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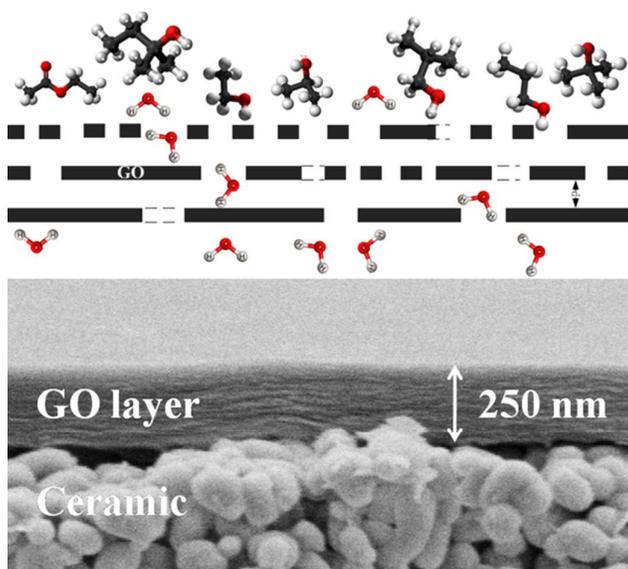


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Porous Al₂O₃ tube supported GO composite membranes with submicron thickness and improved mechanical strength were fabricated via an opposite charges attraction and pressure deposition method. High separation performance (flux, selectivity and stability) was achieved in the pervaporation of water-organic azeotropes.

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ARTICLE TYPE

Efficient dehydration of the organic solvents through graphene oxide (GO) / ceramic composite membranes

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Porous Al₂O₃ tube supported GO composite membranes with submicron thickness and improved mechanical strength were fabricated via a filter-pressing deposition method. High separation performance (flux, selectivity and stability) was achieved in the pervaporation of ethanol, n-propanol, isopropanol, ethyl acetate and butanol isomers aqueous mixture.

Dehydration of organic solvents is an important industrial separation process. Traditional thermal processes have always been energy intensive and cannot separate azeotropics with low energy penalty. Membrane separation has been widely studied as a viable alternative to these traditional methods because it offers advantages of high efficiency, low cost and energy saving. Pervaporation is one such type of membrane process with wide application in azeotropic separation. Numerous studies have been devoted to the application of polymeric, inorganic and hybrid membranes in this area. However, the process economics strongly depends on the membrane performance of flux, separation factor, and stability. Therefore, higher performance and fabrication simplicity is urgently required to overcome the current limitations of common membrane.

GO¹, with hexagonally arrayed carbon atoms binding with -OH, -OOH and -O- groups, has generated a significant amount of interest for membrane separation due to their intrinsic properties of single-atom thickness, excellent flexibility, hydrophilicity and regular interlamination distance. In addition, the structural defects of GO also can be utilized for high selectivity toward light gases.² Recently, the demonstration of fast permeation of water through GO membrane³ has triggered many proposals to use GO for water permselective separation in waste water treatment and desalination.⁴⁻¹² The rejected objects from the water solution by GO membrane include cations, anions, nanoparticles, and macromolecule.^{4, 8-12} Very recently, the pervaporation permeation behaviours of water-organic solvents through GO based membranes was also reported.^{6, 7, 13, 14}

However, the integral mechanical strength of GO membranes is considered as the critical challenge for the practical separation due to the weak interaction between GO flakes, although the building unit of GO membranes, single-layered GO flake, has high mechanical strength.¹⁵ Ceramic porous supports, which is widely employed in inorganic membranes, are the most promising candidate to improve the strength and availability of GO based membranes due to their characters of rigidity, easy sealing / integration and scale up. However, the key points of this

proposal are to achieve defect-free and ultrathin selective layer as well as strong interaction forces between support and GO layer.

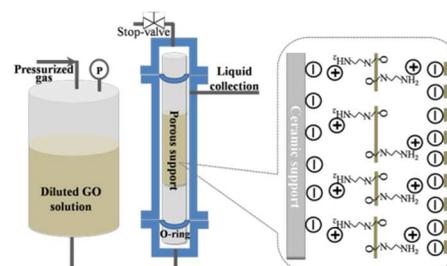


Fig.1 Schematic of GO/ceramic composite membrane preparation

Here, we prepared ultrathin GO composite membrane on porous Al₂O₃ tube through pressure driven filtration deposition. A very thin GO interlayer existed between support surface and GO body layer was charge modified to enhance the interaction of the support and GO membrane. The pervaporation separation behaviours of a term of organic aqueous mixtures, such as EtOH, n-propanol (NPA), IPA, ethyl acetate (EA) and butanol isomers, over the GO/ ceramic membranes were systemically investigated. GO suspension was prepared from graphite powders by the Hummers' method with further post treatments of ultrasonic processing and centrifugation.¹⁶ The GO size was then ordered by centrifugation treatments at different speed between 2000-10000 rpm. The small size GO, ca. 0.3*0.4 μm², was obtained from the supernatant of GO aqueous after 10000 rpm centrifugation (Fig. S1 & S2). The large size GO, ca. 1.2*1.4 μm², was collected by re-dispersing the sediment of GO after 3000 rpm treatment (Fig. S1 & S2). Porous alumina tubes (Inopor, Germany), inner / outer diameters, length, nominal surface pore size and weight of the tubes are 7/10 mm, 65 mm, 100 nm and ca. 7.5 g, respectively, were used as support. The diluted suspensions of these two kinds of GO were sequentially deposited on the inner surface of Al₂O₃ tube to form asymmetric GO layers under an incremental driving-pressure from 2 to 15 bar (Fig. 1). Before deposition, charge modification was carried out only for the large size GO. The negatively charged GO was treated with ethanediamine (EDA) to reverse the surface charge⁴, which should enhance the interaction between the interface of Al₂O₃ surface (negative charge) and positively charged GO (Fig. 1). In a typical synthesis, ca. 0.2 mg large size GO was diluted to 200 mL by DI water. Then 5 mg 1-[3-(Dimethylamino) propyl]-3-ethylcarbodiimide (DEC) methiodide and 0.5 mL EDA were added into the large size GO

solution followed by 30 min ultrasonic treatment at room temperature. The charge modified larger size GO was firstly deposited under 2–4 bar drive pressure to form a very thin layer to cover the possible defects of the support and prevent crowding of the following small size GO into the pore of support under pressure. The small size GO was used to create more boundaries between GO flakes, which benefits water interaction in the separation. In a typical synthesis, ca. 0.2 mg small size GO was diluted to 200 mL by DI water. Then it was deposited on the surface of large size GO layer drove by a pressure from 8–15 bar. The as-prepared membranes were dried and solidified overnight at 45 °C in vacuum. See more experimental details in ESI.

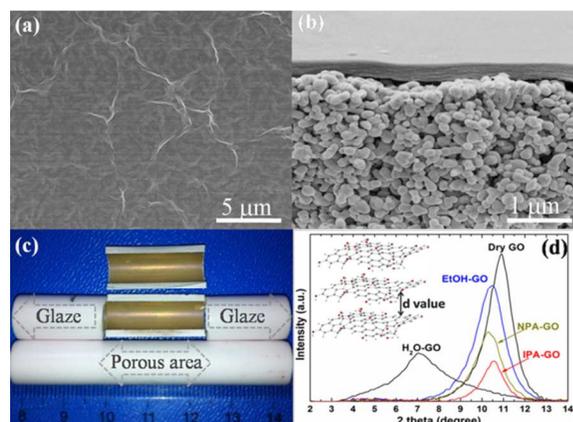


Fig. 2 (a) SEM top views; (b) SEM cross-section view; (c) optical image of GO/Al₂O₃ membrane; (d) XRD patterns of GO membrane in solvents.

Fig. 2 a & b show the morphology of GO / ceramic membrane. The surface of GO layer exhibited highly smooth surface and no visible defects were observed under SEM. Wrinkles, probably formed during the shrinkage after the dehydration of the as-deposited GO membrane, were naturally distributed on the surface (Fig. 2a). They are helpful for the membrane's mechanical stability because wrinkles can provide a buffer space as the membrane is swelling in water / solvent media. The Al₂O₃ substrate morphology underneath the GO layers can be clearly observed from the top view (Fig. 2a) because of the supported GO layer was as thin as ca. 260 nm (Fig. 2b). The cross-section of the GO membrane shows a uniform thickness with highly ordered and well-packed 2D lamellar structure. A homogenous light-brown colour was observed from the optical image of the broken membrane (Fig. 2c), which is typical for GO.³ The crystalline structure of GO layer in different solvents was measured by XRD over the 2θ range of 2° and 15°. The dried GO layer exhibited an intense peak at 10.9° which corresponds to a d-space value of 8.1 Å (Fig. 2d). It agrees well with that of GO laminates in air i.e. 9 ± 1 Å.¹ After introducing H₂O to the dried GO layer, the peak shifted to 7.1°, which translated to a larger 12.4 Å d-space value. However, the d-space of GO layer treated by EtOH, NPA and IPA were fixed around 8.4 ± 0.1 Å, only slightly larger than that of the dried GO layer. It indicated that the organic molecules were not intercalating the GO inter-lamellas, which might be the result of incompatibility between hydrophilic GO layers and the hydrophobic alcohols. TG-MS results show that the N-contained species, NH₃ and NO, were released at the temperature 140 and 204 °C, respectively (Fig. S3). XPS result reveals that 5.9 at.% N was detected from amine treated GO layer

(Fig. S4a). Furthermore, amide group was existed in the C1s peak simulation (Fig. S4c), which suggested that amide was formed through the carboxylic acid group of GO and the amine terminal group of EDA. This deduction is further supported by the FT-IR (Fig. S5). Amino and amide stretch at 1590 and 1634 cm⁻¹, respectively, in the modified GO sample, which is consistent with the literature.⁴ It demonstrated that the apparent charge of large GO flakes were changed from negative to positive, successfully, which is beneficial to effectively combine support and GO by oppositely charge pairs. The tensile test revealed that the breaking strength and the elongation at break of GO layer were 15.9 MPa and 0.81%, respectively (Fig. S6). It indicated that the integrated mechanical strength of the composite membrane was most contributed by the rigid ceramic support.

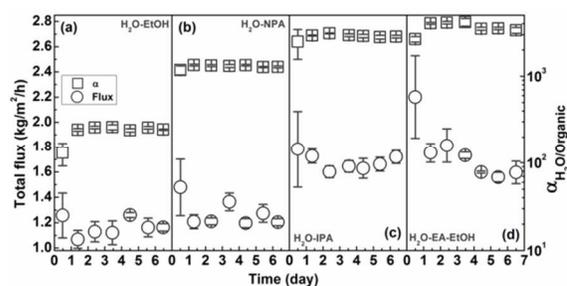


Fig. 3 Separation behaviors of GO/ceramic membranes for the water /organic (1/9) mixtures at 70 °C. a) H₂O / EtOH, b) H₂O / NPA, c) H₂O / IPA and d) H₂O / EA / EtOH (1/8/1).

The pervaporation separation of GO membranes for water-organic mixtures was carried out in a flow system (Fig. S5). The membrane performance was evaluated by the flux (*J*) and separation factor (*α*) determined as follows:

$$J = \frac{W}{A \times t} \quad (1)$$

$$\alpha = \frac{P_{\text{water}}}{P_{\text{organic}}} \times \frac{F_{\text{organic}}}{F_{\text{water}}} \quad (2)$$

Where *W* is the weight of permeation (kg), *A* is the membrane area (m²), *t* is the permeation time (h), *P_i* and *F_i* are the concentrations on the permeation and feed side, respectively. The permeation rate and composition of permeated liquid were analyzed 4 times each day with 1–2 h sample collection intervals. Fig. 3 shows the daily average pervaporation performance of GO composite membranes (parameters listed in Table S1) at 70 °C for 10 wt. % H₂O contained EtOH (Fig. 3a), NPA (Fig. 3b), IPA (Fig. 3c) binary mixtures and 10% H₂O–80% EA–10% EtOH ternary mixture (Fig. 3d), respectively. For H₂O–EtOH separation, the flux decreased from 1.4 to 1.1 kg/m²/h on the first day and remained at 1.2 ± 0.1 kg/m²/h in the next 6 days test. The separation factor (*α*_{H₂O/EtOH}) initially increased from 98 to ~250 and remained at 250 ± 13 in the following days (Fig. 3a). It seems that the GO composite membrane went through a dynamic process before reaching the steady state. Similar tendencies were observed for the other systems (Fig. 3b–d). The fluxes of H₂O–NPA and H₂O–IPA systems decreased from 1.7 and 2.1 kg/m²/h to 1.3 ± 0.1 and 1.7 ± 0.1 kg/m²/h, respectively, while *α*_{H₂O/NPA} and *α*_{H₂O/IPA} were fluctuating in 1293 ± 81 and 2942 ± 152. To compare with alcohol-water systems in the same H₂O wt.%, the dehydration behaviours of 0.1H₂O–0.8EA–0.1EtOH ternary

azeotrope over GO membrane was investigated as the maximum solubility of EA in water is ca. 10 wt.% at ambient temperature. Similarly permeation flux was dropped from 2.6 to 1.8 kg/m²/h and $\alpha_{\text{H}_2\text{O}/\text{organics}}$ increased from 2350 to 4400 followed by a slight decrease to 3500 in 7 d test (Fig. 3d). Higher separation factors, i.e. >5000, and similar fluxes, i.e. 1.6-1.8 kg/m²/h, were achieved for the binary mixtures of H₂O-*iso*-butanol, H₂O-2-butanol and H₂O-*tert*-butanol under the same conditions (Table S1).

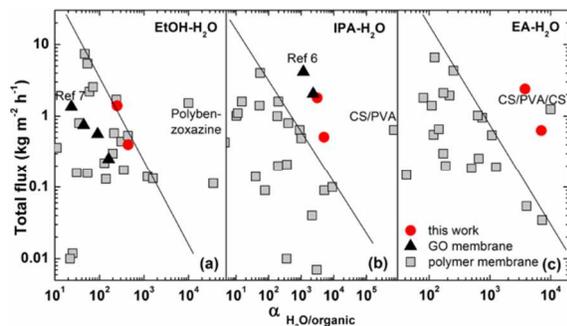


Fig. 4 The comparison of GO/ceramic membranes with polymer membranes and GO membrane in literature.

Obviously, the separation factors of the GO membrane for different mixtures increased with the size of organic molecules, which is well consistent with the observation of Joshi et al.⁹ The thickness of single layer GO is ~3.5 Å, so the distance between hydrated GO layers is ~8.9 Å (=12.4-3.5 Å, Fig. 2d), which is close to the hydro-dynamic diameter of NPA (8.96 Å).⁹ It means that molecules larger than NPA will be rejected by the GO membrane due to a molecular sieving mechanism. Therefore, the separation factors significantly increased as the EtOH was replaced by NPA, IPA, EA and butanol isomers. On the other hand, the GO membrane also can block the permeation of molecules smaller than the distance between GO inter-lamellas (e.g. high $\alpha_{\text{H}_2\text{O-EtOH}}$), which might be attributed to the incompatibility between hydrophilic GO and hydrophobic organics. The separation performance of the GO composite membrane was compared with the upper bound plot of polymeric membranes as well as GO based membranes^{6, 7, 17-19} (Fig. 4). In the case of H₂O-EtOH separation, the GO composite membrane is located on the asymptotic line of the upper boundary of polymeric membranes and shows an adequate performance in comparison with others (Fig. 4a).¹⁷ For larger molecules e.g. IPA and EA, however, the performance of the GO membrane is better than that of most of polymeric membranes (Fig. 4b&c).^{17a, 18, 19} It demonstrates that GO / ceramic membrane has extraordinary separation properties for azeotropes separation. On the other hand, the flux of GO/ceramic membrane for H₂O-EtOH separation was similar to that of the ca. 10 μm thick and unsupported GO membrane⁷ (Fig. 4a). But the H₂O/ethanol separation factor is little bit higher than that of it due to the thinner GO selective layer of our membrane. For the IPA-H₂O separation, the GO/ceramic membrane shows a higher separation factor but lower permeability than the ca. 1 μm thick GO / modified polyacrylonitrile (mPAN) membrane.⁶ Suhas et al. reported GO doped sodium alginate membranes for IPA-H₂O pervaporation separation, in which a flux of 2.7 kg/m²/h and a selectivity of 4623 were achieved.¹³ The separation performance of GO/ceramic membrane is also comparable to that kind of GO modified membranes.

The permeation behaviour of the GO membrane was investigated for various mixtures with 10% H₂O at different temperature. The permeation flux increased with temperature rise from 30-70 °C (Fig.5), which can be expressed by an Arrhenius equation:

$$P = P_0 e^{-\frac{E_a}{RT}} \quad (3)$$

P and P_0 are permeation rate and the pre-factor, respectively. Various steps, such as adsorption / desorption of H₂O on / from GO and H₂O diffusion through oxide / pristine regimes of GO lamellas, may contribute to the apparent activation energy, though the details of such processes is not clear. For the mixture separation, E_a of H₂O permeate through GO composite membrane were very close, between 29.1 and 32.1 kJ / mol (Fig. 5), which suggests that these organics have the similar effect on the H₂O permeation. In addition, slightly lower E_a , 25.5 kJ / mol, was derived from the permeation of pure water feedstock (Fig. 5). It indicates that these organics in the mixtures have weak interaction with the GO membrane, which is also supported by the XRD results in Fig 2. It should be noted that the stability of GO composite membrane in pure water atmosphere is significantly weaker than it in the mixture atmosphere.

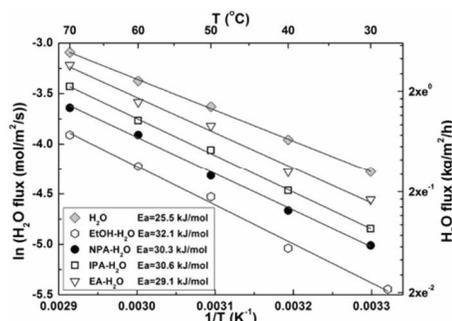


Fig. 5 Temperature dependence of GO composite membranes. H₂O fluxes of pure water have been divided by 2 for clarity of display.

In summary, extremely flexible GO was successfully combined with rigid porous ceramic tubes to form an ultrathin composite membrane by a preparation method that integrated opposite-charges attraction and pressure driven asymmetric deposition. Charge modification of GO not only improved the stability of the composite membrane but also protected the original properties of GO by introducing a short amine. Extraordinary separation performances of the GO membranes were achieved from the pervaporation of water-contained binary and ternary azeotropes. The high separation factor towards water is mainly attributed to the molecular sieving effect from the narrow opening (distance) between GO layers (especially for molecules larger than NPA). The incompatibility between the hydrophilic GO layers and the hydrophobic organic molecules also contribute to the separation. The stability of GO composite membranes was proved through one week pervaporation testing. The temperature dependence of H₂O permeation suggests that organic molecules have weak interaction with GO membranes during the separation.⁹⁰ This work was supported by National 863 Project (No: 2012AA050104) and Advanced Coal Project of Chinese Academy of Sciences (No: XDA07040401).

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† Electronic Supplementary Information (ESI) available: experimental details and AFM, FTIR and XPS results. See DOI: 10.1039/b000000x/

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