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Synthesis of ZIF-8 based composite hollow fiber membrane with a dense skin layer for facilitated biogas upgrading in gas-liquid membrane contactor

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Abstract:

Gas-liquid membrane contactor (GLMC) has been regarded as a promising alternative to conventional contacting processes for CO₂ [absorption](#). In this work, a composite hollow fiber (HF) membrane with an aminosilane-modified zeolitic imidazolate framework-8 (mZIF-8) based dense skin layer was designed and synthesized for high-efficiency biogas upgrading in the GLMC process, by dispersing mZIF-8 nanocrystals into poly(dimethylsiloxane) matrix and then depositing on a porous polyvinylidene fluoride (PVDF) substrate. [\(3-aminopropyl\)triethoxysilane was introduced to modify the ZIF-8 nanocrystals, thereby enabling the chemical bonding with PDMS chains for avoiding interfacial voids and further enhancing hydrophobicity.](#) Compared with the control membrane, the newly developed mZIF-8 based composite membrane with a dense skin exhibited competitive hydrophobicity with a contact angle of 130°, ensuring its anti-wetting ability. It exhibited an enhanced biogas upgrading performance with the absorption fluxes of 2.3 and $3.8 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ using water and 1M monoethanolamine (MEA) as absorbents, respectively (liquid velocity = $0.25 \text{ m} \cdot \text{s}^{-1}$). In particular, a comparable selectivity of CO₂/CH₄ with the value of ~20 was achieved by using MEA as absorbent in the GLMC process. A robust long-term stability of the mZIF-8 based composite HF membrane was also achieved in a 15-day operation. This work offers a new perspective for promoting CO₂ mass transfer with mZIF-8 based composite HF membranes, thereby improving the biogas upgrading performance in GLMC applications.

Keywords: Zeolitic imidazolate framework-8; (3-aminopropyl)triethoxysilane; Composite membrane; CO₂ absorption; Membrane contactor

1 Introduction

Historical trends indicate that fuel sources will be gradually decarbonized over time [1]. Biogas, also known as bio-methane, is a carbon-constrained clean and renewable energy source that composes of methane (CH_4 , 55~65%), carbon dioxide (CO_2 , 30~45%), and other traces of gases [2]. As a major acid impurity in biogas, CO_2 leads to pipeline corrosion, energy content reduction, and occupation of pipeline space during transportation [3]. Therefore, CO_2 removal for biogas upgrading is of great importance for the practical utilization of CH_4 . Current conventional technologies (*e.g.*, physical/chemical absorption, adsorption, and cryogenic separation) are usually energy-intensive, and require large infrastructure and high cost [4]. Membrane technologies are characterized by their compact modular appearance, which allow the use of non-selective (separation with liquid absorbent) or selective (separation without liquid absorbent) membranes, easy prediction, linear scale-up, elimination of typical problems associated with the conventional packed towers (*e.g.*, foaming, channelling, flooding, weeping, excessive loading, and entrainment) [5, 6]. Gas-liquid membrane contactor (GLMC) process has been investigated as a promising alternative to conventional absorption processes [7], presenting main operational and economical advantages of high surface area with compact structure, individual flow of gas and absorbent, high efficiency, small plant footprint, low cost, and low energy consumption [8, 9]. The membrane in the GLMC process normally offers no selectivity due to its porous structure with low mass transfer resistance. Unlike membrane gas separation process, the utilized liquid absorbent is responsible for the selectivity of the separation, which presents a higher efficiency even when fed with CO_2 low concentration [4, 10].

In a typical GLMC module, a microporous membrane provides a physical interfacial barrier to separate gas and liquid phase with individual flows. The gas diffuses to the gas-membrane interface then passes through membrane pores, subsequently transferring from the liquid-membrane interface to the bulk liquid by physical or chemical absorption [11], as illustrated in Fig. 1. Traditional hydrophobic polymeric membranes such as polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), polyvinylidene fluoride (PVDF), polyether-imide (PEI), and polysulfone (PSf) membranes have been generally applied in GLMC processes [11-14]. However, most of them are prone to membrane wetting,

swelling, and degradation by corrosive solvents such as monoethanolamine (MEA), diethanolamine, methyldiethanolamine, *etc.* [15], thereby restricting gas mass transfer and GLMC's long-term performance [16, 17]. Thus, surface modification on pre-fabricated membrane substrates has been widely applied for preventing wetting by endowing the membrane surface with high hydrophobicity, suitable and narrowly distributed pore size, and good thermal and chemical resistance without changing the internal porous structure of the membrane. Several chemical and physical methods have been employed for surface modification of porous membranes, such as chemical grafting, surface coating, solution casting, plasma and laser treatments, *etc.* [6, 17]. However, these porous membranes are still subjected to a trade-off: a high CO₂ transfer flux is often accompanied by membrane wetting, which affects their long-term operations and large-scale utilization.

Fig. 1. The CO₂ absorption process in a porous hollow fiber gas-liquid membrane contactor. Adapted from [11].

Beside porous membranes, dense membranes have also been attempted for CO₂ removal in GLMC processes [18-20]. This indeed offers a remarkable wetting protection due to their non-porous structures, along with enhanced biogas upgrading derived from their idiopathic selectivity for specific gases [21]. In addition, the dense membrane could be better regenerated by drying process once water vapour

condensed in porous substrate [43]. However, dense membranes normally present limited gas mass transfer because of high transmission resistance [22, 23]. Therefore, the rational design of novel composite dense membranes for CO₂ absorption in GLMC processes is highly desired by synergistically combining high CO₂ permeability with desirable anti-wetting properties to overcome the mentioned trade-off effect.

Construction of composite membranes skinned with thin dense layers on porous membrane substrates could provide the possibility for reducing the inevitable membrane resistance as well as achieving wetting prevention for GLMC applications [20]. The thin dense layer may generate a reduced mass transfer resistance for CO₂ permeability [23], meanwhile ensuring the wetting protection and a maximal intensification potential. In addition, the porous membrane substrate could maintain high overall mass transfer and offer a support for the dense layer. Our group developed a high-efficiency composite membrane composed of a coated poly(dimethylsiloxane) (PDMS) layer on a PEI hollow fiber (HF) substrate by controlling the depth of PDMS intrusion into the porous substrate, of which the overall mass transfer coefficient could achieve 7.5 times higher than that of commercial pure PDMS membranes [24]. Similarly, Scholes *et al.* [25] designed different polymeric composite dense membranes for CO₂ absorption, of which the thinner poly(1-trimethylsilyl-1-propyne) and a polymer of intrinsic microporosity based dense layers presented higher mass transfer. However, the dense skin layer still contributed to the primary mass transfer resistance for CO₂ transport, resulting in limited flux despite its reduced thickness [23, 26]. Therefore, further elevating the CO₂ flux of dense skin layer is the main challenge for applying the composite dense membrane in GLMC processes.

In recent years, the development of metal-organic frameworks (MOFs) has been evolved as a promising strategy for developing desired composite membranes for CO₂ capture. The microporous crystalline solids of MOFs are composed of metal-base nodes coordinated with organic bridging ligands or struts, which present a three-dimensional extended network with regular pore sizes ranging from 3 to 20 Å [27, 28]. In comparison to other MOFs, zeolitic imidazolate frameworks (ZIFs) have permanent porosity and exceptional chemical stability, which is ideally suited for gas separation [29]. The developed ZIFs based composite membranes presented admirable separation performance with

improved gas permeability, based on provided extra channels in MMMs, especially for dense membranes [30-32]. Ordoñez *et al.* [33] reported that the gas permeability of the fabricated ZIF-8/Matrimids[®] MMMs could be enhanced by increase of the ZIF-8 loading within certain limits. In another attempt, ZIF-8 fillers were dispersed into poly(vinyl chloride)-g-poly(oxyethylene methacrylate) matrix, and expressed a 8.9 times higher CO₂ permeability than that of the original co-polymer dense membrane and a reasonable selectivity of CO₂/CH₄ [34].

Although progress has been witnessed for ZIF-8 based MMMs in improving CO₂ transfer, synthesizing a uniform, defect-free, and hydrophobic ZIF-8 based composite dense membrane is still challenging [35]. In order to develop active sites for further enhancing the compatibility, the surface functionalization of ZIF-8 by covalent linkers has been proposed to improve the selectivity of ZIFs based MMMs [36, 37]. The free imidazole in the ZIF-8 framework allows covalent functionalization with the active groups of covalent linkers, which offers a promising strategy to design novel ZIF-8 based MMMs with enhanced gas separation performance. Despite this, there have been very few works reporting on the construction of functionalized ZIF-8 based MMMs for biogas upgrading in GLMC. The interaction mechanism of functionalized ZIF-8 in enhancing CO₂ removal from biogas was also rarely investigated.

In this study, we aim to develop a MOF based composite HF membrane with a dense skin layer to enhance mass transfer for biogas upgrading in the GLMC process. Specifically, aminosilane-modified ZIF-8 (mZIF-8) nanocrystals dispersed into PDMS matrix formed a non-porous top layer on a porous PVDF substrate. The ZIF-8 nanocrystals were aminosilane-modified for 1) increasing the CO₂ flux, based on the unique structures/groups of ZIF-8 and (3-aminopropyl)triethoxysilane (APTES); 2) enhancing the hydrophobicity due to the alkyl chain in APTES structure; and 3) improving the interfacial compatibility, derived from the space steric hindrance of APTES structure. We envisage that through chemically modifying the ZIF-8 nanocrystals, the CO₂ flux stability and anti-wetting property in the long-term operation will be improved. The optimum loading of mZIF-8 nanocrystals was investigated to obtain a defect-free and high-efficiency composite HF membrane with a thin dense layer for CO₂ absorption. The hierarchical structure and surface chemistry of the prepared composite

membranes were characterized comprehensively. The performance of CO₂ removal from biogas and the long-term stability were examined via a bench-scale GLMC process by using water and MEA as absorbents, respectively. Its performances and the selectivity of CO₂/CH₄ were studied and compared against those of other dense and porous membranes reported in literature to ascertain its applicability for biogas upgrading.

2 Experimental

2.1 Materials and chemicals

Commercial hydrophobic PVDF HF membranes [38] with the inner/outer diameter of 760/1470 μm and the pore size of $\sim 100\text{ nm}$ were used as substrates. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, designated as Zn^{2+}), 2-methylimidazole (99%, designated as Hmim) and APTES (99%) were supplied from Sigma-Aldrich for synthesizing ZIF-8 nanocrystals and subsequent modification. Sylgard® 184 silicone elastomer kit (Dow Corning) was used to prepare PDMS coating solution with a weight ratio of 10 (base):1 (curing agent). Methanol (MeOH , $\geq 99.9\%$) and *n*-hexane ($\geq 96.0\%$) were purchased as solvents from Merck. Pure CO₂ and biogas (CO₂: CH₄ = 40: 60) (Singapore Oxygen Air Liquide Private Ltd.) were applied as feed gas for the GLMC. MEA ($\geq 99.0\%$) was purchased from Sigma-Aldrich to prepare chemical absorbent for CO₂ absorption. Deionized (DI) water was produced by Milli-Q system (Millipore, USA).

2.2 Synthesis of ZIF-8 nanocrystals and aminosilane-modification

0.74 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.05 g of Hmim were separately dissolved in 50 ml of MeOH with sufficient stirring. The Zn^{2+} solution then mixed with the Hmim solution under magnetical stirring for 30 min at room temperature of 25 °C, with the molar ratio of 1:10:1000 (Zn^{2+} : Hmim: MeOH) [39]. The resultant homogeneous milky suspension was centrifuged at 10000 rpm for 10 min and then washed with MeOH. Finally, ZIF-8 nanocrystals were obtained after repeating the centrifugation-washing process for three times.

For the aminosilane-modification of ZIF-8 nanocrystals, a batch of prepared ZIF-8 nanocrystals were added in 60 ml of 5 wt.% APTES methanol solution under vigorous stirring at 70 °C for predetermined times (6—24 h) [40]. The mZIF-8 products were obtained through three runs of the high-speed centrifugation (same as the method of ZIF-8 synthesis). Hereon, the prepared aminosilane-modified ZIF-8 nanocrystals are designated as the m(x)ZIF-8, in which ‘x’ refers to the time of the aminosilane-modification.

For fabrication of ZIF-8 based composite membranes, the synthesized ZIF-8 and mZIF-8 nanocrystals were further washed with *n*-hexane and centrifuged to improve the compatibility with PDMS solution. The as-washed ZIF-8 and mZIF-8 nanocrystals were then re-dispersed in MeOH/*n*-hexane under ultrasonic treatment at 25 kHz (FB 15068, Fisher Scientific, USA), followed by vacuum-drying at 50 °C overnight for characterization.

2.3 Fabrication of mZIF-8 based composite dense HF membranes

A 5 wt.% PDMS solution was firstly prepared by blending vinyl-type PDMS base and hydrosilyl-type curing agent as cross-linker in *n*-hexane solvent stirring for 1 h at room temperature of 25 °C [41]. Certain amounts of ZIF-8 and mZIF-8 in *n*-hexane suspensions were transferred into the PDMS solution under vigorous stirring for 30 min. The resultant PDMS, ZIF-8/PDMS, and mZIF-8/PDMS mixed solutions were separately poured into three petri dishes for complete evaporation of the solvent. Then they were transferred into an oven for curing at 80 °C for 48 h to afford the PDMS matrix, ZIF-8@PDMS, and mZIF-8@PDMS mixed matrixes for subsequent characterizations.

The sealed PVDF HF with epoxy were soaked in each of the as-prepared mixtures of PDMS, ZIF-8/PDMS, and mZIF-8/PDMS (different loadings of ZIF-8: 2.5—20 wt.%) under stirring for 4 h, and then rinsed thoroughly with MeOH and then cured at 80 °C for 48 h. The PDMS, ZIF-8@PDMS, and mZIF-8@PDMS coated PVDF membranes are referred to as Pp, Z-Pp and m(x)Z(y)-Pp composite HF membranes, respectively, in which x refers to the aminosilane-modification time for ZIF-8 crystals, and y refers to ZIF-8 loading in the PDMS dense layer. The schematic illustration of the development protocol for the mZIF-8 based composite HF membranes is shown in Fig. 2.

Fig. 2. Schematic diagram of construction of the mZIF-8 based composite dense HF membrane.

2.4 Characterizations for nanocrystals and nanocrystals based membranes

The morphologies of powder ZIF-8 and mZIF-8 nanocrystals and the outer surface and cross-section morphologies of the prepared HFs were observed using a field emission scanning electron microscopy (FE-SEM, JSM-7600F JOEL, Japan) at 5 kV. Ultrasonic treatment (FB 15068, Fisher Scientific, USA) of the HFs was performed before the observation. The associated electron dispersive X-ray (EDX) spectroscopy was employed to detect the elemental distribution on the cross-sections of the HF samples. A field emission transmission electron microscopy (FE-TEM, JEM 2100 F, JEOL, Japan) at 200 kV was further used for visualization of ZIF-8 and mZIF-8 nanocrystals. X-ray diffraction (XRD) patterns of powder ZIF-8 and mZIF-8 nanocrystals and prepared ZIF-8/mZIF-8@PDMS mixed matrixes were obtained on a Bruker D8 Advance diffractometer. A dynamic light scattering (DLS) device (Malvern Zetasizer Nano, DKSH Technology Pte Ltd) was introduced to measure the particle size distributions and zeta surface potentials of powder ZIF-8 and mZIF-8 nanocrystals.

A fourier-transform infrared spectroscopy—attenuated total reflectance (ATR-FTIR, IRPrestige-21, Shimadzu, Japan) was used for measuring the functional groups of ZIF-8 and mZIF-8 nanocrystals

and outer surfaces of the HF membranes. An X-ray photoelectron spectrometer (XPS, AXIS Supra, Kratos Analytical, UK) was applied for further investigation of the chemical state of ZIF-8 and mZIF-8 nanocrystals and outer/inner surfaces of hollow.

An electrokinetic analyzer (SurPASS™ 3, Anton Paar, Austria) was used for measurement of the membrane surface charge. A 0.5 mM NaCl electrolyte solution was applied, adjusting the pH in a region of 3—9.5 by dosing with NaOH/HCl. Thermal stabilities of the prepared nanocrystals and nanocrystals based mixed matrixes were measured by thermal gravimetric analyzer (TGA, SDT Q600–V20.9 Build 20, USA) under a nitrogen flow of 100 ml/min at a heating rate of 10 °C/min from 50 to 800 °C. An atomic force microscopy (AFM, XE-100, Park System) was used to investigate the roughness of membrane surfaces. A tensiometer (DCAT11, Data physics, Germany) was applied to measure the dynamic contact angle in water for evaluation of the hydrophobicity of HFs. Each sample measurement was repeated at least three times.

2.5 CO₂ absorption performance of mZIF-8 based composite HF membranes

A lab-scale membrane contactor module was assembled with five pieces of HFs sealed into a PTFE tubing with an effective length of 11 cm and an effective membrane area of 25 cm². The operation of the membrane contacting process for CO₂ absorption can refer to the previous report [42, 43]. The feed gas (pure CO₂ or biogas) flowed in the lumen side of the HF membranes, and the liquid absorbent (DI water or 1M MEA) counter-currently flowed over the out side of the HFs. A micro gas chromatograph (6890 Hewlett Packard, TCD) was used to measure the the gases compositions. Based on the gas flow rate difference between inlet and outlet, the CO₂ absorption flux (J , mol·m⁻²·s⁻¹) can be calculated by the Eq(1):

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

where Q_{in} and Q_{out} are the gas inflow rate and outflow rate (10⁻³ m³·s⁻¹), R is the ideal gas constant (0.083 bar·L·mol⁻¹·K⁻¹), T is the operating temperature (K), A_m is the membrane surface area (m²), and P is the

absolute pressure in gas phase (1.07 bar).

Unlike membrane separation process (separation without liquid absorbents), the gas separation efficiency is determined by the permeability and selectivity of membranes toward a certain gas species [32]. In contrast, the membrane applied in a GLMC system normally acts as a non-selective barrier to offer a gas-liquid interface. The selectivity is mainly functioned by the absorbent liquid (*e.g.*, type, concentration, and flow rate of liquid) [6]. Therefore, the selectivity (*S*) based on the GLMC process was selected to describe the separation efficiency, which is expressed by the ratio of gas component in retentate stream to gas component in feed stream as follows [14]:

$$S = \left(\frac{C_{CH_4(R)}}{C_{CO_2(R)}} \right) / \left(\frac{C_{CH_4(F)}}{C_{CO_2(F)}} \right)$$

where $C_{CO_2(F)}$ or $C_{CH_4(F)}$ and $C_{CO_2(R)}$ or $C_{CH_4(R)}$ are the concentrations (%) of CO₂ or CH₄ in the feed and retentate streams, respectively.

2.6 Long-term performance for CO₂ absorption

The CO₂ absorption process of the prepared HF membrane in long-term operation was carried out periodically. When finishing each run of membrane contacting process, the shell side of HFs in a module was filled with the liquid absorbent to ensure that the shell surface of membranes could be constantly in contact with the liquid absorbent.

3 Results and discussion

3.1 Aminosilane-modification of ZIF-8 nanocrystals

The crystal structures of synthesized powder ZIF-8 and mZIF-8 nanocrystals were identified with XRD patterns and the results are shown in Fig. 3(a). The characteristic crystal planes of synthesized powder ZIF-8 and mZIF-8 matched well with that of simulated ZIF-8 (CCDC number: 823083) collected from the database in the Cambridge Crystallographic Data Center (CCDC) [31, 44], which indicated their highly crystalline structures, thereby confirming the successful synthesis of powder ZIF-

8 nanocrystals. Meanwhile, it also indicated that the crystalline structure of ZIF-8 after aminosilane-modification did not cause collapse or decomposition.

The functional groups of powder ZIF-8 and mZIF-8 were confirmed by the ATR-FTIR spectra as shown in Fig. 3(b). The sharp absorption peak at 420 cm^{-1} was related to Zn–N stretching vibration, which was the characteristic band of ZIF-8 nanocrystals [44]. The absorption peaks below 800 cm^{-1} was associated with the out-of-plane imidazole ring bending, whereas the region of $950\text{--}1350\text{ cm}^{-1}$ was related to the bending of the in-plane ring [45]. In particular, the intense bands at 995 and 1146 cm^{-1} were associated with C–N stretching of ZIF-8 [34, 44]. The convoluted band in the range of $1350\text{--}1550\text{ cm}^{-1}$ was assigned as the entire imidazole ring stretching. The peak at 1584 cm^{-1} was specifically assigned to the C=N stretching. The characteristic absorption peaks at 3135 and 2930 cm^{-1} were associated to the aromatic ring and the aliphatic chain of C–H stretching from imidazole, respectively [45, 46]. After aminosilane-modification, the distinctive peak at 868 cm^{-1} due to the Si–C stretching was observed. And with increasing modification time, the characteristic peaks of the ring involved as well as C–N were enhanced, further demonstrating the successful modification of ZIF nanocrystals with APTES. Besides, the elemental compositions of the ZIF-8 and m(12h)ZIF-8 analyzed from XPS spectra are summarized in Table A. 2, which could also verify the APTES modification procedure.

Fig. 3. XRD patterns (a) and ATR-FTIR spectra (b) of powder ZIF-8 and mZIF-8 nanocrystals.

Fig. 4 shows the morphological features of synthesized ZIF-8 and mZIF-8 nanocrystals. The FE-

SEM image revealed the homogeneous rhombic dodecahedral shape of ZIF-8 nanocrystals with the size of around 45 nm (Fig. 4(a1)). The corresponding FE-TEM images (Fig. 4 (a2)) presented their sharp hexagonal faceted shape, which was in good agreement with literature [39]. However, the original sharp edge of ZIF-8 nanocrystals became round mildly after the aminosilane-modification (Fig. 4 (b), sampled with m(12 h)ZIF-8), although their crystal structures were still obvious. This could be attributed to the increased surface energy of mZIF-8 nanocrystals that promoted amorphization of the dodecahedral/hexagonal-like structure to a spherical-like structure under protracted exposure time of FE-SEM/FE-TEM electron beam [31]. Comparing the FE-SEM/FE-TEM images of ZIF-8 and mZIF-8 (see Fig. 4, Fig. A.1, and Fig. A.2), the estimated particle size (~ 40 nm) of mZIF-8 was smaller than that of ZIF-8. This result was similar with the tendency of the crystal size (listed in Table A. 1) calculated from XRD patterns by Scherrer's equation (Eq. A.1), which was attributed to the slight dissolving of nanocrystals induced by the reaction between APTES and imidazole struts of ZIF-8 [40].

Fig. 4. Morphologies of (a) ZIF-8 and (b) m(12 h)ZIF-8 nanocrystals observed with (1) FE-SEM and (2) FE-TEM.

The mZIF-8 based composite HFs with different APTES modification times (ZIF-8/mZIF-8 loading of 5 wt.% as example) were prepared for hydrophobicity characterization, and their dynamic water contact angles are shown in Fig. 5(a). The m(12h)Z-Pp composite HF membrane presented the highest hydrophobicity, as compared to the ZIF-8 based membrane and other mZIF-8 based membranes. Zeta potentials for ZIF-8/mZIF-8 nanocrystals and Z-Pp/m(12h)Z-Pp composite membranes were

measured to provide information on the modification mechanism and its effect on hydrophobicity enhancement. As shown in Table A. 1, powder ZIF-8 and mZIF-8 were both positively charged. The m(6—24h)ZIF-8 nanocrystals presented higher zeta potentials due to the protonated $-\text{NH}_2$ and $-\text{NH}_2^+$, indicating the modification was based on the reaction between alkoxy of APTES and imidazole of ZIF-8 [17, 18], which improved the hydrophilicity of mZIF-8 nanocrystals. By extending the modification time, the amount of free alkoxy for APTES increased, thereby resulting in reduced zeta potential when the modification process exceeded a certain time. Therefore, the zeta potential of m(24h)ZIF-8 was lower than that of m(12h)ZIF-8. However, the water contact angle measurement of Z-Pp and mZ-Pp composite membranes mentioned above showed the opposite results. In comparison to the Z-Pp composite membrane, the m(12h)Z-Pp membrane was more negatively charged when pH exceeded 5 (Fig. 5(b)). This could be explained by the reaction of amino groups from APTES attached on the outer surfaces of mZIF-8 nanocrystals with the chains of PDMS dope solution, thus resulting in more siloxy groups in polymer matrix layer. In addition, the attached aminosilane created a space steric hindrance between ZIF-8 nanoparticles. Therefore, the dispersibility and compatibility of mZIF-8 in PDMS matrix were enhanced (Fig. 6(b)), and the hydrophobicity of the constructed mZIF-8 based dense layer was improved accordingly. Comparably, the unmodified ZIF-8 in PDMS matrix presented agglomeration to a certain extent (Fig. 6(a)), which induced defects such as interfacial voids in the PDMS matrix [47]. In this study, Considering the subsequent application in CO_2 absorption, m(12h)ZIF-8 nanocrystals were selected for the subsequent mZIF-8 based composite HF membrane construction. The discussion on mZIF-8 loading and other membrane characterizations will be provided in Section 3.2.

Fig. 5. (a) Hydrophobicity and (b) zeta potential of different composite dense HF membranes.

Fig. 6. Surface morphologies of the ZIF-8 based composite membranes without (a) and with (b) aminosilane-modification for nanofillers.

3.2 mZIF-8 based composite HF membranes

The prepared ZIF-8 and mZIF-8 nanocrystals, and the pure PDMS, ZIF-8@PDMS and mZIF-8@PDMS membranes (the loading of ZIF-8/mZIF-8 is 5 wt.% as example) were selected for TGA and DTG analysis, as shown in Fig. 7(a). The as-synthesized powder ZIF-8 and mZIF-8 showed similar decomposition process in which imidazolate species firstly decomposed from 490 °C followed by the decomposition of carbon species from 600 °C [34, 48]. However, the mZIF-8 nanocrystals presented a reduced thermal stability in the region of 500—750 °C in TGA curve, which was attributed to organic decomposition of attached APTES functionalities accompanied by imidazolate disintegration [49]. It also could be confirmed by exothermic peak of mZIF-8 nanocrystals shift to the left around 590 °C in

DTG curve. The pure PDMS membrane showed strong thermal stability with only 35.7% weight loss from 300 to 800 °C, which could be associated to the tight Si–O frameworks [50]. However, with the introduction of ZIF-8/mZIF-8, the resultant ZIF-8@PDMS and mZIF-8@PDMS exhibited significant thermal stability reduction. This was possibly caused by the disruption of inherent cross-linking of PDMS chains and generation of fractional free volume in the PDMS matrix [51, 52], which may enhance the gas mass transfer through membrane for CO₂ absorption. Evidently, in the region of 450 to 650 °C, the dramatic decline of weight loss for ZIF-8@PDMS/mZIF-8@PDMS as compared to pure PDMS membrane indicated the disintegration of ZIF-8/mZIF-8 nanocrystals, which further confirmed the interaction between MOFs-based fillers and PDMS.

To verify the crystalline structure, XRD patterns of pure PDMS, ZIF-8@PDMS and mZIF-8@PDMS membranes are shown in Fig. 7(b). The pure PDMS showed a typical broad peak without crystalline reflections, indicating its amorphous structure [53]. The XRD pattern of ZIF-8@PDMS and mZIF-8@PDMS combined the pattern features of ZIF-8 and PDMS, which further revealed the presence of the crystal phase in polymer matrix [30]. The crystalline structures of ZIF-8 and mZIF-8 were maintained during the preparation procedure of mixed matrix membrane.

Fig. 7. TGA and DTG curves (a) and XRD patterns (b) of ZIF-8 nanocrystals, mZIF-8 nanocrystals, PDMS, ZIF-8@PDMS and mZIF-8@PDMS mixed matrixes.

In order to investigate the influence of mZIF-8 loading on the morphology of composite membrane, FE-SEM was applied to observe shell surfaces and cross-sections of composite HF membranes. As shown in Fig. 8(a) and Fig. 9(a), the pure PDMS coated PVDF membrane (mZ(0%)-Pp or Pp) presented

a smooth and non-porous surface, which indicated the uniform deposition of PDMS layer on porous pristine PVDF substrate (see in Fig. A.3). With an increase of mZIF-8 loading from 2.5 to 20 wt.%, more bumps appeared evenly on the surfaces of coated layers and uniformly distributed in PDMS bulks, deriving from the embedment of mZIF-8 in PDMS matrix. Apparent crystals aggregation and/or interfacial voids could be observed in the mZIF-8 based composite membranes with mZIF-8 loading above 10 wt.%, which would result in membrane wetting in the GLMC process. The surface roughness of the prepared membranes was also investigated, as shown in Table A. 3. In comparison to the PVDF substrate, the surface roughness of the Pp membrane was reduced due to its dense structure. With an increase of mZIF-8 loadings, the surface roughness of the mZ-Pp composite membranes increased accordingly, which was in agreement with the FE-SEM images.

Fig. 8. FE-SEM images of the outer surface of mZIF-8 based composite membranes with different

mZIF-8 loadings ((a—f) representing 0, 2.5, 5, 10, 15 and 20 wt.%).

Fig. 9. FE-SEM images of the cross-sections of mZIF-8 based composite membranes with different mZIF-8 loadings ((a—f) representing 0, 2.5, 5, 10, 15 and 20 wt.%).

Moreover, the cross-section of PVDF substrate, Pp, Z-Pp and mZ-Pp membranes (5 wt.% ZIF-8/mZIF-8 loading as example) were also observed using FE-SEM, as shown in Fig. 10 and Fig. A.4. The top layers of Pp, Z-Pp and mZ-Pp membranes presented dense structures with similar thicknesses around 3.5 μm , indicating the negligible effect of ZIF-8/mZIF-8 nanofillers addition on the thickness of the PDMS matrix. The EDX scanning images of mZ-Pp membranes (Fig. 10(d-Si) and (d-Zn)) showed that Si and Zn elements uniformly distributed on the coated layer, demonstrating the formation of a continuous mZIF-8 based PDMS layer on the PVDF substrate. A minor amount of Si could be identified in the PVDF substrate (indicated with F element). This is due to that the PDMS dope solution diffused into the substrate pores during the coating process, which could enhance the mechanical performance of the formed composite membranes.

Fig. 10. FE-SEM images of cross-sections of (a) PVDF substrate, (b) Pp, (c) Z-Pp and (d) mZ-Pp HF membranes (the loading of mZIF-8 is 5 wt.% as example), of which the EDX mappings for F, Si and Zn elements.

To verify that the modified ZIF-8 mixed with PDMS was coated on the PVDF substrate, ATR-FTIR spectra of the outer surface of substrate, Pp, Z-Pp and mZ-Pp hollow membranes were detected and shown in Fig. 11. Compared with the PVDF spectrum, the characteristic absorption peaks of PDMS attributed to the Si-C, Si-O-Si, and Si-C stretching could be detected at 1258, 1085—995 and 865—755 cm^{-1} , respectively [54]. After embedding ZIF-8 nanocrystals in PDMS matrix, emerging absorption peaks at 1240, 1095, and 884/740 cm^{-1} were associated with the in-plane imidazole ring bending, C-N stretching, and out-of-plane ring bending of ZIF-8, respectively [45]. As for coating with mZIF-8@PDMS dense layer, the absorption peaks of Si-O (1085 and 1050 cm^{-1}) and Si-C (865 and 843 cm^{-1}) stretching were stronger. This was due to APTES grafted on ZIF-8 nanocrystals introducing more Si-O and Si-C functional groups in the top layer.

Fig. 11. (a) ATR-FTIR spectra and (b) XPS survey spectra of the shell surfaces of PVDF substrate, Pp, Z-Pp and mZ-Pp membranes.

XPS analyses were measured to further explore the elemental compositions and chemical bindings of obtained membranes, of which the elemental compositions of inner and outer surfaces of membranes can be seen in Table 1. The elemental compositions of inner surfaces of Pp, Z-Pp, mZ-Pp membranes were almost equal and all detected Si element in a certain amount. It indicated that PDMS could partially penetrate through the macropores of the PVDF, which was consistent with the result of EDX. As illustrated in Fig. 11(b), the peaks of the F 1s and Cl 2p (feature elements of applied PVDF) were significantly weakened, while the peaks of O 1s, Si 2p, and Zn 2p presented strongly enhancement, due to the coated PDMS-based dense top layers on PVDF substrates. The deconvolution of C 1s spectrum in Fig. 12(a) was curve-fitted to three components, which are C-Si/C-C/C-H (284.5 eV), CH₂/C-O/C-N (285.5 eV), and CF₂ (289.5 eV). The O 1s spectrum (Fig. 12(b)) was curve-fitted with three components of Si-O-Si (531.6 eV), CO_x bounds (532.1 eV), and O-Si-O (532.2 eV). The Si 2p spectrum (Fig. 12(c)) was curve-fitted with two components of Si-O-Si (101.3 eV) and O-Si-O (102.4 eV) [42, 55, 56]. The Zn 2p_{3/2} core-level spectrum (Fig. 12(d)) presented one peak component at binding energy of 1022.0 eV, which was assigned to the Zn²⁺ of ZIF-8. The XPS analyses results were consistent with previous studies [57, 58].

Fig. 12. Deconvolution XPS spectra of (a) C 1s, (b) O 1s, (c) Si 2p, and (d) Zn 2p on the shell surface of mZ-Pp membranes.

Table 1. Elemental compositions of the PVDF substrate, Pp, Z-Pp, and mZ-Pp membranes.

	C 1s (%)	F 1s (%)	O 1s (%)	Cl 2p (%)	Si 2p (%)	Zn 2p (%)	N 1s (%)
Outer surface							
PVDF	65.4	17.0	9.8	5.8	2.1	—	—
Pp	47.2	4.7	26.2	1.7	20.2	—	—
Z-Pp	49.8	3.2	26.0	1.5	19.3	0.2	0.1
mZ-Pp	53.6	5.1	22.9	1.9	14.6	0.3	1.6
Inner surface							
PVDF	53.1	28.9	4.2	13.8	—	—	—
Pp	47.1	11.0	21.5	4.0	16.4	—	—
Z-Pp	51.2	10.1	15.5	5.8	17.4	—	—
mZ-Pp	48.6	16.9	17.2	5.2	12.0	—	—

The dynamic water contact angles of PVDF substrate, Pp, Z-Pp, mZ(2.5—20%)-Pp HF membranes were measured to investigate their hydrophobicities, as shown in Fig. 13. The hydrophobicity of Pp HF was significantly improved due to the coating of dense hydrophobic PDMS on the surface of porous PVDF substrate, and the contact angle increased from 98 ° to 115 °. The contact angle of Z(5%)-Pp HF increased slightly, which was caused by the rougher shell surface of membrane after introducing the ZIF-8 nanocrystals into the PDMS matrix. With the addition of mZIF-8 into PDMS, the overall hydrophobicity of mZ-Pp membrane was enhanced, which was consistent with the discussion in Section 3.1. The highest dynamic water contact angle was achieved by mZ(5%)-Pp composite membrane. However, the hydrophobicity of composite membrane would decrease when continuously improving the loading of mZIF-8. This could be ascribed to more hydrophilic amino groups of mZIF-8 exposing in the PDMS matrix and the interfacial voids formed by nanocrystals agglomeration, which are in agreement with other studies [59, 60]. Therefore, in view of its superb hydrophobic property, the mZ(5%)-Pp composite HF membrane was selected for the following investigation of CO₂ removal performance in a GLMC.

Fig. 13. Contact angles of PVDF, Pp, Z(5%)-Pp and mZ(2.5—20%)-Pp membranes.

3.3 Biogas upgrading in GLMC

A series of mZ-Pp membranes were measured to verify the CO₂ absorption performance using water as liquid absorbent and fed with biogas (40% CO₂) in GLMC process. In Fig. 14(a), the CO₂ flux was improved by embedding the ZIF-8 nanocrystals into PDMS matrix deposited on PVDF substrate due to ZIF-8 nanocrystals creating multiple pore channels for molecule transportation pathway [30]. Meanwhile, the mZ-Pp composite membranes with modified ZIF-8 exhibited significantly higher CO₂ flux compared to Z-Pp membrane (ZIF-8/mZIF-8 loading is 5 wt.%). It could be explained by [formation of more free volumes in matrix for gas transport, derived from the chemical bonding of APTES between ZIF-8 and PDMS chains, and attraction of amine group to CO₂ \[61\]. The free -NH₂ of APTES could offer extra affinity for CO₂ thus promoting the CO₂ transport through PDMS matrix.](#) The CO₂ removal flux of Z-Pp membrane showed a gently rising trend with increasing liquid velocities, and even reduced when velocity over 0.25 m·s⁻¹. It could be explained by the partial-wetting of membrane caused by its weaker hydrophobicity and generated interfacial voids derived from weaker compatibility between ZIF-8 nanocrystals and PDMS matrix. The CO₂ removal performances of mZIF-8 based composite HF membrane with different mZIF-8 loadings were evaluated and shown in Fig. 14(b). With increasing mZIF-8 loading from 2.5 to 5 wt.%, the CO₂ flux was significantly improved, which could be ascribed

to the more pore channels supplied by mZIF-8 nanocrystals. When the loading is 5 wt.%, the CO₂ absorption flux of composite membrane reached $2.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at $0.3 \text{ m} \cdot \text{s}^{-1}$. However, the CO₂ absorption fluxes of mZ-Pp membranes decreased by further increasing mZIF-8 loadings from 5 wt.%. The severe agglomeration of mZIF-8 nanocrystals in PDMS matrix at high loading, as indicated in FE-SEM images (Fig. 8), would generate more non-selective interfacial defects, leading to accelerated membrane wetting. Therefore, the composite membrane with 5 wt.% of mZIF-8 nanocrystals loading was selected for following CO₂ absorption investigation. The CO₂ removal performance of mZIF-8 based composite membranes using water and 1M MEA as absorbents were presented in Fig. 14(c). Due to much higher CO₂ loading capacity of MEA [42], the CO₂ flux of using MEA presented around 188% higher than that of using water. In the biogas-water system, the average CO₂/CH₄ selectivity of mZ-Pp membrane was ~ 1.5 , while the selectivity was remarkably improved to ~ 17.0 using 1M MEA solvent, which was comparable with other studies [30, 34, 52].

Fig. 14. CO₂ absorption fluxes for Pp, Z-Pp and mZ-Pp membranes (a), and mZIF-8 based composite dense HF membranes (b) with different mZIF-8 loadings and (c) using different liquid absorbents; and selectivity on their each GLMC system.

3.4 Long-term performance

Long-term CO₂ removal from biogas with mZ-Pp composite HF membranes were examined for 15 days using water and 1 M MEA as absorbents to investigate the stability of membranes. As shown in Fig. 15, the mZ-Pp composite membrane presented a reasonable stability throughout 15 days of operation, with $\sim 11\%$ and 13% reductions of the initial CO₂ fluxes in biogas–water and biogas–1M MEA systems, respectively. In our previous study [38], the CO₂ absorption flux of pristine PVDF (the same material as this work) in the same biogas–1M MEA system showed a $\sim 80\%$ drop from the initial

flux after 10 days of operation, in which the membrane had been completely wetted. It indicates that a significant improvement in long-term stability after construction of a mZIF-8 base PDMS dense layer on porous PVDF substrate was achieved. The slightly flux decline of mZ-Pp composite membrane seems to be inevitable. Since the prepared HF membranes were immersed in water or 1M MEA during long-term testing after each test, the capillary condensation of the water or MEA vapor would occur in the pores of the membrane substrate [42].

Fig. 15. Long-term stability of mZIF-8 based composite HF membrane.

3.5 Comparison of CO₂ absorption fluxes of various membranes

The CO₂ absorption performances in GLMC processes of various dense/porous HF membranes are summarized in Table 2. It is worth noting that our developed mZIF-8 based dense composite membrane (5 wt.% m(12h)ZIF-8 loading) reached a high CO₂ absorption performance with the flux values of 2.3 and $3.8 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at a liquid velocity of $0.25 \text{ m} \cdot \text{s}^{-1}$ using water and 1M MEA as absorbents, respectively. It demonstrated a significantly enhanced CO₂ mass transfer efficiency as compared to other dense membranes, and even outperformed some other porous membranes applied with higher concentrations of feed CO₂ and chemical absorbents. Therefore, we can say that the aminosilane-modified ZIF-8 based composite HF membrane is well-designed to facilitate CO₂ mass transfer for biogas upgrading in GLMC processes.

Table 2. Comparison of CO₂ absorption flux of the various HF membranes in GLMC.

Membrane substrate	Modification layer	Pore size (nm)	Lumen side	Feed gas	Absorbent	Operating pressure (bar)	Liquid velocity (m·s ⁻¹)	CO ₂ flux (10 ⁻³ mol·m ⁻² ·s ⁻¹)	Reference
PVDF	mZIF-8@PDMS	Non-porous (NP)	Gas (G)	40% CO ₂	Water	1.1	0.25	2.3	Current work
PVDF	mZIF-8@PDMS	NP	G	40% CO ₂	1M MEA	1.1	0.25	3.8	Current work
Poly(acrylonitrile) ^a	PolyActive™-PDMS ^b	NP	—	Pure CO ₂	Water	2.0	0.36	2.9 ^c	[22], 2016
Commercial P-240	PolyPhenylene Oxide	NP	G	30 %CO ₂	Water	2.5	0.0004	0.03	[23], 2016
Commercial P-240	PolyPhenylene Oxide	NP	G	35 %CO ₂	Water	8.0	0.09	0.3 ^c	[26], 2018
PAI	Octadecylamine	—	G	Pure CO ₂	Water	1.0	0.25	1.8	[62], 2012
PVDF	—	55	G	Pure CO ₂	Water	1.0	0.25	0.2	[63], 2013
PEI	Fluorinated (f) SiO ₂	40	G	Pure CO ₂	Water	1.0	0.25	1.3	[64], 2013
PVDF	CA-PDA/PEIm ^d	26	G	Pure CO ₂	Water	1.0	0.25	2.5	[43], 2019
PTFE	—	30-80	Liquid (L)	Pure CO ₂	30 wt.% MEA	1.0	28 mL·min ⁻¹	1.1	[65], 2014
Al ₂ O ₃	fZrO ₂	200	L	12.5% CO ₂	5 wt.% MEA	1.0	10 mL·min ⁻¹	1.3	[66], 2015
PVDF	fTiO ₂	25	G	Pure CO ₂	1M MEA	1.0	0.25	10.9	[38], 2018
PVDF	fTiO ₂ -SiO ₂	25	G	40% CO ₂	1M MEA	1.0	0.25	3.2	[42], 2018
PTFE	Silica nanoparticles	—	G	40% CO ₂	20 wt.% K ₂ CO ₃	10.0	75 mL·min ⁻¹	1.5	[67], 2018

^a flat sheet membrane;^b PolyActive™ represents for poly(ethylene oxide) PEO (amorphous)–poly(butylene terephthalate) PBT (crystalline) block copolymer;^c after conversion of mol·m⁻³·s⁻¹ to mol·m⁻²·s⁻¹;^d CA-PDA/PEIm refers to carbonic anhydrase-polydopamine/polyethylenimine.

4 Conclusions

In this study, MOF based composite dense HF membranes were successfully constructed for biogas upgrading in the membrane contacting process by dispersing aminosilane-modified ZIF-8 nanocrystals into PDMS matrix deposited on porous PVDF substrate. The modification mechanism was revealed

with zeta potential analysis, which was based on the dual link of APTES with ZIF-8 structure and PDMS matrix. As the modifier, APTES significantly ameliorated the compatibility of ZIF-8 with dense PDMS layer and improved the overall hydrophobicity of composite membranes, thereby enhancing the anti-wetting ability in the GLMC process. Benefitting from the extra pore channels provided by mZIF-8 nanocrystals, the optimized composite membrane achieved a competitive CO₂ mass transfer efficiency as well as good selectivity of CO₂/CH₄ using water and aqueous amine absorbents. Furthermore, robust long-term stability of the mZIF-8 based composite HF membrane with a dense layer was confirmed in a 15-day operation. This study provides a new strategy to enhance the biogas upgrading efficiency of the composite dense HF membrane with modified MOFs in GLMC applications.

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Appendix A.

The crystallite size can be calculated by the Scherrer's equation using XRD data.

$$D_p = \frac{0.94\lambda}{\beta_{1/2} \cos\theta} \quad (\text{A.1})$$

where D_p is the average crystallite size, β is the line broadening in radians, θ is the Bragg angle, λ is the X-ray wavelength ($\lambda = 1.54 \text{ \AA}$).

Table A. 1. Calculated average crystallite sizes and zeta potentials of ZIF-8 and m(6—24h)ZIF-8 nanocrystals

Nanocrystal	Crystallite size (nm)	Zeta potential (mV)
ZIF-8	22.3 ± 7.0	15.7 ± 0.9
m(6h)ZIF-8	19.3 ± 5.9	16.5 ± 1.3
m(12h)ZIF-8	19.9 ± 6.9	22.1 ± 1.8
m(24h)ZIF-8	18.4 ± 5.4	17.5 ± 1.1

Fig. A.1. FE-SEM images of m(6h)ZIF-8 (a) and m(24h)ZIF-8 (b) nanocrystals.

Fig. A.2. FE-TEM images of m(6h)ZIF-8 (a) and m(24h)ZIF-8 (b) nanocrystals.

Table A. 2. Elemental composition of the powder ZIF-8 and m(12 h)ZIF-8 nanocrystals.

	C 1s (%)	N 1s (%)	O 1s (%)	Zn 2p (%)	Si 2p (%)
ZIF-8	62.2	23.2	5.8	8.8	—
m(12mh)ZIF-8	60.8	24.7	7.1	7.0	0.4

Fig. A.3. FESEM images of the shell surface of the PVDF hollow fiber substrate.

Table A. 3. Surface roughness parameters of the PVDF, Pp, Z-Pp and mZ-Pp hollow fiber membranes.

Membrane	Roughness	
	R_a (nm)	R_q (nm)
PVDF	19.18 ± 3.70	24.66 ± 4.39
Pp	12.65 ± 1.01	16.32 ± 1.65
Z-Pp	33.19 ± 2.33	42.93 ± 3.21
mZ(2.5%)-Pp	34.23 ± 3.76	45.99 ± 3.09
mZ(5%)-Pp	40.07 ± 5.59	52.29 ± 6.68
mZ(10%)-Pp	59.44 ± 4.10	64.18 ± 4.72
mZ(15%)-Pp	66.32 ± 6.14	79.50 ± 7.11
mZ(20%)-Pp	68.83 ± 5.72	83.92 ± 6.2

Fig. A.4. FE-SEM images ($\times 50$ k) of cross-sections of (a) PVDF substrate, (b) Pp, (c) Z-Pp and (d) mZ-Pp HF membranes (the loading of mZIF-8 is 5 wt.% as example).