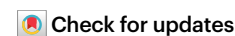


# Polyimide-derived carbon molecule sieve membranes for gas separations

Zhongyun Liu, Yuhe Cao & William J. Koros



Polyimide-derived carbon molecular sieve (CMS) membranes mark an important step for various current, key energy-intensive separations. The excellent separation performance combined with economical scalability make CMS membranes ready to enable energy-transition-focused gas separations.

Gas separations are crucial to the energy transition to lower energy-intensive processes with reduced carbon footprints. Such processes will reduce the environmental impacts of industrial gas separations while maintaining sustainable economic growth despite an increasing global population. Over the past several decades, membrane-based separation processes, such as aqueous reverse osmosis, have provided a model that can be emulated with a full order of magnitude reduction in energy intensity. To be such change agents, gas separations need both materials innovations and economical high surface-to-volume hollow fiber modules, as gas fluxes are typically an order of magnitude lower than that of water fluxes in reverse osmosis. Highly selective carbon molecular sieve (CMS) hollow fibers meet such needs for a broad spectrum of key separation targets. In this Comment, the engineering of such devices to meet the energy transition needs is described, along with the challenges for large-scale implementation.

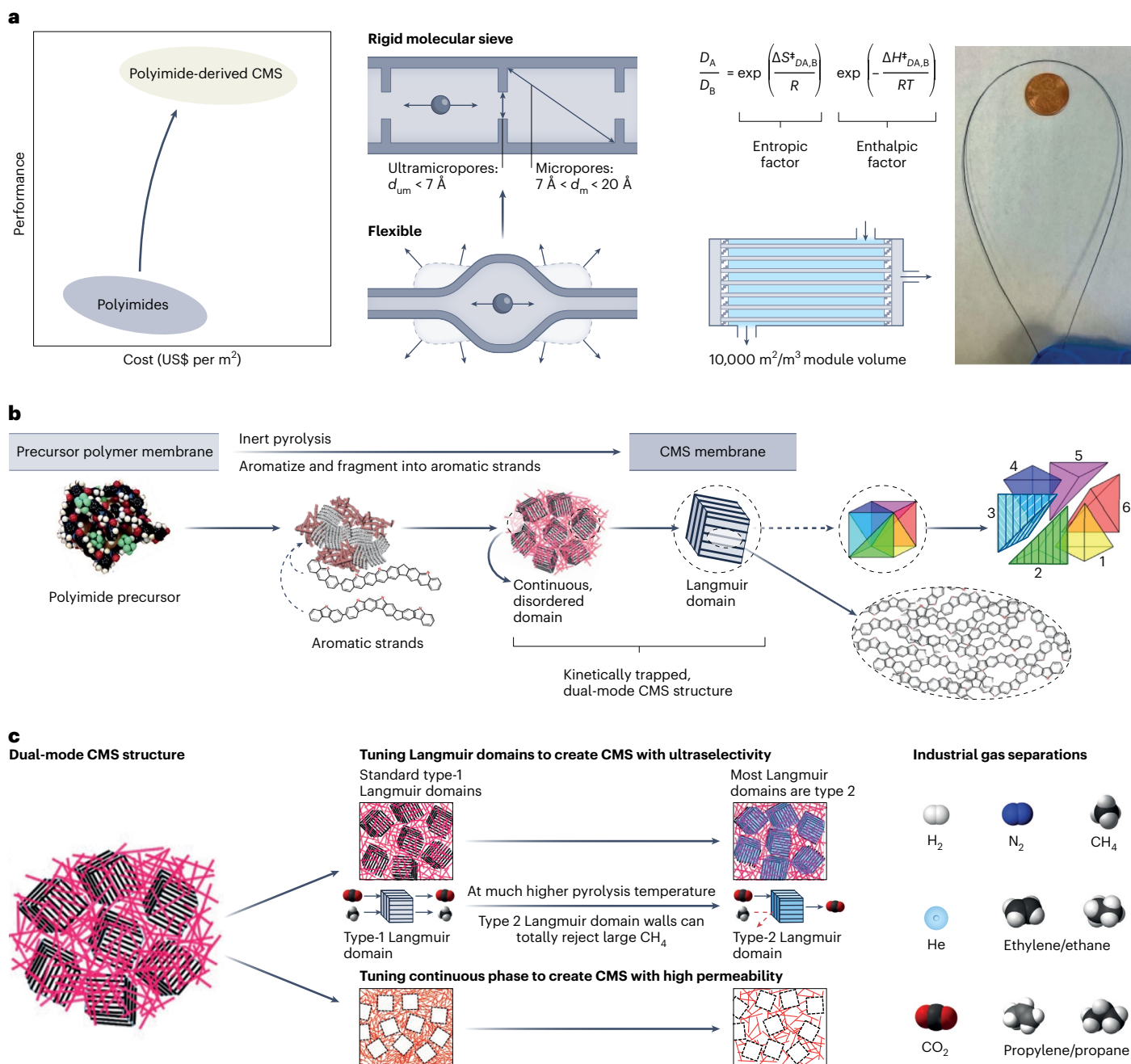
## Enabling features of CMS membranes

Tunable ångström-level discrimination between gas molecules combined with suitable mechanical properties to create economical modules with thousands of square meters per cubic meter volume make CMS membranes appealing<sup>1</sup>. These features are not easily matched by polymeric or even other high-performance molecular sieving materials. Transformation of suitable precursor polymeric, asymmetric, thin-skinned hollow fibers into CMS modules occurs in a seamless integrated process<sup>2</sup>. At the microscopic level, flexible polymer coils are transformed into locally rigid entities with specialized bimodal pore size distributions to deliver size discrimination with other special CMS properties. Large 7–20 Å micropores provide high sorption capacities and long penetrate jump lengths for high intrinsic gas permeabilities, while ultramicropores (<7 Å) enable enthalpic and entropic molecular-sieving selectivity factors (Fig. 1a). The ability to deform without failure during hollow-fiber module formation further distinguishes CMS membranes from other molecular sieving membrane materials in high surface-to-volume modules that are ideal for large-scale industrial gas separations. Although freshly made CMS membranes show self-retarding physical aging, such physical aging can be accelerated to allow CMS membranes to reach a more stable thermodynamic state within

much shorter times compared with the lifetime of the membrane<sup>3</sup>. The stabilized CMS membranes show highly attractive stable gas permeability and selectivity, indicating that physical aging of CMS membranes is not a problem for practical applications. The intrinsic properties of the precursor polymers to create the CMS membranes are important, and we comment on this topic next in a self-consistent discussion that considers the above-mentioned multiple unique features.

## Fundamentals of CMS membranes

Here ‘self-consistent’ means connecting the information about the pyrolytically created CMS elemental compositions to the properties probed by the gas penetrants and spectroscopic techniques to infer a reasonable picture of the fascinating CMS state of matter. The 6FDA-based polyimide precursor family (6FDA = (4,4′-hexafluoroisopropylidene) diphthalic anhydride) has been studied to connect the mechanical properties and structure evolution of CMS membranes derived from specific precursors to penetrant sorption, diffusion and permeation. This Comment provides our integrated vision (Fig. 1b) based on our work on the key transformations that occur during pyrolysis of the 6FDA:BPDA-DAM member of this polyimide family (BPDA = 3,3′,4,4′-biphenyltetracarboxylic dianhydride, DAM = 2,4,6-trimethyl-m-phenylenediamine). Specifically, entangled polyimide chains that experience backbone aromatization, scission and fragmentation can transform into shorter, rigid aromatic carbon strands, accompanied by the evolution of gas species including CF<sub>3</sub>H, CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub> (ref. 4). Entanglement of random-coil, high-molecular-weight (150–300 kDa) polyimide precursors that are undergoing aromatization creates strong mechanico-chemical stresses. Such stresses at weak bonds, such as in the biphenyl unit, can be relieved by scission to provide a source of short strands such as those shown in Fig. 1b. X-ray photoelectron spectroscopy showed the coexistence of *sp*<sup>2</sup> and *sp*<sup>3</sup> hybridized carbon in the formed carbon stands and clarified the chemical speciation of nitrogen in the carbon strands to include a mixture of pyrrolic and pyridinic nitrogen. The rapid evolution of the above-mentioned small molecules (CF<sub>3</sub>H, CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub>) creates a temporary general increase in the free volume to provide a high-free-volume environment with elevated local mobility for the short strands shown in Fig. 1b. We reason that this phenomenon, coupled with the stress-induced effects mentioned above, allows locally sufficient mobility of the relatively short, high-aspect-ratio strands to move and reorganize. Classic work by Flory indicates, “Steric repulsions between the solute particles are principally responsible for order in lyotropic liquid-crystalline systems. In the case of rigid rods, the axial ratio of the particles governs the concentration at which separation of a nematic or cholesteric phase sets in.”<sup>5</sup> In Flory’s review, he identifies rigid strands with aspect ratios of three or more as prone to such ordering. Clearly, the strands in Fig. 1b more than meet this standard. In this case, some formed aromatic carbon strands may further arrange into more ordered ‘graphene-like’ plate structures driven by entropy,



**Fig. 1 | Key features and engineering of CMS membranes for industrial gas separations.** **a**, Combined advantages of separation performance and economical scalability (left graph) and mechanical properties (right; image of hollow fiber) of CMS membranes. The schematics (middle) show the transformation of a flexible polymer coil to a locally rigid entity with a bimodal pore size distribution and the high surface-to-volume CMS module. **b**, Envisioned mechanism of transformation of polyimide precursors to CMS membranes.

**c**, Envisioned engineering of CMS microstructures for tuning separation performance for important gas separations.  $d_{um}$ , ultramicropore diameter;  $d_m$ , micropore diameter;  $D_A$  and  $D_B$  are the diffusion coefficients of A and B gas molecules, respectively;  $\Delta S_{DA,B}^\ddagger$  and  $\Delta H_{DA,B}^\ddagger$  are the differences in the diffusion transition state entropy and enthalpy for A and B gas molecules, respectively;  $R$  is the universal gas constant; and  $T$  is absolute temperature. Figure adapted with permission from: **a**, ref. 1, Springer Nature Ltd; **b**, ref. 3, Wiley.

analogous to that for liquid crystals. Neighboring carbon strands in such 'plates' with slit-shaped ultramicropores offer exceptional size and shape discriminating abilities for gas molecules. Ultramicropore

distributions within such plates depend strongly on the shape and packing of the carbon strands in the plates, which will be influenced by precursor structures. Kinetic factors hamper organization, leading to

non-stacked, imperfectly packed polygonal entities idealized as tetrahedra and cubes, while randomly oriented carbon strands can connect the cell structures through a disordered, continuous phase. Micropores within polygonal pore geometries offer a high uptake capacity for gas molecules, and gas sorption in such geometries is consistent with a Langmuir sorption model. A second Langmuir isotherm could, of course, be used to describe deviations from a single Langmuir isotherm. Fortunately, however, even for a high-pressure, multicomponent gas mixture, using Henry's law as a limiting case of such a second Langmuir isotherm works well for CMS membranes. On this basis, for gases of great practical importance, a Langmuir plus Henry's law framework (so-called dual-mode sorption model) adequately describes key chemical engineering performance features with the two sorption populations linked by local equilibrium. Such final CMS membranes derived from polyimide precursors show dual-mode morphologies consisting of a disordered, continuous phase and distributed Langmuir domains. Such a unique dual-mode morphology enables the CMS membranes to be highly tunable to optimize the continuous and Langmuir environments for target gas pair separation. Moreover, the dual-phase morphology provides desirable mechanical and transport properties (Fig. 1a–c). The insights discussed above may help to understand structure evolution in non-polyimide precursors, such as polyaramides<sup>6</sup>, polymers of intrinsic microporosity<sup>7</sup> and cellulose precursors<sup>8,9</sup>, to produce CMS membranes; however, detailed work similar to that done for the polyimide family materials is needed for these non-polyimide precursors.

## Engineering CMS structure and separation performance

Tools to tailor the intrinsic CMS dual-mode structure and separation performance rely on the molecular engineering of precursors, as well as on the pyrolysis conditions and post-pyrolysis treatments. Engineering of the polyimide precursors and pyrolysis conditions allows the shapes and lengths of the resultant carbon strands to be tailored, which affects strand packing and properties in the continuous and Langmuir domains. For example, forming shorter and straighter carbon strands during pyrolysis using low-cost Matrimid, a commercial polyimide, as a precursor illustrates this strategy. Indeed, high-temperature pyrolyzed Matrimid with high strand packing in the Langmuir domains reduces the ultramicropore size of CMS membranes<sup>2</sup>. Such tailored ultramicropores in CMS membranes not only increases diffusion selectivity but also enables thermodynamic exclusion sorption selectivity at high pyrolysis temperatures by excluding larger CH<sub>4</sub> versus CO<sub>2</sub> (Fig. 1c) to enable ultrasensitivity<sup>2</sup>. Further reduced CMS ultramicropore sizes can largely exclude CH<sub>4</sub> and even CO<sub>2</sub> while still allowing super-slim H<sub>2</sub>, to show ultrasensitivity, with a H<sub>2</sub>/CH<sub>4</sub> selectivity as high as 40,000 (ref. 2) and H<sub>2</sub>/CO<sub>2</sub> selectivity of 156 (ref. 6). Reduced CMS permeance created at high pyrolysis temperatures can be offset by the high surface-to-volume capabilities of CMS hollow fibers in compact, high-productivity modules to produce a high-purity gas product without using 'polishing' recycle stages, thereby making membrane technology even more appealing. Moreover, such ultrasensitive CMS membranes can even enable the efficient recovery of dilute helium from natural gas feeds<sup>2</sup>.

For larger, even more similarly sized gas penetrants (such as C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>), a promising strategy is to introduce low volume fractions of packing to inhibit features such as crosslinkable groups and kinked backbones in precursors. Such features seem to prevent excessive packing of the formed carbon strands in the continuous phase, while still allowing carbon strand packing in the Langmuir domains to increase gas permeability with adequate selectivity. Other ultramicropore tuning

tools, such as controlled electron irradiation<sup>10</sup>, and the approaches noted above provide a large toolbox for CMS engineering to meet the diverse needs for a broad spectrum of challenging gas separations.

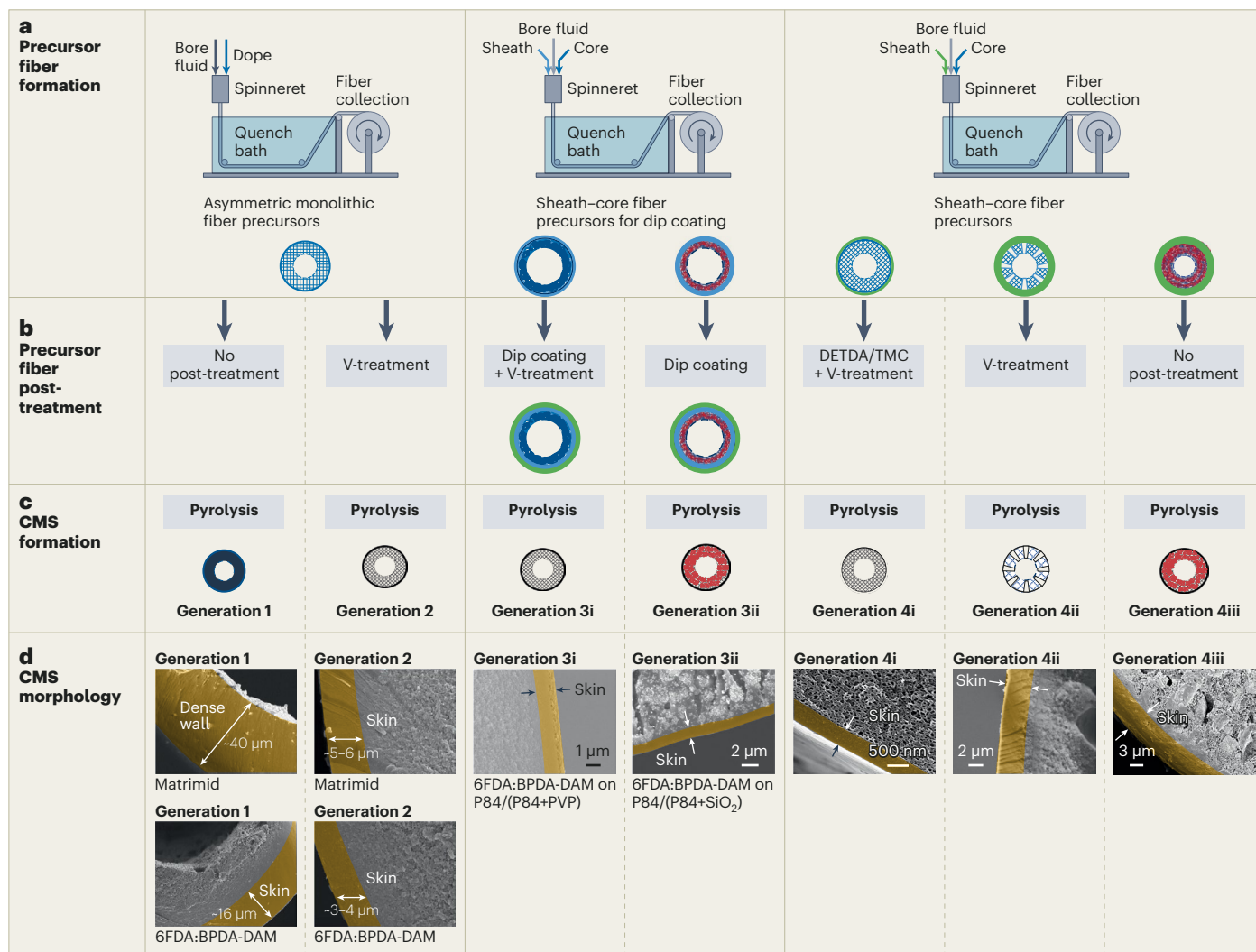
## Engineering asymmetric CMS hollow fibers for gas separation

Figure 2 summarizes the evolving nature of CMS hollow-fiber membranes, which are already in their fourth generation. An early (generation 2) form of CMS hollow-fiber membranes is already undergoing scale up and preparation for field testing for deployment, in collaboration between industrial entities, in the large Libra oil field offshore of Brazil<sup>11</sup>. Translating polyimide precursor materials, as discussed above, relies on chemical engineering principles to create practical CMS hollow fibers and modules. This translation process requires thin, defect-free selective layers to deliver maximum practical impact. Natural gas purification has been the focus of this translational work, thus we use it to discuss the evolution of this feature of CMS membrane development; however, the approaches apply to most gas pairs. Most importantly, our experience shows that pyrolyzing asymmetric, polymeric hollow-fiber membrane precursors to final CMS structures is preferable, instead of using ceramic or other expensive support layers. Porous supports for generation-1 Matrimid and many other precursors in Fig. 2 collapsed as the pyrolysis temperature passed the precursor glass transition temperature ( $T_g$ ), thereby causing the loss of the asymmetric morphology introduced during fiber spinning<sup>12</sup>. The collapse of the substructure morphology caused the generation-1 CMS hollow fibers (Fig. 2) to have low gas permeance due to thick fiber walls. Precursor asymmetric fibers based on 6FDA materials maintain differing degrees of asymmetry, depending on the precursor segmental rigidity. Fortunately, a simple sol-gel pre-pyrolysis treatment (termed V-treatment) was developed to restrict the collapse of the substructure morphology in virtually all cases to create generation 2, so even Matrimid precursors lose little asymmetry. This sol-gel treatment creates highly porous organo-silica on the fiber pore walls to prevent substrate collapse with negligible added support transport resistance<sup>12</sup>.

Another challenge, the cost of the exotic precursors, such as of 6FDA-based polymers, was overcome in generation 3 to reduce material costs and to allow intrinsically high permeability 6FDA-derived CMS hollow-fiber membranes to be used. Specifically, in generation 3i and generation 3ii fibers with attractive separation performance, only roughly 10% of the total wall is based on 6FDA polyimides, greatly reducing costs. Generation 3i supports use low-cost P84 polyimide (a commercial polyimide) plus pore former additive to create precursor supports. A related generation 3ii also uses P84 in support precursors, but relies on SiO<sub>2</sub> nanoparticles as anti-collapse agents for the porous CMS support. Both generation 3i and 3ii supports enable scalable dip-coating processes, avoiding the need to spin defect-free precursor fibers as a platform for diverse sheath precursors for CMS fibers. Despite some uncertainty regarding the interface boundaries between support and 'skin' zones, appealing performance is achieved.

Generation 4i–iii defines the state of the art with lower-cost CMS hollow fibers relying on co-spun sheath-core precursors with suitably thin selective layers to eliminate the generation-3 dip-coating steps. Generation 4i achieves ultrathin-skin CMS hollow-fiber membranes using Matrimid-derived CMS supports and 6FDA:BPDA-DAM sheath precursors with CO<sub>2</sub> permeances an order of magnitude above monolithic 6FDA:BPDA-DAM precursors, with attractive CO<sub>2</sub>/CH<sub>4</sub> separation factors<sup>13</sup>. Generation 4i uses a final precursor pre-treatment with





**Fig. 2 | CMS hollow-fiber formation options.** **a**, Different generations of precursor fiber formation processes. **b**, Precursor fiber post-treatment approaches. **c**, CMS formation illustrations. **d**, Featured scanning electron microscopy images showing CMS morphologies. Approximate selective skin

layers are challenging to define perfectly. PVP, polyvinylpyrrolidone. Figure adapted with permission from: **a**, ref. 16, Wiley; **d** (generation 1 and 2), ref. 12, Elsevier; **d** (generation 4i), ref. 13, Wiley; **d** (generation 4ii), ref. 14, Wiley; **d** (generation 4iii), ref. 15, American Chemical Society.

diethyltoluenediamine (DETDA) and trimesoyl chloride (TMC) to hybridize and seal any selective-layer defects before pyrolysis. This simple step is a variant of interfacial polymerization used in state-of-the-art reverse osmosis membranes, but at much lower reagent concentrations than for reverse osmosis membranes. The generation-4ii morphology relies on a novel precursor morphology, termed ‘pseudo-wheel+hub and spoke’, to provide the selective-layer support that benefits from very high modulus carbon ‘spokes’ to minimize porous flow resistance for high feed pressures and fluxes<sup>14</sup>. Again, domain boundaries are difficult to define precisely, but performance in terms of permeance equal to partial-pressure-normalized fluxes is excellent. Simultaneous optimization of precursor asymmetric morphology, along with an engineered pyrolysis process, creates defect-free CMS composite generation-4ii CMS hollow-fiber membranes with a sheath-core spun precursor with a 6FDA-DAM sheath and a Matrimid core.

This generation-4ii approach avoids the need for post-treatment to seal precursor defects, while providing a CO<sub>2</sub>/CH<sub>4</sub> (50:50) mixed gas feed with an attractive CO<sub>2</sub>/CH<sub>4</sub> selectivity of 64.3 and CO<sub>2</sub> permeance of 232 gas permeation units (GPU) at 35 °C. Finally, generation 4iii (Fig. 2), involving co-extrusion spun nanoparticle-filler composite hollow-fiber membranes, avoids the need for a V-treatment, and may fill several specialty niches<sup>15</sup>. Further advances using the above approaches for high-performance composite CMS fiber fabrication are likely with other sheath or core precursors. We see this as the future of CMS hollow-fiber development for various gas pair separations shown in Fig. 1c, beyond the specific applications mentioned above.

This Comment shows that CMS hollow fibers can be change agents suitable for the ongoing evolution to meet the needs of globally sustainable gas separations. Generation of new advanced membranes for oxidatively active feeds can also benefit from the above

approaches by calcining alternative precursors analogous to those discussed here.

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## Competing interests

W.J.K. notes that Air Liquide has licensed the Georgia Institute of Technology V-treatment intellectual property (IP) mentioned in Fig. 2.

## Additional information

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