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Supporting Information

A highly permeable graphene oxide membrane with fast and selective transport nanochannels for efficient carbon capture

Shaofei Wang, Yingzhen Wu, Ning Zhang, Guangwei He, Qingping Xin, Xingyu Wu, Hong Wu, Xingzhong Cao, Michael D. Guiver*, and Zhongyi Jiang*

Experimental Section

Materials:

Natural graphite flake (12000 mesh) was purchased from Qingdao Tianhe Graphite Co. Ltd. (Shandong, China). Polyethersulfone microfiltration membrane with an average pore size of 0.22 μ m was obtained from Haining Yibo Filter Co. Ltd. (Zhejiang, China). Potassium tetraborate (K₂B₄O₇) was supplied Aladdin Chem Co. Ltd. (Shanghai, China). Concentrated sulfuric acid (H₂SO₄, 98 wt%), hydrochloric acid (HCl) and potassium permanganate (KMnO₄) were obtained from Tianjin Kewei Ltd. (Tianjin, China). Hydrogen peroxide aqueous solution (H₂O₂, 30 wt%), sodium nitrate (NaNO₃) were purchased from Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China). All the reagents were of analytical grade and used without further purification. Deionized water was used in all experiments.

Preparation of B-GO/PES membrane:

Graphene oxide was prepared by the modified Hummers method.¹ For a typically preparation, a certain amount of graphite powder and NaNO₃ was added to 98 wt% H_2SO_4 cooled in an ice bath. Afterwards, KMnO₄ was added in batches. After stirring for 2 h, the mixture was stirred for 30 min at 35 °C. The temperature was then raised to 98 °C and maintained at that temperature for 3 h to ensure a high degree of oxidation in the graphite oxide. Following this, H_2O_2 was added to dilute the resulting resulting viscous mud. Then, the

mixture was centrifuged and washed with water several times, and the concentrate was diluted with water and sonicated for 1 h. Finally, a yellow–brown graphene oxide (GO) aqueous dispersion was obtained by centrifuging at 11,000 rpm to remove the not fully exfoliated portions from the mixture. A certain amount of GO dispersion was diluted by adding 1 M $K_2B_4O_7$, then stirring at room temperature for 2 h. The dilute suspension was sonicated and then filtered on a PES membrane substrate by using the vacuum-assisted filtration method. Before coating with GO, the PES substrate had been previously immersed in water for two days to remove any residues in the pores. The prepared membranes were heated in an oven at different temperatures for 5 h. The membranes are denoted as B-GO(X) or GO(X), where X represents the treatment temperature. Pristine GO membrane with different treatment temperatures (GO(X)) were also prepared for comparison, *via* the same procedure, but without the addition of $K_2B_4O_7$. For each type of membrane, three samples were prepared and tested for experimental reproducibility.

Characterization:

The morphology of GO was observed by transmission electron microscopy (TEM, JEOL JEM-100CXII). The samples were sonicated in water for 10 min then dipped onto support films and dried for observation. The chemical properties of the GOs were characterized by Fourier transform infrared spectra (FT-IR, Bruker Vertex 70). Wide-angle XRD patterns were used to investigate the *d*-spacing of stacked GO nanosheets by a D/MAX-2500 X-ray diffractometer (CuK α) at a speed of 3°/min. Membranes with thick separation layers (thickness > 1 µm) were utilized for some measurements of the GO layers alone, such as density, since they are more easily peeled off from the supports. Membranes with a thick separation layer (~1 µm) were prepared by filtering the GO suspension on PES supports, and the resulting GO layer membranes were carefully peeled off. For wet membranes, the membranes were first immersed in water for 1 day to ensure sufficient hydration, and then set

in the apparatus for subsequent measurements. The chemical compositions of GO were characterized by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 1600 ESCA) with a monochromatic Mg K α source and a charge neutralizer. The cross-sectional morphology of the membranes was observed by FESEM (NanoSEM 430). Before analysis, membranes were cryogenically fractured in liquid nitrogen and then sputtered with a thin layer of gold. To probe the interfacial structure at the angstrom level, VEPAS was used by implanting positrons to the specimens with moderate energy, and the depth profile of free volume can be evaluated by the *S* parameter. The mean implantation depth (*R*, nm) of the energetic positrons is expressed by the equation:

$$R = (\frac{40}{\rho})E^{1.6}$$

where E is the positron incident energy (keV) and ρ is the density (g/cm³) of the materials.

Density of GO membranes was measured by the buoyancy method using an electronic balance equipped with a density determination kit². Silicon oil with known density ($\rho_0 = 0.972$ g/cm³) was employed as the auxiliary liquid. The GO membranes (~1 µm) were carefully peeled off from the polyethersulfone (PES) supports and weighed both in air and silicon oil. Density of GO membranes (ρ_{GO}) was calculated by the following equation:

$$\rho_{\rm GO} = \frac{m_{\rm A}}{m_{\rm A} - m_{\rm L}} \rho_{\rm C}$$

Where m_A and m_L are the membrane weights in air and in silicon oil, respectively. Each sample was measured three times and the average value was used to calculate the membrane density. The results are listed in Table S1.

Gas permeation tests:

Separation performances of the membranes were measured by a conventional constant

pressure - variable volume technique with pure N₂, CH₄ and CO₂ and gas mixtures (CO₂:N₂ 50:50, CO₂:CH₄ 50:50, O₂:N₂ 50:50) as feed gases. H₂ was employed as the sweep gas. The apparatus is shown in Figure S7. Both the humidified state and dry state tests were conducted at 30 °C. Before testing in the humidified state, membranes were immersed in water for 1 day to ensure sufficient hydration and to wash out residual ions. Liquid water was pumped into the apparatus at controlled flow rates, vaporized, and then mixed with the feed gas and sweep gas in their respective humidifiers. The same system was used for the dry state tests, but the water vapor feed section was removed. The flow rates of the feed gas and permeate gas were measured or controlled by two gas mass flowmeters. The flow rate of sweep gas was fixed at 30 mL min⁻¹, while the feed gas flow rate at fixed pressure was 30~50 mL min⁻¹, depending on the permeation properties of the membranes. After reaching steady state (about 1 h), gas permeance (P/l, GPU, 1 GPU = 1×10^{-6} cm³(STP)/cm² s cmHg) of the membranes was calculated from the average value of three individual membrane tests, using the equation: $(P/l)_i = Q_i l/\Delta p_i A$, where Q_i represents the gas volumetric flow rate of "i" (cm³/ s)(STP), Δp_i is partial pressure difference across the membrane (cmHg), A represents the effective membrane area (12.56 cm² in this study). The standard deviation from the mean values of permeabilities was within ca.±5%. The ideal gas selectivity (α_{ij}) was calculated by: $\alpha_{i/j} = (P/l)_{i/(P/l)_j}$.



Figure S1. Cross-sectional FESEM images of membranes with different filtration volumes of B-GO. (a) and (b) 20 mL B-GO suspension, (c) 40 mL B-GO suspension and (d) 80 mL B-GO suspension. The selective layer thickness increases with the increased filtration volume.



Figure S2. Photograph of the B-GO/PES membrane. The membrane surface shows a uniform color, implying the uniform stacking of GO.



Figure S3. TEM images of GO after being treated with potassium tetraborate at 70 °C. About four layers of GO stack together, manifesting that borate induces the crosslinking of GO nanosheets.



Figure S4. Chemical structures of GO and B-GO membranes. (a) XPS of GO. (b) XPS of B-GO. (c) EDX mapping, top view of the B-GO/PES membrane surface.



Figure S5. FT-IR of membranes that have undergone different treatments. With increasing treatment temperatures, fewer bands associated hydroxyl groups are observed in the spectra, implying that higher temperatures induce borate to chemically attach onto the GO nanosheets and form borate orthoester bonds.



Figure S6. XRD patterns of the membranes in the dry and wet states. In the wet state, all the membranes show larger *d*-spacing. Higher treatment temperature leads to smaller *d*-spacing.



Figure S7. Apparatus for membrane gas separation. The apparatus contains two water reservoirs to humidify the feed and sweep gases. The humidity of the gases is controlled by the water pumps.



Figure S8. Effect of selective layer thickness on gas separation performance. Selective B-GO layers of less than 5 nm are not sufficiently compact to obtain defect-free composite membranes. Therefore, high CO_2 permeance and low CO_2 /gas selectivity is observed. As the selective layer thickness increases, the multilayered GO sheets seal any defects, allowing gas selectivity and gas molecule size discrimination in the interlayer nanochannels.



Figure S9. Effect of feed gas pressure on gas separation performance. The decreased CO_2 permeance and CO_2 /gas selectivity at higher feed gas pressure indicates carrier saturation in facilitated transport membranes.



Figure S10. CO_2 permeance stability of B-GO(50)/PES membrane over a 200 h time period (at 1 bar, 30 °C). The membrane shows good stability primarily due to the crosslinking effect of borate and enhanced interface adhesion between GO and PES.



Figure S11. Exploratory results of gas separation performances of GO membranes after treatment with various ions. The solid symbols represent gas separation performance tested in the wet state. The open symbols represent gas separation performance tested in the dry state.

Dry Membranes	Density (g/cm ³)
GO	1.583
GO(50)	1.625
GO(70)	1.687
GO(90)	1.711
B-GO(50)	1.445
B-GO(70)	1.535
B-GO(90)	1.611

 Table S1. Density of the membranes

Membrane	O ₂ permeance (GPU)	N ₂ permeance (GPU)	O ₂ /N ₂ selectivity
B-GO(70) wet	54.6	9.8	5.6
B-GO(70) dry	6.7	5.9	1.1

Table S2. O_2/N_2 separation performance of B-GO(70) membrane

To examine the size sieving effect, gases with low solubility coefficients and different kinetic diameters should be employed as feed gases. The O_2/N_2 gas pair have similar solubility coefficients, much lower than that of CO_2 , but different kinetic diameters. O_2/N_2 separation performance was investigated by using O_2/N_2 (50/50 vol%) gas mixtures. B-GO(70) membrane showed O_2/N_2 selectivity of 5.6, as shown in Table S2, which provides the supporting evidence for a molecular sieving effect. The B-GO(70) dry membrane with smaller nanochannel size exhibits much weaker molecular sieving effect.

Membrane	CO ₂ permeance (GPU)	CO ₂ /CH ₄ selectivity	CO ₂ /N ₂ selectivity	Reference
B-GO/PES	650	75	57	This study
TeO ₃ ²⁻ -GO/PES	232	53	48	This study
GO/PES	120	28	55	3
GO/PES	95	23	33	3
PVAm-PIP/PS	450	-	80	4
XL3/P1	1210	-	22	5
Ultem+zeolite	6.2	44	30	6
Poly4.0k/PAN	1770	13.9	59.9	7
Matrimid-ZIF8	23	23	27	8
AMT/PSf	842	140	123	9
Pebax-PEG/PAN	93	23	70	10
PVAm/PPO	440	-	183	11
DNMDAm-DGBAmE-TMC/PSf	1600	53	138	12

Table S3. Comparison of the membrane separation properties of GO-based and other composite and asymmetric membranes.

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