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Review

Graphene in gas separation membranes—State-of-the-art and potential spoors

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Abstract: Graphene and derivatives have been frequently used to form advanced nanocomposites. A very significant utilization of polymer/graphene nanocomposite was found in the membrane sector. The up-to-date overview essentially highlights the design, features, and advanced functions of graphene nanocomposite membranes towards gas separations. In this concern, pristine thin layer graphene as well as graphene nanocomposites with poly(dimethyl siloxane), polysulfone, poly(methyl methacrylate), polyimide, and other matrices have been perceived as gas separation membranes. In these membranes, the graphene dispersion and interaction with polymers through applying the appropriate processing techniques have led to optimum porosity, pore sizes, and pore distribution, i.e., suitable for selective separation of gaseous molecules. Consequently, the graphene-derived nanocomposites brought about numerous revolutions in high-performance gas separation membranes. The structural diversity of polymer/graphene nanocomposites has facilitated the membrane selective separation, permeation, and barrier processes, especially in the separation of desired gaseous molecules, ions, and contaminants. Future research on the innovative nanoporous graphene-based membrane can overcome design/performance-related challenging factors for technical utilizations.

Keywords: graphene; polymer; nanocomposite; membrane; gas separation; selectivity; permeation

1. Introduction

For environmental remediation purposes, membrane technology has been widely adopted, especially for the separation of desired or toxic gaseous species [1]. Among membranes, polymeric membranes have durability, long functioning, and efficient performance, so they have achieved significance for separation applications. The graphene-filled nanocomposite membranes possess superior characteristics for technical fields such as gaseous, water molecules, and chemical separations [2]. The subsequent membranes were formed for large-scale gas separation, water decontamination, fuel cells, and several other applied fields [3,4]. Primarily, the graphene-derived nanocomposite membranes have been developed with torturing pathways in the matrices to promote gaseous, water molecules, ions, or diffusion of other species [5]. Consistent graphene dispersion in the membranes was found to improve the targeted impurities and toxic molecules from the medium of interest [6,7]. The membrane processes studied for these nanocomposites include ultrafiltration, microfiltration, nanofiltration, and reverse osmosis [8–10]. The resultant membranes were competently applied for eliminating the pollutants [11]. The graphene-reinforced membranes revealed superior structural benefits than the pristine polymer designs due to facile manufacturing and performance advantages [12]. Research developments have reported technical growth of these membranes for numerous sectors [13].

In the polymeric membranes, graphene, graphene oxide, and other modified graphene forms have been applied [14]. It is worth mentioning that the thin layer of neat graphene nanosheet has been designed for selective permeation of gaseous molecules [15]. In polymeric matrices, graphene has revealed fine reinforcement effects relative to other carbon nanofillers (fullerene, carbon nanotube, etc.) [16]. Including multilayered graphene or graphene oxide in the polymer membranes has been known to form two-dimensional nanochannels for the selective permeation and barrier effects of gaseous molecules [17]. Efficient and facile processing technologies have been applied, such as solution casting, doctors blading technique, in situ method, phase inversion, infiltration, lift-off/float-on, etching, etc. [18,19]. Mostly, thermoplastic matrices have been examined to form graphene-derived nanocomposites and membranes for gas separation [20–22]. The pore sizes and graphene dispersion patterns directly affect the gaseous molecular permeability and diffusivity features of these membranes [23–25]. Consequently, graphene scattering and layering in matrices have been known to develop percolation trails for the diffusing gaseous molecule [26]. However, fine graphene dispersion, optimization of pore sizes, and processing conditions have yet to be attained towards high-performance commercial-scale gas separation membranes. Applications of gas separation membranes for gaseous pollutants and desired molecules were found in the fields of fuel cells, gas sensors, chemical industries, etc. [27,28].

This review basically focuses on the design, development, and aspects of graphene-derived nanocomposite membranes for selective gas permeation applications. Fine graphene dispersion, interface effects, and optimum pore formation in the membranes have broadened the potential of the gas partition membranes. This overview is groundbreaking to portray the methodical progressions of graphene resultant membranes for gas separation. For the separation of gaseous species from mixtures, various polymer matrices have been filled with the graphene nanofillers to form the selectively permeable membranes. To the best of knowledge, this state-of-the-art review is innovative to depict the advancements in gas separation membranes, including the membrane designs, physical properties, and effect of graphene inclusion on the gas transportation features. This manuscript has been found indispensable for the future advances of gas separation graphene nanocomposite membranes, and so it can be a helpful guide for the interested field researchers.

2. Graphene

A two-dimensional nanosheet like carbon nanostructure is referred to as graphene [29]. It is constituted of sp^2 hybridized carbon atoms, discovered in 2004 [30]. Graphene was synthesized using numerous strategies like mechanical or liquid exfoliation of graphite, chemical vapor deposition, laser technique, plasma practice, and chemical synthesis methods [31–33]. Graphene is a thin, layered, transparent nanostructure [34]. Graphene has high electron mobilization of around 200,000 $cm^2V^{-1}s^{-1}$ and high thermal conductivity of 3000–5000 W/mK [35]. Excellent mechanical properties of graphene include a high Young's modulus of 1 TPa and a strength of >200 times that of steel [36]. Graphene nanosheets have a wrinkling effect due to the van der Waals interactions [37]. To enhance the dispersion effects and final features, graphene nanosheets have been functionalized to introduce various surface functionalities such as hydroxyl, carbonyl, carboxylic, epoxide, etc. [38]. The properties of graphene have been synergistically combined with other nanomaterials to form the nanocomposites. Graphene-based nanocomposites revealed numerous superior electrical, mechanical, thermal, and physical features [39–41]. Consequently, the graphene-derived nanomaterials have been applied in wide-ranging technological structures and applications like electronics, sensors, actuators, energy devices, including fuel cells, batteries, membranes, engineering structures, and biomedical advanced devices [42].

3. Graphene and nanocomposites in gas separation

Graphene-based nanoporous membranes have been applied for gas molecule transport [43–45]. The ultrathin graphene nanosheets have been designed for gas separation [46–48]. Lee et al. [49] studied the selective separation of carbon dioxide CO_2 molecules from CO_2/CH_4, CO_2/O_2, and CO_2/N_2 gas mixtures. Graphene nanosheets have affinity for CO_2 molecules, and pores in graphene nanosheets were suitable for the passage [50–52]. Among the gas mixtures, a high gas flux was observed for CO_2/O_2 at 0.43 [53]. Jiang et al. [54] used first principles density functional theory to examine the permeability and selectivity of nanoporous graphene nanosheets. **Figure 1** shows graphene nanosheet with hydrogen-passivated pore. The nanopore width was 0.02 Å according to electron density isosurface isovalue. The snapshot of gas molecules passing is given in **Figure 2**.

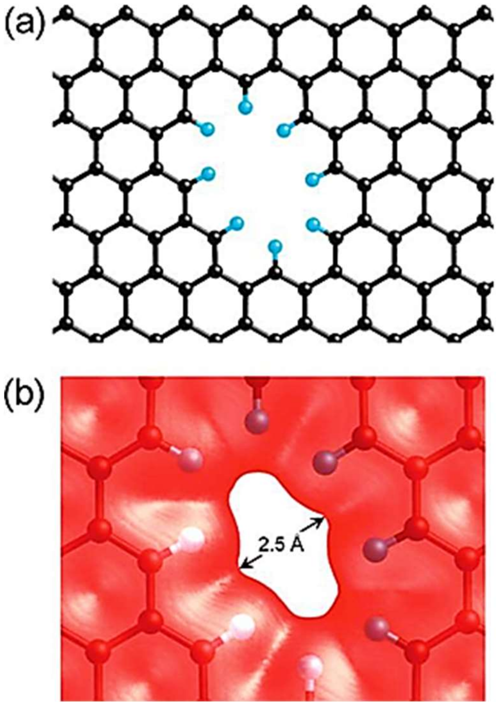

Figure 1. (a) An all-hydrogen passivated pore in graphene; **(b)** pore electron-density isosurface Isovalue is at 0.02 e/Å3 [54]. Reproduced with permission from ACS.

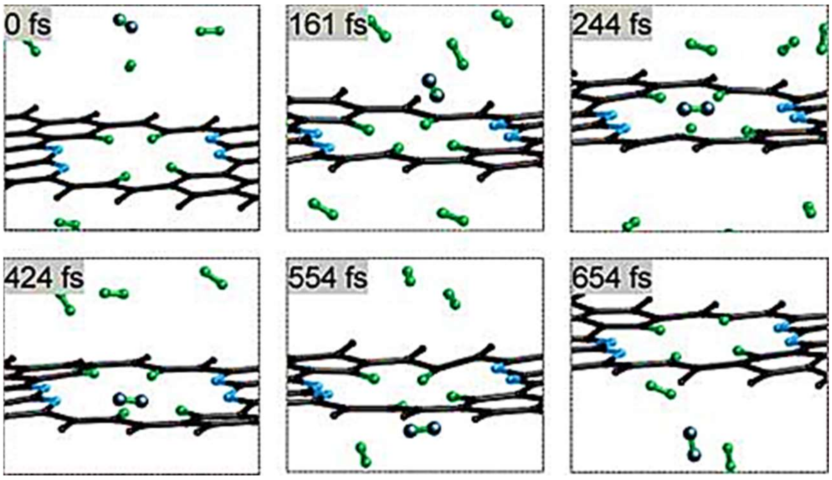

Figure 2. Molecular dynamics simulations of H_2 diffusing through nitrogen functional pore (600 K) [54]. Reproduced with permission from ACS.

According to geometry optimization studies, H_2 molecules entered through pores at 244 fs, and molecules stayed there for 180 fs. Then molecules diffuse out through pores at 424 fs. High H_2/CH_4 permselectivity was observed, as per first principles molecular dynamics simulation studies on porous graphene. It has been observed that hydrogen atoms on graphene nanopores decreased the pore width to 2.5 Å, while the pore length remained the same as 3.8 Å (**Figure 3**). Consequently, the interaction energy of incoming molecules with graphene nanosheets and diffusion barriers affected molecular adsorption or transportation. The resulting van der Waals density functional barrier for H_2 and CH_4 was observed as 0.22 and 1.60 eV, respectively.

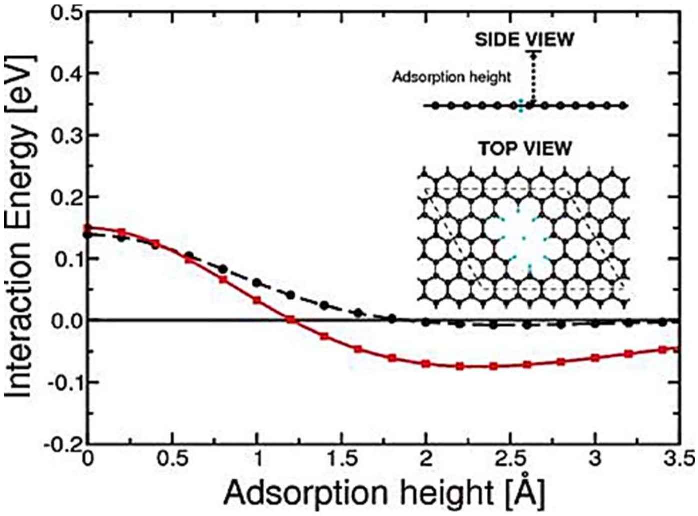

Figure 3. Interaction energy between H_2 vs. adsorption height. Inset: adsorption height and orientation of H_2. Red squares/solid lines = vdW-DF; black circle/dashed lines = PBE [54]. Reproduced with permission from ACS.

The graphene membranes having porous nanostructures were designed and studied aiming for gas separation [55–57]. Graphene and graphene oxide membranes were designed with fine pores for molecular sieving purposes. Koenig and colleagues [58] deposited the single-layered graphene on a silicon oxide substrate. The graphene layer was studied for the permeation of gas molecules. The etching process was applied for the separation of the membrane from the substrate. The pristine graphene nanosheet is not permeable to gas molecules; however, the etched graphene membrane had a porous nanostructure for gas molecule passage. Consequently, the etched graphene nanosheet was permeable to H_2 and CO_2 gas molecules [59–61]. Li and researchers [62] designed the ultrathin porous graphene oxide membranes with pore sizes of −0.34 nm to 1 nm. The membranes were studied for permeability and selectivity properties of CO_2, H_2, N_2, and gases. The H_2/CO_2 selectivity of 3400 and H_2/N_2 of 900 were observed [63,64]. Smaller gas molecules revealed facile permeation relative to the larger molecules through the porous membranes [65–67].

For gas separation applications, poly(methyl methacrylate) was applied for effective membrane thermoplastic material [68–70]. For the formation of polymer/graphene nanocomposite membranes, facile methods have been used [71,72]. Most commonly, the solution casting procedure has been applied [73]. In this method, the polymer is dissolved in an appropriate solvent. The nanoparticles of interest are also dispersed in a solvent. Afterwards, both the dispersions are mixed to yield a consistent phase. The mixed solution is spread on an open surface to evaporate the solvent. The phase inversion method has also been used for the fabrication of graphene-filled nanocomposite membranes [74]. In this procedure, polymer is transformed from the liquid to solid phase. During this process, controlled solution evaporation and immersion precipitation are involved. Additionally, interfacial polymerization has been used for the formation of graphene nanocomposite membranes [75]. Interfacial polymerization consists of various steps such as oil phase formation, emulsification, and finally solvent evaporation. All the membrane formation methods have capabilities for fine dispersion of graphene nanofiller in the polymeric matrices.

Baldanza and co-workers [76] developed the graphene-filled poly(methyl methacrylate) nanocomposite membranes by applying the wet deposition process. Here, the ‘lift-off/float-on’ method was used for obtaining membrane [77–79]. For the preparation of fine graphene nanosheets, the chemical vapor deposition practice was used. **Figure 4** illustrates the lift-off/float-on procedure for the membrane formation. The poly(methyl methacrylate)/graphene nanocomposite membrane with 0.06% loading had a thickness of 550 nm. According to the scanning electron microscopy images, graphene nanosheets were found to be sequentially layered in the polymeric membranes. According to permeability coefficients of humidified or pure O_2 and CO_2 measured for varying R.H. levels for poly(methyl methacrylate) and poly(methyl methacrylate)/graphene, the resultant membranes own a lower permeability coefficient of 1.30×10^{-17} and 0.21×10^{-17} $\text{mol·m·m}^{-2}\text{·Pa}^{-1}\text{·s}^{-1}$, respectively, for CO_2 and O_2, than the unfilled polymeric membrane (**Figure 5** and **Table 1**). The reduced permeability values of gases were attributed to the formation of better dispersion and the development of more twisted gas diffusion paths for gas molecule permeation [80]. Nevertheless, few studies have reported the poly(methyl methacrylate) and graphene nanocomposite-based gas separation systems, and more concentrated future research efforts may lead to the formation of high-performance selective gas permeation membranes.

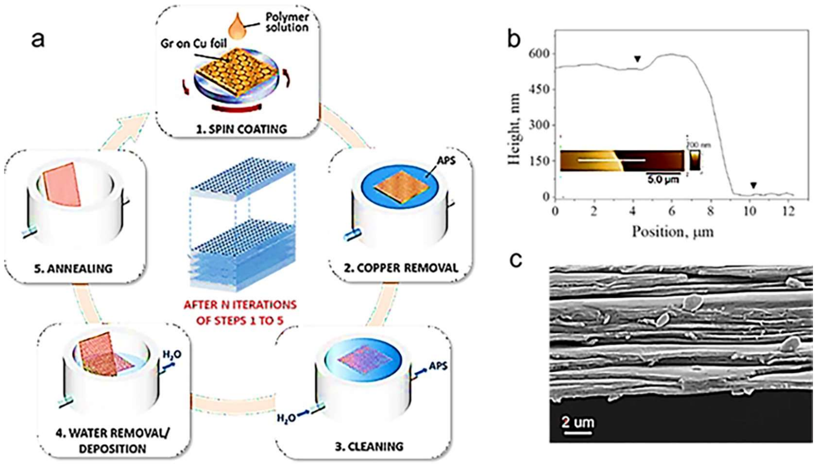

Figure 4. (a) 'Lift-off/float-on' and wet depositions adopted to produce poly(methyl methacrylate); **(b)** thickness of single nanocomposite layer on Si wafer (inset: cross-section AFM); **(c)** SEM cross-section plane of nanolaminate [76]. Reproduced with permission from MDPI.

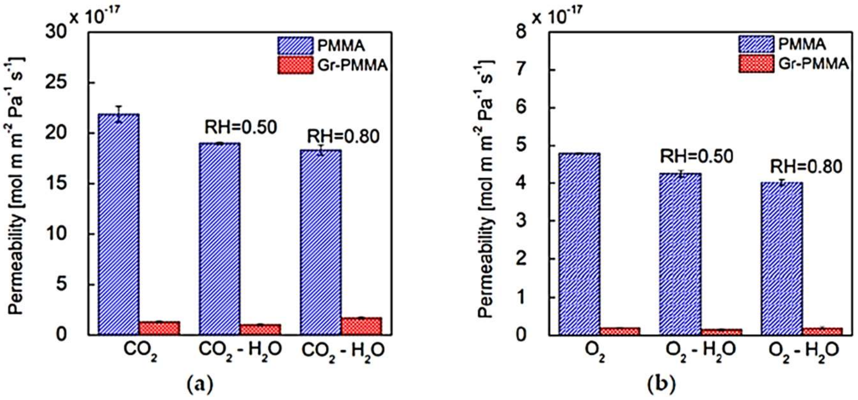

Figure 5. Gas permeability coefficients (25 °C), PMMA (blue bars) and Gr-PMMA (red bars): **(a)** CO_2 and humidified CO_2; **(b)** O_2 and humidified O_2 [76]. Reproduced with permission from MDPI.

Table 1. Permeability coefficients of CO_2 or O_2 through PMMA nanocomposite [76]. Reproduced with permission from MDPI.

Nanolaminate/Permeating Gas	P [mol·m·m^{-2}·Pa^{-1}·s^{-1}]	P [Barrer]
PMMA/CO_2	21.9 (± 0.8) × 10^{-17}	6.5 (± 0.2) × 10^{-1}
Gr-PMMA/CO_2	1.30 (± 0.1) × 10^{-17}	0.39 (± 0.03) × 10^{-1}
PMMA/O_2	4.79 (± 0.01) × 10^{-17}	1.434 (± 0.003) × 10^{-1}
Gr-PMMA/O_2	0.21 (± 0.01) × 10^{-17}	0.063 (± 0.003) × 10^{-1}

Poly(dimethyl siloxane) was investigated towards essential material aiming membrane formation [81–83]. The separation processes of carbon dioxide and other toxic gases have been studied using the poly(dimethyl siloxane) membranes. Here, membrane thickness has been found to affect the gas permeability and separation properties [84]. To enhance the membrane features, nanofillers have been reinforced in the matrices for fine performance. Ha and co-workers [85] reported on the graphene oxide-filled poly(dimethyl siloxane) membranes through solution processing. The kinetic diameters of CO_2, O_2, N_2, and CH_4 gases (in the range of 0.16 to 0.50 Å) affected the selectivity and permeability performance according to membrane porosity and microstructures. The membrane permeability was observed up to 99.9% by including 8 wt.% graphene oxide. Moreover, selectivity properties of the CO_2/CH_4, CO_2/O_2, and CO_2/N_2 have been observed. The gas transportation features were found to be reliant on the fine nanoparticle scattering in the polymer matrix. The microstructure and matrix-nanofiller interactions were also observed to be linked with the nanofiller alignment and scattering in the matrix for the formation of gas transportation pathways. Koolivand and researchers [86] fabricated the poly(dimethyl siloxane) and graphene oxide-derived membranes. Facile Hummer's method was used to form graphene oxide [87]. For these membranes, the combination of solution and ultrasonication processing methods have been applied. Adding 5 wt.% graphene oxide loading, CO_2 permeability and CO_2/CH_4 selectivity of 29% and 112%, respectively, were observed. Berean et al. [88] opted for solution processing and ultrasonication for the formation of poly(dimethyl siloxane)/graphene nanocomposite membranes. Due to the interactions, graphene dispersion and matrix-nanofiller interactions have been perceived. **Figure 6** shows a change in the permeability behavior of the membranes with graphene loading. The membrane permeability was about 60% enhanced with the nanofiller loading for CO_2, N_2, Ar, and CH_4 gases. Among these, CO_2 had greater permeation with the 0.5 wt.% graphene than other gases showing permeation at 0.25 wt.%. The greater permeation of CO_2 at higher nanofiller contents was observed due to its fine affinity towards graphene nanosheets.

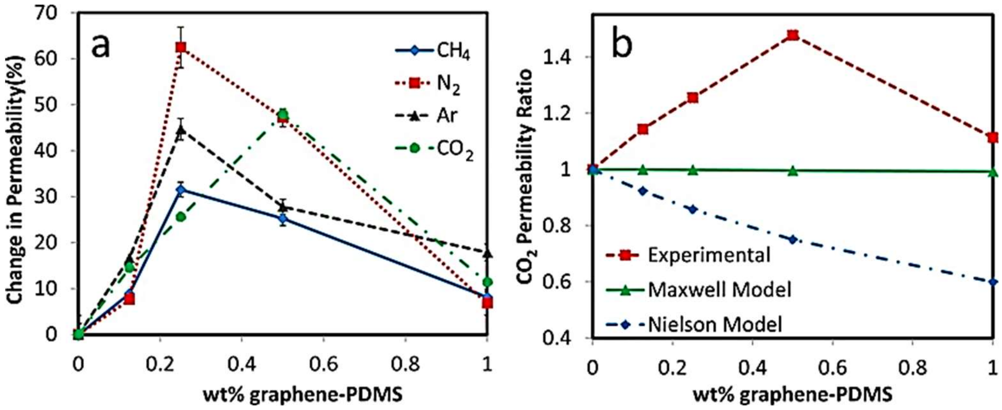

Figure 6. (a) change in permeability for gas species with graphene concentration; **(b)** experimental data, Maxwell model & Nielson model for CO_2 permeation (0.25 wt.% nanocomposite) [88]. Reproduced with permission from ACS.

Figure 7 depicts the formation and behavior of diffusion pathways in poly(dimethyl siloxane) and graphene-reinforced poly(dimethyl siloxane) nanocomposites. Aligned graphene nanosheets developed layered nanostructures with voids in the matrix. The formation of continuous gas diffusion trails was responsible for the passivation of the gaseous molecules through the matrix. Gas permeability of N_2, CO_2, Ar, and CH_4 was enhanced up to 60% with just 0.2 wt.% graphene contents. Consequently, neat poly(dimethyl siloxane) had CO_2/CH_4 selectivity of 3.6, which was increased up to 4.2 in the poly(dimethyl siloxane)/graphene membrane.

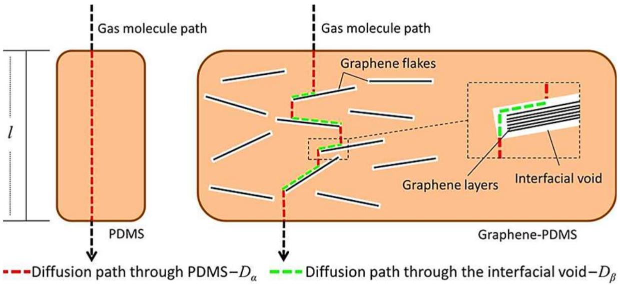

Figure 7. Diffusion paths for PDMS and PDMS/graphene nanocomposites, path length = l; diffusion path (Dα) = red; diffusion path through interfacial void (Dβ) = green [88]. Reproduced with permission from ACS.

Polysulfone has been used as a popular matrix for membrane formation and also for the gas separation application [89–91]. In this context, the mixed matrix membranes of polysulfone have been reported [92–94]. The resulting polysulfone membranes have been observed to be functional for toxic gas separation such as carbon dioxide, nitrogen, and sulfur oxides [95]. Zahri and co-workers [96] reported on polysulfone and graphene oxide-based membranes through the dry wet phase inversion process. The polysulfone-based nanocomposite membranes revealed high CO_2 permeability of 64–87 GPU. In addition, with the nanofiller loading, CO_2/CH_4 selectivity was increased in the range of 19–25. The fine selectivity of the nanocomposite membranes was credited to the dispersal patterns in the polymer matrix [97]. Sainath and co-worker [98] designed the mixed matrix gas separation polysulfone/graphene oxide nanocomposite membrane for gas separation using the solution method. As compared to a pristine polysulfone membrane, the graphene oxide-filled system revealed >3 times higher selectivity for CO_2/CH_4. Fine selectivity was attributed to the homogeneous dispersion and formation of efficient diffusion trails in the matrix. Zhu and co-workers [99] opted for the vacuum infiltration process to form graphene oxide-filled nanocomposite membranes of the phosphotungstic acid-grafted polyphenylsulfone-pyridine matrix. Transmission electron micrographs of polyphenylsulfone-pyridine, phosphotungstic acid, and graphene oxide-based systems are given in **Figure 8**. The nanofiller was observed to be homogeneously dispersed in the polymer matrix.

With the increasing nanofiller concentrations, fine nanoparticle distribution was observed in the matrix. In addition, with increasing nanoparticle loading, pore diameter as well as porosity have been found to enhance. It has been observed that the grafting of polymer matrix was also effective to disperse the nanofiller particles in the matrix. Henceforth, polysulfone and derivative-based membranes with graphene or graphene oxide have been developed with superior morphology, gas separation, selectivity, and permeation performance.

Some membrane systems based on polyimide and graphene have been reported for efficient gas separation [100–102]. An attempt by Melicchio and colleagues [103] used the knife casting method to form graphene oxide-filled Matrimid® 5218 polyimide-derived membranes. The membranes were studied for the permeability and selectivity of H_2 and CO_2 gases. H_2/CO_2 selectivity was found as 3.5, while the permeability of H_2 and CO_2 gases was 8–28 Barrer. The nanocomposite membrane permeability and selectivity were found to rely on the nanofiller contents and dispersion in the polymer matrix.

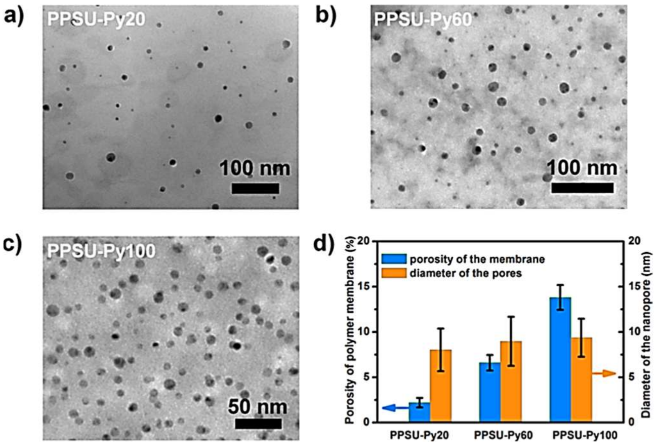

Figure 8. Transmission electron microscopy images with different pyridine moiety proportions in PPSU-Pyx (polyphenylsulfone-pyridine) **(a)** 20%; **(b)** 60%; **(c)** 100%; **(d)** porosity and diameter of membranes [99]. Reproduced with permission from ACS.

For membrane application, poly(1-trimethylsilyl-1-propyne) matrix material has been found useful [104–106]. Albertoa and co-workers [107] formed graphene-reinforced poly(1-trimethylsilyl-1-propyne for CO_2 separation. Accordingly, the CO_2 permeability of poly(1-trimethylsilyl-1-propyne)/graphene nanocomposite membrane was 3.5×10^3 Barrer, i.e., 39% lower than the neat polymer membrane. For poly(1-trimethylsilyl-1-propyne), graphene oxide has been rarely used as a nanofiller. Olivieri et al. [108] designed the graphene oxide-filled poly(1-trimethylsilyl-1-propyne) using solvent technique with chloroform. For the membranes, the CO_2, N_2, and CH_4 gases had diffusion coefficients of 25%, 14%, and 9%, respectively. The membrane systems based on poly(2,6-dimethyl-1,4-phenylene oxide) have also been researched [109–111]. Rea and colleagues [112] developed 0.3–15 wt.% graphene-filled poly(2,6-dimethyl-1,4-phenylene oxide) membranes. According to scanning electron micrographs, the matrix-nanofiller interfaces have been observed with the nanofiller flakes dispersed in the membrane matrix (**Figure 9**). The membrane permeability was studied at 35 and 65 °C (**Figure 10**).

For He, CO_2 and N_2, the membrane permeability was found to slightly decrease with the nanofiller loading levels. The decreasing permeability was attributed to the increased nanofiller dispersion and membrane selectivity towards these gases. The dispersed graphene nanoplatelets were supposed to develop percolation pathways for the diffusion of gaseous species. **Table 2** shows the permeability behavior of the membranes with different nanofiller loadings at 35 and 65 °C. In this way, efficient graphene-filled nanocomposite membranes have been designed for the selective gas separation or permeation properties [113–115]. The selective permeability of the membranes was found to depend upon nanofiller scattering plus alignment in the matrix [116,117]. Future studies on advanced graphene nanocomposite membranes may lead to better gas molecule separation from mixtures of gases.

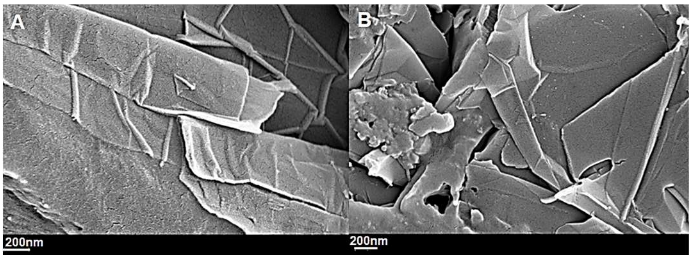

Figure 9. SEM images of membranes. **(A)** PPO/0.3 wt.% graphene; **(B)** PPO/1 wt.% graphene [112]. SEM=scanning electron microscopy; PPO = poly(1-trimethylsilyl-1-propyne). Reproduced with permission from MDPI.

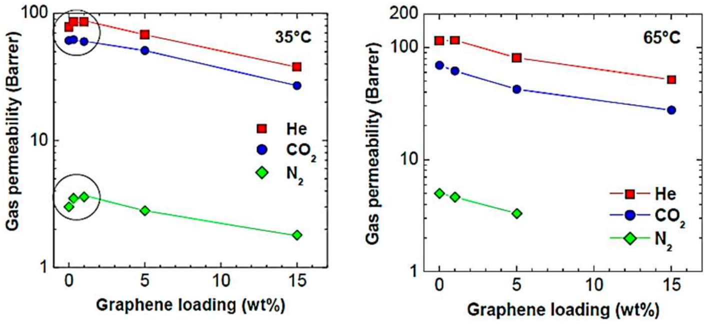

Figure 10. Gas permeability. **(a)** 35 °C; **(b)** 65 °C; and after graphene addition (as a function of graphene loading in poly(1-trimethylsilyl-1-propyne) matrix [112]. Reproduced with permission from MDPI.

Table 2. Permeability of the various gases in PPO and nanocomposite membranes [112]. PPO = poly(1-trimethylsilyl-1-propyne). Reproduced with permission from MDPI.

Permeability at 35 °C, Barrer	**PPO**	**PPO/0.3 wt.% graphene**	**PPO/1 wt.% graphene**	**PPO/5 wt.% graphene**	**PPO/15 wt.% graphene**
He	78 ± 3.8	86 ± 4.2	86 ± 4.1	68 ± 2.0	38 ± 3.2
N_2	3.0 ± 0.2	3.5 ± 0.2	3.6 ± 0.2	2.8 ± 0.1	1.8 ± 0.2
CO_2	61 ± 2.0	62 ± 2.9	60 ± 2.9	51 ± 1.5	27 ± 2.3
Permeability at 65 °C, Barrer	PPO	PPO/0.3 wt.% graphene	PPO/1 wt.% graphene	PPO/5 wt.% graphene	PPO/15 wt.% graphene
He	114 ± 5.0	-	116 ± 6.7	81.0 ± 2.4	51.6 ± 4.4
N_2	5.00 ± 0.4	-	4.64 ± 0.3	3.31 ± 0.1	-
CO_2	69.3 ± 2	-	61.9 ± 3.6	42.3 ± 1.2	27.6 ± 2.4

4. Prospects, challenges and gaps

In the formation and application of graphene nanocomposites as high-performance membrane materials, numerous challenges have been faced during the field research efforts. Generally speaking, not much effort has been observed for various categories of polymer/graphene nanocomposite membranes such as poly(dimethyl sulfoxide)/graphene, polysulfone/graphene, poly(methyl methacrylate)/graphene, polyimide/graphene, polyamide/graphene, etc. The experimental designs of the polymer/graphene nanocomposite membranes have been reported using the matrices, graphene nanofillers, processing techniques (solution, phase inversion, infiltration, etc.), and related preparation parameters.

Table 3 outlines the experimental design of the gas separation nanocomposite membranes used in important studies. Adding graphene in polymer matrices affected the membrane morphology, physical properties, permeability, selectivity, and separation properties. Polysulfone-based nanocomposite membranes have efficient CO_2/CH_4 selectivity of 45%–74%. For gas separation membranes of poly(dimethyl siloxane) nanocomposites, N_2, CO_2, and other gases permeability was observed >99.9%. Similarly, higher selectivity values for gases like CO_2/CH_4 have been observed. Hence, there is huge scope for fabrication and investigations on graphene-based air/water purification membranes.

Development and investigation of more designs definitely can lead to better analysis of optimum fabrication, selectivity, permeation, and gas separation performance, along with better understandings on the structure-property relationship and mechanism of innovative graphene membranes [118]. Major challenges hindering the gas separation membrane performance have been observed as graphene dispersion depending upon nanofiller contents, functionality, matrix nanofiller interactions, and interface formation [7]. The formation of interweaving pathways due to graphene dispersion in the polymer matrices has directly influenced the gas transportation properties. Controlled pore sizes, shapes, and distribution in the matrices have also been found indispensable to promote the gas membrane performance. Important solutions to the nanofiller dispersion have been proposed depending upon the graphene modification as well as by applying appropriate processing techniques and steps with the optimized conditions [119]. Further challenges have been observed regarding the fabrication of graphene-based membranes on a large scale and subsequent commercialization. Here, the appropriate fabrication techniques and processing parameters need to be implemented for the massive production of graphene nanocomposite membranes. In this case, the development of nanofibrous polymer/graphene membranes must be developed with a high surface area and well-dispersed nanoparticles for separating the desired gaseous molecules [120]. By controlling and overcoming all the above-mentioned graphene and graphene nanocomposite membrane design and processing challenges leading to the fine microstructure, robustness, permeability, selectivity, and barrier characteristics [121]. Briefly speaking, further research on the mentioned line may lead to the proposition of high-tech future gas transportation membranes for commercial purposes.

Table 3. Significant features of polymer/graphene nanocomposite membranes for gas separation.

Polymer	**Nanofiller**	**Fabrication way**	**Physicochemical properties**	**Membrane properties**	**References**
Polymer	Graphene or graphene oxide	Solution casting	Ion-molecule interaction; 1.8–20 nm thickness	H_2/N_2 selectivity 900; H_2/CO_2 selectivity 3400; pore size 0.34 nm	[62]
Poly(dimethyl siloxane)	Graphene oxide	Solution casting	Matrix-nanofiller interactions; interaction between graphene oxide and polymer	8 wt.% nanofiller; H_2, O_2, N_2, CH_4 and CO_2 permeability 99.9%	[85]
Poly(dimethyl siloxane)	Graphene oxide	Solution/ultrasonication methods; tetrahydrofuran solvent	Interfacial interactions between functional groups of graphene oxide and polymer; density 1.09–1.12; Thickness 1.9–2.8 nm	5 wt.% nanofiller; CO_2/CH_4 selectivity 112%; CO_2 permeability 29%.	[86]

Table 3. (*Continued*).

Polymer	Nanofiller	Fabrication way	Physicochemical properties	Membrane properties	References
Poly(dimethyl siloxane)	Graphene	Solution casting; p-xylene solvent	π-π interactions in matrix-nanofiller	0.2 wt.% nanofiller; N_2, CO_2, Ar, and CH_4 permeation 60%; CO_2/CH_4 selectivity 4.2	[88]
Polysulfone	Graphene	Phase inversion; hollow fiber mixed matrix membrane	Nanosize synthesized graphene; Interfacial interaction between graphene and polymer matrix	CO_2/N_2 selectivity 158%; CO_2/CH_4 selectivity 74%	[97]
Polysulfone	Graphene oxide	Solution route; N-Methyl-2-pyrrolidone solvent	Physical interaction between oxygenated functional groups of graphene oxide and polymer; Interactions between functional groups of nanocomposites and gas molecules	CO_2/CH_4 selectivity 45	[98]
Polyphenylsulfone-pyridine	Graphene oxide	Vacuum infiltration technique	Wettability and surface charge response to pH; acidic pH = 3 form hydrophilic state contact angle 63.3°; alkaline pH = 11 form hydrophobic state contact angle 106.5°; charge-density-tunable nanoporous; power of ≈ 0.76 W m^{-2}	Dispersion; morphology	[99]
Poly(1-trimethylsilyl-1-propyne)	Graphene oxide	Solution casting; chloroform solvent	Anchoring of graphene oxide nanosheets lowers membrane flexibility; less free volume; covalent cross-linking of polymer	1 wt.% graphene; diffusion coefficients CO_2 (25%); N_2 (14); CH_4 (9%)	[108]
Poly(1-trimethylsilyl-1-propyne)	Graphene	Solution route	Interaction between filler andpolymer matrix; 0.93–1.36 MPa; 38–44 MPa	0.05 wt.% nanofiller; CO_2 permeability 3.5 × 10^3 Barrer	[107]
Poly(2,6-dimethyl-1,4-phenylene oxide)	Graphene	Solution route	Void formation at interface; glassy polymer filled with graphene; graphene inclusion for physical constraint to relaxation of polymer chains	0.3–15 wt.% nanofiller reduced permeability	[112]

The research progress on the polymer/graphene nanocomposite membranes has led to several advances in the kinds, design, and applications to overcome the crucial foremost problems in this field. These separation membranes have been used for the efficient removal of gaseous pollutants with optimally high flux and permeation. For this purpose, microstructure and mechanical features like strength and flexibility have been considered important. For the enhancements in these properties, nanoparticle dispersion has been found significant for the matrix-nanofiller interactions to advance the ultimate membrane characters. In this context, compatibility of graphene nanoparticles with matrices must be enhanced for better miscibility and reinforcing effects. The pore shape, size, and distribution in the matrices have been found to affect the membrane selectivity/permeability features. The most important challenges of graphene-based gas separation membranes include graphene nanosheet aggregation, phase separation, and uncontrolled and undefined fabrication parameters. Such undefined conditions may lead to the different pore shapes, sizes, and random distribution in the matrices. The membranes with various pore sizes and shapes may cause major hinderances towards the separation of particular gaseous molecules of specific types. The random pore distribution in membranes also affects the strength, durability, and life of the membranes. In addition, poor membrane performance may result in restricted cyclic uses. Consequently, the uncontrolled membrane features may cause poor barrier effects and selective molecular transportation. Hence, perfect membrane design features need to be identified before commercial-scale production of these membranes. Investigations on the membrane separation mechanisms may be used to overcome the barrier, molecular selective diffusion, and performance challenges. In addition, advanced and facile fabrication methods need to be designed to form efficient membranes with controlled pore dimensions and essential features. Future research to resolve the stated challenging directions can be beneficial for the formation of high-performance gas separation membranes.

5. Conclusions

In this state-of-the-art review article, the design, physical properties, and gas partition features have been scrutinized for important graphene and nanocomposite-based membranes. Consequently, graphene has been filled in various polymeric matrices to form the efficient gas separation membranes. These membranes have been studied for the selective separation or permeation of various toxic or desired gas molecules such as O_2, N_2, CO_2, CH_4, etc. from the gas mixtures. Consequently, the membrane performance has been analyzed based on the microstructure, pore size, pore distribution, and specific tests related to the separation or permeation of the gaseous molecules. It has been observed that by varying the nanofiller contents and nanofiller functionalities, as well as polymer type and fabrication methods, the resulting membrane performance has been rehabilitated. In addition, the graphene alignment and dispersion pattern in the polymer matrices resulted in advanced membrane performance with optimum porosity and tortuous pathway formation for the passage of gas molecules. In the future, well-organized graphene-based membranes need to be designed by overcoming the dispersion and processing challenges behind the development of high-performance systems.

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