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Graphene oxide nanosheets to improve permeability and selectivity of PIM-1 membrane for carbon dioxide separation

Mengmeng Chen, Faizal Soyekwo, Qiugen Zhang*, Chuan Hu, Aimei Zhu, Qinglin Liu

Department of Chemical & Biochemical Engineering, Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, College of Chemistry & Chemical Engineering, Xiamen University, Xiamen 361005, China

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ABSTRACT

Polymers of intrinsic microporosity (PIMs) have attracted increasing interest in gas separation membranes due to their high permeability. However, the moderate selectivity limits their wide applications in CO_2 separation. Herein we report a facile strategy to improve simultaneously the permeability and CO_2 selectivity of PIMs membrane using the prepared PIM-1/graphene oxide (GO) nanosheets mixed matrix membrane. The GO nanosheets improves the hydrophilicity and surface roughness of PIM-1 membrane whereas the uniform assembly of GO nanosheets in the PIM-1 matrix creates the hydrophilic/hydrophobic microphase segregation in the membrane. The as-prepared mixed matrix membrane is also very porous and has a pore size of about 0.78 nm. The combination of these properties significantly contributes to the enhancement of the gas separation performance of PIM-1 membrane, with the resultant membrane exhibiting an exceptionally high CO_2 permeability of up to 6169 barrer as well as a high CO_2/N_2 selectivity of 123.5, which is more than 7 times that of the pure PIM-1 membrane. The developed PIM-1/GO mixed matrix membrane should have a wide application in the CO_2 separation.

Introduction

Nowadays, membrane gas separation is an attractive technology for the separation of CO_2, oxygen enrichment and hydrogen purification from several gas sorption processes due to energy and environmental concerns [1–5]. Polymers are the most favourable membrane materials for this process owing to their good mixed gas selectivity and controllable structure and properties, but with corresponding relatively low gas permeability nonetheless [6,7]. Recently, a new class of polymers have been developed and utilized to produce highly permeable gas separation membranes amongst which include microporous organic polymers (MOPs), hyper crosslinked polymers (HCPs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs) and conjugated microporous polymers (CMPs) [8–12]. This genre of polymers exhibit high-specific surface area, good physicochemical stability, diverse pore dimensions and chemical functionalities, and thus show a great potential as next generation membrane materials for gas separation [13–16]. In particular, PIMs synthesized from rigid monomers with sites of contortion are chemically and mechanically stable. Meanwhile, the poor packing of its rigid chains creates a unique interconnected micropores leading to a high fractional free volume in PIMs, which allows the high gas permeability. Subsequently, PIMs display remarkable polymeric molecular sieve capabilities with the representative PIM-1 a focus of increasing attention in CO_2 separation [17–21]. However, whereas membranes based on PIM-1 polymer show sufficiently high CO_2 permeability, the ideal CO_2 selectivity in the separation of various mixed gas *e.g.* CO_2/N_2 and CO_2/CH_4, is moderately low [16,17].

With the intention of improving the gas selectivity of PIM-1 membrane, researchers developed several strategies such as thermal crosslinking, grafting of functional group, blending with other polymers, and solution mixing with nanofillers [1,22–26]. The grafting of functional groups with a special affinity for a target gas molecule can effectively improve the gas selectivity of the PIMs membranes. For example, Khan et al. demonstrated that by grafting trifluoromethyl and phenylsulfone groups to PIM-1 chains, the CO_2/N_2 selectivity improved from 15 to 22 [25]. In another study, the carboxylation of PIM-1 increased the CO_2/N_2 selectivity from 11 to 26, but at the expense of decreased CO_2 permeability from 8310 to 620 barrer [27]. Polymer blending on the other hand is effective by introducing new properties into the PIM-1 matrix. For instance, Yong et al. blended PIM-1 with the matrimid polymer to improve their CO_2/N_2 selectivity [28]. We have also recently shown that the PIM-1 blended membrane containing the 3.5 wt% of 20 kDa polyethylene glycol, which has the high CO_2

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* Corresponding author.
E-mail address: qgzhang@xmu.edu.cn (Q. Zhang).

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permeability and CO_2/CH_4 selectivity of 1952 barrer and 39 respectively [1]. Additionally, the thermal treatment was demonstrated to significantly improve the selectivity due to the improved molecular sieving properties of membrane, it happens at the cost of an overall loss in gas permeability. For instance, heating the PIM-1 membrane at 300 °C for 2 days improved its CO_2/N_2 selectivity from 20.4 to 41.7 accompanied with a 57.5% reduction in the CO_2 permeability [29].

The incorporation inorganic nanofillers to form PIM-1 mixed matrix composite membranes represents the most feasible strategy to simultaneously improve the permeability and selectivity of gases and allow the composite membranes to surpass the 2008 upper bound. Incidentally, whereas the permeability are improved, the corresponding enhancements in selectivity are still small for the practical separations of industrially and environmentally important gases. A combination of controlled thermal oxidative crosslinking and filling with zeolitic imidazolate framework (ZIF-8) nanoparticles was shown to enhance the CO_2 permeability from 2745 barrer to 3944 barrer, with decreased CO_2/CH_4 selectivity from 38 to 27 and a constant CO_2/N_2 selectivity of 27 [30]. Meanwhile, when silica nanoparticles are employed, the CO_2 permeability is improved from 1200 barrer to 2615 barrer but with a drop in CO_2/CH_4 selectivity from 64 to 33 [26]. This kind of inherent “trade-off” relationship between permeability and selectivity of gas separation membrane therefore necessitates the continued exploration of more membrane design approaches with the capacity to achieve both high gas permeability and excellent CO_2 selectivity for the application of PIM-1 based as well as other microporous polymers.

Currently, 2D nanosheets like graphene oxide (GO) that is only one carbon atom manometer thick represent a new class of advanced membrane materials from which gas transport nanochannels could be generated by their facile assembly into ultrathin films and utilized for high performance gas separation [31–33], photocatalysis [34], bioimaging [35] and conductive switching [36]. For example Li et al. reported the fabrication of the ultrathin GO nanosheets membrane with high selectivity of up to 3400 and 900 for H_2/CO_2 and H_2/N_2 mixtures while the coating of ultrathin GO nanosheets membrane on macroporous polyethersulfone membranes results in high CO_2 permeability of ~8500 barrer and CO_2/N_2 selectivity of ~20 [37,38]. Likewise, in an effort to enhance the gas properties of GO membrane, Wang et al. recently reported that providing a suitable interlayer nanochannel spacing and physical microenvironments are conducive for the selective and facilitated fast transport of gas molecules [39]. GO nanosheets filled polymer nanocomposite is also shown to improve gas separation performance of polymer membranes like the GO nanosheets filled poly(ether block amide) membrane developed by Shen et al, which exhibited the high CO_2/N_2 selectivity of 91, but with a low CO_2 permeability of only 100 barrer [40]. Obviously, the GO nanosheets are promising membrane materials for CO_2 capture, but it is challenging to produce GO nanosheets filled polymer membranes that are able to achieve both high CO_2 selectivity and permeability.

In this study, we demonstrate that controlled incorporation of the GO nanosheets can effectively tune the micropores in the PIM-1 creating diffusion channels for excellent selectivity and permeability of gas molecules for application in CO_2 capture. The as-prepared composite membrane achieves CO_2/N_2 selectivity as high as 123.5 with high CO_2 permeability of 6168.9 barrer, and hence presents a great potential application in CO_2 separation.

Experimental

Materials

The monomers, 5, 5′, 6, 6′-tetrahydroxy-3, 3, 3′, 3′-tetramethyl-1, 1′-spiobisindane (TTSBI), 3,4-dimethoxyphenol, and GO nanosheets with the thickness of 0.55–1.2 nm and the diameter of 0.5–3.0 μm were purchased from *J&K Scientific Ltd*. The monomers were purified through crystallization with chloroform. 2, 3, 5, 6-Tetrafluoroterephthalonitrile (TFTPN) was obtained from *Sigma–Aldrich*. Potassium carbonate, dimethylformamide (DMF) and other chemicals were purchased from *Shanghai Chemical Reagent Ltd*. Potassium carbonate was dried in a vacuum oven at 80 °C for 12 h before usage.

Preparation of the PIM-1/GO composite membrane

The PIM-1 was synthesized from the monomers TTSBI and TFTPN with the potassium carbonate as the catalyst according to our previous work, adaptation of the low temperature Budd/McKeown method [1]. In brief, the equimolar amounts of TTSBI, TFTPN, and excessively potassium carbonate were added into a three-neck round-bottom flask with DMF as solvent, and reacted in N_2 atmosphere with constant magnetic stirring at 80 °C for 48 h. The resulting mixture cooled to room temperature and then precipitated in methanol aqueous solution (1:1 v/v). The precipitate was purified by Soxhlet extraction in methanol for 12 h, and then dried in the vacuum oven at 80 °C for 12 h to obtain the expected yellow powder of PIM-1.

The PIM-1/GO composite membrane was prepared *via* the typical solution casting and solvent evaporation process. Firstly, the PIM-1 powder (1 ± 0.02 g) dissolved in the chloroform (20 mL) to form homogeneous PIM-1 solution and then filtered by a polytetrafluoroethylene filter with 0.45 μm pores. Secondly, GO nanosheets dispersion was prepared by dispersing GO nanosheets powder (0.2 ± 0.005 g) in chloroform (100 mL) by stirring for 12 h followed by ultrasonic treatment at below 35 °C for 72 h. Finally, the GO dispersion (1 mL) was mixed into the PIM-1 solution (5 mL) under gentle stirring for 1 h followed by ultrasonic treatment for 4 h. The obtained uniformly dispersed solution was cast into a Teflon folder and then dried in an oven at 35 °C for 3 days for evaporation of chloroform [41]. The resulting PIM-1/GO mixed matrix membrane was peeled off and then dried in an oven at 35 °C for another 12 h to remove any residual solvent.

Characterizations

Scanning electron microscopy (SEM) (S-4800, *Hitachi*) and atomic force microscopy (AFM) (Nanoscope-MultiMode/Dimension, *Digital Instruments*) was used to observe morphology and microstructure of the membrane. The sample was prepared by freezing and cutting the membrane in liquid nitrogen for cross-sectional SEM observation. The AFM image was obtained under the tapping mode at ambient condition (25 °C, 65% relative humidity). FT-IR spectra was recorded on a Nicolet Avatar 330 spectrophotometer (*Thermo Electron Co.*). The hydrophilicity was measured by pendant drop method using a contact angle meter (DSA30, *Kruss*) at room temperature. The thermostability was characterized by thermogravimetric analysis (TGA) (TG 209 F1, *NETZSCH-Gerätebau GmbH*) in N_2 atmosphere. The surface area and porosimetry analyzer (ASAP 2020 HD88, *Micrometrics Instrument Co.*) was used to measure sorption characteristics with respect to nitrogen at 77 K.

Gas permeation measurements

The permeability of CO_2 and N_2 through the composite membrane were determined by the traditional constant pressure/variable volume method. The measurement was carried out at a feed pressure of 0.4 MPa and 30 °C. The permeability (P, barrer) and ideal selectivity (α) were determined using the relationship,

$$P = 10^{10}\frac{273.15dV}{T}\frac{l}{dt\,\Delta pA} \tag{1}$$

$$\alpha = P_A/P_B \tag{2}$$

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