure 4 Photographs of the oil-water separation process using (a, b) the ZIF-8-coated mesh membrane, (c, d) the large-area ZIF-8-coated mesh membrane and (e, f) the ZIF-8-coated “boat” (cyclohexane was dyed with Sudan III).

the oil phase is rejected completely. Similarly, the oil-water separation process of the ZIF-8-coated mesh membranes with 400 and 800 mesh were shown in Videos S3 and S4, respectively.

Encouraged by the simple preparation methods under ambient temperature and pressure, the large-area fabrication of the ZIF-8-coated mesh membrane was easily

realized. As shown in Fig. 4c, the large-area ZIF-8-coated mesh membrane (10.0 cm×10.0 cm) was placed on two tilted beakers, and then the oil-water mixture was poured onto the membrane. The dyed red oil phase flowed over the ZIF-8 membrane to the left beaker, while the pure water was collected in the right beaker (Fig. 4d and Video S5). However, the bare stainless steel mesh could not separate the oil-water mixture obviously (Figs S11c–f). Furthermore, as shown in Fig. 4e, the ZIF-8-coated mesh membrane (10.0 cm×10.0 cm) was folded into a “boat” and placed on a beaker. To evaluate the cleanup capability of ZIF-8-coated “boat”, several oil-water mixtures were continuously poured into the beaker through the mesh. It can be seen that all the dyed red oil successfully remained in the “boat” while the water quickly permeated through the mesh, and no obvious flux decrease occurred (Fig. 4f and Video S6). Compared with preparation methods of most of the inorganic coated membranes, such as hydrothermal synthesis, chemical vapor deposition or annealing method, the ZIF-8-coated mesh membrane can be readily enlarged to separate a lot of oil-water mixtures continuously and exhibits potential industrial application.

To quantitatively demonstrate the separation efficiency of the ZIF-8-coated mesh membrane for the oil-water mixture, the residual oil content in the collected water was measured by an infrared spectrometer oil content analyser. The result indicated that high purity water with less than 4 ppm oil could be readily obtained through oil/water separation by using the ZIF-8-coated mesh membrane. Besides, ZIF-8-coated mesh membrane can be applied to separate water from various oils including diesel, soybean oil, cyclohexane and pump oil, which exhibited superior oil-water separation performance (Fig. 5a). To analyze the oil-water separation efficiency, the oil rejection coefficient R (%) was calculated by the equation: $R = (1 - C_1/C_0) \times 100\%$ (3), where C_0 is oil con-

Figure 5 Oil-water separation performances of the ZIF-8-coated mesh membrane. (a) The separation efficiency and residual oil contents in the collected water for various oils. (b) The influence of different mesh number on water flux and intrusion pressure of oil (calculated by cyclohexane).

centration in the oil-water mixture before separation, C_1 is oil concentration in collected water after separation. The membrane shows a high separation efficiency of over 99.99% for various oils. And the water flux and intrusion pressure of oil were introduced to further study the separation properties. The water flux (F) was calculated by the equation: $F=VS/t$ (4), where V and t were volume and time of water penetrating through the membrane, respectively, and S was the area of the membrane. The intrusion pressure (P) values can be calculated using the equation: $P=\rho gh$ (5), where ρ is the density of oil, g is the acceleration of gravity, and h is the maximum height of oil that the ZIF-8-coated mesh membrane can support.

The pore sizes of ZIF-8-coated mesh membrane were easily adjusted by the stainless steel mesh with different mesh number. With the decrease of the mesh number, the pore size of the membrane increased. It was obvious that the larger pore size of the ZIF-8-coated mesh membrane was more favorable for water permeation, but the membrane cannot support too much oil, because it had not enough surface tension. The higher oil intrusion pressure of 6,400 Pa and water flux of $10.2 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$ were achieved, respectively (Fig. 5b). The performances of the ZIF-8-coated membrane were among the best reported [12]. In addition, after the oil-water mixtures were

separated, the ZIF-8-coated mesh membrane can be easily recovered by simply washing the surface with ethanol, possessing good recyclability.

Stability and durability of the ZIF-8-coated mesh membrane

To explore the stability of the ZIF-8-coated mesh membrane, the high temperature and organic solvent resistance were evaluated. The thermal stability of the ZIF-8-coated mesh was examined by putting the as-prepared meshes into the oven with different temperatures from 100 to 200°C for 20 h. Moreover, the as-prepared ZIF-8 meshes were immersed in various organic solvents including tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), dichloromethane (DCM) and *n*-hexane for 20 h to evaluate the chemical stability. After high temperature and various organic solvents treatment, the XRD patterns of these membranes showed they were in consistent with the simulated pattern, suggesting the fully crystalline integrity of the coated ZIF-8 crystal layer (Figs S2, S3). The morphology of these treated ZIF-8-coated mesh membranes were characterized by SEM, the results showed that ZIF-8 nanocrystals remained compactly covered the mesh, and no visible cracks were formed on the membrane surface

Figure 6 Stability and recyclability of ZIF-8-coated mesh membrane (500 mesh). (a, b) Underwater oil contact angles (UWOCAs) of the ZIF-8-coated mesh membrane after heating treatment under different temperatures and immersing in various organic solvents for 20 h. The inset: photos of underwater oil droplets (dichloroethane) standing on ZIF-8-coated mesh membranes after heating and immersing treatment. (c, d) Water flux and separation efficiency for oil-water mixtures of ZIF-8-coated mesh membrane during the 10 cycles.

(Figs S9, S10). Analyzed by the CA measurements, these ZIF-8-coated mesh membranes still exhibited closed underwater superoleophobic properties (Fig. 6a, b). And then to study the recyclability of the ZIF-8-coated mesh membrane, the membrane was recycled 10 times. The intrusion pressure of cyclohexane maintained a high value and average height of oil column could reach 40 cm after 10 times (Fig. S12). The separation efficiency for cyclohexane and water mixture had been above 99.99%, and water flux of ZIF-8-coated mesh membrane remained about $7.9 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$ during repeated experiments (Fig. 6c, d). Furthermore, in order to explore the stability of the ZIF-8-coated mesh membrane in water, it was immersed in water for 20 days. SEM image revealed that the ZIF-8-coated mesh membrane retained micro and nano hierarchical rough surface (Fig. S13a), and the ZIF-8-coated mesh membrane kept near underwater superoleophobic properties after 20 days (Fig. S13b). Moreover, there was no obvious change on the water flux and separation efficiency for oil-water mixtures compared with the new membrane, which indicated that the membrane had long-term stability in the water (Fig. S14). In addition, the ZIF-8-coated mesh membrane was stable in solution from pH 6 to 12 for 20 h, and the oil-water separation efficiency remained about 99.99% (Fig. S15). These properties indicated that the ZIF-8-coated mesh membrane had excellent thermal and chemical stabilities and durability.

CONCLUSIONS

In summary, the ZIF-8-coated mesh membrane with underwater superoleophobicity has been fabricated *via* a facile method under ambient temperature and pressure, which displays excellent oil-water separation properties. It can separate various oil and water mixtures driven by gravity, with outstanding separation efficiency over 99.99% and water flux as high as $10.2 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$. Importantly, the membrane exhibits excellent stabilities towards high temperature and various organic solvents immersion, durability and extensibility of the preparation process, which indicates the ZIF-8-coated mesh membrane will be a promising candidate for wastewater treatment applications and clean-up of oil spills. And this work paves the way for further development of functional applications of MOF membrane materials.

Received 27 June 2018; accepted 27 August 2018;
published online 19 September 2018

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- Acknowledgements** This work was financially supported by the National Natural Science Foundation of China (21571076, 21390394, 21571079 and 61701543), "111" project (B07016), the Ministry of Science and Technology of SINOPEC (A381) and Open Projects of State Key Laboratory of Safety and Control for Chemicals (SKL-038). Song M, Zhao Y, and Xue M are inventors of a Chinese patent (CN201810148543.6).
- Author contributions** Xue M, Zhao Y, and Qiu S conceived and designed this work. Song M and Xue M conducted the synthesis and analyzed the data. Song M, Zhao Y, Mu S, Jiang C, Li Z, Yang P and Fang Q performed the characterization. Song M, Zhao Y, and Xue M wrote the paper. All authors contributed to the general discussion. Song M and Zhao Y contributed equally to this work.
- Conflict of interest** The authors declare no conflict of interest.
- Supplementary information** Supplementary data are available in the online version of the paper.

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利用简易方法制备稳定的具有微纳结构的ZIF-8高效油水分离膜

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摘要 在常温常压条件下, 以金属网为载体, 成功地制备出表面具有微纳结构的ZIF-8分离膜, 该膜显示出优异的水下超疏油性能. 该方法制备的ZIF-8分离膜, 可以高效地分离多种油水混合物, 油水分离效率高达99.99%, 同时具有较高的水通量 $10.2 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$, 以及耐压性. 进一步, 通过高温处理以及多种常见有机溶剂浸泡, 该膜仍然可以保持高效的油水分离性能, 并且可以循环使用. 由于制备方法简单, 该类ZIF-8油水分离膜可以实现大面积制备, 这对于油水分离的实际应用至关重要.