

Synthesis of highly stable UiO-66-NH₂ membranes with high ions rejection for seawater desalination



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ABSTRACT

Compact and phase-pure UiO-66-NH₂ membranes were synthesized on the 3-aminopropyltriethoxysilane (APTES) modified macroporous Al₂O₃ tubes through a repeated synthesis strategy. APTES acts as a molecular linker for anchoring the metal ions onto the support surface to promote the nucleation and the crystallization of UiO-66-NH₂ membrane. Therefore, well-intergrown UiO-66-NH₂ membranes could be prepared through a repeated synthesis method on the APTES-modified macroporous Al₂O₃ tubes. The developed UiO-66-NH₂ membranes were evaluated for seawater desalination by pervaporation. It is found that the UiO-66-NH₂ membranes show high desalination performances attributing to the narrow pore size which is exactly in between the size of water molecules and hydrated ions. With increasing the feed temperature from 318 to 363 K, the water fluxes increase from 1.5 to 12.1 kg m⁻² h⁻¹, with ions rejections of above 99.7%. Further, the UiO-66-NH₂ membranes display high stability for a long time in seawater desalination, which is very promising for seawater desalination.

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1. Introduction

Water scarcity has increasingly become a global issue due to the increase of water demand and aggravation of water pollution [1]. Therefore, the development of renewable freshwater resources such as seawater desalination has attracted much attention to resolve the problem of water supply [2–4]. The membrane-based RO is considered to be one of the most promising technologies due to its low energy consumption and ease of operation [5–7]. However, the present polymeric RO membranes usually suffer from biofouling, oxidation, metal oxide fouling, abrasion and mineral scaling because of their low stability [8,9]. Inorganic membranes, such as zeolite membranes [10–17], carbon membrane [18] and graphene oxide (GO) membrane [19–22], are expected to break through these material-based limitations for desalination due to their high thermal and chemical stability. However, it is still highly desired to develop novel molecular sieving membranes that can be facilely prepared and activated, and thus effectively used for seawater desalination.

Microporous metal-organic frameworks (MOFs) have drawn much attention for the fabrication of membranes/films due to their

highly diversified pore structures and pore sizes as well as specific adsorption affinities. In particular, no SDAs are used in the synthesis of MOF membranes, thus MOF membranes can be easily activated easily under mild conditions (e.g. vacuum or heating with activation temperatures below 423 K). Therefore, MOFs have emerged as a novel type of microporous materials for the fabrication of molecular sieve membranes [24–28]. Especially, zeolitic imidazolate framework (ZIF) membranes have attracted intense interest for gas separation due to their exceptionally thermal and chemical stability [29–41]. Recently, we have reported the synthesis of ZIF membranes for seawater desalination [42]. Attributing to the small aperture size as well as high stability in seawater, the developed ZIF membranes display high separation performances for seawater desalination.

Attributing to the high hydrothermal and chemical stability of UiO-66 [43], especially its high resistance towards humidity, UiO-66 has been drawn much interest for many practical applications in dye separation and seawater desalination [43–45]. Further, the BDC linker can be modified by introducing functional groups like -NH₂, -Br, -F, -OH, -COOH, -CH₃ to obtain derivatives of UiO-66 with special adsorption properties [46]. Among these derivatives, UiO-66-NH₂ is of special interest for gas adsorption and separation [47,48]. UiO-66-NH₂ has a same topological structure with UiO-66, consisting of highly symmetric Zr₆(OH)₄O₄ clusters and 2-amino-1,4-benzenedi-carboxylate (NH₂-BDC) linkers (Fig. 1). As reported

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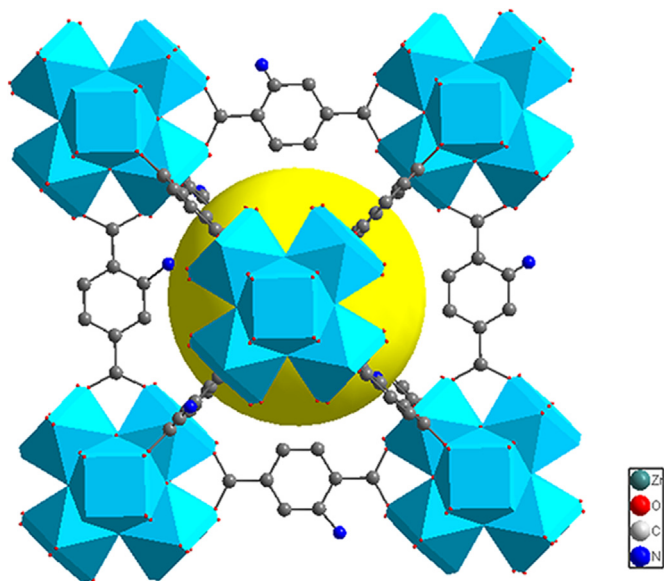


Fig. 1. Topological structure of UiO-66-NH₂ consisting of Zr₆(OH)₄O₄ clusters and NH₂-BDC linkers.

previously [49], UiO-66-NH₂ shows permanent microporosity with narrow pores size (about 0.52 ± 0.02 nm), which is located between the size of water molecules (0.26 nm) and hydrated ions [50] (e.g. Na⁺ 0.72 nm, K⁺ 0.66 nm, Ca²⁺ 0.82 nm, Mg²⁺ 0.86 nm, Cl⁻ 0.66 nm, Table 1). It can be expected that UiO-66-NH₂ membranes can show high ion rejections in seawater desalination by ionic sieving. To the best of our knowledge, however, no studies on UiO-66-NH₂ membranes have been reported for seawater desalination. In the present work, we report the synthesis of high stable UiO-66-NH₂ membranes for seawater desalination by using 3-aminopropyltriethoxysilane (APTES) as a covalent linker between the UiO-66-NH₂ membrane and the porous α -Al₂O₃ support [51,52].

2. Experimental

2.1. Materials

All chemicals were obtained commercially and used without further purification: zirconium (IV) chloride (ZrCl₄, Sigma, $\geq 99.5\%$ metals basis), 2-aminoterephthalic acid (2-NH₂-BDC, Alfa Aesar, 99%), N, N-dimethylformamide (DMF, Aladdin, $>99.9\%$ GC), 3-aminopropyltriethoxysilane (APTES, Aladdin, 98%). Porous α -Al₂O₃ tubes (Jiexi Lishun Technology Co., Guangdong, China: 12 mm

Table 1

Ion concentrations in the feed and permeate as well as ion rejection of the UiO-66-NH₂ membrane prepared on APTES-modified α -Al₂O₃ tube for desalination of 3.5 wt% seawater at 348 K.

Main ions in feed	Hydrated diameter ^a (nm)	Ion concentration (ppm)		Rejection (%)
		Feed	Permeate	
Na ⁺	0.72	14061.00	8.05	99.94
K ⁺	0.66	609.50	n.a. ^b	100.00
Mg ²⁺	0.86	894.20	0.39	99.96
Ca ²⁺	0.82	141.30	n.a.	100.00
NH ₄ ⁺	0.66	223.30	n.a.	100.00
F ⁻	0.70	3.57	n.a.	100.00
Cl ⁻	0.66	27765.00	3.02	99.98
NO ₃ ⁻	0.68	3527.40	5.64	99.84

^a Hydrated diameters are adopted from Ref. [50].

^b Below the detection limit of equipment.

outside diameter, 9 mm inside diameter, 75 mm length, ca. 1.0 μ m pore size, 30% porosity) were used as supports.

2.2. Synthesis of UiO-66-NH₂ membranes

The UiO-66-NH₂ membranes were prepared on non-modified or APTES-modified α -Al₂O₃ tubes according to the procedure as reported in elsewhere [45] with minor modification. Before membrane synthesis, the α -Al₂O₃ tubes were modified with APTES (0.2 mM in 10 mL toluene) at 383 K for 1 h under argon, leading to an APTES monolayer deposited on the surface of α -Al₂O₃ supports [51, 52]. In order to prepare UiO-66-NH₂ membrane on the non-modified or APTES-modified α -Al₂O₃ tube, a synthesis solution with the molar ratio of 1 ZrCl₄: 1 NH₂-BDC: 1 H₂O:500 DMF was prepared by mixing ZrCl₄, NH₂-BDC, H₂O and DMF under vigorous stirring, and stirring was continued to produce a clear and homogenous solution. The non-modified or APTES-modified α -Al₂O₃ tubes were vertically placed in a Teflon autoclave, and then the synthesis solution was poured into the autoclave. After in-situ growth for 24 h at 393 K, the UiO-66-NH₂ membranes were grown in-situ on the outside of the APTES-modified Al₂O₃ tubes. Afterwards, the as-synthesized membrane was washed with DMF and dried at room temperature for characterization and seawater desalination permeation measurement. In order to prepare denser UiO-66-NH₂ membranes, the above process of hydrothermal synthesis was repeated.

2.3. Characterizations of UiO-66-NH₂ membranes

The morphology and thickness of the UiO-66-NH₂ membrane were characterized by field emission scanning electron microscopy (FESEM) on an S-4800 (Hitachi) with a cold field emission gun operating at 4 kV and 10 μ A. X-ray diffraction (XRD) was applied to confirm the phase structure of the UiO-66-NH₂ membranes at room temperature under ambient pressure, which was recorded on a Bruker D8 Advance operating at 40 kV and 40 mA with a Cu K α 1 radiation source ($\lambda = 0.154056$ nm) at a stepwise increase of $2^\circ \cdot s^{-1}$ in the Bragg angle (2θ) range from 5 to 50 $^\circ$.

2.4. Seawater desalination measurement through the UiO-66-NH₂ membranes by pervaporation

The integrity of the as-synthesized UiO-66-NH₂ membrane is confirmed by measurement of single gas permeation by a soap-film flow-meter. For the single gas permeation, the UiO-66-NH₂ membrane prepared on the APTES-modified α -Al₂O₃ tube was sealed in a permeation tubular module, and the permeation of the single gas CO₂, N₂ was tested at 298 K and 1 bar across the membrane. The separation performance of the UiO-66-NH₂ membrane was evaluated for seawater desalination by pervaporation [19,20]. The seawater was prepared by dissolving sea salts in deionized water with concentrations ranging from 2 to 10 wt%. Unless mentioned, the conventional concentration of the seawater is 3.5 wt%, and the details of the corresponding ion concentration in the 3.5 wt% seawater was listed in Table 1. The supported UiO-66-NH₂ membranes were sealed in a permeation module with silicone O-ring, and the seawater preheated to 318–363 K was fed to the membrane side. The whole membrane module was heated in a thermostatic water bath together with the feed solution. The permeate side of the membrane was evacuated with a vacuum pump. Two freezing traps with liquid N₂ cooling were used to collect the permeation at every time interval. Continuous stirring and recirculation of the feed solution was utilized to prevent the concentration polarization on the contact membrane side. The water flux has been determined by the amount of water collected in the two cooling traps. For the

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