# **Electronic Supplementary information**

Effects of cationic concentrations on controlling the interlayer spacings

for highly effective ions rejection via graphene oxide membranes

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### **PS1** Materials and methods

#### Fabrication of GO suspension

Graphene oxide (GO) suspension was prepared from graphite powder according to modified Hummers method.<sup>S1-S3</sup> The graphite powders were added into concentrated H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and P<sub>2</sub>O<sub>5</sub> solution and stirred continuously for several hours. Then the mixture was diluted using deionized (DI) water, centrifuged and washed with DI water. Then, the pre-oxidized graphite was obtained after drying treatment under vacuum. Then, these pre-oxidized graphite were further oxidized in concentrated H<sub>2</sub>SO<sub>4</sub> and KMnO<sub>4</sub>, diluted with DI water, and then 30% H<sub>2</sub>O<sub>2</sub> was added. The product was centrifuged and washed with 1:10 HCl aqueous solution and DI water sequentially to remove ion species. The concentration of as-prepared GO suspension is approximately 5 mg/mL.

#### Fabrication of supported GO membranes

GO membranes supported by mixed cellulose ester (MCE, 50 mm diameter, 0.22  $\mu$ m pore size) substrates were fabricated by vacuum filtration method. For GO membrane with 100 nm thickness, 20 mL GO dispersion with concentration of 0.01 mg/mL was applied for GO membrane fabrication. GO membranes with thicknesses of 30, 180 and 280 nm were also prepared for comparison. These membranes with different thicknesses were noted as GO-30, GO-100, GO-180 and GO-280, respectively.

#### **Experimental setup for XRD detection**

GO membranes prepared by vacuum filtration method were immersed in a certain concentration of KCl solution at room temperature for one hour, respectively. Then the wet membranes with salt solution were taken out and characterized with XRD.

### **PS2** Characterization methods

As-prepared GO membranes were characterized by scanning electron microscope (SEM, Hitachi, S-4800), X-ray diffraction (XRD, Siemens,

08DISCOVER,  $\lambda$ =0.15418 nm) and UV-vis (Shimadzu UV-25500 PC UV/vis absorption spectrometer).

### **PS3** Ion permeation tests

Ion permeation experiments were carried out using a self-made device as shown in the Fig. 1. The effective membrane area is 1.77cm<sup>2</sup>. Take the initial ions concentration is 0.25M of MgCl<sub>2</sub>, 0.25M KCl-controlled GO-100 membrane as an example: for the test of membrane untreated GO membrane , 80 mL 0.25M MgCl<sub>2</sub> aqueous solution was added into draw side, and 80mL DI water was added into feed side at the same time. For 0.25M KCl-controlled GO membrane, the membrane was first immersed into 0.25 M KCl solution for 1h. Then 80 mL 0.25M KCl solution was added into feed side, while 80 mL mixture of 0.25 M KCl and 0.25 M MgCl<sub>2</sub> aqueous solution was added into the draw side. The introduction of KCl is to prevent the leakage of KCl in the membrane. After free penetration for 8 h, the solution on the both feed sides was taken for ICP measurement. During the tests, the GO layers were facing to the draw side all the time and to avoid concentration gradients, magnetic stirrings were applied to both sides.

The water flux J<sub>w</sub> was calculated by

$$J_{\rm w} = \frac{\Delta V}{A\Delta t}$$

Where  $\Delta V$  is the volume change of draw side, A is the effective membrane area,  $\Delta t$  is the permeation time.

The ions permeation rate P<sub>i</sub> was calculated by

$$P_{\rm i} = \frac{C_i V}{A\Delta t}$$

Where  $C_i$  is the ion concentration of draw side, V is the volume of draw side, A is the effective membrane area, and  $\Delta t$  is the permeation time.

Further, we have experimentally studied the K<sup>+</sup> leakage without KCl solutions on both sides of GO membrane, as shown in Fig. S1. We used the 1.50M KCl-controlled GO-100 membranes and 0.25 M MgCl<sub>2</sub> initial concentration as the example. In details, 80mL DI water and 80 mL 0.25M MgCl<sub>2</sub> aqueous solutions were added into the feed side and draw side, respectively. During the test, the GO layer were facing in the draw side. Magnetic stirrings were applied to both sides to avoid possible concentration gradient.



Fig. S1. (a) Schematic of the experimental setup for Mg<sup>2+</sup> permeation test on 1.50 M KClcontrolled GO membrane without KCl solutions in feed side and draw side. (b) 0.25M Mg<sup>2+</sup> permeation rates of untreated, KCl-controlled GO membrane without KCl solutions in both sides and KCl-controlled GO membrane added KCl solutions in both sides.

As shown in Fig S1 b, the  $Mg^{2+}$  permeation rate in this experiment (KClcontrolled GO membrane without KCl in both sides) is 0.78 mol m<sup>-2</sup> h<sup>-1</sup>, which is comparable to the  $Mg^{2+}$  permeation rate of untreated GO membrane (0.92 mol m<sup>-2</sup> h<sup>-1</sup>). Further, this rate is much higher than the  $Mg^{2+}$  permeation rate of KCl-controlled GO membranes added KCl in both sides (0.024 mol m<sup>-2</sup> h<sup>-1</sup>, as shown in Fig 2 and S1 b). Thus, it can be reasonable asummed that when KCl is lacked in both sides, the high permeation rate is due to the leakage of K<sup>+</sup> in the GO membrane.

Therefore, it is necessary to add KCl into both sides of the membrane during the permeation process to confine the K<sup>+</sup> in the GO membrane and to keep the interlayer

spacings stable.



Fig. S2. The rejection of untreated GO membrane and GO membrane controlled by different concentration KCl with the initial 0.25 M MgCl<sub>2</sub> solution.

Fig. S2 shows that with the increasing concentrations of controlling ions (K<sup>+</sup>), the  $Mg^{2+}$  rejection of controlled membranes is increasing. In particular, for the 1.50 M KCl-controlled GO-100 membranes, the rejection of  $Mg^{2+}$  achieved above 97.5%. This picture is related to Fig. 1e.



Fig. S3. The rejection of untreated GO-100 membrane and GO-100 membrane controlled by different concentrations of KCl solutions as a function of filtration time. Error bars indicate the standard deviation from three different samples.

The different concentrations KCl-controlled GO-100 membranes and untreated GO-100 membranes all showed an outstanding stability with rejection of Mg<sup>2+</sup> as shown in Fig. S3.



**Fig. S4. Liquid level changes of different membranes in ion permeation test.** (a)untreated GO-100 membrane;(b) 0.25M KCl controlled GO membrane;(c) 1.5 M KCl controlled GO-100 membrane. The underlined position is the initial liquid level.

Membrane	Untreated	0.25M KCl	1.5M KCl Controlled
	$(L/m^2h)$	Controlled(L/m <sup>2</sup> h)	$(L/m^2h)$
GO-100	1.85	1.16	0.47
GO-30	3.70	2.20	1.85

Table S1 Comparison of water flux of GO-100 and GO -30 membranes.

The water fluxes of the membrane are listed in Table S1. The initial salt concentration  $(Mg^{2+})$  of all flux tests were 0.25 M. The results showed that the water flux increased significantly as the film thickness decreased. Further, the water flux decreased after controlled by KCl owing to the fact that the interlayer spacings of GO membranes were reduced after treatment with higher concentrations of K<sup>+</sup>. Therefore, the water flux can be improved by decreasing the thickness of the GO membranes.





We tested GO membranes with thicknesses of about 100 (GO-100), 180(GO-180), and 280 (GO-280) nm. The feed side included 80 mL DI water, and the draw side included 80 mL 0.25M MgCl<sub>2</sub> aqueous solution. For the 1.5M KCl-treated GO membranes, the feed side included 80 mL 0.25 M KCl aqueous solution, and the draw side included 1.5 M KCl with 0.25 M MgCl<sub>2</sub> aqueous solution. The introduction of KCl is to prevent the leakage of KCl in the membrane. Error bars indicate the standard deviation from three different samples.

We also examined how membrane thickness affected the Mg<sup>2+</sup> permeation

behaviour. The results are shown in Fig. S5. The  $Mg^{2+}$  permeation rate was decreased with the increased thickness of GO membranes for both untreated and 1.50M KClcontrolled GO membranes. Further, for these three thickness of GO membranes, the ratio of the permeation rate of 1.50 M KCl-controlled GO membranes to untreated GO membranes maintain at about 1/50, indicating that the ratio is relatively independent of the thickness. Further, the 1.50M KCl-controlled GO membranes with different thickness exhibited almost totally rejection for the  $Mg^{2+}$ .



Fig. S6. Permeation rates of high initial concentrations of Mg<sup>2+</sup> in untreated and 1.50 M KCl-controlled experiments.

We have also performed new permeation tests for higher concentration (1.0 M, 1.5 M) of Mg<sup>2+</sup> solution using 1.50 M KCl-controlled GO membrane, as shown in Fig. R2. The result shows that the permeation rate of Mg<sup>2+</sup> were 0.029 mol m<sup>-2</sup> h<sup>-1</sup> and 0.043 mol m<sup>-2</sup> h<sup>-1</sup> for 1.0 and 1.5 M Mg<sup>2+</sup> solution, while the corresponding permeation rate of Mg<sup>2+</sup> using untreated GO membrane were 1.26 mol m<sup>-2</sup> h<sup>-1</sup> and 3.80 mol m<sup>-2</sup> h<sup>-1</sup>, respectively, indicating a high rejection performance of KCl-controlled GO membranes for Mg<sup>2+</sup> (See Fig. S6).

The above results demonstrated that, for higher concentrations of  $Mg^{2+}$  solutions, the KCl-controlled GO membrane is still maintain an excellent controlling effect in the permeation experiment, which is coincident with the lower concentration of  $Mg^{2+}$ .

## **Reference:**

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