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PS1: Materials and methods

Fabrication of freestanding GO membranes

Graphene oxide (GO) was prepared from natural graphite powder via a modified Hummers method\(^{S1-S3}\). Graphite powders were put into concentrated \(\text{H}_2\text{SO}_4\), \(\text{K}_2\text{S}_2\text{O}_8\), and \(\text{P}_2\text{O}_5\) solution and stirred continuously for several hours. Then the mixture was diluted with deionized water (DI), centrifuged, and washed with DI water. After drying, preoxidized graphite was obtained. Then, they were further oxidized in concentrated \(\text{H}_2\text{SO}_4\) and \(\text{KMnO}_4\), diluted with DI water, followed by the addition of 30% \(\text{H}_2\text{O}_2\). The product was centrifuged and washed with 1:10 HCl aqueous solution and DI water sequentially to remove ion species. Finally, few-layer graphene oxide was separated by centrifugation at 4000 rpm. The concentration of the as-prepared GO suspension was approximately 5mg/mL. Freestanding GO membranes could be prepared by drop-casting the GO suspension (5 mg/mL, 1 ml) droplets onto a smooth paper substrate\(^1,S4\).

In order to speed up the preparation process without affecting the quality of GO membranes, the freestanding GO membranes in our study were drying thoroughly at 60 °C for 12 hours. After that, they were peeled off, rinsed and soaked with DI water for more than half hour to remove the absorbed metal ions, then dried in a dry dish at room temperature for three days. These prepared freestanding membranes were used for ion controlling and salt solution adsorption experiments.

Fabrication of GO membranes supported by ceramic substrates

GO membranes supported by ceramic disks were fabricated by filtration method. The GO layer thickness was easily tuned by changing the deposition amount of GO materials on the substrates. For GO membrane with 750 nm thickness, 55 mL GO dispersion with concentration of 0.01 mg/mL was applied for membrane fabrication. Thinner membranes with thicknesses of 550 and 280 nm were also prepared for comparison. These membranes with different thicknesses were noted as GO-750, GO-550 and GO-280, respectively. Homemade \(\text{Al}_2\text{O}_3\), ceramic disks with diameter of 2.8 cm and average pore size of 200 nm were used as substrates. Ceramic supported rGO membranes were fabricated by the same method, except using rGO dispersion. The rGO dispersion was prepared by the reported methods\(^{S5}\) using L-ascorbic acid (also known as vitamin C, VC) as the reducing agent. Typically, 0.01 mmol VC was first added into a 20 mL GO suspension (0.01 mg/mL), and then 40 \(\mu\)L of ammonia solution (25% w/w) was added. The mixture was vigorously shaken for a few minutes and then stirred at 95°C for more than 10 min. The mixture was subsequently cooled to room temperature and the resulting stable black suspension was centrifuged at 3000 rpm and washed with water three times. The obtained rGO sheets were redispersed in water and stored before further processing.

Characterization methods for freestanding GO membranes

As-prepared GO membranes were characterized by scanning electron microscope (SEM, Hitachi, S-4800), atomic force microscopy (AFM, Bruker, Multimode-8), X-ray photoelectron spectroscopy (XPS, ESCALAB, 250Xi), X-ray diffraction (XRD, Siemens, 08DISCOVER, \(\lambda=0.15418\) nm) and synchrotron wide-angle X-ray scattering (WAXS, BL16B1 beamline at Shanghai Synchrotron Radiation Facility).
Using a fixed wavelength of 0.124 nm, a sample to detector distance of 5 m, and an exposure time of 200 s. In the adsorption experiments, the GO membranes after immersion in solution were dewatered using SIGMA 2-16PK with 12148 rotors. The water adsorption storage was also characterized using NETZSCH STA 449C TG-DTA/DSC. These TGA experiments were recorded at 5 K/min under constant He flow of 50 mL/min.

**Fig. S1. Schematics and characterizations of freestanding GO membranes.** (A) Photograph of a freestanding GO membrane prepared by drop-casting of a 5 mg/mL GO suspension. SEM images of (B), (C) the surface and (D) a cross-section of the freestanding GO membrane. (E) AFM images of the GO sheets. (F) Thermogravimetric analysis (TGA) of pristine GO membranes (black curve) at a heating rate of 5 K/min from 20K to 500K in He flow. Differential Thermal Analysis (DTA, orange curve) and first derivative of the thermogravimetric data (DTG, green curve). (G) Mass of freestanding GO membranes after remove surface free water by different centrifugal speed, normalized by the corresponding dry mass of pristine GO membranes. Error bars indicate the standard deviation from three different samples.

The thermogravimetric analysis (TGA) curves of pristine GO in Fig. S1F show two main regions with considerable weight loss. The first weight loss is below 120 °C due to the removal of adsorbed water (about 11%) from the freestanding GO membranes. The removal of water is also confirmed by the first derivative of the thermogravimetric data (DTG) and thermal analysis (DTA) curves. Both of them...
show an endothermic peak at about 80 °C respectively, corresponding to the evaporation of water. The second weight loss (about 30%) in the freestanding GO membranes occurs below 280 °C, due to the pyrolysis of the labile oxygen-containing functional groups. The DTA signal also shows a marked exothermic peak at about 160 °C, suggesting the removal of functional groups.

Experimental setup for XRD detection

The freestanding GO membranes were immersed in KCl, NaCl, CaCl₂, LiCl and MgCl₂ solution of 0.25 mol/L (M) concentration at room temperature for one hour. Then the wet membranes with salt solution were taken out and characterized with XRD or WAXS. To manifest the controlled interlayer spacing with KCl solution, GO membranes were soaked in pure water and then immersed to KCl solution for half hour for pretreatment. The same concentration solutions of other ion were added at ratio of 1:1 (corresponding added salt solution to KCl solution), and the membranes were soaked in the mixed salt solution (KCl + M, M = NaCl, CaCl₂, or MgCl₂) for another half an hour.

For the interlayer spacings observation with Na⁺ concentrations, the freestanding GO membranes were immersed in NaCl solution at concentrations ranging from 0.01 to 1 M for half hour; then the wet membranes with salt solution were taken out and characterized with XRD. To manifest the controlled interlayer spacing with KCl solution, GO membranes were soaked in KCl solution (0.25M) for half hour for pretreatment; then the KCl-controlled GO membranes were taken out and soaked in mixed KCl (0.25 M) + NaCl solution (0.01 to 1M) at volume ratio of 1:1 for another half hour and characterized with XRD.

Experimental setup for adsorption of salt solutions

The freestanding GO membranes were placed in the centre of the centrifuge tube to ensure its full exposure to added DI water or salt aqueous solutions. After immersion at room temperature for half hour, the free bulk solution was removed from the tubes, followed by centrifuging at 2000 rpm for 1 minute to remove solutions on the surface of membranes. Salt solutions inside GO membranes can be retained due to a strong capillary effect. At last, the membranes were dried at 60 °C for 12 hours and kept in a dry dish for three days. Initial masses of wet (the freestanding GO membrane together with the inside solution) and subsequent dry (the freestanding GO membrane together with the inside salt) GO membranes were weighed.

During dehydrating tests, the mass of membranes after immersion in water decreased as the centrifugal speed increased from 100 rpm to 2200 rpm, normalized by the corresponding dry mass of pristine GO membranes, as shown in Fig. S1G, while it tended to be constant when the rotational speed was faster than 1000 rpm. Thus, we believe that the free water on the membrane surface was effectively separated under the centrifugal speed of 2000 rpm. And the residual adsorption solution was mainly stored in GO membranes due to strong capillary effect.
Experimental setup for adsorption isotherms

The adsorption isotherms for NaCl and mixed KCl + NaCl solution were investigated at pH 7 and a temperature of 298 K. For a single NaCl system, the freestanding GO membranes of 25 mg were added with 3.0 ml NaCl solution at certain initial concentrations ranging from 0.01 to 1.0 M. For mixed KCl + NaCl system, the freestanding GO membranes of 25 mg were immersed to 3.0 ml KCl solution (0.25 M) for one hour for pretreatment; then, the KCl-controlled GO membranes were taken out and soaked in 3.0 ml mixed KCl (0.25 M) + NaCl solution (0.01 to 1M) at volume ratio of 1:1. The samples were shaken at 160 rpm for one hour. The concentration of Na⁺ and K⁺ were determined using PS7800 inductively coupled plasma optical emission spectrometer (ICP-OES). Metal ion equilibrium concentrations were used to calculate the equilibrium adsorption capacities, as described by \( q_e = (C_0 - C_e) V_m / M \), where \( q_e \) is the equilibrium adsorption capacity (mmol/g), \( C_0 \) is the initial metal ion concentration (mmol/L), \( C_e \) is the metal ion equilibrium concentration (mmol/L), \( V_m \) is the volume of the metal ion solution (L), and \( M \) is the mass of the adsorbent (g).

Theoretical computational methods:

Ab initio molecular dynamics (MD) simulations

The simulation system contained two periodic GO sheets, 44 water molecules and a NaCl ion in a periodic box with the dimensions 12.25 × 17.10 × 30.00 Å, see Fig. S2. The period boundary conditions were applied to all three dimensions in the simulation. Based on the Shi-Tu structure model\(^{24}\), the GO nanosheet was constructed with a formula of C\(_{10}\)O\(_{1}\)(OH)\(_{1}\), which contains 12 hydroxyl groups (-OH) and 12 epoxy groups (-O-). In the simulation, all atoms were free. The motion of the atoms is performed at the DFT level of theory. We represent all electrons and use the PBE exchange-correlation functional and DZVP basis sets. The simulation was carried out in the canonical ensemble (NVT) using a time step of 0.1 fs with CP2K-2.6.1\(^{29}\). The temperature was kept at 300K by Nose-Hoover thermostat\(^{10,11}\). The program VMD\(^{12}\) was used for data analysis and molecular graphics.
Fig. S2. Model of the *ab initio* molecular dynamics simulation. Spheres in cyan, white, pink, and red represent carbon, hydrogen and oxygen atoms in the oxygen functional group, oxygen atoms in water molecules. Blue and yellow spheres represent Na\(^+\) and Cl\(^-\).

**Density functional theory (DFT) calculations**

In the DFT calculation, structures of the cation@GO and cation-(H\(_2\)O)_6 were optimized at B3LYP/6-31G(d) level, in which cations or hydrated cations were located in between two unoxidized graphene (C\(_{54}\)H\(_{25}\)) regions\(^{S13}\) of GO sheets. The geometry optimizations were performed via the Berny algorithm\(^{S14}\) with the convergence criteria of a maximum step size of 0.0018 au and a root mean square (RMS) force of 0.0003 au. These calculations were carried out with the Gaussian 09 software package\(^{S15}\).

The hydrated cation–GO interaction (\(\Delta E_{\text{hydrated cation–GO}}\)), cation–GO interaction (\(\Delta E_{\text{cation–GO}}\)) and hydrated energy (\(\Delta E_{\text{hydrated energy}}\)) were calculated as follows:

\[
\begin{align*}
\Delta E_{\text{hydrated cation–GO}} &= E_{\text{cation-(H}_2\text{O)}_6@GO} - E_{\text{cation-(H}_2\text{O)}_6} - E_{\text{GO}} \\
\Delta E_{\text{cation–GO}} &= E_{\text{cation@GO}} - E_{\text{cation}} - E_{\text{GO}} \\
\Delta E_{\text{hydrated energy}} &= E_{\text{cation-(H}_2\text{O)}_6} - E_{\text{cation}} - E_{\text{(H}_2\text{O)}_6}
\end{align*}
\]

where \(E_{\text{GO}}\) and \(\Delta E_{\text{cation}}\) are the total energy of optimized GO sheets and cations.

**PS2: X-ray diffraction for freestanding GO membranes in solution**
**Fig. S3.** (A) X-ray diffraction and for dry GO membranes, immersed in pure water and various 0.25 mol/L (M) salt solutions. (B) X-ray diffraction for GO controlled by KCl, GO immersed in pure water (dark yellow line) first, then in KCl solution of 0.25 M (blue line), finally add corresponding salt solution to KCl solution at ration of 1:1 (MgCl$_2$: red, CaCl$_2$: orange, NaCl: green).

**PS3: Synchrotron wide-angle X-ray scattering 2D patterns of freestanding GO membranes in dry state and solutions of 0.25M KCl, NaCl, pure water, CaCl$_2$, LiCl and MgCl$_2$**

Fig. S4 shows the two-dimensional (2D) synchrotron WAXS patterns of dry GO, GO in pure water and in salt solution (KCl, NaCl, CaCl$_2$, LiCl and MgCl$_2$). The 2D WAXS patterns exhibit typical diffusive arcs with a corresponding interlayer spacing between GO sheets, which are 8.0 Å, 9.4 Å, 10.2 Å, 11.6 Å, 12.1 Å and 13.2 Å for pristine dry GO, KCl, NaCl, CaCl$_2$, LiCl and MgCl$_2$ solution, respectively. This order is consistent with our experimental results from the XRD detection.

For CaCl$_2$, LiCl and MgCl$_2$ solution, it is clear that the diffusive arcs form crescent diffusive patterns, indicating the increasing degree of lamellar orientation in GO membranes. This shows that the rippling or wrinkled structure is aligned more flat by these salts. The clear increase of the degree of the lamellar orderings from monovalent cations (K$^+$, Na$^+$ and Li$^+$) to divalent ions (Ca$^{2+}$ and Mg$^{2+}$) reflects the deswelling of ripples in membranes, which results in the reduction of storage space of solution. This is agreement with our adsorption experimental results (Fig. 2A). For ions with the same valence, the order of salt solution adsorption was consistent with the order of interlayer spacings controlled by the corresponding salt solutions, and that there is not clear order for the adsorbed salt solution for the ions with different valences. We attribute the observation to the existence of ripples in the membranes, together with the method used to obtain the values of the interlayer spacings. The ripples considerably increase the solution volume in the membrane, but have a negligible effect on the XRD spectrum peak and the interlayer spacings.
Fig. S4. The two-dimensional (2D) synchrotron wide-angle X-ray scattering (WAXS) patterns of freestanding dry GO, GO in pure water and in salt solution (KCl, NaCl, CaCl₂, LiCl and MgCl₂).

Table S1. Interlayer spacings (Å) between GO sheets from XRD and WAXS. Uncertainty values indicate the standard deviation from three different points of a sample.

<table>
<thead>
<tr>
<th></th>
<th>XRD</th>
<th>WAXS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry pristine GO</td>
<td>7.9 ± 0.1</td>
<td>8.0</td>
</tr>
<tr>
<td>KCl</td>
<td>11.4 ± 0.1</td>
<td>9.4</td>
</tr>
<tr>
<td>NaCl</td>
<td>12.1 ± 0.2</td>
<td>10.2</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>12.9 ± 0.2</td>
<td>11.6</td>
</tr>
<tr>
<td>LiCl</td>
<td>13.5 ± 0.2</td>
<td>12.1</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>13.6 ± 0.1</td>
<td>13.2</td>
</tr>
</tbody>
</table>

**PS4: X-ray photoelectron spectrometer spectra (XPS) of freestanding GO membranes: Pristine GO membrane and GO membrane immersed in KCl solution**

We used XPS to detect the atomic concentrations and oxygen-containing group distribution. Fig. S5A shows the survey XPS scans of the pristine GO membranes. We can see that there are no observable ion signals. The C/O atomic concentration ratio of
pristine GO membrane is 1.1, indicating many oxygen-containing groups were introduced into the graphite during oxidation. Fig. S5B shows high-resolution C1s XPS spectra for the pristine GO membranes which can be fitted using four components centred at 284.5, 286.7, 287.8, and 288.9 eV corresponding to aromatic C-C/C=C (48.0%), C–O/C–O–C (31.8%), C=O (17.5%) and O–C=O (2.7%) chemical shifts, respectively\textsuperscript{S16,S17}.

For the GO membranes treated by KCl solution, the XPS spectra (Fig. S5C) indicates that there is a small amount of K ions. This is consistent with the adsorption experiments of pure KCl solution that there were very few KCl penetrated into the GO membranes from Fig. 2A.

**Fig. S5.** X-ray photoelectron spectrometer spectra (XPS) of freestanding GO membranes. (A) Pristine GO membrane, (B) at the C1s of the pristine GO membranes. (C) GO membrane immersed in KCl solution.

**PS5: Interlayer spacing and KCl solution adsorption of freestanding GO membranes with time**

In order to test whether the adsorption measurements have reached equilibrium, we performed experiments on GO controlled by NaCl, KCl and NaCl + KCl, and the solution adsorption of freestanding GO membranes with different ions to illustrate the saturation effect of the interlayer spacings and adsorption masses of GO controlled by cations. Fig. S6A shows that the interlayer spacings of GO membranes for immersion in KCl and NaCl as well as KCl + NaCl remain consistent from 0.05 to 144 hour (h). Fig. S6B shows the wet masses of GO membranes immersed in pure KCl solution are all very close to from 0.5 to 96 h, indicating that there is a saturation effect of the interlayer spacings and adsorption masses of GO controlled by cations.
Fig. S6. Interlayer spacing and KCl solution adsorption of freestanding GO membranes with time. (A) Interlayer spacings for GO membranes immersed in 0.25 M KCl, NaCl and KCl + NaCl mixed salt solutions. Interlayer spacings of GO membranes in mixed salt solution, first soaked in KCl solution and then immersed in NaCl solutions. (B) The normalized masses of GO membranes soaked in KCl solution. The red dashed lines correspond to the normalized mass of GO membranes for KCl at 0.5 hour (h). Error bars indicate the standard deviation from three different samples.

PS6: Salt solution adsorption of freestanding GO membranes controlled by NaCl/CaCl$_2$

We also used NaCl/CaCl$_2$ to determine and fix the interlayer spacing of freestanding GO membranes and tested the rejection for the cations which can induce a larger interlayer spacing by NaCl/CaCl$_2$. We firstly soaked the GO membranes in pure water and next immersed to NaCl solution. Then, the solutions of CaCl$_2$ or MgCl$_2$ were added to them as the case of KCl. In Fig. S7A, the spectra for subsequent addition of salts (CaCl$_2$ and MgCl$_2$) only showed very small difference from the spectrum of membranes with pure NaCl solution. The interlayer spacing of GO membranes in the mixed solution of NaCl + CaCl$_2$, or MgCl$_2$ was 12.3 ± 0.3 Å and 12.2 ± 0.1 Å, respectively, which is coincident with the interlayer spacing of GO membrane with pure NaCl solution (see Fig. S7B). Similarly, the interlayer spacing of
12.7 ± 0.2 Å in the mixed solution (CaCl$_2$ + MgCl$_2$) was very close to that of 12.9 ± 0.2 Å in pure CaCl$_2$ solution, showing the rejection of Mg$^{2+}$ by CaCl$_2$ (Fig. S7C and S7D).

Fig. S7. Controllable interlayer spacing in freestanding GO membranes by NaCl/CaCl$_2$. (A) X-ray diffraction for GO controlled by NaCl. GO was first immersed in NaCl solution of 0.25 M (green line), then added corresponding salt solution to NaCl solution at ration of 1:1 (MgCl$_2$: red, CaCl$_2$: orange, NaCl: green). (B) Interlayer spacing of GO membranes immersed in salt solution which was controlled by NaCl. (C) X-ray diffraction for GO controlled by CaCl$_2$. GO was immersed in CaCl$_2$ solution of 0.25 M, then added corresponding MgCl$_2$ solution to CaCl$_2$ solution at ration of 1:1. (D) Interlayer spacing of GO membranes immersed in MgCl$_2$ solution which controlled by CaCl$_2$. Error bars indicate the standard deviation from three different points of a sample.

PS7: Ion permeation tests of GO membranes supported by ceramic substrates

The ion permeation tests were carried out using a diffusion cell shown in Fig. S8. The effective membrane area is 1.13 cm$^2$. Take the single-ion permeation tests of Na$^+$ as an example: for testing GO membrane without being treated by KCl solution, 35 ml DI water and 35 ml 0.25 M NaCl aqueous solution were added into the feed side and draw side, respectively. During the test, the GO layers were facing to the draw side. Magnetic stirrings were applied to both sides of the feed and the draw solutions to avoid possible concentration gradients. For GO membrane treated with KCl, the GO membrane with the same GO deposition amount was immersed in the 0.25 M
KCl solution for 1h. Then, 35 ml 0.25 M KCl aqueous solution was added into the feed side, while 35 ml mixture of 0.25 M KCl and 0.25 M NaCl aqueous solution was added into the draw side. The introduction of KCl was aimed to prevent the leakage of K\(^+\) from the treated GO membrane. Inductive Coupled Plasma Emission Spectrometer (Optima 7000DV, Perkin Elmer, USA) was used to obtain the cation concentrations in solutions. The data were recorded after the system reached steady-state. The test temperature was about 25 °C. The mixed-ions permeation tests were carried out with similar method, by adding the mixture of controlling salts and testing target salts into the draw side.

The water flux \(J_w\) (L/m\(^2\) h\(^{-1}\)) can be calculated by:

\[
J_w = \frac{\Delta V}{A \Delta t}
\]

where \(\Delta V\) is the volume change of draw solution, \(A\) is the effective membrane area, and \(\Delta t\) is the test time.

**Fig. S8. Schematic of the experimental setup for single-ion permeation test of Na\(^+\).**

(A) For GO membrane without being treated by KCl solution, 35 ml DI water and 35 ml 0.25 M NaCl aqueous solution were added into the feed side and draw side, respectively. (B) For GO membrane treated by KCl solution, 35 ml 0.25 M KCl aqueous solution was added into the feed side, while 35 ml mixture of 0.25 M KCl and 0.25 M NaCl aqueous solution was added into the draw side. The introduction of KCl was aimed to prevent the leakage of K\(^+\) from the treated GO membrane. Arrows show the penetration direction of water and Na\(^+\) (blue for H\(_2\)O, purple for Na\(^+\)).
Mixed-ion permeation tests with a Na\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+} mixture:

Fig. S9. Mixed-ion permeation tests with Na\textsuperscript{+}, Mg\textsuperscript{2+}, and Ca\textsuperscript{2+}. In the ion permeation tests for the untreated GO-750 membrane, the feed side included 35 mL DI water, and the draw side included 35 mL of a mixture of 0.25 mol/L NaCl, 0.25 mol/L CaCl\textsubscript{2}, and 0.25 mol/L MgCl\textsubscript{2} aqueous solutions. For the K\textsuperscript{+}-treated GO-750 membranes, the feed side included 35 mL 0.25 mol/L KCl aqueous solution, and the draw side included 35 mL of a mixture of 0.25 mol/L KCl, 0.25 mol/L NaCl, 0.25 mol/L CaCl\textsubscript{2}, and 0.25 mol/L MgCl\textsubscript{2} aqueous solutions. Error bars indicate the standard deviation from three different points of a sample.

The GO membrane maintained effective ion rejection even with mixed-ion permeation, which involved exposure to a solution with a high salt concentration. As shown in Fig. S9, the Na\textsuperscript{+} permeation rates decreased by a factor of around 43 when controlled by KCl. For divalent cations of Mg\textsuperscript{2+} and Ca\textsuperscript{2+}, the KCl-treated GO-750 membrane still rejected over 93\% of ions relative to the untreated GO-750 membranes. The decreased rejection performance with mixed-ion compared to single-ion permeation tests may have been due to the much higher salt concentration gradient, generating an enhanced driving force behind the ion permeation. Additionally, the mixed-ion permeation tests involved a more complicated interaction between ions and the membrane layers.

Single-ion permeation of divalent cations (Ca\textsuperscript{2+} or Mg\textsuperscript{2+}) with NaCl- or KCl-treated GO membranes.
Fig. S10. Single-ion permeation of divalent cations (Ca\(^{2+}\) or Mg\(^{2+}\)) for the NaCl-treated, KCl-treated, and untreated GO-750 membranes. Dashed lines indicate the detection limits for different cations. In the ion permeation tests for the untreated GO membrane, the feed side included 35 mL DI water, and the draw side included 35 mL 0.25 mol/L target salt aqueous solution (NaCl, CaCl\(_2\), or MgCl\(_2\)). For the ion-treated GO-750 membranes, the feed side included 35 mL 0.25 mol/L KCl or NaCl aqueous solution, and the draw side included 0.25 mol/L KCl or NaCl with 0.25 mol/L target salt aqueous solution (NaCl, CaCl\(_2\), or MgCl\(_2\)). Error bars indicate the standard deviation from three different samples.

Fig. S10 shows that not only K\(^+\) but also Na\(^+\) can effectively control the GO layers for rejecting other cations if they require a larger interlayer spacing, as the results of adsorption experiments also demonstrated. It can be seen that after controlling by NaCl, the GO membrane showed decreased permeation rates of Ca\(^{2+}\) and Mg\(^{2+}\), with the ion rejection higher than 90% relative to the untreated GO membranes. This indicates the feasibility of our proposed ion-controlling strategy, or, GO membranes controlled by one kind of cation can exclude other cations with a larger hydrated volume, which can only be accommodated with a larger interlayer spacing.

**Mixed-ion permeation tests of K\(^+\) and Na\(^+\) using DI water as the feed side solution:**

![Mixed-ion permeation tests of K\(^+\) and Na\(^+\) using DI water as the feed side solution](image-url)

The mixed-ion permeation tests were performed using DI water as the feed side solution. The permeation rates for K\(^+\) and Na\(^+\) ions are shown in the graph. The permeation rates for K\(^+\) are higher than those for Na\(^+\) due to the higher charge density. Error bars indicate the standard deviation from three different samples.
Fig. S11. Mixed-ion permeation tests of K⁺ and Na⁺ using deionized (DI) water as the feed side solution. (A) Schematic of mixed-ion permeation tests of K⁺ and Na⁺ mixture, where the feed side included 35 mL DI water, and the draw side included 35 mL of a mixture of 0.25 mol/L KCl and 0.25 mol/L NaCl aqueous solution. (B) K⁺ and Na⁺ mixed-ion permeation performance for untreated and KCl-treated GO-750 membranes. Error bars indicate the standard deviation from three different samples.

We assessed the permeation rates of a mixture of K⁺ and Na⁺, using DI water as the feed side solution. The untreated GO membrane had K⁺ and Na⁺ permeation rates of 0.23 and 0.20 mol m⁻² h⁻¹, respectively. In comparison, the K⁺ and Na⁺ permeation rates were decreased by a factor of over 50 for the KCl-treated GO membrane, demonstrating that the K⁺ confined within the GO layers could reject other ions as well as K⁺ itself in solution. Notably, the ion rejection performance here was inferior to that in the single-ion permeation tests, due to the enhanced salt concentration gradient caused by the use of DI water as the feed side solution. The water flux decreased from 0.22 to 0.12 L m⁻² h⁻¹, demonstrating that water could still transport through the membrane.

Effect of membrane thickness on Na⁺ permeation behaviour:

Fig. S12. Effect of membrane thickness on Na⁺ permeation behaviour. We tested GO membranes with thicknesses of about 280 (GO-280), 550 (GO-550), and 750 (GO-750) nm. The dashed line indicates the Na⁺ detection limit. In the ion permeation tests for all of the untreated GO membranes, the feed side included 35 mL DI water, and the draw side included 35 mL 0.25 mol/L NaCl aqueous solution. For the KCl-treated GO membranes, the feed side included 35 mL 0.25 mol/L KCl aqueous solution, and the draw side included 0.25 mol/L KCl with 0.25 mol/L NaCl aqueous solution. Error bars indicate the standard deviation from three different samples.
We also examined how membrane thickness affected the Na\(^+\) permeation behaviour. Compared to the untreated GO-280 membrane, the Na\(^+\) permeation rate was decreased by a factor of 148 for the KCl-controlled GO-280 membrane. Compared to the untreated GO-550 membrane, the Na\(^+\) permeation rate was decreased by a factor of 163 for the KCl-controlled GO-550 membrane. With a thickness of about 750 nm, the KCl-treated membrane rejected almost all of the Na\(^+\). Thus, increased GO membrane thickness was associated with enhanced Na\(^+\) rejection performance. This is because of the highly ordered laminar structure that gradually forms during the self-assembly of GO nanosheets on porous substrates\(^{18}\). The comparison of water flux is shown in Table S2. The water flux decreased owing to the fact that the GO interlayer spacing was reduced after treatment with K\(^+\) (Figs. 1C-D), which is also verified by adsorption experiments (Fig. 2B).

**Effect of NaCl concentration on Na\(^+\) permeation behaviour:**

![Graph showing effect of NaCl concentration on Na\(^+\) permeation rate](image)

**Fig. S13. Effect of NaCl concentration on Na\(^+\) permeation behaviour.** In ion permeation tests, the feed side included 35 mL 0.25 mol/L KCl aqueous solution, and the draw side included a 35 mL mixture of 0.25 mol/L KCl and 0.01–2.5 mol/L NaCl aqueous solutions.

With NaCl concentrations of 0.01 to 0.25 mol/L, the Na\(^+\) permeation rates were below 0.005 mol m\(^{-2}\) h\(^{-1}\), demonstrating efficient control of KCl in GO layers. Even with 0.5 mol/L NaCl, the Na\(^+\) permeation rate was 0.042 mol m\(^{-2}\) h\(^{-1}\), which is about 95\% lower than that of the untreated GO membrane. However, when the NaCl concentration exceeded 1 mol/L, the Na\(^+\) permeation rates increased dramatically. This was because the significantly greater salt concentration increased the driving force behind Na\(^+\) permeation, overcoming the KCl control, and enabling fast transport of Na\(^+\).

**Na\(^+\) permeation through reduced graphene oxide (rGO) membrane:**
Fig. S14. Single-ion (Na\(^+\)) permeation tests for untreated and KCl-treated rGO membranes with a thickness of ~280 nm. In ion permeation tests for untreated rGO membrane, the feed side included 35 mL DI water, and the draw side included 35 mL 0.25 mol/L NaCl aqueous solution. For the KCl-controlled rGO membranes, the feed side included 35 mL 0.25 mol/L KCl aqueous solution, and the draw side included a 35 mL mixture of 0.25 mol/L KCl and 0.25 mol/L NaCl aqueous solutions.

To improve the membrane stability during long-term operation, we fabricated reduced GO (rGO) membranes and conducted ion permeation tests. Compared to untreated rGO membrane, the KCl-treated rGO membrane showed a much lower Na\(^+\) permeation rate of 0.063 mol m\(^{-2}\) h\(^{-1}\). Moreover, the rGO membrane showed better stability during long-term operation (stable performance for over 24 h). This indicates promising potential for practical applications of this ion-controlling method. The rGO membranes showed decreased water flux, which is attributed to the reduced interlayer spacing. Additionally, the KCl-treated rGO membrane showed an increased Na\(^+\) permeation rate compared to the GO membrane (Fig. 3E), which may be due to micro-defects and holes generated by the reduction process.

Table S2. Comparison of water flux of GO membranes with thicknesses of 280 (GO-280), 550 (GO-550), and 750 (GO-750) nm tested by single-ion permeation of Na\(^+\).
PS8: Ab initio MD simulation to illustrate the underlying physical mechanism taking place in GO membranes treated by cations

We take Na\(^+\) as an example, based on an *ab initio* MD simulation (CP2K), to illustrate the picture. In the simulation, we build a periodic system with the dimensions Å, which contains two layers of GO membranes, 44 water molecules and one NaCl ion. Fig. S15A shows the details of the MD simulation, that the Na\(^+\) moves from the middle between two GO sheets to a position close to the bottom GO sheet during the first 14 ps, and then adsorbs at the coexistence regions of oxidized groups and aromatic rings. We then analyze the lifetime (\(<\tau_{sw}\>) of this hydrogen bonds, belonging to those water molecules which around the Na\(^+\) ion and take part in the connection between the two GO membranes, as shown highlighted in Fig. S15B. Here the H-bond is defined based on the paper\(^{S19}\). As shown in Fig. S15C, the character H-bond lifetime (\(<\tau_{sw}\>) and water-water character H-bond time-correlation function (\(S_{ww}(t)\)) is fit to

\[
S_{ww}(t) = e^{-\frac{t}{\tau_{sw}}}
\]

with the \(\tau_{sw} \approx 15\) ps. We note that the MD computation is very intensive that 12.5 ps simulation together with the 14 ps for equilibrium reaches the maximal storage of the data. In the simulation, the initial loci of oxygen groups on GO are set according to the distribution reported our previous paper\(^{S18}\), and the initial distance between GO sheets was set as the interlayer spacing measured in the corresponding XRD experiments. The ions and two GO sheets are free in whole simulation.

We also used the same software to perform the simulation of pure water. Comparing with the initial structure of the Na\(^+\) in the GO membranes, the contrast system is the same in size (Å) and just replaces the Na\(^+\) and Cl\(^-\) ion by two water molecules. As shown in Fig. S15D, the character H-bond lifetime in pure water is about ~0.5 ps. These results show that the character lifetime of H-bonds of the water molecules which around the Na\(^+\) ion and take part in the connection between the two GO membranes is about ~30 times of the H-bond lifetime in pure water, indicating that the hydrated Na bind the GO sheets through a stable hydrogen bond network.
**Fig. S15.** A snapshot of the *ab initio* MD simulation at 27 ps. Spheres in cyan, white, pink, and red represent carbon, hydrogen and oxygen atoms in the oxygen functional group, oxygen atoms in water molecules. Blue and yellow spheres represent Na\(^+\) and Cl\(^-\). (B) A snapshot at 27 ps. Water molecules surrounding the Na\(^+\) ion and participating in the connection between the oxygen functional group of the two GO membranes are highlighted. Red helixes represent the hydrogen bonds connecting these water molecules to each other and to the oxygen functional groups of the two GO membranes. (C) Water–water H-bond time-correlation function (black line) marked in (B), together with the exponential fitting \(S_{ww}(t) = e^{-t/\tau_{H,bond}}\), red line) with the character H-bond lifetime of 15 ps. (D) Water–water H-bond time-correlation function (black line) for pure water, together with the exponential fitting \(S_{ww}(t) = e^{-t/\tau_{H,bond}}\) with the character H-bond lifetime of 0.6 ps (red line) and 0.3 ps (blue line), respectively.

**PS9: DFT calculations on the hydrated cations in between two GO sheets**

We also have performed optimization of cations between to GO sheets to further illustrate the underlying physics. We firstly optimized the structures of cation@graphene clusters at B3LYP/6-31G(d) level in gas phase, and the loci of oxidized groups on GO sheet comes from our previous paper\(^{58}\). Their most stable optimized structures are shown in Fig. S16. For cation@graphene clusters, the most stable adsorption position of cations (K\(^+\), Na\(^+\), and Li\(^+\)) on the GO sheet is the coexistence regions of oxidized groups and aromatic rings. The adsorption energies are -53.6, -75.5, and -87.0 kcal/mol, respectively, which is clearly higher than the corresponding cations-\(\pi\) interaction (-28.7, -39.9, and 55.2 kcal/mol)\(^{26}\) between cations (K\(^+\), Na\(^+\), and Li\(^+\)) on the graphene sheet. This demonstrates that the oxidized groups on GO sheets assistant to cations adsorption on sheets.
We analyzed the molecular orbitals to further understand the strong interaction between the GO sheet and cations. In Fig. S16B, an occupied state of the molecular orbitals (HOMO-7) of a GO sheet with Na\(^+\) is plotted, representing all of the molecular orbitals with interactions between the Na\(^+\) and GO. The plot clearly shows coupling between the lone pair of electrons of the oxygen atoms in the oxygen functional group and the delocalized \(\pi\) states of the aromatic ring structure in GO and the empty orbitals of Na\(^+\). This indicated that the interaction between GO and cations was mainly between the cations and the oxidized groups and aromatic ring on the GO sheet.

We further computed the adsorption of hydrated cations between two unoxidized graphene regions of GO sheets. Fig. 4 shows their most stable optimized structures. The average interlayer spacings of two unoxidized graphene regions of GO sheets in cation-(H\(_2\)O)_6@GO clusters (cation = K\(^+\), Na\(^+\), and Li\(^+\)) were 9.09 Å, 9.75 Å and 10.24 Å, respectively. The order of the interlayer spacing from DFT calculations is consistent with our results of XRD and WAXS experiments. In fact, our theoretical computation results first inspired the idea to use the ions themselves to control and fix the interface spacing of GO membranes.

On the hydrated divalent cations of Mg\(^{2+}\) and Ca\(^{2+}\), since there will be a large hydrated layer, the theoretical calculation to determination of the interlayer distances is still beyond the computation capacity. This is similar to the difficulty in the theoretical recover of the radii order of hydrated cations observed by experiment simply in water solution. However, the radii of hydrated cations decrease in the order Mg\(^{2+}\)\(_{aq}\) > Ca\(^{2+}\)\(_{aq}\) > Li\(^+\)\(_{aq}\) > Na\(^+\)\(_{aq}\) > K\(^+\)\(_{aq}\)\(^{2,S20}\), which is consistent with our observations except for Li\(^+\). We attribute the exception to the much smaller cation-(H\(_2\)O)_6@GO interaction of Li\(^+\) relative to Ca\(^{2+}\), meaning that Li\(^+\) is less able to control the interlayer spacing. Values of effective ionic radius and the hydrated radius for K\(^+\), Na\(^+\), Ca\(^{2+}\), Li\(^+\) and Mg\(^{2+}\) can be found in the literature\(^{2,S20}\) and are shown in Table S3.
Fig. S16. Most stable optimized geometries of cation@graphene clusters and an occupied state of the molecular orbitals (HOMO-7) of a GO sheet with Na⁺.

Table S3. Radius of effective and hydrated ions studied in this work in the literature.²⁰

<table>
<thead>
<tr>
<th></th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Li⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective ionic radius (Å)</td>
<td>1.38</td>
<td>1.02</td>
<td>1.00</td>
<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>Hydrated radius (Å)</td>
<td>3.31</td>
<td>3.58</td>
<td>4.12</td>
<td>3.82</td>
<td>4.28</td>
</tr>
</tbody>
</table>

PS10: UV absorption spectral experiments to demonstrate the existence of the cation–π interactions between hydrated cations and the aromatic ring structure in GO.

The UV absorption spectra of GO and GO in KCl, NaCl, CaCl₂, LiCl and MgCl₂ solution are showed in Fig. S17. The UV spectrum of GO at ~ 230 nm, which is assigned to a conjugate double bond of the aromatic group that easily generated π-π*
transition\textsuperscript{S21-S23}. Compared with the UV intensity of GO in pure water, the intensity of GO in the various salt solution markedly decreased (Fig. S17), indicating that the conjugate double bonds of the aromatic group in GO are greatly affected in the various salt solution. We note that an analogous UV difference spectrum has been observed for an indolyl model compound (Gly-Asn-His-Trp-NH\textsubscript{2})\textsuperscript{S23} and tryptophan\textsuperscript{S21} of the cation-π interaction, in which Cu\textsuperscript{2+} ion bound by the four nitrogen ligands or oxygen groups in tryptophan is located at the indole ring plane of tryptophan. The similarity between the UV difference spectrum observed by us and those reported early indicates the existence of the cation-π interaction in cation-(H\textsubscript{2}O)\textsubscript{6}@GO clusters, which is consistent with the molecular orbital analysis result of theoretical computation.

\textbf{Fig. S17}. UV absorption spectra of GO suspension (50 mg/L) 1:1 mixed with various 0.025 M salt solutions.

\textbf{PS11: XAFS measurements of GO membranes treated by CuCl\textsubscript{2} solution}

We take the CuCl\textsubscript{2} as an example to perform XAFS measurements at Cu K-edge in fluorescence mode to show the hydrated cations interacted with GO sheets. We used Cu\textsuperscript{2+} since Cu\textsuperscript{2+} is the minimal detectable element in XAFS measurements at the BL14W1 in Shanghai Synchrotron Radiation Facility (SSRF), and the CuCl\textsubscript{2} solution also has good ability to control the interlayer spacing of the GO membrane, which was 11.3 Å Fig. S18C. Fig. S18A shows that the spectrum in Cu-GO sample is dominantly attributed to the first-shell X atoms around the Cu\textsuperscript{2+}. The Cu-X nearest-neighbor distance in Cu-GO is coincident with the Cu-O nearest-neighbor distance in CuO, but obviously shorter than the Cu-Cl nearest-neighbor distance in the CuCl\textsubscript{2} and the Cu-Cu nearest-neighbor distance in the
Cu foil. It can be deduced that the first shell X around the Cu\(^{2+}\) in Cu-GO most probably are O atoms, rather than Cl atoms. However, it is hard to differentiate the C atoms from the O atoms. The Cu-O bond can start to form in the aqueous condition. As shown in Fig. S18B, the Cu-X in the CuCl\(_2\) solution is more likely to be Cu-O bond rather than Cu-Cl bond. It suggests that after the Cu-Cl broken down in the solution, the Cu\(^{2+}\) can be very easily surrounded by the O atoms, which is consistent with our theoretical computation result.
**Fig. S18.** X-ray absorption fine structure (XAFS) analyses of Cu species in GO membrane immersed in 0.25 M CuCl$_2$ solution, CuO, CuCl$_2$, CuCl$_2$ solution and Cu foil. (A) EXAFS spectra of Cu species. (B) EXAFS signals obtained by Fourier transforms of the radial structure function for the various Cu species. Dash line at the peaks corresponds to the Cu-Cu, Cu-Cl, Cu-C and Cu-O bond, respectively. (C) X-ray diffraction for GO membrane immersed in 0.25 M CuCl$_2$ solution.

**PS12: Adsorption isotherms for single species, competitive adsorption isotherms for Na$^+$ and K$^+$, and corresponding interlayer spacing observation**

The adsorption isotherm for Na$^+$ on the untreated GO membranes in solution is shown in Fig. S15A. We can see that the Na$^+$ ions reach adsorption equilibrium from the 0.25 mol/L. At the higher concentration (≥ ~ 1.0 mol/L), more Na$^+$ ions are adsorbed in which there may be more complex reasons, such as cation aggregations at graphitic surface$^{26}$, which requires further study.

The competitive adsorption isotherms for Na$^+$ and K$^+$ on the K$^+$-controlled GO membranes in mixed NaCl + KCl solution is shown in Fig. S15B. The Na$^+$ adsorption only slightly enhances at high NaCl concentration.

Interlayer spacings of untreated GO membranes with respect to the NaCl concentration is shown in Fig. S15C, which shows the efficient control of GO layers in all NaCl concentration.

Figure S15D shows the interlayer spacings of K$^+$-controlled GO membranes with different NaCl concentrations. We can see that the interlayer spacings only slightly enhance in the high NaCl concentration, which is consistent with the experiment results of Na$^+$ adsorption on K$^+$-controlled GO membranes.
Figure S15. Adsorption isotherms of Na$^+$ and K$^+$ on GO membranes in solution and corresponding interlayer spacings. (A) Adsorption isotherms of Na$^+$ on GO membranes in solution. (B) Adsorption isotherms of Na$^+$ and K$^+$ on KCl-controlled GO membranes in NaCl and KCl mixed solution. (C) Interlayer spacings of untreated GO membranes with NaCl concentration. (D) Interlayer spacings of K$^+$-controlled GO membranes with NaCl concentration. Error bars indicate the standard deviation from three different samples.
References and Notes