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Supporting Information

Fabricating preoxide graphene-based nanofiltration membranes and their good performance with tunable porosity

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Supporting information list

1. Experimental section

2. The vacumm membrane distillation and the stability of the membrane

3. The surface morphology of rPGMs at different reduction time of 40, 60 and 80 min

4. The XRD patterns of PG and rPG

5. The contact angles of PGM and rPGMs

6. Summarize of some GO-based membranes for salt and dye rejection

7. Characterization

8. Notes and References

1. Experimental section

Preparation of Preoxide Graphene (PG) from Graphene Oxide (GO): GO was synthesized from natural graphite (300 μm, Qingdao Graphite Company) by a modified Hummers method.[1] Typically, H_2SO_4 (300 mL) and natural flake graphite (50 mesh, 10 g) were mixed in a round-bottom flask (1000 mL) cooled with an ice bath, and then magnetically stirring the mixture for 30 min, forming $KMnO_4$ (0.15 g) was added gradually and stirred for 30 min before $KMnO_4$ (3.0 g) was added to maintain the temperature no more than 10°C. After 2h magnetically stirring, the beaker was heated at 35°C, and kept it overnight. Then, distilled water (300 mL) was slowly mixed with the suspension at this temperature and further hydrogen preoxide (30%, 50 mL) was mixed, forming a bright yellow suspension. The solution obtained was repeatedly centrifuged and washed with dilute hydrochloric acid (3%, 100 mL) and distilled water until the pH of the solution became neutral. Finally, the precipitates were diluted in distilled water to make a solution of 6 mg mL^{-1} concentration for storage. The above aqueous GO suspension (2.5 mL) was diluted to 1 mg mL^{-1} by DI water and added into concentrated HNO_3 (70%, 375 mL) in a sealed flask vial continuous stirring. Based on the previous attempts, a GO suspension/70% HNO_3 volume ratio of 1:12.5 were added into the system and refluxed for 18h with constant stirring. After that, the mixture was sonicated for 4h, 6h, 9h and settled at room temperature staying overnight. Further, wash the compound and repeat the centrifugation procedure several times to remove the acid in order to obtain the PG.

Preparation of Preoxide Graphene Membranes (PGMs) and Reduced PGMs (rPGMs): First of all, the obtained PG solution with micropores and the GO suspension were diluted to 1 mg mL^{-1} and then coated on the commercialized micro-filtration membranes through a rod coating method.[2] It only needed solution of 250 μL every time and repeating the coating step three times. After that, stewing 12 hours for drying the films naturally and finally the PGMs could be acquired. Before the reduction of PG solution by hydrogen, a calculated amount of $PdCl_2$ aqueous solution (Pd content: 6 g L^{-1}) was added into the PG dispersion (30 mg, weight ratio of Pd to PG is 0.1). The rPGMs were executed in a hydrogen generator (300 mL) at room temperature. After a certain time (20 min, 40 min, 60 min, 80 min, 100 min), a range of the resulting reduction preoxide graphene membranes at different times can be obtained. The reduced samples are labeled rPGM-20, rPGM-40, rPGM-60, rPGM-80, rPGM-100.

Stability performance evaluation for PGMs and rPGMs at high salt concentration and pressure: The stability of PGMs and rPGMs are investigated through vacuum membrane distillation by using a laboratory setup. The effective membrane area was 15.00 cm^2. Sodium chloride solution raging from 0.05 to 4 mol L^{-1} was pumped to the feed side of the membrane by a digital peristaltic pump (WT600-2J, Baoding Longer Co., Ltd., China) at a constant flow rate of 1.0 L min^{-1}.

NF performance evaluation for PGMs and rPGMs: All the NF performance evaluation was carried out in a filtration device. The pure water flux F (L m^{-2} h^{-1} bar^{-1}) was recorded after 1h of filtration when it went steady at 1 bar and neutral pH. After the salt or dye solution was switched, the permeate flux was determined when the retention rate became stable. Retentate (*Cr*) and permeate concentrations (*Cp*) were recorded both during and at the end of each run to monitor the evolution of rejection rate. The rejection rate can be calculated by the following equation:

$$R = \frac{C_{\mathrm{r}} - C_p}{C_r} \times 100\%$$

The rejection rate of different salts was measured by the sequence of Na_2SO_4, $MgSO_4$, NaCl and $MgCl_2$ at the concentration of 0.005 M. The capabilities of separating organic dyes from water were test applying Methyl Orange. First, the rejection rate for Na_2SO_4 of a new membrane sample was tested to make sure the membrane is of proper quality. Moreover, the membrane surface was exposed to dye and salts solution (25 mL) for more than 8 h to rule out the adsorption effect by the membrane. Finally, the rejection rate for dye solution and salts solution were measured by UV-vis spectra and by electrical conductivity by collecting permeated samples.

For each group of samples, the tests for NF performance were performed in triplicate to ensure reproducibility.

2. The vacumm membrane distillation and the stability of the membrane

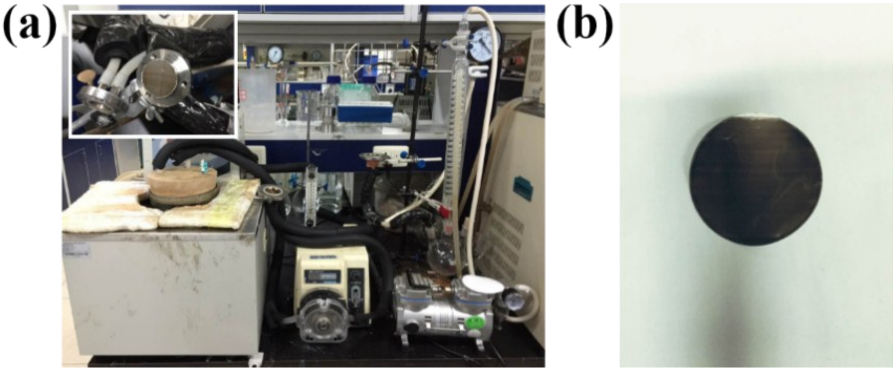

Fig. S1. (a) Optical photograph of the vacuum membrane distillation (VMD) experimental system, the inset is the membrane; (b) Optical photograph of the rPGM membrane after VMD at a salt concentration of 4 mol L^{-1} with the pressure of 2 bar.

3. The surface morphology rPGMs at different reduction time of 40, 60 and 80 min

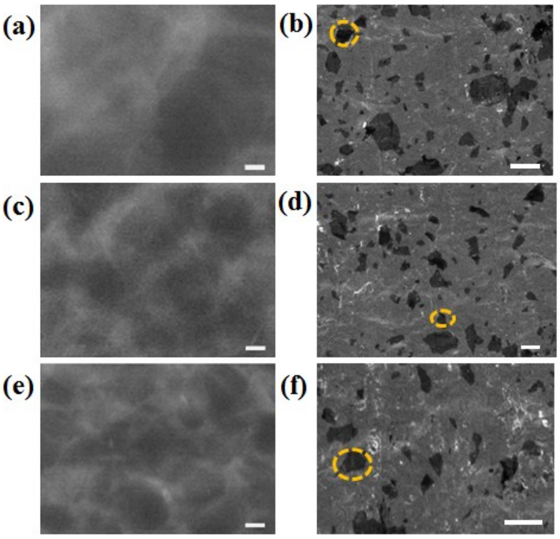

Fig. S2. The surface morphology of the (a-b) rPGM-40, (c-d) rPGM-60, (e-f) rPGM-80. Scale bars, (a), (c), (e) 100nm, (b), (d), (f) 1μm.

4. The XRD patterns of PG and rPG

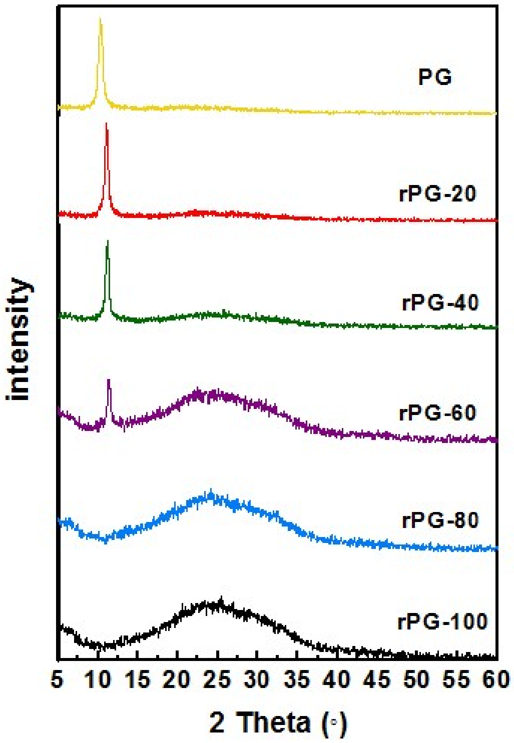

Fig. S3. XRD patterns of PG, rPG-20, rPG-40, rPG-60, rPG-80, rPG-100.

5. The contact angles of PGM and rPGMs

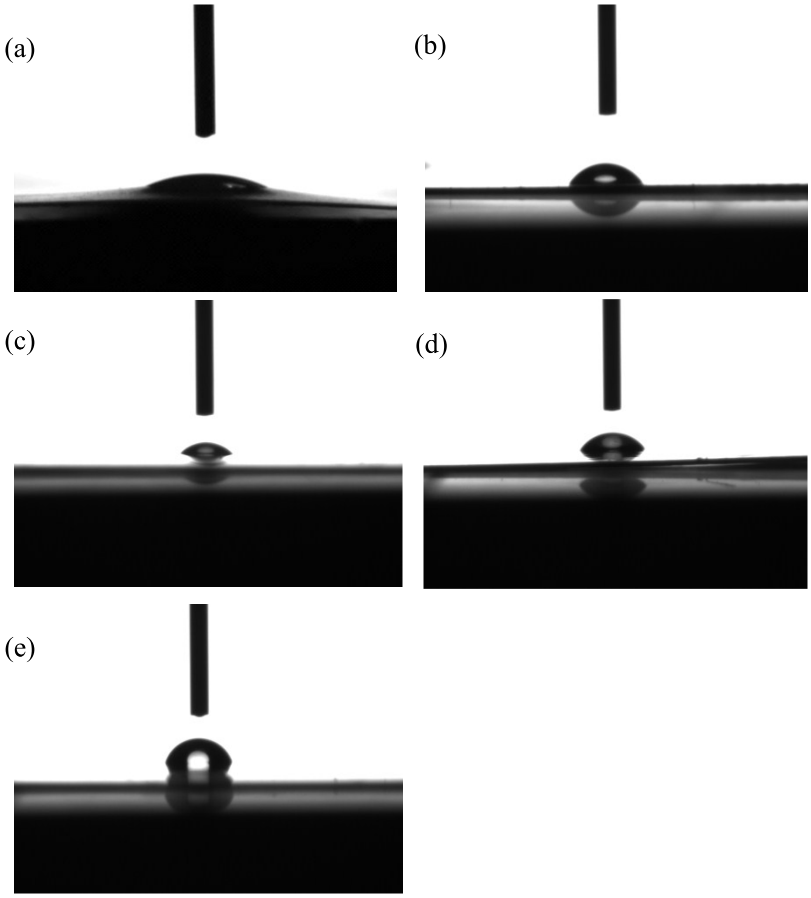

Fig. S4. Digital photos of water drops on (a) PG membrane, (b) rPG-20 membrane, (c) rPG-40 membrane, (d) rPG-60 membrane, (e) rPG-80 membrane, and the water contact angles are 11.9°, 45.3°, 85.8°, 101.3° and 121.2°.

6. Summarize of some GO-based membranes for salt and dye rejection

Table S1. Summarize of some GO-based membranes for salt and dye rejection.

Sample description	**Cited literature**	**Conditions**	**NaCl (R%)**	**Na_2SO_4 (R%)**	**Dye (R%)**
rPGM-80	Our work	1 bar, 5 mM (salt) 0.025 g L^{-1} (dye)	53.9	69.0	97.5 **(MO)**
G-CNTm(8:1)	ref 3	5 bar, 10mM (salt) 0.05g L^{-1} (dye)	39.6	71.2	92.0 **(MO)**
uGNMs	ref 4	5 bar, 20 mM (salt) 0.02mM (dye)	~ 40	~ 60	99.8 **(MB)**
GO/TMC	ref 5	3.4bar, 10mM (salt) 7.5mg L^{-1} (dye)	29	26	46-66 **(MB)**
GO/PECs	ref 6	5 bar	Na^+:43.2	Na^+:43.2	87.6 **(MO)**
PSF/GO (1000 ppm)	ref 7	4 bar	~ 50	~ 65	
NSC-GO membrane	ref 8	13 bar, 15µM (EB)			83 **(EB)**
0.5 wt% GO/PES	ref 9	4 bar, 30 mg L^{-1}			96 **(DR16)**

MO: Methyl Orange; MB: Methylene Blue; EB: Evans Blue; DR: Direct Red

7. Characterization

The morphology and thickness of as-prepared PGM and rPGMs were investigated using Hitachi S4800 scanning electron microscopy (SEM) and JEOL 2100F transmission electron microscopy (TEM). Besides, the detailed functional group information was obtained by X-ray Photoelectron Spectroscopy (XPS, ESCALAB250Xi); the X-ray diffraction (XRD) measurements involve the interlayer spacing were carried out on a RigakuD/max-2500B2 + /PCX system with Cu Ka radiation. Contact angle measurement was taken using a VCP Optima XE system. The pure water flux and retention measurements were performed on a dead end filtration device. UV−vis spectra were obtained to determine the concentrations of dye solutions on a Varian Cary 300 Bio UV−vis spectrophotometer. Salt concentrations were measured using electrical conductivity (DDS-307, Shanghai Leici Instrument Co.).

8. Notes and References

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