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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 MoS$_2$ content in the membranes were varied and their H$_2$ permeance and H$_2$/CO$_2$ selectivity are reported. A 60 nm hybrid membrane containing $\sim$75% by weight of MoS$_2$ exhibited the highest H$_2$ permeance of $804 \times \times 10^{-9}$ mol/m$^2$·s·Pa with corresponding H$_2$/CO$_2$ selectivity of 26.7; while a 150 nm hybrid membrane with $\sim$29% MoS$_2$ showed the highest H$_2$/CO$_2$ selectivity of 44.2 with corresponding H$_2$ permeance of $287 \times 10^{-9}$ mol/m$^2$·s·Pa. The hybrid membranes exhibited much higher H$_2$ permeance compared to graphene oxide membranes and higher selectivity compared to MoS$_2$ 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 (MoS$_2$), 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 H$_2$/CO$_2$ selectivity of 3400 (for 1:1 H$_2$:CO$_2$ mixture) reported to-date. Chi et al [16] fabricated ~20 nm GO membranes using spin coating method and reported H$_2$/CO$_2$ selectivity of around 250 with H$_2$ permeance of ~340×10$^{-9}$ mol/m$^2$·s·Pa. Layered transition metal chalcogenides such as MoS$_2$ have also been recently demonstrated in membrane based gas separation application. Achari et al [17] employed a 500 nm thick layered MoS$_2$ membrane which showed H$_2$/CO$_2$ selectivity of ~8.2 (more than the ideal Knudsen value of 4.7) with a very high H$_2$ permeance (780×10$^{-9}$ mol/m$^2$·s·Pa) whereas Wang et al [18] reported very thin (17-60 nm) MoS$_2$ membranes that exhibited H$_2$/CO$_2$ selectivity of 3.4 to 4.4 with a very high H$_2$ permeance in the range of 818–9186×10$^{-9}$ mol/m$^2$·s·Pa. Based on these results it is clear that GO membranes show high gas selectivity but low gas permeance, whereas MoS$_2$ 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 MoS$_2$ sheets. Hence, if using GO as a packing agent, it may help improve the performance of MoS$_2$ membrane.

Motivated by the results from both GO and MoS$_2$ membranes, we report here for the first time, to the best of our knowledge, hybrid sub-micron thick membranes containing both GO and MoS$_2$ mixed together, to synergistically utilize the unique gas separation properties of both materials. The gas separation performance of the membranes was
investigated for $\text{H}_2$ and $\text{CO}_2$ separation as a function of MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ (from the stock solution) was dispersed in 50 ml DI water (50 ml of 45/55 vol% of ethanol/water for MoS$_2$) 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-MoS$_2$ composition, two dispersions of GO and MoS$_2$ in 25 ml DI water (for GO) and 25 ml of 55/45 vol% DI water/ethanol (for MoS$_2$) were prepared and sonicated for 5 min, followed by mixing them together using 10 min sonication to get homogeneously mixed GO-MoS$_2$ 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 MoS$_2$ content. The amount of GO and MoS$_2$ 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% MoS$_2$, 50% GO-50% MoS$_2$ and 25% GO-75% MoS$_2$. 
Table 1 lists the details of fabricated membranes (pure GO, pure MoS$_2$ and GO-MoS$_2$ hybrid membranes).

To fabricate membranes with controlled thickness, known amount of given nanomaterial (GO, MoS$_2$ or GO + MoS$_2$) was added in 50 ml of DI water (or DI water + ethanol for MoS$_2$) 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 μm). The thickness of the fabricated membranes (four representative membranes: GO, MoS$_2$ 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 cm$^2$) and the nanomaterial density (GO density = 1.5 mg/ml; MoS$_2$ density = 5 mg/ml).

Table 1: Membrane details fabricated using vacuum filtration

<table>
<thead>
<tr>
<th>Membrane</th>
<th>GO wt%</th>
<th>MoS$_2$ wt%</th>
<th>Thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>100</td>
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<td>50</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>GM-60-1</td>
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<td>27.53</td>
<td>59</td>
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<td>GM-60-2</td>
<td>51.37</td>
<td>49.62</td>
<td>61</td>
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<td>25.28</td>
<td>74.71</td>
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<td>150</td>
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<tr>
<td>GM-150-3</td>
<td>24.75</td>
<td>75.25</td>
<td>151</td>
</tr>
</tbody>
</table>
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 MoS\(_2\)) and a drop of the diluted dispersion was transferred to TEM grid followed by drying under vacuum at 40\(^\circ\)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 \(^\circ\)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 MoS\(_2\) were measured using Micromeritics ASAP 2050 sorption analyzer at 0\(^\circ\)C and 25\(^\circ\)C for pressure up to \(~102\) kPa. Before each isotherm measurement, the samples were degassed under vacuum at 60\(^\circ\)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,

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

4.1 Materials and membrane characterization

Figure 2a shows the digital photograph of the as synthesized GO and MoS$_2$ 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 MoS$_2$ nanosheets which shows that the exfoliated GO and MoS$_2$ nanosheets were flat with a uniform thickness. The GO thickness calculated from the three AFM height profiles was around 1.1 nm ($\pm$ 0.15 nm), while that for MoS$_2$ was around 3.1 nm ($\pm$ 0.14 nm). Based on the monolayer thickness of GO [15] and MoS$_2$ [21], it can be deduced that the exfoliated GO was monolayer while MoS$_2$ was tri-layer. Most of the GO flakes were in the ~0.5 to 1.5 $\mu$m size range, whereas the MoS$_2$ flakes were in the ~0.8 - 2 $\mu$m size range. The UV-vis spectra for GO, MoS$_2$ and GO-MoS$_2$ (50:50 w/w) dispersions are shown in Figure 4. The spectrum of GO shows a characteristic peak at 230 nm, associated with $\pi-\pi^*$ interactions, and a broad absorption peak (shoulder) at 300 nm, attributed to n-$\pi^*$ interactions [22]. For MoS$_2$, 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) MoS$_2$

Figure 4: UV-vis spectra for GO, MoS$_2$ and 50/50 GO/MoS$_2$ mixture

Figure 5: TEM images of (a) GO and (b) MoS$_2$ nanosheets
Figure 6 shows the FT-IR spectra for GO, MoS$_2$ and GO-MoS$_2$ 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 MoS$_2$, 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 MoS$_2$ are observed, suggesting that there is no chemical interaction between the GO and MoS$_2$ nanosheets.

![FT-IR spectra for GO, MoS$_2$ and GO-MoS$_2$ mixture](image)

Figure 6: FT-IR spectra for GO, MoS$_2$ and 50/50 GO/MoS$_2$ mixture

The digital pictures of five membranes fabricated using vacuum filtration technique (GO, GM-100-1, GM-100-2, GM-100-3 and MoS$_2$) 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 MoS$_2$ 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].

![Surface SEM images](image-url)

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 MoS$_2$ nanosheets were stacked in a random and irregular way in the MoS$_2$ 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 MoS$_2$ nanosheets, which basically contribute to “pop up” the hybrid GO-MoS$_2$ layers. As also seen from the cross-section SEM, the higher the content of MoS$_2$ in the hybrid membrane, the higher the density of voids.

![Cross section SEM images](image)

Figure 10. Cross section SEM images for (a) GO membrane, (b) MoS$_2$ membrane, (c) GO-MoS$_2$ (50/50) hybrid membrane and (d) GO-MoS$_2$ (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, MoS\(_2\) and GM-60-2 are shown in Figure 11. GO membranes exhibit the lowest gas permeance among the three membranes, while MoS\(_2\) the highest. H\(_2\) (0.28 nm) being the smallest among the gases tested, permeates faster than other gases such as CO\(_2\) (0.33 nm), N\(_2\) (0.364 nm) and CH\(_4\) (0.38 nm). The order of gas permeance for all membranes is H\(_2\) >> CH\(_4\) > CO\(_2\), N\(_2\). Although the sorption amount of CO\(_2\) in both materials is much higher than that of H\(_2\) and CH\(_4\) as shown in Figure 12, its lower permeance compared to, especially, CH\(_4\) is counter-intuitive and needs to be investigated further, but is speculated to be due to the molecular shape of the gases (the spherical CH\(_4\) molecule might permeate easier through the pores of the membrane due to less steric hindrance than the rod shaped CO\(_2\) or N\(_2\) molecule) and steric hindrance [16]. The H\(_2\) permeance through GO membranes was 188 × 10\(^{-9}\) mol/m\(^2\)·s·Pa with H\(_2\)/CO\(_2\) selectivity of 69.9 whereas for MoS\(_2\) membranes the figure-of-merits were 1047 × 10\(^{-9}\) mol/m\(^2\)·s·Pa and 6.7, which are comparable to those reported in literature [16-18]. In case of GM-60-2, the H\(_2\) permeance was 749 × 10\(^{-9}\) mol/m\(^2\)·s·Pa with H\(_2\)/CO\(_2\) selectivity of 31. Thus, the hybrid membrane exhibited much higher H\(_2\) permeance than pure GO membranes and higher H\(_2\)/CO\(_2\) selectivity compared to pure MoS\(_2\) membranes. The high selectivity, in case of GO indicates molecular sieving mechanism for gas transport while for MoS\(_2\) it is
Knudsen mechanism. The hybrid membrane draws its transport properties from both the mechanisms in a synergistic way.

For H\textsubscript{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\textdegree 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, MoS\textsubscript{2}, GO-MoS\textsubscript{2} hybrid membrane (GM-60-2; before and after heat treatment).](image-url)
Figure 12. Gas sorption isotherms of CO$_2$, CH$_4$ and H$_2$ at 273 K and 293 K for (a) GO and (b) MoS$_2$

H$_2$ permeance as a function of MoS$_2$ content for membranes with different thickness is shown in Figure 13 (pure and 1:1 H$_2$/CO$_2$ mixture experiments). The first observation from the Figure 13a (pure gas testing) is that the permeance of both gases increased (whereas the H$_2$/CO$_2$ selectivity decreased) with increasing MoS$_2$ content in a membrane of a given thickness. This is because, the MoS$_2$ contribution with regards to permeance in the hybrid membrane becomes larger with increasing MoS$_2$ content, albeit accompanied by loss of selectivity. Also, increasing the membrane thickness while keeping the MoS$_2$ 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, H$_2$ permeance and the H$_2$/CO$_2$ selectivity dropped whereas the CO$_2$ 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.
Another effect, which may contribute to the differences between the single and the mixed gas data, is the preferential interaction of CO\(_2\) with the edge carboxylic groups of the GO nanosheets, as well as with MoS\(_2\) nanosheets which could inhibit the flow of H\(_2\); as evidenced by sorption isotherms (cf. Figure 12).

![Figure 13: H\(_2\) and CO\(_2\) permeance as a function of MoS\(_2\) content in the hybrid membranes listed in Table 1 for (a) pure gas and (b) mixed gas (1:1 H\(_2\):CO\(_2\) mixture)](image)

The pure and mixed gas H\(_2\)/CO\(_2\) selectivity as a function of MoS\(_2\) content for hybrid membranes is shown in Figure 14, along with the pure gas selectivity for pure GO and MoS\(_2\) membranes. Introducing MoS\(_2\) in the GO stacking reduces the selectivity when compared with GO membranes but significantly increases it in comparison to pure MoS\(_2\) membranes. The effect of MoS\(_2\) content in the hybrid membrane reveals that increasing MoS\(_2\) decreases the selectivity due to larger gas transport contribution from MoS\(_2\). In terms of membrane thickness (with constant MoS\(_2\) 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 CO\(_2\) 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 $804 \times 10^{-9}$ 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 $287 \times 10^{-9}$ 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*)

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<thead>
<tr>
<th>Membrane</th>
<th>Thickness</th>
<th>H2 permeance</th>
<th>H2 permeability**</th>
<th>H2/CO2 selectivity</th>
<th>Reference</th>
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<td>9</td>
<td>100</td>
<td>2.7</td>
<td>3400</td>
<td>[15]</td>
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<tr>
<td>GO</td>
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<td>100</td>
<td>5.4</td>
<td>333</td>
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<td>GO</td>
<td>20</td>
<td>490</td>
<td>29.3</td>
<td>44</td>
<td>[16]</td>
</tr>
<tr>
<td>GO</td>
<td>20</td>
<td>335</td>
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<td>218</td>
<td>[16]</td>
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<tr>
<td>GO-EFDA</td>
<td>1000</td>
<td>281</td>
<td>839.6</td>
<td>29</td>
<td>[27]</td>
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<tr>
<td>GO-EFDA</td>
<td>1000</td>
<td>402</td>
<td>1199.5</td>
<td>33</td>
<td>[27]</td>
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<tr>
<td>MoS2</td>
<td>17</td>
<td>919</td>
<td>466.5</td>
<td>3.4</td>
<td>[18]</td>
</tr>
<tr>
<td>MoS2</td>
<td>35</td>
<td>236</td>
<td>246.5</td>
<td>3.7</td>
<td>[18]</td>
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<tr>
<td>MoS2</td>
<td>60</td>
<td>819</td>
<td>146.8</td>
<td>4.4</td>
<td>[18]</td>
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</table>
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.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>MoS₂</th>
<th>GO</th>
<th>500</th>
<th>790</th>
<th>1179.4</th>
<th>8.3</th>
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<td>28.0</td>
<td>69.9</td>
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<td>105 ($\pm$10)</td>
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<tr>
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<tr>
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<td>GM-150-2</td>
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<td>151</td>
<td>466 ($\pm$12)</td>
<td>140.0</td>
<td>26.9</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>GM-150-3</td>
<td>151</td>
<td>151</td>
<td>287 ($\pm$7)</td>
<td>126.5</td>
<td>44.2</td>
<td>this work</td>
<td></td>
</tr>
</tbody>
</table>

* Mixed gas 1:1 H₂/CO₂ mixture

** 1 Barrer = 3.348×10⁻¹⁶ mol·m⁶·m⁻²·s⁻¹·Pa
Figure 15. \( \text{H}_2, \text{CO}_2 \) permeance and \( \text{H}_2/\text{CO}_2 \) selectivity as a function of temperature in the hybrid membrane GM-100-2, under mixed gas environment (1:1 \( \text{H}_2/\text{CO}_2 \) mixture).

Figure 16 compares the separation performance of the hybrid membranes reported here with GO [15, 16, 27], MoS\(_2\) [17, 18] and other inorganic membranes (silica[6-8], zeolites[9-12], ZIF’s[13, 14]) reported in the literature in a \( \text{H}_2 \) permeability vs \( \text{H}_2/\text{CO}_2 \) selectivity plot along with the 2008 Robeson upper bound. From Figure 16, it can be seen that the performance of the hybrid GO-MoS\(_2\) membranes exceeds the upper bound with the added advantage of tuning the membrane property by adjusting the amount of MoS\(_2\).

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 ($P_{\text{eff}}$) of the hybrid membranes can thus be calculated from the following EMA equation:

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

where $P_g$ and $P_m$ represent the gas permeability of the pure GO and MoS$_2$ membranes (cf. Table 2) while $\phi_g$ and $\phi_m$ represents their respective volume fraction in the membranes. Subscript “$i$” denotes either H$_2$ or CO$_2$ gas. The H$_2$/CO$_2$ selectivity for the hybrid membranes can then be calculated as:

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

The effective permeability versus the H$_2$/CO$_2$ selectivity calculated from the pure GO and MoS$_2$ 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-MoS\textsubscript{2} membranes performance (ideal H\textsubscript{2}/CO\textsubscript{2} selectivity vs H\textsubscript{2} permeance) with other membranes reported in the literature (silica\textsuperscript{[6-8]}, zeolites\textsuperscript{[9-12]}, ZIF’s\textsuperscript{[13, 14]}, MoS\textsubscript{2}\textsuperscript{[17, 18]} and GO\textsuperscript{[15, 16, 27]}). Dashed line represents calculated permeability and selectivity from EMA model. The black line denotes the 2008 upper bound for H\textsubscript{2}/CO\textsubscript{2} 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 H\textsubscript{2} and CO\textsubscript{2} 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 H\textsubscript{2} (Figure 17a) followed by 72 h test under CO\textsubscript{2} (measurements were taken every 8 hours). Again, no considerable change in the membrane performance was observed. Note that in Figure 17a, H\textsubscript{2}/CO\textsubscript{2} 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 submicrometer 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.
Acknowledgement

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References


Highlights

- GO-MoS$_2$ hybrid membranes exhibited high selectivity and high permeance.
- GO assists in packing the MoS$_2$ nanosheets.
- The membranes were stable under long term testing.


