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2017

Lin, Y., Xu, Y., Loh, C. H., & Wang, R. (2018). Development of robust fluorinated TiO₂/PVDF composite hollow fiber membrane for CO₂ capture in gas-liquid membrane contactor. *Applied Surface Science*, 436, 670-681. doi:10.1016/j.apsusc.2017.11.263

<https://hdl.handle.net/10356/85345>

<https://doi.org/10.1016/j.apsusc.2017.11.263>

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**Development of Robust Fluorinated TiO₂/PVDF Composite Hollow Fiber
Membrane for CO₂ Capture in Gas-liquid Membrane Contactor**

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Abstract

Gas-liquid membrane contactor (GLMC) is a promising method to attain high efficiency for CO₂ capture from flue gas, biogas and natural gas. However, membranes used in GLMC are prone to pore wetting due to insufficient hydrophobicity and low chemical resistance, resulting in significant increase in mass transfer resistance. To mitigate this issue, inorganic-organic fluorinated titania/polyvinylidene fluoride (fTiO₂/PVDF) composite hollow fiber (HF) membranes was prepared via facile in-situ vapor induced hydrolyzation method, followed by hydrophobic modification. The proposed composite membranes were expected to couple the superb chemical stability of inorganic and high permeability/low cost of organic materials. The continuous fTiO₂ layer deposited on top of PVDF substrate was found to possess a tighter microstructure and better hydrophobicity, which effectively prevented the membrane from wetting and lead to a high CO₂ absorption flux ($12.7 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$). In a stability test with 21-day operation of GLMC using 1M monoethanolamine (MEA) as the absorbent, the fTiO₂/PVDF membrane remained to be intact with a CO₂ absorption flux decline of ~16%, while the pristine PVDF membrane suffered from a flux decline of ~80% due to membrane damage. Overall, this work provides an insight into the preparation of high-quality inorganic/organic composite HF membranes for CO₂ capture in GLMC application.

Keywords:

Inorganic/organic composite membrane; gas-liquid membrane contactor; in-situ vapor induced hydrolyzation method; CO₂ capture; chemical resistance.

1. Introduction

Global warming is a challenging issue for the international community, and the rise of atmospheric temperature is likely correlated to the increasing anthropogenic greenhouse gas emissions. Carbon dioxide (CO_2) is one of the key contributors to the greenhouse effect: according to the most recent Intergovernmental Panel on Climate Change report, the share of CO_2 emission was 76% in 2010 [1]. Therefore, CO_2 capture is of great importance in addressing the global concern of climate change. At present, a wide variety of technological options has been proposed to capture CO_2 , such as absorption, adsorption, distillation and cryogenics. Conventional techniques such as packed towers and bubble columns are energy-intensive processes and not easy to operate because of the frequent problems, including flooding, foaming, channeling and entrainment [2, 3]. Membrane contactor, on the other hand, integrates the acid gas absorption process with the membranes and is increasingly seen as a promising alternative to capture CO_2 . By using hollow fiber (HF) membranes in membrane contactor, several advantages, such as energy and cost savings, device size reducing, operation flexibility increasing and easy scale-up, can be achieved [4, 5].

In gas-liquid membrane contactor (GLMC) for CO_2 capture, a gas stream and an alkaline liquid solution flow on different sides of a microporous membrane, and the target gas transports through the membrane and is absorbed by the liquid absorbent. The membrane acts as a barrier between the liquid and gas phases to increase the gas-liquid contact area without dispersing one phase into the other. Therefore, CO_2 selectivity is determined by the alkaline absorbent, rather than the membrane itself [6]. Since the transport of gas through the membrane is based on the diffusion mechanism, it is preferable to run the process with non-wetted membrane, that is, the membrane pores are gas-filled. When the pores are partially or totally liquid-filled, the mass transfer flux can be significantly reduced due to the lower CO_2 diffusion rate in the liquid [7, 8].

Three kinds of techniques have been proposed to prevent membrane wetting by the absorbent solution: (1) surface modification (membrane surface energy), (2) tuning of membrane structural

parameters (pore size distribution and membrane porosity), and (3) adjusting of operating conditions [9, 10]. Generally, membranes having lower surface energies are less prone to wetting. Therefore, various surface modification techniques, such as coating, grafting and plasma polymerization, have been employed to deposit a layer of low surface energy material on the membranes to enhance GLMC efficiency [11, 12]. For instance, Rahbari-Sisakht et al. [13] blended hydrophobic macromolecules with polyvinylidene difluoride (PVDF) to prepare hydrophobic HF membranes. The resultant membranes exhibited a maximum CO₂ flux of $7.7 \times 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at 300 ml·min⁻¹ of absorbent flow rate due to improved membrane hydrophobicity and wetting resistance. In addition to surface hydrophobicity, membrane wettability is also influenced by pore size and porosity. According to the Young-Laplace equation, the critical liquid entry pressure is higher for membranes with smaller pores, and thus they are less prone to wetting [14, 15]. Effects of different operating parameters, such as absorbent temperature, CO₂ pressure, absorbent flow velocity, were proven to affect the membrane wetting and GLMC performance as well [16, 17].

Several hydrophobic materials with low surface energy, such as polytetrafluoroethylene (PTFE), polypropylene (PP), and PVDF, have been used directly to make microporous membranes for CO₂ absorption in membrane contactors [18, 19]. However, these organic materials suffer from severe pore wetting over prolonged period of operation. It is widely accepted that chemical reactions between the membrane and the absorbent in a membrane contactor will lead to membrane degradation and thus wetting. Lv et al. [20] reported that the absorbent caused absorption-swelling of PP membranes, resulted in morphology change and membrane wetting. Wang et al. [21] also attributed the membrane wetting to possible chemical reactions between the membrane and absorbent solutions, as evidenced by the deformation of surface morphology and change in hydrophobicity. Therefore, to prevent organic membrane degradation and subsequently wetting due to chemical reaction with absorbents, development of membranes with excellent chemical resistance is of great importance for feasible GLMC operation. However, there have only been few literatures reporting on the surface modification of membranes to enhance their chemical resistance for long term process.

Inorganic membranes, made from metal oxides such as TiO₂, Al₂O₃, and ZrO₂, have received much

attention due to their excellent mechanical properties, chemical resistance and thermal stability, and thus have been employed in harsh conditions [22, 23]. Most inorganic membranes used for GLMC are modified to be hydrophobic to prevent wetting. A commonly used modification technique is the grafting of hydrophobic substances with active sites such as hydroxyl groups on the membranes surface [24]. Yu et al. [25] modified the Al_2O_3 membranes with fluorinated ZrO_2 layer for membrane contactor, generating superhydrophobic surface that led to good long-term operation stability. Sirichai et al. [26] applied hydrophobically modified Al_2O_3 membranes in GLMC system for CO_2 stripping using monoethanolamine (MEA) solution, and found that the inorganic Al_2O_3 membranes presented better thermal stability compared with organic membranes. Despite the several advantages of inorganic membranes, the much higher capital cost and the brittleness are the drawbacks that limit their wide applications. According to the literature, the fabrication cost per effective membrane area of superhydrophobic inorganic membranes used for GLMC is 12.5 times of the cost for organic membranes [25].

Inorganic-organic composite membrane is a new class of hybrid membranes where the organic membrane substrate serves as a low-cost, flexible, and highly porous support, while the thin inorganic layer provides protection by preventing the organic substrate from direct contacting with chemicals or other harsh operating conditions [27]. By coupling the advantages of inorganics and organics, they could be ideal candidates to overcome the aforementioned problems of weak solvent resistance and high capital cost [28]. By further grafting molecules with low surface energy onto the inorganic layer, it is possible to prepare inorganic/organic composite membranes with hydrophobic surface that are suitable for GLMC. To date, most inorganic-organic composite membranes have been prepared by blending inorganic particles in organic matrix, limiting the effectiveness of performance [29, 30]. The preparation of high-performance composite HF membranes with a thin continuous inorganic layer on top of organic substrate for GLMC applications has rarely been reported. A particular challenge deterring the development is the difficulty in depositing a defect-free continuous hydrophobic inorganic layer onto the surface of organic HF substrates due to the curved structure of the substrate surface and the relatively large surface pore size of the substrate.

In this study, novel hydrophobic composite HF membranes with a continuous inorganic layer of TiO_2 on a PVDF substrate were developed for CO_2 capture via GLMC. The inorganic layer was deposited on the PVDF substrate via the in-situ vapor induced hydrolyzation method. Subsequently, grafting 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFTS) onto the TiO_2 layer was carried out to modify the surface hydrophobicity. Compared with the commonly used atomic layer deposition (ALD) method for preparation of inorganic/organic composite membrane, the in-situ vapor induced hydrolyzation method has been proven to be a simple and low-cost membrane preparation process. This is because the thin inorganic membrane could be in-situ fabricated after the vapor hydrolyzation and condensation process, replacing hundreds of complicated cycles of “pulse–exposure–purge” process of ALD method [31]. The schematic illustration for fabrication of the composite membranes and their anticipated effects in GLMC application is shown in Fig. 1. This study aims to demonstrate that the inorganic/organic composite HF membranes with hydrophobic modification could be a low-cost alternative that provides excellent chemical and wetting resistances for high-performance GLMC application.

Fig. 1 Illustration for development of fTiO_2 /PVDF composite membranes and CO_2 capture process in GLMC application.

2. Experimental

2.1 Preparation of fTiO_2 /PVDF composite HF membranes

(1) Preparation of titania precursor solution

The titania precursor solution was prepared as follows: a desired amount of titanium isopropoxide (TTIP, Sigma-Aldrich, 97 wt.%) used as the metal precursor was dissolved into isopropyl alcohol (IPA, Sigma-Aldrich, 99.7 wt.%) with vigorous stirring for 60 min. After that, the copolymer of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEO-PPO-PEO, P123, Sigma-Aldrich, Mw 2000), and 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 120 min, then a transparent solution was obtained. The compositions of the precursor solutions were summarized in Table 1.

Table 1. Compositions of precursor solutions for preparation of TiO₂/PVDF composite membranes.

Membrane No.	TTIP (g)	PEO-PPO-PEO (g)	DEA (g)
TiO ₂ -1	1	0.3	0.25
TiO ₂ -2	2	0.6	0.5

*Note: IPA content = 60 g.

(2) Preparation of TiO₂/PVDF composite HF membrane

Commercial PVDF HF with an outer diameter (OD) of 1.46 mm and an inner diameter (ID) of 0.76 mm provided by a company were used as the substrates. Before surface modification, the HF was dried in oven at 50 °C for 24 h. The dried HF was immersed into the prepared precursor solution (from step 1) with stirring for 30 min, and the titanium precursors were expected to be deposited mainly on the outer surface of the substrate by then. Inorganic deposition was carried out on the outer surface in this study due to the fact that the selective layer of the substrate was located at the shell side. However, deposition can easily be carried out on the inner surface of substrate as well, by injecting the precursor solution into the fiber lumen. The HF was then dried in oven at 50 °C for 30 min. After that, the titanium-deposited HF was placed in a humidity chamber for in-situ vapor induced hydrolyzation, under the reaction temperature of 100 °C for 30 min. The hydrolyzation of Ti

precursor resulted in the formation of TiO_2 on PVDF membrane surface. After the reaction, the prepared membranes were rinsed with abundant deionized water (DI water, produced by Milli-Q system, Millipore, USA) to remove loosely bound and stacked layer of TiO_2 nanoparticles from the membrane surface, followed by drying in oven at 40 °C for 12 h.

(3) Hydrophobic modification

For hydrophobic modification, the prepared TiO_2 /PVDF membranes were further immersed in hydrophobic modification solution, composing of 2 wt.% of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFTS, Sigma-Aldrich, 97%) in ethanol at 60 °C for 24 h. Then, the HF's were dried at 60 °C for 12 h. After the drying process, the membranes were rinsed with abundant ethanol and deionized water to remove the unreacted PFTS residue. Based on the composition of the precursor solution used, the resultant fTiO_2 /PVDF composite membranes were designated as fTiO_2 -1 and fTiO_2 -2, corresponding to the designation of their TiO_2 /PVDF counterparts in Table 1.

2.2 Membrane characterizations

The membrane samples were characterized by a Field Emission Scanning Electron Microscope (FESEM, JSM-7600F JOEL) at an operating voltage of 5 kV. The membrane samples were broken in liquid nitrogen and then sputtered with a thin layer of platinum using an EMITECH SC7620 sputter coater prior to analysis. EDX spectroscopy was employed to detect the elemental composition on the surface and cross-section of fTiO_2 /PVDF composite membranes, at an operating voltage of 15 kV. The surface microstructures were obtained by AFM (XE-100, Park System, Korea) operated in the noncontact mode, in which the membrane surfaces were imaged in a scan size of $5\ \mu\text{m} \times 5\ \mu\text{m}$. The surface roughness of the membranes was expressed in terms of the mean roughness (R_a).

The average membrane pore size and pore size distribution were measured by capillary flow porometer (CFP 1500A, from Porous Material. Inc. (PMI)), and the detailed description for the

measurement can be found in a previous literature [32]. The chemical compositions and states were determined by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, USA). Non-monochromatic Mg-K α X-ray ($h\nu=1253.64$ eV) was used as the excitation source while XPS spectra were calibrated with C 1s peak of pure carbon sample (energy position 284.6 eV).

The overall membrane porosity ε_m is defined as the volume of the pores over the volume of the membrane, which is usually examined by gravimetric method [33], Eq (1):

$$\varepsilon_m = 1 - \frac{\rho_{membrane}}{\rho_{polymer}} = 1 - \frac{m/V_{membrane}}{\rho_{polymer}} \quad (1)$$

Where m is the weight of the dry membranes; $V_{membrane}$ is the volume of certain membrane which can be calculated by the ID/OD and the length of the membrane; and $\rho_{polymer}$ is the specific gravity of the certain polymer material (ρ_{PVDF} is 1.78g/cm³).

To evaluate the surface hydrophobicity of fibers, a tensiometer (DCAT11 Dataphysics, Germany) was used to measure the dynamic contact angle (CA). The CA was calculated from the wetting force based on the Wilhelmy method. Three immersion/emersion cycles were carried out for each specimen, and each run was repeated three times to confirm the reproducibility. In addition, the static CA was also measured by using a goniometer (Data Physics Instruments GmbH) via sessile drop method. To minimize experimental errors, the CAs were obtained by averaging three measurements.

2.3 Performance of fTiO₂/PVDF composite HF membranes in CO₂ absorption

Hollow fibers were sealed with epoxy-based adhesive (Araldite 2012, USA) into a glass tube to make a lab-scale module. Since the modification processes were carried out on the outer surface of the hollow fiber membranes. Pure CO₂ (Singapore Oxygen Air Liquid Private Ltd.) was used as feed gas which flowed through the lumen side of HF membranes. According to literature, MEA concentration

used for CO₂ capture via conventional carbon scrubbing ranges from 5-30 wt.% ($\approx$ 1-5 M) [34], while the MEA concentration used in membrane contactor process is usually below 2 wt.% as most membranes were subject to chemical damage in solutions with high MEA concentration. To explore the potential applications of our developed membrane in the harsher condition, CO₂ absorption tests using MEA solutions of 1 M, 2 M and 5 M as the chemical absorbent were carried out. The liquid absorbent was flowed through the shell side of the HFs, while the CO₂ gas was flowed at the HF lumen, using the counter-current mode. The characteristics of the membrane modules and the operation conditions are given in Table 2.

Table 2. Characteristics of membrane modules and operation conditions of GLMC process.

Characteristics of membrane modules		Operation conditions	
Module ID, mm	6.4	Temperature, °C	25
Module length, mm	83	Absolute pressure, bar	1
Fiber ID, mm	1.46	Relative pressure, bar	0
Fiber OD, mm	0.76	Feed gas	Pure CO ₂
Fiber length (eff.), mm	44	Feed absorbent	1M/2M/5M MEA
Contact area (eff.), mm ²	807	Gas phase	lumen side of hollow fiber
Number of fibers, N	4	Liquid phase	shell side of hollow fiber
Overall porosity of membrane, %	89		

The specific CO₂ absorption flux was used to evaluate the CO₂ removal efficiency of the membranes, which could be calculated by Eq (2):

$$J = \frac{P(Q_{in} - Q_{out})}{RTA_m} \times 10^3 \quad (2)$$

where J is the specific CO₂ absorption flux of the HF membrane (mol·m⁻²·s⁻¹); Q is the volume flow (m³·s⁻¹) measured by mass flow controller (Cole-Parmer, USA); R is the ideal gas constant of 0.083 bar·L·mol⁻¹·K⁻¹; T is the operating temperature of 298 K; A_m is the membrane surface area (m²); and P is the operating pressure of 1 bar [35].

Different liquid velocities was used to evaluate the CO₂ absorption performance. The liquid velocity was calculated by Eq (3):

$$v = \frac{Q_l}{\pi \cdot (ID_{module}/2)^2 - n\pi \cdot (OD_{membrane}/2)^2} \quad (3)$$

where v is the velocity of the fluid flowed through the shell side of the hollow fibers in the membrane module ($\text{m}\cdot\text{s}^{-1}$); Q_l is the liquid flow rate ($\text{m}^3\cdot\text{s}^{-1}$) controlled by a digital peristaltic pump (MasterFlex® L/S, USA); ID_{module} is the inner diameter of the glass module (m^2); $OD_{membrane}$ is the outer diameter of the hollow fiber membranes (m^2); n is the number of the hollow fiber in each module.

Long term performance of the $\text{fTiO}_2/\text{PVDF}$ HF membranes were evaluated by alternating CO_2 absorption run and soaking in MEA. After each running of CO_2 absorption test, the membranes modules were filled with the liquid absorbent until the next absorption test, to ensure that the outer surface of membranes was continuously in contact with the chemical absorbent of MEA. The membrane surface morphologies, CA, and CO_2 absorption flux were examined periodically over the testing period. To test the bonding stability between the inorganic layer and the substrate, the prepared fTiO_2 -2/ PVDF composite HF membranes were subject to ultrasonic oscillation test at 25 kHz for 5 min, followed by measurement of dynamic CA.

3. Results and discussion

3.1 Morphologies and microstructures of $\text{fTiO}_2/\text{PVDF}$ composite membranes

The surface morphologies of PVDF substrate and TiO_2/PVDF composite HF membranes are presented in Fig. 2. As can be seen from Fig. 2 (a), the PVDF substrate presented a smooth and porous shell surface with the most frequent pore size of ~ 100 nm and a maximum pore size of 157 nm. After the fTiO_2 modification, as shown in Fig. 2 (b), the clusters of nanoparticles could be clearly observed and the surface pores became significantly smaller, with the most frequent pore size of ~ 60 nm and a maximum pore size of 68 nm. With a further increase in doping amount of Ti precursors, an uniform and continuous fTiO_2 layer was formed and large pores were no longer visible, as shown in Fig. 2 (c).

The most frequent pore size of this membrane was measured to be ~25 nm, while its maximum pore size was 32 nm.

Fig. 2. FESEM images of the shell surface of (a) PVDF substrate, (b) fTiO₂-1/PVDF composite HF membrane, and (c) fTiO₂-2/PVDF composite HF membranes.

The AFM test was employed to characterize the fTiO₂/PVDF composite HF membranes prepared with different Ti precursor doping amounts. As shown in Fig. 3, the smooth surface of the PVDF substrate (shown in Fig. 3(a)) became rougher after fTiO₂ deposition. The average roughness (R_a) increased from 16 nm for PVDF substrate to 38 nm for fTiO₂-1/PVDF membrane (Fig. 3(b)). However, a further increase in the doping amount of Ti precursor led to a smoother surface, as evidenced by the decreased R_a from 29 nm for fTiO₂-2/PVDF membrane (Fig. 3(c)). This could be ascribed to the reason that the deposited TiO₂ nanoparticles filled in the low-lying “valleys” during the in-situ hydrolyzation process, resulting in the formation of a denser surface. The AFM results further demonstrated that the microstructures and morphologies of the membrane surfaces could be tuned by controlling the Ti precursor doping amount.

Fig. 3. AFM images of the surface of (a) PVDF substrate, (b) fTiO₂-1/PVDF composite HF membrane, and (c) fTiO₂-2/PVDF composite HF membrane.

EDX was employed to characterize the distribution of fTiO₂ on the membrane surface. Considering that the hydrophobic group of C-F from PFTS may be confused with the C-F group from PVDF substrate, the elemental distributions of Si from PFTS and Ti from TiO₂ nanoparticles were selected as the distribution indicator for the fTiO₂ layer. As shown in Fig. 4, the Ti and Si elements were evenly distributed throughout the membrane surface, verifying the formation of continuous inorganic layer composed of uniform fTiO₂ nanoparticles without aggregation.

Fig. 4. (a) The surface image of fTiO₂-2/PVDF composite HF membrane, and the EDX mappings of (b) C , (c) Ti, (d) Si elements.

The elemental compositions of fTiO₂/PVDF composite HF membranes prepared with different Ti precursor dopings were summarized in Table 3. As presented, the atomic concentration of Si and F increased with increasing Ti doping amount. This was because there were more hydroxyl site for the PFTS grafting when the amount of TiO₂ nanoparticles increased, leading to formation of higher amount of fTiO₂.

Table 3. Elemental composition (%) of membrane surface prepared with different Ti doping amounts

Membrane No.	C	F	Cl	O	Si	Ti
PVDF	62.75	34.93	2.33	-	-	-
fTiO ₂ -1/PVDF	50.54	43.75	1.22	3.41	0.73	0.35
fTiO ₂ -2/PVDF	39.05	51.34	1.25	5.98	1.20	1.18

FESEM and EDX analyses were carried out on the cross-section of the PVDF substrate and fTiO₂-2/PVDF composite HF membrane to examine their morphology and the distribution of fluorinated particles. As shown in Fig. 5(a), the PVDF substrate exhibited a sponge-like structure with highly porous skin layer. The fTiO₂-2/PVDF composite HF membrane, on the other hand, had a dense top layer deposited directly on the surface of the macroporous substrate, as shown in Fig. 5(b). The

dense layer, with a thickness of about 1 μm , was composed of nanoparticles that formed the packed structures. Moreover, to some extent, it could be observed that the deposited skin layer was infiltrated into the substrate, which may lead to an enhancement in the mechanical performance of $\text{fTiO}_2/\text{PVDF}$ membranes. According to the EDX line scanning results in Fig. 5(c), the Ti elements were mostly deposited on the surface of the prepared HF membrane, with a less amount deposited on the inner structure of the PVDF substrate. The minor amount of internal distribution of Ti element might be ascribed to the diffusion of Ti precursors into substrate pores during modification. The distribution of Si element was observed to be similar to that of Ti element, which could be explained that the fluorinated Si was grafted via bonding with the hydroxyl groups of TiO_2 .

Fig. 5. The cross-section images of (a) PVDF substrate, (b) fTiO_2 -2/PVDF composite HF membrane, and the (c) EDX line scans of Ti and Si elements across the cross-section of fTiO_2 -2/PVDF composite HF membrane.

3.2 Chemical compositions on the surface of $\text{fTiO}_2/\text{PVDF}$ composite HF membranes

The surface chemical compositions of the PVDF substrate and the fTiO₂-2/PVDF composite membrane were characterized using XPS. As shown in Fig. 6 (a) and (b), the Ti 2p showed the peaks at 458.3, 458.6 and 464.5 eV, corresponding to Ti-O-Ti, Ti-O-Si (bonding of TiO₂ with Si from PFTS), and Ti-O-Ti bonds, respectively. The XPS results further proving the formation of inorganic layer composed of interconnected TiO₂ nanoparticles via vapor induced hydrothermal treatment. The Si 2p characteristic peak could also be divided into three peaks located at the binding energy of 102.8, 103.0 and 103.8 eV, representing the Si-O-Ti bond, the Si-O bond from PFTS, and the O-Si-C bond from PFTS which consisted of the fluorinated silane, respectively [36, 37], shown in Fig. (c) and (d). For the F element shown in Fig. 6 (e) and (f), the divided peaks were attributed to the -CF₃ from PFTS, -CF₂-CF₂- from PFTS, and -CH₂-CF₂- from PVDF, further confirming the successful fluorination of the inorganic layer [38, 39]. For the C 1s shown in Fig. 6 (g) and (h), considering the chemically inert nature of PVDF substrate, the presented C-O bond could be attributed to the ether bond of PEO-PPO-PEO. The amphiphilic nature of PEO-PPO-PEO might help enhancing integrity between the hydrophilic TiO₂ and the hydrophobic PVDF substrate [40].

According to the above results, it was believed that the formation of the TiO₂ layer and subsequent hydrophobic modification was based on the following mechanism: Ti precursors, together with amphiphilic copolymer of PEO-PPO-PEO as bridging aid, were firstly deposited on the surface of PVDF substrate. During the vapor-induced hydrolyzation, the deposited Ti precursors were exposed to water vapor at high temperature of about 100 °C and thus hydrolysis occurred, resulting in nucleation and growth of Ti nanoparticles via condensation (formation of Ti-O-Ti bonding). When the amount of Ti precursors was sufficiently high, the nucleation and growth would lead to interconnected clusters of nanoparticles, finally forming the continuous TiO₂ layer.

For the subsequent hydrophobic modification, the silane groups of PFTS were first hydrolyzed to form silanol groups, followed by reaction with hydroxyl groups of TiO₂ on the membrane surface via condensation [41]. This resulted in the formation of Si-O-Ti bonding. The long fluorinated chains of PFTS grafted on the TiO₂ surface were with low surface energy, thus were believed to remain at the

outermost surface of the resultant composite membranes and rendered the surface hydrophobic.

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

3.3 Surface hydrophobicity and bonding stability of fTiO₂/PVDF composite membranes

The surface hydrophobicity of PVDF substrate and TiO₂/PVDF composite HF membranes were investigated. As shown in Fig. 7, it could be observed that the CA of the PVDF substrate was 107°.

After deposition of the TiO_2 layer, the CA of the resultant membrane decreased to 81° due to the hydrophilic nature of the newly formed inorganic layer. The successive grafting of PFTS on the TiO_2 -2/PVDF composite membranes resulted in a significant enhancement in CA to 119° for the fTiO_2 -1/PVDF composite HF membrane. This is believed due to the low surface free energy generated by the grafted PFTS layer. Moreover, a further increase in dynamic CA to 125° was observed when the Ti precursor doping amount increased, as there were more hydroxyl sites for the PFTS grafting. The similar trend of static CA could also be observed, further proving that the more hydroxyl sites brought the better hydrophobicity after PFTS modification. The bonding stability between the fTiO_2 layer and the PVDF substrate was investigated by assessing the change in hydrophobicity before and after the ultrasonication. It could be observed that the hydrophobic performance of fTiO_2 -2/PVDF composite HF membrane presented no significant change, with the dynamic CA decreasing of less than $\sim 2\%$. It confirmed the good bonding stability of the top fTiO_2 layer with the PVDF substrate.

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

3.4 GLMC performance for CO_2 absorption

3.4.1 Membrane absorption performance

Fig. 8 presents the CO absorption flux of the pristine PVDF membranes and the modified

composite hollow fiber membranes prepared with different amounts of doped Ti precursor. The CO₂ absorption flux were tested using the absorbents of 1 M, 2 M and 5 M MEA, under different absorbent velocities. As shown in Fig. 8 (a), the CO₂ absorption flux for all of the membranes increased gradually when the absorbent flow velocity increased from 0.1 to 0.25 m·s⁻¹. This reveals that the main resistance exists in the liquid phase where the CO₂ absorption takes place. Since the reaction between the chemical absorbent of MEA and CO₂ occurs at the gas-liquid boundary, the depletion of untreated MEA might have limited the rate of CO₂ absorption. Therefore, an increase in MEA flow velocity allowed a sufficient amount of unreacted MEA to flow through the gas-liquid boundary, thus enhancing the CO₂ absorption flux [39].

Fig. 8. CO₂ absorption flux tested under different absorbent velocities: (a) flux of different membranes, (b) flux of fTiO₂-2/PVDF using different absorbent concentrations.

For the pristine PVDF membrane, however, the CO₂ flux started decreasing when the absorbent flow rate exceeded 0.25 m·s⁻¹. This was probably because the partial wetting of the membranes pores by the absorbent became more severe due to the higher shear forces generated by the higher absorbent flow velocity. It has been well known that a wetted membrane could significantly increase the mass transfer resistance for gas transport in GLMC application [10]. For the TiO₂-2/PVDF composite HF membrane, the CO₂ absorption flux remained relatively low, which could be ascribed to the membrane wetting due to the hydrophilic nature of the TiO₂ layer. For the fTiO₂-1/PVDF composite HF membrane, the CO₂ absorption flux increased nearly linearly with a slight decrease at a higher liquid velocity of 0.4 m·s⁻¹, which might also be due to partial membrane wetting. The delayed onset of wetting compared with the pristine PVDF membrane could be ascribed to the improved hydrophobic

surface with fTiO₂ modification, but the membrane was still not sufficiently hydrophobic to prevent wetting at a higher liquid velocity. In contrast, for the fTiO₂-2/PVDF composite HF membrane, the CO₂ absorption flux increased linearly without declining, and reached a value of $12.7 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ that was nearly equal to the CO₂ flux of the pristine PVDF membrane, reaching a relatively high CO₂ absorption flux via better hydrophobicity and more suitable pore size of HF membrane for GLMC application. Considered that the fTiO₂-2/PVDF membrane possessed a better wetting resistance and a higher CO₂ flux, it was selected for further study using higher MEA concentrations to explore its potential applications in a harsher condition.

As shown in Fig. 8 (b), the CO₂ absorption flux increased significantly when the absorbent concentration increased from 1 M to 2 M. This is because the active component absorbing CO₂ in the liquid boundary layer increased with the absorbent concentration, resulting in a higher CO₂ absorption capacity at the same liquid flow rate [42]. By further increasing the absorbent concentration to 5 M, however, the CO₂ absorption flux showed no significant improvement. This could be mainly attributed to the reason that the mass-transfer resistance of the liquid boundary layer is not a key controlling factor any more, as the highly concentrated absorbent (5M) has a sufficient capacity to absorb CO₂. There is also no need to increase the absorbent velocity to bring in more fresh absorbent to the membrane surface. The results suggest that it is not necessary to use a highly concentrated MEA absorbent. A balance between the absorbent concentration and liquid velocity needs to be considered to achieve high mass-transfer efficiency of CO₂ absorption [43, 44].

3.4.2 Long term performance of fTiO₂/PVDF composite HF membranes in GLMC

It is widely accepted that chemical reaction between the membrane and the absorbent in membrane contactor will lead to membrane degradation and thus wetting, consequently deteriorating its long term performance. In this study, the long-term CO₂ absorption performance of the PVDF substrate and fTiO₂-2/PVDF composite HF membrane were carried out for 21 days by using 1M MEA solution as the absorbent.

As shown in Fig. 9(a), the CO₂ absorption flux of the pristine PVDF membrane continuously decreased since the beginning of the test, suggesting progressive wetting of the membrane which resulted in an increase in membrane resistance. The CO₂ flux was stabilized at a value of $\sim 3.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, or $\sim 20\%$ of initial value after 10 days of testing, which might be attributed to complete wetting. On the other hand, CO₂ absorption flux of fTiO₂-2/PVDF composite membrane decreased merely $\sim 16\%$ over the 21-day testing and maintained a relatively high value of $\sim 10.1 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. The slight flux decline could be attributed to the partial wetting caused by capillary condensation of MEA vapors in the HF substrates. Considering that the HFs were soaked stagnantly in MEA solution for long-term operation test in each CO₂ absorption run, diffusion and condensation of MEA vapors into the membranes was inevitable, hence resulted in the CO₂ absorption flux and hydrophobicity decline.

Fig. 9. Long term performance of (a) CO₂ absorption flux (at the absorbent velocity of $0.25 \text{ m} \cdot \text{s}^{-1}$) and (b) contact angle for PVDF substrate and fTiO₂-2/PVDF composite HF membrane.

The dynamic CAs were tested periodically during the long-term operation in MEA solution. As shown in Fig. 9(b), the dynamic CA of PVDF membrane decreased from $\sim 101^\circ$ to 78° , suggesting that chemical or physical properties of the membrane surface might have changed due to interaction with MEA. According to Sadoogh et al. [45], there might be chemical reaction between PVDF and MEA that resulted in dehydrofluorination of the former. By examining the surfaces morphologies of the pristine PVDF membrane after the 21-day immersion in MEA solution as shown in Fig. 10(a), enlargement of surface pores could be observed, confirming the damage of PVDF membrane surface

caused by reaction with MEA for 21 days. Both the reduction in membrane hydrophobicity and enlargement of surface pores could induce membrane wetting for GLMC operation, which explains the significant drop in CO₂ flux since the beginning of the test.

On the other hand, the CA for the fTiO₂-2/PVDF membrane showed only slight decrease from ~125° to 117°, as presented in Fig. 9(b). In addition, no significant difference could be observed on the membrane surface according to the FESEM images shown in Fig. 10(b). Apparently, the presence of highly hydrophobic and chemically robust fTiO₂ top layer effectively prevented the PVDF support from corrosion in MEA solution, and thus ensuring relatively stable CO₂ flux during the long-term GLMC operation.

Fig. 10. FESEM images of the surfaces of (a) PVDF substrate, (b) fTiO₂-2/PVDF composite HF membrane before and after 21-day immersion in MEA solution.

3.5 Comparison of CO₂ flux of various membranes used in GLMC

Different types of membranes used in GLMC are listed in Table 4 to compare their CO₂ absorption

performance, and MEA was the most commonly employed absorbent in GLMC application. Compared with the state-of-the-art CO₂ absorption performance in recent years, the membrane prepared in current work exhibited comparable performance in terms of CO₂ absorption flux under a relatively low MEA concentration and liquid velocity, implying its highly efficient CO₂ removal capacity. The fTiO₂/PVDF composite HF membrane is able to present a superb CO₂ absorption flux while maintaining high performance stability, mainly because the inorganic layer formed on top of the organic substrate, which combines the advantages of highly porous organic membrane and chemically robust inorganic.

Table 4. Overall comparison of CO₂ absorption flux of various membranes used in GLMC.

Membrane type	Modification layer	Pore size (nm)	Water contact angle (°)	Lumen side	Feed gas	Absorbent	Liquid velocity (m·s ⁻¹)	CO ₂ flux (10 ⁻³ mol·m ⁻² ·s ⁻¹)	Reference
#1 PVDF	N.A.	20	N.A.	Gas	Pure CO ₂	Water	0.25	0.8	[4], 2006
#2 PEI	Polydimethylsiloxane	278	114	Gas	Pure CO ₂	Water	0.11	0.8	[46], 2015
#3 PEI	Hydrophobic montmorillonite	79	86	Liquid	Pure CO ₂	Water	0.25	0.7	[47], 2015
#4 PEI	Fluorinated SiO ₂	30	121	Gas	Pure CO ₂	2M Sodium taurinate	0.25	6.8	[48], 2014
#5 PP	N.A.	20	N.A.	Gas	14% CO ₂	1M MEA	0.10	5.9 ^a	[42], 2007
#6 PVDF	N.A.	200	100	Liquid	Pure CO ₂	2M MEA	2.1	2.6	[24], 2007
#7 fTiO ₂ /PVDF	Fluorinated TiO ₂	25	125	Gas	Pure CO ₂	1M MEA	0.25	10.9	Current work
#8 fTiO ₂ /PVDF	Fluorinated TiO ₂	25	125	Gas	Pure CO ₂	2M MEA	0.25	12.6	Current work
#9 fTiO ₂ /PVDF	Fluorinated TiO ₂	25	125	Gas	Pure CO ₂	5M MEA	0.25	13.0	Current work

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

4. Conclusions

The in-situ vapor induced hydrolyzation process incorporated with PFTS grafting was used to prepare fTiO₂/PVDF thin-film composite HF membranes. It was found that the surface microstructure and pore size of the membranes could be modified by controlling the Ti precursor doping amount. The fabricated membrane exhibited a promising CO₂ absorption flux of $12.7 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at a higher absorbent liquid velocity of $0.4 \text{ m} \cdot \text{s}^{-1}$. Compared with the pristine PVDF membrane, the long-term performance of the fTiO₂/PVDF composite HF membrane was significantly improved due to its high chemical resistance and hydrophobicity that effectively prevented PVDF membrane from corrosion by MEA. The results demonstrate the feasibility of inorganic/organic thin-film composite membranes in GLMC application by combining the advantages of inorganics and organics. Moreover, the demonstrated in-situ vapor induced hydrolyzation process incorporated with PFTS grafting provides an alternative method to develop inorganic-organic composite membranes, and thus it is anticipated to facilitate practical applications of membrane contactor technology.

Acknowledgements

We acknowledge funding support from the Singapore Economic Development Board to the Singapore Membrane Technology Centre.

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Table 1. Compositions of precursor solutions for preparation of TiO₂/PVDF composite membranes.

Membrane No.	TTIP (g)	PEO-PPO-PEO (g)	DEA (g)
TiO ₂ -1	1	0.3	0.25
TiO ₂ -2	2	0.6	0.5

*Note: IPA content = 60 g.

Table 2. Characteristics of membrane modules and operation conditions of GLMC process.

Characteristics of membrane modules		Operation conditions	
Module ID, mm	6.4	Temperature, °C	25
Module length, mm	83	Absolute pressure, bar	1
Fiber ID, mm	1.46	Relative pressure, bar	0
Fiber OD, mm	0.76	Feed gas	Pure CO ₂
Fiber length (eff.), mm	44	Feed absorbent	1M/2M/5M MEA
Contact area (eff.), mm ²	807	Gas phase	lumen side of hollow fiber
Number of fibers, N	4	Liquid phase	shell side of hollow fiber
Overall porosity of membrane, %	89		

Table 3. Elemental composition (%) of membrane surface prepared with different Ti doping amounts.

Membrane No.	C	F	Cl	O	Si	Ti
PVDF	62.75	34.93	2.33	-	-	-
fTiO ₂ -1/PVDF	50.54	43.75	1.22	3.41	0.73	0.35
fTiO ₂ -2/PVDF	39.05	51.34	1.25	5.98	1.20	1.18

Table 4. Overall comparison of CO₂ absorption flux of various membranes used in GLMC.

Membrane type	Modification layer	Pore size (nm)	Water contact angle (°)	Lumen side	Feed gas	Absorbent	Liquid velocity (m·s ⁻¹)	CO ₂ flux (10 ⁻³ mol·m ⁻² ·s ⁻¹)	Reference
#1 PVDF	N.A.	20	N.A.	Gas	Pure CO ₂	Water	0.25	0.8	[4], 2006
#2 PEI	Polydimethylsiloxane	278	114	Gas	Pure CO ₂	Water	0.11	0.8	[46], 2015
#3 PEI	Hydrophobic montmorillonite	79	86	Liquid	Pure CO ₂	Water	0.25	0.7	[47], 2015
#4 PEI	Fluorinated SiO ₂	30	121	Gas	Pure CO ₂	2M Sodium taurinate	0.25	6.8	[48], 2014
#5 PP	N.A.	20	N.A.	Gas	14% CO ₂	1M MEA	0.10	5.9 ^a	[42], 2007
#6 PVDF	N.A.	200	100	Liquid	Pure CO ₂	2M MEA	2.1	2.6	[24], 2007
#7 fTiO ₂ /PVDF	Fluorinated TiO ₂	25	125	Gas	Pure CO ₂	1M MEA	0.25	10.9	Current work
#8 fTiO ₂ /PVDF	Fluorinated TiO ₂	25	125	Gas	Pure CO ₂	2M MEA	0.25	12.6	Current work
#9 fTiO ₂ /PVDF	Fluorinated TiO ₂	25	125	Gas	Pure CO ₂	5M MEA	0.25	13.0	Current work

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