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

# Guihua Li<sup>a, b</sup>, Lei Shi<sup>c</sup>, Gaofeng Zeng<sup>a, \*</sup>, Yanfeng Zhang<sup>a, \*</sup> and Yuhan Sun

a, CAS Key Laboratory of Low-carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China b, College of Sciences, Shanghai University, Shanghai 200444, China c, State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 20050, China

### **Experimental details**

1. Graphene oxide synthesis

Graphite powders of 8000 mesh were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). GO was prepared by the Hummers' method with further post treatments of ultrasonic processing and centrifugation<sup>1</sup>. Typically, graphite powder (8000 mesh, 5g) and NaNO<sub>3</sub> (2.5g) were mixed with sulfuric acid (115mL, 98wt %) under magnetic stirring for 0.5h. Then the mixture was put into an ice bath before KMnSO<sub>4</sub> (15g) was slowly added, and make sure the temperature remains below 20 °C. Subsequently, the reaction system was transferred to a water bath of 35 °C and maintained for 0.5 h. After that, 230 mL of water was slowly added into the system. The diluted suspension was then stirred at 98 °C for 15 min, followed by another 700 mL of water added. And the reaction was terminated by the addition of  $H_2O_2$  (50 mL, 30wt %). The mixture was filtered and washed with HCl (1 L, 1 mol/L) and a large amount of distilled water in sequence. The resulting solid was dried and dissolved. The dispersion of graphite oxide was ultrasonicated under 40 kHz for 30 min and centrifugated at 3000 rpm for 30 min, obtaining stable GO colloid of specific concentration.

GO aqueous with narrow dispersed size were obtained by centrifugation at different speed and sonication treatments. In detail, as prepared GO aqueous was centrifugated at 2,000 rpm for 100 min. The sediment was discarded and the supernatant was collected for another 100 min centrifugation at 10000 rpm. The supernatant was collected as the minimum size GO (marked as GO-S, ca. 0.2 mg GO/ml) and the sediment was resolved in de-ioned water followed by 30 min sonication and 100 min centrifugation at 6000 rpm. Then the sediment was dissolved in DI water followed by 30 min sonication and 100 min centrifugation at 3000 rpm. The largest GO dispersion

was obtained by dissolving the sediment in water (labelled as GO-L, ca. 0.4 mg GO/ml). The size of GO-S and GO-L were measured by atomic force microscopy (AFM) and particle size analyzer, which were showed in Fig. S1 and S2.



Fig. S1 AFM measurement of GO suspension with different size: supernatant of high speed (10000 rpm) centrifugation (left); sediment of low speed (3000 rpm) centrifugation (right).



Fig. S2 GO size distribution in the large size and small size samples.

2. GO / ceramic composite membrane deposition

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 layer 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 cm<sup>2</sup> surface area for membrane deposition. The supports were cleaned sequentially by ethanol, 4% aqueous KOH solution and deionized water before membrane synthesis.

Ceramic support was mounted into the tube housing and sealed with two O-rings on the both ends of support. The upper end of tube housing was closed by stop-valve and the bottom end was connected to the GO solution container. The GO diluted solution was drove to the lumen side of tube through the bottom end by pressurized nitrogen. Liquid was collected and measured from the permeation side of ceramic tube. In a typical synthesis, 0.5 mL GO-L and 1 mL GO-S solution were diluted to 200 mL by DI water, respectively. In addition, 5 mg 1-[3- (Dimethylamino) propyl] -3- ethylcarbodiimide (DEC) methiodide and 0.5 mL ethanediamine were added into the diluted GO-L solution. Both solutions were sonicated 30 min at room temperature for homogenous mixing as well as degassing. Then the diluted GO solutions were separately transferred to the synthesis container. For the GO-L diluted solution, 2-4 bar N<sub>2</sub> was introduced. The inner pressure of GO-L diluted solution was kept at 2-4 bar until 195 ml liquid was collected from the permeation side. Then the diluted GO-S solution was introduced to the container and drove by an increasing N2 pressure from 8-15 bar. The pressure associated deposition was considered as reaching the end when the flow rate of permeation side was lower than 1 mL/h. The GO/ceramic membrane was taken out after slowly release the inner pressure. The as-prepared composite membrane was vertically dried overnight at 45 °C in vacuum. TG-MS, XPS and FT-IR characterization results of charge modification GO were showed in Fig. S3, Fig. S4 and Fig. S5, respectively. The stress-strain measurement was showed in Fig. S6. The membranes fabricated for this work were listed in Table S1 and showed in Fig. S7.



Fig. S3 TG-MS results of GO layer from 30-700 oC in Ar. (a) TG, DSC and DTG; (b) TG and MS information.



Fig. S4 XPS results of GO membrane: a) treated with amidation (red) and without treatment (black); b) Simulation of C1s of GO without treatment; c) Simulation of C1s of GO treated by EDA.



Fig. S5 FT-IR results of GO treated with amidation (blue) and without treatment (black)



Fig. S6 Stress-Strain result of GO layer. The breaking strength and the elongation at break of GO layer were 15.9 MPa and 0.81%, respectively

Membr	Thickness (nm)	Mixture (10wt%H <sub>2</sub> O)	PV temperature (°C)	Flux (kg/m2/h)	Separation factor
			70	1.30	250
M1	250	H <sub>2</sub> O-EtOH	60	0.95	230
			50	0.70	320
			40	0.43	335
			28	0.30	410
M2	220	H <sub>2</sub> O-NPA	70	1.70	1290
			60	1.30	1240
			50	0.91	1670
			40	0.61	1730
			30	0.43	1740
M3	190	H <sub>2</sub> O-IPA	70	2.10	2940
			60	1.50	3020
			50	1.10	2830
			40	0.75	4340
			30	0.51	4020
			70	2.39	3600
M4	190	H <sub>2</sub> O-EA-EtOH	60	1.66	3330
			50	1.31	3950
			40	0.83	3650
			30	0.63	5030
M5	175	H <sub>2</sub> O-SBA	70	1.82	6910
		H <sub>2</sub> O-TBA	70	1.63	5120
		H <sub>2</sub> O-IBA	70	1.68	6110
			70	5.88	-
M6	190	H <sub>2</sub> O	60	4.44	-
			50	3.44	-
			40	2.48	-
			30	1.64	-

Table S1 The key parameters of GO /composite membranes employed in this work



Fig. S7 SEM cross-section views of M1-M6 prepared for the pervaporation test in this work.

## 3. Pervaporation of H<sub>2</sub>O-organic azeotropes

The separation performance of GO / ceramic composite membrane for water contained azeotropes were carried out with the pervaporation (PV) method in the temperature range from 30-70 °C (Fig. S8). The GO composite membrane was fixed with O-rings in the separator, which has the same configuration as the tube housing for membrane deposition. Then the separator was vertically fixed in an oven. Alcohols and ethyl acetate were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). 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 1 to 2 h. The composition of permeation liquid as well as feedstock was analysed by a GC with TCD detector (Shimadzu GC-2014C, HP Plot/U 0.2  $\mu$ m\*30 m). Based on the result of GC analysis, the concentration of H<sub>2</sub>O-organic mixture feedstock was corrected everyday by adding water in the long term test.



### Fig. S8 Schematic of pervaporation system

## 4. Characterizations

The size of GO single layer were analyzed in tapping mode using atomic force microscopy (AFM, NanoScope IIIa). The size distribution of GO was also measured by particle size analyzer (Mastersizer 2000, Malvern Instruments). The concentration of the resulting GO dispersion was measured by UV-vis (UV2700, SHIMADZU) absorption at 600 nm wavelength<sup>2</sup>. Membrane fragments were characterized by scanning electron microscopy (SEM, S 4800 Hitachi) at an accelerating voltage of 5 kV. The structure of GO layers were determined by X-ray diffraction (XRD, Rigaku Ultima IV) using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm, 40 kV, 40 mA). The near-surface compositions of membrane fragments were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Al K $\alpha$  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 GO films 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 40-700 °C with a 2 °C/min heating rate. Mechanical property measurements of GO layer were performed on a tensile tester (XQ-1C, Shanghai New Fiber Instrument Co., Ltd.).

References

(1) Hummers, W. S.; Offeman, R. E. *Journal of the American Chemical Society* **1958**, *80*, 1339.

(2) Li, H.; Song, Z.; Zhang, X.; Huang, Y.; Li, S.; Mao, Y.; Ploehn, H. J.; Bao, Y.; Yu, M. *Science* **2013**, *342*, 95.