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Graphene oxide – molybdenum disulfide hybrid membranes for hydrogen separation

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Abstract

Graphene oxide – molybdenum disulfide hybrid membranes were prepared using vacuum filtration technique. The thickness and the MoS₂ content in the membranes were varied and their H₂ permeance and H₂/CO₂ selectivity are reported. A 60 nm hybrid membrane containing ~75% by weight of MoS₂ exhibited the highest H₂ permeance of 804×10^{-9} mol/m²·s·Pa with corresponding H₂/CO₂ selectivity of 26.7; while a 150 nm hybrid membrane with ~29% MoS₂ showed the highest H₂/CO₂ selectivity of 44.2 with corresponding H₂ permeance of 287×10^{-9} mol/m²·s·Pa. The hybrid membranes exhibited much higher H₂ permeance compared to graphene oxide membranes and higher selectivity compared to MoS₂ membranes, which fully demonstrated the synergistic effect of both nanomaterials. The membranes also displayed excellent operational long-term stability.

Keywords: Graphene oxide; molybdenum disulfide; composite membranes; vacuum filtration; gas separation.

1 Introduction

Gas separation through membranes offers many advantages over traditional separation techniques (such as cryogenic distillation, absorption, etc.), namely, high energy efficiency, smaller footprint, and ease of scale-up [1]. Membrane-based gas separation is suitable for a range of applications such as H₂ separation from various gas streams, N₂ removal from air, and CO₂ separation from flue gas to name a few [2, 3]. In particular, separation of H₂ from gasification, steam reforming or water gas shift process products (gases such as CO₂, CO, CH₄) is an important application as H₂ is considered as a clean energy source.

To be an operationally and economically viable option compared with the current industrial separation technologies, membranes with high selectivity and high permeability are desired, as these two parameters influence the capital and operational costs of the membrane process. In general, the thinner the membrane (the separating layer) is, the higher the flux (i.e. permeance) is, which in turn reduces the capital cost. On the other hand, a highly selective membrane results in lower operational costs. However, membranes are always limited by a trade-off between the selectivity and permeance, as shown by the Robeson trade-off plot [4, 5]. As noted above, thinner membranes are generally desirable as they increase the gas flux, but to fabricate defect-free sub-micrometer thick membranes is challenging.

To this end, development of microporous membranes such as silica [6-8], zeolites [9-12] and ZIF's (zeolitic imidazolate frameworks) [13, 14] among others have shown promising gas separation properties. In addition, recent advances in the development of

sub-micrometer thick membranes fabricated from single-atom-thick nanosheets or 2D layered materials, such as graphene oxide (GO) or molybdenum disulfide (MoS₂), have made the realization for enhanced gas separation membranes possible. These materials, in general, can be easily fabricated into thin films with high chemical robustness. Li et al [15] fabricated very thin GO membranes (1.8–18 nm) that showed the highest H₂/CO₂ selectivity of 3400 (for 1:1 H₂:CO₂ mixture) reported to-date. Chi et al [16] fabricated ~20 nm GO membranes using spin coating method and reported H₂/CO₂ selectivity of around 250 with H₂ permeance of $\sim 340 \times 10^{-9}$ mol/m²·s·Pa. Layered transition metal chalcogenides such as MoS₂ have also been recently demonstrated in membrane based gas separation application. Achari et al [17] employed a 500 nm thick layered MoS₂ membrane which showed H₂/CO₂ selectivity of ~8.2 (more than the ideal Knudsen value of 4.7) with a very high H₂ permeance (780×10^{-9} mol/m²·s·Pa) whereas Wang et al [18] reported very thin (17-60 nm) MoS₂ membranes that exhibited H₂/CO₂ selectivity of 3.4 to 4.4 with a very high H₂ permeance in the range of $818\text{--}9186 \times 10^{-9}$ mol/m²·s·Pa. Based on these results it is clear that GO membranes show high gas selectivity but low gas permeance, whereas MoS₂ membranes exhibit high permeance but low gas selectivity. To explain the contrast performance of these materials, our hypothesis is that GO sheets can pack much more efficiently than MoS₂ sheets. Hence, if using GO as a packing agent, it may help improve the performance of MoS₂ membrane.

Motivated by the results from both GO and MoS₂ membranes, we report here for the first time, to the best of our knowledge, hybrid sub-micron thick membranes containing both GO and MoS₂ mixed together, to synergistically utilize the unique gas separation properties of both materials. The gas separation performance of the membranes was

investigated for H₂ and CO₂ separation as a function of MoS₂ content and membrane thickness, and was found much better than what was expected from the mixed matrix membrane modelling.

2 Experimental

2.1 Materials

Graphite and molybdenum disulfide powders, and chemicals including sulfuric acid, hydrochloric acid, hydrogen peroxide, n-butyl-lithium (1.6 M in hexane) and potassium permanganate, were all supplied by Sigma-Aldrich and were used as received. Absolute ethanol and HPLC grade hexane were procured from VWR chemicals. DI water from Millipore Milli-Q system was used. Anodisc 25 (AAO: Anodic Aluminum Oxide) supports (20 nm pore size, 25 mm diameter) for membrane fabrication were purchased from GE healthcare.

2.2 Graphene oxide (GO) synthesis

Graphene oxide nanosheets were synthesized using the modified Hummer's method [19, 20]. Briefly, 450 ml of sulfuric acid was added to 10 g graphite powder in a beaker under continuous stirring (90 mins). The beaker was kept in an ice bath so as to maintain the solution temperature below 10°C. 30 g of potassium permanganate was slowly added to the above mixture under continuous stirring and the resulting solution was stirred for 3 hours which changed the solution color from black to dark green. After this, the solution temperature was raised to 40°C and further stirred for 1 hour. 450 ml of DI water was added to the solution slowly while maintaining the temperature below 50°C. During this step, the solution turned brown. Following this, 300 ml of hydrogen peroxide (30 wt%) was added to the solution and was then stirred for 2-3 hours, with the resulting solution

turning golden yellow in color. The solution was then filtered to obtain GO cake and washed with 10 wt% hydrochloric acid multiple times and subsequently centrifuged at 10,000 rpm for 30 min in 10 wt% hydrochloric acid. Finally, the GO was washed and centrifuged in water to remove any remaining impurities and un-exfoliated graphite. The resulting solution was filtered and dried at 40°C under vacuum for 24 hours followed by drying at 60°C under vacuum for 24 hours. The dried GO was dispersed in DI water with 30 min sonication to obtain 0.3 mg/ml dispersion, which was then used as stock dispersion for membrane fabrication.

2.3 Molybdenum disulfide (MoS_2) synthesis

MoS_2 nanosheets were synthesized using the controlled exfoliation method described by Fan et al [21]. Briefly, 4 g of MoS_2 powder were added in three-neck round bottom flask and dried at 70°C under vacuum for 24 hours. Following the drying, a continuous argon flow was maintained in the flask for 1 hour to remove air and moisture. Subsequently 40 ml hexane was added in a drop-wise fashion to the flask under continuous argon flow and the resulting solution was stirred for 30 min. To this, 2.5 mmol of n-butyl-lithium was added very slowly. The solution was then stirred at room temperature for 3 days under argon environment. After 3 days, the solution was filtered over a nylon support and the resulting MoS_2 cake washed with copious amount of hexane to remove any unreacted n-butyl-lithium. The cake was then dried under vacuum at room temperature for one day. 300 mg of dried MoS_2 (stable 2H phase) nanosheets were then dispersed in 20 ml of ethanol/water (45:55) mixture and sonicated for 2 hours. After sonication, the resulting dispersion was centrifuged at 6000 rpm for 30 min and the top two-third supernatant was collected and used as stock solution for membrane fabrication.

The dispersion concentration was measured by carefully drying 5 ml of stock solution under vacuum at 40°C and subsequently, measuring the weight of dried MoS₂ nanosheets. This was done on 4-5 batches of the obtained dispersion. The dispersion concentration thus obtained was 0.76 mg/ml.

2.4 Membrane fabrication

Simple vacuum filtration technique was used to fabricate all the membranes, using 25 mm Millipore vacuum filter holder with fritted glass support, over 25 mm AAO supports with 20 nm pores. In general, for pure membranes known amount of GO or MoS₂ (from the stock solution) was dispersed in 50 ml DI water (50 ml of 45/55 vol% of ethanol/water for MoS₂) and further sonicated for 10 min, followed by vacuum filtering the diluted solution over AAO supports to get pure membranes. In case of hybrid membranes, depending on the desired thickness and GO-MoS₂ composition, two dispersions of GO and MoS₂ in 25 ml DI water (for GO) and 25 ml of 55/45 vol% DI water/ethanol (for MoS₂) were prepared and sonicated for 5 min, followed by mixing them together using 10 min sonication to get homogeneously mixed GO-MoS₂ dispersion.

The amounts of nanomaterials were chosen so as to get membranes of desired thickness. For a particular thickness, three membranes were fabricated using different GO and MoS₂ content. The amount of GO and MoS₂ in these membranes was not only adjusted so as to get the desired composition, but also to get membranes that were about similar thickness. The membranes were approximately 60, 100 and 150 nm thick, with composition around 70% GO-30% MoS₂, 50% GO-50% MoS₂ and 25% GO-75% MoS₂.

Table 1 lists the details of fabricated membranes (pure GO, pure MoS₂ and GO-MoS₂ hybrid membranes).

To fabricate membranes with controlled thickness, known amount of given nanomaterial (GO, MoS₂ or GO + MoS₂) was added in 50 ml of DI water (or DI water + ethanol for MoS₂) and then filtered through the AAO support. During filtration, there was no material loss as the support pore size (20 nm) was much smaller than the nanosheets (~1 μ m). The thickness of the fabricated membranes (four representative membranes: GO, MoS₂ and two hybrid membranes) was then measured by cross section SEM images. The thickness obtained from the cross-section SEM for the four representative membranes were then used to calculate or estimate the thickness of the membranes reported in Table 1. The thickness of the membranes can also be calculated from the amount of the nanomaterial filtered, the AAO support filtration area (=3.8 cm²) and the nanomaterial density (GO density = 1.5 mg/ml; MoS₂ density = 5 mg/ml).

Table 1: Membrane details fabricated using vacuum filtration

Membrane	GO wt%	MoS ₂ wt%	Thickness, nm
GO	100	0	50
MoS ₂	0	100	100
GM-60-1	72.46	27.53	59
GM-60-2	51.37	49.62	61
GM-60-3	25.28	74.71	60
GM-100-1	70.30	29.70	108
GM-100-2	47.90	52.10	98
GM-100-3	24.80	75.20	101
GM-150-1	71.15	28.84	148
GM-150-2	50.53	49.46	150
GM-150-3	24.75	75.25	151

3 Characterization

3.1 Materials

The synthesized materials were characterized using Transmission electron microscopy (TEM), Atomic force microscopy (AFM) and Ultraviolet–visible spectroscopy (UV-vis spectroscopy). TEM images were taken on Titan CT (FEI) transmission electron microscope operated at 300 kV. The stock dispersion was diluted by 100 times in DI water (+ ethanol in case of MoS₂) and a drop of the diluted dispersion was transferred to TEM grid followed by drying under vacuum at 40°C for 6 hours before TEM analysis. UV-vis spectra of the diluted (1:20 dilution of the stock solution) dispersions were recorded using an Agilent Cary-100 UV-vis spectrometer. Atomic force microscopy (AFM) was performed on an Agilent 5400 Scanning Probe Microscope (SPM). 2-3 drops of the diluted suspension (1:100 times dilution of stock solution) were transferred onto Si wafers and dried at 40 °C for 6 h before being analyzed by AFM. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet iS10 smart FTIR spectrometer (Thermo Scientific, USA) equipped with a smart OMNI transmission ranging from 4000 cm⁻¹ to 400 cm⁻¹. Gas sorption isotherms on exfoliated GO and MoS₂ were measured using Micromeritics ASAP 2050 sorption analyzer at 0°C and 25°C for pressure up to ~102 kPa. Before each isotherm measurement, the samples were degassed under vacuum at 60°C for 24 h.

3.2 Membranes

The fabricated membranes were characterized by X-ray diffraction, RAMAN spectroscopy and Scanning electron microscopy (SEM). Bruker AXS D-8 Advance

diffractometer operated at 40 kV voltage and 40 mA current, was used to measure the XRD diffraction pattern of the samples. The Raman spectra of the membranes were collected using Horiba LabRam HR 800 microscope. Surface and cross section SEM images for the membranes were obtained on FEI Nova Nano630 and Magellan XHR SEM respectively.

3.3 *Transport measurements*

Steady state pure and mixed gas experiments were performed in order to measure the transport properties of gases through the membranes. The schematic for the experimental setup is shown in Figure 1. The feed flow rates were controlled using mass flow controllers while on the permeate side, argon (flowrate = 20-50 ml/min) was used as a sweep gas to carry the permeating gas to gas chromatograph (Agilent 7980) for gas composition analysis. The absolute feed pressure was maintained at 1 bar with a total flow rate of 250-400 ml/min and the measurements were done at room temperature. The membranes were capped with Kapton tape with a 6 mm hole (thus effective membrane area = 0.285 cm²) and were installed in 25 mm Millipore stainless steel filter holders for permeation study. Before every measurement, both feed and permeate lines were flushed with argon for 20 min so as to remove any air from the experimental setup. Enough time (3-4 h) was allowed for the gas permeation to reach equilibrium before the measurements were taken. The permeance was reported in the unit of 10⁻⁹ mol/m²·s·Pa since this unit has the following simple relationship with GPU, another commonly used non-SI unit,

$$1 \times 10^{-9} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa} = 3 \text{ GPU}$$

Figure 1: Schematic of the permeation setup

4 Results

4.1 Materials and membrane characterization

Figure 2a shows the digital photograph of the as synthesized GO and MoS₂ dispersions. The dispersions exhibited the Tyndall effect (Figure 2b), which confirmed the presence of nanoparticles or the colloidal nature of the dispersions. Figures 3a and 3b show the AFM images and the corresponding height profiles of GO and MoS₂ nanosheets which shows that the exfoliated GO and MoS₂ nanosheets were flat with a uniform thickness. The GO thickness calculated from the three AFM height profiles was around 1.1 nm (± 0.15 nm), while that for MoS₂ was around 3.1 nm (± 0.14 nm). Based on the monolayer thickness of GO [15] and MoS₂ [21], it can be deduced that the exfoliated GO was monolayer while MoS₂ was tri-layer. Most of the GO flakes were in the ~ 0.5 to 1.5 μm size range, whereas the MoS₂ flakes were in the ~ 0.8 - 2 μm size range. The UV-vis spectra for GO, MoS₂ and GO-MoS₂ (50:50 w/w) dispersions are shown in Figure 4. The spectrum of GO shows a characteristic peak at 230 nm, associated with π - π^* interactions, and a broad absorption peak (shoulder) at 300 nm, attributed to n - π^* interactions [22]. For MoS₂, two characteristic peaks at 610 and 670 nm, associated with the A and B direct

excitonic transitions in MoS_2 , respectively [21], were observed. The UV-vis spectrum for the mixed dispersion exhibit the characteristic peaks of both GO and MoS_2 , and is indicative of a homogenously mixed dispersion. The AFM height profiles and the UV-vis spectra for both dispersions thus demonstrate that both exfoliated materials can serve as perfect building blocks for assembling a hybrid-stacked membrane. The TEM images as shown in Figure 5 reveal smooth and transparent layers of both GO and MoS_2 while exhibiting wrinkles and folds/bends and in case of MoS_2 exhibits some overlapped nanosheets.

Figure 2: (a) As synthesized dispersions of GO and MoS_2 and (b) dispersions exhibiting Tyndall effect

Figure 3: AFM images and corresponding height profiles of (a) GO and (b) MoS₂

Figure 4: UV-vis spectra for GO, MoS₂ and 50/50 GO/MoS₂ mixture

Figure 5: TEM images of (a) GO and (b) MoS₂ nanosheets

Figure 6 shows the FT-IR spectra for GO, MoS₂ and GO-MoS₂ mixture. The IR spectra for GO reveal the characteristic bands at 3420 cm⁻¹ (-OH stretching), 1740 cm⁻¹ (C=O stretching), 1620 cm⁻¹ (C=C stretching), 1400 cm⁻¹ (-OH vibration), 1250 cm⁻¹ (C-O vibration of C-OH) and 1080 cm⁻¹ (C-O vibration of epoxy) [23], whereas for MoS₂, a weak absorption peak at 467 cm⁻¹ related to Mo-S stretching can be observed [24]. In the spectra for the mixture, no additional new peaks other than those observed for pure GO and MoS₂ are observed, suggesting that there is no chemical interaction between the GO and MoS₂ nanosheets.

Figure 6: FT-IR spectra for GO, MoS₂ and 50/50 GO/MoS₂ mixture

The digital pictures of five membranes fabricated using vacuum filtration technique (GO, GM-100-1, GM-100-2, GM-100-3 and MoS₂) are shown in Figure 7, showing thin transparent films on the AAO support. The Raman spectra of the as-prepared membranes are shown in Figure 8a. The spectrum of the pure GO membrane exhibits the characteristic D and G bands at around 1335 and 1586 cm⁻¹, respectively [15], whereas the spectrum of the pure MoS₂ membrane displays two peaks at 384 and 407 cm⁻¹ that

correspond to the E_{2g}^1 and A_{1g} phonon modes, respectively [21]. The spectrum of the hybrid membrane exhibits all these peaks, indicating the presence of both types of nanosheets in the membrane. Moreover, the $I(D)/I(G)$ ratio of 1.1 for the GO membrane increased to 1.3 for the mixed membrane. This may be due to the introduction of distortions in the GO assembly by MoS_2 .

Figure 7: Digital pictures of the fabricated membranes on 25mm AAO support. From left to right: GO, GM-100-1, GM-100-2, GM-100-3 and MoS_2 . (cf. Table 1)

Figure 8: (a) RAMAN and (b) XRD spectra GO, MoS_2 and GM-100-2 (50/50 GO- MoS_2 membrane, 100nm)

The X-ray diffraction spectra of the as-prepared membranes are shown in Figure 8b. For the GO membrane, a diffraction peak at 9.26° was observed, which corresponds to an interlayer spacing (or d-spacing) of 0.95 nm, while for MoS_2 , the observed diffraction

peak at 14.23° corresponds to a d-spacing of 0.62 nm, calculated according to Bragg's law. These values are similar to those reported in the literature [21, 25]. In the case of the hybrid membrane, the peaks are slightly shifted, but are broadened compared to those of its components taken separately. This could be due to structural or stacking distortions/disruptions in GO due to the presence of MoS_2 and vice versa.

Figure 9 shows the surface SEM images of three membranes. The GO membrane surface looked smooth with some wrinkles. This could originate from the method of preparation, i.e. vacuum filtration, in which the only force applied is a vertical pulling force, which limits the horizontal alignment of the GO sheets [16]. The MoS_2 surface appeared irregular, with MoS_2 flakes covering the surface of the support with pinholes or defects i.e. it did not form a homogenous smooth membrane layer. The hybrid membranes displayed a clearly different surface morphology from that of the pure membranes. A mix of 2D sheets along with homogeneously distributed nanoparticles was observed. The former are GO nanosheets, whereas the latter some agglomerated MoS_2 nanosheets [26].

Figure 9. Surface SEM images for (a) GO membrane, (b) MoS_2 membrane and (c) GO- MoS_2 (50/50) hybrid membrane

The cross-section images shown in Figure 10 reveal a much clearer picture of the effect of mixing the two types of nanosheets. The GO membrane cross-section shows a very regular lamellar stacking of GO nanosheets without any defects. In contrast, the MoS₂ nanosheets were stacked in a random and irregular way in the MoS₂ membrane. In the case of the hybrid membrane, the stacking was lamellar, as in the pure GO membrane, but with voids created by some agglomerated MoS₂ nanosheets, which basically contribute to “pop up” the hybrid GO-MoS₂ layers. As also seen from the cross-section SEM, the higher the content of MoS₂ in the hybrid membrane, the higher the density of voids.

Figure 10. Cross section SEM images for (a) GO membrane, (b) MoS₂ membrane, (c) GO-MoS₂ (50/50) hybrid membrane and (d) GO-MoS₂ (75/25) hybrid membrane. (*Note:*

the hybrid membranes were made thicker for cross-section SEM images, so as to get good quality images)

4.2 Gas transport results

Gas permeance as a function of the kinetic diameter of the gases, for three membranes; namely GO, MoS₂ and GM-60-2 are shown in Figure 11. GO membranes exhibit the lowest gas permeance among the three membranes, while MoS₂ the highest. H₂ (0.28 nm) being the smallest among the gases tested, permeates faster than other gases such as CO₂ (0.33 nm), N₂ (0.364 nm) and CH₄ (0.38 nm). The order of gas permeance for all membranes is H₂ >> CH₄ > CO₂, N₂. Although the sorption amount of CO₂ in both materials is much higher than that of H₂ and CH₄ as shown in Figure 12, its lower permeance compared to, especially, CH₄ is counter-intuitive and needs to be investigated further, but is speculated to be due to the molecular shape of the gases (the spherical CH₄ molecule might permeate easier through the pores of the membrane due to less steric hindrance than the rod shaped CO₂ or N₂ molecule) and steric hindrance [16]. The H₂ permeance through GO membranes was 188×10^{-9} mol/m²·s·Pa with H₂/CO₂ selectivity of 69.9 whereas for MoS₂ membranes the figure-of-merits were 1047×10^{-9} mol/m²·s·Pa and 6.7, which are comparable to those reported in literature [16-18]. In case of GM-60-2, the H₂ permeance was 749×10^{-9} mol/m²·s·Pa with H₂/CO₂ selectivity of 31. Thus, the hybrid membrane exhibited much higher H₂ permeance than pure GO membranes and higher H₂/CO₂ selectivity compared to pure MoS₂ membranes. The high selectivity, in case of GO indicates molecular sieving mechanism for gas transport while for MoS₂ it is

Knudsen mechanism. The hybrid membrane draws its transport properties from both the mechanisms in a synergistic way.

For H_2 separation, the thermal stability of the membranes is critical and thus, the same was evaluated for GM-60-2 membrane. The membrane was heated to 120°C for four hours under helium atmosphere and was then subsequently cooled to room temperature. The gas permeation properties of the heat-treated membrane were then measured at room temperature and the results are shown in Figure 11. Heat treating the membrane did not significantly affect the permeation properties of the membrane (slight drop in the permeance) indicating that the membrane was thermally stable.

Figure 11. Gas permeance versus kinetic diameter for GO, MoS₂, GO-MoS₂ hybrid membrane (GM-60-2; before and after heat treatment).

Figure 12. Gas sorption isotherms of CO₂, CH₄ and H₂ at 273 K and 293 K for (a) GO and (b) MoS₂

H₂ permeance as a function of MoS₂ content for membranes with different thickness is shown in Figure 13 (pure and 1:1 H₂/CO₂ mixture experiments). The first observation from the Figure 13a (pure gas testing) is that the permeance of both gases increased (whereas the H₂/CO₂ selectivity decreased) with increasing MoS₂ content in a membrane of a given thickness. This is because, the MoS₂ contribution with regards to permeance in the hybrid membrane becomes larger with increasing MoS₂ content, albeit accompanied by loss of selectivity. Also, increasing the membrane thickness while keeping the MoS₂ content constant results in decreasing permeance due to the increased diffusion pathway length. The results of mixed gas permeation tests (50:50 v/v mixture) are shown in Figure 13b. Under mixed gas environment, H₂ permeance and the H₂/CO₂ selectivity dropped whereas the CO₂ permeance increased compared to the respective pure gas data. This can be explained by the frequent collisions occurring between different gas molecules in narrow pores, which lead to a transfer of momentum from the lighter molecules with higher velocities to the heavier ones, which in turn can affect the individual gas flows

[17]. Another effect, which may contribute to the differences between the single and the mixed gas data, is the preferential interaction of CO₂ with the edge carboxylic groups of the GO nanosheets, as well as with MoS₂ nanosheets which could inhibit the flow of H₂; as evidenced by sorption isotherms (cf. Figure 12).

Figure 13: H₂ and CO₂ permeance as a function of MoS₂ content in the hybrid membranes listed in Table 1 for (a) pure gas and (b) mixed gas (1:1 H₂:CO₂ mixture)

The pure and mixed gas H₂/CO₂ selectivity as a function of MoS₂ content for hybrid membranes is shown in Figure 14, along with the pure gas selectivity for pure GO and MoS₂ membranes. Introducing MoS₂ in the GO stacking reduces the selectivity when compared with GO membranes but significantly increases it in comparison to pure MoS₂ membranes. The effect of MoS₂ content in the hybrid membrane reveals that increasing MoS₂ decreases the selectivity due to larger gas transport contribution from MoS₂. In terms of membrane thickness (with constant MoS₂ content), relatively small changes in selectivity are observed. In general, the pure gas selectivity is higher than the mixed gas selectivity, which could be due to the CO₂ sorption effect as explained above.

Figure 14: H₂/CO₂ selectivity as a function of MoS₂ content in the hybrid membranes, listed in Table 1, under pure and mixed gas (1:1 H₂:CO₂ mixture) conditions. Also shown is the pure gas H₂/CO₂ selectivity for pure GO and MoS₂ membranes.

In case of hybrid membranes, the highest H₂ permeance was 804×10^{-9} mol/m²·s·Pa with corresponding H₂/CO₂ selectivity of 26.7 (membrane GM-60-3). The highest H₂/CO₂ selectivity of 44 with corresponding H₂ permeance of 287×10^{-9} mol/m²·s·Pa was obtained for membrane GM-150-1. Thus, hybrid membranes exhibited high selectivity w.r.t. to MoS₂ membranes and high permeance w.r.t. GO membranes. For example, in case of GM-60-# membranes, by increasing the MoS₂ content from ~25% to ~75% by weight, the H₂ permeance increased by a factor of 3.6 to 4.2 respectively when compared with pure GO membranes, whereas the selectivity increased by a factor of 5.5 to 3.9 respectively when compared with pure MoS₂ membranes. The gas transport through GO membranes has been identified to take place in the interlayer spaces and/or through defects on the basal plane [15, 16], while that through MoS₂ membranes (specifically for the 2H MoS₂ phase) occurs in the inter-bundle spaces [17]. Thus, both these mechanisms are exploited in a synergistic fashion in the hybrid membranes reported here. Table 2

compares the gas transport performance of the membranes reported here with similar membranes reported in the literature. From Table 2, it can be seen that, the hybrid membranes exhibit a much higher permeability (= permeance x membrane thickness) than pure GO membranes reported in the literature as well as pure GO membrane reported here. In terms of selectivity, the hybrid membranes show far superior performance with respect to MoS₂ membranes. Hybrid GO-MoS₂ membranes have H₂ permeability in the 120-150 Barrers range with H₂/CO₂ selectivity of 26-44, depending on the membrane thickness and MoS₂ content.

Table 2: H₂ permeance and H₂/CO₂ selectivity for hybrid membranes (and pure GO and MoS₂ membranes) reported here along with those reported in literature. (*The values in parentheses are standard deviations in H₂ permeance*)

Membrane	Thickness nm	H ₂ permeance 10 ⁻⁹ mol/m ² ·s·Pa	H ₂ permeability** Barrer	H ₂ /CO ₂ selectivity	Reference
GO*	9	100	2.7	3400	[15]
GO	18	100	5.4	333	[15]
GO	20	490	29.3	44	[16]
GO	20	335	20.0	218	[16]
GO-EFDA	1000	281	839.6	29	[27]
GO-EFDA	1000	402	1199.5	33	[27]
MoS ₂	17	919	466.5	3.4	[18]
MoS ₂	35	236	246.5	3.7	[18]
MoS ₂	60	819	146.8	4.4	[18]

MoS ₂	500	790	1179.4	8.3	[17]
GO	50	188 (± 9)	28.0	69.9	this work
MoS ₂	100	105 (± 10)	312.7	6.7	this work
GM-60-1	59	686 (± 14)	120.1	37.0	this work
GM-60-2	61	749 (± 35)	137.4	31.0	this work
GM-60-3	60	804 (± 38)	143.0	26.7	this work
GM-100-1	107	399 (± 10)	127.0	43.5	this work
GM-100-2	98	437 (± 22)	127.5	32.8	this work
GM-100-3	101	466 (± 12)	140.0	26.9	this work
GM-150-1	148	287 (± 7)	126.5	44.2	this work
GM-150-2	150	310 (± 9)	138.5	33.4	this work
GM-150-3	151	328 (± 11)	147.7	27.1	this work

* Mixed gas 1:1 H₂/CO₂ mixture

** 1 Barrer = 3.348×10^{-16} mol·m/m²·s·Pa

H₂ separation needs to be carried out at higher temperatures (for example in pre-combustion). Thus, the performance characteristics of the membranes at higher temperatures is important. The separation performance of a hybrid membrane (GM-100-2) in mixed gas environment (1:1 H₂:CO₂) as a function of temperature is shown in Figure 15. From Figure 15, it can be seen that the permeance for both H₂ and CO₂ increases as the temperature is increased. Increasing the temperature from 20 to 100°C, the H₂ permeance almost doubled whereas CO₂ permeance increased by a factor of ~7. The faster increase in the CO₂ permeance as compared to H₂ permeance, led to a decrease in the H₂/CO₂ selectivity from ~25 (at 20°C) to ~8 (at 100°C) i.e. the selectivity decreased by a factor of ~3 when the temperature increased from 20 to 100°C. The faster increase in the CO₂ permeance compared to H₂ could be due to the more activated CO₂ diffusion through the membrane at higher temperatures. Similar gas permeation behavior as a function of temperature has been reported earlier [15, 16] for GO membranes. The temperature was restricted to 100°C because the support used in this study was not suitable for higher temperatures.

Figure 15. H₂, CO₂ permeance and H₂/CO₂ selectivity as a function of temperature in the hybrid membrane GM-100-2, under mixed gas environment (1:1 H₂:CO₂ mixture).

Figure 16 compares the separation performance of the hybrid membranes reported here with GO [15, 16, 27], MoS₂ [17, 18] and other inorganic membranes (silica[6-8], zeolites[9-12], ZIF's[13, 14]) reported in the literature in a H₂ permeability vs H₂/CO₂ selectivity plot along with the 2008 Robeson upper bound. From Figure 16, it can be seen that the performance of the hybrid GO-MoS₂ membranes exceeds the upper bound with the added advantage of tuning the membrane property by adjusting the amount of MoS₂.

The transport properties of the membranes were modeled using the effective medium approximation (EMA) theory [28, 29]. The benefit of using the EMA theory is that it does not distinguish between the continuous or dispersed phase in the membranes and thus treats the contribution from both the phases equally. In the hybrid membranes reported here, the two materials are randomly mixed and hence EMA is useful as it is derived for completely random distributions. It is also valid for any composition range of

the materials in the hybrid membranes. The effective permeability (P_{eff}) of the hybrid membranes can thus be calculated from the following EMA equation:

$$\phi_g \frac{P_{g,i} - P_{eff,i}}{P_{g,i} + 2P_{eff,i}} + \phi_m \frac{P_{m,i} - P_{eff,i}}{P_{m,i} + 2P_{eff,i}} = 0 \quad (1)$$

where P_g and P_m represent the gas permeability of the pure GO and MoS₂ membranes (cf. Table 2) while ϕ_g and ϕ_m represents their respective volume fraction in the membranes. Subscript “*i*” denotes either H₂ or CO₂ gas. The H₂/CO₂ selectivity for the hybrid membranes can then be calculated as:

$$\alpha = \frac{P_{eff,H_2}}{P_{eff,CO_2}} \quad (2)$$

The effective permeability versus the H₂/CO₂ selectivity calculated from the pure GO and MoS₂ membrane data and equations (1) and (2) are plotted in Figure 16 as a dashed line. As can be seen from Figure 16, the permeability-selectivity predicted from EMA theory is much lower than those measured from the experiments. This indicates that there is synergistic effect of both 2D materials on the hybrid membrane performance.

Figure 16. Comparison of GO-MoS₂ membranes performance (ideal H₂/CO₂ selectivity vs H₂ permeance) with other membranes reported in the literature (silica[6-8], zeolites[9-12], ZIF's[13, 14], MoS₂[17, 18] and GO[15, 16, 27]). Dashed line represents calculated permeability and selectivity from EMA model. The black line denotes the 2008 upper bound for H₂/CO₂ separation.

From a practical application point of view, the long-term stability of the membranes is of utmost importance. Three measurements of long-term stability were carried out on the hybrid membranes under different conditions. Firstly, the GM-100-1 membrane underwent a cyclic permeation test for 60 h under alternating H₂ and CO₂ feed gas (each gas was tested for 3 h and then switched), with a measurement of the permeance towards the end of each cycle. The corresponding data is shown in Figure 17a, and it can be seen that the membrane was stable as no hysteresis and no considerable change in the membrane performance in terms of permeance and selectivity were observed. Secondly, membrane GM-100-2 was subjected to a 72 h continuous test under H₂ (Figure 17a) followed by 72 h test under CO₂ (measurements were taken every 8 hours). Again, no considerable change in the membrane performance was observed. Note that in Figure 17a, H₂/CO₂ selectivity is only shown for the first test (for membrane GM-100-1) where the gases were alternated every 3 hours and selectivity can be calculated after each cycle. Similar results were obtained with mixed gas long-term stability tests as shown in Figure 17b. On the basis of these tests, it can be concluded that the membranes were stable, and did not undergo any obvious structural changes.

Figure 17. Long-term stability tests for hybrid membranes (a) pure gas testing (GM-100-1 tested under alternate gas mode and GM-100-2 under continuous mode) and (b) mixed gas (1:1 H_2/CO_2 mixture) testing for GM-100-1

Conclusions

In conclusion, we have demonstrated for the first time the preparation of sub-micrometer thick composite hybrid membranes using two 2D building blocks, namely GO and MoS_2 , by simple vacuum filtration technique. The hybrid GO- MoS_2 membranes exhibited both high H_2 permeance and high H_2/CO_2 selectivity and these can be tuned by controlling the GO and MoS_2 contents as demonstrated here, to suit a given application. The voids created in the GO assembly by the introduction of MoS_2 may contribute to the high H_2 permeance observed through the membranes. The figure-of-merits (H_2 permeance and H_2/CO_2 selectivity) are well above the upper bound of the trade-off plot as shown in Figure 16. This methodology could be extended to prepare defect-free ultrathin membranes from 2D materials (from which the membrane fabrication is not trivial; like COF's, MOFs etc.) by employing GO as a packing agent.

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Highlights

- GO-MoS₂ hybrid membranes exhibited high selectivity and high permeance.
- GO assists in packing the MoS₂ nanosheets.
- The membranes were stable under long term testing.