Supporting Information

Ultrahigh water permeance of a composite reduced graphene oxide / graphene oxide membrane for efficient rejection of dyes

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PS 1 Materials and method

1.1. Materials

Graphite (325 mesh) was purchased from Sinopharm Chemical Reagent Co., Ltd . Aqueous ammonia (NH_3 • H2O) was obtained by McLean Biochemical Technology Co., Ltd (Shanghai, China). Hydrochloric acid(HCI), sulfuric acid(H_2SO_4), nitric acid (HNO_3), phosphoric acid(H_3PO_4) potassium persulfate ($K_2S_2O_5$), phosphorus pentoxide(P_2O_5), hydrogen peroxide solution(H_2O_2), potassium permanganate ($KMnO_4$), sodium hydroxide (NaOH), sodium chloride (NaCl) and Sodium sulphate (Na_2SO_4) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Congo red (CR) was bought from Shanghai Xushuo Biotechnology Co., Ltd. Methylene blue (MB), and Rhodamine B (RB) were purchased from Shanghai Boer Chemical Reagent Co., Ltd (China). All reagents were used without any purification. Mixed Cellulose Ester (MCE) membranes were bought from Shanghai Xingya Purifying Material Factory (China), and the nominal pore diameter was 0.22 um. The de-ionized water (DI)used for all the experiment in this paper was taken from Milli-Q purification system (Millipore, USA).

1.2. Preparation of the rGO suspension

GO suspension was prepared by improved hummers methods as reported by previous works [S1-S3]. Using L-ascorbic acid (commonly referred to as vitamin C, VC) as the reducing agent, the rGO dispersion was made according to the documented procedures [S4]. Usually, 20 mL of GO suspension (0.01 mg/mL^{-1}) was first mixed with certain amount VC (mass ratio (VC: GO) = 10:1), and after that, 40 μL of ammonia solution (25% w/w) was added. After a few minutes of vigorous shaking, the mixture was mixed for more than ten minutes at 95°C. After the mixture was allowed to settle to room temperature and was centrifuged several times, a stable black rGO suspension was produced.

1.3. Fabrication of the GO/rGO composite membranes

Then, the GO solution (3.8 mg mL^{-1}) was diluted with DI water to prepare a 20 mL uniform GO dispersion (10 mg L^{-1}). Afterward, the 20 mL rGO aqueous solution (10 mg L^{-1}) was mixed with the obtained 20 mL 10 mg L^{-1} GO solution and the mixed solution was sonicated for 10 min to obtain the 40 mL uniform rGO/GO suspension. Subsequently, rGO/GO composite membranes were fabricated using 40 mL rGO/GO suspension by vacuum filtration under a fixed pressure of 1 bar with MCE membrane as support membrane. After membrane preparation, rGO/GO composite membrane swere filtered using 50 mL of DI water to clean any residual reactants before membrane performance tests.

1.4 Membrane performance

The separation filtration experiment was carried out by lab-scale vacuum filtration device (Fig. S1. Various dye aqueous solutions (e.g., methylene blue (MB), Rhodamine B (RB), Congo red (CR)) were used as the feeding solution to investigate the water permeance and retention performance of membranes. The water permeance (J_w) was measured by using the following equation:

$$J_w = \frac{V}{\Delta t \times A \times P} \quad (1)$$

A is the effective membrane area (11.34 cm^2), Δt is the test time, and V is the volume of the permeate solution during the test time, respectively.

The feed concentration and the permeate solution were used to calculate the rejection rate (R) of the dyes. The rejection rate was measured using the following equation:

$$R = (1 - \frac{C_P}{C_f}) \times 100\% \quad (2)$$

where C_p and C_f are the concentration of permeate and feed dyes solution. To verify the correctness of the data, three parallel permeation experiments were performed to obtain the average water permeance and rejection rate.

A Mettler Toledo Conductivity Meter was used to detect the salt concentrations, and an

ultraviolet-visible (UV-vis) spectrometer (HITACHI UH 5300) was employed to determine the dye concentrations.

1.5 Characterization

The XRD patterns were recorded on a D8 Advance X-ray diffractometer with Cu Ka radiation (A 0.15418 nm, Bruker Corp., Billerica, MA, USA).The tests were implemented in the reflection mode at room temperature with 20 in the range of 5-25, and scanning speed at 10 deg min-1,and step size at 0.02.The X-ray photoelectron spectroscopy (XPS)spectra were recorded from a Thermo Scientific Escalab 250Xi (Thermofisher, USA).Raman Spectra were collected on Renishaw in Via plus laser Raman spectrometer using an excitation wavelength of 532 nm. The contact angles were measured by dropped a 5 uL water droplet onto the surface of GO-based membranes under air atmosphere by using an JY-82 Automatic Video Contact Angle Detector. The micro-morphologies of GO and hybrid membranes were characterized by field-emission scanning electron microscope (FE-SEM, JSM-6700F,JEOL Ltd., Tokyo, Japan) at 10 kV. The absorbance spectra of GO solution, rGO solution, and mixed solution were measured by ultraviolet-visible spectroscopy (UV-Vis, Japan Hitachi HITACHI double beam spectrophotometer UH5300).

PS.2 AFM results of pristine GO nanosheets

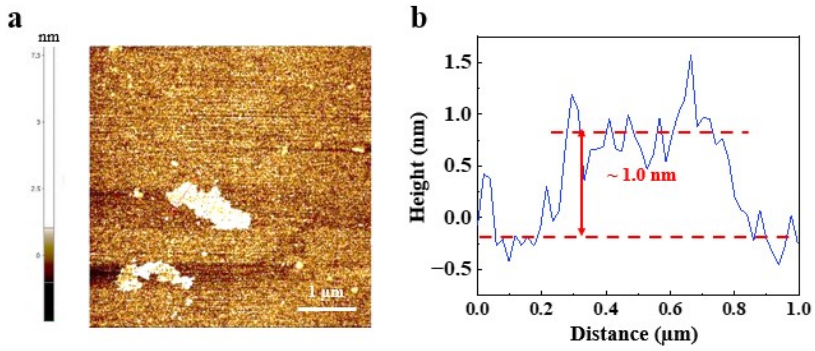

Fig. S1. (a) AFM image of pristine GO nanosheets. (b) The corresponding height profile of pieces from(a).

PS 3 Photos of GO, rGO, and rGO/GO solutions and membranes

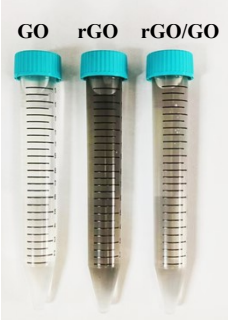

Fig. S2. Photos of GO, rGO, and rGO/GO solutions with the concentration of 10 mg L^{-1}.

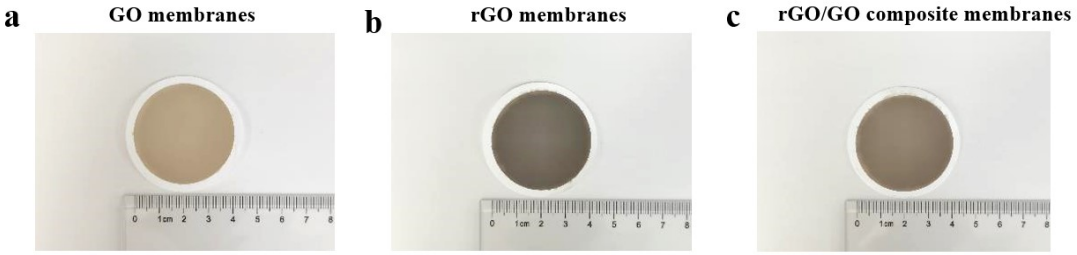

Fig. S3. Optical images of (a) GO, (b) rGO and (c) rGO/GO hybrid membranes.

PS 4 Water contact angles (CA) of GO and rGO membranes

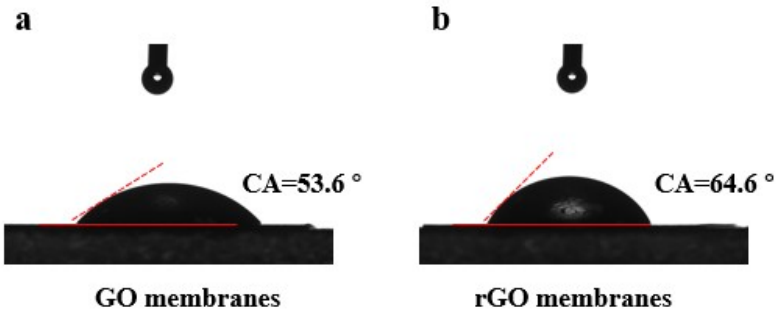

Fig. S4. Water contact angles (CA) of (a) GO and (b) rGO membranes.

PS 5 Cross-sectional SEM images of GO and rGO membranes

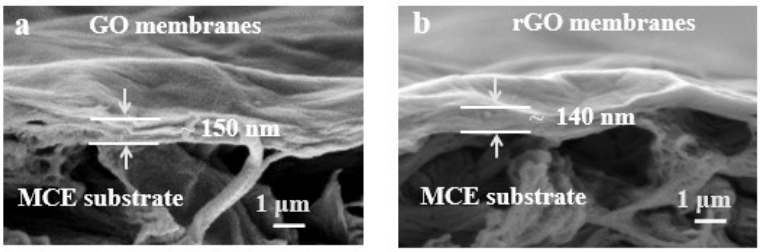

Fig. S5. Cross-sectional SEM images of (a) GO and (b) rGO membranes.

PS 6 Absorption spectra of GO, rGO, and rGO/GO solutions

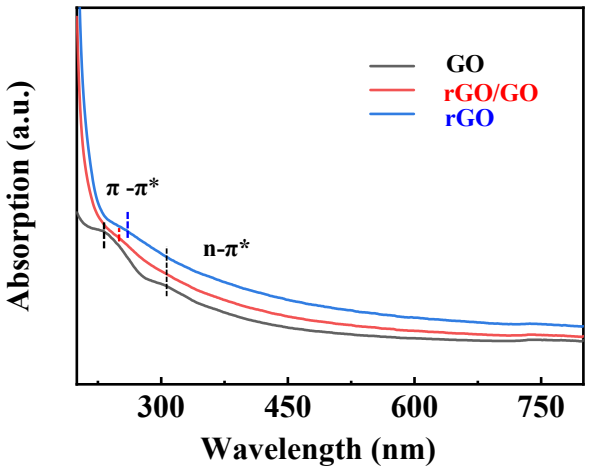

Fig. S6. Absorption spectra of GO, rGO, and rGO/GO solutions.

PS 7. Zeta potential of GO, rGO, and rGO/GO suspensions

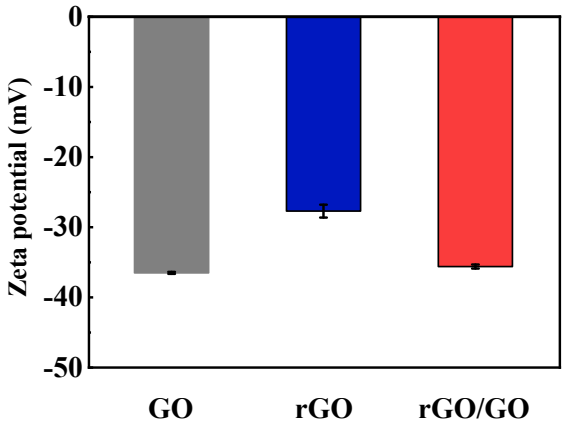

Fig. S7. Zeta potential of GO, rGO, and rGO/GO suspensions.

PS 8. FT-IR spectrum of GO, rGO, and rGO/GO composite membranes

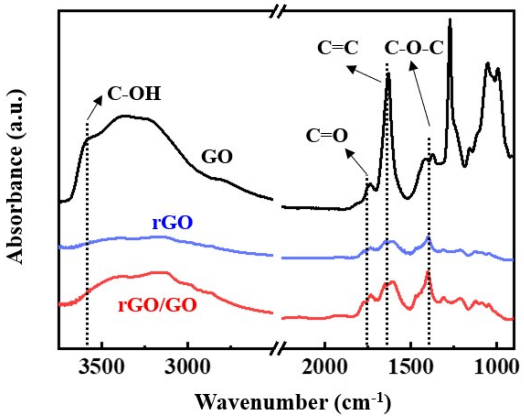

Fig. S8. FT-IR spectrum of GO, rGO, and rGO/GO composite membranes.

PS 9 Analysis of XPS content on GO, rGO, and rGO-GO composite membranes

Table S1. Analysis of XPS contents on GO, rGO, and rGO-GO composite membranes.

Membranes	Element composition		O/C
	C (at.%)	O (at.%)	
GO	69.65	30.35	0.44
rGO-GO	70.98	29.02	0.41
rGO	73.42	26.58	0.36

PS 10 Photos of filtrate and feed solution of rGO/GO hybrid membrane for rejecting different dyes

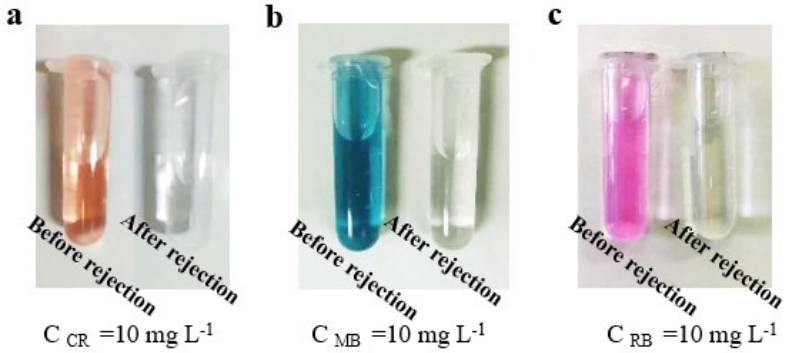

Fig. S9. Photos of filtrate and feed solution of rGO/GO composite membrane for rejecting (a) CR, (b) MB, and (c) RB solutions.

PS.11 Stability performance of rGO/GO composite membranes immersed in different pH solutions.

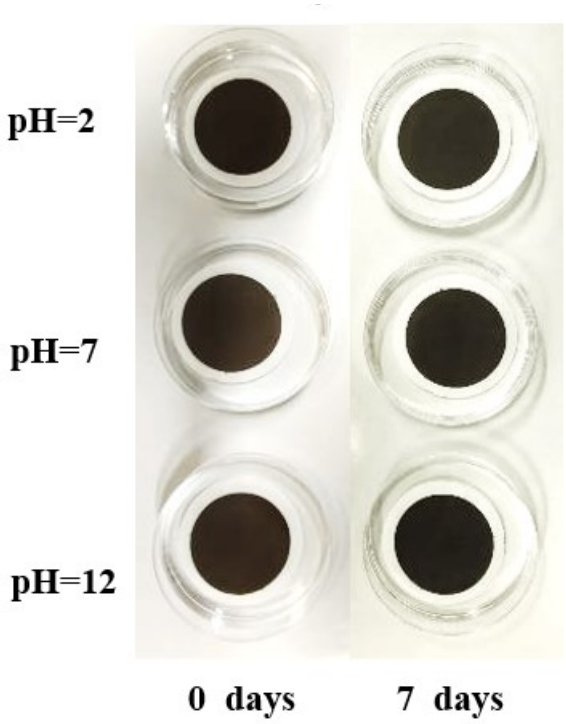

Fig. S10 Stability performance of rGO/GO composite membranes immersed in different pH solutions.

References:

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