



Carbon membranes for CO₂ removal: Status and perspectives from materials to processes

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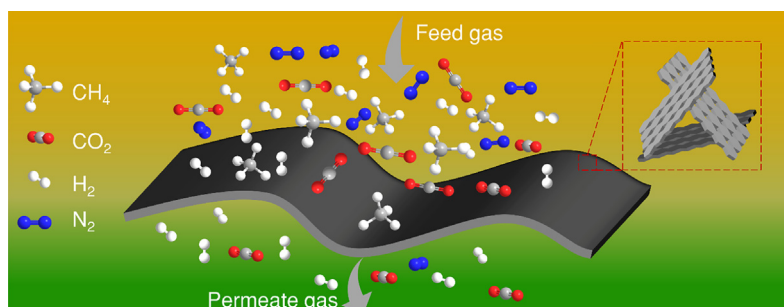
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HIGHLIGHTS

- Tuning carbon membrane structure and performance was critically reviewed.
- Technology advances of carbon membrane for CO₂ removal was discussed.
- Future perspectives for carbon membrane development and application was proposed.

GRAPHICAL ABSTRACT

The outstanding separation performance coupled with excellent mechanical and chemical stabilities makes carbon membranes-based separation process as an energy-efficient and environmentally friendly technology for CO₂ removal.



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ABSTRACT

CO₂ removal from gas streams using energy-efficient and environmentally friendly separation technologies can contribute to achieving a low-carbon energy future. Carbon membrane systems for hydrogen purification, post-combustion CO₂ capture, and natural gas (NG) sweetening are considered as green processes because of their low energy consumption and negligible environmental impact. Much effort has been devoted to enhancing gas permeance and/or selectivity of carbon membranes by tailoring micropore structures to accomplish different CO₂ removal processes. In this review, the status of tuning microstructure and fabrication of the ultrathin selective layer of carbon membranes, as well as membrane module upscaling was analyzed. The precursors made from a clean process using the solvent of ionic liquids have a particular interest, and high-performance asymmetric carbon hollow fiber membranes (CHFMs) without complex pre-treatment were highlighted towards technology advances of carbon membrane development. Energy-efficient processes of carbon membranes for CO₂ removal in oil/gas/chemical industries and power plants were discussed for decreasing production costs, environmental impact, energy consumption, and improving process flexibility. Future perspectives on advanced carbon membrane material development based on renewable precursors and simple carbonization processes, as well as module design and process optimization, were proposed.

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1. Introduction

The rapid growth in greenhouse gas emissions has stimulated worldwide attention to look for green and clean energy resources alternatives to traditional fossil fuels. Hydrogen and methane, as clean and low-carbon energy sources, have shown the increased demands in the energy system and transport sector such as electricity generation, heating, and vehicle fuels [1]. However, raw gas streams usually contain some impurities such as CO₂ and water which should be removed to reach the purity requirement for end-users. Compared to the conventional separation technologies of chemical absorption, pressure-swing adsorption (PSA), and cryogenic distillation, membrane-based separation technology as an energy-efficient and environmentally friendly process is currently attracting particular interest for selected CO₂ removal applications. Various membrane materials such as polymeric membranes [2,3], inorganic-based membranes like carbon molecular sieve (CMS) [4-7], graphene oxide (GO) [8], zeolite imidazolate framework (ZIF) [9,10], and metal-organic frameworks (MOFs) [11] have been developed for CO₂-related separations. Among them, carbon membranes have great advantages of providing strong mechanical and chemical stabilities and high separation performance, especially for high-temperature and -pressure demanded scenarios such as H₂/CO₂ separation in steam methane reforming process, and CO₂/CH₄ separation in natural gas (NG) sweetening [12-14].

The first carbon membranes were prepared by carbonization of cellulose hollow fibers [15], and since then carbon membranes have been developed from different precursors such as cellulose derivatives [4,16-20], polyimide derivatives [5,21-26], poly(vinylidene fluoride) (PVDF) [27], and polyacrylonitrile (PAN) [28]. Carbon hollow fiber membranes (CHFMs) derived from polyimide-based precursors were prepared for different gas separations (NG sweetening and olefin/paraffin separation [21,29,30]) and demonstrated excellent performance. The PVDF based CHFMs with an average pore size of 6 Å were developed for organic solvent separations [27], and a high ideal p-xylene/o-xylene selectivity of 26 was reported at lab-scale. The cellulose acetate (CA) based CHFMs have been developed for biogas upgrading, natural gas sweetening and H₂ separation [4,31-33], which showed high CO₂/CH₄ selectivity, but relatively low gas permeance (e.g., CO₂: < 0.04 m³(STP)/(m²·h·bar)) due to a thick wall (ca. 20–30 μm) made in symmetric structure [17]. Reducing the thickness of the carbon matrix can potentially enhance gas permeance, but the mechanical strength of membrane materials may decrease. Moreover, the main challenge of cellulose regeneration from CA precursors still hindered the large-scale production of cellulosic-based CHFMs [33]. Recently, the preparation of carbon membranes directly from cellulose hollow fibers was reported by Lei et al. [4], which partly addressed the challenge of CA-based carbon membranes. However, the gas permeances of the reported carbon membranes are still relatively low, which should be further improved by making either asymmetric or supported carbon membranes.

Moreover, by carefully controlling carbonization conditions (e.g., final carbonization temperature, heating rate, and environment) and proper post-treatment such as post-oxidation and chemical vapor deposition (CVD), the pore structure and porosity of carbon membranes based on the specific precursors can be tailored to efficiently separate gas molecules which are much alike in both size and physical properties (e.g., H₂-CO₂ and olefin-paraffin) [18,21,34]. The improvement of carbon membrane performances may offset the relatively high fabrication cost compared to polymeric membranes. However, the up-scaling of carbon membrane modules is still challenging especially related to membrane mounting, potting, and sealing for high-pressure and high-temperature applications. Therefore, this is a need to make flexible carbon membranes and identify a suitable potting material to make modules with high packing density and high-pressure tolerance. Ceramic supported carbon membranes present much stronger mechanical strength and are easier for module construction, which has

been widely studied for high-temperature H₂ purification. However, the challenges of making defect-free, thin selective carbon layer on top of support still hinder its up-scaling for large-scale commercial applications [35]. In this work, a review of the status and challenges of both self-supported and supported carbon membranes from materials to applications was conducted. Moreover, carbon membrane development with respect to renewable precursors and low-cost carbonization procedures as well as the applications for CO₂ removals with respect to energy efficiency were clearly highlighted. Finally, future perspectives on material, module, and process development for CO₂ removal with advanced carbon membranes were also proposed.

2. Carbon membrane development

2.1. Precursor selection and preparation

In the past decades, different polymeric precursors have been employed for fabrication of high-performance carbon membranes, including cellulose and derivatives [4,20,36,37], polyimide (PI) and derivatives [26,38-42], polyacrylonitrile (PAN) [28,43], poly(p-phenylene oxide) (PPO) [44-46] and phenolic resin [47,48]. Besides the optimization of carbonization conditions and the implementation of post-treatment, the selection of suitable precursors is also a crucial factor to determine membrane separation performance. Moreover, the polymer precursor-determined properties such as chemical structures, glass transition temperature, decomposition temperature, and fractional free volume (FFV) should be well considered for making high-performance carbon membranes [49,50]. The effect of the microstructure of polyimide precursors on the gas permeation properties of the derived carbon membranes was investigated by comparing three block-copolyimides with a different number of methyl substituent groups as reported by Park et al. [49]. Gas permeability of carbon membranes can be improved by introducing the methyl substituent groups into polymer backbone to increase FFV. The current researches on carbon membrane preparation are mainly based on two representative precursors: cellulose and polyimide, and the comparison of the two materials are given in Table 1. Carbon membranes made from cellulose precursors usually present a relatively low cost with moderate separation performance. While polyimide-derived carbon membranes in general show higher performance, but production cost might be relatively higher.

To date, N-methyl-2-pyrrolidone (NMP) remains the dominant solvent for making carbon membrane precursors. However, it has now been faced with restriction for industrial use in some EU countries due to the risks to the health of workers exposed to NMP [52]. Thus, alternative green solvents are required to achieve a cleaner precursor preparation process. Recently, ionic liquids (ILs), which are suggested as a green solvent because of the advanced properties of negligible volatility, high thermal and chemical stability, easy recyclability [53,54], has been successfully used for fabrication of cellulose

Table 1

Comparison of cellulose and polyimide precursors for making carbon membranes.

Property	Cellulose	Polyimide
Availability	High (abundant)	Limited
Sustainability	Renewable biopolymer	Synthetic material
Processability	Moderate (difficult to dissolve)	High (can be dissolved in conventional solvents)
Free volume	Low to Moderate	Moderate to high
Fusing risk during carbonization	Moderate	Very high
Mechanical strength	High	High
Material cost ratio ^a	1	10

^a : Cost estimation is basically due to the availability of the material [51].

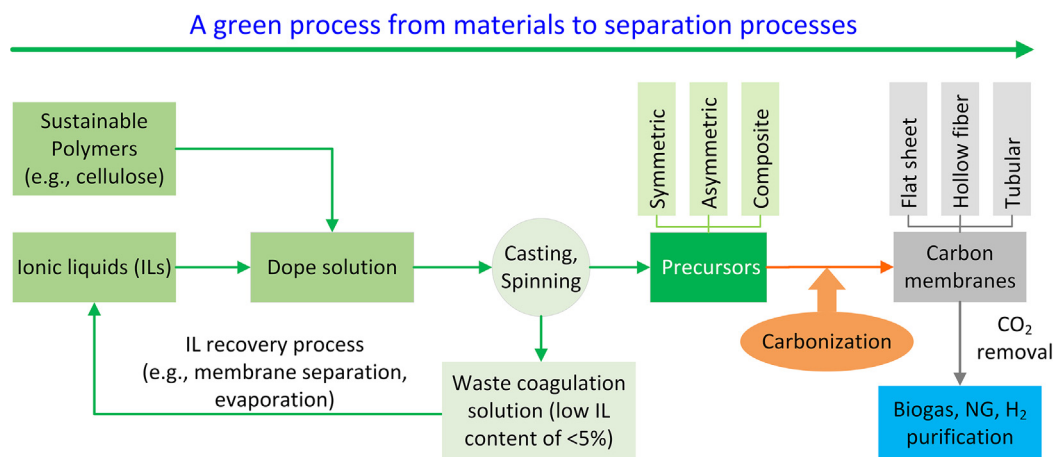


Fig. 1. Schematic illustration of a green process for preparation of carbon membrane precursors using ionic liquids. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

precursors [4,20]. Besides, several ILs recycling methods have been investigated involving freeze crystallization [55], membrane separation [56], and evaporation [57]. This shows great potential on the fabrication of CMS membranes at a low environmental impact. A conceived illustration on the preparation of CMS membranes from sustainable polymer materials and the solvent of ionic liquids (ILs) is depicted in Fig. 1. The membrane precursors with tunable structures, such as symmetric, asymmetric, and composite, can be prepared from renewable materials (e.g. cellulose) that are dissolved in ILs. The diluted ILs in the waste coagulation solution can be recycled by evaporation or membrane separation processes. Then, the carbon membranes are constructed into various types of modules for energy-efficiency CO₂ removals. The green advances of carbon membrane compared to conventional separation technologies for gas separations were discussed in section 3.

2.2. Carbon membrane preparation

Carbon membranes are typically formed with a rigid structure via a controlled carbonization procedure applied to polymer precursors at a high temperature (e.g., 500–900 °C). During carbonization, the entangled precursors are transformed to rigidly carbonized aromatic strands, and afterward forming organized plates to approach a higher system entropy, which results in a bimodal structure of ultramicropores and micropores [29,58]. Although carbon membranes can be prepared from diverse precursors and present different structures and separation performance, the general carbonization mechanism from polymeric precursors to carbon membranes is very similar. Rungta et al. [29] and Ma et al. [58] proposed an envisioned evolution mechanism for the preparation of CMS membranes by carbonization of the coil polymer precursors as illustrated in Fig. 2. The entangled precursor is initially activated to start aromatization and fragmentation at the temperature ramping process and afterward generates periodic scissions along the polymer backbone due to enough localized stresses (Fig. 2(i) & (ii)) [29,58]. By removing most of oxygen and hydrogen atoms, the backbone scissions are transformed to rigidly aromatic carbon strands [58]. Besides, the rigid carbon strands align and form carbon “plates” to yield higher entropy to the system and reduce the excluded volume effects that existed with the random packing of the strands (Fig. 2(iii)) [29]. During the final thermal soaking phase, it is difficult to form long-range perfect stacking of plates due to the kinetic restrictions (limited time at high temperature). Thus, the final carbon membranes usually present a microstructure with imperfectly packed plates that are formed by organized strands (ultramicropores) as depicted in Fig. 2(iv). During the end cooling stage, the micropore “cells” are stacked to form a cellular

structure (Fig. 2(v)) in which the ultramicropores share the “walls” between micropores [58]. The pore size distribution of CMS membranes is depicted in Fig. 2(vi), which can be adjusted by different methods listed in Fig. 2 (Red dashed square) to get larger pores (Fig. 2 (Vii)) or smaller pores (Fig. 2 (Viii)). The ultramicropores of ca. 3–7 Å are suggested to govern gas selectivity, while the micropores (7–20 Å) contribute to a high gas permeability with larger sorption sites [25,26,58].

Carbon membranes are composed of sp²- and sp³- hybridized carbon structure [26,58]. The sp²-hybridized carbon (i.e., a two-dimensional (2D) layered graphitic carbon) is beneficial for plate packing to form a more compact ultramicropore structure. While the three-dimensional (3D) sp³-hybridized carbon will prevent the plate packing, which enhances gas permeability due to the widening of micropores. However, the sp³-hybridized carbon structure is thermodynamically unstable, which can be partly transformed to sp²-hybridized carbon at higher temperatures [59,60]. Moreover, adjusting of carbon structure can be implemented either during carbonization or in an extra post-treatment process, which makes carbon membranes flexible for different applications. Tuning carbonization conditions (e.g., carbonization temperature, atmosphere, doping) and applying post-treatment steps can provide some facile ways to modify the microstructures of carbon membranes, and thus improve separation performance (especially membrane selectivity). It should be noted that the pore size controlling approach applies to all carbon membrane configurations (e.g., flat-sheet, hollow fiber and tubular). Various methods by tailoring micropores/ultramicropores of carbon membranes during carbonization or post-treatment step (illustrated in Fig. 2 and listed in Table 2 for details) were reported to tune carbon membrane structures, which can either improve gas permeability and/or enhance selectivity.

H₂-assisted tailoring of ultramicropores can dramatically improve gas permeability with a low selectivity loss as reported by Ma et al. [58]. The H₂-contained carbonization environment can modulate the carbon hybridized structures (sp² and sp³), and the ratio of sp³/sp² hybridization carbon increases when the carbonization environment contains a higher H₂ concentration, which results in a more permeable but less selective membrane [58]. That method provides a facial way for tuning micropore size and distribution.

Oxidative treatment of fresh-made carbon membranes has been successfully employed to obtain wider pores [32,61–63]. Carbon membranes exposed in the air at an oxidation treatment of 350 °C increased H₂ permeance from 5 to 18 m³(STP) m⁻²h⁻¹ bar⁻¹ due to the increase of the sp³ hybridized carbon atoms in carbon matrix [62]. Moreover, the increase of pore size via oxidation treatment was verified by N₂ adsorption reported by Lee et al. [61]. Compared with the fresh-

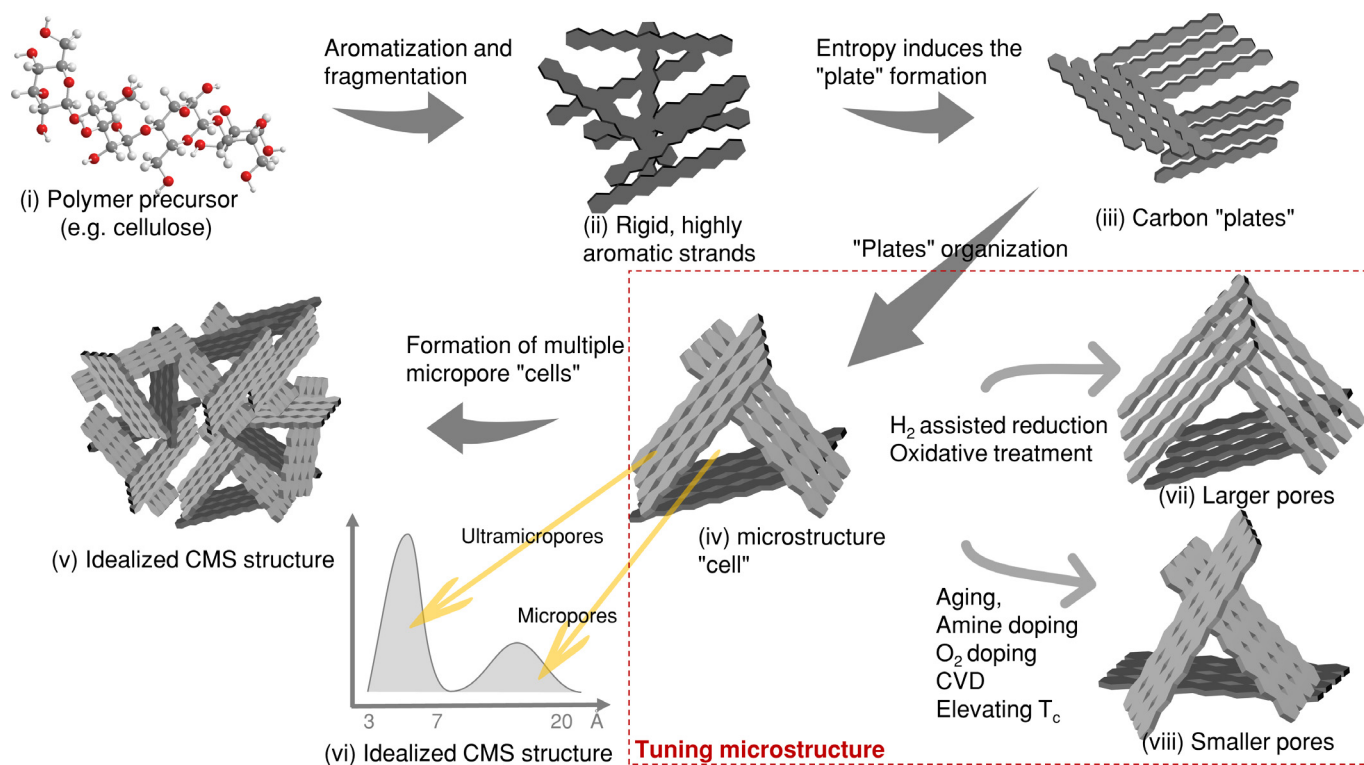


Fig. 2. Illustration of the formation process of a CMS structure from a polymeric precursor based on the ref [29,58]. The red dashed line encloses the methods for tuning the microstructures of carbon membranes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

made carbon membranes, the average pore size of the post-oxidation processed membranes increases from 0.53 to 0.68 nm which significantly decreases membrane selectivity.

However, introducing a trace amount of O_2 at high temperature (i.e., O_2 doping) can tighten the pore structure of carbon membranes to make more selective CMS membranes [29,64,65]. The oxygen molecules can bind to active sites for narrowing ultramicropore size, and thus improve membrane selectivity [64]. Moreover, introducing other doping species such as ozone [66] and amine [67] can also adjust pore size. Huang et al. [66] reported the implementation of an ozone-based post-synthetic method to enhance H_2/CH_4 selectivity from 13.3 to 50.7. Similar doping concept by applying a dopant of paraphenylenediamine (PPDA) (fit to the pore size of carbon membranes) was conducted by Wenz and Koros [67] to react with the adjacent CMS sheets to form new covalent bonds, and thus decreasing ultramicropore size.

A physical aging process, named hyperaged was introduced by Qiu et al. [25] to improve H_2/C_2H_4 selectivity. The distance of adjacent carbon strands can be compressed when the fresh-made CHFMs were

hyperaged at a hot flow of air atmosphere at a certain temperature range (e.g., 90 to 250 °C), and thereby resulting in smaller ultramicropores with a 10-fold increase of H_2/C_2H_4 selectivity. Therefore, proper aging methods can be introduced to adjust separation performance and enhance the stability of carbon membranes.

Elevating carbonization temperature was reported to reduce pore size in the literature [16,19,26,38,42,68]. A CO_2/CH_4 selectivity of > 3000 was obtained by increasing the carbonization temperature to 900 °C [26]. When carbonization temperature raises, the micropores surrounded by refined ultramicropores can be formed to provide the sorption sites for CO_2 , O_2 and N_2 , but rejects the CH_4 molecules. Because of the narrowed pathways, both sorption and diffusion selectivities can be improved.

Post-treatment by the integration of post-oxidation, post-reduction and CVD was applied to improve separation performance by Haider et al [32]. The post-oxidized membranes exhibited a rapid clogging when contaminated with water vapor or any other hydrogen bonding molecules. Thus, the following post-reduction step should be employed

Table 2
Representative methods for tuning carbon membrane structures and performances.

Tune carbon structure	Methods	Membrane performance	ref.
Pore widening	H_2 -assisted environment (introduce H_2 into purge gas)	Dramatic increase permeability with little loss selectivity	[58]
	Oxidative treatment (in air at different temperatures of below 400 °C)	Improve gas permeability but may scarify gas selectivity	[32,61-63]
Pore reducing	Chemical doping (Ozone, O_2 , amine, etc.)	Increase selectivity, but may reduce gas permeability	[29,64-67]
	Hyperaging (at a specific temperature, e.g., below 250 °C)	Enhance gas selectivity, enhance stability of gas permeability	[25]
	Elevating carbonization temperature	Enhance gas selectivity but reduce permeability	[16,19,26,38,42,68]
Increase porosity, but narrow pore size distribution	Integrating of post-treatments (post-oxidation, reduction and chemical vapor deposition (CVD))	Simultaneously enhance gas permeability and selectivity	[32]

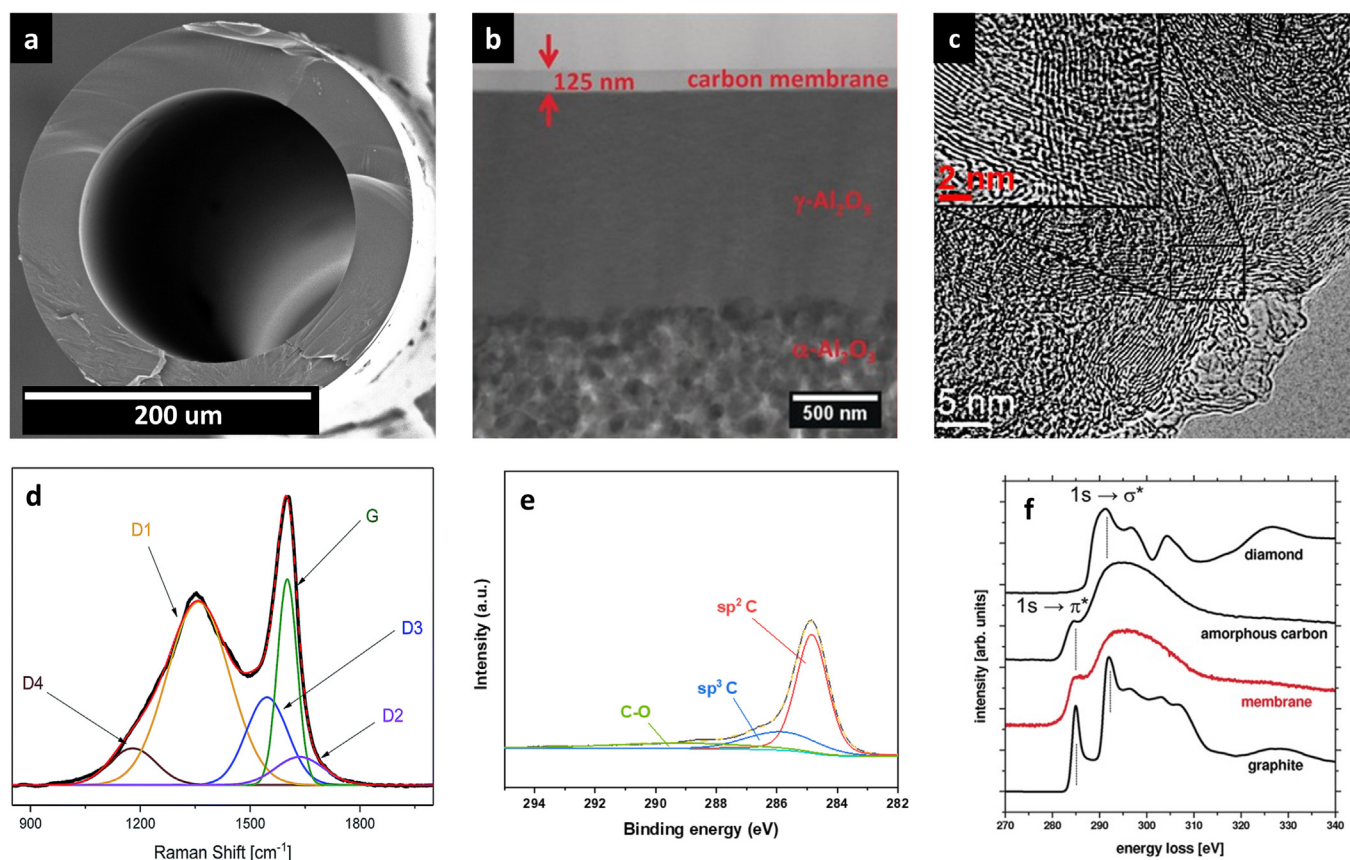


Fig. 3. Typical characterization methods for the analysis of CMS membranes. a) SEM image of a self-supported hollow fiber CMS membrane [4]; b) SEM image of a support carbon membrane [62]; c) High-resolution TEM image of a CMS membrane [69]; d, e, and f) Raman spectrum, C1s XPS spectrum, and EELS of carbon membranes reported in ref. [73,58], and [62], respectively.

to deactivate the membrane surface but extend the micropores further. The optimized CHFMs presents 50,000 times higher in terms of CO₂ permeance and 41 times higher of CO₂/CH₄ selectivity compared to the original carbon membranes by the employment of a proper post-treatment, which is considered as a promising way to enhance carbon membrane separation performance. However, the production cost increases due to the extra treatments included.

2.3. Structural characterization of carbon membranes

As mentioned previously, the microstructure of CMS membranes is a typical bimodal pore model, which consists of micropores (~7–20 Å) and ultramicropores (< 7 Å). Different techniques have been employed to characterize the structures and properties of carbon membranes. Membrane morphology is widely characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Moreover, different hybridized carbons (sp² and sp³) existed in the carbon matrix can be revealed by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electron energy loss spectroscopy (EELS).

Fig. 3a–c show the SEM and TEM images of CMS membranes prepared from different precursors, which are usually used for determining the thickness of the selective layer of a CMS membrane. For example, Fig. 3a shows a typical cross-sectional SEM image of CHFMs with a symmetrical morphology where the selective layer for gas separation is the whole wall of the hollow fiber. For a supported carbon membrane, the CMS layer is commonly fabricated on a porous inorganic material (e.g., ceramic or alumina support), as shown in Fig. 3b. The fine microstructure of carbon membranes can be determined using high-resolution TEM [69–71], as shown in Fig. 3c, where a typical turbostratic

carbon is presented in CMS membranes. If electron microscopy equipped with energy-dispersive X-ray spectroscopy (EDX), then the elemental composition of CMS membranes can be obtained. This could provide interfacial adhesion information between CMS membrane and support when applied to a supported CMS membrane. For example, Tseng et al. [72] used the SEM-EDX line scanning method to detect mechanical interlocking between the CMS layer and the TiO₂/Al₂O₃ composite support. The superimposed carbon signal that existed in the composite support indicated that carbon has penetrated the support, which can be used as the index of the depth of mechanical interlocking [72].

Raman spectroscopy can provide the ordered or disordered information within CMS membrane structures. In general, as shown in Fig. 3d, a G band (located at ~1600 cm⁻¹), and a D band (located at ~1380 cm⁻¹) can be observed for CMS membranes. The spectrum can be further deconvoluted into five bands: G, D1, D2, D3, and D4. The G band is assigned to the characteristic peak of the ideal graphitic vibration mode (E_{2g}-symmetry). The D1 band is the disordered graphite peak (graphene layer edges, A_{1g}-symmetry), while the D2 band corresponds to graphitic lattice vibrations mode with E_{2g}-symmetry but involving isolated graphene layers [25]. When the D3 and D4 bands exist, the carbonaceous materials normally are highly disordered [73]. Besides, hybridized carbon in the CMS membranes can be distinguished by the intensity ratio of D1 to D2. It was suggested that the sp³ hybridization carbon defect occurs when the ratio is ~13, while vacancy like-defects dominated when ratio closes to 7 [74].

XPS can provide the surface elemental composition and chemical state of the elements for carbon membranes. By deconvoluting the C1s XPS spectrum, it can provide the information of the chemical state of different carbons, like sp²-hybridized carbon, sp³-hybridized carbon,

and C-N, C-O, and C = O bonds. The calculated ratio of sp^2/sp^3 can then be used as an indicator of the graphitization degree of the carbon [75]. Fig. 3e shows a deconvoluted C1s XPS spectrum of CMS membrane prepared from a PIM-1 precursor where sp^2 -hybridized are mainly observed in the prepared membrane [58]. The sp^2 and sp^3 carbons can be discerned by EELS as is reported by Richter et al. [62]. For carbon materials, the EELS of K-edge represents the electron transition from 1s electronic core state to antibonding π^* states (π^* band) or to the antibonding σ^* states (σ^* band) [59]. Specifically, the hybrid orbitals of sp^3 carbon do not possess π states, indicating that only one major feature edge at about 293 eV (σ^* band) will be observed, whereas the EELS spectrum of sp^2 hybrid carbon exhibits two major features located at about 285 eV (π^* band) and 295 eV (σ^* band). Fig. 3f shows an EELS spectra of different carbon materials reported by Richter et al. [62].

It is important to obtain the pore size distribution of CMS membranes as it directly determines the separation performances of CMS membranes. This is because the gas transport through CMS membranes relies on the combination of the selective surface flow mechanism happening in micropores (7–20 Å) and the molecular sieving mechanism happening in ultramicropores (< 7 Å) [12,29,76,77]. The micropores usually provide sorption sites for gas molecules, which results in a significant sorption selectivity for gas separations. Thus, the more condensable gas molecules, like CO_2 , having a higher sorption capacity, which presents enhanced gas permeability and also higher selectivity over less condensable gases. The ultramicropores, on the other hand, provide precise discrimination between similarly sized gas molecules (such as C_2H_4/C_2H_6), leading to an effective diffusion selectivity. As a result, the unique bimodal distribution of pores, combining micropores and ultramicropores, offers CMS membranes to achieve both high gas permeability and selectivity.

N_2 and CO_2 physisorption, and CO_2 high-pressure sorption are the common methods for determining the pore size distribution of CMS membranes. N_2 physisorption at 77 K can provide a pore size distribution of micropores, as reported in many works [42,58,69,70]. The limitation to using N_2 physisorption is that N_2 molecules (3.64 Å) are difficult to diffuse into the ultramicropores. For example, when a CMS membrane is prepared at a carbonization temperature of above 1000 °C, pore size distribution is not detectable by N_2 physisorption [42]. To overcome this problem, the smaller molecule of CO_2 (3.3 Å) used as probe molecules conducted at 273 K is normally employed to analyze the ultramicropores and micropores. The bimodal pore size distribution was observed from CO_2 physisorption as reported [4,26,78]. The structure properties, such as micropore volume and average micropore width, can be also obtained by high-pressure CO_2 adsorption at 298 K [4,18,20], which is based on the Dubinin-Radushkevitch (DR) equation [79] and the Stoekli equation [80].

2.4. Flat-sheet and tubular carbon membranes

Unsupported flat-sheet carbon membranes are widely prepared to investigate material properties such as sorption–diffusion properties and membrane morphology. Table 3 summaries the representative unsupported flat-sheet carbon membranes made from the respective precursors at specific carbonization conditions (CC) as well as the reported separation performances obtained at given testing conditions (TC). Ning and Koros [3] investigated the sorption and diffusion coefficients of dense CMS films and found that membrane selectivity can be enhanced by increasing carbonization temperature while gas permeability reduces concomitantly, which is similar with the results reported in other literature [19,26]. High CO_2 permeability of > 4000 barrer was obtained from a carbon-rich intrinsically microporous polyimide precursor (SBFDA-DMN) by making an ultra-selective CMS dense film [42]. Moreover, dense CMS films with the surpass of the O_2/N_2 and H_2/N_2 Robeson upper bounds [81] were prepared from the regenerated cellulose precursors [20], and the prepared CMS membranes exhibited good stability in the presence of 75 – 77% relative humidity at 25 °C.

Although unsupported flat-sheet CMS membranes exhibit promising performance for gas separations, the brittleness and fragility have limited their wide potential applications where modules with large membrane surface areas are required, especially compared with supported carbon membranes or CHFMs.

Supported CMS membranes manufactured on porous support (e.g. ceramic, stainless steel) exhibit strong mechanical strength. Different technologies such as dip coating [73,88], spin coating [89–92], spray coating [93] and chemical vapor deposition (CVD) [94] have been employed to coat polymeric precursor on top of support and followed by carbonization. These methods can reduce the thickness of the carbon membrane selective layer to provide higher gas permeance compared to unsupported dense carbon membranes. The representative supported carbon membranes are listed in Table 4.

It should be noted that the properties of porous supports can directly affect the structure of supported CMS membranes and consequently affect its separation performance. Commercial ceramic supports are usually porous (e.g., pore size ~ 200 nm), which will lead to a lower quality of the derived CMS membranes due to the occurrence of interfacial defects during the formation of selective layer [77]. Thus, the multilayer substrates are widely used for the fabrication of supported CMS membranes, and carbon selective layer is usually combined to a coated porous intermediate layer (normally 1–10 nm pore size) on top of macroporous support. To avoid the existence of large pores inside α - Al_2O_3 tubular support that might cause pinholes in CMS membranes, a thin γ - Al_2O_3 layer with a moderate pore size of ~ 4 nm was deposited [73]. The smaller pores of γ - Al_2O_3 layer were formed by repeating the dip-coating of a boehmite (γ - $AlOOH$) sol and followed by a calcination procedure [73,102,103]. The separation performances of supported CMS membranes can be improved by tuning the properties of the intermediate layer. Tseng et al. [72] reported an enhanced H_2/CO_2 separation performance by modifying Al_2O_3 support with the TiO_2 intermediate layer. The intermediate layer could provide a networking interlocking pattern with CMS membranes, which is beneficial to both gas permeability and selectivity.

Moreover, developing ultrathin supported CMS membranes (i.e., < 500 nm) is a promising way of making high-performance CMS membranes. The state-of-the-art ultrathin supported CMS membranes are summarized in Table 4. The ultrathin (~200 nm) and defect-free CMS membranes were prepared by carbonization of polyimide precursors made by dip-coating of an inner layer of porous supports [73], and the prepared CMS membranes presented a high H_2 permeance of up to 3253 GPU and ideal H_2/CO_2 selectivity of 24 at 200 °C. Moreover, Huang et al. [66] also prepared CMS films with a thickness of 100 nm by employing a novel fabrication route (named transfer technique) to reach attractive H_2 permeance of 3060 GPU. Although the development of supported CMS membranes with ultrathin selective layer shows a very promising approach to enhance gas permeance, fabrication of defect-free ultrathin CMS membranes is still challenging due to the fragile thin layer. It should also be noted that supported thin CMS membranes usually present to a relatively lower selectivity which significantly influences separation efficiency. Thus, modification of porous support (e.g., enhancing chemical bonding between the support and CMS layer) and introducing post-treatment is usually applied to improve membrane selectivity. Nevertheless, the remaining challenge of high production cost for supported carbon membranes limits their large-scale applications.

2.5. Carbon hollow fiber membranes

Membranes made in hollow fiber configuration have the advantage of higher packing density (up to 30,000 m^2/m^3) compared to spiral wound, plate-and-frame, and tubular modules [104], which is the industrially preferred configuration. Moreover, CHFMs can also withstand high transmembrane pressures [58], and thus show promising applications in the high-pressure separation scenarios such as CO_2

Table 3
Representative unsupported flat-sheet carbon membranes for gas separation.

Precursors	CC(Temp. (°C)/Purge gas)	TC(Temp. (°C)/feed pressure (bar))	Separation performance				Gas pair selectivity				ref
			Permeability (barrer)				Selectivity				
			H ₂ (He)	CO ₂	O ₂	CH ₄	CO ₂ /CH ₄	O ₂ /N ₂	Others		
Cellulose	650/ vacuum	30/2	1300	480	130	4.4	109	8.7	H ₂ /CO ₂ = 2.7	[16]	
Cellulose	550/N ₂	25/1	206	13.4	5.16	–	–	32.3	CO ₂ /N ₂ = 83.8	[20]	
Cellophane paper	550/N ₂	29.5/2	168.1	17.0	4.87	0.17	100	11.3	H ₂ /CO ₂ = 9.9	[82]	
Matrimid®	550/Ar (1 ppm O ₂)	30/3.4	(6.05)	1049	301	17	80.7	4.8	CO ₂ /He = 1.7	[83]	
Polyimide	550/ N ₂	35/-	–	428.2	377.6	23.9	17.9	4.2	–	[23]	
6FDA/BPDA-DAM	550/Ar (1 ppm O ₂)	30/3.4	(5.30)	7170	1530	247	29	7.5	CO ₂ /He = 13.5	[83]	
6FDA/DETDA:DABA (3:2)	550/Ar	30/2	–	21,740	4293	723	30.1	4.9	–	[34]	
6FDA/1,5-ND:ODA (1:1)	550/Ar	30/2	–	9791	2038	217	45.1	6.0	–	[34]	
TB-PI	650/N ₂	35/1	6552	4200	1092	68	62	9.3	H ₂ /CH ₄ = 96	[84]	
SBFDA-DMN	1000/N ₂	35/2	(96)	30	7.5	0.02	1475	11	He/CO ₂ = 3.3	[42]	
PIM-6FDA-OH	800/N ₂	35/10	–	512	–	–	88	–	–	[85]	
PIM-6FDA-OH	800/N ₂	35/2	2177	556	149	6	93	8.9	H ₂ /CO ₂ = 3.9	[86]	
PBI	900/N ₂	150/11	54	–	–	0.68	–	–	H ₂ /CO ₂ = 80	[87]	

Table 4
Representative (ultrathin) supported CMS membranes for gas separation.

Support/Geometry	Precursor	CMS membrane thickness (μm)	CC(Temp. (°C)/Purge gas)	TC(Temp. (°C)/feed pressure (bar))	Separation performance			Selectivity			ref.
					Permeance(GPU) ^a			Selectivity			
					H ₂ (He)	CO ₂	O ₂	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄	
Carbon/Disk	Matrimid	1–2	700/vacuum	25/1	(8.0)	10.8	2.4	–	–	23	[95]
Carbon/Disk	PMDA–ODA polyimide	2	700/Ar	RT/1	161	26	22	76.3	10.4	–	[96]
Al ₂ O ₃ / Disk	PI/PPO	~ 5.3	600/vacuum	25/1	273.3	248.7	–	171.9	–	156.9	[97]
Al ₂ O ₃ / Disk	PEI/PPO	~ 1.6	600/vacuum	25/1	507.2	320.3	–	136.2	–	86.1	[97]
Al ₂ O ₃ / Disk	PPO/PVP	~ 3.2	700/vacuum	25/2	350.3	–	–	163	–	–	[46]
Al ₂ O ₃ / Disk	PEI	2.1	600/vacuum	25/1	265	80.3	20.4	197	8.2	59.7	[72]
TiO ₂ - Al ₂ O ₃ / Disk	PEI	~ 3	600/vacuum	25/1	355	98.7	27.9	246	9	68.2	[72]
α-Al ₂ O ₃ /Tube	Novolac resin	3	550/N ₂	RT/1	414 (171)	157-	25.1	117	7	–	[98]
Al ₂ O ₃ /Tube	Resorcinol-formaldehyde resin	3	550/N ₂	25/2	149 (132)	6.7	3.1	> 586	> 11.5	–	[99]
Pencial, α-Al ₂ O ₃ /Tube	PFA	8.8	550/Ar	RT/4	103	29.6	22.2	58	13	–	[100]
α, β-Al ₂ O ₃ /Tube	Polyimide	0.2	700/vacuum	200/2	3250	135	–	114	–	8.1	[73]
AAO/Disk	BFDA – DMN	1	700/N ₂	21/-	152.3	210.7	35.8	25.8	6.1	47.3	[91]
Carbon nanotube (CNT), AAO/Disk	PFA	0.322	500/Ar	25/1	56.0	9.4	5.3	141	13.4	44.2	[90]
Cu foil, Macroporous W	Matrimid	0.1	500/(H ₂ /Ar)	25/1.5	761	497	–	H ₂ / CH ₄ = 24.1	–	14.0	[66]
PVA, AAO/Disk	Matrimid	0.2	500/(H ₂ /Ar)	130/1.5	453	69	–	H ₂ / CH ₄ = 106	–	17.4	[66]
Al ₂ O ₃ / Disk	SBF-DMN	0.082	600/N ₂	21/1.5	195 (107)	320	59.1	156	7.4	56.5	[101]

^a : the performance reported in permeabilities (barrer) are converted to permeance (GPU) based on the reported thickness.

Table 5
Representative symmetric CHFMs for gas separation.

Precursors	CC(Temp. (°C)/Purge gas)	TC(Temp. (°C)/feed pressure (bar))	Separation performance				Selectivity			ref
			Permeability(barrer)				Selectivity			
			H ₂	CO ₂	O ₂	CH ₄	CO ₂ /CH ₄	O ₂ /N ₂	others	
Cellulose	600/CO ₂	25/2	–	239	68	1.3	186	10.9	–	[4]
Cellulose acetate	550/CO ₂	30/2	–	346	87	–	–	7.9	CO ₂ /N ₂ = 31.5	[36]
Cellulose acetate	550/CO ₂	30/2	–	410	63	4.0	102	6.9	CO ₂ /N ₂ = 44.6	[37]
Cellulose acetate	550/CO ₂	30/2	637	268	71.5	4.1	65.5	7.4	H ₂ /CH ₄ = 156	[18]
Matrimid®	900/Ar	35/6.9	266	24.1	0.14	0.0066	3650	21	H ₂ /CO ₂ = 11	[26]
Matrimid®	750/Ar	35/6.9	1671	370	105	2.43	152	10	H ₂ /CO ₂ = 4.5	[26]
PPO	650/vacuum	25/1	1900	544	126	5.36	101	9.8	H ₂ /CH ₄ = 350	[45]
TMSPPPO	650/vacuum	25/1	1314	216	56	1.82	118	11.6	H ₂ /CH ₄ = 719	[45]
SPPO	700/N ₂	90/1	2260	900	277	22	40	5.6	H ₂ /CH ₄ = 101	[107]

removal from natural gas [4,5,29,67], and hydrogen purification [105,106]. It should be noted that CHFMs can be made in symmetric and asymmetric morphologies. Symmetric CHFMs with a thick dense layer usually provide a remarkable gas selectivity compared to CHFMs made in asymmetric morphology with a thin selective layer. Table 5 summarizes the latest symmetric CHFMs reported in the literature. Among them, CHFMs with ultra-high permselectivities derived from Matrimid polyimide precursors were reported by Zhang et al. [26]. The

polymer precursors and prepared CHFMs displayed symmetric structure with a well-defined separation layer. The membrane carbonized at 900 °C presented the highest ideal selectivity for different gas pairs reported so far (e.g., α[CO₂/CH₄] = 3650, α[H₂/CH₄] = 40350). The enhanced CO₂/CH₄ selectivity at higher carbonization temperatures was caused by the simultaneously enhanced diffusion and sorption selectivities [26]. However, most of the reported symmetric carbon membranes presented relatively low gas permeability/permeance as

Table 6
Representative asymmetric CHFMs for gas separation.

Precursor	Thickness of skin layer (μm)	CC(Temp. ($^{\circ}\text{C}$)/Purge gas)	TC(Temp. ($^{\circ}\text{C}$)/feed pressure (bar))	Separation performance			ref
				Permeance(GPU)	CO ₂	Selectivity CO ₂ /CH ₄ others	
Matrimid*	4–5	550/Ar	35/6.9	216		~30	[108]
Matrimid*	–	675/Ar	35/6.9	–	C ₂ H ₄ : 1.1	–	C ₂ H ₄ /C ₂ H ₆ =11.1 [109]
Matrimid*	3–4	550/Ar	35/3.4	164	–	55	– [110]
6FDA: BPDA-DAM (1:1)	3–4	550/Ar	35/6.9	394	–	~26	– [108]
6FDA: BPDA-DAM (1:1)	~10	675/Ar	-/3.4	–	H ₂ : 96.1	–	H ₂ /C ₂ H ₄ = 249 [25]
6FDA/BPDA (1:1)-DAM	3	550/Ar	35/124	~100	–	~60	– [29]
BTDA-TDI/MDI	–	900/Ar	60/-	0.42	O ₂ : 0.119	49.4	O ₂ /N ₂ = 11.9 [105]
					H ₂ : 6		H ₂ /CO ₂ = 14.3
BTDA-TDI/MDI	2.4	800/N ₂	25/2.1	1108	C ₂ H ₄ : 210	21	C ₂ H ₄ /C ₂ H ₆ =8.7 [111]
6FDA-DAM: DABA (3:2)	2.7	575/Ar	35/1	956	–	50.2	– [112]
6FDA-DETDA: DABE	0.5	550/Ar	35/2	1000	–	25	– [24]
6FDA: BPDA-DAM	0.3	675/Ar	35/3.4	310	–	58.8	– [5]
6FDA/BPDA-DAM	0.5	550/Ar	35/6.9	2546	–	24	– [113]
PIM-1	5	575/Ar	35/2	13.8	O ₂ : 2.9	96.8	O ₂ /N ₂ = 9.8 C ₂ H ₄ /C ₂ H ₆ = 7 [114]
PEI/PVP	–	650/N ₂	RT/7	1.66	N ₂ : 0.04	55.3	CO ₂ /N ₂ = 41.5 [115]

shown in Table 5. Thus, recent research activities are focusing on the development of asymmetric CHFMs to improve gas permeance while maintaining a relatively good selectivity. Moreover, polyimide derived carbon membranes may provide a better potential for high-pressure natural gas sweetening with relatively high CO₂ permeance and comparable CO₂/CH₄ selectivity compared to cellulose-based carbon membranes.

Table 6 summaries the representative asymmetric CHFMs developed from different precursors and their performances for gas separations. It can be seen that CO₂/CH₄ separation performance varies from 20 to 60 for the carbon membranes prepared from similar polyimide-based polymers, which is mainly due to the different precursor structure, carbonization condition as well as the testing condition reported in the literature. It is difficult to directly predict carbon membrane performance from polymer structure based on quantitative structure–property relationship (QSPR) modeling. However, increasing carbonization temperature can in general enhance both sorption and diffusion selectivities because of the narrowed pathways. Moreover, the precursor with a relatively thinner selective layer will usually lead to the derived carbon membranes with higher CO₂ permeance. Therefore, the methodology based on the DPCOI platform [37] may provide a guideline for systematic optimization of carbon membrane development and can be applied to different polymer precursors. Moreover, the asymmetric structures of precursors can be obtained by adjusting spinning conditions, but an extra pre-treatment step (often refers to cross-linking) is required to maintain asymmetric structure during carbonization. Koh et al. [27] reported the preparation of asymmetric CHFMs from PVDF hollow fibers. To avoid pore collapse inside the membrane caused by the loss of storage modulus of PVDF precursor, a cross-linking method with a base treatment (NaOH + MeOH) and following a nucleophilic attack with *para*-xylylenediamine (see Fig. 4a) was used to form covalent bonds between PVDF chains. Compared to the neat PVDF hollow fibers, the cross-linked PVDF precursors maintained a high storage modulus at above 300 $^{\circ}\text{C}$, and the asymmetric porous structure was well-kept after carbonization.

A V-treatment method was used to restrict morphology shrinking of asymmetric hollow fiber membranes during carbonization [5,22,108,113], which can avoid a chemical reaction between polymer precursors and agents as the cross-linking reaction happens between organic-alkoxy silane (vinyltrimethoxysilane, VTMS) and moisture at room temperature. As shown in Fig. 4b, the cross-linked layer provides the reinforced sheaths on the “struts” and thus restricting substructure collapse during carbonization. Benefiting from the reduced skin layer, the gas permeance of asymmetric CHFMs was improved 4 times comparing to non-treated membranes while CO₂/CH₄ selectivity only slightly decreased [22]. However, the associated crosslinking steps may

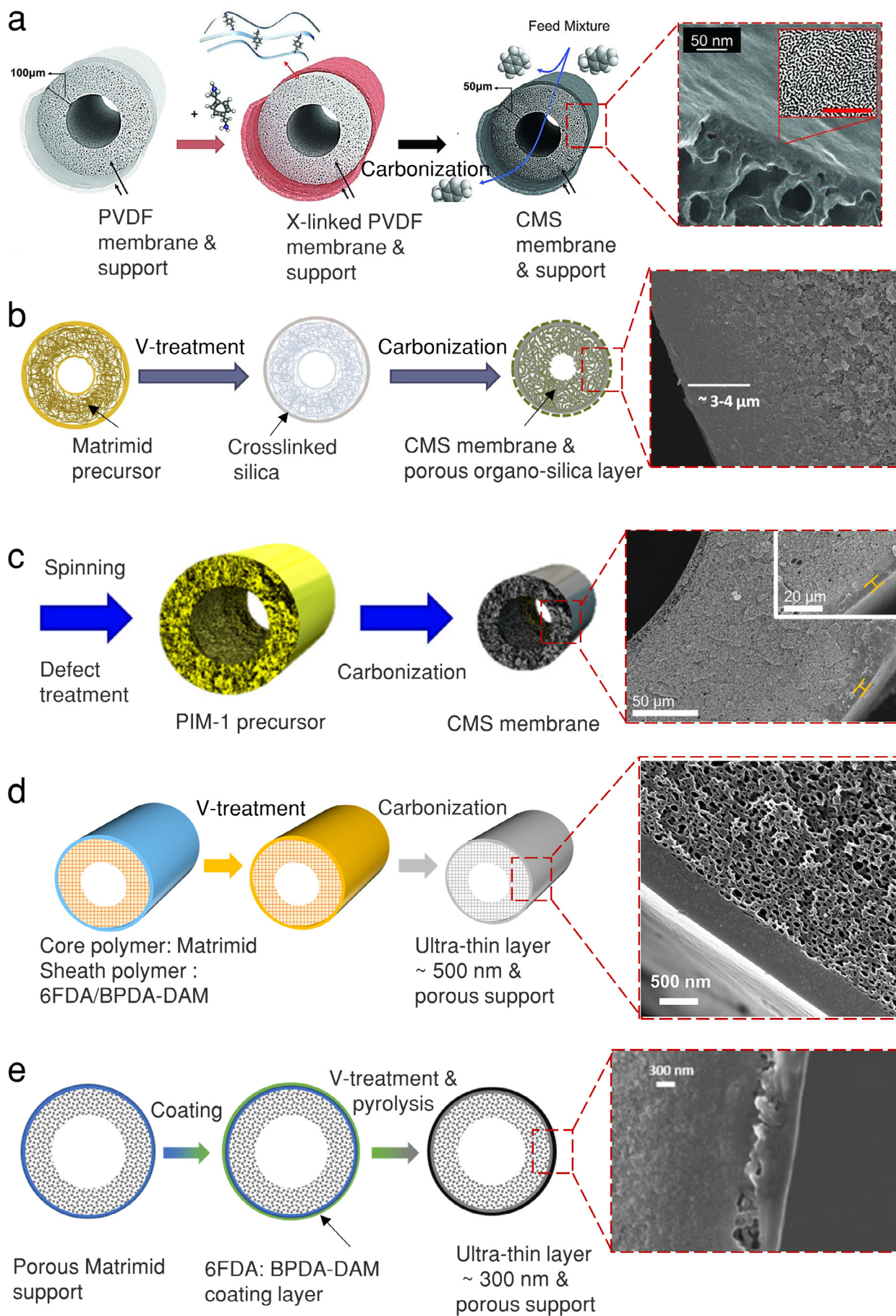
account for ~40% cost increment of the overall membrane fabrication process [114]. Thus, the development of CHFMs without extra treatments can reduce the production cost towards a more sustainable process for carbon membrane fabrication. Recently, asymmetric CHFMs were directly prepared from PIM-1 precursors without cross-linking or other pretreatments (see Fig. 4c) by Jue et al. [114]. The collocation of polymer glass transition and decomposition temperature can maintain asymmetric structure without significant changes in storage modulus during carbonization [114].

It should be noted that most of CHFMs reported so far still present a relatively thick selective layer (e.g., > 3 μm), which restricts to reach very high gas permeance. Further reducing carbon membrane thickness can provide significantly enhanced gas permeance, and thus reduce the required membrane area for a specific application. Zhang et al. reported a dual-layer precursor spinning process by co-extruding a sheath polymer dope and a core polymer dope from a multichannel spinneret [113], as illustrated in Fig. 4d. The dual-layer structure of precursor was well maintained after V-treatment and carbonization to obtain CHFMs with ultra-thin skin layers (~500 nm). The dual-layer precursors comprise different sheath and core layer polymers can also reduce the cost of polymer materials. Moreover, a composite precursor made by spin coating of an expensive dense skin layer on top of cheap porous support can reduce the material cost of a 25-fold compared to monolithic precursors [5], and the asymmetric carbon membranes with 300 nm thin layer prepared from the composite precursors (see Fig. 4e) provide excellent performance.

Although different methods have been reported to make asymmetric CHFMs, most of them need complex pre-treatment (e.g., cross-linking) to prevent pore collapse, which increases the carbon membrane production cost. Besides, fabrication of ultra-thin selective layer CHFMs normally requires more complicated precursor preparation, such as co-spinning of sheath and core polymer dopes, a combination of spinning and dip-coating. This may limit the production of carbon membranes in large-scale applications. Thus, making asymmetric CHFMs without costly pre-treatment should be pursued towards the green advances of carbon membrane development. Moreover, carbon membranes preparation in a continuous process needs to be addressed to further reduce production costs.

2.6. Carbon membrane upscaling

When membrane materials are going to be produced at a large scale, using renewable materials (e.g., cellulose) as precursors have an important advantage to secure a steady and reliable supply chain of raw materials. The general challenge for batch-wise production is to obtain equal conditions for each precursor inside a chamber or container.



(caption on next page)

Fig. 4. Formation of asymmetrical CHFMs. a) base-treated crosslinking method to fabricate asymmetric CHFMs [27]; b) schematic representation of V-treatment process in the overall asymmetric polyimide-based CHFMs formation [22]; c) asymmetric CHFMs were formed directly without cross-linking or other pretreatments [114]; d) Formation of ultra-thin CHFMs by dual-layer spinning [116], and; e) dip-coating to create multi-layer asymmetric CHFMs [5].

Karvan et al. [117] reported that polyimide-based hollow fibers were in contact with each other during carbonization, and fused together at higher temperatures. While cellulose hollow fibers are less prone to fusing, and a large quantity of cellulose precursors can be carbonized in the same batch. Haider et al. [118] reported that 1600–4000 regenerated cellulose hollow fibers were carbonized simultaneously by using 2 m-long perforated plates with square openings. However, they also reported that it is crucial to drain the tars and vapors by setting an angle (e.g., 6°) between support and furnace during the carbonization of a large bundle of fibers. It should be noted that continuous fabrication may be pursued for the commercialization of carbon membranes in the future.

Another challenge on carbon membranes up-scaling is related to module design and construction, typically CHFMs mounting, potting and sealing for high temperature/pressure applications. A suitable potting material (e.g., epoxy resin) that easily penetrates a bundle of fibers at a high module packing density should be identified. Module upscaling of cellulose-based carbon membrane to m² surface area with thousands of CHFMs bundling together was reported by Haider et al. [33] to move towards a higher technology readiness level (TRL). However, there are still challenges related to further development and upscaling of CA-based carbon membranes due to 1) the high production cost with the extra cellulose regeneration step involved; 2) the difficulty of keeping fibers straight during fiber drying after CA deacetylation. Recently, development of CHFMs directly from cellulose precursors may address some of these challenges [4]. For supported carbon membranes, Parsley et al. [119] demonstrated a membrane module consisting of tubular carbon membranes with a surface area of 0.76 m² and a packing density of 222 m²/m³. A bundle of supports was fabricated beforehand the application of carbon layers via dip-coating and carbonization. It is expected that large-scale production of supported carbon membranes will be challenging, and production cost is still quite high, which may limit the applications only in small-volume gas separation processes.

3. Carbon membrane applications for CO₂ removal

Membrane technology for gas separation is considered a green process with respect to decreasing production costs, footprint, energy consumption, and improving process flexibility [120]. Carbon membranes with high separation performance under high-pressure and/or high-temperature conditions provide a significant green advance when applied to the integration of CO₂ capture with low-carbon or renewable energies (e.g., H₂ purification from syngas, biogas upgrading, and natural gas sweetening). Permeability and selectivity (separation factor) are commonly used to describe the membrane separation performances, which influences the productivity and separation efficiency of a membrane separation process. Generally, gas permeability (P_i) is described as the product of diffusion coefficient (D_i) and solubility coefficient (S_i): $P_i = D_i \times S_i$. Accordingly, the gas pair selectivity is expressed by $\alpha_{i/j} = (D_i/D_j)(S_i/S_j)$. The diffusion coefficient is a kinetic factor that characterizes the ability of gas molecules to penetrate through the membrane. It depends on the size and shape of the penetrated gas molecules and the critical ultramicropores dimensions [34]. For highly adsorbing gases like CO₂, a thermodynamically corrected concentration-independent diffusion coefficient is used, refers to Maxwell-Stefan diffusivity. On the other hand, the solubility coefficient is a thermodynamic factor that determining the amount of absorbed gas by a membrane at a given temperature and pressure. Thus, for a CMS membrane-based separation process, gas permeability is significantly dependent on operating temperature. The kinetic diffusion coefficient is

enhanced by rising operating temperature following the Arrhenius relationship, while the thermodynamic sorption coefficient is inhibited concomitantly. It should be noted that module design and process operating parameters will also significantly influence the process performance of carbon membrane systems besides the material property itself (i.e., ideal selectivity and gas permeability) which is usually characterized by single gas permeation testing.

3.1. Carbon membranes for hydrogen purification from syngas

Hydrogen production from natural gas through combined steam methane reforming and water–gas shift (WGS) process is considered as one of the most promising technologies for the implementation of a hydrogen economy for a low-carbon energy future, the reduction of greenhouse gas emissions and the increased demand of sustainable energy. However, the produced hydrogen stream usually contains a significant amount of CO₂ that needs to be removed to obtain high purity hydrogen (for fuels or feedstocks in the petrochemical industry). Purification of hydrogen from this gas stream requires novel separation technologies to improve energy efficiency as it consumes ca. 60% of the total energy required in the whole hydrogen production process. The state-of-the-art pre-combustion CO₂ capture technologies of pressure swing adsorption (PSA) and cryogenic distillation [121–123] are energy-intensive, while membrane gas separation technology exhibits a great potential for this application. Different types of membranes such as palladium, polymeric, mixed matrix and carbon membranes have been investigated for H₂/CO₂ separation. Among them, great effort has been devoted to developing palladium-based membranes for H₂ purification [123]. However, the cost of palladium membranes is still high, which cannot yet compete with PSA. The polymeric and mixed matrix membranes have the challenges to achieve a high H₂ purity (e.g., > 99%) due to the low H₂/CO₂ selectivity (usually < 10) [124–128].

Carbon membranes have great advantages of high mechanical and chemical stabilities, and also high separation performance that can exceed the Robeson upper bound 2008 for H₂/CO₂ separation [81], which can reach the industrially attractive region for this application [14]. The technology feasibility of carbon membranes (with H₂/CO₂ selectivity of 40) for purification of hydrogen from a gas stream containing 35 mol.% CO₂/65 mol.% H₂ has been documented by He [129], and the cost was theoretically evaluated to \$1/kg H₂ produced at a feed pressure of 20 bar. Developing higher performance carbon membranes can further bring down the purification cost. Recently, CMS membranes for H₂/CO₂ separation at high temperatures were reported in the literature [62,73,106], and the membrane performances were found to be enhanced compared to the state-of-the-art organic and inorganic membranes for H₂/CO₂ separation (see Table 7). The CMS membranes exhibit present competitive performance with relatively good H₂/CO₂ selectivity and H₂ permeance compared to other high-performance inorganic membranes. In general, the higher operating temperatures will be favorable to enhance H₂/CO₂ separation performance especially H₂ permeance, which is typically suitable for hydrogen purification in the steam methane reforming process.

Moreover, one membrane module consisting of tubular carbon membranes with a surface area of 0.76 m² and a packing density of 222 m² m⁻³ was reported by Parsley et al. [119], which was field-tested for hydrogen recovering from raw coal-delivered and biomass-delivered syngas with stable performance over 500 h. The integration of carbon membranes to water–gas shifting (WGS) reaction (a membrane reactor) was reported to improve CO conversion [130]. Those carbon membranes showed high stability against H₂S, NH₃ and other

Table 7

Comparison of carbon membranes with polymeric and other inorganic membranes for H₂/CO₂ separation. The membrane thickness was assumed to be 3 μm when converting the permeability (barrer) to permeance (GPU).

Membrane materials	Performance		Test conditions			ref
	H ₂ permeance (GPU)	α_{H_2/CO_2}	Type of analysis	Temperature(°C)	Feed pressure (bar)	
PBI	0.53	132.8	Single gas	150	14	[131]
POF	24.2	39.5	Mixed gas	150	2	[132]
MOF JUC-150	452.4	30.2	Mixed gas	200	1	[133]
Al ₂ O ₃ /SAPO-34	214.7	23.0	Mixed gas	200	3.5	[134]
ZIF-8/ZIF-9@P84	250	9.6	Mixed gas	150	–	[9]
ZIF-90	739.2	7.3	Single gas	200	1	[10]
GO	30	30	Single gas	140	1	[8]
MoS ₂	240	8.5	Mixed gas	160	1	[135]
CMS	118.4	14.5	Single gas	150	–	[106]
CMS	3250	24	Single gas	200	2	[73]
CMS	1827.5	8	Single gas	150	1	[62]

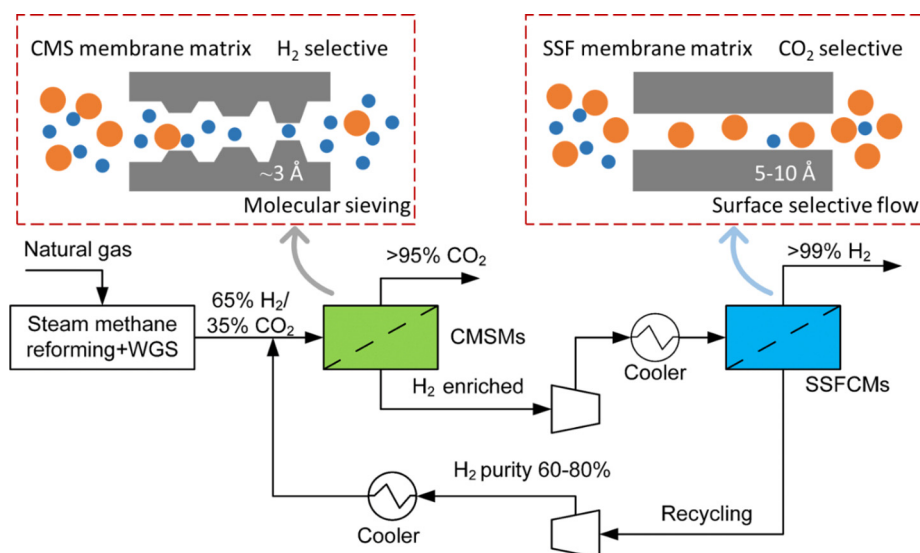


Fig. 5. The concept of a two-stage carbon membrane system for integrated CO₂ removal and H₂ purification. CMSMs (H₂-selective membranes) used in the first stage will capture CO₂, and the SSFCMs (CO₂-selective membranes) in the second stage can produce high purity H₂ (> 99 mol.%) at a high H₂ recovery (> 90%) with permeate recycling back to the first stage.

contaminants in syngas compared to palladium membranes [119,130]. Moreover, by combining both H₂-selective and CO₂ selective carbon membranes, a two-stage membrane system (the first stage H₂-selective CMSMs and the second stage selective surface flow carbon membranes (SSFCMs)) can be designed for integration of CO₂ capture and H₂ purification as shown in Fig. 5. This process is expected to achieve at least 20% of cost reduction compared to the state-of-the-art technologies for hydrogen purification in a steam methane reforming plant. The produced high purity H₂ (> 99%) from the 2nd-stage retentate is particularly interested as H₂ resource for downstream petrochemical industries and/or catalytic conversion to chemicals or fuels (not for fuel cells where ultrapure H₂ (99.999 mol.%) is usually required). However, experimental validation at a pilot-scale should be conducted in the future work to prove the technology advance and potentially expand hydrogen economy.

3.2. Carbon membranes for CO₂ capture from flue gas

In addition to H₂ purification and pre-combustion CO₂ capture as discussed in section 3.1, post-combustion CO₂ capture, which can be retrofitted to existing power plants, presents the closest marketable technology for contributing to the reduction of CO₂ emissions [136,137]. The major challenges for CO₂ capture from flue gas are the low feed pressure (~1 bar), the low CO₂ concentration (usually < 20%), and the requirement of large gas volume to be processed [136]. Besides, the discrimination of gas molecules with similar sizes like CO₂, O₂, and N₂, is another obstacle for archiving a high-efficient separation.

The state-of-the-art technology for post-combustion carbon capture is amine-based absorption that occupies > 90% of the market [137]. However, the high energy demands for absorbent regeneration directs to seek for alternative technologies. Membranes-based separation processes have shown promising advantages beyond amine absorption due to their low energy consumption, small footprint, and easy scale-up [70,138,139]. Various membrane materials have been developed for the application in post-combustion carbon capture, such as fixed-site-carrier membranes [140,141], and mixed matrix membranes [142,143]. Some commercial membranes have been tested in power plants for the post-combustion CO₂ capture, such as PRISM™ from Air Products [144] and Polaris™ from MTR Inc. [145]. A detailed summary of the commercial membranes for CO₂ removal from flue gas and their main issues is recently reviewed by Kárászová et al. [138].

CMS membranes have been considered for post-combustion CO₂ capture due to their high separation performance of CO₂/N₂ that can surpass the Robeson upper limit. Recently, Yang et al. reported a fluorinated CMS membrane with high CO₂ permeability of 2140 barrer and CO₂/N₂ selectivity of 36 in pure gas test [70]. When tested in a mixture of 15 mol.% CO₂-85 mol. % N₂, the membranes showed a slightly increased CO₂ permeability of 3712 barrer and CO₂/N₂ selectivity of 27. Besides, a retained CO₂ permeability and slightly reduced CO₂/N₂ selectivity under high relative humidity (~90%) testing within a CO₂/N₂ 50/50 mol.% mixed gas indicated that the membrane can endure the situation of water vapor that normally presented in flue gas streams, which presents a great potential for CO₂ removal from flue gas [70]. However, the reported CMS membrane is such thick with a

symmetric structure of 75 μm selective layer that the low CO_2 permeance (e.g. ~ 50 GPU) was recorded.

Another major obstacle of CMS membranes used for CO_2 capture from flue gas is the performance deterioration caused by species sorption on the carbon matrix. CMS membranes prepared from deacetylated cellulose acetate have been systematically investigated for CO_2 capture from flue gas by He et al. [17,36,37]. A long-term aging test over ~ 7 months where the membrane module was exposed to the laboratory air without any protection showed the gas permeabilities of the fabricated CHFMs dropped by $\sim 55\%$ within the first 2 months, and afterward slightly reduced [17]. When a membrane module was exposed to a real flue gas containing 12.4% CO_2 /4.5% O_2 /70.1% N_2 /1.3% H_2O (also impurities of 89 mg Nm^{-3} SO_2 , and 246 mg m^{-3} NO_x) for 3 weeks, it was found that the permeance of the CMS membranes decreased about 40%, which was caused by pore blocking with physisorption and/or chemisorption of water vapor and oxygen [37].

Capturing CO_2 from flue gas using a hybrid process of membrane/cryogenic distillation under sub-ambient operating temperature (e.g. below -20°C) has documented a cost-effective process as reported by Air Liquide [146]. This strategy provides a highly-effective CMS membranes-based separation process for post-combustion carbon capture because reducing operating temperature can dramatically improve CO_2/N_2 selectivity. Recently, Joglekar et al. reported that a CHFMs presented 4.5 times higher CO_2/N_2 selectivity at -20°C than tested at 35°C (increasing from 29 to 109), whereas only $\sim 33\%$ loss in CO_2 permeance was observed (dropped from 160 to 108 GPU) [147]. The significant improved CO_2/N_2 selectivity can thus reduce the module productivity, and therefore may offset the increased membrane area due to the reduction on gas permeance and also the cooling loading.

Although good CO_2/N_2 selectivity has been reported, the application of CMS membranes for post-combustion carbon capture is however still challenging: (1) the CO_2 permeance is relatively lower compared to many polymeric materials, which requires larger membrane area to achieve a given CO_2 capture ratio; (2) most of CMS membranes are sensitive to water vapor that normally exists in flue gas stream; (3) the fragility of CMS membranes. To address this challenge, the development of ultra-thin supported CMS membranes with highly hydrophobic membranes may be considered. For example, cellulose-based CMS membranes [20] and fluorinated CMS membranes [70] have shown good stabilities under $> 85\%$ RH conditions.

3.3. Carbon membranes for biogas upgrading

Biogas is a renewable energy source that can be produced in a controlled manner by microbial digestion of biomass (agricultural waste, manure, municipal waste, sewage, food waste, etc.) in the absence of O_2 [148,149]. The major components are CH_4 , CO_2 , H_2O together with traces of H_2S and some other gases. The state-of-the-art technology for separation of CO_2 from biogas in European region is water scrubbing, pressure swing adsorption (PSA), chemical absorption (e.g. amines) [150–152]. Although gas separation membranes have only 4% of the market today [152], the advantages of green, energy-saving, space-saving, easy to scale-up stimulate its further development on new membrane materials and processes for CO_2 - CH_4 separation. The choice of suitable separation technology is mainly dependent on the specific condition at a plant, such as the availability of low-price thermal energy, electricity, and water, as well as the amount of gas to be handled. Fig. 6 shows the comparison of the key performance indicators (KPIs) such as power consumption, footprint, CH_4 purity, CH_4 loss, and process flexibility of different technologies for biogas upgrading with respect to green and sustainable solutions.

Membranes show good process flexibility and smaller footprint compared to other separation methods, but the main challenge of a polymeric membrane system for biogas upgrading is to simultaneously obtain a high CH_4 purity and a low CH_4 loss (also power consumption). It should be noted that a high CH_4 loss is negatively related to the

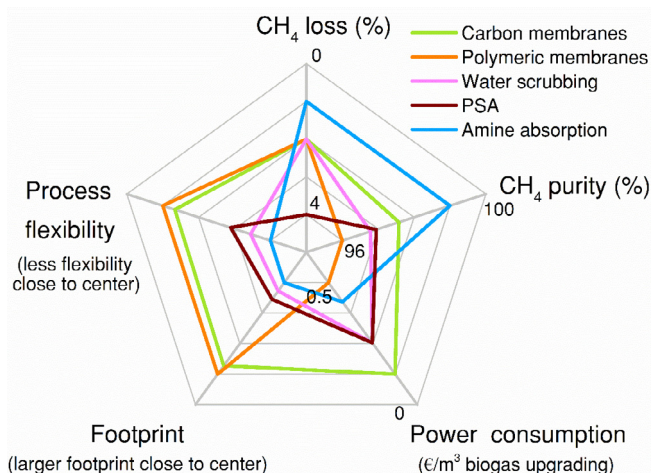


Fig. 6. Comparison of the KPIs of carbon membranes with other technologies for biogas upgrading. A larger area implies a better performance. Part of data are taken from references [153,154].

economy and greenhouse gas performance. By using a multi-stage membrane system can reach high purity methane, but energy consumption will then be higher. Thus, the development of highly CO_2/CH_4 selective membranes is crucial to expand the applications of membranes for biogas upgrading. The trade-off between permeability and selectivity of commercially polymeric membranes (e.g., SEPURAN®, Carbox®®, Prism®) directs to the development of alternative CMS membranes for biogas upgrading. Since CMS membrane separation is based on the molecular size difference, and pore structure can be tailored to achieve a high selectivity of specific gas pairs, it provides an overall technology advance (especially low power consumption as a high membrane selectivity can significantly reduce the operating cost to achieve specific separation requirement). However, the challenge up to now has been the sufficiently high CO_2 permeance to bring down capital cost and upscaling of modules.

In general, the composition and quality of biogas vary a lot, and are highly dependent on the source or substrate on which the bacteria are fed. Thus, the customizations/adaptations are usually required for each individual plant. On top of that, the intended use of upgraded biomethane may also put constraints on an upgrading process. Similarly, local or global legislations on methane emissions in the slip (rejected stream or permeate) may add to the complexity of the biogas plant. A small-scale carbon membrane system for biomethane production in the Southern part of Norway was conducted by MemfoACT (the company closed in 2014), and the intended use of biomethane is vehicle fuels complying to the Swedish biomethane standard that requires the methane content of 96–98 mol.% and also specifies the allowable water content ($< 32 \text{ mg Nm}^{-3}$) and H_2S content (23 ppm) in the gas product. Several tests of stability and durability have previously been conducted with modules containing up to 2000 fibers at varying feeds reported by Lie et al. [155], and no change after 16 days (10 bar feed, 1 bar on permeate side) was found regarding the testing of one module with a 5.5% CO_2 and balance CH_4 at a rate of 1 Nm^3/h . However, by adding 1000 ppm n-heptane, the CO_2 permeance reduced 23% at the same operating condition. The effect of relative humidity and sulfur loading was also tested in a large 30-fiber module (30 cm long) exposed (dynamically) to biogas over 6 months. This was done on-site using the very same biogas source and only with limited pretreatment consisting of water knockout using a heat exchanger (dewpoint ca 10°C), H_2S adsorption in activated carbon granulates (two 4 L tanks in parallel but no warning system for H_2S breakthrough) and particle removal (2 μm nominal size). The results of this pre-study showed a 60% drop in CO_2 permeance and a quadrupling of the CO_2/CH_4 selectivity. Thus, proper pre-treatments such as the removal of water vapor or H_2S from the gas

stream might be necessary to keep high performance and a longer lifetime of carbon membranes in the real applications. Moreover, several modules of the same type as above were exposed to real biogas (63 mol.% CH₄, 1 ppm H₂S, balance CO₂), and tested with a 10 Nm³ h⁻¹ of biogas at 15–20 °C and 20 bar feed pressure [33]. After 200 days in operation, the CO₂ permeance was reduced by 30%. They reported that the single-stage pilot system can reach a methane purity of 96 mol.% at a high methane recovery of > 98% [33]. It was worth noting that a significant performance increase (10 to 15%) by letting the gravity pull the CO₂ out of the bore (i.e., permeate outlet pointing downwards was significantly better). However, the challenges of getting a high mass transfer coefficient and increasing effective membrane area should be addressed due to the manually sorted and randomly packed CHFMs. Moreover, they also pointed out bore-side feeding configuration may provide a better overall module performance [33].

In order to evaluate the techno-economic feasibility of carbon membrane for biogas upgrading, a two-stage carbon membrane system was designed to achieve high methane purity of > 96 mol.% from biogas containing 35 mol.% CO₂/65 mol.% CH₄ [153,156]. Moreover, Haider et al. conducted the comparison of carbon membranes with polyimide-based membranes for biogas upgrading based on their pilot testing results [156], and they found that two-stage polyimide membrane system is not commercially viable for biogas upgrading due to high recycle ratio, and carbon membrane system presented a 22% energy reduction compared to a three-stage polyimide membrane system, which is very promising for this application. The membrane production cost at a semi-industrial production plant based on CMS membranes from regenerated cellulose was estimated at about \$100 m⁻². The MemfoACT cost estimations of a large-scale production facility (24–7 operation) the cost of \$100 per m² was reasonable (the production would easily be profitable for the company if the selling prize was in the range of \$100 per m²). The current preparation of CMS membranes directly from cellulose contains the majority of the same procedures part from the two steps: 1) direct spinning from cellulose requires more costly solvent (ionic liquid), that would need to be recovered and re-used in large-scale production; 2) there would be no need to deacetylate the cellulose acetate used by the previous company so those chemicals and handling efforts would be saved.

It is then estimated that these added costs and saved costs would cancel out and hence an estimation of \$100 per m² cost would still be acceptable. However, due to the decrease of membrane effective area, the membrane cost doubled for a biogas pilot plant, which ultimately increased the total capital cost of further upscaling of the plant. Thus, the site owner chose to build their full-scale plant based on water scrubbing technology, and the pilot carbon membrane system developed by the previous company MemfoACT was sadly obsolete [33]. However, a biogas processing cost of 0.078 \$/m³ at the feed pressure of 8.5 bar in a 1000 m³(STP) h⁻¹ biogas plant was evaluated by He et al. [153], which is lower compared to 0.15 € m⁻³ of amine absorption if carbon membrane cost of 50 \$ m⁻² can be achieved. Therefore, carbon membranes show great potential for biogas upgrading if the membrane material cost at a large-scale production can be reduced.

3.4. Carbon membranes for natural gas sweetening

Though raw natural gas varies in composition from different sources, the major impurity of CO₂ should be removed before natural gas is transported to the pipeline network [157]. Amine absorption is the most used technology for CO₂ removal from natural gas, but it faces high capital and operating cost, complex operation process, and environmental pollutions [157]. A membrane system is a potential alternative for CO₂ removal in offshore or remote regions where small footprint, flexibility, low capital and operating costs are highly desirable [4,29]. Yeo et al. [158] conducted a comprehensive review on the comparison of membrane technology with conventional methods for CO₂ removal from natural gas. It was suggested that membrane

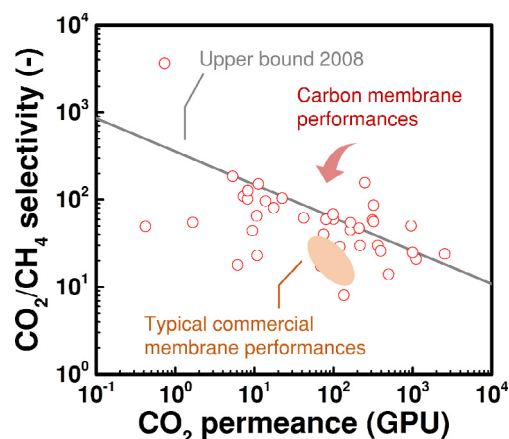


Fig. 7. The CO₂/CH₄ separation performances of different carbon membranes (Data are taken from Tables 3-6). The excellent separation performance is converted to permeance (GPU) based on the reported thickness. Gray line represents the 2008 Robeson upper bound [81] based on 1 μm selective layer, and the commercial membrane performances were taken from the reference [159] assuming 1 μm selective layer.

technology was economically superior [158]. The commercial polymeric membranes such as cellulose acetate, polyimide, and perfluoro membranes have been used for natural gas sweetening [4,157]. However, polymeric membranes suffer the loss of selectivity induced by membrane compaction and plasticization when exposed to high-pressure of 60–90 bar. CMS membranes with rigid structure can provide a good compact- and plasticization-resistance, and thus are good candidates for CO₂ removal from high-pressure natural gas. Fig. 7 summarizes the performances of carbon membranes for CO₂/CH₄ separation, which clearly exhibits better performances in both selectivity and permeability compared to typical commercial membranes.

Swaidan et al. investigated the CO₂/CH₄ separation performance of CMS membranes derived from PIM precursors (PIM-6FDA-OH) under the testing pressure up to 30 bar [85]. They found that CO₂/CH₄ selectivity and CO₂ permeability deteriorated in the mixed gas measurement, while CH₄ permeability increased with feed pressure. Recently, the developed polyimide-derived CHFMs were tested with supercritical natural gas (1800 psia [124 bar]) at different feed compositions (including the impurities of high hydrocarbons such as toluene and n-heptane). The separation factors for each scenario were almost the same as 50–60 within the tested feed pressure range [29]. The CHFMs also presented stable separation factors when exposed to hydrocarbon impurities while CO₂ permeance reduced with the increase of impurity concentration. The decreased CO₂ permeances were caused by the competitive sorption behavior happening inside of the micropores of carbon membranes where heavy hydrocarbons reduce sorption sites for CO₂ and CH₄. With attractive and stable separation performance at aggressive feed conditions, the developed CHFMs showed great potential for CO₂ removal from natural gas.

In order to develop an energy-efficient and cost-effective carbon membrane process for CO₂ removal from natural gas, process design and operating parameter optimization are also crucial besides the development of advanced membrane materials. A two-stage CMS membrane system with different CO₂ concentrations in feed gas was investigated to achieve the separation requirements by Chu and He [160]. Based on HYSYS simulation, they found that the cost for a specific natural gas sweetening process was significantly affected by membrane performance, especially CO₂/CH₄ selectivity. Moreover, the 2nd-stage permeate pressure will have a great influence on the cost when the feed CO₂ content is higher. Chu et al. [161] also developed a membrane model to simulate CO₂ removal from natural gas by hollow fiber membranes, which enables to predict the flow rate, concentration and pressure profiles along hollow fiber length in both feed and permeate

sides. The modeling results indicated that total pressure drop along module length can be ignored if the inner diameter of CHFMs (with total 0.6 m) is $> 200 \mu\text{m}$, and extremely high packing density can lead to a significant pressure drop in shell side. Moreover, it was also found that the required membrane area and methane loss increased with the increase of CO_2 content in the feed gas, while feed pressure showed an opposite effect.

It should be noted that achieving high purity products is still challenging using commercial membranes in the real natural gas sweetening since those polymeric membranes suffer low selectivity at high-pressure operation. While the higher purity gas obtained in an amine process is paid by high capital investment and a potentially harmful environmental process. Thus, the development of advanced CMS membranes with excellent separation performance (high CO_2/CH_4 selectivity) not only provides an environmentally friendly process but also offers a membrane process to reach the high purity requirement. Haider et al. reported the pilot-scale testing of carbon membrane modules at high pressures (50 bar) for the potential application of natural gas sweetening [32]. The separation performance was basically maintained at higher pressures, which shows an extraordinary advantage of carbon membranes for high-pressure CO_2/CH_4 separation. Moreover, the reported carbon membranes showed no signs of CO_2 plasticization which has been a drawback for most polymeric membranes. Therefore, carbon membranes with rigid structures are promising for CO_2 removal from high-pressure natural gas.

4. Future perspectives

This review highlights the status of carbon membrane development with respect to precursor selection and preparation, tuning carbon membrane structure, membrane up-scaling and their potential applications as a green and environmentally friendly technology for CO_2 removal. Both self-supported and ceramic-supported carbon membranes in flat-sheet and hollow fiber configurations show the potentials for selected gas separations. The most promising precursors of polyimide and cellulose are identified to balance production cost and separation performance. Even though the current carbon membranes present good performances for CO_2/CH_4 , CO_2/N_2 , and H_2/CO_2 separations, none of them have been successfully brought to the market at an industrial scale. A sustainable process from precursors to carbon membranes should be pursued, and making asymmetric CHFMs without costly pre-treatment needs to be focused on the technology advances of carbon membrane development. A potential commercialization CMS membrane for separation process basically requires that 1) the membrane retains high separation performance, robust durability under harsh conditions, and good mechanical strength; 2) the membrane production process is easily scaled up with acceptable cost; 3) constructed membrane module adapts to different scenarios.

Although the fabrication of carbon membranes is more complicated compared to polymeric membranes as a separate process of carbonization is implemented, however, the more means that can be applied during carbonization provide more ways to enhance performances further. On the one hand, modification on the precursors, such as the FFV adjustment by grafting functional groups and element doping, has been documented as effective ways to improve the performances of resulted CMS membranes. On the other hand, diverse methods to tune microstructure/properties during the carbonization and post-treatment steps provide CMS membranes with more competitive separation performances. In the future work, applying such facile methods, like widening micropores by post-reduction and -oxidation, and narrowing micropores by chemical species doping and hyperaging, to adjust microstructure and then to meet required separation performances. Furthermore, the stability under the existence of water vapor in the feed stream must be considered as the water vapor is normally presented in flue gas and raw natural gas. Thus, the design of highly hydrophobic CMS membranes to allow a fast transport of water molecules in the

micropores is crucial. The CMS membranes prepared from cellulose membranes and fluorinated triazine-based membranes have illustrated a high durability under $> 85\% \text{RH}$, which can be further investigated. The functionalization of CMS membranes by heteroatom-doped active sites to modify their surface properties should be promoted. Besides, to enhance the mechanical strength of CMS membranes, the carbonization process could be optimized. For example, HCl is considered as carbonization catalysts, which can make carbon hollow fibers mechanically stronger. For safety issues, ammonium chloride (NH_4Cl) can put inside the quartz tube and using a sweep gas to slowly release HCl when carbonization temperature reaches $340 \text{ }^\circ\text{C}$ (i.e., the NH_4Cl decomposition temperature).

It is necessary to optimize the membrane production process, which can be scaled up in an industrial capacity. Polyimide derived hollow fiber precursors have been developed into different configurations and have shown promising performances for required separations. Nevertheless, the challenges, such as using NMP as a solvent, involving complex procedures to maintain micropores during carbonization, easily in contact with each other hollow fibers and fused together during carbonization, are needed to be addressed if a large production capacity considered. On the other hand, cellulose hollow fibers are less prone to fusing, and many cellulose fibers can be carbonized in the same batch, which can significantly bring down the production cost for commercialization. Renewable polymers of cellulose show a particular interest by using ionic liquids (ILs) as a solvent to achieve green advances on carbon membrane production. A novel methodology by the combination of experiment, chemometrics, and molecular modeling can be introduced to spin defect-free, asymmetric cellulose hollow fiber precursors with desired structure and property by screening ILs and cellulose feedstocks will have a great potential to flexibly tune precursor structure and property (e.g., porosity, degree of polymerization, crystallinity, and hydrophilicity, etc.). Moreover, the carbonization process must be very fine-tuned to get a high yield of perfect carbon membranes. The conventional carbonization process using horizontally placed furnace suffers the problems of low gas permeance and defect-formation due to the accumulation/sintering of residual carbon ashes on carbon surface/matrix. Thus, a novel carbonization process might be applied to prepare straight and mechanically strong carbon hollow fibers with high porosity and less dead-end pores by setting an angle of furnace or using a vertically placed furnace during the carbonization to drain the tars and vapors can be a solution. Moreover, the challenge of high production cost due to the difficulty on fabrication of carbon membranes in a continuous process needs to be addressed. However, the excellent separation performance reported in the latest literature indicates that the research for more robust membranes will be solved. With the possibility of tailoring membrane pore size and distribution which these membranes have, there are a huge number of potential gas separation applications for carbon membranes.

Membrane module design and construction for high temperature/pressure applications is another challenge on up-scaling of carbon membranes, which is related to membrane mounting, potting and sealing. It is worth noting that the shell-side feeding configuration may not be very efficient as CHFMs can be damaged or broken at a high-pressure feed flow. Thus, future module design should be focused on bore side feeding. Moreover, due to the fragility and brittleness characteristics, CMS membranes should be fabricated in a free-stand hollow fiber configuration if considering large-scale. It is also expected that large-scale production of supported carbon membranes will be challenging, and the production cost is still quite high, which may limit the applications only in small-volume gas separation processes. One should bear in mind even though most of the reported modules are potted in both ends the individual arrangement of the carbon hollow fibers inside a module cover would probably vary slightly depending on orientation. In case of vacuum permeate operation, the feed from bottom and retentate on the top may provide a better membrane performance due to the gravity helping in keeping the heavy CO_2 from flowing to the

retentate- this should be further tested in the future work.

Carbon membrane technology is considered as energy-efficient processes for CO₂ removals in different scenarios. Hydrogen purification from syngas may become a major application, but also CO₂ removal from natural gas or biogas (CO₂/CH₄ separation) has a very promising potential. However, in order to compete with the currently commercialized polymeric membranes for selected gas separation applications, the above-mentioned challenges for carbon membranes must be overcome. Moreover, collaboration with industry to test out the green advances (especially high energy efficiency and low greenhouse gas emissions) of carbon membranes technology is also essential to bring the technology to future commercialization. For some gas streams containing water vapor or higher hydrocarbons, regeneration of carbon membranes will have to be put up to recover membrane performance over time. Moreover, process design with proper pre-treatment steps (water and particle removals) should be well considered to protect carbon membranes for longer lifetime, which can reduce the capital cost of carbon membrane systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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