Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Electronic Supplementary Information

Chemical vapor crosslinking of graphene oxide membranes for controlling nanochannels

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Experimental details:

Materials

The graphite oxide power was purchased from XFnano chemical Co., Ltd., China. Ethylenediamine (EDA) was purchased from Xinhong Chemical Reagent Co., China. Sodium sulphate (Na_2SO_4), sodium chloride (NaCl), magnesium sulphate ($MgSO_4$), magnesium chloride (MgCl), and polyethersulfone (PES) with pore size of 0.2 μm were obtained from Kutai Chemical Reagent Co., China.

Fabrication of GO and GO-EDA membranes

To produce GO suspension with concentration of 1.0 mg mL^{-1}, 50 mg of graphite oxide was added to 50 mL of deionized (DI) water, followed by ultrasonication for 2 h. A certain volume of the GO suspension was diluted to 20 μg mL^{-1} and 40 μg mL^{-1}. The diluted solution (10 mL) was filtered onto a PES substrate with pore size of 0.2 μm by vacuum filtration to prepare the GO membrane. The EDA monomer was added to GO suspension (60 mL, 20 μg L^{-1}) to prepare a 0.1 M solution. After stirring for 2 h at room temperature, 10 mL of GO-EDA solution was filtered onto the PES substrate by vacuum filtration to prepare the GO-EDA-V membrane. The GO-EDA membrane was prepared by chemical vapor deposition (CVD). The GO membrane was dried at room temperature for 24 h before it was crosslinked by EDA. Briefly, 20 mL of EDA was poured into a beaker, and a holder was placed above EDA. The holder was not contacted with EDA. The GO membrane was placed on the holder with GO facing EDA. Then, the beaker was sealed and thermally treated at 40 ^{o}C for vapor deposition. The deposition durations were 15, 30, and 45 min, respectively. After deposition, the obtained GO-EDA membrane was heat-treated at 80 ^{o}C for 1 h to realize further crosslinking of GO and EDA, and then immersed into DI water for 10 h to remove uncrosslinked EDA. Ultimately, the prepared GO-EDA membrane was dried at room temperature.

Characterizations

The top and cross-section morphologies of membranes were observed by a scanning electron microscope (SEM, Ultra-55, Zeiss Co.). The acceleration voltage was 5 kV. Fourier transform infrared spectrometer (FTIR, IRTracer-100, Shimadzu Co.) was employed to investigate the chemical structures of membranes. X-ray photoelectron spectroscopy (XPS) was applied to analyze the chemical compositions of membranes. The crystalline properties of membranes were acquired by an X-ray diffractometer (XRD) at 30 kV and 10 mA. The interlayer spacing was calculated by Bragg's Law:

$$\lambda = 2d\sin\theta \qquad (1)$$

where λ is the wavelength of Cu X-ray beam (0.15406 nm), d is the interlayer spacing of GO laminates, and θ is the diffraction angle.

Separation performance

A cross-flow filtration system with an effective filtration area of 7.0 cm^2 was used to investigate permeance of DI water and the salt rejection of the membranes. The desalination tests were performed with different salt solutions with the concentration of 500 ppm, an applied pressure of 2.0 bar, and a flow of 30 L h^{-1} at room temperature.

The data were recorded after the system ran stably. To ensure repeatability, the experiments were carried out at least three times. The conductivity of the collected permeation was measured with a conductivity meter, and the water permeance and the rejection rate was calculated by the following equations, respectively:

$$P = \frac{V}{Ap\Delta t} \tag{2}$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{3}$$

where P is the permeance of DI water, V is the volume of permeate water, A is the effective filtration area, p is the applied pressure, Δt is the permeate time, R is the rejection, C_p and C_f are the salt concentrations of the feed and permeate solutions, respectively.

Ion permeation

The ion permeation experiment of the membrane was performed by U-tube. Thirty milliliters of DI water was added in the permeate side and 30 mL of salt solution with concentration of 2.0 M was added in the feed side. The membrane was facing the permeate solution. The solutions on both sides were stirred by magnetic rotors. The conductivity of the permeate solution was measured at regular intervals for 2 h.

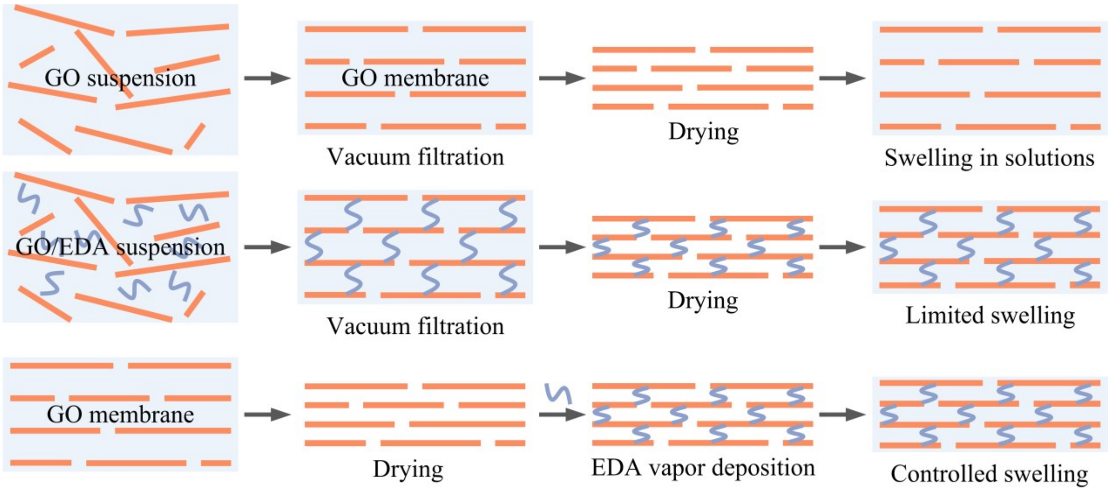

Fig. S1 Illustration of the GO membrane and the GO-EDA memebranes prepared by vacuum filtration and CVD.

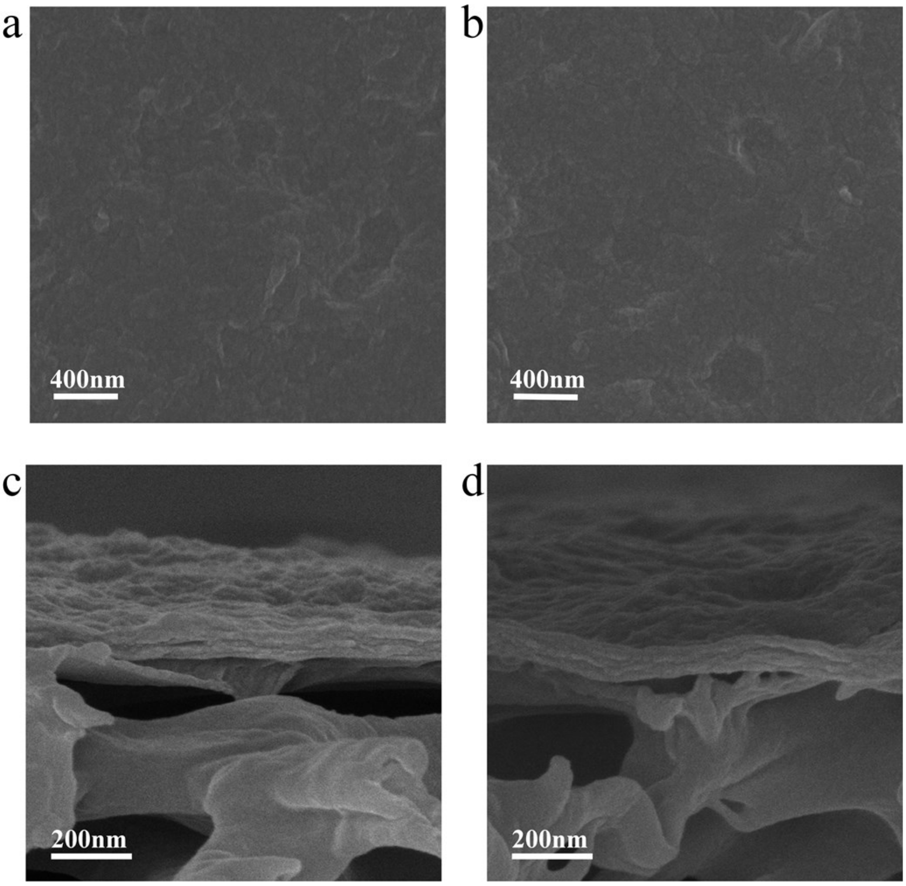

Fig. S2 SEM images of (a,b) top and (c,d) cross-sectional views of the GO-EDA membrane vapor-deposited for (a,c) 15 min and (b,d) 45 min. These membranes were prepared with concentration of 20 μg mL^{-1}.

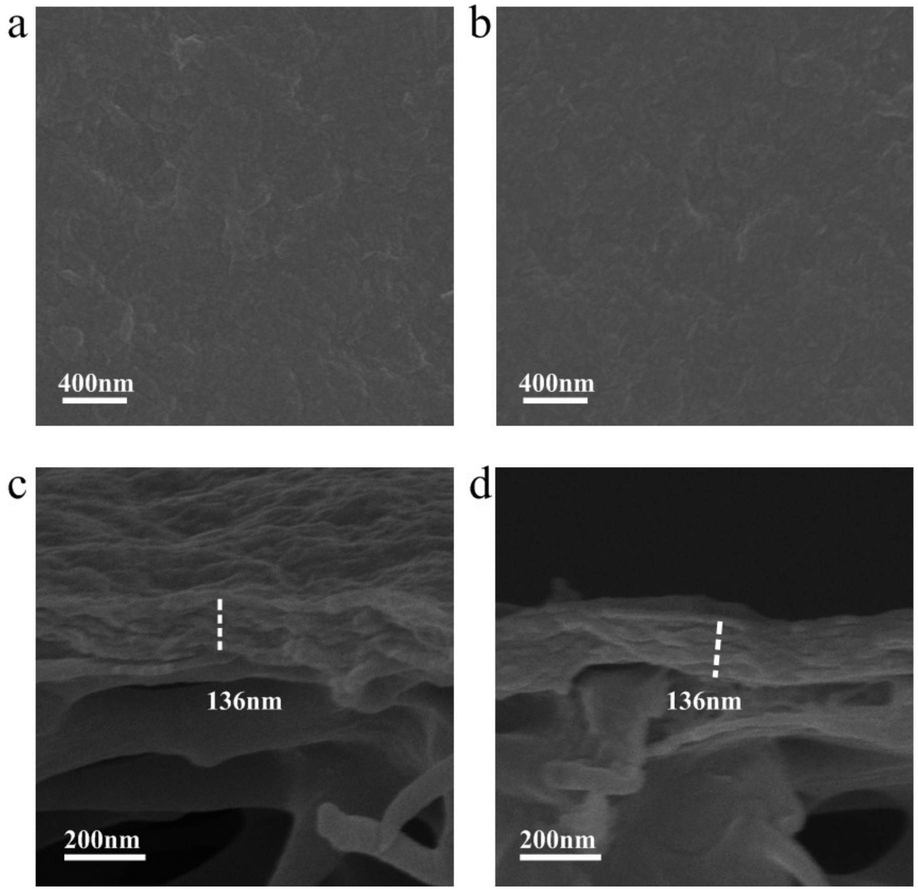

Fig. S3 SEM images of (a,b) top and (c,d) cross-sectional views of (a,c) the pristine GO membrane and (b,d) the GO-EDA membrane vapor-deposited for 30 min. These membranes were prepared with concentration of 40 μg mL^{-1}.

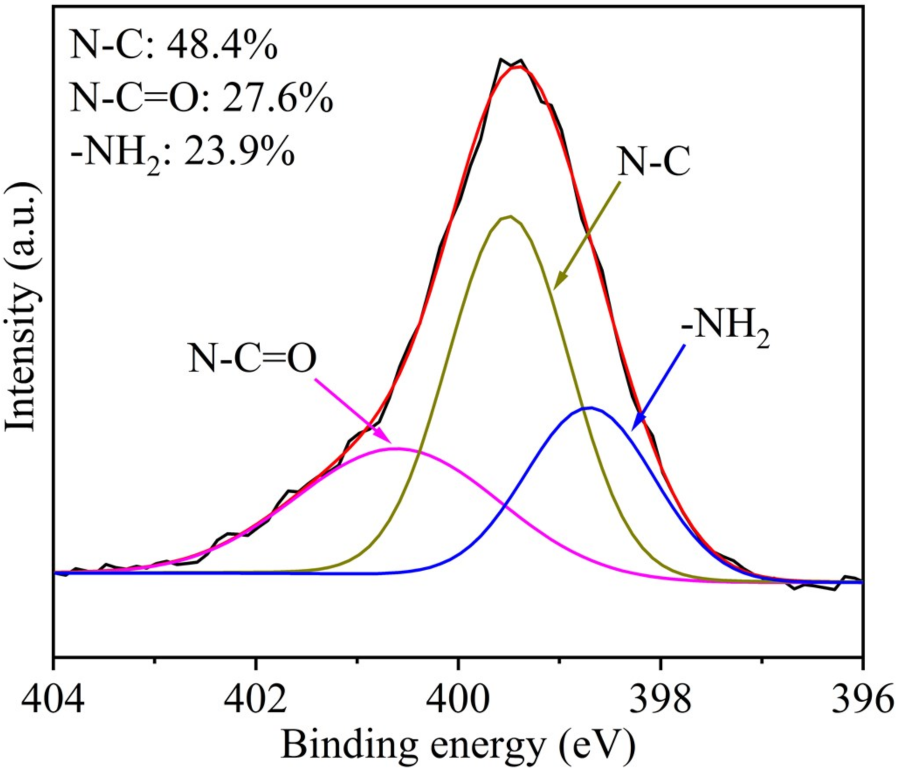

Fig. S4 XPS N 1s spectrum of the GO-EDA membrane.

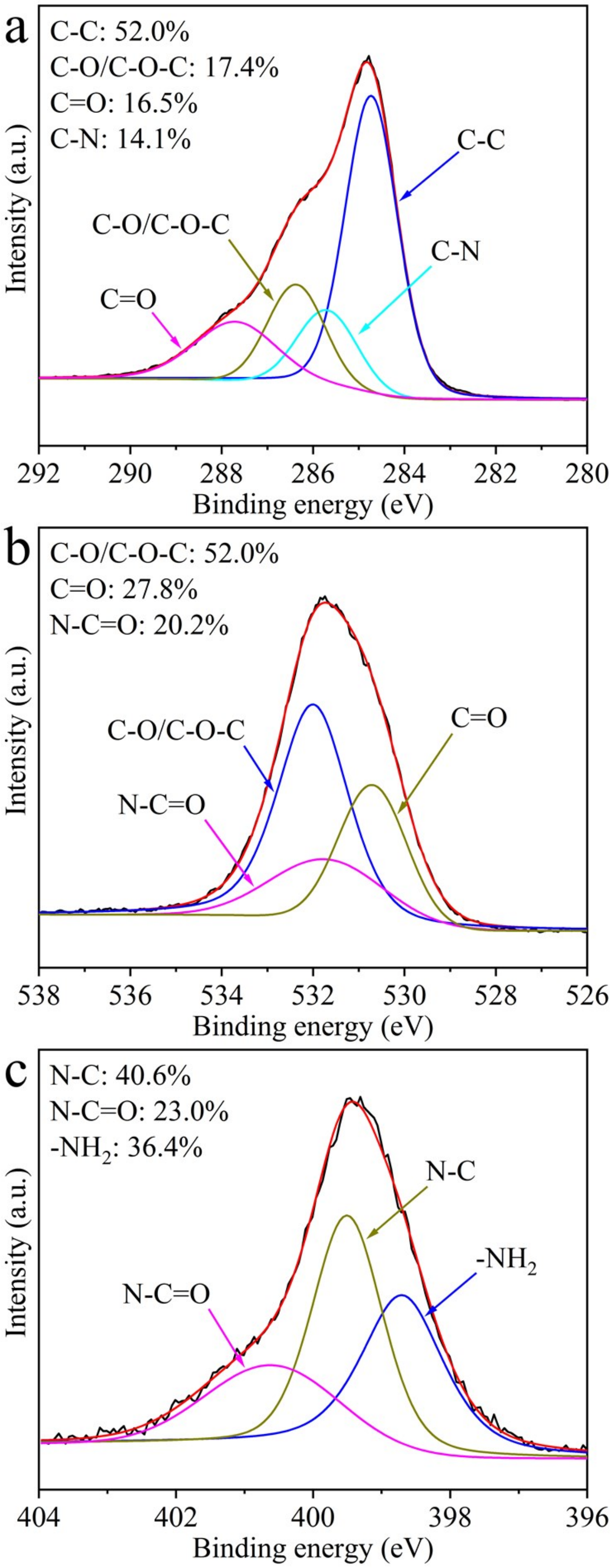

Fig. S5 XPS (a) C 1s, (b) O 1s, and (c) N 1s spectra of the GO-EDA-V membrane.

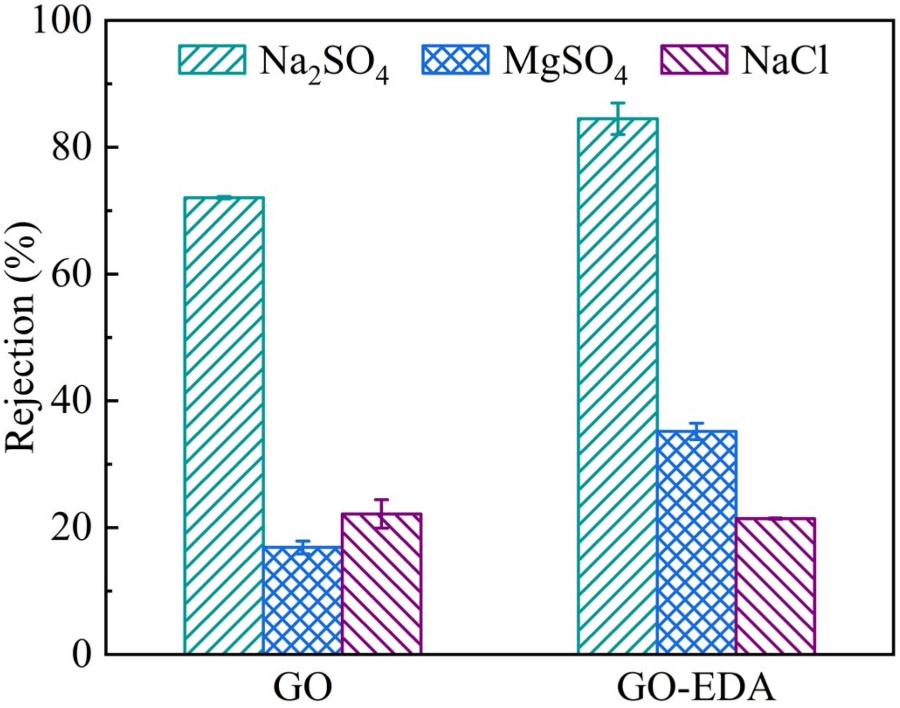

Fig. S6 Na_2SO_4, $MgSO_4$, and NaCl rejections of GO and GO-EDA membranes with GO loading of 400 μg.

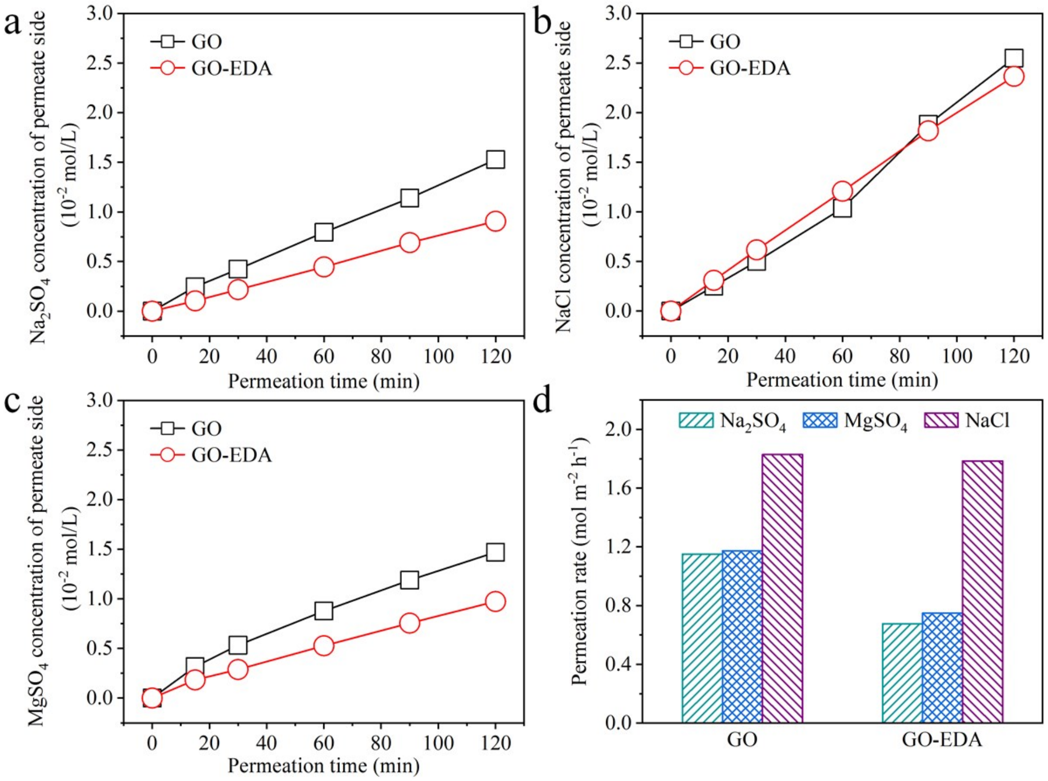

Fig. S7 (a) Na_2SO_4, (b) NaCl, and (c) $MgSO_4$ concentrations of permeate side with permeation time. (d) Na_2SO_4, NaCl, and $MgSO_4$ permeation rates of GO and GO-EDA membranes. These membranes were prepared with concentration of 20 μg mL^{-1}.

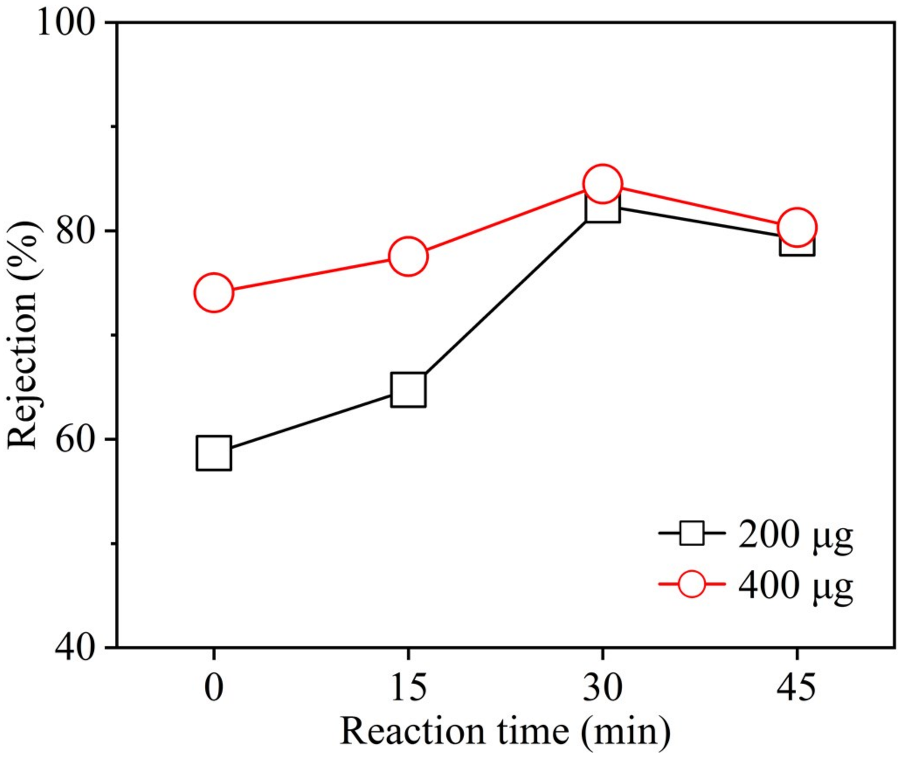

Fig. S8 Na_2SO_4 rejection of GO-EDA membranes with different reaction durations.

Table S1 Desalination performance of different GO membranes for Na_2SO_4 solution.

Membrane	Concentration (ppm)	Water permeance (L m^{-2} h^{-1} bar^{-1})	Rejection (%)	Ref
TMPyP/GO	2000	1.2	87.7	1
TMC/GO, Polydopamine	1420	276	26	2
GO @ PAN	-	2.0	56.7	3
brGO	2840	3.26	60.0	4
BPPO/EDA/GO	1000	4.1	56.2	5
GO/TiO_2	710	89.6	60.6	6
GO-EDA	500	2.3	82.4	This work

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