



# Highly permeable and selective graphene oxide-enabled thin film nanocomposite for carbon dioxide separation



Kar Chun Wong, Pei Sean Goh\*, Ahmad Fauzi Ismail

Advanced Membrane Technology Research Centre (AMTEC), Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia (UTM), 81310, Johor, Malaysia

## ARTICLE INFO

### Keywords:

Graphene oxide  
Thin film nanocomposite  
Gas separation

## ABSTRACT

Membrane technology appeals as an environmental friendly approach for CO<sub>2</sub> capture application due to its modest energy requirement and scalability but high performing membranes are constantly sought after to make this technology economically competitive to the conventional amine absorption process. This study focuses on a relatively new class of membrane known as the thin film nanocomposite (TFN) which is characterized with extremely thin selective layer for high productivity. Using the interfacial polymerization (IP) technique, TFNs embedded with graphene oxide (GO) were successfully fabricated to investigate the effects of GO loading on the morphology and gas separation performance of the resultant membrane. Permeance and selectivity of the TFN is a positively correlated with GO content. The optimum sample, TFN-0.5 exhibited more than twice the CO<sub>2</sub> permeance of neat thin film composite (TFC) while achieving CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation factor of 41 (26% increment) and 25 (26% increment) respectively. The enhancement in TFN performance was attributed to the increased tortuosity in polymer matrix and the introduction of rapid diffusion passages resulted from incorporation of rigid GO sheets. GO-TFN demonstrated attractive potential for low pressure post-combustion CO<sub>2</sub> separation to reduce emission of the greenhouse gas and mitigate the global warming issue.

## 1. Introduction

Global warming is a serious environmental issue that could lead to drastic climate fluctuation, loss of biodiversity, food insecurity and threaten the public well-being (Maibach et al., 2015). Since CO<sub>2</sub> is the major contributor to global warming, carbon capture and storage (CCS) is deemed as a viable strategy to overcome this issue. CCS involves capturing or separating the CO<sub>2</sub> from the emission source, processing the captured CO<sub>2</sub> into storable form and transporting it to the holding facilities. Through this approach, CO<sub>2</sub> released from anthropogenic activities can be regulated in hope to bring down the atmospheric CO<sub>2</sub> concentration to a healthy level. Contemporary, the CO<sub>2</sub> separation stage alone comprises up to 70% of the total cost of CCS (Favre, 2011). Hence, economical CO<sub>2</sub> separation technologies are crucial to make CCS implementation sustainable in the long run (Belaisaoui et al., 2012). Among the existing CO<sub>2</sub> separation technologies, membrane technology is recognized as a cost-effective, environmentally benign and sustainable candidate (Adewole et al., 2013; Scholes et al., 2010). Additionally, it can be easily operated and scaled up while requiring little maintenance. The recent advancement made in material sciences allows the tailoring of membrane properties for high CO<sub>2</sub> selectivity.

Some recent efforts include the use of CO<sub>2</sub>-affinitive materials in amino-starch incorporated membrane and supported ionic liquid membrane (SILM) (Saedi et al., 2013; Sun et al., 2015). Despite their potential for large-scaled industrial applications, most of the CO<sub>2</sub> selective membranes are still at the developmental stage and their separation efficiency is relatively low compared to the conventional amine-adsorption process. One of the major hiccups to achieving high performing membrane is the inherent limitation of polymeric materials which commonly known as the Robeson's trade-off. Mondal and Mandal (2013) processed amine carriers blended polyvinyl alcohol (PVA) into membranes with different skin thickness. While they observed higher CO<sub>2</sub> permeation rate from membrane with thinner skin (9 μm), selectivity of the membrane was consistently lower at a range of testing condition (90–125 °C, 2–7 atm) compared to its counterpart with a 14 μm thick skin. The trade-off was due to the fact that, albeit the shorter travel path of gases through the thinner skin, the gases were not adequately sieved by the polymer network.

In recent years, hybrid composite membranes have been developed to overcome this trade-off. The success of hybrid composite membrane relies greatly on the presence of inorganic fillers which introduce highly selective and permeable pore systems to elevate the membrane

\* Corresponding author.

E-mail address: [peisean@petroleum.utm.my](mailto:peisean@petroleum.utm.my) (P.S. Goh).

performance (Deng and Hägg, 2014; Kiadehi et al., 2015). Mixed matrix membrane (MMM) is the most studied hybrid composite membrane due to the facile fabrication involved and its promising separation performance. MMM is commonly fabricated via phase inversion technique which involves casting a dope solution containing dispersed fillers on a flat surface or extruding it through a spinneret then subjecting the dope to rapid solvent exchange in a coagulation bath to obtain flat sheet or hollow fiber MMM respectively. Currently, the progress of MMM is concentrated on developing high performing nanofillers and improving the homogeneity of fillers within the polymer matrix. Wu et al. and Zhao et al. (2014) reported a 2–3 folds boost in separation performance of their MMM by incorporated 20 wt% polyethylenimine functionalized mesoporous silica and 33 wt% amino functionalized carbon nanotube (CNT) respectively into Pebax membrane. The performance enhancement was ascribed to the introduction of CO<sub>2</sub>-selective diffusion passages by the incorporated nanofillers within the polymer matrix and good filler-matrix compatibility.

While nanofillers such as zeolite, metal organic framework (MOF) and carbon nanotube (CNT) with well-define structures and precise molecular sieving pores can be rather costly to be manufactured, ingenious membrane design and sparing use of these precious materials can lead to a sensible cost-to-performance ratio. Here is where the TFN stands out compared to MMM. TFN is generally a dual-layer polymeric composite which consists of a dense skin layer formed atop of a porous support. Compared to MMM, the distribution of inorganic nanofillers can be well controlled by selectively dispersing them in the dense layer or/and the porous layer. This configuration allows nanofillers to be concentrated at the desired layer to maximize the nanofillers utility and cut-down fabrication cost. Among the different TFC fabrication methods, interfacial polymerization (IP) technique is advantageous in producing extremely thin skin layer (< 0.5 μm) to give highly productive membrane and the process is self-sealing which minimizes defect formation (Freger, 2005; Lau et al., 2015). Moreover, it has been suggested that the polyamide (PA, common polymer yield from IP) layer of TFC exhibited CO<sub>2</sub> facilitated transport mechanism due to the presence of unreacted amine and amino groups in the film (Andrew Lee et al., 2013). Yu et al. (2010) fabricated TFC with good separation performance (CO<sub>2</sub> permeance = 173 GPU; CO<sub>2</sub>/N<sub>2</sub> selectivity = 70, 1 GPU = 1 × 10<sup>-6</sup> cm<sup>3</sup> (STP) cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>) by choosing the appropriate monomer containing tertiary amino groups. The flexibility of IP technique and wide selection of monomers allows the tailoring or designing of TFC membranes to suit different applications (Wong et al., 2016).

One of the major challenges in developing defect free TFN is nanofillers agglomeration and inorganic-organic incompatibility. While past studies showed that nanofiller modification can overcome these problems (Guo et al., 2015; Wu et al., 2014), our previous works indicated that the size and shape of inorganic particles are also important considerations to yield defect-free membrane especially when dealing with the submicron thick skin layer of TFN (Wong et al., 2015a, 2015b). In regard to this matter, GO could be a key solution. This two-dimensional (2D) flake-like material which consists only a few layers of atomic thin carbon sheets are dimensionally well-suited for embedment into the TFN skin. GO shares many resemblance with graphene and CNT including good mechanical and thermal stability (Zhou et al., 2016). Besides, the abundance of functional groups such as carboxyl, epoxy and hydroxyl groups on the GO surface warrants good dispersion and compatibility with the polymer matrix (Yazici et al., 2017).

Dong et al. (2016) reported good CO<sub>2</sub> separation (CO<sub>2</sub> permeability = 119 barrer, CO<sub>2</sub>/N<sub>2</sub> selectivity = 104, 1 barrer = 1 × 10<sup>-10</sup> cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>) through the incorporation of porous reduced GO (PRG) in Pebax. The high performance of their MMM was attributed to the presence of nanopores on the PRG which enabled fast gas permeation while the appropriate interlayer spacing of PRG stacks afforded good sieving properties. On the other hand, Peng et al. found that properly oriented GO

sheets can intensify the tortuosity of polymeric network, leading to better membrane selectivity. Their optimum sample which comprised of zinc ion and dopamine (DA) functionalized GO showed a 78% increment in CO<sub>2</sub>/CH<sub>4</sub> selectivity (CO<sub>2</sub> permeability = 138 barrer, CO<sub>2</sub>/CH<sub>4</sub> selectivity = 31) compared to the neat membrane. Meanwhile, Li et al. (2015) attributed the enhancement in the CO<sub>2</sub> selectivity of MMM incorporated with mixed CNT-GO fillers to the strong interaction between the gas and the functional groups on the fillers. Clearly, GO is an excellent nanofiller that could propel the advancement of gas separation membrane to greater height.

Contemporary, the progress of GO-based membranes in the field of gas separation revolves around GO-MMM (Peng et al., 2017; Wang et al., 2015b) and GO film (Athanasakou et al., 2016; Chi et al., 2016). No attempt has yet been made to investigate the effects of GO incorporation on the CO<sub>2</sub> separation performance of TFN. Hence, this work shall be the first to elucidate the potentials of GO-TFN in alleviating the impact of global warming.

## 2. Experimental

### 2.1. Materials

Graphite powder (< 20 μm, synthetic), potassium permanganate (KMnO<sub>4</sub>, 99%), sodium nitrate (NaNO<sub>3</sub>, 99%), Diethylene glycol bis (3-aminopropyl) ether (DGBAmE, 97%) and 3,3'-diamino-N-methyldipropylamine (DNMDAm, 96%) were purchased from Sigma Aldrich while sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95–97%), hydrochloric acid (HCl, 37%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), hexane (99%) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99%) were purchased from Merck Millipore. Other materials used in this study include trimesoyl chloride (TMC, 98%, Acros Organics) and ultrafiltration (UF) polysulfone (PSf) flatsheet membrane (PS35, MWCO: 20 kDa, Nanostone).

### 2.2. Synthesis of GO

GO was synthesized via an adapted Hummers method (Chen et al., 2015; Hummers and Offeman, 1958). Firstly, graphite powder (6 g) and NaNO<sub>3</sub> (3 g) were mixed with H<sub>2</sub>SO<sub>4</sub> (138 mL) under vigorous stirring in an ice bath (≈ 5 °C) for 10 min. Then, KMnO<sub>4</sub> (18 g) was cautiously added into the mixture while maintaining the slurry temperature below 20 °C. The viscous slurry was stirred at 300 rpm for 2 h before transferred out from the ice bath onto a hotplate to be heated up to 40 °C and stirred for another 30 min at 500 rpm. Next, 300 mL of pre-heated water (≈ 60 °C) was gradually added and the mixture temperature was adjusted to 90 °C. After stirring for 15 min, 900 mL of water was rapidly added to quench the mixture. The mixture was stirred for 45 min and the reaction was terminated by drop-wise addition of H<sub>2</sub>O<sub>2</sub> (90 mL) during which the dark brown solution turned to yellowish brown. The solution was stirred for 30 min before alternately centrifuged (10k rpm, 5 min) and washed with 5% aqueous HCl for several times to remove metal ions. The washing process was repeated by replacing HCl solution with water to bring the pH of final product to about 6. Finally, the brown paste was dried overnight in vacuum oven at 70 °C, ground into fine powder and kept in glass bottle for further use.

### 2.3. Fabrication of GO embedded TFNs

GO-TFN was prepared via IP technique which involves polycondensation of amine with acid chloride to produce a thin PA layer at the aqueous-organic interface when the two phases containing the essential monomers were brought into contact. Organic phase (Solution A) was prepared by dissolving TMC (0.28%w/v) in hexane while the aqueous phase (Solution B) was prepared by dissolving DGBAmE (0.25%w/v), DNMDAm (0.17%w/v), Na<sub>2</sub>CO<sub>3</sub> (0.4%w/v) and a certain amount of GO (0.0 g/L–1.0 g/L) in water. Solution B was sonicated for 1 h before use to ensure GO remained well-suspended. In a typical

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