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Electronic Supplementary Information

In-plane mesoporous graphene oxide nanosheets assembled membranes for molecular separation

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1. Experimental section:

1.1 Graphene oxide synthesis:

Similar to by the modified Hummers method[1, 2], the graphite powders (0.1873g) were adding to an 80 °C solution mixed with concentrated H_2SO_4 solution (3.3ml), $K_2S_2O_8$ (0.6250 g), and P_2O_5 (0.6250 g). Then the mixture was kept at 80 °C for 4.5h while stirring. After the reaction was finished, the mixture was cooled down to room temperature and diluted with 250ml distilled (DI) water. Then the mixture was filtered, washed on the filter until the pH of the filtrate was closed to 7. Then, the $KMnO_4$ powders (3.75g) and the pre-oxidized graphite powders were adding into a concentrated H_2SO_4 solution (30 ml) and cooled in the ice-water bath under stirring. The mixture was heated to 35 °C and kept it for 2h. Again, the mixture was diluted with 62.5 ml DI water and kept at 35 °C for another 2h. Subsequently, the mixture was diluted with 175ml cold DI water. After that, 10 ml of 30% H_2O_2 was added leading to a brilliant yellow dispersion. 10ml of hydrochloric acid 37% was added into the solution and stored for 2 days. The resulted sediment was centrifuged and washed with hydrochloric acid solution (10%) for 5 times followed by DI water 5 times to fully remove the acid and metal ions. The product was dried in a vacuum chamber at 50 °C for several days and re-dispersed in ultrapure water to make 0.1 mg/ml dispersion by ultrasonication, and named as GO-1.

1.2 The re-oxidation of GO:

The re-oxidized step was followed by the method we reported previously[3]. Briefly, 0.15 g GO was added into 100 ml of DI water, and dispersed by ultrasonic dispersion method. Then 0.1816 g KMnO4 was added into the above solution, and subsequently stirred for 10 min. Finally the resulting suspension was heated using a household microwave oven for 5 min, and treated by oxalic acid for 6 h, and named as GO-2. Similar to GO-2, GO-3 was prepared by adding 1.089 g $KMnO_4$ keep the other condition as the same. Finally, the products were centrifuged and washed with oxalic acid and hydrochloric acid (v/v, 1:1) and water for several times and dried in a vacuum chamber at 50 °C for several days. 0.1 mg/ml dispersions of GO-2 and GO-3 were prepared by ultrasonication the products in ultrapure water.

1.3 Preparation of GO-related membranes:

The membranes of GO-1, 2 and 3 were fabricated by vacuum filtration through a 0.2 micron polycarbonate membrane (Whatman, 25 mm diameter, 200 nm pore size). 3.2 ml GO solutions (0.1 mg/ml) were filtered on PC membranes, respectively, and resulting in the corresponding membranes with nearly 1 μm in thickness and 21 mm in diameter.

1.4 Separation test:

The GO membrane fabricated by vacuum filtration was transferred onto a filter holder (Millipore p158, 25 mm) separation system which was driven by high pressure nitrogen gas. And the effective area for water permeation in this device was 2.83 cm^2. The pure water flux was calculated by measuring the mass of filtrates collected every 1 hour under a certain pressure and the rejection was calculated by measuring the absorption intensity of the filtrates and the origin solution.

1.5 Characterization:

SEM images were recorded by Hitachi S-4800 field-emission SEM at 5kV and the TEM images were recorded by Philips CM200 field-emission TEM at 160 kV. AFM images were recorded by the Veeco multimode AFM under tapping mode. The XRD spectra were carried out on a X'Pert PRO (PANalytical, Netherlands) XRD analyzer with Cu Ka of 1.5406 Å at room temperature. The Raman spectra were carried out on a Renishaw inVia Raman microscope with a 532 nm argon ion laser. The FT-IR spectra were conducted on a Tensor 27 FT-IR spectrometer (Bruker Inc) with samples prepared as KBr pellets

UV-Vis absorption spectra of the filtrates and residues were collected using a SHIMAZU 360 UV-Vis spectrometer. The XPS spectra were acquired in an ESCALAB-250Xi X-ray photoelectron spectrometer with Al Ka X-ray as the excitation source. The pore width distribution figures were collected using a Quantachrome Autosorb-1 apparatus by Brunauer-Emmett-Teller (BET) method.

Zeta potentials were measured by the dynamic light scattering (DLS, Zetasizer3000HSA, Malvern Instruments, UK) method at pH 7 which was the water flux test condition. All the characterizations were carried at room temperature.

2.1 Additional TEM, SEM images, FTIR and XPS spectra and pore size distribution.

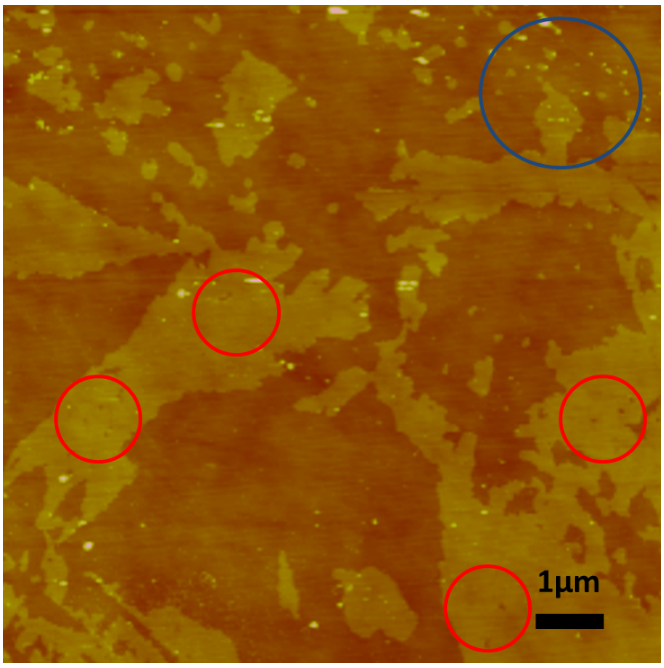


Figure S1. The AFM image of the GO sheets after re-oxidizing for 18 hours under the same condition as used for GO-3. The GO sheets breaks down to small pieces (blue circle). Besides, pores in tens to hundred nanometer size are observed (red circles).

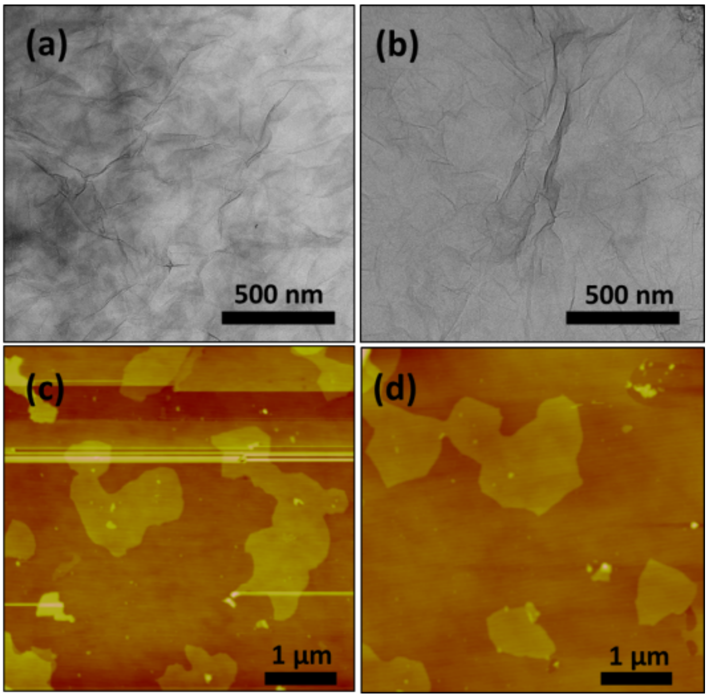


Figure S2. TEM image of GO-1 (a) and GO-2 (b), AFM image of GO-1 (c) and GO-2 (d).

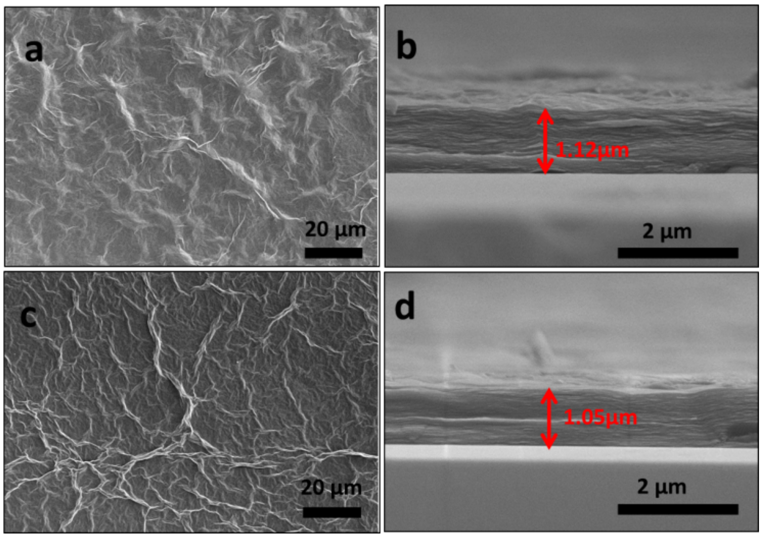


Figure S3. (a) Surface and (b) Cross-section SEM images of GO-1 membrane, (c) Surface and (d) Cross-section SEM images of GO-2 membrane.

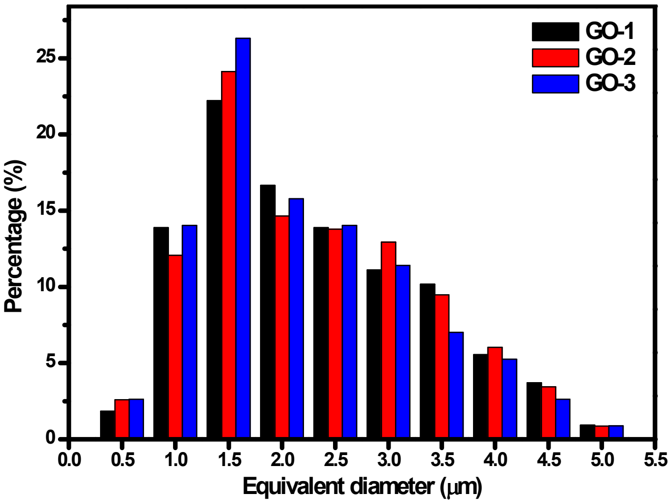


Figure S4. The corresponding histogram of GO size of samples GO-1, GO-2, and GO-3 sheets on a silicon substrate. The histograms of GO size distributions were obtained by counting more than 100 sheets for each sample.

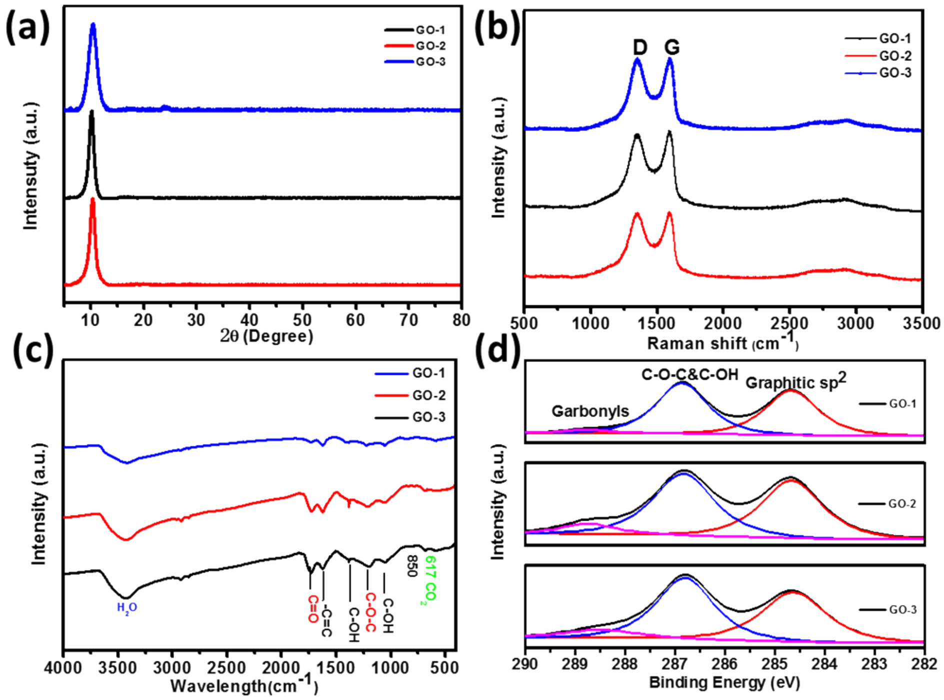


Figure S5. (a) XRD image, (b) Raman spectra and (c) FT-IR spectra and (d) XPS spectra of GO-1, GO-2, and GO-3 samples.

The X-ray diffraction (XRD) patterns of the GO membranes show typical GO peaks near 10° without any other phases in Figure S5a. Raman spectra with three characteristic peaks of D, 2D and G are observed in Figure S5b without any obvious differences. Infrared absorbance spectra of membranes made up from GO suspensions with different oxidative degrees in transmission are shown in Figure S5c. The sharp and absorption bands are the same as those in other works.[4] The absolute intensities of bonds which are related to the amount of GO on the KBr pellets are meaningless, but the relative intensities may offer some evidences for the oxidative degree. An obvious difference among these three spectra in C=O and C=C in Figure S6a from the XPS figures. The related amount of C=O groups are increased with more re-oxidation..

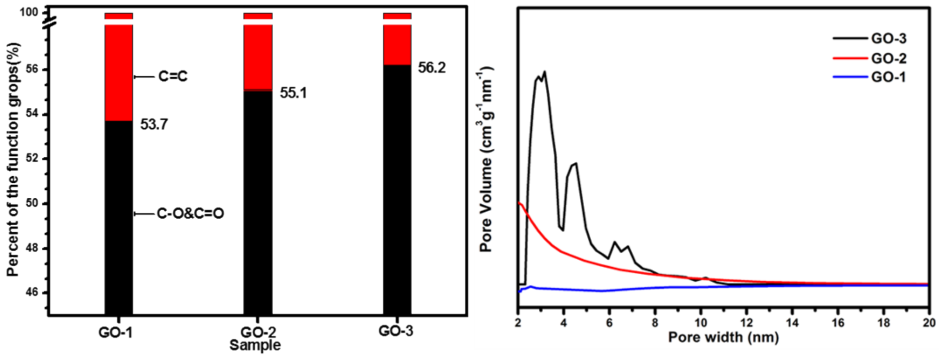
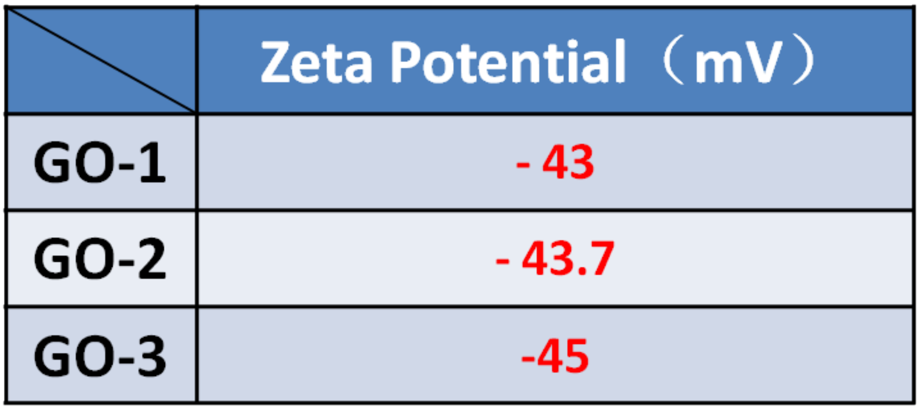


Figure S6. (a) The detail analytical figures of the XPS spectra of the GO sheets, (b) The pore-size distributions of the GO-1, GO-2 and GO-3. And nitrogen was the absorbate used in BET. The pore-size distributions were measured on desorption.

2.2 Zeta potential of GO suspension

The zeta potential of GO suspension was negative even at low pH (−18 mV at pH 2) and became more negative with increasing pH (−50 mV at pH 6), then reverse and stable (nearly -40 mV from pH 7 to pH 12), as expected from its oxygen-containing groups, which has been demonstrated by our former experiments.[5] In this article, the test of flux and rejection were hold at neutral environment (pure aqueous solution). So only the zeta potential figures at pH 7 were done, -43 mV for GO-1, -43.7 mV for GO-2 and -45 mV for GO-3. These were responsible for the stability of GO dispersions,[6, 7] which is very important for the formation of membranes by vacuum filtration method.

Table S1. The figures of the Zeta potential of the GO sheets



	Zeta Potential（mV）
GO-1	- 43
GO-2	- 43.7
GO-3	-45

References:

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