

Supporting Information

Shear-aligned Graphene Oxide Laminate/Pebax Ultrathin Composite Hollow Fiber Membranes Using a Facile Dip-coating Approach

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1. Experimental Section

1.1 Materials

The polyvinylidene fluoride (PVDF) hollow fiber membrane was generously provided by the Beijing Origin Water Technology Co., Ltd. (China). The average pore size of the membrane was 0.05 μm . The outer diameter, inner diameter and thickness were 1.1, 0.5 and 0.3 mm respectively. Pebax-1657 was purchased from Arkema, Australia and used for the preparation of polymer solution for composite hollow fiber membranes. The chemical structure of Pebax is shown in Figure S1. Pebax-1657 contains 60 wt% PEO and 40 wt% polyamide 6 (6 repeated units of PA). Poly (1-trimethylsilyl-1-propyne) (PTMSP) (Figure S1) was purchased from Gelest, USA and used as a gutter layer to minimize polymer solution intrusion. Graphene oxide (GO) nanosheets were prepared by oxidizing natural graphite powders (Sinopharm Chemical Reagent Co., Ltd, 45 μm) based on a modified Hummers' method. The detailed process can be found in other publication ^[1] All other chemicals were of the highest purity and used without further purification.

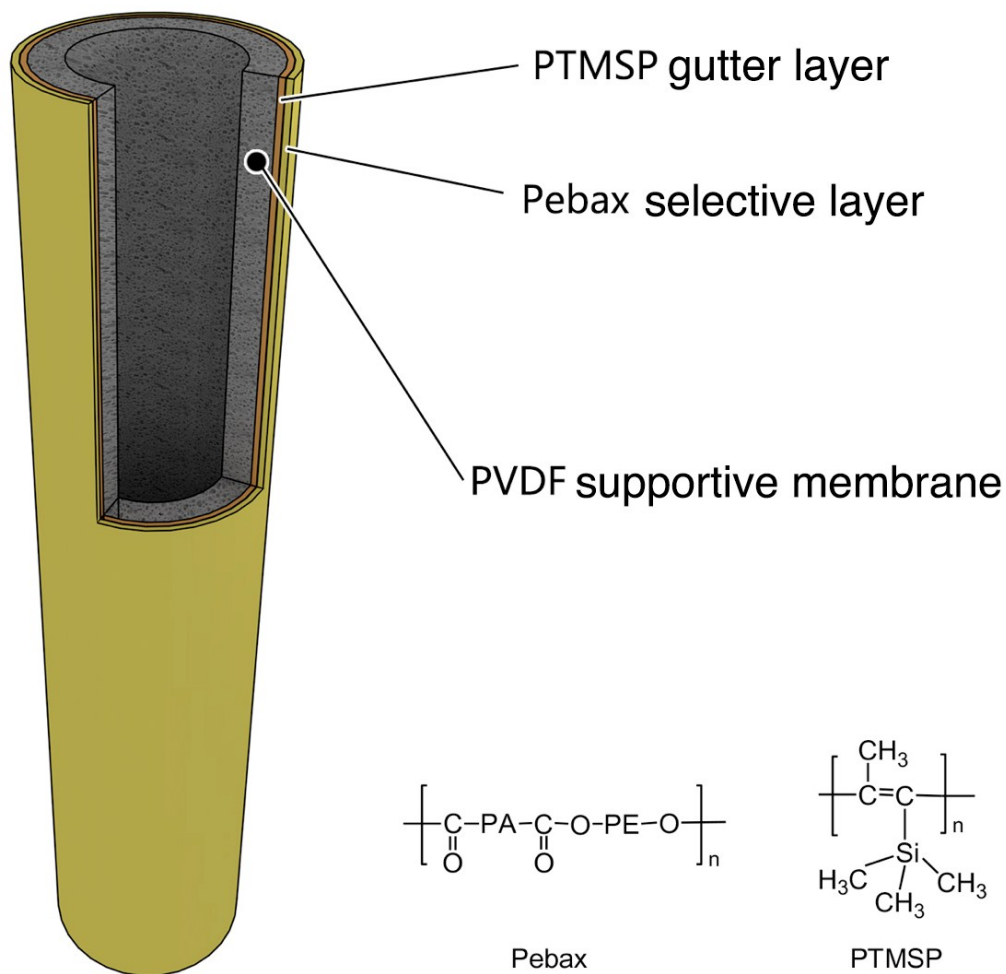


Figure S1 Schematic diagram of the dip-coated composite membrane

1.2 Membrane fabrication and Characterization

1.2.1 Membrane fabrication

In order to minimize the intrusion of the polymer solution into the supportive membrane pores, the PVDF membrane was firstly soaked in Milli-Q water to fill the pores. Initially PTMSP gutter layer was coated onto the polymeric membrane. The dip-coating solution contained 10 wt % PTMSP dissolved in n-Hexane. Four coating cycles were applied for the gutter layer. The PVDF membrane was immersed into

coating solution at a constant speed (0.8 cm/s), followed by 60 s of immersion. Then the hollow-fiber membrane was withdrawn at a constant speed of 0.3 cm/s. The dip-coating was carried out at 25 °C and 60 % relative humidity. The coated membrane was placed in over at 50 °C for 8 h after each cycle. In order to ensure the evenness of the coating layer, after each coating cycle the membrane was turned upside down for the subsequent coating cycle. In terms of the Pebax coating, the PTMSP pre-coated membrane was soaked into 3 wt % Pebax solution (70% ethanol/30% water). The coating parameters were identical to the gutter layer coating. In this work, at least three samples were fabricated for each recipe to investigate the reproducibility.

1.2.2 Characterization of the GO

The samples were characterized by various techniques. FTIR spectra were performed at 2 cm⁻¹ resolution with Thermo Nicolet IR 200 spectroscope (Thermo Nicolet Corporation, USA). Typically, 64 scans were signal-averaged to reduce spectral noise. The spectra were recorded in the 400-4000 cm⁻¹ range using KBr pellets. XRD pattern was obtained using a Philips X Pert-Pro diffractometer with Cu K α ($\lambda=0.154$ nm) radiation operating at 35 kV and 25 mA and a step width of 0.04°. The morphology of samples was observed by a FEI Model TECNAI G² TEM (200 kV acceleration voltages). The pore size distribution of the supporting membrane is characterized by the porometer (CFP-1200-AEXL Capillary Porometer). The samples of GO nanosheets were dispersed in solvent, then the suspended particles were transferred to a copper grid (400 meshes) coated with a strong carbon film. Dispersion (3 μ L) of GO

was dropped on freshly cut mica followed by air drying for AFM analysis. AFM analysis was performed on the AFM apparatus (DI Nanoscope IIIa, Veeco, USA).

1.2.3 Characterization of the composite membrane

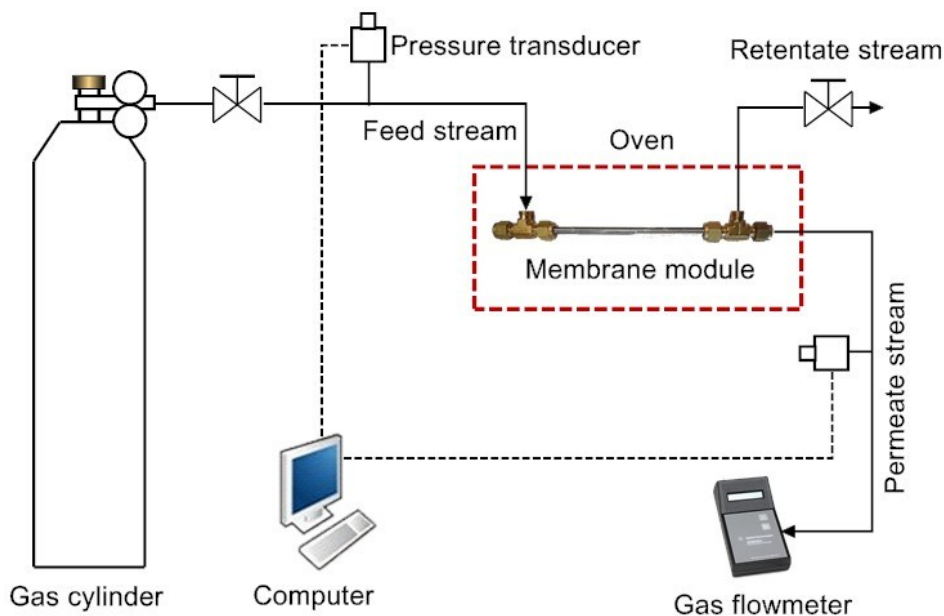
The dried samples were sputter-coated with chromium for SEM images by the FEI Nova NanoSEM 230 FESEM, operating in backscatter mode at 5 kV or 15 kV accelerating voltage. In terms of the TEM imaging, the samples of Pebax/GO membrane were embedded in epoxy resin and cross sections with a thickness of 60 nm were obtained by sectioning with a Leica Ultracut UCT ultramicrotome. Then these thin sections were mounted on the carbon-coated TEM copper grids.

The gas adsorption isotherm was carried out with Micromeritic Tristar 3000 analyzer. Prior to the test, all samples are placed in a 50 degree oven for at least 48 h. At least 1 g sample was loaded into the sample vial and dried under vacuum for 3 h at 120 degree. For the nitrogen test, the isotherm test was carried out with liquid nitrogen environment with the pressure range of 0-1 bar, and the obtained data were analyzed based on the Brunauer, Emmett, and Teller (BET) and Barrett, Joyner and Halenda (BJH) models. In terms of the CO₂ adsorption test, it was carried out with icy water condition with the pressure range of 0-0.03 bar.

The tensile strength of the hollow fibre membranes was tested with the textural analyzer (TA-XT2, Stable Micro Systems). The sample length was 100 mm, and the testing speed was 0.5 mm/s. The change of the stress under different elongation rate was recorded.

1.2.4 Gas permeation test

The gas permeation tests were carried out in a hollow fiber membrane gas separation rig (scheme 1). The membrane was mounted in a quarter inch steel membrane module prepared with stainless steel Swagelok tube fittings. The membrane was sealed with epoxy resin. In all tests, the feed gas pressure was fixed at 2 bar (gauge pressure), and the permeate side pressure was atmospheric. The gas flux was monitored by the Agilent ADM1000 gas flowmeter. The shell side was set as the feed side. The ideal selectivity was calculated as the ratios of pure gas permeances and expressed in terms of $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ and gas permeation units (GPU).



Scheme 1 Gas permeation apparatus

1.2.5 Viscosity and surface tension test

The viscosity GO/Pebax solution was analyzed with the Brookfield Rheometer DV3T viscometer. 1 ml solution was added and the total analyzing time was 90 s. In terms of the liquid surface tension, it was monitored with the Pendant drop method (KSV Cam

200 Instrument, Finland) and further calculated with the Young-Laplace equation.

2. Result and discussion

2.1 Characterization of GO

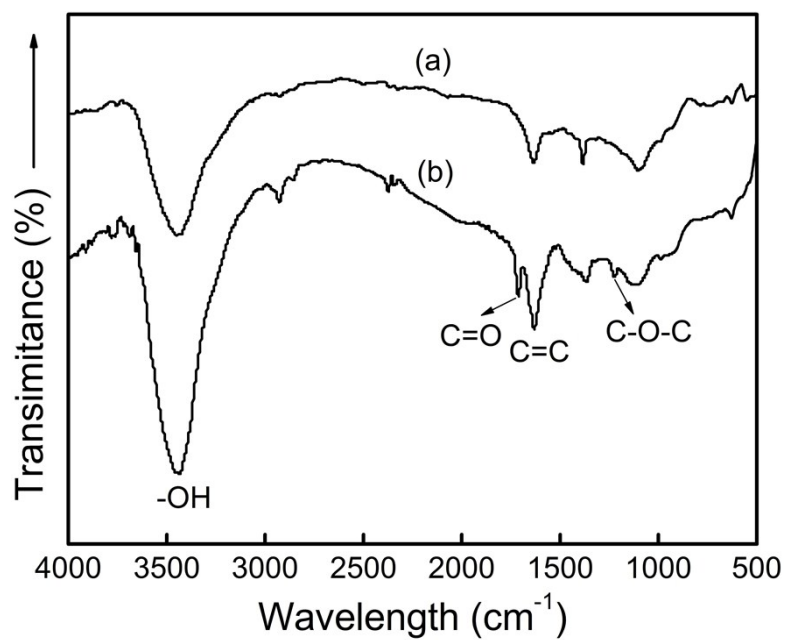


Figure S2 FTIR spectra of (a) graphite and (b) graphene oxide

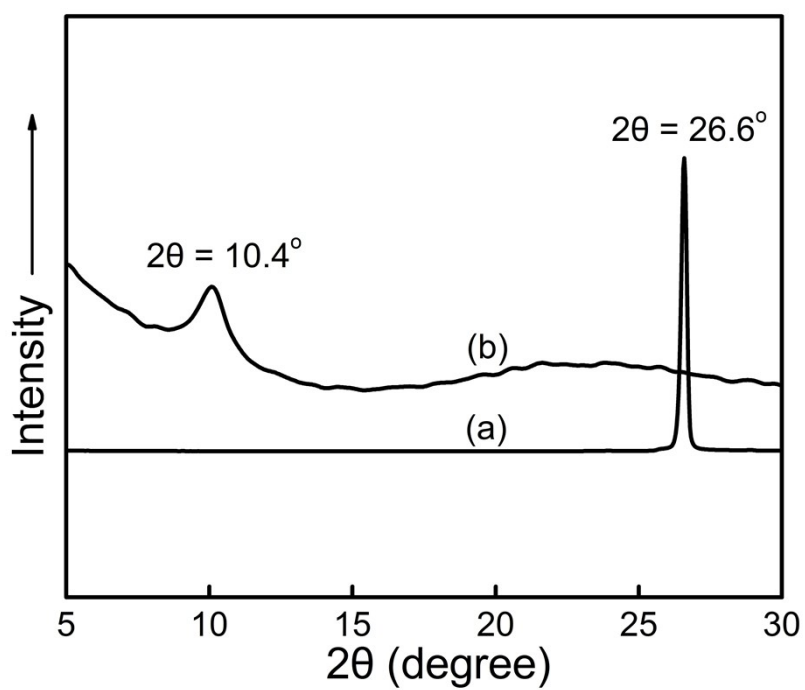


Figure S3 XRD patterns of (a) graphite and (b) graphene oxide

2.2 Characterization of the composite membrane

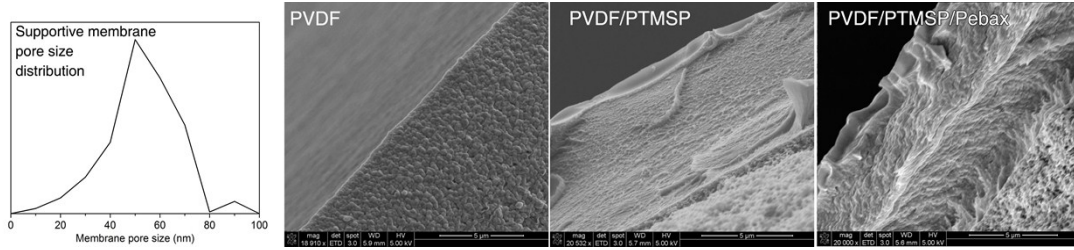


Figure S4 Supporting membrane pore size distribution and SEM images of the original PVDF, PTMSP coated and PTMSP-Pebax coated membrane

2.3 Calculation of the liquid film thickness

The dip-coating process is a wide-spread industrial process that consists of the deposition of a liquid film onto a solid surface. Based on the Landau-Levich mensicus theory, when the capillary number Ca_0 is lower than 1, the film thickness (h_0) formed by the dip-coating process can be calculated with:^[2]

$$h_0 \sim 0.94aCa_0^{2/3} \quad (1)$$

when the Ca_0 is higher than 1, the h_0 value can be calculated with:

$$h_0 \sim aCa_0^{1/2} \quad (2)$$

where the capillary length a can be determined by:

$$a = \sqrt{\lambda / \rho g} \quad (3)$$

In equation 3, γ is the surface tension (25.5 mN/s), ρ is the density of the GO/Pebax coating solution (0.845 g/ml), and g is the gravitational acceleration (9.8 m/s²).

The Ca_0 can be determined by:

$$Ca_0 = \eta V_0 / \gamma \quad (4)$$

where η is the viscosity of the GO/Pebax coating solution (3.90 mPa). V_0 is the withdrawn speed during the dip-coating process (0.1-1 cm/s in this work).

Within the tested withdrawn speed, as the capillary number Ca_0 in this work is lower than 1, the liquid film thickness h_0 can be calculated as Figure S5.

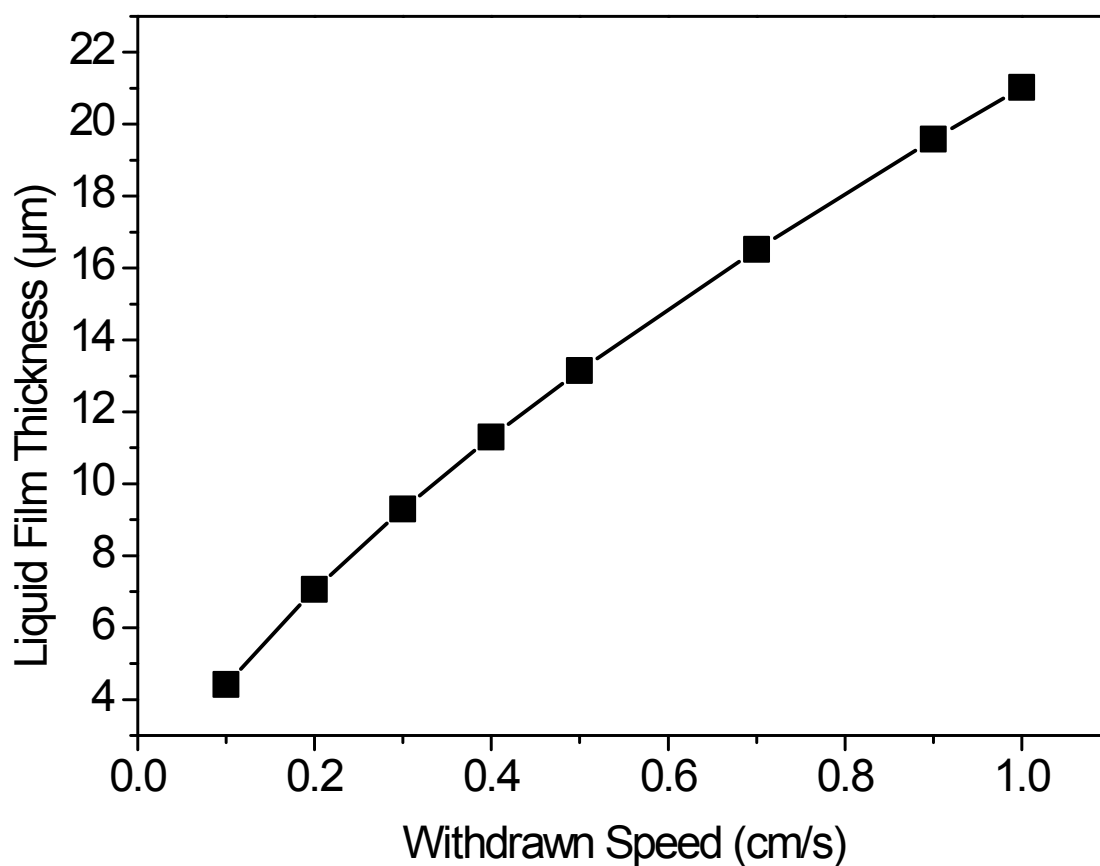


Figure S5 The liquid film thickness with different withdrawn speed (3 wt% Pebax, 0.1 wt % GO)

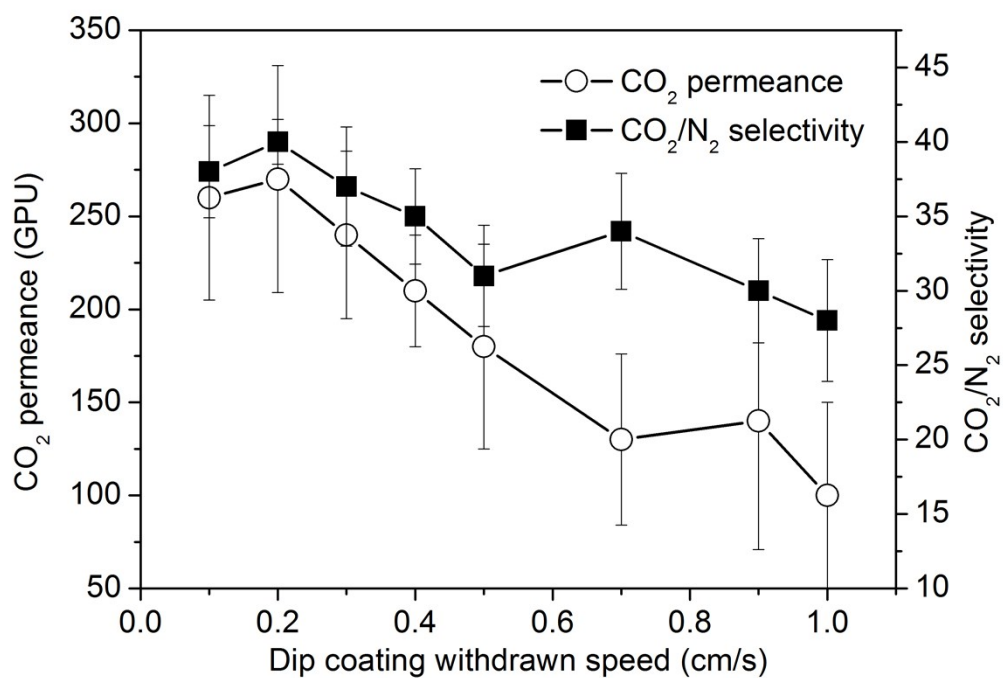


Figure S6 Membrane performance with different withdrawn speed (0.2 wt % GO)

3. Reference

- [1] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS nano* **2010**, *4*, 4806-4814.
- [2] M. Maleki, M. Reysat, F. Restagno, D. Quéré, C. Clanet, *Journal of Colloid and Interface Science* **2011**, *354*, 359-363; bE. Ramé, *Physics of Fluids* **2007**, *19*, 078102.