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# Two-dimensional materials for gas separation membranes

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The next generation of gas separation membranes requires from novel membrane materials with superior performance, sufficient mechanical stability, and long-term stability under harsh operation conditions. Two-dimensional (2D) materials offer several advantages over conventionally used polymeric materials. However, gas separation membranes containing 2D materials have not reached commercialization yet,

despite having been discovered almost two decades ago. Difficulties in membrane scalability and high costs associated with the manufacturing processes are the main challenges. This review focuses on the current state and prospects of the

technology and highlights novel 2D materials and strategies to fabricate ultrathin membranes that have been developed during the last three years. A multidisciplinary approach, covering the fields of physics, chemistry, and chemical engineering, needs to be taken to achieve the preparation of robust, large-scale, and economically affordable (2D material)-based membranes capable of breaking into the gas separation market.

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### Introduction

Since the first commercial membrane for hydrogen separation in 1980, this technology has experienced a rapid growth; the global gas separation membrane market in 2021 (USD 0.9 billion) has sextupled from 2000, when the market size was USD 0.15 billion [1], and is projected to reach USD 1.2 billion by 2026 [2]. The main applications are in the natural gas industry, nitrogen generation and oxygen enrichment, and hydrogen recovery.

The implementation of membrane technologies in various fields, including seawater desalination, the most widespread application, has been possible due to the development of fabrication techniques that allow for the reduction in thickness of the selective membrane layer. Gas permeance through a membrane scales inversely proportionally to its thickness. It is therefore expected that the next generation of commercial membranes for gas separation will target an even further reduction in thickness to maximize gas permeance without interfering in the membrane capability of selectively separating gas molecules.

Since the publication of the first graphene oxide (GO) laminate membrane [3], the development of membranes from two-dimensional (2D) materials has generated a growing interest in the separations field. The initial excitement for these selective and fast-permeating materials in liquid applications soon jumped to gases [4,5], and in recent years, many groups have focused on the preparation of ultrathin films with graphene-based materials and other interesting 2D materials, including hexagonal boron nitride (hBN), porous graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), transition metal dichalcogenides (TMDs), layered double hydroxides (LDHs), metal organic frameworks (MOFs), covalent organic frameworks (COFs), and 2D polymers (Figure 1).

Other fascinating 2D candidates for highly permeable and selective membranes are graphynes, which are graphene analogs that contain intrinsic uniformly distributed pores. Qiu et al. [6] carried out computational research that showed these 2D materials offer advantages over other atomically thin membranes such as porous graphene in terms of controllability in pore geometry. The size of graphyne nanopores is comparable





Number of publications containing keywords "Polymeric membranes+gas separation", "2D membranes+gas separation", "COFs+gas separation", and "Atomically thin membranes+gas separation". Source: Web of Science on October 2022.

to the size of target gas molecules, and therefore size sieving would be the gas transport mechanism, which would allow highly selective separation of small species. However, challenges remain with the fabrication of highquality and large-area graphyne materials; the first scalable synthesis of multilayered graphyne has been successfully performed very recently [7]. Molecular simulations have recently shown the potential of 2D metal trihalides MX3 (AsI<sub>3</sub>, ScI<sub>3</sub>, SbI<sub>3</sub>, YI<sub>3</sub>, BiI<sub>3</sub>, ScCl<sub>3</sub>, ScBr<sub>3</sub>, and YBr3) for gas separation applications [8].

The big majority of experimental-based research articles report the preparation of extremely thin films with bidimensional nanomaterials using rigid porous substrates  $(Al_2O_3, Si_3N_4)$  as they are flatter and smoother than polymeric porous supports. From the materials point of view, this is extremely exciting and allows for elucidating gas transport properties at much lower level. However, from the commercial point of view, these configurations will hardly make it to the market. Developed membranes should not only outperform existing polymeric ones for economic viability, but the fabrication should be scalable. Therefore, the optimization of polymeric supports to produce very flat surfaces needs to be a priority.

Using 2D materials as nanofillers to enhance the permselectivity properties of existing polymeric membranes may find its way to faster commercialization. 2D materials can impart antiaging properties in super glassy polymer and can increase gas affinity.

Some of the most recent review papers on 2D materials for gas separation were published in 2018 [9–11]. This short review aims at highlighting the latest breakthroughs

from 2019 up to the present in the manufacturing of membranes with 2D materials, briefly discussing their underpinning gas transport mechanisms and the associated hurdles that need to be overcome to reach commercialization. Figure 2 represents the different sort of assemblies of 2D materials that are discussed in this current opinion review.

## **Conventional gas separation membranes**

Most commercial gas separation membranes are thin polymeric dense layers supported onto a highly porous structure. The selective passage of gas molecules takes place through the thin top layer through a pressuredriven solution-diffusion mechanism, where the gaseous species are dissolved on the surface of the membrane, then diffuse through the polymer matrix, and finally are desorbed and exit the system. There is a trade-off between how fast a gas can permeate through a polymer film and how selective the film is; large gas diffusivity (high free volume) leads to low selectivity and vice versa. This is graphically represented as the Robeson upper bound in log-log plots of selectivity versus permeability for different gas pairs of industrial interest. However, this upper bound can be overcome using other types of membrane materials such as zeolites, MOFs, and thermally rearranged polymers.

## Nanoporous atomically thin membranes

In nanoporous atomically thin membranes (NATMs), the gas transport takes place through the rigid nanopores in a continuous and atomically thin film, whose permselectivity properties can be tuned by creating high-enough density of pores with an angstrom precision. The production of continuous 'electronic-grade' large-area films of chemical vapor deposition (CVD) graphene with



#### Figure 2

Representation of the different sort of membranes containing 2D materials. The 3D structures of the 2D materials were produced with VESTA software [12].

minimum defects, makes this 2D material a great candidate for the production of large-scale membranes, but pores must be created. Different strategies such as focused ion beam (FIB), ultraviolet-induced oxidative etching, and defect formation during CVD have led to the formation of nanometer-size pores in CVD-grown graphene, and membranes of extremely small area have been prepared. We recommend the review paper by Yuan et al. [13], where experimental advances focusing on perforation strategies, pore-size distributions, and supporting layers for NATMs are comprehensively reviewed.

The difficulty when preparing CVD graphene-based NATMs lies in controlling the formation of pores, for instance, FIB-drilled pores vary in a relatively broad range between 10 nm and 1  $\mu$ m, and different approaches have been reported. A novel strategy based on partially decoupled defect nucleation and pore expansion using O<sub>2</sub> plasma and O<sub>3</sub> treatment reported by Zhao et al. [14] led to the production of high-density H<sub>2</sub>-selective pores. The nanoporous film achieved a maximum H<sub>2</sub> permeance of 6045 GPU with a decent separation factor for the H<sub>2</sub>/CH<sub>4</sub> mixture (15.6–25.1). They were able to transfer the film onto a macroporous W substrate hosting arrays of 5-µm pores over a 1-mm<sup>2</sup> area without producing cracks or tears.

The formation of cracks during the transfer of the perforated graphene onto the porous support is indeed another hurdle toward the scalability of such membranes. Yet, novel strategies on transferring, including functional coatings for the substrates, have very recently led to cmscale nanoporous single-layer graphene membranes with selective gas separation properties [15].

Another approach for the formation of high gas separation performance of monolayer nanoporous graphene (NPG) membranes that has been recently reported is the drop-coating of an ultrathin layer of imidazolium-based ionic liquid (IL) [16]. The ultrathin ILs tuned the size and chemical affinity of the nanopores while preserving the high-permeance NPG membrane, and a high  $CO_2$ permeance of 4000 GPU and an outstanding  $CO_2/N_2$ selectivity up to 32 were obtained. A similar strategy, based on coating NPG with an ultrathin layer of a  $CO_2$ selective polymer such as PIM-1, resulted in membranes with  $CO_2$  permeances and  $CO_2/N_2$  selectivities within the ranges of 960–2470 GPU, and 21–33, respectively [17].

Despite the recent advances on top-down methods, we are still lacking the ability to create high-density pore membranes containing subnanometer pores with atomic precision. Emergent bottom-up surface-assisted synthesis, which is mainly focused into optoelectronics applications of 1D graphene nanoribbons, could fill the gap of the required pore accuracy. Newly 2D bottom-up synthetized NPG has demonstrated the ability to create high-density membranes ( $10^{13}$  pores/cm<sup>-2</sup>) with pores of  $3 \text{ Å} \times 8 \text{ Å}$  [18], and more recently, even to include functional groups at precise pore edge positions [19]. These membranes hold high promise for the efficient separation of H<sub>2</sub>/N<sub>2</sub> [20]. According to theoretical calculations,

the  $H_2/N_2$  selectivity can reach 10 orders of magnitude in comparison with other membranes as well as high permeability due to its ultrahigh pore density. Furthermore, theoretical calculations also predict ultrahigh selectivity, since only He and H<sub>2</sub> are allowed to permeate at room temperature [21]. Consequently, the NPG membrane could elevate the performance level far beyond the 2015 Robeson upper bound and make it a prospective ultrathin membrane with outstanding performance for He and H<sub>2</sub> separation.

## Laminate membranes

The most promising approach to developing the next generation of commercial membrane with 2D materials is perhaps the stacking of 2D flakes on top of each other and directing the gas permeation through the interlayer channels or slits between the nanosheets, that is, interlayer diffusion. Liquid exfoliation of oxidized graphite and other multilayer materials such as hBN leads to 2D flakes with a wide lateral size distribution ranging from few tens of nanometers to several micrometers. Higher permeation can be achieved by creating shorter interlayer pathways with smaller flakes (it is possible to narrow the size distribution by sonication and centrifugation). Additional passage of gas molecules can take place through in-plane pores that can be created in the bidimensional nanosheets by scalable methods such as chemical etching [22].

2D laminate membranes have been prepared very recently with black phosporene nanoflakes, reporting a very good separation performance for  $H_2/CO_2$  ( $H_2$  permeance > 1000 GPU and  $H_2/CO_2$  selectivity > 100) [23]. This work demonstrates experimentally and by means of density functional theory calculations that the interlayer galleries allow for  $H_2$  passing while blocking other gases with bigger kinetic diameters.

Another 2D-layered material that has received increasing attention over the past few years in the membranes field is MXene. For gas separation, titanium carbide ( $Ti_3C_2T_x$ ) laminate membranes have been produced onto porous anodic aluminum oxide (AAO) supports and have shown excellent properties for H<sub>2</sub> separation [24–26].

Ultrathin (30–70 nm) 2D-LDH laminate membranes have been fabricated onto polymeric porous substrates, showing ideal gas selectivity toward  $CO_2$  ( $CO_2/CH_4$  selectivity of 33) and a  $CO_2$  permeance of 150 GPU [27].

Few-layered TMD nanosheets  $WSe_2$ ,  $MoSe_2$ , and  $MoS_2$ were investigated for the fabrication of H<sub>2</sub>-selective membranes [28]. The prepared  $WSe_2$  membrane using polycarbonate substrates and a thickness of 0.6 µm showed a H<sub>2</sub> permeance of 47 000 GPUs with a H<sub>2</sub>/CO<sub>2</sub> selectivity of ca. 7, surpassing the Robeson's upper bound.

Recent works have shown that ILs can improve gas permeation through laminate membranes. Dou et al. [29] introduced reactive ionic liquids (RILs) within boron nitride (BN) nanochannels to favor the alignment of the cations and anions of the RILs for a fast and selective ethylene transport. These membranes exhibited a very high  $C_2H_4$  permeance of 138 GPU and  $C_2H_4/$  $C_2H_6$  selectivity of 128, outperforming the reported state-of-the-art membranes.

Wan et al. [30] confined magnetic ionic liquid (MIL) [P6,6,6,14][FeCl4] into the 2D nanochannels of a laminated BN membrane (prepared onto polyvinylidene fluoride, PVDF, with thickness of ~11 µm), leading to selectively accelerated  $CO_2$  transport that was supported by molecular dynamic simulations.  $CO_2$  permeability of about 227 Barrer and  $CO_2/N_2$  selectivity of 90, that is above the 2008 Robeson upper bound, were obtained.

1-ethyl-3-methylimidazole acetate ([EMIm][AcO]) was confined in the 2D channels of  $g-C_3N_4$ -laminated membrane, showing high CO<sub>2</sub> permeance (~1000 GPU), good selectivity for CO<sub>2</sub>/N<sub>2</sub> (52.49) and CO<sub>2</sub>/CH<sub>4</sub> (48.41), and good thermal stability and durability [31].

Lamellar stacking of 2D zeolite nanosheets has been also used for the fabrication of gas-selective membranes. Min et al. [32] used porous mordenite framework inverted (MFI) nanosheets of lateral size ca. 2 µm to coat an alumina hollow fiber support that underwent a further two-step hydrothermal treatment to form a continuous film where voids had been filled without significant overgrowth and also without delamination or crack formation. The membrane exhibited high performance for the separation of n-butane from i-butane. Another strategy to prevent the nonselective defects created upon the exfoliation-reassembly method is to use an *in situ* synthetic route; Song et al. [33] fabricated a 2D MOF membrane with a thickness of ca. 80 nm on an alumina substrate modified with a ZnO buffer layer and obtained a  $H_2/CH_4$  selectivity of ~60.

2D COFs are a relatively new class of porous materials considered as potential candidates for the fabrication of gas separation membranes. However, their pores are generally too large for gas selectivity and different stacking strategies have to be followed in order to obtain membranes with good separation performance. For instance, Wang et al. [34] used large-aspect ratio COF nanosheets to create laminate structures with staggered stacking patterns of ca. 10 nm in thickness onto  $\alpha$ -alumina. They achieved a commercially feasible performance for syngas separation (CO<sub>2</sub> permeance of 328 GPU and CO<sub>2</sub>/H<sub>2</sub> separation factor of 22), but the hotdrop coating method they used and the rigid substrate would limit the scalability of membrane fabrication.

Bottom-up fabrication approaches have been also recently reported for the fabrication of COF-based multilaver architectures. Ying et al. [35] carried out a direct layer-by-layer interfacial reaction of two COFs (TpPa-SO<sub>3</sub>H and TpTGCl) with different pore sizes to form narrowed apertures at the COF-COF interfaces. A 155nm-thick ultrathin COF membrane was fabricated on a relatively large-pore COF-LZU1 film, which displayed a H<sub>2</sub> permeance up to 2163 GPU and a H<sub>2</sub>/CO<sub>2</sub> selectivity of 26, exceeding the 2008 Robeson upper bound. Another successful bottom-up strategy for the implementation of 2D COFs into gas separation membranes is the synthesis of H<sub>2</sub>P-DHPh COF onto a UiO-66 MOF film supported on a porous silica substrate [36]. The highly oriented 2D COF layer comprising porphyrin arrays leads to a composite membrane with ultrahigh H<sub>2</sub> permeability  $\sim 1 \times 10^5$  Barrer and H<sub>2</sub>/CO<sub>2</sub> gas mixture selectivity of 32.9, also surpassing the Robeson upper bound.

### Mixed matrix membranes

Embedding 2D materials within a polymer membrane is a widespread strategy to improve the performance of conventional polymeric membranes. This can be done by enhancing the solubility or the diffusivity of target gas molecules, slowing down physical aging or increaseing plasticization resistance.

## Two-dimensional materials for improved permeance and facilitated transport

The presence of selective functional groups on 2D materials can lead to enhanced solubility for a desired gas. For instance, 2D  $Ti_3C_2T_x$  MXene nanosheets were added to Pebax membranes, where the CO<sub>2</sub>-selective channels provided by the  $Ti_3C_2T_x$  multilayers led to membranes with superior CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> separation performances above the 2008 Robeson's upper bounds [37].

Porous 2D materials have the additional advantage over nonporous ones of shorter molecular pathways and thus higher gas diffusivity. g-C<sub>3</sub>N<sub>4</sub> nanosheets with intrinsic in-plane nanopores and CO<sub>2</sub>-philic nature coming from its amine groups were incorporated into polyether block amide (Pebax) membrane for CO<sub>2</sub> separation [38]. A filler loading of 0.25 wt% led to simultaneous enhancement in CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity compared with pure Pebax membrane. 2D MOF Cu(BPY)(2) (OTF)(2) was added to rubbery Pebax for CO<sub>2</sub>/CH<sub>4</sub> separation, leading to improved CO<sub>2</sub> permeability and selectivity (increased by 86.65% and 47.59%, respectively) [39]. Grafting porous nanoparticles (NPs) to the surface of 2D materials can prevent NP agglomeration and allows for controlled openings of the 2D nanochannels within the mixed matrix membranes (MMMs). GO nanosheets were decorated with porous ZIF-8 and added to ethyl cellulose-thick freestanding membranes to enhance gas permeability (increase the size and connectivity of gas transfer passage) [40]; 20 wt% fillers in the polymer matrix led to a CO<sub>2</sub> permeability of 203.3 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 33.4 (139% and 65% improvements, respectively). In another work, ZIF-90 was grown on the pores of g-C<sub>3</sub>N<sub>4</sub> 2D nanosheets and added to a rubbery polymer matrix to improve the CO<sub>2</sub>/N<sub>2</sub> separation [41]. Higher  $CO_2$  permeability and higher selectivity toward this gas were obtained, surpassing the 2008 Robeson upper bound.

# Two-dimensional materials for physical aging and plasticization resistance

Highly gas-permeable polymers suffer from a phenomenon called physical aging. Polymeric chains tend to rearrange toward the equilibrium, consequently reducing polymer free volume and gas permeability over time. 2D materials have been proven good candidates for mitigation of physical aging in the polymer of intrinsic microporosity PIM-1 due to their high surface area and large lateral size, which can 'freeze' the polymer chains [42–44]. Very recently, our group has reported that physical aging can also be prevented in a very thin film of PIM-1 membranes prepared with 1 wt% of (tris (4-aminophenyl)-amine)-functionalized holey reduced GO [45].

2D materials have also shown antiplasticization properties achieving effective preservation of membrane selectivity when MMMs are exposed to high pressure of the plasticizing agent. The most significant findings are well explained by Moghadam et al. in their review article from 2018 [10].

# Two-dimensional materials for other gas separation membrane configurations

2D graphene has been used to create subnanoscale interfacial gaps around porous zeolites for ultrafast separation of hydrogen/methane [46]. Despite the relatively large thickness of the graphene-wrapped membranes (150  $\mu$ m), gas permeabilities of  $5.8 \times 10^6$ Barrer and mixed gas selectivities of 50 were reported.

Attractive interactions between negatively charged MXene nanosheets and cations have been used for the fabrication of multilayer hybrid membranes containing 2D nanosheets and NPs. Thus, ZIF-67 was grown between Mxene nanosheets that resulted in He permeance of around 200 GPU and He/N<sub>2</sub> and He/CH<sub>4</sub> selectivity above 13, much higher as compared with other MOF-based membranes, which was attributed to the narrower





Analysis of the strengths and weaknesses of NATMs, laminate membranes, and MMMs based on five key parameters (a), and double-logarithmic plot of  $CO_2/N_2$  selectivity versus  $CO_2$  permeability for commercial polymeric membranes – cellulose acetate (black diamond [16]) and MTR Polaris (black star) [50] – and (2D material)-based membranes – NATMs (blue filled square [16] and blue unfilled square [17]), laminate membranes (red filled circle [31], red unfilled circle [27], and red half-filled circle [30]), and MMMs (green unfilled triangle [38] and green filled triangle [45]) – (b). In (a), the five key parameters have been evaluated based on the literature search conducted for this review, for example, 'current performance at lab scale' is exemplified in (b).

window of ZIF-67, that is, 0.33 nm [47]. In another work, Pd NPs were intercalated between Mxene nanosheets leading to relatively thin membranes, that is, 780 nm of selective layer [48]. These membranes showed high  $H_2$ permeances (800 GPU due to the increased d-spacing and an ultrahigh  $H_2/CO_2$  selectivity of 242 due to the Hspillover effect from the Pd NPs). Novel freestanding MXene-(ZIF-8) dual-layered composite membranes were prepared using a quick, facile, and scalable fabrication procedure based on electrophoretic deposition, for fabrication of the MXene lamellar structure, and fast current-driven synthesis, for growth of the ZIF-8 layer on top of the 2D laminates [49]. The dual-layered membrane exhibited an outstanding  $H_2/CO_2$  selectivity of 77 and a  $H_2$  permeance of 178 GPU.

### Outlook, challenges, and future trends

Owing to the incipient status of the research, commercialization of (2D material)-based membranes for gas separation seems unfeasible yet. They are at a very low technology readiness level, TRL4 at much, and moving to higher TRLs will take time.

The strengths and weaknesses of the three main fabrication strategies involving 2D materials (blends with polymers, laminate membranes, and NATMs) are summarized in Figure 3a. The biggest advantage of MMMs is that, in principle, is more scalable and cost-effective as compared with the fabrication of few nanometer-thin gas-selective layers purely made of 2D materials. While 2D materials are relatively new, the concept of MMMs was introduced more than three decades ago, which makes 2D material-based MMMs a more mature technology than NATMs and laminate membranes. Outstanding gas separation performances have been reported for small-scale devices of NATMs and, although scaling up is possible, fabrication of larger-scale (i.e. few  $cm^2$ ) robust membranes is often accompanied by loss of membrane performance. Therefore, in order to reach a closer-to-commercialization stage, future research on NATMs must address both technological and economic feasibility issues. Laminate membranes offer several advantages over other strategies due to the large number of available 2D materials and configurations that can be used. The permeability and selectivity of the membranes can be tuned by controlling the size of the inter- and intraflake nanopores and the d-spacing of the 2D nanochannels (e.g. by intercalating NPs). Figure 3b shows a comparison (double-logarithmic plot of CO<sub>2</sub>/N<sub>2</sub> selectivity versus CO<sub>2</sub> permeance) between commercial polymeric membranes, cellulose acetate (black diamond) and MTR Polaris (black star), and selected 2D materialbased membranes for CO<sub>2</sub>/N<sub>2</sub> separations that are of industrial relevance for flue gas treatment [50]. Even though this graph does not represent the whole picture — a variety of materials and configurations have been reported and distinct goals have been targeted — this exemplifies the current state of (2D material)-based membranes. NATMs (blue unfilled and filled squares) generally exhibit high flux due to their ultrathin nature but struggle to achieve a sufficiently attractive  $CO_2$  selectivity. Laminate membranes (red unfilled, half-filled, and filled circles) are capable of achieving high selectivity derived from the molecular sieving effect of 2D nanochannels or intercalated NPs. MMMs (green uppointing unfilled and filled triangles) highly depend on the intrinsic permselective nature of the polymer and, despite the positive effect of the 2D material, highly permeable polymers or ultrathin-selective layers are required to get closer to the area of interest [50].

Ironically, the Achilles heel of 2D atomically thin membranes is not the membrane itself but, in many cases, the porous support that enables its freestanding configuration. The material support must be atomically flat and provide enough mechanical strength to enable one-atom-thick membrane to withstand the pressure required for filtration while avoiding the generation of cracks or defects. In addition, the support must have high interconnected porosity, higher permeance than the one-atom-thick layer, high chemical resistance, and allow for strong interactions with the 2D materials to prevent detachment during operation. Thin laminate membranes have been successfully prepared using conventional porous polymeric substrates [27,29,31], which raise less concerns over their scalability, and significantly reduce the membrane manufacturing cost as compared with smoother inorganic supports such as microfabricated silicon ones. Laminate membranes certainly are less sensitive to rough surfaces as compared with NATMs, since gas transport through the multilayer structure is mainly governed by the d-spacing and the influence of the support roughness becomes smaller as the number of lavers increases. However, for the fabrication of ultrathin laminate membranes and NATMs, the presence of defects becomes an issue, and then a flat support with suitable compatibility with the 2D material must be pursued. Porous AAO supports are then the most common choice [25,34,35] as they are flat, highly porous, and offer good compatibility with most inorganic materials. Nonetheless, they are extremely brittle and highly expensive, which limits their use to lab-scale applications. An interesting approach is the preparation of an intermediate layer between the support and the selective layer [36] (so-called 'gutter layer' in conventional thin-film composite membranes). From the experience over the years with conventional polymer membranes, the incorporation of the intermediate layer offers several advantages, such as i) improving interfacial compatibility between the support and the selective layer, ii) creating new permeation pathways, iii) preventing the formation of defects, iv) synergetic effects between the intermediate and selective layer, and v) allowing for some control over the growth of the selective layer. To sum up, the development of 2D material membranes must be accompanied by research in the rational design of novel membrane supports.

Gas separation membranes market is nowadays governed by polymeric membranes due to their cost-effective fabrication processes, high stability, and reproducibility. However, they cannot afford the more significant evervday niche market of high-temperature applications. due to plasticization. It is precisely such weakness which 2D materials can harness to reach the membrane market. Furthermore, 2D materials are metallic, semimetallic, semiconductors, and superconductors [51]. All these rich arenas of physical properties could be potentially exploited to develop the next generation of multifunctional membranes where some external stimuli such as light [52] or electric field [53] could play a central role in the development on disruptive solutions. Particularly interesting, it could be to revisit the possibility to use superconductors [54], now with the recently discovered 2D counterparts [55], to separate diamagnetic (N<sub>2</sub>, Ar, and CO<sub>2</sub>) and paramagnetic (O<sub>2</sub>, NO) mixture of gases by means of the Meissner effect.

2D materials also show promise for future quantum sieves [56–58] since quantum effects dominate when the membrane pore size is in the Angstrom level. It is therefore expected that such materials could be used to separate isotopes where the investigation in novel solutions is scarce, and the methods used are energy-consuming and up to some extent inefficient. Alternatively, 2D materials could perform isotope separation at room temperature in a more efficient way.

Olefin/paraffin separations are another interesting application in which polymer membranes fail to deliver the required separation performance due to the similar physical and chemical properties of the gases. 2D material-based membranes, capable of achieving precise size-sieving abilities at high permeances [29,59], outperform conventional polymer membranes and could potentially give rise to the first generation of membranes for this particular separation. In addition, 2D materials may also serve as platforms for the deposition of compounds with molecular recognition abilities, which can be used in combination with their size-sieving abilities to further improve membrane performance [59].

## **Data Availability**

Data will be made available on request.

## **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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