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Decorating a metal–organic framework UiO-66 layer on ceramics substrate by the seed-assisted solvothermal method for high-performance desalination

Xin Ren[a], Xuebin Zhang[a,*], Dawei Tang[a], Aifeng Yang[b], Yi Feng[a]

[a]*School of Materials Science and Engineering, Hefei University of Technology, Hefei Anhui 230009, China, Tel. +86 551 2901362/ +86 13865517460; email: zzhhxxbb@126.com (X. Zhang), Tel. +86 18756937701; email: rxstc123@outlook.com (X. Ren), Tel. +86 18862601109; email: 1840288496@qq.com (D. Tang), Tel. +86 551 62904715; email: fyhfut@163.com (Y. Feng)*
[b]*School of Management, Hefei University of Technology, Hefei Anhui 230009, China, Tel. +86 551 62901485; email: aifengy@163.com*

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ABSTRACT

UiO-66 is one kind of zirconium-based metal-organic framework, and $Zr_6O_4(OH)_4$ clusters are the cornerstones of the three-dimensional framework. To obtain enough strength for desalination, a dense continuous UiO-66 membrane was synthetized by the seed-assisted solvothermal synthesis method on the alumina substrate. The thickness of the dense UiO-66 membrane on the alumina substrate could be reduced to 1 μm. The thin layer achieved a high permeate flux of 0.344 L m^{-2} h^{-1} μm^{-1} with the ion rejections of Ca^{2+} and Mg^{2+} respectively reaching 82.1% and 98.2%. Such excellent performances were much better than those of reverse osmosis and nanofiltration membranes. Na^+ and K^+ could also be rejected by the UiO-66 membrane based on the ligand effect, whose ion rejections were 49.8% and 45.8%, respectively. Due to the exceptional chemical stability of UiO-66, no degradation of membrane performance was observed by test up to 180 h toward the saline solution. These results show that the UiO-66 membrane on the alumina substrate gives a good promise in the desalination application.

Keywords: Metal–organic framework; Porous ceramic membrane; Desalination

1. Introduction

Metal-organic framework (MOF) materials, constructed by the metal ion joints and the organic linkers [1], have gained a wide range of attention due to their variety of potential applications in the fields of sensors, drug delivery, gas storage and molecular separations [2,3]. MOFs exhibit high surface area and have unlimited number of microporous structures with adjustable pore size. Among the reported MOFs, zirconium-carboxylate MOF shows an excellent stability against chemical, mechanical stress and temperature. Furthermore, different framework topologies, a wide range of pore sizes, and various functional groups can be easily designed by controlling the synthesis process [4]. UiO-66, synthetized by University of Oslo (Norwegian) firstly, is a prototypical Zr-MOF with the formula of $Zr_6O_4(OH)_4(BDC)_6$ [5,6]. It composes of $Zr_6O_4(OH)_4$ clusters and benzene-1,4-dicarboxylate ligand [7,8]. The aperture size of UiO-66 has been reported as ~6.0 Å according to the crystallography analysis, which suggests the theoretical possibility of UiO-66 membrane for desalination to reject the bigger hydrated ions (6.6 Å~) and deliver smaller H_2O molecules (~2.8 Å) [7,9].

However, the strength of the polycrystalline MOF membranes is not high enough when used in some demanding conditions [2,4]. For instance, the thin UiO-66 membrane undergoes an extremely high water-pressure when it is used for practical water treatment process [9,10]. Although considerable effects have been applied on the enhancement of membrane mechanical property, little progress is made. As a result, there are few reports on

* Corresponding author.

UiO-66 membrane for application of water desalination. Thus, a permeable support with durable property is highly needed for overcoming the weakness of the membrane.

In this paper, a thin and dense UiO-66 membrane was synthesized using a new seed-assisted solvothermal synthesis method. A porous alumina ceramic tube was chosen as a support to enhance the membrane durability. It is found that the membrane could work stably for more than 180 h without any changes. Also, it exhibited high water flux and good ions rejection.

2. Experimental

2.1. Materials

The porous ceramic tube was supplied by Hefei Jinar New Material Co. Ltd., China. The pore size, water flux, and porosity of the porous ceramic tube were 1 μm, 29.07 L m^{-2} h^{-1} bar^{-1} and 35.6%, respectively. BDC (p-phthalic acid), DMF (N, N-Dimethylformamide) and $ZrCl_4$ were purchased from Sigma-Aldrich. All chemicals were used as received.

2.2. Fabrication of UiO-66 functional membrane on the ceramic tube

The internal diameter of porous ceramic tube was 1.9 cm. A seed-assisted solvothermal method was applied to synthesize the UiO-66 membrane on the inner side of the tube. Several factors would influence the preparation of UiO-66 polycrystalline membranes including the concentration of solvents, duration and temperature during the synthesis process [6,11–13]. The seed-assisted solvothermal synthesis method contains two steps: (1) preparation of seed grains and (2) the following solvothermal synthesis. In each step, the same reaction precursor solution with a molar composition of Zr^{4+}/BDC/H_2O/DMF = 1:1:1:380 was used. Specifically, 0.159 g of $ZrCl_4$ and 0.102 g of BDC were respectively dissolved in 20 mL DMF and 0.015 mL of H_2O with ultrasonic treatment for 10–30 min. For seed grain synthesis, the autoclave with the solution inside was placed in a pre-heated convective oven at 120°C for 24 h. After heating, the autoclave was cooled down to room temperature with the oven, which could ensure the quality of the membranes. The prepared UiO-66 nanocrystals dispersed in the solution and were collected by solution centrifugation at 8,000 rpm for 5 min for further use in the next step. In the solvothermal synthesis, 1.5 g of as-prepared UiO-66 seeds were mixed in 4 mL deionized water (DI) water using ultrasonic to get a thick liquid. Then it was dropped into one-end-sealed ceramic tube and the tube was heated at 60°C for 2 h. After that, the tube was placed into the autoclave and the following process was the same as the seed grain synthesis step. At last, the prepared product was washed by DI water and dried at 40°C for 12 h.

2.3. Characterizations

The surface and cross-section morphologies of the membranes were observed by field emission scanning electron microscopy (FESEM) (Model SU-8020, Hitachi, Japan). X-ray diffraction (XRD) patterns were collected on PANalytical X'Pert PRO MPD using Cu-Kα radiation. To test the desalination performance, the samples were equipped on a dead-end system with four kinds of different saline water solutions at the pressure of 10.0 bar. In the same system, the flux of the membranes was tested under the pressure of 3.0, 5.0, 8.0, and 10.0 bar. The saline water was the solo solvent of KCl, NaCl, $CaCl_2$ and $MgCl_2$ with the concentration of 0.1 wt.% (1,000 ppm). The rejection rate was determined according to the remaining concentration of the ions using a TDS detector (Xiaomi Technology Co. Ltd, Foshan, China).

3. Results and discussion

To determine the formation of crystalline UiO-66 inside the ceramic tube, XRD test was carried out. As shown in Fig. 1, UiO-66-modified alumina ceramic tube had the typical diffraction peaks of UiO-66 crystals and ceramic tube, which confirmed crystalline UiO-66 had been successfully fabricated on the surface of ceramic by the seed-assisted solvothermal synthesis.

FESEM was applied to investigate the morphology of the prepared UiO-66 membrane on ceramic tube. In comparison to the porous ceramic support (Fig. 2a), continuous UiO-66 membrane was prepared evenly and tightly attached to the surface of ceramic tube. The size of UiO-66 grains varied from 200 to 400 nm. These grains were well-intergrown and the prepared membrane totally became an overlap on the surface. Meanwhile, unlike the typical UiO-66 crystals which had sharp edges [9,14], the UiO-66 crystals in this work nearly melt together and generated a large layer without a visible gap or crack. Obviously, this is helpful for the desalination effect. Furthermore, the controllable nucleation could not only facilitate the uniformity but also control the thickness of the layer. It had been reported that the thickness of membrane would approach to 2 μm in the conventional method [10]. With our new seed-assisted method, the thickness of the dense UiO-66 membranes could achieve to 1 μm (Fig. 2e), which would surely improve the water flux and ensure superior desalination property.

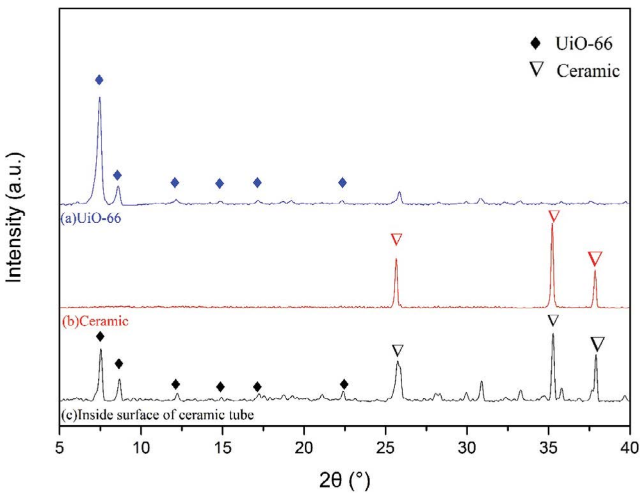

Fig. 1. XRD patterns of (a) UiO-66 crystals, (b) pure ceramic tube, and (c) UiO-66 membrane on the inside surface of ceramic tube.

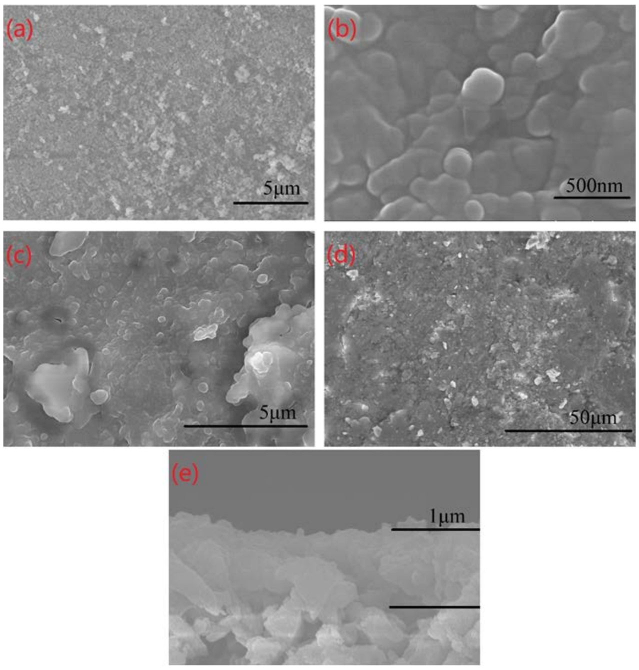

Fig. 2. SEM images of surface morphology of (a) ceramic, (b)–(d) UiO-66 membrane in different scales, and (e) cross-section morphology shows the membrane thickness is 1 μm.

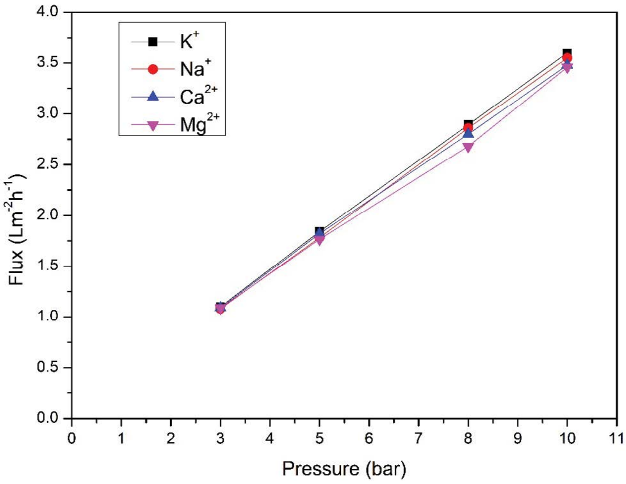

Fig. 3. Flux of the membrane. Four different saline water solutions with the same concentration (0.1 wt.%) were applied respectively as a feed at 26°C under different pressures. We used binomial fitting method to obtain the flux data.

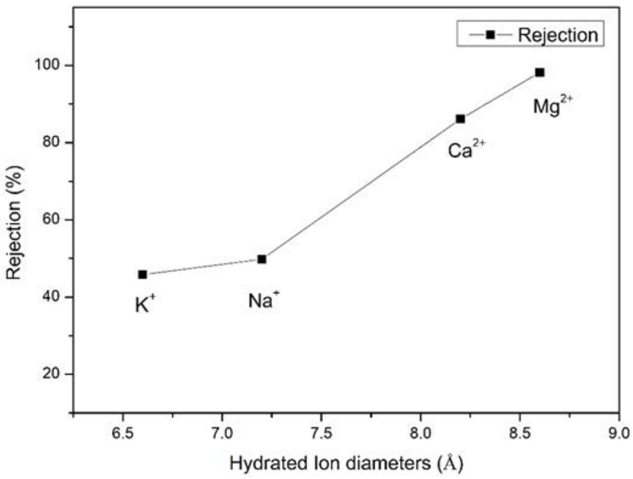

Fig. 4. Rejection of the membranes was tested. Four different saline water solutions with the same concentration (0.1 wt.%) were applied respectively as a feed at 26°C under a pressure difference of 10.0 bar. The rejection is 45.8% for K^+(6.6 Å), 49.8% for Na^+(7.2 Å), 86.1% for Ca^{2+}(8.2 Å) and 98.2% for Mg^{2+}(8.6 Å).

To evaluate the desalination performance, the samples were equipped on a dead-end system with four kinds of different saline water solutions. The saline water solutions were the solo solvent of KCl, NaCl, $CaCl_2$ and $MgCl_2$ respectively, and the concentrations were controlled at the same value of 0.1 wt.% (1,000 ppm). The desalination properties were obtained from average values of five samples prepared using the same method for two cycles in the order of K^+, Na^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, Ca^{2+}, Mg^{2+}. The samples were rinsed by DI and performed ultrasonic clean for 10 min after each test.

In general, four kinds of saline solutions were respectively used as a feed to determine the membrane flux, as shown in Fig. 3. We used binomial fitting method to obtain the flux data which were 3.44 L m^{-2} h^{-1} (K^+), 3.47 L m^{-2} h^{-1} (Na^+), 3.48 L m^{-2} h^{-1} (Ca^{2+}) and 3.45 L m^{-2} h^{-1} (Mg^{2+}), respectively. The membrane flux and pressure normalized flux were determined as 3.44 and 0.344 L m^{-2} h^{-1} bar^{-1}. Then, the thickness normalized water permeance of the UiO-66 was calculated as 0.344 L m^{-2} h^{-1} bar^{-1} μm, which could be ranked at the level of upper reaches contrasting to reverse osmosis and nanofiltration membranes (0.047–0.72 L m^{-2} h^{-1} μm) [15,16]. In comparison to 0.28 L m^{-2} h^{-1} bar^{-1} μm of a 2 μm thickness membrane reported by Liu et al. [14], our membranes indeed had a higher flux because of the decreasing thickness.

The ion rejection of the membranes was examined. As shown in Fig. 4, the rejection value increased with increasing the diameter of the hydrated ions, which could be called the size-selective diffusion desalination. The rejection of the monovalent ion (K^+:6.6 Å; Na^+:7.2 Å) was moderate (i.e., 45.8 and 49.8% for K^+ and Na^+, respectively). This phenomenon was attributed to the ligand defects or the change of ligand coordination [17–19]. These defects could expand the aperture and made the pass of the monovalent ions possible [20]. For other two kinds of ions, Ca^{2+} (8.2 Å) and Mg^{2+} (8.6 Å), the membranes synthetized by the seeding method exhibited a high rejection level (i.e., 86.1% and 98.2% for Ca^{2+} and Mg^{2+}, respectively), this is because the size of these hydrated ions was much larger than the effective aperture of the membranes. According to the current theory, rejection of ions was determined by both size effect and electrostatic effect. Marcus Y. [21] pointed out that the electrostatic effect was considerable only when the ionic strength was in the magnitude of mol/L. Also, Wang et al. [22] proved that $CaCl_2$ solution had a weaker electrostatic effect compared with NaCl solution, considering only the shielding or screening effect at neutral pH. However, we could observe great differences in the rejection of Ca^{2+} and Na^{+} in our work. It could be concluded that the size effect played a significant role in desalination process on the UiO-66 membrane and electrostatic effect had no obvious effect.

In order to verify the working durability of the membranes, we carried out a test around 180 h with a $CaCl_2$ solution at the transmembrane pressure of 10.0 bar. As shown in Fig. 5, no degradation of membrane performance was observed during the test. This result led to the suggestion that the saline solution and water pressure were harmless to the crystal structure and the pore blockage didn't occur on UiO-66 membrane. The structure and morphology of the UiO-66 membrane remained unchanged after the test as characterized by the XRD (Fig. 6) and scanning electron microscopy (SEM) (Fig. 7), respectively. After flushing with DI water, no salt residues were left on the membrane, according to the element analysis data.

Considering the promising high flux and rejection level, UiO-66 is expected to be a promising water desalination

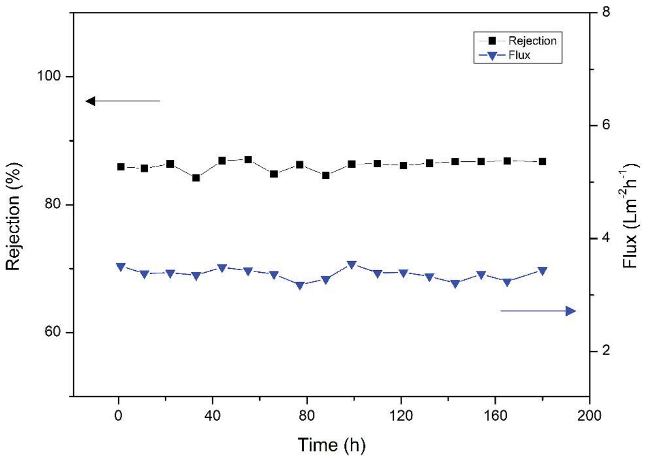

Fig. 5. Rejection ability and flux of the membrane for Ca^{2+}. The UiO-66 membrane was tested at the pressure of 10.0 bar for 180 h.

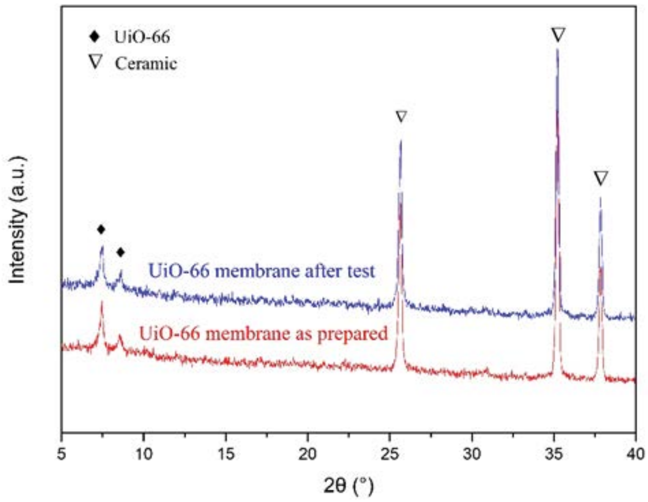

Fig. 6. XRD patterns of the UiO-66 membrane before and after the 180 h test.

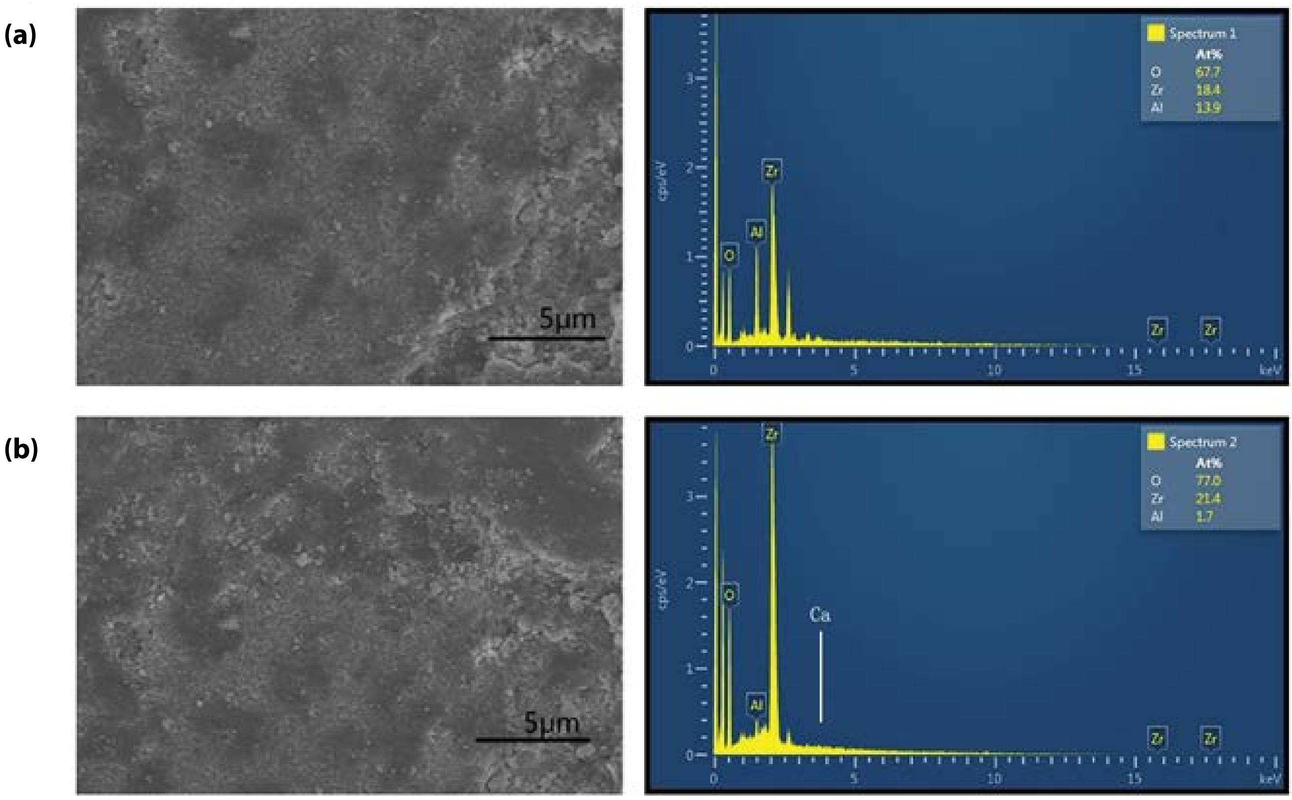

Fig. 7. SEM images and EDXS data of ceramics substrate supported UiO-66 membrane before (a) and after (b) test.

material. With more control of the ligand to get rid of the ligand defects, a suitable flux and great ion rejection will be achieved.

4. Conclusions

A continuous Zr-MOF UiO-66 membrane was synthetized on the surface of porous ceramics tube by a seed-assisted solvothermal approach. The as-synthesized membranes exhibited excellent multivalent ions rejection (e.g., 86.1% for Ca^{2+}, 98.2% for Mg^{2+}) and a moderate water flux (0.344 L m^{-2} h^{-1} bar^{-1} μm). As expected, the UiO-66 showed promising in water treatment application, and the seed-assisted approach was proved to be an efficient way to control the thickness of UiO-66 membranes. The further study will focus on a more optimized membrane with proper thickness, and the reaction parameters for controllable synthesis of the UiO-66 membranes would be investigated.

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