

**Sharp molecular-sieving of alcohol-water mixtures over phenyl-
diboronic acid pillared graphene oxide framework (GOF)
hybrid membrane**

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Experiments

1. Graphene oxide synthesis

GO was prepared by the Hummers' method with further post treatments of ultrasonic processing and centrifugation¹. Briefly, graphite powder (235 meshes, 1.5 g, Aladdin Chemistry Co. Ltd), NaNO₃ (1.5 g), and H₂SO₄ (98%, 69 mL) were mixed and stirred in an ice-water bath for 30 min followed by adding 9 g KMnO₄. The mixture was then stirred for 1 h at room temperature. 100 mL deionized water was added to the mixture followed by stirring for 30 min at 90 °C. Additional 300 mL of water was poured into the mixture followed by slowly adding 30% H₂O₂ (10 mL). The reaction mixture was filtered and re-dispersed in water several times until its pH value was closed to 7. Finally, the filtrated GO was dried in vacuum overnight.

2. Graphene oxide framework synthesis

The benzenediboronic acid linked graphene oxide framework (GOF) materials were synthesized by solvothermal method^{2, 3}. Briefly, GO (40.7 mg), 1, 4-benzenediboronic acid (14PDBA, 213.3 mg) and 30 mL methanol were mixed in a capped vial and stirred at 90 °C for 60 h. Then the solid product GOF was separated by centrifugation at 10000 rpm for 20 min. The sediments were re-dispersed in methanol and centrifuged for several times to remove residual reagents. The washed GOF was dried at 55°C in vacuum before use.

3. GOF/PVA composite membrane preparation

Asymmetric porous alumina tubes supplied by Inopor Co. (Germany) were used as support. The inner and outer diameters and the length of the tubes are 7, 10 and 65

mm, respectively, and the nominal pore size of the inner surface is ~100 nm. Both ends of support were glazed at 900 °C (Duncan, Fresno, CA) but left with a ~3.0 cm middle section corresponding to 6.5 cm² surface area for membrane deposition⁴. The supports were cleaned sequentially by ethanol, 4% aqueous KOH solution and deionized water before membrane synthesis⁵. Dried GOF was re-dispersed in water by stirring for 30 min and pulse ultrasonic treatment (125 watt, 20 kHz) for 60 min to prepare 0.5 mg / mL GOF suspensions. Polyvinyl alcohol (PVA) aqueous solution (5 wt.%, 0.514 g) are added to GOF suspensions (0.5 mg / mL, 21 mL) by stirring for 30 min to form stable GOF / PVA suspensions with a mass ratio of 3:7 (GOF:PVA). Then the suspension was degassed for 60 min before membrane preparation.

Ultrathin GOF/PVA composite membrane was prepared on the inner surface of porous Al₂O₃ tube with dip-coating method. The tube was vertically immersed into the GOF/PVA suspension with a descent rate of 5 mm / s. After dwelling in the suspension for 30s, the tube was pulled out with a lift rate of 1 mm / s. The as-prepared membranes were dried at 55 °C in vacuum overnight.

4. Pervaporation separation

The separation performances of GOF / PVA composite membranes for water contained azeotropes and methanol contained solvent mixtures were carried out with the pervaporation (PV) method in the temperature range from 30-70 °C. The setup was described in our previous work^{5, 6}. The GOF/PVA composite membrane was fixed with O-rings in the separator. Then the separator was vertically fixed in an oven. The water-organic mixture (4 L each) was fed into the lumen side of membrane with a

flow rate of 2 ml / min by a constant flow pump. Liquid of lumen side was returned back to the feedstock. The retentate side of separator was connected in sequence with sample collector, which is immersed in liquid nitrogen cold trap, and vacuum pump, by which the pressure of retentate side was kept around 100 Pa. Permeation liquid was begun to collect after 60 min running of PV system under the certain pressure and temperature. The weight of permeated liquid was calculated from the weight different of sample collector. The collection interval, which depends on the permeability of membrane, is in the range of 2 to 5 h. The composition of permeation liquid as well as feedstock for water-alcohols was analyzed by a GC with TCD detector (Shimadzu GC-2014C, HP Plot/U 0.2 μm \times 30 m). In the case of de-methanol separation, permeation liquid was analyzed by GC with FID detector (Shimadzu GC-2014C, DB-FFAP 0.53 mm \times 30 m). Based on the result of GC analysis, the concentration of mixture feedstock was corrected everyday by adding component.

5. Material characterizations

The size and thickness of mono-dispersed GO and GOF were analyzed in tapping mode using atomic force microscopy (AFM, NanoScope IIIa). The surface and cross-sectional morphology of the membranes were characterized by scanning electron microscopy (SEM, S 4800 Hitachi, 5 kV) and transmission electron microscopy (TEM, JEM-2100, 200 kV). The structure of GOF layers in air or organics were determined by X-ray diffraction (XRD, RigakuUltima IV) using Cu K α radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA). The near-surface compositions of GOF were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Al K α radiation, 1486.6 eV, 12

kV, 3 mA). XPS peak positions were calibrated with the help of the C 1s peak at 285.0 eV. The surface chemistry of GOF was analyzed by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, Thermo Fisher). The thermal properties of GO membranes were analyzed by Thermal Gravimetry - Quadrupole Mass Spectrometer (TG-MS, STA 449F3/ QMS 403, NETZSCH) in the temperature scale of 40-600 °C with a 2 °C/min heating rate. Mechanical property measurements of GO layer and GOF/PVA layer were performed on a tensile tester (XQ-1C, Shanghai New Fiber Instrument Co., Ltd.). Both the GO layer and GOF/PVA composite layer for the tensile stress test were free-standing. For the preparation of free-standing GO membrane, firstly, supported GO membrane with ca. 15 microns thickness was deposited on the inner surface of porous ceramic tube by filter-pressing method. The as-prepared GO/ceramic membrane was dried in vacuum at 65 °C for 72 h. The GO layer would be peeled off from the support during the thermal treatment because of the shrinkage of GO. GO layer was cut into pieces with size of 3mm*20mm. For the preparation of free-standing GOF/PVA membrane, the suspension of GOF and PVA was decanted into a retainer ring supported on glass board. Then the casted membrane was dried on a hotplate at 60 °C for 72 h. The GOF/PVA layer was peeled off from glass. GOF/PVA layer with thickness ~20 microns was cut into pieces with size of 3mm*20mm before tensile stress test. The tensile stress was calculated as Tensile stress (MPa) = Force at broken (cN)/sectional area (m²) = F/thickness of layer/width of sample.

Results

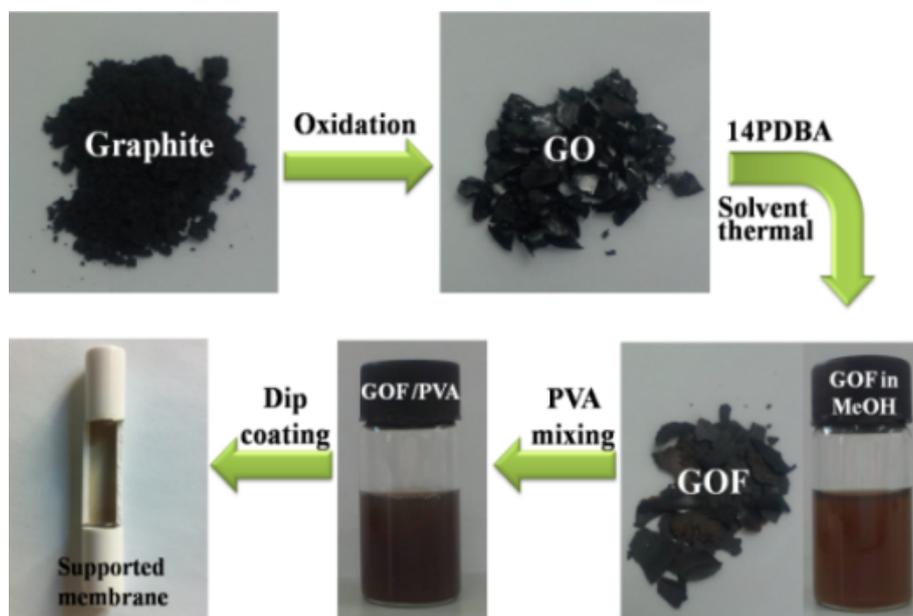


Fig.S1 Preparation procedures of GOF/PVA composite membranes.

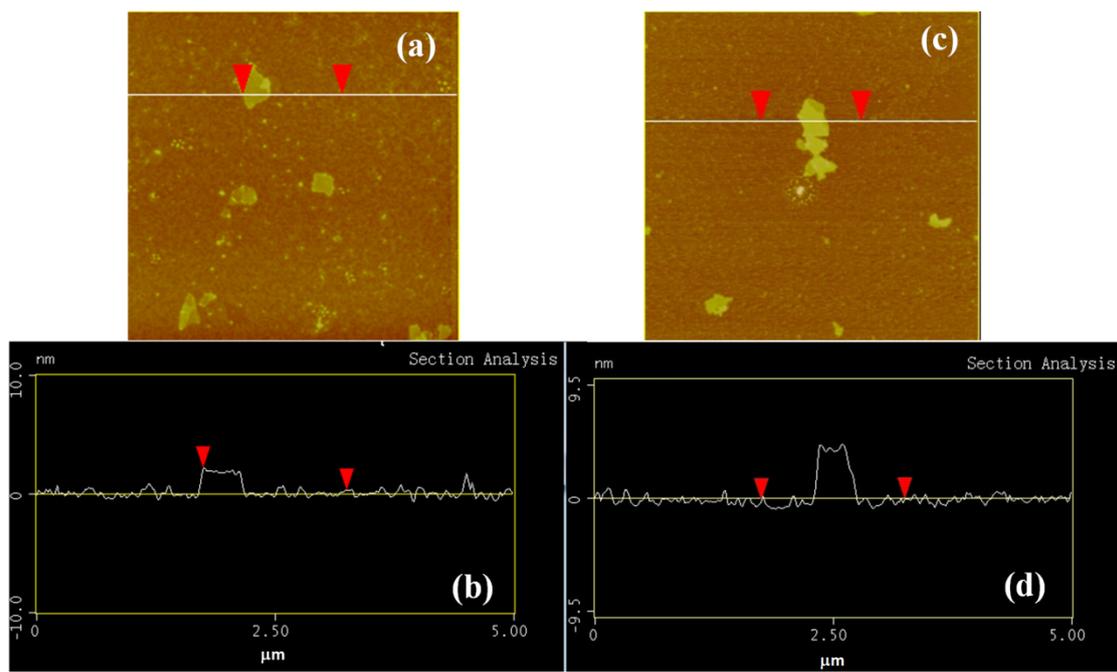


Fig. S2 AFM section analysis of GO (a) & (b) and GOF (c) & (d) mono-disperse.

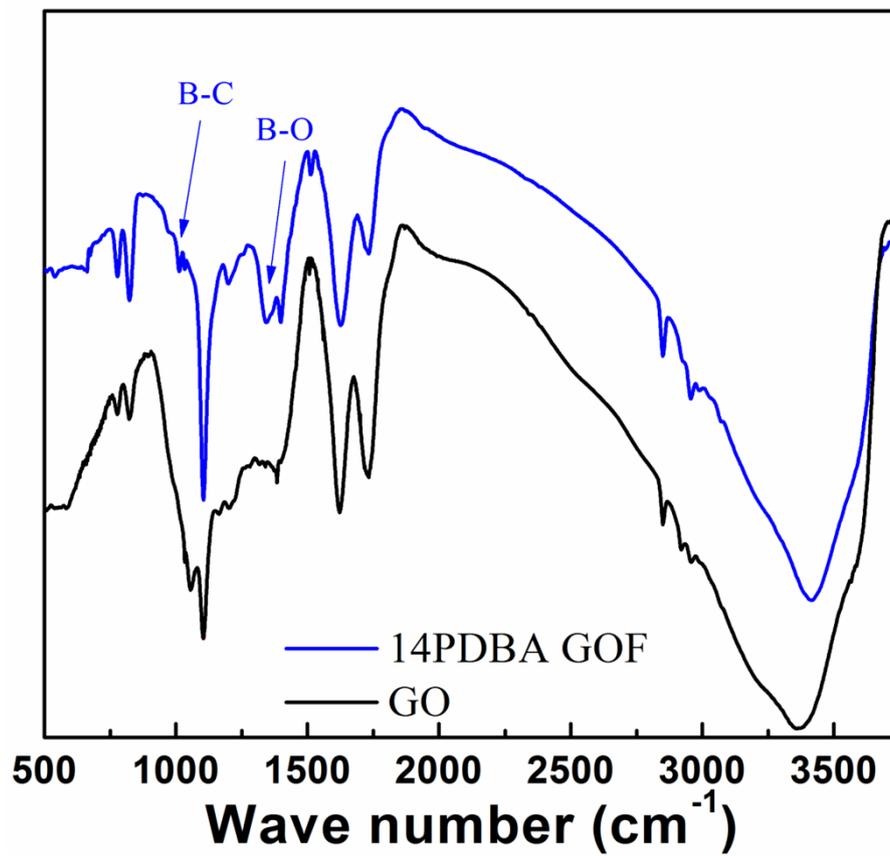


Fig. S3 FTIR measurements of GO and 14PDBA -GOF.

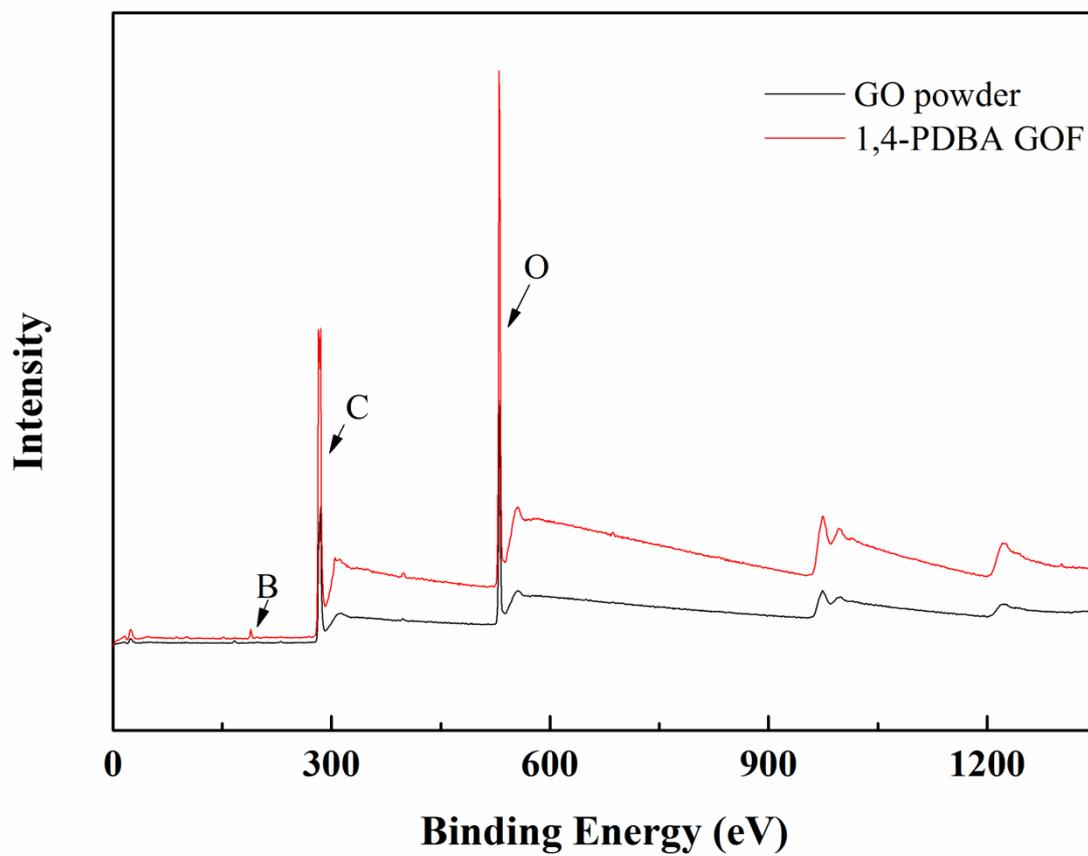


Fig. S4 XPS results of GO and GOF.

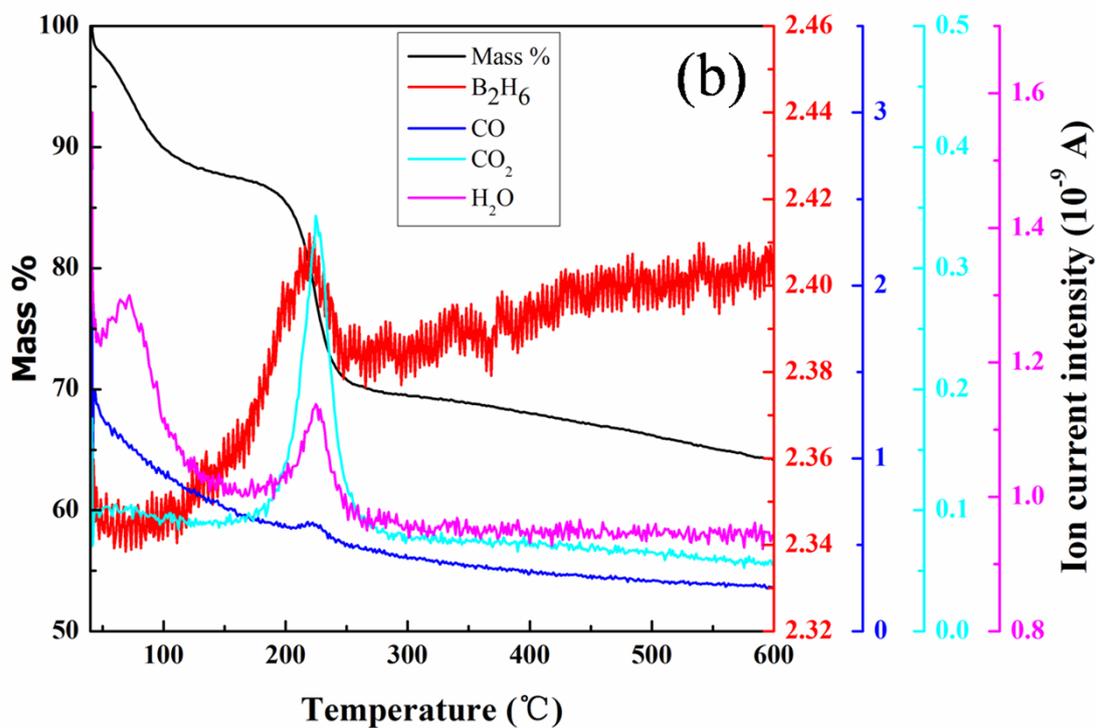
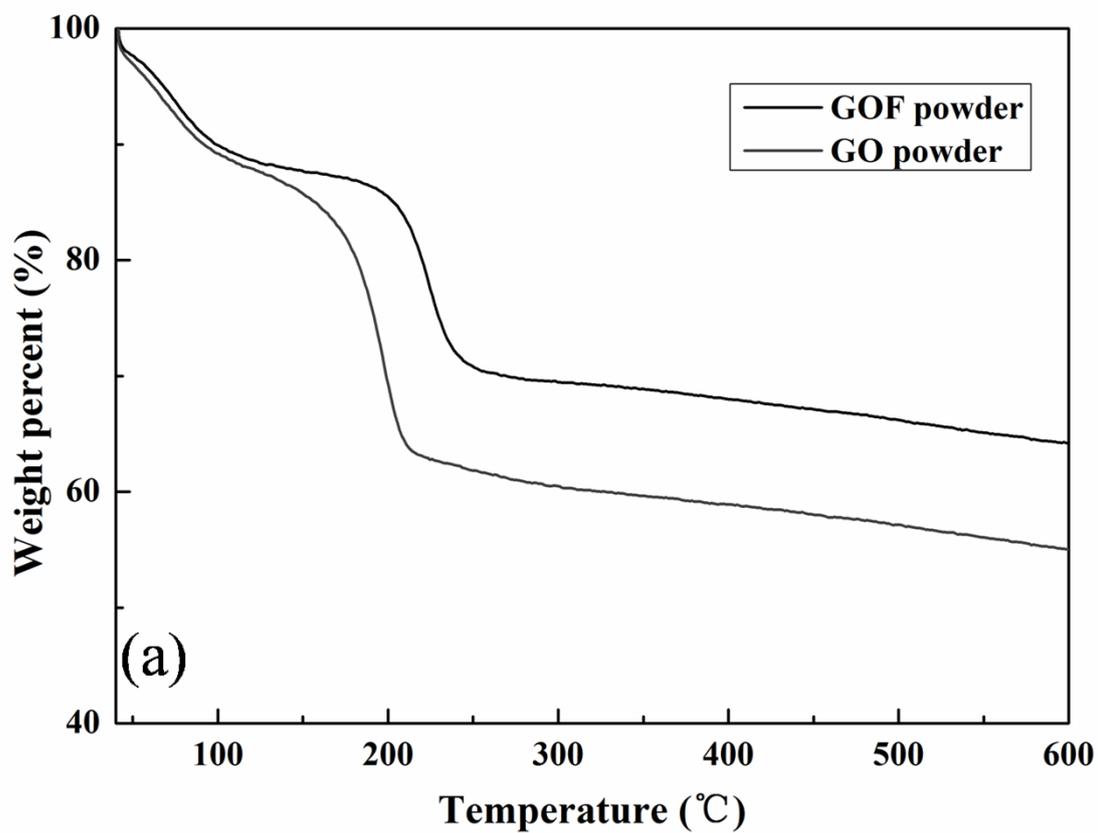


Fig. S5 TG-MS results of GOF from 40-600 oC in Ar. (a) TG; (b) TG and MS information.

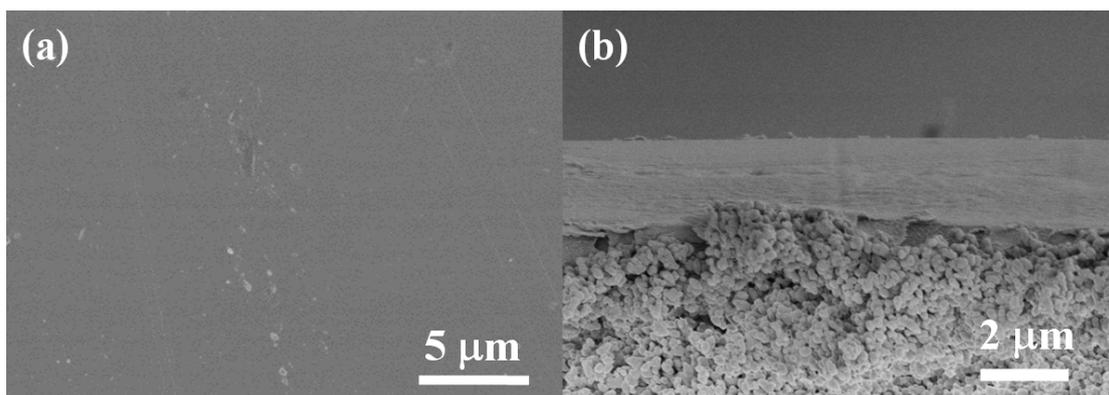


Fig. S6 SEM views of ceramic supported PVA membrane. (a) top view and (b) cross-section view.

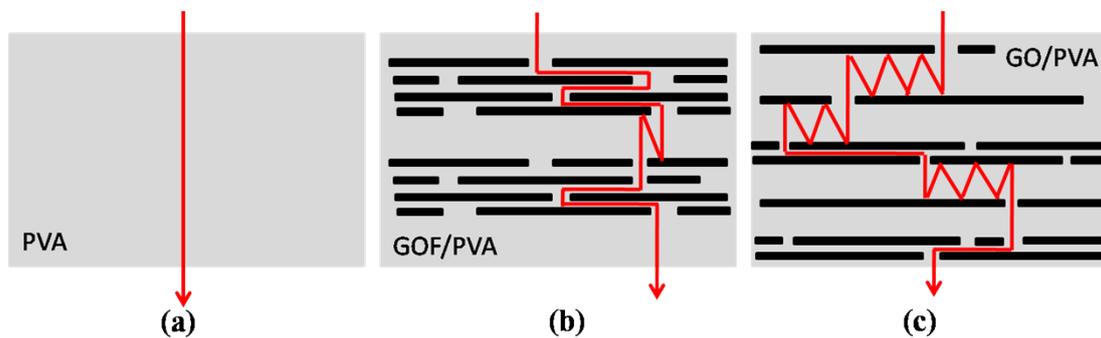


Fig. S7 The diffusion path of molecular in the PVA (a), GOF/PVA (b) and GO/PVA membrane (c).

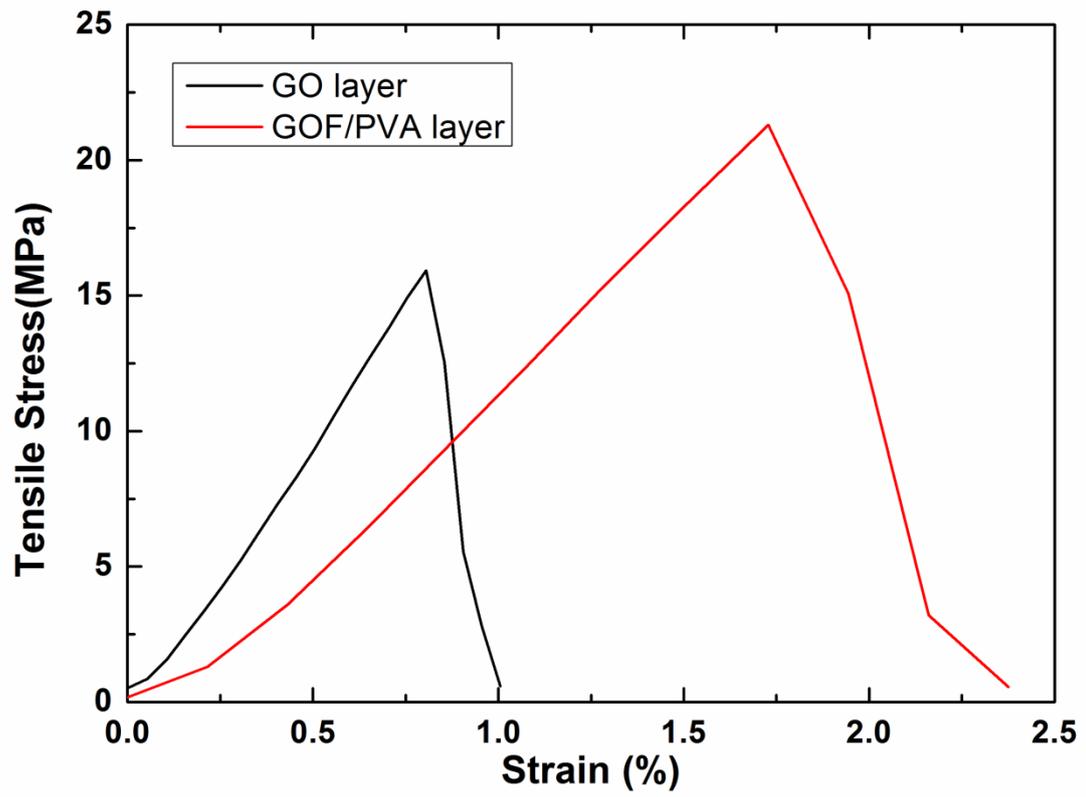


Fig. S8 Stress-Strain results of GO layer and GOF/PVA layer.

Table S1 Key parameters of PVA and GO /PVA membranes employed in pervaporation.

	Supported PVA membrane	Supported GO/PVA membrane
Composition (wt%)	100% PVA	30%GO/PVA
Thickness (μm)	2	0.5
Membrane Area (cm^2)	6	6

Table S2 Separation performance of GOF/PVA hybrid membrane for methanol contained mixtures at 70 °C.

Mixtures		Total flux ($\text{kg}/\text{m}^2/\text{h}$)	SF
Phase 1	Phase 2		
10% MeOH	90% DMM ^a	0.08	370
10% MeOH	90% DMC ^b	0.11	350
10% MeOH	90% IPA	0.12	230

a, DMM dimethoxyl methane; b, DMC dimethyl carbonate

Reference

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