Development of low mass-transfer-resistance fluorinated TiO₂-SiO₂/PVDF composite hollow fiber membrane used for biogas upgrading in gas-liquid membrane contactor

Xu, Yilin; Lin, Yuqing; Lee, Melanie; Malde, Chandresh; Wang, Rong

2018

Xu, Y., Lin, Y., Lee, M., Malde, C., & Wang, R. (2018). Development of low mass-transfer-resistance fluorinated TiO₂-SiO₂/PVDF composite hollow fiber membrane used for biogas upgrading in gas-liquid membrane contactor. *Journal of Membrane Science*, 552, 253-264. doi:10.1016/j.memsci.2018.02.016

<https://hdl.handle.net/10356/85344>

<https://doi.org/10.1016/j.memsci.2018.02.016>

© 2018 Elsevier B.V. All rights reserved. This paper was published in *Journal of Membrane Science* and is made available with permission of Elsevier B.V.

Downloaded on 26 Apr 2023 22:34:15 SGT

Development of Low Mass-Transfer-Resistance Fluorinated TiO₂-SiO₂/PVDF Composite Hollow Fiber Membrane Used for Biogas Upgrading in Gas-liquid Membrane Contactor

Yilin Xu^{a,b,1}, Yuqing Lin^{b,1}, Melanie Lee^b, Chandresh Malde^c, Rong Wang^{b,d*}

^a Interdisciplinary Graduate School, Nanyang Technological University, Singapore [639798](#), Singapore

^b Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore

^c Johnson Matthey Technology Centre, Reading RG4 9NH United Kingdom

^d School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

¹These authors contributed to the work equally as first authors

*Corresponding author at: School of Civil and Environmental Engineering,

Nanyang Technological University, 639798 Singapore,

Singapore. Tel.: +65 6790 5327; fax: +65 6791 0676.

E-mail address: rwang@ntu.edu.sg (R. Wang).

Abstract:

An inorganic-organic fluorinated titania-silica (fTiO₂-SiO₂)/polyvinylidene fluoride (PVDF) composite membrane was fabricated, via facile in-situ vapor-induced hydrolyzation method followed by hydrophobic modification. This low mass-transfer-resistance membrane, composing of a mesoporous layer deposited onto macroporous substrate, was designed for biogas upgrading in gas-liquid membrane contactor (GLMC) application. The surface hydroxylation was introduced to facilitate the bridging of TiO₂-SiO₂ nanoparticles and PVDF substrate, which resulted in a more coherent deposition of the fTiO₂-SiO₂ layer onto the substrate. The surface microstructure was fine-tuned by controlling the amount of doped Si precursor, forming an integrated mesoporous fTiO₂-SiO₂ layer. The resultant fTiO₂-SiO₂/PVDF composite hollow fiber membrane exhibited a tighter pore size of ~25 nm and a desired water contact angle of ~124°, which effectively prevented membrane wetting. The CO₂ absorption fluxes of 8.0 and $5.6 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ were achieved due to the lower mass transfer resistance, by using 1 M of monoethanolamine (MEA) and sodium taurinate as absorbents with a liquid velocity of 0.25 m·s⁻¹, respectively. The long-term stability test showed a good integrity between the fTiO₂-SiO₂ layer and the PVDF substrate after 31-days of GLMC operation. The main benefit is the robust fluorinated inorganic layer which exhibited strong chemical resistance and high hydrophobicity, thus preventing membrane damage and pore wetting. Overall, this work provides an insight into the preparation of high-performance inorganic/organic composite hollow fiber membranes for carbon dioxide (CO₂) removal in GLMC application.

Keywords:

Fluorinated TiO₂-SiO₂; inorganic/organic composite membrane; mass transfer resistance; gas-liquid membrane contactor; CO₂ removal

Introduction

While historical trends indicate gradual decarbonization of fuel sources over time, there is an increasing interest in biogas for mitigating carbon dioxide (CO₂) emissions [1-3]. The major components of biogas are 55~65% CH₄, and 30~45% CO₂. The purity of CH₄ used in fuel should be above 95% [4-5]. Thus, biogas upgrading by CO₂ removal is of great importance for its practical utilization. Conventional techniques for carbon capture such as chemical and physical absorptions, solid adsorption and cryogenic distillation suffer many limitations due to their high energy consumption and process complexity [6-7]. To overcome these problems, membrane technology based on gas-liquid membrane contactor (GLMC) has been proposed as a promising alternative with the main advantages of being energy and space efficient, low cost, high operation flexibility and facile scalability [8-9].

In a GLMC for CO₂ capture, a gas and liquid absorbent flow on different sides of a microporous membrane, through which the target gas transporting is absorbed by the liquid absorbent. The membrane acts as a non-selective interfacial barrier between the liquid and gas phases to provide a large gas-liquid contact area without dispersing one phase into the other. Therefore, CO₂ selectivity is determined by the loading capacity of the absorbent, rather than the membrane itself [10-12]. It is preferable to run the process with non-wetted mode, i.e., the membrane pores are always filled with gas. As such, the transport of gas through the membrane is not blocked by the liquid phase. When the pores are partially or totally filled with liquid, the mass transfer of gas can be significantly reduced due to the lower CO₂ diffusion rate in the liquid [13-14]. To date, the pore sizes of the most of hollow fiber membranes employed in GLMC application are less than 200 nm to prevent the penetration of adsorbents, thus reducing mass transfer resistance [15-16]. For instance, Korminouri et al. [17] prepared polysulfone (PSf) membranes with different pore sizes ranging from 21-774 nm for CO₂ removal via GLMC. They found that the maximum absorption flux of $4.8 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ was achieved by using the hollow fiber with a pore size of 21 nm due to the higher critical water entry pressure. Atchariyawut et al. [9] reported the use of polyvinylidene

fluoride (PVDF) hollow fiber membranes in GLMC for CO₂ absorption, in which the hollow fiber with an average pore size of 20 nm presented the highest CO₂ absorption flux of $0.8 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Despite the advantages of tight pore structure for improving wetting resistance, the gas phase transportation in the tighter pore structure might also be retarded, resulting in lower CO₂ flux. Ideally, the membrane itself should possess a hydrophobic layer with a small pore size distributed on a highly porous substrate with large pores. It is theoretically accepted to be highly efficient for CO₂ removal in GLMC [18-19]. However, the preparation of such composite membranes is still in the proof-of-concept stage. A particular challenge impeding the development is the difficulty in depositing an integrated hydrophobic layer onto the substrate surface that has large pore sizes. The top mesoporous layer should be as thin as possible, but it has to cover the macro-pores to prevent the membrane from wetting.

Most of the current hollow fiber membranes used for GLMC are made from organic materials such as polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), PVDF, PSf, and polyether-imide (PEI) [5,20]. Except PTFE membrane [21-22], most of these membranes suffer from membrane swelling and degradation caused by chemical attacks from the absorbents over prolonged periods of operation, resulting in significant increments in mass transfer resistance [16-17, 23-25]. Inorganic membranes, made from metal oxides such as TiO₂, Al₂O₃, SiO₂ and ZrO₂, have received much attention due to their excellent chemical resistance, thermal stability, and mechanical properties, and thus have been employed in harsh conditions [26-28]. By fabricating an inorganic layer on a porous organic substrate, it is possible to obtain membranes with combined merits of both materials to broaden their applications. To design and fabricate the desired microstructure of an inorganic top layer on a polymeric substrate, the atomic layer deposition was the most commonly used method. This method involved hundreds of preparation cycles of “pulse–exposure–purge” to form a uniform and defect-free inorganic layer [29]. The nature of the complicated process makes it unviable to be employed in preparing integrated inorganic/organic composite membranes in hollow fiber configuration for GLMC. Thus, developing a new method to make such inorganic/organic composite membranes with desired microstructure is of great interest. Our

previous works [30-31] have successfully prepared an inorganic/organic composite ultra-filtration hollow fiber membrane by using an amphiphilic copolymer to facilitate the bonding between the hydrophobic organic substrate and hydrophilic inorganic layer. However, for the GLMC application, the copolymer bonding might limit the degree of adhesion stability, as it can easily be damaged by the chemical absorbent vapor in GLMC operation, thus affecting its long-term performance.

In this study, we aimed to design and fabricate a low mass-transfer resistance $\text{fTiO}_2\text{-SiO}_2/\text{PVDF}$ composite membrane via facile in-situ vapor-induced hydrolyzation method, followed by hydrophobic modification. The surface hydroxylation was employed for generating stable and permanent anchoring sites on macroporous PVDF substrates by alkali treatment. The microstructure of the $\text{TiO}_2\text{-SiO}_2$ layer was tuned by controlling the amount of doped Si precursor. The physical and chemical properties of the prepared $\text{fTiO}_2\text{-SiO}_2/\text{PVDF}$ membranes were characterized. The CO_2 absorption performance and the long-term stability were examined by using two types of absorbents (sodium taurinate [32-33] and MEA) in GLMC process. The schematic illustration (Fig. 1) showed the development of the inorganic/organic composite hollow fiber membranes and their anticipated effects in GLMC application.

Fig. 1 Schematic illustration of the $\text{fTiO}_2\text{-SiO}_2/\text{PVDF}$ composite hollow fiber membrane and CO_2 removal in GLMC application.

1. Experimental

2.1 PVDF surface hydroxylation

In-house made PVDF hollow fibers with outer diameter of 1.2×10^{-3} m and inner diameter of 0.7×10^{-3} m were used as substrates for fTiO₂-SiO₂/PVDF composite hollow fiber membrane development, and their specific information will be discussed later. The chemical modification of surface hydroxylation involves PVDF surface treatment using an aqueous alkali solution. Firstly, the PVDF membranes were thoroughly rinsed with deionized water (DI water, produced by Milli-Q system, Millipore, USA) to remove the glycerol preservatives. Secondly, the cleaned PVDF hollow fibers were immersed into 1 M sodium hydroxide solution (NaOH, Merck, 99 wt.%) under magnetic stirring for 3, 6 and 12 h, at a heating temperature of 60 °C. After alkali treatment, the hollow fibers were rinsed with DI water, and then dried at 50 °C in an oven for 12 h.

2.2 Preparation of fTiO₂-SiO₂/PVDF composite hollow fiber membranes.

The pretreated PVDF hollow fibers were used as substrates for TiO₂-SiO₂ film deposition. The modification solution was synthesized as follows: a desired amount of titanium isopropoxide (TTIP, Sigma-Aldrich, 97 wt.%) and/or tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 99 wt. %) were dissolved into isopropyl alcohol (IPA, Sigma-Aldrich, 99.7 wt.%) with vigorous stirring for 120 min. After that, a desired amount of diethanolamine (DEA, Sigma-Aldrich, ACS) used for tuning the reaction rate of hydrolyzation were sequentially dissolved into the as-prepared solution with vigorous stirring for 60 min, and then the precursor solution was obtained. The compositions of the precursor solutions are summarized in Table 1.

Table 1. Compositions of precursor solutions for preparation of TiO₂-SiO₂/PVDF composite hollow fiber membranes

Membrane*	TEOS (g)	DEA (g)
TiO ₂ -SiO ₂ -0/PVDF	0	0.5
TiO ₂ -SiO ₂ -0.5/PVDF	0.5	0.8
TiO ₂ -SiO ₂ -1/PVDF	1	1.0

*Note: IPA content = 60 g; TTIP content = 2 g (same amount for all types of membranes).

The surface modification was carried out by immersing dried pretreated PVDF hollow fibers into the as-prepared solutions via stirring for 30 min. The membranes were then placed in a humidity chamber for in-situ vapor-induced hydrolyzation reaction at 100 °C for 30 min. Hydrolyzation of Ti and Si precursors resulted in formation of TiO₂ and SiO₂ on the PVDF membrane surface during the reaction. After that, the prepared membranes were rinsed with excess DI water to remove loosely bound and stacked layer of TiO₂ and SiO₂ nanoparticles on the inorganic film layer, followed by drying at 50 °C for 12 h.

For hydrophobic modification, the prepared TiO₂-SiO₂/PVDF membranes were further treated by 2 wt.% of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFTS, Sigma-Aldrich, 97%) in ethanol (Sigma-Aldrich, 97%) at 60 °C for 24 h. The membranes were then dried in an oven at 70 °C for 12 h. After the drying process, the membranes were rinsed with excess ethanol and DI water to remove any unreacted PFTS residue. The membranes were subsequently dried at 50 °C for 12 h.

2.3 Membrane characterizations

The membrane samples were observed using a field emission scanning electron microscope (FESEM, JSM-7600F JOEL) at an operation voltage of 5 kV, which were sputtered with a thin layer of platinum prior to analysis. EDX spectroscopy was employed to detect the elemental composition on cross-section of fTiO₂-SiO₂/PVDF composite hollow fiber membranes. The average membrane pore size and pore size distribution were measured by a capillary flow porometer (CFP 1500A, from Porous Material. Inc. (PMI)). The chemical composition and states were investigated by X-ray photoelectron spectroscopy (XPS, Thermo

ESCALAB 250, USA). The XPS spectrum were analyzed by CasaXPS software, and the C 1s peak with the corrected energy at 284.5 eV was used as reference for spectra calibration. The detailed description for the measurement can be found in literature [34].

To evaluate the surface properties of fibers, a tensiometer (DCAT11 Dataphysics, Germany) was used to perform dynamic water contact angle measurement. In addition, the static water contact angle was also measured by using a goniometer (Data Physics Instruments GmbH) via sessile drop method. To minimize experimental errors, water contact angles were obtained by averaging three measurements.

2.4 Performance of fTiO₂-SiO₂/PVDF composite hollow fiber membrane in CO₂ absorption

Six pieces of fibers were sealed into a glass tube to make a lab-scale module with an effective length of 4.4×10^{-2} m and an effective membrane area of about 1.0×10^{-3} m². Pure CO₂ or biogas (CO₂/CH₄ = 40/60) (Singapore Oxygen Air Liquid Private Ltd) was used as feed gas which flowed into the lumen side of the hollow fiber membranes, and the liquid absorbent of 1 M MEA or sodium taurinate solution was transported over the shell side of the hollow fibers in counter-current direction.

The micro gas chromatograph (6890 Hewlett Packard, TCD) was used to analyze the inlet and outlet mixed gas compositions. All data collected after the experiment were operated for 30 min at 25 °C to ensure that the system has reached steady state. The results of each run were averaged from five times of sampling.

The specific CO₂ absorption flux was used to evaluate the membrane CO₂ removal efficiency rate, which could be calculated by Eq (1):

$$J = \frac{P(Q_{in} - Q_{out})}{RTA_m} \quad (1)$$

where J is the specific CO₂ absorption flux (mol·m⁻²·s⁻¹) of the hollow fiber membrane, Q the

volume flow rate ($10^{-3} \text{ m}^3 \cdot \text{s}^{-1}$) measured by mass flow controller (Cole-Parmer, USA), R the ideal gas constant of $62.4 \text{ mmHg} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, T the operating temperature of 298 K, A_m the membrane surface area (m^2), and P the operating pressure of 753 mmHg.

Long term performance test of the $\text{fTiO}_2\text{-SiO}_2/\text{PVDF}$ hollow fiber membranes was carried out periodically. After each running of CO_2 absorption test, the membranes modules were filled with the liquid absorbent MEA or sodium taurinate to ensure that the outer surface of membranes were continuously in contact with the chemicals. The membranes surface morphologies and water contact angles were also examined periodically over the testing period.

To test the bonding stability between the inorganic layer and the substrate, the $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membranes were subject to ultrasonication bath (FB 15068, Fisher Scientific, USA) at 25 kHz for 5 min, followed by testing the surface hydrophobicity and morphology.

2. Results and discussion

3.1 Surface hydroxylation of PVDF substrates by alkali treatment

The dynamic water contact angle and mechanical strength were utilized to evaluate the surface hydroxylation of PVDF substrates after alkali treatment. As shown in Fig. 2(a) and (b), the surface hydrophilicity increased while the mechanical property decreased during the test, indicating that the PVDF surface might have changed due to the dehydrofluorination after alkali treatment [35-36]. Thus, high surface-energy functional groups of carbonyl ($\text{C}=\text{O}$, 531.5 eV) and hydroxyl ($\text{C}-\text{O}$, 533.2 eV) were generated, and the dehydrofluorinated CHF (288.6 eV), $\text{CF}_2\text{-CHF}$ (290.8 eV) and CF_3 (293.8 eV) could also be detected, as shown in Fig. 3(c) and (d) [37-39]. It should be noting that a significant enhancement of hydrophilicity (dynamic water contact angle of 71° , which is $\sim 36.0\%$ drop from initial value) with only a slight mechanical property deterioration (tensile strength of 16.2 MPa, which is $\sim 7\%$ drop from

initial value), and this could be obtained after 6 h of alkali treatment. Therefore, the PVDF substrate obtained by surface hydroxylation for 6 h was selected for further study.

Fig. 2 Comparisons of (a) surface hydrophilicity, (b) mechanical property, and XPS spectra on (c) C 1s and (d) O 1s of PVDF substrate after surface hydroxylation with different hours of treatment.

The PVDF substrate morphologies and microstructures were further characterized before and after surface hydroxylation for 6 h, as shown in Fig. 3. As can be seen from Fig. 3(a), the pristine PVDF substrate was highly porous with a peak pore size of 530 nm. From the surface SEM, however, the largest surface pore size was $\sim 1 \mu\text{m}$ that may result in the penetration of

the top modification layer and forming defects. Apparently, this type of surface structure was not suitable for GLMC. The mesoporous layer deposited onto such macroporous substrates should be an intergated layer, which will be discussed in section 3. After surface hydroxylation process, shown in Fig. 3(b), there was no significant change in surface morphology and microstructure. This implies that the surface hydroxylation for 6 h has not caused severe damage of the microstructure of the substrate.

Fig. 3 FESEM images of the shell surface and pore size distributions of PVDF substrate (a) before and (b) after surface hydroxylation process for 6 h.

3.2 Membrane Characterization

3.2.1 Morphologies and microstructures of fTiO₂-SiO₂/PVDF composite hollow fiber membranes

The surface morphologies of fTiO₂-SiO₂/PVDF composite hollow fiber membranes with different amounts of doped Si precursors are presented in Fig. 4. For the fTiO₂-SiO₂-0/PVDF membrane (without Si), shown in Fig. 4(a), it could be observed that the fTiO₂ nanoparticles deposited on the PVDF substrate, but could not cover the big pores and form the continuous layer. Moreover, an additional peak showing a slightly smaller pore size after modification with fTiO₂ layer emerged, and this is due to the blocking of some large macropores by the

inorganic particles. After adding 0.5 g of Si precursor dopant, the $\text{fTiO}_2\text{-SiO}_2\text{-0.5/PVDF}$ membrane was formed. From this, the clusters of nanoparticles could be observed more obviously, and the surface pore size significantly decreased to 260 nm with a narrow pore size distribution, shown in Fig. 4(b). By continuing to increase the amount of Si doped, shown in Fig. 4(c), a relatively uniform and integrated $\text{fTiO}_2\text{-SiO}_2$ layer was formed with a peak pore size of 25 nm. This indicates that the Si precursor doping induced a microstructure tuning effect on the macroporous substrate. In addition, for the $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ membrane (1 g of Si precursor), a small amount of pores with an average size of ~ 180 nm could also be observed. This is likely to be as a result of the PVDF substrate possessing large surface pores ($> 1 \mu\text{m}$), which cannot be fully covered by the $\text{TiO}_2\text{-SiO}_2$ modification layer.

Fig. 4 FESEM images of the shell surface and pore size distributions of (a) $\text{fTiO}_2\text{-SiO}_2\text{-0/PVDF}$ composite hollow fiber membrane, (b) $\text{fTiO}_2\text{-SiO}_2\text{-0.5/PVDF}$ composite hollow fiber membrane, and (c) $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membranes.

There is a trend for the pore size of the fTiO₂-SiO₂ layer to decrease with an increasing amount of doped Si precursor. This could be due to water attacking the strained Si-O-Si bonds at high temperature during the hydrothermal treatment, leading to bond cleavage via hydrolysis. Thus the bond cleavage promoted the reconstruction of the Si-O-Si network, and then the relatively stable bonds accompanied with densified silica network were formed via condensation by water molecule removal [40-41]. Consequently, the fusion of SiO₂-TiO₂ nanoparticles sealed the grain boundaries and large pores during the hydrothermal process of vapor-induced in-situ hydrolyzation, thereby forming an integrated layer.

FESEM and EDX analysis were carried out on the cross-section of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane to examine its morphology and the distribution of TiO₂-SiO₂ particles. As shown in Fig. 5(a), the PVDF substrate exhibited a sponge-like structure. The fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane, on the other hand, had a denser top layer deposited on the macroporous PVDF substrate, as shown in Fig. 5(b). The top layer, with a thickness of 1.4 μm, was composed of inorganic nanoparticles that formed the packed pore structures. According to the EDX line scanning result in Fig. 5(c), the Ti (red line) and Si (blue line) elements were mostly deposited on the surface of the prepared hollow fiber membrane, with a small amount deposited on the inner structure of the PVDF substrate. The minor amount of internally distributed Ti and Si elements might be ascribed to the diffusion of precursors into substrate pores during modification. Moreover, to some extent, it proved that the skin layer has infiltrated into the substrate, which also leads to an enhancement in mechanical and bonding performance for fTiO₂-SiO₂/PVDF membranes.

Fig. 5 The cross-section images of (a) PVDF substrate, and (b) fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane, and (c) EDX line scan of Ti (red) and Si (blue) elements across the cross-section of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane.

3.2.2 Chemical composition of fTiO₂-SiO₂/PVDF composite hollow fiber membranes

The chemical composition and the nature of the chemical bonding of the fTiO₂-SiO₂/PVDF composite hollow fiber membrane was analyzed using XPS, as shown in Fig. 6(a) and (b). The Ti 2p peaks at 458.8 and 464.6 eV were corresponding to the Ti-O-Ti bonds [42-43]. The Si 2p peak at 102.2 eV was corresponding to Si-O-Si bond located at from SiO₂, as shown in Fig. 6(c) and (d) [43-44]. For the C 1s shown in Fig. 6(e) and (f), the

reduction of the presented $\text{CH}_2\text{-CF}_x$ peak could be attributed to surface hydroxylation. The stronger peak of CF_3 could be ascribed to the PFTS modification.

Fig. 6 The XPS spectra of (a) Ti 2p, (c) Si 2p, and (e) C 1s on fTiO₂-SiO₂-1/PVDF membrane and PVDF substrate; and the corresponding curve fittings of (b) Ti 2p, (d) Si 2p, and (f) C 1s for fTiO₂-SiO₂-1/PVDF membrane.

According to the above results, it is believed that the formation of the inorganic layer and subsequently hydrophobic modification are based on the following mechanism: Ti and Si precursors were firstly exposed to water vapor at a high temperature of ~ 100 °C and thus

hydrolysis occurred, resulting in nucleation and growth of inorganic nanoparticles via condensation, and formed the Ti-O-Ti, Si-O-Si and Ti-O-Si bonds. When uniform Ti and Si precursors were deposited on the PVDF substrates, the hydrolyzed nucleation would lead to interconnected clusters, which finally grew and formed the integrated layer [45-46].

For the subsequent hydrophobic modification, the silane groups of PFTS were first hydrolyzed to form silanol groups. This was followed by reaction with hydroxyl groups from TiO₂ or SiO₂ on the membrane surface via condensation. The long fluorinated chains of PFTS grafted on the TiO₂-SiO₂ surface had low surface energy, thus rendered the surface to be hydrophobic as discussed below.

3.2.3 Surface hydrophobicity and adhesion characterization of fTiO₂-SiO₂/PVDF composite hollow fiber membranes

The surface hydrophobicity of hollow fiber membranes with different Si precursor modifications were investigated, as shown in Fig. 7. It could be detected that the dynamic water contact angle decreased to 68° after surface hydroxylation treatment. After deposition of the fTiO₂-SiO₂ layer, water contact angle increased to 117°, and this is believed to be due to the successful grafting of low surface-energy PFTS. By continuously increasing the amount of doped Si precursor to 1 g, a further enhancement in dynamic water contact angle up to ~124° was detected. This is because the more integrated surface of fTiO₂-SiO₂-1/PVDF membrane ratherly introduce more hydroxyl sites for PFTS grafting. Thus, the fTiO₂-SiO₂-1/PVDF membrane was selected for further adhesion characterization studies. The bonding stability between the fTiO₂-SiO₂ layer and the PVDF substrate was investigated by assessing the change in hydrophobicity before and after ultrasonication for 5 min. It could be observed that the hydrophobicity of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane presented no significant change, with the dynamic water contact angle decreasing by less than ~5%. This confirmed the good bonding stability between the top fTiO₂-SiO₂-1 layer with the PVDF substrate.

Fig. 7 Surface hydrophobicity with different modification treatments and adhesion characterization after ultrasonication.

The adhesion of the top inorganic layer with the PVDF substrate was examined through ultrasonication, shown in Fig. 8. It could be observed that the surface of fTiO₂-SiO₂-1/PVDF membrane without surface hydroxylation was not integrated well with a large amount of big defects (Fig. 8(a)) as compared to the more integrated membrane with surface hydroxylation (Fig. 8 (c)). After ultrasonication, the fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane without surface hydroxylation was significantly stripped off (Fig. 8(b)), in which the pore size and pore size distribution of the large defects expanded. In contrast, for the fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane with surface hydroxylation treatment, a slight change in surface morphology could be observed. A minor peak at 55 nm emerged, by shifting from the smallest pores of 26 to 39 nm, shown in Fig. 8(c) and (d). The improved adhesion stability could be attributed to the coordination between the surface anchoring groups of carbonyl and hydroxy functionalities, and the Ti, Si precursors. This facilitated the bonding and growth of the inorganic particles, and verified that the surface hydroxylation was one of the key steps to fabricate a coherent membrane by improving the bonding strength of fTiO₂-SiO₂ layer with the PVDF substrate.

Fig. 8 FESEM images of (a) $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membrane without surface hydroxylation before and (b) after ultrasonication, (c) $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membrane with surface hydroxylation before and (d) after ultrasonication.

3.3 Performance of $\text{fTiO}_2\text{-SiO}_2\text{/PVDF}$ composite hollow fiber membranes in GLMC application

3.3.1 The pure CO_2 absorption and synthetic biogas upgrading performance

In order to examine the performance of the $\text{fTiO}_2\text{-SiO}_2\text{/PVDF}$ composite hollow fiber membranes were prepared with different amounts of doped Si precursor. The CO_2 absorption flux and the synthetic biogas upgrading performance of the pristine PVDF substrate, $\text{fTiO}_2\text{-SiO}_2\text{-0.5/PVDF}$ and $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membranes were tested using the absorbents of 1 M MEA and sodium taurinate, shown in Fig. 9. For both pure CO_2 and synthetic biogas feeds, the composite hollow fiber membranes exhibited higher CO_2 flux compared to the pure PVDF membrane. In fact, there is a trend of increasing CO_2 flux

with an increased amount of Si precursor doping. This becomes more pronounced at higher absorbent flow rates and using pure CO₂ as the feed.

Fig. 9 (a) pure CO₂ absorption flux and (b) synthetic biogas upgrading performance of various membranes with different modification treatments. (ST: sodium taurinate)

The CO₂ absorption flux presented a rising trend when the absorbents of MEA and sodium taurinate flow velocities increased from 0.1 to 0.3 m·s⁻¹, indicating that the liquid phase boundary layer governs most of the mass transfer resistance. Since the reaction between the chemical absorbents and CO₂ occurred near the gas-liquid boundary, the depletion of untreated MEA or sodium taurinate might have limited the rate of CO₂ absorption. Therefore, an increase in absorbent flow velocity allowed a sufficient amount of unreacted absorbents to flow through the gas-liquid boundary, thus enhancing the CO₂ absorption flux [8]. Moreover, the CO₂ absorption flux was higher when using the MEA absorbent than sodium taurinate. This could be attributed to the faster reaction rate for CO₂-MEA depletion compared to CO₂-sodium taurinate according to the mechanism of reaction kinetics [32-33].

For the pristine PVDF substrate, the CO₂ flux remained relatively low and started decreasing when the absorbent flow rate exceeded 0.2 m·s⁻¹. This may be due to the partial wetting of the membrane pores which becomes more severe when higher shear forces are generated by the absorbent flow velocity. This leads to a significant increase in mass transfer resistance for CO₂ diffusion in GLMC application. For the fTiO₂-SiO₂/PVDF composite

hollow fiber membranes, in contrast, the CO₂ absorption flux increased almost linearly with an increase in absorbent flow velocity. This indicates a non-wetted improvement compared with the pristine PVDF substrate, which could be ascribed to the tighter and more hydrophobic surface after fTiO₂-SiO₂ modification. Moreover, it is noted that the fTiO₂-SiO₂-0.5/PVDF membrane was also subjected to pore intrusion by absorbents at a higher liquid velocity of 0.3 m·s⁻¹. However, the CO₂ absorption flux of fTiO₂-SiO₂-1/PVDF membrane increased linearly and reached a relatively high value of 8.6 and 6.3 × 10⁻³ mol·m⁻²·s⁻¹ for absorbents of MEA and sodium taurinate, respectively. One possibility that the fTiO₂-SiO₂-1/PVDF membrane had a more suitable pore size and better hydrophobicity, hence presenting a higher wetting resistance for GLMC application.

The CO₂ separation performance in synthetic biogas upgrading using MEA chemical absorbent provided insight into the performance of the composite hollow fiber membranes in a more realistic scenario. As shown in Fig. 9(b), the CO₂ absorption flux of the pristine PVDF substrate and fTiO₂-SiO₂/PVDF membranes with biogas was relatively lower than that with pure CO₂ as feed gas. It could be explained by the fact that biogas with 40% CO₂ concentration was employed in GLMC process. The lower CO₂ concentration led to the lower driving force of CO₂ diffusion from the lumen side (gas phase, high CO₂ concentration) to shell side (liquid phase, low CO₂ concentration), thus resulted in lower CO₂ absorption flux. The CO₂ absorption performance of the PVDF support and the fTiO₂-SiO₂-0.5/PVDF membrane with biogas decreased gradually with the liquid velocity increasing, which is similar to the case of using pure CO₂. This could also be attributed to the partial wetting of large pores or defects caused by infiltration of chemical absorbents. However, the CO₂ absorption of fTiO₂-SiO₂-1/PVDF membrane increased linearly without declining, which further verifies its desirable CO₂ removal capacity in GLMC due to its better integrated membrane surface.

3.3.2 Long-term performance in GLMC

Long-term deterioration in membrane stability due to the reaction between the membrane and the chemical absorbents can strongly affect their performance and efficiency. In this study, the long-term CO₂ absorption performance of the PVDF substrate and fTiO₂-SiO₂-1/PVDF composite hollow fiber membranes were carried out for 31 days by using 1 M MEA and sodium taurinate solution as absorbents, respectively.

As shown in Fig. 10(a), for the MEA absorbent, the CO₂ absorption flux of pristine PVDF continuously decreased, implying the occurrence of progressive wetting, resulting in an increase in membrane mass transfer resistance. The CO₂ flux was eventually stabilized at a value of $1.8 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, or a 61% drop from the initial value after the 18-day test. This could be complete wetting. In contrast, the CO₂ absorption flux of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane decreased by merely 10% over the 31-day test and maintained a relative high value of $6.1 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, indicating a significant improvement in GLMC long-term operation. The slight flux decline could be attributed to the partial wetting caused by capillary condensation of MEA vapors in the hollow fiber substrates. Considering that the hollow fibers were soaked stagnantly in MEA solution during the long-term operation tests in each CO₂ absorption run, diffusion and condensation of MEA vapors into the membranes was inevitable, hence resulted in slight declines of the CO₂ absorption flux and hydrophobicity.

Fig. 10 Long term performances of (a) CO₂ absorption flux (at absorbent velocity of 0.25 m s⁻¹) and (b) surface hydrophobicity of PVDF substrate and fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane under the absorbents of MEA and sodium taurinate over a period of

31 days.

The dynamic water contact angles were tested periodically during the long-term operation in MEA solution. As shown in Fig. 10(b), the dynamic water contact angle of the pristine PVDF membrane decreased from $\sim 112^\circ$ to 85° , implying that a chemical and/or physical change(s) occurred on the membrane surface due to the interaction with MEA. Nevertheless, the water contact angle of the $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ membrane showed only a slight decrease from $\sim 124^\circ$ to 119° . According to Sadoogh et al. [47], the PVDF substrate performance drop might be ascribed to the chemical degradation at the PVDF and MEA interface, and this resulted in dehydrofluorination of the PVDF surface. In addition, for the long-term performance tests using sodium taurinate as the absorbent, the curves of CO_2 absorption flux and dynamic water contact angles were similar to the MEA absorbent, but they presented a lower degree of performance deterioration. It could be explained by the higher surface tension of sodium taurinate as well as its lower non-volatile property. This leads to a reduced tendency for pore intrusion, and better long-term performance was achieved compared to the MEA absorbent [48]. The presence of a highly hydrophobic and chemically robust $\text{fTiO}_2\text{-SiO}_2$ top layer effectively prevents the PVDF substrate from corrosion in MEA and sodium taurinate solution, and thus ensuring relatively stable CO_2 flux during long-term GLMC operation.

The morphologies and pore size distributions were also characterized after the 31-day operation in MEA and ST solutions, as shown in Fig. 11. It could be observed that after the 31-day operation, most of the $\text{fTiO}_2\text{-SiO}_2$ surface layer still remained its original morphology as compared to the pristine PVDF membrane with larger surface pore structures, which further verified that the robust $\text{fTiO}_2\text{-SiO}_2$ layer prevented chemical absorbents attacking and pore wetting during the long-term test. However, some small defects could also be observed over the $\text{fTiO}_2\text{-SiO}_2$ layer, probably due to the vapour condensation of MEA or ST in the PVDF support from the large pores of $\text{fTiO}_2\text{-SiO}_2$ layer, causing a bit PVDF swelling and thus cracks formed on the $\text{fTiO}_2\text{-SiO}_2$ layer. This also explained the reduced tendency of long-term

CO₂ absorption flux in Fig. 10.

Fig. 11 FESEM images and pore size distributions of PVDF support and fTiO₂-SiO₂-1/PVDF composite HF membranes (a1-b1) before and after 31-day operation in (a2-b2) MEA and (a3-b3) ST solution, respectively.

3.4 CO₂ flux comparison in various membranes for GLMC

Compared with the state-of-the-art CO₂ removal performance in GLMC applications from literature, the fTiO₂-SiO₂ composite hollow fiber membrane prepared in the current work exhibited competitive performance in terms of CO₂ absorption flux under a relatively low MEA concentration and liquid velocity, shown in Table 2. It could be explained by the lower

mass-transfer-resistance nature of the macroporous PVDF substrate with relatively large pore sizes, and the mesoporous fTiO₂-SiO₂ modification layer deposited onto the substrate. This combines the advantages of highly porous organic membranes with chemically robust inorganic materials.

Table 2. Overall comparison of CO₂ absorption flux on various membranes in GLMC

Membrane substrate	Modification layer	Feed gas	Absorbent	Lumen side	Substrate pore size (nm)	Surface pore size (nm)	Liquid velocity (m·s ⁻¹)	CO ₂ flux (10 ⁻³ mol·m ⁻² ·s ⁻¹)	Reference
PVDF	— ^a	Pure CO ₂	Water	Gas	20	—	0.25	0.8	[9], 2006
PEI	Polydimethyl-siloxane	Pure CO ₂	Water	Gas	148 ^c	—	0.11	0.8	[11], 2015
PEI	Hydrophobic montmorillonite	Pure CO ₂	Water	Liquid	331	79	0.5	1.1	[25], 2015
PSf	Surface-modifying macromolecules	Pure CO ₂	Water	Gas	—	21	300 ml·min ⁻¹	4.8	[17], 2015
PAI ^b	Fluorolink S10	Pure CO ₂	Water	Gas	—	—	0.25	0.7	[49], 2011
PEI	Fluorinated SiO ₂	Pure CO ₂	2M sodium taurinate	Gas	30	—	0.25	6.8	[50], 2014
PP	— ^a	14% CO ₂	1M MEA	Gas	20	—	0.1	5.9 ^d	[51], 2007
PVDF	Low-density polyethylene	20% CO ₂	1M MEA	Gas	—	—	50 ml·min ⁻¹	3.1	[52], 2013
PVDF-Cloisite	— ^a	Pure CO ₂	1M MEA	Liquid	—	—	1.1	20.3	[53], 2017
PVDF	— ^a	Pure CO ₂	2M MEA	Liquid	—	—	12.4 ml·min ⁻¹	13.0	[10], 2013
PTFE	— ^a	Pure CO ₂	30 wt% (≈ 4.9M) MEA	Liquid	30-80	—	28 ml·min ⁻¹	1.1 ^e	[7], 2014
Al ₂ O ₃	Fluorinated ZrO ₂	12.5 % CO ₂	5 wt% (≈ 0.8M) MEA	Liquid	—	200	10 ml·min ⁻¹	1.3	[12], 2015
PVDF	Fluorinated TiO ₂ -SiO ₂	Pure CO ₂	1M MEA	Gas	530	25	0.25	8.0	This work
PVDF	Fluorinated TiO ₂ -SiO ₂	Pure CO ₂	1M sodium taurinate	Gas	530	25	0.25	5.6	This work

^a non-modified membrane; ^b PAI: polyamide-imide; ^c predicted pore size;

^{d, e} after converting the units of (mol·m⁻²·h⁻¹), (mol·m⁻²·min⁻¹) to (10⁻³ mol·m⁻²·s⁻¹), respectively.

3. Conclusions

The in-situ vapor-induced hydrolyzation process incorporated with PFTS grafting was used to prepare fTiO₂-SiO₂/PVDF composite hollow fiber membranes for biogas upgrading in GLMC. The surface hydroxylation was found to be effective in bridging the TiO₂-SiO₂ nanoparticles and the PVDF substrate due to its hydrophilic nature. The surface microstructure could be fine-tuned by controlling the amount of doped Si precursor, and an integrated mesoporous fTiO₂-SiO₂ layer onto a macroporous PVDF substrate. The fabricated membrane exhibited a high CO₂ absorption flux of $8.0 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Compared with the pristine PVDF membrane, the long-term performance of the fTiO₂-SiO₂/PVDF composite hollow fiber membrane was significantly improved due to its high chemical resistance and hydrophobicity that effectively prevented the PVDF substrate from corrosion by chemical absorbents of MEA and sodium taurinate. Overall, the fTiO₂-SiO₂/PVDF composite hollow fiber membrane prepared in this work out-performed most of the state-of-the-art membranes for CO₂ removal in GLMC applications. This work may provide useful insights and routes into the preparation of a new generation of inorganic-organic composite hollow fiber membranes for the GLMC process.

Acknowledgements

This work was funded by the Johnson Matthey Technology Centre. We also acknowledge funding support from the Singapore Economic Development Board to the Singapore Membrane Technology Centre.

References

- [1] T. C. Merkel, H. Q. Lin, X. T. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: An opportunity for membranes, *J. Membr. Sci.*, 359 (2010) 126-139.
- [2] Z. E. Zhang, Y. F. Yan, L. Zhang, Y. X. Chen, J. Y. Ran, G. Pu, C. L. Qin, Theoretical study on CO₂ absorption from biogas by membrane contactors: Effect of operating parameters, *Ind. Eng. Chem. Res.*, 53 (2014) 14075-14083.
- [3] N. Tippayawong, P. Thanompongchart, Biogas quality upgrade by simultaneous removal of CO₂ and H₂S in a packed column reactor, *Energy*, 35 (2010) 4531-4535.

- [4] K.H. Kim, K.J. Baik, I.W. Kim, H.K. Lee, Optimization of membrane process for methane recovery from biogas, *Sep. Sci. Technol.*, 47 (2012) 963-971.
- [5] Y. Zhang, J. Sunarso, S.M. Liu, R. Wang, Current status and development of membranes for CO₂/CH₄ separation: A review, *Int. J. Greenh. Gas Con.*, 12 (2013) 84-107.
- [6] S. Atchariyawut, R. Jiratananon, R. Wang, Separation of CO₂ from CH₄ by using gas-liquid membrane contacting process, *J. Membr. Sci.*, 304 (2007) 163-172.
- [7] F. Bougie, I. Iliuta, M.C. Iliuta, Absorption of CO₂ by AHPD-Pz aqueous blend in PTFE hollow fiber membrane contactors, *Sep. Purif. Technol.*, 138 (2014) 84-91.
- [8] J.L. Li, B.H. Chen, Review of CO₂ absorption using chemical solvents in hollow fiber membrane contactors, *Sep. Purif. Technol.*, 41 (2005) 109-122.
- [9] S. Atchariyawut, C. Feng, R. Wang, R. Jiratananon, D.T. Liang, Effect of membrane structure on mass-transfer in the membrane gas-liquid contacting process using microporous PVDF hollow fibers, *J. Membr. Sci.*, 285 (2006) 272-281.
- [10] S. Rajabzadeh, S. Yoshimoto, M. Teramoto, M. Al-Marzouqi, Y. Ohmukai, T. Maruyama, H. Matsuyama, Effect of membrane structure on gas absorption performance and long-term stability of membrane contactors, *Sep. Purif. Technol.*, 108 (2013) 65-73.
- [11] S.A. Hashemifard, A.F. Ismail, T. Matsuura, M.R. DashtArzhandi, Performance of silicon rubber coated polyetherimide hollow fibers for CO₂ removal via a membrane contactor, *RSC Adv.*, 5 (2015) 48442-48455.
- [12] X. Yu, L. An, J. Yang, S.-T. Tu, J. Yan, CO₂ capture using a superhydrophobic ceramic membrane contactor, *J. Membr. Sci.*, 496 (2015) 1-12.
- [13] M. Rahbari-Sisakht, D. Rana, T. Matsuura, D. Emadzadeh, M. Padaki, A.F. Ismail, Study on CO₂ stripping from water through novel surface modified PVDF hollow fiber membrane contactor, *Chem. Eng. J.*, 246 (2014) 306-310.
- [14] Y. Liao, R. Wang, A.G. Fane, Engineering superhydrophobic surface on poly (vinylidene fluoride) nanofiber membranes for direct contact membrane distillation, *J. Membr. Sci.*, 440 (2013) 77-87.
- [15] K.J. Lu, J. Zuo, T.S. Chung, Tri-bore PVDF hollow fibers with a super-hydrophobic coating for membrane distillation, *J. Membr. Sci.*, 514 (2016) 165-175.
- [16] R. Wang, H.Y. Zhang, P.H.M. Feron, D.T. Liang, Influence of membrane wetting on CO₂ capture in microporous hollow fiber membrane contactors, *Sep. Purif. Technol.*, 46 (2005) 33-40.
- [17] F. Korminouri, M. Rahbari-Sisakht, T. Matsuura, A.F. Ismail, Surface modification of polysulfone hollow fiber membrane spun under different air-gap lengths for carbon dioxide absorption in membrane contactor system, *Chem. Eng. J.*, 264 (2015) 453-461.
- [18] A. Lautenschleger, E.Y. Kenig, A. Voigt, K. Sundmacher, Model-based analysis of a gas/vapor-liquid microchannel membrane contactor, *AIChE J.*, 61 (2015) 2240-2256.
- [19] P.T. Nguyen, E. Lasseguette, Y. Medina-Gonzalez, J.C. Remigy, D. Roizard, E. Favre, A dense membrane contactor for intensified CO₂ gas/liquid absorption in post-combustion capture, *J. Membr. Sci.*, 377 (2011) 261-272.
- [20] Y. Zhang, R. Wang, Gas-liquid membrane contactors for acid gas removal: recent advances and future challenges. *Curr. Opin. Chem. Eng.*, 2 (2013) 255-262.
- [21] O. Falk-Pedersen, H. Dannström, Separation of carbon dioxide from offshore gas turbine exhaust. *Energ. Convers. Manage.*, 38 (1997) S81-S86.
- [22] H. Tang, Y. Zhang, F. Wang, H. Zhang, Y. Guo, Long-term stability of polytetrafluoroethylene

- (PTFE) hollow fiber membranes for CO₂ capture, *Energ. Fuel.*, 30 (2016) 492-503.
- [23] S.M. Sedghi, J. Brisson, D. Rodrigue, M.C. Iliuta, Chemical alteration of LDPE hollow fibers exposed to monoethanolamine solutions used as absorbent for CO₂ capture process, *Sep. Purif. Technol.*, 80 (2011) 338-344.
- [24] R. Naim, A.F. Ismail, A. Mansourizadeh, Effect of non-solvent additives on the structure and performance of PVDF hollow fiber membrane contactor for CO₂ stripping, *J. Membr. Sci.*, 423-424 (2012) 503-513.
- [25] M. Rezaei DashtArzhandi, A.F. Ismail, T. Matsuura, B.C. Ng, M.S. Abdullah, Fabrication and characterization of porous polyetherimide/montmorillonite hollow fiber mixed matrix membranes for CO₂ absorption via membrane contactor, *Chem. Eng. J.*, 269 (2015) 51-59.
- [26] Y. Lin, D. Zou, X. Chen, M. Qiu, H. Kameyama, Y. Fan, Low temperature sintering preparation of high-permeability TiO₂/Ti composite membrane via facile coating method, *Appl. Surf. Sci.*, 349 (2015) 8-16.
- [27] Y. Lin, Y. Cai, M. Qiu, E. Drioli, Y. Fan, Environment-benign preparation of Ag toughening TiO₂/Ti tight ultrafiltration membrane via aqueous sol-gel route, *J. Mater. Sci.*, 50 (2015) 5307-5317.
- [28] Y. Lin, Y. Cai, E. Drioli, Y. Fan, Enhancing mechanical and photocatalytic performances on TiO₂/Ti composite ultrafiltration membranes via Ag doping method, *Sep. Purif. Technol.*, 145 (2015) 29-38.
- [29] D.B. Farmer, R.G. Gordon, Atomic layer deposition on suspended single-walled carbon nanotubes via gas-phase noncovalent functionalization, *Nano Lett.*, 6 (2006) 699-703.
- [30] Y. Lin, C.H. Loh, L. Shi, Y. Fan, R. Wang, Preparation of high-performance Al₂O₃/PES composite hollow fiber UF membranes via facile in-situ vapor induced hydrolyzation, *J. Membr. Sci.* 539 (2017) 65-75.
- [31] Y. Lin, Y. Xu, C.H. Loh, R. Wang, Development of robust fluorinated TiO₂ /PVDF composite hollow fiber membrane for CO₂ capture in gas-liquid membrane contactor, *App. Surf. Sci.*, 436 (2018) 670-681.
- [32] R. Wang, D.F. Li, D.T. Liang, Modeling of CO₂ capture by three typical amine solutions in hollow fiber membrane contactors, *Chem. Eng. Process.: Process Intensification*, 43 (2004) 849-856.
- [33] Y. Zhang, R. Wang, L. Zhang, A.G. Fane, Novel single-step hydrophobic modification of polymeric hollow fiber membranes containing imide groups: Its potential for membrane contactor application, *Sep. Purif. Technol.*, 101 (2012) 76-84.
- [34] X. Yang, R. Wang, L. Shi, A.G. Fane, M. Debowski, Performance improvement of PVDF hollow fiber-based membrane distillation process, *J. Membr. Sci.*, 369 (2011) 437-447.
- [35] Z. Zheng, Z. Gu, R. Huo, Z. Luo, Superhydrophobic poly (vinylidene fluoride) film fabricated by alkali treatment enhancing chemical bath deposition, *Appl. Surf. Sci.*, 256 (2010) 2061-2065.
- [36] S. Sairiam, C.H. Loh, R. Wang, R. Jiratananon, Surface modification of PVDF hollow fiber membrane to enhance hydrophobicity using organosilanes, *J. Appl. Polym. Sci.*, 130 (2013) 610-621.
- [37] Y. Han, S.J. Song, Y. Lu, D.F. Zhu, A method to modify PVDF microfiltration membrane via ATRP with low-temperature plasma pretreatment, *Appl. Surf. Sci.*, 379 (2016) 474-479.
- [38] C.D. Wagner, G.E. Muilenberg, *Handbook of X-ray photoelectron spectroscopy: A reference*

book of standard data for use in X-ray photoelectron spectroscopy, Perkin-Elmer, 1979.

- [39] D.R. Baer, M.H. Engelhard, G.E. Johnson, J. Laskin, J. Lai, K. Mueller, P. Munusamy, S. Thevuthasan, H. Wang, N. Washton, A. Elder, B.L. Baisch, A. Karakoti, S.V.N.T. Kuchibhatla, D. Moon, Surface characterization of nanomaterials and nanoparticles: Important needs and challenging opportunities, *J. Vac. Sci. Technol. A.*, 31 (2013) 050820.
- [40] A. Matsuda, T. Kogure, Y. Matsuno, S. Katayama, T. Tsuno, N. Tohge, T. Minami, Structural-changes of sol gel-derived TiO₂-SiO₂ coatings in an environment of high-temperature and high humidity, *J. Am. Ceram. Soc.*, 76 (1993) 2899-2903.
- [41] T. Tsuru, Nano/subnano-tuning of porous ceramic membranes for molecular separation, *J. Sol-Gel Sci. Technol.*, 46 (2008) 349-361.
- [42] A. Eshaghi, A. Eshaghi, Optical and hydrophilic properties of Cr doped TiO₂-SiO₂ nanostructure thin film, *Appl. Surf. Sci.*, 258 (2012) 2464-2467.
- [43] L. Zhai, Y. Wang, F. Peng, Z. Xiong, R. Liu, J. Yuan, Y. Lan, Synthesis of TiO₂-SiO₂/waterborne polyurethane hybrid with amino-siloxane terminated via a sol-gel process, *Mater. Lett.*, 89 (2012) 81-85.
- [44] M. Barberio, S. Veltri, A. Imbrogno, F. Stranges, A. Bonanno, P. Antici, TiO₂ and SiO₂ nanoparticles film for cultural heritage: Conservation and consolidation of ceramic artifacts, *Surf. Coat. Technol.*, 271 (2015) 174-180.
- [45] C.A. Wilson, R.K. Grubbs, S.M. George, Nucleation and growth during Al₂O₃ atomic layer deposition on polymers, *Chem. Mater.*, 17 (2005) 5625-5634.
- [46] L. Wang, J.J. Travis, A.S. Cavanagh, X. Liu, S.P. Koenig, P.Y. Huang, S.M. George, J.S. Bunch, Ultrathin oxide films by atomic layer deposition on graphene, *Nano Lett.*, 12 (2012) 3706-3710.
- [47] M. Sadoogh, A. Mansourizadeh, H. Mohammadinik, An experimental study on the stability of PVDF hollow fiber membrane contactors for CO₂ absorption with alkanolamine solutions, *RSC Adv.*, 5 (2015) 86031-86040.
- [48] S. Masoumi, M.R. Rahimpour, M. Mehdipour, Removal of carbon dioxide by aqueous amino acid salts using hollow fiber membrane contactors, *J. CO₂ Util.*, 16 (2016) 42-49.
- [49] Y. Zhang, R. Wang, S. Yi, L. Setiawan, X. Hu, A.G. Fane, Novel chemical surface modification to enhance hydrophobicity of polyamide-imide (PAI) hollow fiber membranes, *J. Membr. Sci.*, 380 (2011) 241-250.
- [50] Y. Zhang, R. Wang, Novel method for incorporating hydrophobic silica nanoparticles on polyetherimide hollow fiber membranes for CO₂ absorption in a gas-liquid membrane contactor, *J. Membr. Sci.*, 452 (2014) 379-389.
- [51] S.P. Yan, M.X. Fang, W.F. Zhang, S.Y. Wang, Z.K. Xu, Z.Y. Luo, K.F. Cen, Experimental study on the separation of CO₂ from flue gas using hollow fiber membrane contactors without wetting, *Fuel Process. Technol.*, 88 (2007) 501-511.
- [52] A.L.y. Ahmad, H.N. Mohammed, B.S. Ooi, C.P. Leo, C.P. Leo, A.L. Ahmad, Deposition of a polymeric porous superhydrophobic thin layer on the surface of poly(vinylidene fluoride) hollow fiber membrane, *Pol. J. Chem. Technol.*, 15 (2013) 1-6.
- [53] I. Rudaini, R. Naim, S. Abdullah, N. Mokhtar, J. Jaafar, PVDF-Cloiste hollow fiber membrane for CO₂ absorption via membrane contactor, *J. Teknol. Sci. Eng.*, 79 (2017) 17-23.

Fig. 1 Schematic illustration of the fTiO₂-SiO₂/PVDF composite hollow fiber membrane and CO₂ removal in GLMC application.

Fig. 2

Fig. 2 Comparisons of (a) surface hydrophilicity, (b) mechanical property, and XPS spectra on (c) C 1s and (d) O 1s of PVDF substrate after surface hydroxylation with different treated hours.

Fig. 3

Fig. 3 FESEM images of the shell surface and pore size distributions of PVDF substrate (a) before and (b) after surface hydroxylation process for 6 h.

Fig. 4

Fig. 4 FESEM images of the shell surface and pore size distributions of (a) $f\text{TiO}_2\text{-SiO}_2\text{-0/PVDF}$ composite hollow fiber membrane, (b) $f\text{TiO}_2\text{-SiO}_2\text{-0.5/PVDF}$ composite hollow fiber membrane, and (c) $f\text{TiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membranes.

Fig. 5

Fig. 5 The cross-section images of (a) PVDF substrate, and (b) fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane, and (c) EDX line scan of Ti (red) and Si (blue) elements across the cross-section of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane.

Fig. 6

Fig. 6 The XPS spectra of (a) Ti 2p, (c) Si 2p, and (e) C 1s on fTiO₂-SiO₂-1/PVDF membrane and PVDF substrate; and the corresponding curve fittings of (b) Ti 2p, (d) Si 2p, and (f) F 1s for fTiO₂-SiO₂-1/PVDF membrane.

Fig. 7

Fig. 7 Surface hydrophobicity with different modification treatments and adhesion characterization after ultrasonication.

Fig. 8

Fig. 8 FESEM images of (a) fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane without surface hydroxylation before and (b) after ultrasonication, (c) fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane with surface hydroxylation before and (d) after ultrasonication.

Fig. 9

Fig. 9 (a) pure CO₂ absorption flux and (b) biogas upgrading performance of various membranes with different modification treatments. (ST: sodium taurinate)

Fig. 10

Fig. 10 Long term performances of (a) CO₂ absorption flux (at absorbent velocity of 0.25 m s⁻¹) and (b) surface hydrophobicity of PVDF substrate and fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane under the absorbents of MEA and ST over a period of 31 days.

Fig. 11

Fig. 11 FESEM images and pore size distributions of PVDF support and $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite HF membranes (a1-b1) before and after 31-day operation in (a2-b2) MEA and (a3-b3) ST solution, respectively.