

Electronic Supplementary Material

A Novel Mixed Matrix Membrane Framework for Ultrafast Cation Sieving

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Experimental details

Materials:

Graphene oxide (GO) was prepared by a modified Hummer's method.¹ Sodium p-Styrene Sulfonate was purchased from Energy Chemical Co., Ltd. (Shanghai, China) Divinylbenzene and 2,2-Azobisisobutyronitrile (AIBN) were purchased Aladdin Chemistry Co., Ltd. (Shanghai, China). Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) with a degree of sulfonation of 30% was kindly provided by Tianwei Membrane Co., Ltd. (Shandong, China). Graphite powder (99.8%), potassium permanganate (KMnO₄, AR grade), sulfuric acid (H₂SO₄, 98%, AR grade), phosphoric acid (H₃PO₄, 85%, AR grade), hydrochloric acid (HCl, 37.5%, AR grade), hydrogen peroxide (H₂O₂, 30%, AR grade), N, N-dimethylformamide (DMF, AR grade), lithium chloride (LiCl, AR grade), sodium chloride (NaCl, AR grade), potassium chloride (KCl, AR grade), calcium chloride (CaCl₂, AR grade), magnesium chloride hexahydrate (MgCl₂·6H₂O, AR grade), ferric chloride (FeCl₃, AR grade), and chromium chloride hexahydrate (CrCl₃·6H₂O, AR grade) were purchased from Shanghai-Sinopham Chemical Reagent Co., Ltd. (China). Polyether sulfone (PES) microfiltration membranes and Nylon microfiltration membranes with an average pore size of 0.22 μm were purchased from Jinteng Experimental Equipment Co., Ltd. Deionized (DI) water was used throughout the experiments.

Preparation of Graphene oxide (GO):

Firstly, 5 g of graphite powder was added to a mixed solution of 200 mL concentrated H₂SO₄ and 40 mL H₃PO₄ solution, and then 20 g of KMnO₄ was slowly added under stirring. After 5 hours, the mixed solution was added to 800 mL ice water and 20 mL H₂O₂ solution. After standing overnight, the mixed solution was washed with HCl and water until neutral. Finally, GO powders were obtained by freeze-drying. The quality of GO nanosheets was investigated by TEM, as shown in **Fig. S3**.

Preparation of GO and cross-linked polystyrene sulfonate networks mixed with GO (CPSN@GO) membranes:

The prepared GO powder was dispersed in water after ultrasonication for 1 hour (0.5

mg/mL), and GO membranes were prepared by a pressure-assisted filtration-deposition method through PES microfiltration membranes. Then, the freestanding GO membranes will spontaneously detach from the PES substrate when immersing into water environments after a while. The GO membranes were further dried under vacuum at 40 °C prior to use.

The CPSN@GO membrane was prepared following below procedure. Typically, 20 mg GO powder was dispersed in 100 mL DMF solution after ultrasonication for 1 hour, and then a certain amount of sodium styrene sulfonate and divinyl benzene monomers (5wt% of sodium styrene sulfonate) were added. Finally, AIBN (5wt% of sodium styrene sulfonate) was added. After 4 hours of reaction in oil bath under nitrogen atmosphere at 85 °C, the mixed suspensions were filtered under vacuum to obtain the successful fabrication of CPSN@GO. The freestanding CPSN@GO membranes were obtained by taking the similar procedures for treating GO membranes. To prepare a series of CPSN@GO membranes with varied compositions, 20 mg, 100 mg, and 200 mg sodium styrene sulfonate were used respectively. The corresponding membranes were named as CPSN@GO-I, CPSN@GO- II , and CPSN@GO-III, respectively. For comparison, the CPSN+GO membrane was prepared by the solution casting methods. The solution compositions are identical with those for the CPSN@GO-II fabrication. All the membranes were processed by 1 mol L⁻¹ HCl solutions to exchange the Na⁺ counterions with H⁺.

Characterizations:

Atomic force microscope (AFM) images were recorded on an SPM 9600 microscope (Shimadzu, Japan). Transmission electron microscopy (TEM) images were taken out by using a HT7700 microscope (Hitachi, Japan) at an acceleration voltage of 200 kV. Elemental analysis was collected by using Vario ELc (elementar, Germany). Fourier transform infrared (FT-IR) spectra of GO and CPSN@GO were recorded on LX10-8813 (USA). Scanning electronic microscopy (SEM) images were taken out by using a SU8020 scanning electron microscope (Hitachi, Japan) with an accelerating voltage of 10 kV. X-ray diffraction (XRD) was performed on a X'Pert PRO MPD X-ray

diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm, Palmer naco, Netherland). X-ray photoelectron spectroscopy (XPS) spectra were collected by using an ESCALAB 250XI photoelectron spectrometer (ThermoFisher Scientific, USA). The tensile measurements were carried out using a Q850 dynamic mechanical analyser (DMA, TA Instruments, USA) at a stretch rate of 0.5 N/min.

Ion penetration test:

Ion penetration experiments were carried out with a homemade permeability apparatus (**Fig. S1**). The freestanding GO membrane and CPSN@GO composite membranes were sealed by a piece of copper tape containing a hole with a diameter of 8 mm (an effective area of 0.5 cm²) in its center. The feed compartment was filled with 100 mL 0.2 M salt solution (NaCl, LiCl, CaCl₂, MgCl₂, FeCl₃ or CrCl₃). The permeate side was filled with 100 mL DI water. Stirring on both of sides was performed continuously to minimize the effects of concentration polarization. The conductivity of the permeation side was measured by conductivity meter (DDS 307A) and recorded as a function of permeation time. The ionic conductivity of permeate side was recorded by every 1 h, and the measurements last 5 h. The measured ionic conductivity variations of permeate solutions were converted to corresponding salts concentration according to the molar conductivity calculations: $C = (\kappa/\Lambda_m)$, where C is the concentration, κ is the measured conductivity, and Λ_m is the molar conductivity. The molar conductivities of salt solutions were taken from the literature.²

The ion permeation rate was calculated from the diffusion equation:

$$J = \frac{V_{\text{eff}} \times C}{A_m \times t}$$

Where V_{eff} (L) is the effective volume of the permeation solution, c (mol L⁻¹) is the permeation concentration across the membrane, A_m (m²) is the effective area of the membrane, and t (h) is the testing time. All the collected data were averages of three parallel tests and standard deviation was calculated.

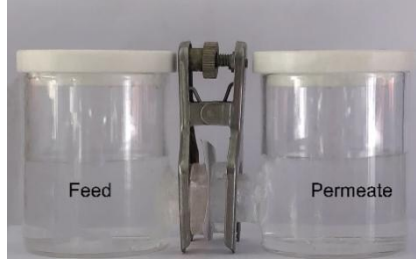


Fig. S1 Schematic of static diffusion device.

Electrodialysis test:

Electrodialysis (ED) testing was taken out by using an ED device with an effective area of 0.5 cm^2 (**Fig. S2**). Firstly, the electrode chamber was filled with 200 mL of 0.3 M Na_2SO_4 solution and the diluted chamber contained 100 mL of 0.1 M NaCl / 0.1 M MgCl_2 or 0.1 M LiCl / 0.1 M MgCl_2 mixed solution. The concentrated compartment was filled with 200 mL of 0.01 M KCl solution. The peristaltic pump was used for circulation at a flow rate of 30 r min^{-1} . The electro dialysis experiment was carried under the constant voltage of 38 V by using a DC electrical potential. After 0.5 h, the concentration compartment solution was detected by ICP-MS (Agilent 7900, USA) to obtain ion concentration. The corresponding flux through the membrane was calculated from the concentration change in the concentrated chamber:

$$J = \frac{(C_t - C_0) \times V}{A_m \times t}$$

Where J is the ion flux ($\text{mol m}^{-2} \text{ h}^{-1}$). C_t (mol L^{-1}) and C_0 (mol L^{-1}) represent the ion concentration at time 0 and t, respectively. V (m^3) is the volume of circulated solution in the concentrated compartment. t (h) is the testing time. A_m (m^2) is the effective area.

The perm-selectivity was calculated according to the following equation as reported³

$$P_{M^{2+}}^{N^+} = \frac{(J_{N^+} \times C_{M^{2+}})}{(J_{M^{2+}} \times C_{N^+})}$$

Where J_{N^+} and $J_{M^{2+}}$ are the ion flux ($\text{mol m}^{-2} \text{ h}^{-1}$). $C_{M^{2+}}$ (mol L^{-1}) and C_{N^+} (mol L^{-1}) are concentrations of M^{2+} and N^+ in the diluted compartment during the ED experiment. All the collected data were averages of three parallel tests and standard deviation was calculated.

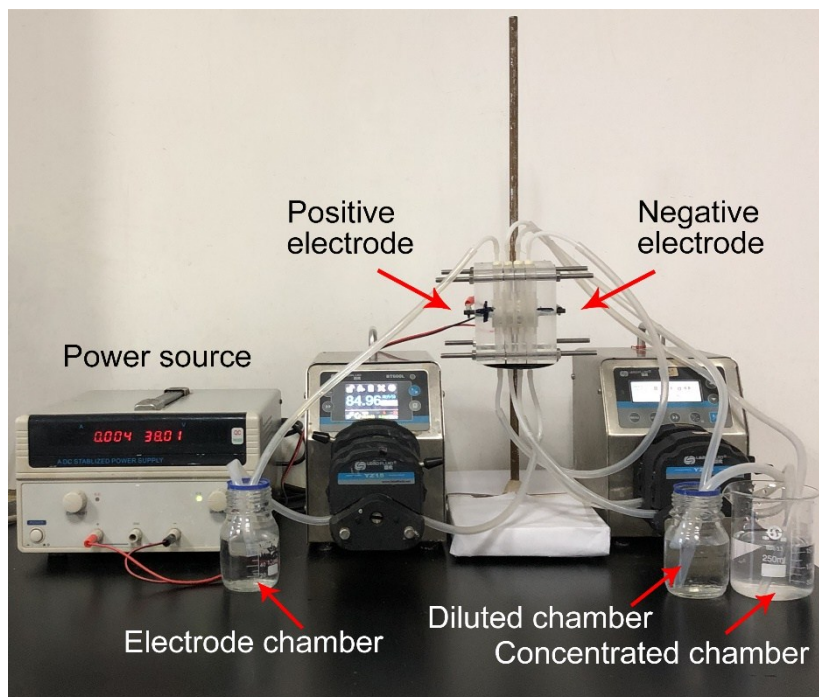


Fig. S2 Schematic of electrodialysis device.

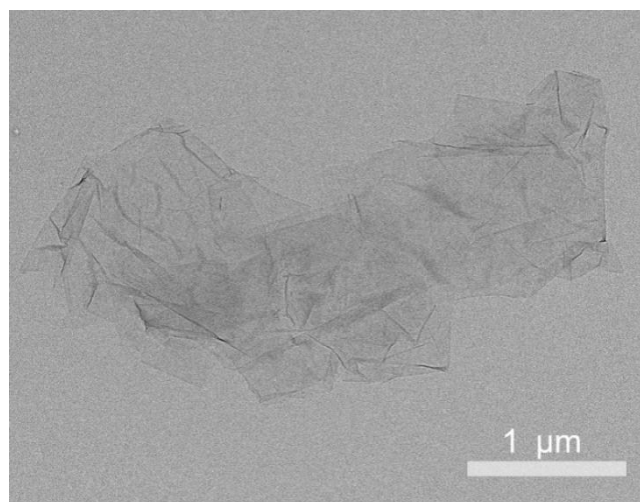


Fig. S3 The TEM image of GO.

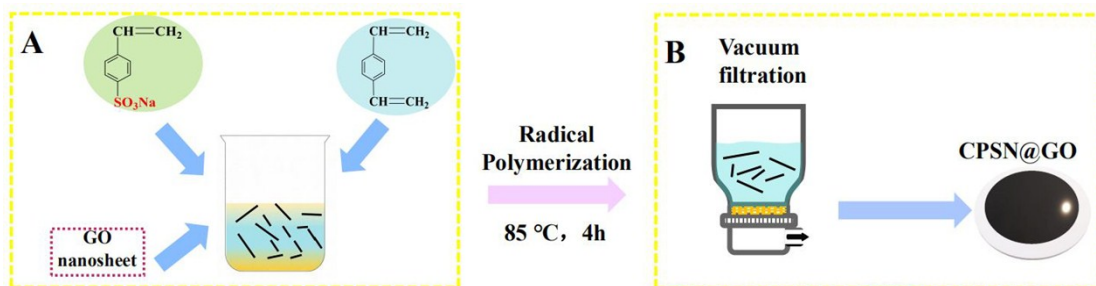


Fig. S4 The preparation procedure of CPSN@GO membranes.

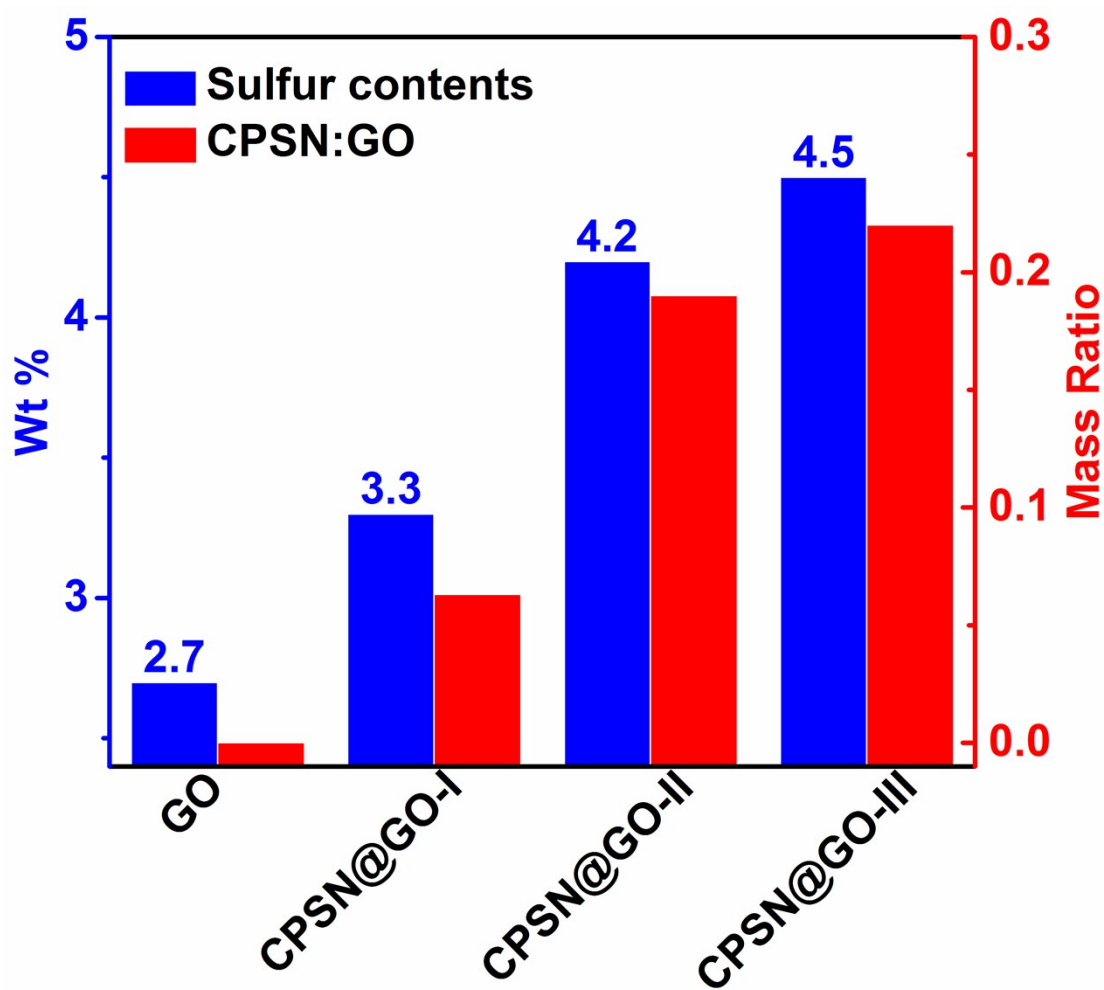


Fig. S5 The realistic sulfur contents and mass ratios of CPSN and GO for the CPSN@GO membranes.

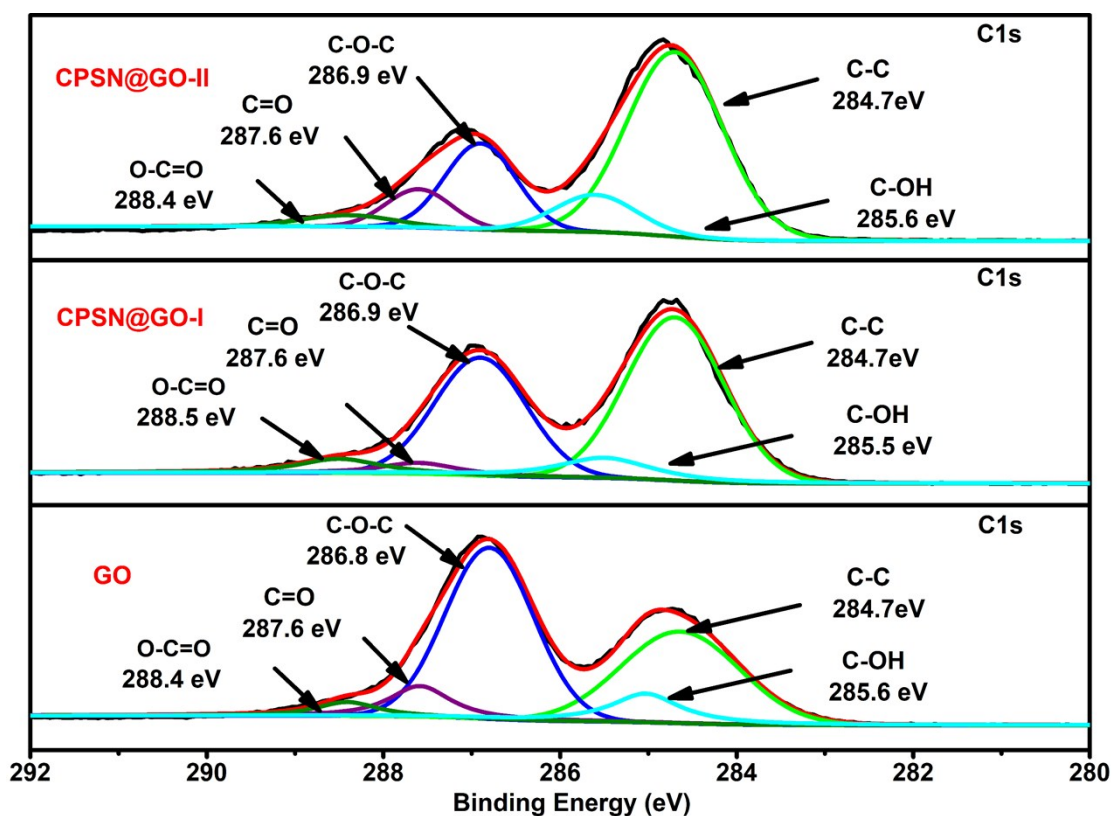


Fig. S6 The C1s XPS spectra of GO, CPSN@GO-I, and CPSN@GO-II.

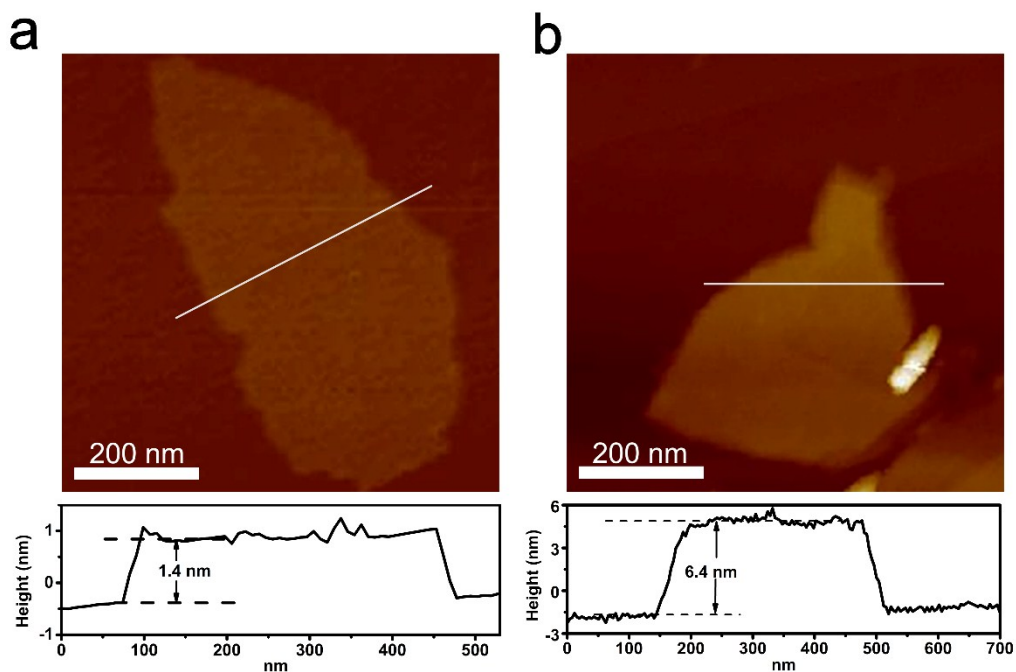


Fig. S7 The AFM images and height profiles of (a) GO sheets; (b) CPSN@GO sheets on freshly cleaved mica.

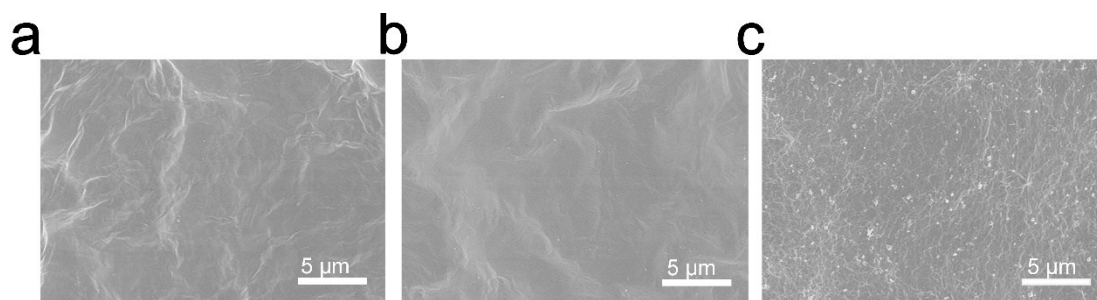


Fig. S8 The surface SEM images of GO, CPSN@GO-I, and CPSN@GO-II.

As shown in Fig. S8, the CPSN@GO membranes display an intact surface without detectable pinholes and cracks, similar to that of the GO membrane. As the increasing CPSN proportion from CPSN@GO-I to CPSN@GO-II, the superficial polymer amounts of the CPSN@GO membranes also gradually increase, leading to visible white dots on the surface of CPSN@GO-II.

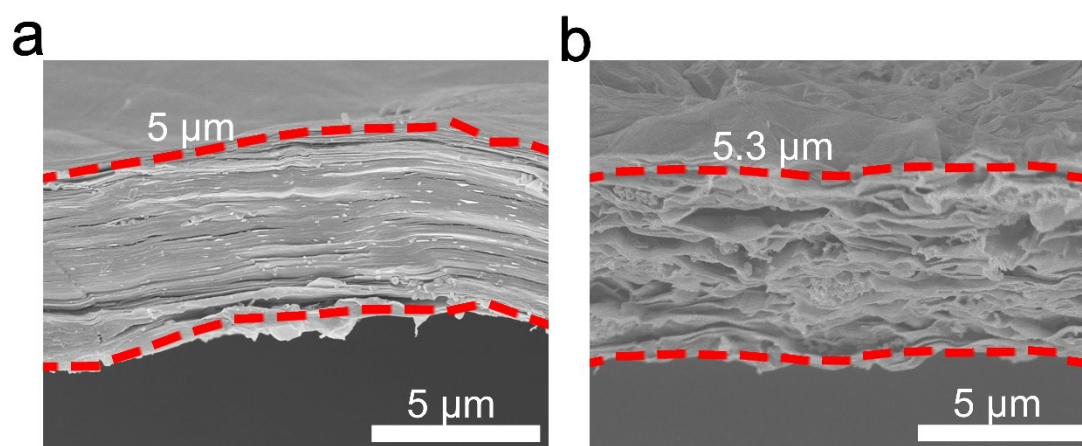


Fig. S9 The cross-sectional SEM images of GO, and CPSN@GO-I.

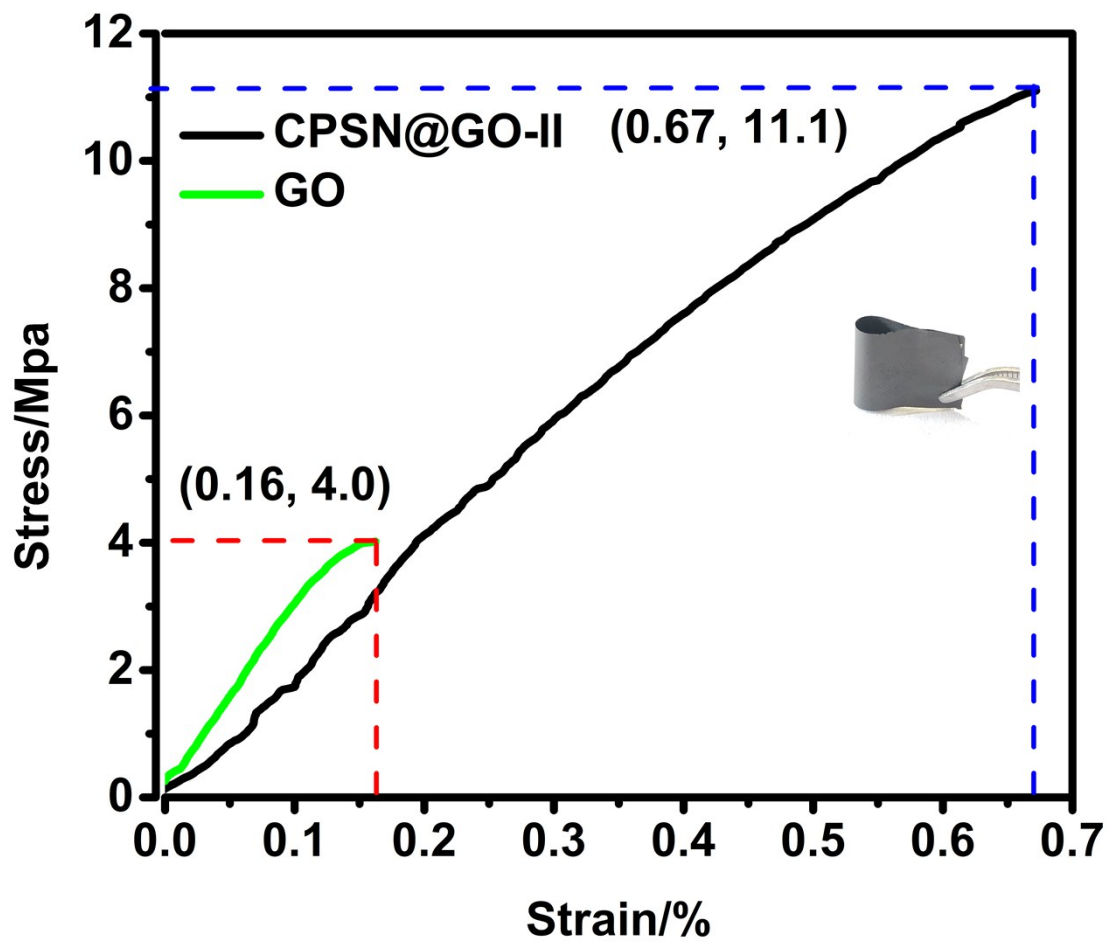


Fig. S10 The stress-strain curves of the GO and CPSN@GO-II membranes (inset: the bending capability of the CPSN@GO-II membrane).

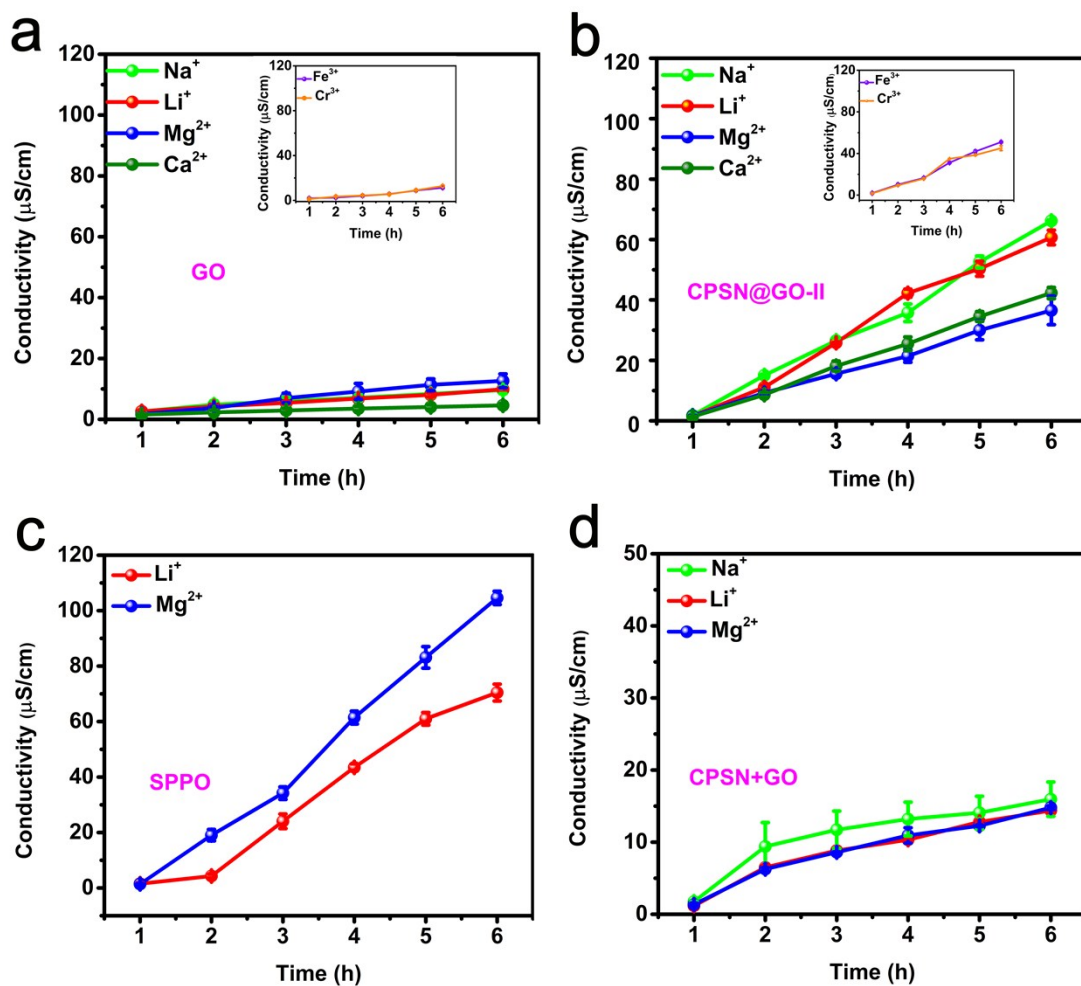


Fig. S11 The conductivity variations as a function of prolonging time for (a) the GO membrane; (b) the CPSN@GO-II membrane; (c) the SPPO membrane; (d) the CPSN+GO membrane.

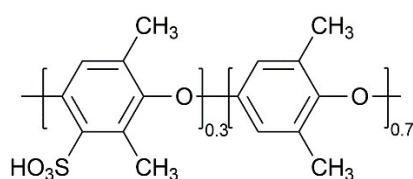


Fig. S12 The chemical structure of SPPO.

The SPPO employed for comparisons exhibits a moderate degree of sulfonation of 30%, which renders SPPO to possess promising membrane formation and ion conduction abilities. Correspondingly, SPPO has a sulphur content of 6.7wt%. The resulting SPPO membrane exhibits an ion exchange capacity of 2.1 mmol/g.

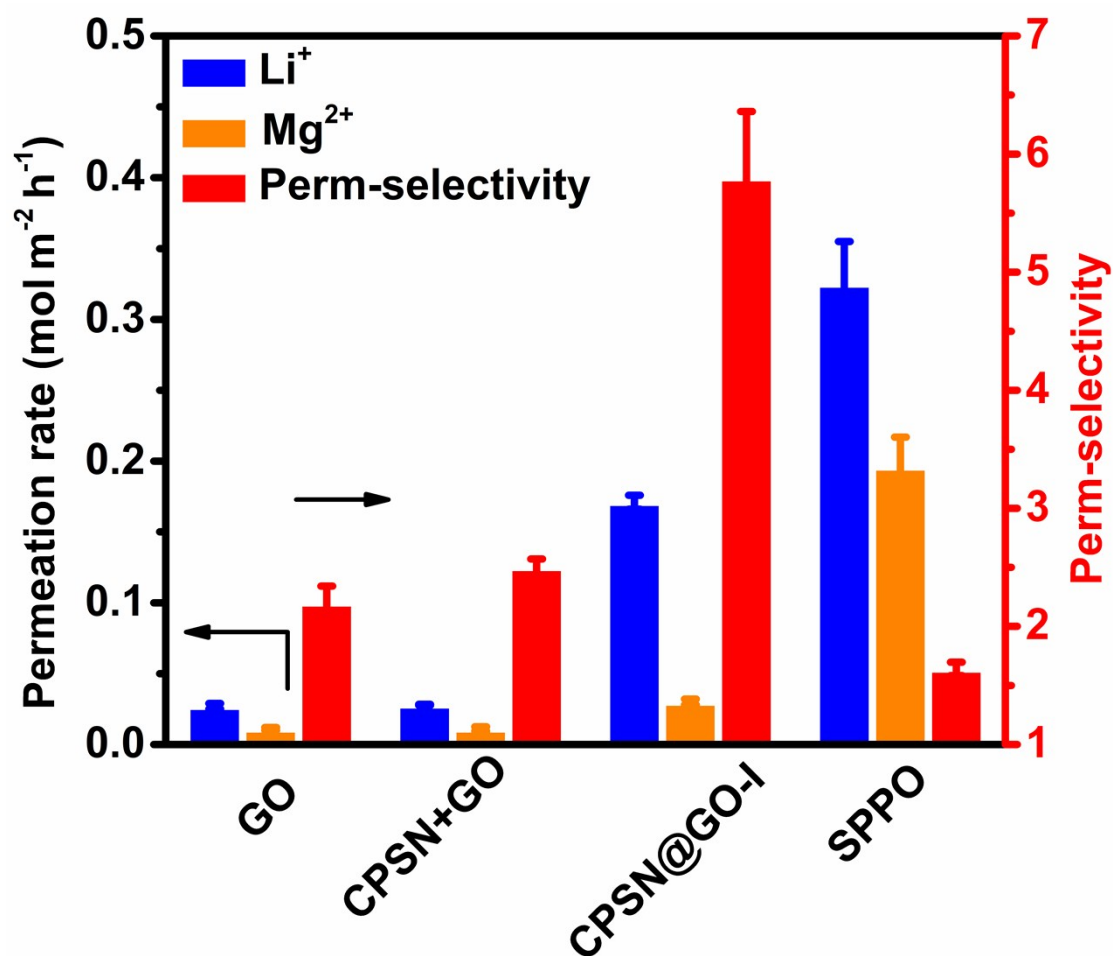


Fig. S13 The permeation rates and perm-selectivity through the GO, CPSN+GO, CPSN@GO-I, and SPPO membranes evaluated by diffusion dialysis.

As shown in Fig. S13, the Li⁺ and Mg²⁺ permeation rates through the CPSN@GO-I membrane fall in between those through the GO laminate and SPPO membrane. And CPSN@GO-I exhibits higher perm-selectivity towards Li⁺ and Mg²⁺ compared to both the GO and SPPO membranes, demonstrating the improving ion sieving ability by the special scheming mixed matrix membrane structure.

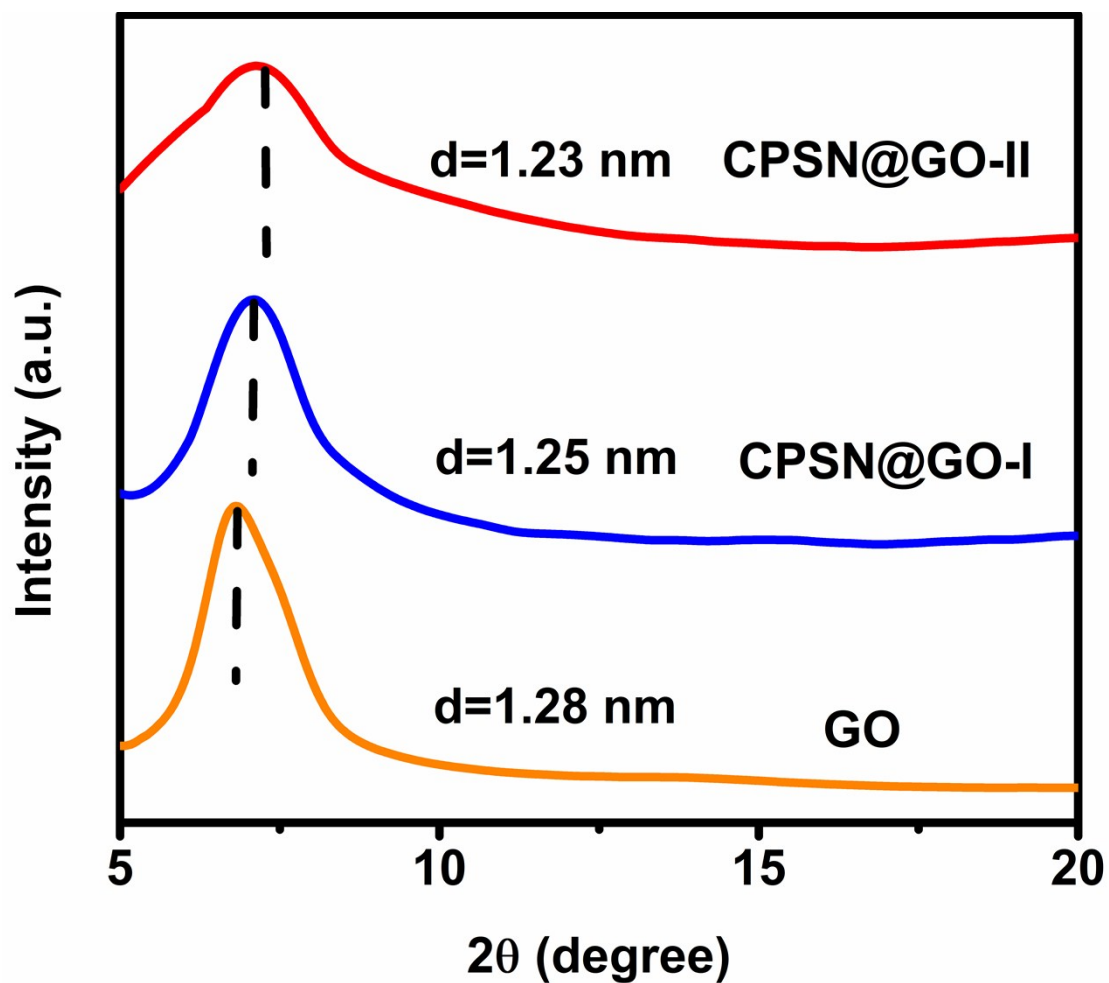


Fig. S14 The XRD patterns of the GO, CPSN@GO-I, and CPSN@GO-II membrane in solvated states.

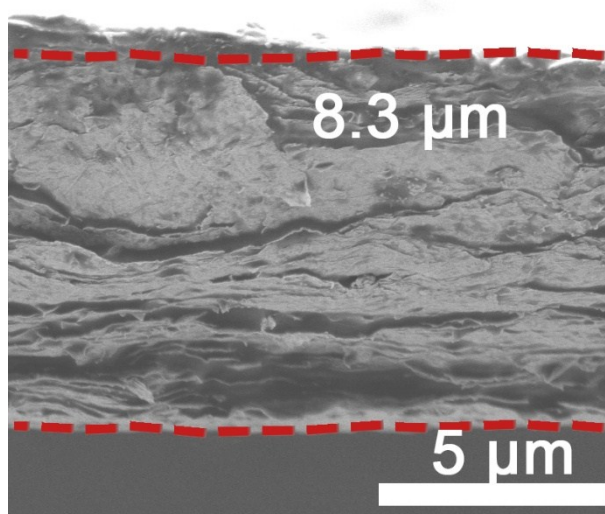


Fig. S15 The cross-sectional SEM image of CPSN+GO.

Table S1 The reported ionic diameters and hydrated ionic diameters are from ref. (4). The hydration enthalpies are from ref. (5). The binding affinities are from ref. (6-8).

Ion	Hydrated ionic diameter (Å)	Hydration enthalpy (kJ mol ⁻¹)	Binding affinity (related to Li ⁺)
K ⁺	6.62	480	2.90
Na ⁺	7.16	390	1.98
Li ⁺	7.64	330	1.00
Mg ²⁺	8.56	1870	3.18
Ca ²⁺	8.24	1520	5.06
Fe ³⁺	9.14	4230	/
Cr ³⁺	9.22	4090	/

Table S2 Comparisons of the ion permeation rate and perm-selectivity through the membranes reported in literature.

Membrane	Ion permeation rate (mol m ⁻² h ⁻¹)		Perm-selectivity		Thickness (μm)	Solution concentration (mol/L)	Driving force	Ref.
	Na ⁺	Li ⁺	Na ⁺ /Mg ²⁺	Li ⁺ /Mg ²⁺				
CPSN@GO	2.4	2.58	32	20	6.7	0.1	Current	This work
QDBPOSS	0.45	/	7.3	/	/	0.1	Current	9
SBQAPPO	0.73	/	2.62	/	/	0.1	Current	10
Mxene	1.53	1.4	9.56	8.75	1.5	0.1	Concentration	11
EDA-GO	0.05	/	2.5	/	/	0.1	Concentration	12
GO-750	0.19	/	7.6	/	0.75	0.25	Concentration	13
NFCMs	1.1	/	1.6	/	114	0.1	Current	14
E-HPAN	1.54	/	3.3	/	97	0.1	Current	15
ENFMs	/	2.1	/	11.3	140	0.1	Current	16

CPSN@GO cross-linked polystyrene sulfonate networks distributed onto GO; **QDBPOSS** monovalent cations perm-selective membranes composed of quaternized poly(2,6-dimethyl

phenylene oxide)s containing different lengths of alkyl spacers; **SBQAPPO** synthesized zwitterionic polyelectrolytes membrane; **Mxene** 2D membrane composed of $Ti_3C_2T_x$; **EDA-GO** GO membranes crosslinked with ethylene diamine; **GO-750** a thickness of the GO membrane is 750 nm; **E-HPAN** hydrolyzed polyacrylonitrile porous substrate immersed in ethylene diamine; **ENFMs** electro-nanofiltration membranes.

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