Understanding water transport through graphene-based nanochannels via experimental control of slip length

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The water transport along graphene-based nanochannels has gained significant interest. However, experimental access to the influence of defects and impurities on transport poses a critical knowledge gap. Here, we investigate the water transport of cation intercalated graphene oxide membranes. The cations act as water-attracting impurities on the channel walls. Via water transport experiments, we show that the slip length of the nanochannels decay exponentially with the hydrated diameter of the intercalated cations, confirming that water transport is governed by the interaction between water molecules and the impurities on the channel wall. The exponential decay of slip length approximates non-slip conditions. This offers experimental support for the use of the Hagen-Poiseuille equation in graphene-based nanochannels, which was previously only confirmed by simulations. Our study gives valuable feedback to theoretical predictions of the water transport along graphene-based channels with water-attracting impurities.
Introduction

Ultrafast water transport through graphene oxide membranes (GOMs) is considered to originate from the friction-free movement of water molecules through sub-nanometre graphene-based channels\(^1,2\). In detail, GOM nanochannels consist of patches of graphitic and functionalized areas. Along the graphitic parts the water transport is considered frictionless and along the functionalized areas the water transport is partially hindered\(^3,4\). The assumption that the water transport is friction-less along graphitic domains originates from the use of the Hagen-Poiseuille (HP) equation to describe the water transport in graphene-based nanochannels. The HP equation allows calculating water flux through a channel if water molecules have zero velocity at the liquid/channel wall interface\(^5\). This condition is called a non-slip condition. In experiments, the liquids often exhibit slip at the channel walls (i.e., the non-zero velocity at liquid/channel wall interface)\(^5\). To describe the amount of slip, the slip length is introduced. In particular, the water flux through graphene-based nanochannels showed a large slip length. Hence, it was concluded that the water flux is frictionless. In the case of GOMs, the water transport is only partially frictionless due to patches of functionalized areas. Nevertheless, the GOMs typically show high slip lengths indicating low friction transport along their nanochannels\(^2\). Recent advances allow a deeper understanding of the unusual water transport along graphene-based planes in nanoconfinement\(^6-8\). However, it was identified that the influence of defects on this transport is yet challenging to access experimentally\(^9\). *Ab initio* molecular dynamic (AIMD) simulations predict that defects in the graphitic plane will cause extra friction to the movement of water inside the nanochannels\(^10\). The effect on the friction is predicted to increase with the number of hydrogen bonds between the water molecules and the defects\(^10\). While simulation studies offer a great understanding of the underlying transport mechanism\(^11\), an experimental observation is still lacking. Experimental studies so far mainly focus on how the ionic transport occurs in these nanochannels\(^3\). However, a systematic study on the water transport in graphene-based nanochannels with water attraction impurities has remained elusive. Thus, controlling the affinity of water molecules towards the nanochannel walls by intercalation of cations with different hydrated diameter may offer a unique platform to tailor and understand the water friction of the unusual water transport in graphene-based nanochannels.
From a potential application point of view, it is important to understand the water transport in graphene-based nanochannels with impurities. For example, GOMs exhibit promising membrane properties\textsuperscript{12,13}. The two key parameters for using GOMs as water purification membranes are first, their capability to reject certain solutes and, secondly, letting pass as much solvent as possible\textsuperscript{12}. The recent advance in controlling the interlayer space of GOMs via intercalation of cations is a promising approach to tune the porosity\textsuperscript{14,15}. With that potentially controlling the rejection of dissolved ions in aqueous solution using GOMs\textsuperscript{16}. Here, the intercalation of K\textsuperscript{+} prevents swelling of GOMs in a wet environment\textsuperscript{16}. Without control, swelling leads to an increase in interlayer space and hence an increase in pore size of the GOMs. Intercalation with K\textsuperscript{+} prevents swelling and reduces the interlayer space of wet GOMs, allowing the rejection of smaller species\textsuperscript{16}. Higher cation concentration led to even lower interlayer space of wet GOMs\textsuperscript{17}. The cation intercalated GOMs exhibit various performance improvements, including long-term aqueous stability and strength, and excellent molecular separation performance\textsuperscript{15,18}.

Previous studies suggest that the water flux is decreased upon intercalation of cations\textsuperscript{19,20}. However, a systematic study on how the intercalation of different cations influences the water transport through the nanocapillaries is still lacking. With that, one of the two key parameters in cation intercalated GOMs remains unexplored: the water permeance. This is not only important for potential water purification applications but also for other applications where water transport in GO and graphitic nanochannels with intercalated cations or other impurities displayed high potential\textsuperscript{21–23}.

In this study, we investigate the influence of cation intercalation on the water transport through GOMs. For that, we intercalate different types of ions (NaCl, KCl, MgCl\textsubscript{2}, CaCl\textsubscript{2} and FeCl\textsubscript{3}) with varying water affinities allowing to manipulate the number of hydrogen bonds attracted to the intercalated cation. This leads to the observation of an unintuitive trend. Water flux is decreasing with increasing cation-controlled interlayer space. Via water flux measurements and AIMD simulations, we show that both the water flux and cation-controlled interlayer space are directly correlated to the size of the hydration shell of the respective cation. The use of cations as controlled impurities with different water affinities allows us to manipulate the number of hydrogen bonds attracted to impurities on the wall of a graphene-based nanochannel and experimentally observe its effect on the water transport through
graphene-based nanochannels. Further, we gain important insights into the water transport mechanism in graphene-based nanochannels in general and support the use of HP equation to describe the water transport in graphene-based nanochannels.

Results

Preparation of cation intercalation GOMs

![Fabrication and characterization of graphene oxide](image)

**Figure 1:** Fabrication and characterization of graphene oxide. Schematic of (A) vacuum filtration setup for membrane preparation, (B) membrane intercalation with cations (X-M-GO), and (C) solution intercalation with cations (X-S-GO); violet and green spheres represent the cations and anions, respectively. Morphology of graphene oxide (D) TEM image of sheets, (E) Cross-sectional SEM image of GOM on PVDF substrate. Chemical characterizations of GOM using (F) XRD of membranes (G) XPS survey scan showing carbon/oxygen ratio, and (H) XPS C1s spectra.
For the intercalation of cations into the GOMs, two different preparation methods (membrane intercalation and solution intercalation) are common and gave promising rejection results in previous studies\textsuperscript{24,25}. To exclude the influence of the different methods, in this study, both methods are used to prepare cation intercalated GOMs. For that, cation intercalated GOMs were fabricated as follows (Figure 1A-C). In the first method (membrane intercalation\textsuperscript{16}), the GOMs were prepared via vacuum filtration (Figure 1A) by filtering GO solution through a porous polymer substrate. Then these membranes were soaked in various salt solutions (Figure 1B). The membranes from this approach are labelled as X-M-GO, where X stands for the corresponding cation of the salt solution and M indicates that the membrane was intercalated by soaking the GOMs. In the second approach (solution intercalation\textsuperscript{23}), the GO solution was mixed with the respective salt solution prior to fabricating the membranes (Figure 1C). Then the salt-GO mixture was filtered by vacuum filtration through a porous polymer membrane to obtain the membrane. The membranes prepared from this approach are labelled as X-S-GO. Here, S indicates that the intercalation of GO was initiated in the GO solution by mixing with respective cation X. According to previous studies, the mass increase of dry, cation intercalated GOMs was equal to the mass of intercalated salts\textsuperscript{16}. Therefore, the number of moles of cations inside the X-M-GO was calculated from the mass gain of the membranes after soaking the membranes in the respective salt solution. Table 1 shows that the number of moles of cations inside the X-M-GO range from 2-7 \( \mu \text{mol} \). The number of moles of cations in the X-S-GO was controlled to match the X-M-GO by adding same number of moles of respective cations into GO solution according to Table 1. In X-M-GO the concentration of intercalated cation is not precisely controllable. To exclude any influence of concentration differences on the water transport, a third group of samples was prepared. Here, the number of moles of intercalated cations was attempted to be constant by mixing appropriate amounts of salt \( (0.2 \mu \text{mol}) \) with GO solution \( (5 \text{ mL of } 0.1 \text{ mg/mL}) \). The molarity of salt was kept low to avoid \( \text{Fe}^{3+} \) induced aggregation in the mixture. To evaluate the effective intercalated cations, the effluent of the X-S-GO preparation was analysed by ICP-OES for cation concentration. Our results suggest that for different cations, the percentage of intercalation may vary independent of its hydration shell. It may be noted that this experimental approach of testing the effective intercalated cations in such small quantities may not fully represent the actual mass loading. Figure 1D-H presents the structural and chemical characteristics of GOM. The lateral size of GO flakes utilized in this study is \( \sim 0.5 \mu \text{m} \).
as displayed in the TEM image in Figure 1D. The thickness of the GOM was ~200 nm according to the cross-sectional SEM analysis (Figure 1E). The interlayer space of the dry, original GOM is ~9.4 Å. After soaking in water for 10 mins, the interlayer space in the original GOM increases to 12.3 Å. The interlayer space is depicted via X-ray diffraction (XRD) analysis as described in the methods section.

**Water transport measurements through cation intercalated GOMs**

The water transport through GOMs was tested via vacuum filtration. Figure 2A shows the water flux values for membranes prepared using two methods. It becomes clear that for both preparation methods, the water flux decreases following the trend Mg$^{2+}$-M/S-GO < Ca$^{2+}$-M/S-GO < Na$^{+}$-M/S-GO < K$^{+}$-M/S-GO. It is thus rational to plot the water flux against the hydrated diameter ($D_H$) of the respective cations as they follow the exact opposite trend of $D_H$, Mg$^{2+}$ > Ca$^{2+}$ > Na$^{+}$ > K$^{+}$. It may be noted that as discussed in the next section the ionic diameter of the ions does not rationally resembles the water flux trend.

As shown in Figure 2B, the interlayer space increases with the hydrated diameter of the intercalated cations. As previously reported, both methods allow controlling the swelling of GO to a certain degree. In particular, K$^{+}$-M/S-GO show a smaller interlayer space compared to pristine GOM as well as Na$^{+}$-M/S-GO. Intercalation of divalent cations (Ca$^{2+}$ and Mg$^{2+}$) increases the wet interlayer spaces in GOMs regardless of the preparation method. In the dry state, X-S-GO show a reduced interlayer space, whereas X-M-GO show an increased interlayer space except for K$^{+}$. The slight differences in the interlayer spaces resulting from different preparation methods are discussed in SI section 1 and Figure S1.

Concentration differences of intercalated cations may be responsible for the observed water flux trend. The number of moles of intercalated cations in the X-M-GO cannot be precisely controlled. However, in the X-S-GO, it is more probable to do so. Therefore, water filtration experiments were conducted on X-S-GO with controlled intercalated cations (0.2 µmol) using K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$ and Fe$^{3+}$. As shown in Figure 2C, we find a similar trend as in Figure 2A that water flux decreased with increasing hydrated diameter of cations. As mentioned above, the number of intercalated cations may also vary for X-S-GO. However, we could not find a matching trend of mass loading and hydrated diameter in any of the experiments. Figure 2A shows that the water flux decreases with increasing hydration diameter despite arbitrary mass loadings of different cations (Table 1). This suggests that the mass loading is not the
primary explanation for the observed trend in water flux.

**Figure 2:** Water transport through cation intercalated GOMs. Variation of (A) water flux and (B) interlayer space of cation intercalated GOMs with hydrated diameters; the hydrated diameters of cations are listed in **Table 1**. (C) Variation of water flux of X-S-GO with controlled...
moles of cation, where H⁺ corresponds to the case of water flux of pure GOM. (D) Variation of slip length with hydrated diameter of cations; slip length is calculated using experimentally observed water flux and interlayer space as described in SI section 2. The dotted black line displays an exponential decay fit with a coefficient of determination (R²) of 0.998. For each data point shown in (A)-(D) three separate membranes were tested. Error bars indicate the standard deviation from these three membranes. (E, F) Schematic diagram of water transport through pure GOM (E) and cation intercalated GOM (F). v(H₂O) corresponds to the velocity of water molecules. The dimension of water molecules, GO sheets and hydrated cations are chosen for illustration and are not intended to represent the realistic scale. Without the influence of cations or H⁺, the water flux through graphitic domains is illustrated as unimpeded².

The water flux for membranes prepared using both preparation methods decrease with increasing interlayer space. This is surprising as a decreased interlayer space should offer less room for the water molecules to travel. As reported in our previous study and by others, this is true for untreated GO where smaller interlayer space resulted in a decline in water flux²⁰,²⁴. It may be further noted that all cation intercalated membranes in this study show a decreased water flux in comparison with untreated GO. Combined with the observation that the water flux declines not only with increasing interlayer space but also with increasing hydrated diameter of the intercalated cations, it seems reasonable to assume that the interaction between the cations and the water travelling through the nanochannels may govern the water transport.

**Water transport mechanism through cation intercalated GOMs**

To explain the water transport mechanism through cation intercalated GOM, we calculated the slip length (lₛ) for the cation intercalated GOMs. We refer to Figure S2 and SI section 2 for understanding the concept of slip length²,²⁶,²⁷. Additionally, a detailed explanation and calculation of slip length based on our water flux and XRD measurements are discussed in SI section 2.1-Calculation of slip length. In brief, the water flux according to the HP equation was calculated based on the membranes thickness and interlayer space. In the calculation of the water flux, the available space for water transport in between the GO layer was estimated using the interlayer space from XRD measurements and the diameter of carbon atoms².

Further, we estimated that the intercalated cations may not change the average available space as the ratio of number of intercalated carbon atoms to cations is ~144 (see also SI section 2.2-Carbon/cation ratio). With that only a limited number of cations exist in the channels causing no substantial changes to the available space for water transport. From the
difference between the experimentally measured and calculated water flux the slip length is determined².

The most obvious assumption that could explain a decreased water flux or changes in slip length by cation intercalation is that the cations cause steric hindrance for the transport of water molecules. If that was true, the water flux trend should follow the ionic diameter of the cations. As shown in (SI section 2.3-Steric hindrance) the water transport does not follow this trend. In contrary the K⁺ would cause the largest steric hindrance as they have the largest ionic diameter. However, the water transport for K⁺ is the highest among tested cations. For Mg²⁺, the cation with the smallest ionic diameter, shows comparably lower water transport, despite showing a larger interlayer space compared to K⁺ intercalated GOMs. With that it can be ruled out that steric hindrance of the cations is the major contributor to the hindrance of water transport upon cation intercalation.

As shown in Figure 2D, the slip length decreases with the increased hydrated diameter. This decrease in slip length can be well fitted with an exponential decay function. Interestingly, when considering H⁺ as the cation intercalated in pure GOM, it also fits the exponential relation. Moreover, the exponential function decays towards zero slip-length (non-slip condition) for the highest hydrated diameters.

This allows us to draw interesting conclusions about the water transport in cation intercalated GOMs and GOMs in general. GO consists of functionalized and graphitic domains. In GOMs the water flux is considered to mainly move along the graphitic domains²³,²⁰. The water flux along graphene-based nanochannels is often described based on the Hagen-Poiseuille equation considering a large slip length that exceeds the channel width²⁸,²⁹. The large slip length describes the low friction of water along the graphitic planes. As shown in Figure 2E for pristine graphitic nanochannels, the slip length is large and has been reported to be around 100-1000 Å². This is in line with our calculated value ~400 Å (Figure 2D) for the original GO based on our experimental result. After cation intercalation, the slip length decreases. Hence, the intercalation of cations causes a hindrance to the water transport in the nanochannels (Figure 2F). This hindrance increases exponentially with the hydrated diameter of intercalated cations, as shown in Figure 2D. This shows that enhanced interaction between water molecules and cation decorated graphitic nanochannel is responsible for the decrease in water flux. The fact that the hydrated diameter of H⁺ fits the exponential function indicates
that hydrated hydrogen ions may govern the water transport in the original GOM (Figure 2E).

Moreover, the exponential decay of the slip length approximates the non-slip condition (see Figure S2C for visualization of the non-slip condition, \(l_s = 0\)). That means that if cations highly increase the interaction between the nanochannel walls and the water, the water transport follows the Hagen-Poiseuille equation. This is a valuable insight as this is experimental support for the use of the Hagen-Poiseuille equation in nanochannels with slip lengths that exceed the channel width. Here it is to be noted that so far, the justification for using the Hagen-Poiseuille equation relied only on molecular-dynamic (MD) simulations \(^{29}\) and is debated in the literature \(^{30}\).

**Stability of intercalated cations**

Differences in cation intercalation stability may be responsible for the water flux trend. To exclude that, a control experiment testing the stability of the intercalated ions was conducted. For that, pure DI water was fed through the membranes, and the permeate of this experiment was collected and analysed by ICP-OES to determine the mass of cations that might have been washed out. The experimental details are discussed in SI section 3. As shown in Figure 3 for all membranes, after 3-5 hours, there were no detectable cation in the permeate. The total mass of washed-out cations is below 5.5 \(\mu\)g (Table S3), which is negligible compared with the measured mass of intercalated cations (Table 1). Hence, we conclude that the cation intercalation is stable in our water flux experiments.

![Figure 3: Stability test of intercalated cations](image)

**Figure 3: Stability test of intercalated cations.** Number of cations in permeate over the course of washing time for (A) X-M-GO and (B) X-S-GO. The membranes were filtered with DI water and the resulting permeate was analysed by ICP-OES to determine the mass of washed-out...
cations. Error bars are standard deviations from three permeate samples.

Since the above reason could be excluded to be responsible for the observed trend in water flux, the following examination further focuses on the interaction between intercalated cations and water molecules. As shown above, the flux declines, and slip length increases with the increase of the hydrated diameter of the intercalated cation. At the same time, the interlayer space is increased with the increase in hydrated diameter as well. A higher increase in the interlayer space upon wetting the membrane is associated with increased intercalated layers of water. We speculate that the cations with higher hydration diameter have a stronger attraction towards water inside the capillaries. To investigate that, we performed ab initio molecular dynamic (AIMD) simulation with several intercalated cations and investigated the water density around the specific cation.

**Simulation study on water affinity towards cation intercalated graphitic nanochannels**

![Simulation study on water affinity towards cation intercalated graphitic nanochannels in a model bilayer graphene.](image)

Figure 4: Simulation study on the water affinity towards cation intercalated graphitic nanochannels in a model bilayer graphene. (A) Schematic diagram of the simulation cell at initial state (0 ps) in ab initio MD simulation. The supercell consists of a graphitic sheet (grey spheres) intercalated with two cations (violet spheres) and filled with water molecules (red and white spheres are oxygen and hydrogen atoms, respectively). The periodic boundary conditions ensure the nanoconfinement. The dimension of the simulation cell is x = 17.23 Å,
y= 17.05 Å and z= 14 Å. (B) Distribution of water molecules at the initial state. Violet circles are the position of cations. X is a placeholder for different types of cations. The number of accumulated water molecules is represented by the colour range in the scale (C-E).

Distribution of water molecules after 4 ps for graphitic sheets intercalated with K+, Na+ and Ca²⁺, respectively.

Error! Reference source not found.A shows a simulation cell used to investigate the behaviour of nanoconfined water in the presence of cations. The simulation cell resembles a bilayer of graphene with two cations attached to the basal plane. The bilayer configuration is achieved by employing periodic boundary conditions. The space between the layers is filled with water molecules. Graphene was chosen as a model as various studies confirm that main group metal cations intercalate mainly via cation-π interaction. With that in GOMs, the main group metal cations would attach to the graphitic areas where π electrons exist. The cations may also attach to functional groups (see the simulation cell in Figure S8A). Hence, simulations were conducted with functionalized graphene sheets as the substrate for cation intercalation (see SI section 4). For both cases, graphitic and functionalized nanochannels, we examined the rearrangement of water molecules by projecting their distribution on the graphitic/functionalize domain plane. Starting with randomly distributed water molecules around the ions (Error! Reference source not found.B and Figure S8B), we let the molecules relax over 4 ps. After that period, the water molecules rearranged more densely around the cations (Error! Reference source not found.C-E and Figure S8C-E). We tried relaxing Mg atoms on graphene; however, the Mg atoms did not bind with the graphene sheet and stabilized far (> 4 Angstrom) from the graphene plane. As such, we did not include Mg atoms in our study.

In the case of functionalized channels, the water molecules rearrange during the relaxation period by getting attracted to the intercalated cations. However, no observable trend in water affinities with different cations is found (Figure S8C-E). Interestingly, in the case of graphitic channels the water molecules show a higher density around the Ca²⁺ than the monovalent cations of K⁺ and Na⁺ (Error! Reference source not found.C-E). The higher density around the Ca²⁺ suggests that cations with larger hydration shells attract water more tightly in the confined environment of graphene nanocapillaries. Despite allowing a larger number of water molecules to intercalate into the capillaries and expanding the space for the water to travel, the flux declines and slip length decreases, as shown in our experimental results. From the simulation results, we may conclude that this decline is based on the increased interaction between water molecules and intercalated cations. As the differences in water affinities of
cations in the simulations was prominent in the case of cation-π interaction and not observable in cation intercalation with functionalized areas, it suggests that the cation-π interaction on the graphitic areas of GO is the more dominant case for governing the slip length. A similar increase in friction was predicted with AIMD simulations of water transport with impurities in the graphitic nanochannel walls\textsuperscript{10}. In this case, the friction was correlated with the hydrogen bond ability of impurities. This increase in interaction between cations and water molecules may affect the slip length in two different ways. The slip length can be interpreted as a description of the friction of water with the nanochannel walls. Increased attraction of water molecules via the absorbed cation would cause increased friction and explains the trend of decreasing slip length with increasing hydrated diameter. The large slip length in graphene-based nanochannels may also be explained by a depletion layer with reduced viscosity close to the channel walls\textsuperscript{26}. Increased interaction between the channel walls and the intercalated cations may also reduce the depletion layer and increase the viscosity close to the channel walls, explaining the increase in slip length with increasing hydration diameter.

**Discussion**

We present a study on water transport through cation intercalated graphene oxide membranes. With that, experimental access to the role of impurities with different water affinities in graphene-based nanochannel is gained. We found that the flux of cation intercalated GOMs was decreased with the increase of interlayer space. We explain this by showing that the slip length of the cation intercalated GOMs scales exponentially with the hydrated diameter of the respective cation. This allows us to hypothesise that the water flux in original GOMs is influenced by hydrated hydrogen, which is omnipresent in aqueous environments. Our simulation study further supports that the hindrance of water transport through the cation decorated nanochannels is due to increased interaction between the water molecules and the nanochannel. Further, the non-slip conditions for high hydrated diameters offer experimental support for using the Hagen-Poiseuille equation in graphene-based nanochannels. Hence, our study suggests that the water transport in graphene-based nanochannels follows the HP equation. The slip length may change dependent on the water affinity of impurities. As we showed, in the case of cation intercalation, the slip length decays exponentially with the hydrated diameter (i.e., water affinity). Future studies may find a way
to further explore and confirm the exponential relationship between hydrated cations and GOM slip length. With that, our study may offer a starting point towards a deeper understanding of the water transport through graphene-based nanochannels with water-attracting impurities. Additionally, these may pose valuable insights for future applications where graphene-based nanochannels in aqueous environments play a promising role.

**Methods**

**GOM preparation.** GO powder containing single-layered laminates with a lateral size of ~500 nm (Jiangsu XFNANO Materials Tech. Co. Ltd) was dispersed in deionized water at the concentration of ~0.1 mg/mL. The GO suspension was then ultrasonicated for 2h under ambient conditions, avoiding GO reduction at elevated temperatures. GOMs were fabricated onto polyvinylidene fluoride (PVDF, 0.1 µm pore size) substrate by filtering 5 mL of GO suspension under vacuum at ~0.9 bar pressure, and the obtained GOMs were air-dried for 24 hours.

**Membrane intercalation (X-M-GO).** GOMs were separately soaked in 10 mL of 10 mM salt solutions using NaCl, KCl, MgCl₂ and CaCl₂ for 24 hours, followed by air-drying for 24 hours. The average mass increase of these GOMs was measured as shown in **Table 1**.

**Solution intercalation (X-S-GO).** NaCl, KCl, MgCl₂ and CaCl₂ powders with the number of moles shown in **Table 1** were mixed with 5 mL, ~0.1 mg/mL GO solution to prepare cation intercalated GO solutions. The dispersibility of the mixture was ensured by incubating the suspension for 24 hours. Then, the suspension was filtered through PVDF substrate under ~0.9 bar pressure. Another set of intercalated GOMs was prepared from 5 mL, 0.1 mg/mL of GO solution containing 0.2 µmol of K⁺, Na⁺, Ca²⁺, Mg²⁺ and Fe³⁺.

| Intercalated cations | Na⁺ | K⁺ | Mg²⁺ | Ca²⁺ |
|----------------------|-----|----|------|------|
| Membrane mass increase (mg) | 0.28 | 0.15 | 0.66 | 0.49 |
| Number of moles of intercalated cations (µmol) | 4.79 | 2.01 | 6.93 | 4.42 |

**Table 1:** Mass of intercalated cations in X-M-GO and their hydrated/ionic diameter

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| Characterized Diameter        | 6.62 | 7.16 | 8.24 | 8.56 |
|-------------------------------|------|------|------|------|
| Hydrated diameter-$D_H$ (Å)   |      |      |      |      |
| Ionic diameter-$D_I$ (Å)      | 1.90 | 2.66 | 1.30 | 1.98 |

**Characterization of GO sheets and GOMs.** Transmission electron microscopy (TEM, JEOL, JEM-2100F, Japan) was used to investigate the dimension of GO sheets on lacey carbon grid. The cross-sectional structure and the thickness of pure GOM on PVDF substrate were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan). The X-ray diffraction (XRD, Bruker D8 focus, Germany) patterns of GOMs in both dry and wet (soaked in deionized water for 10 mins) conditions were obtained using Cu-Kα radiation ($\lambda=1.54$ Å). The chemical compositions of GOMs were analysed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Al-Kα radiation, USA).

**Membrane permeation and separation tests.** Membrane permeation tests were carried out by vacuum filtration. The cation intercalated GOMs on PVDF substrates were tightly clamped between feed and permeate compartments. Deionized water was permeated through GOM for 5 hours, and the cations concentration in permeate and water volumes were recorded every 1 hours. The cation concentration was measured by Inductive Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Varian 710-OES, USA). The flux of cation intercalated GOM was calculated by the following equation:

$$J = \frac{\Delta V}{AtP} \quad (1)$$

Where $J$ is flux in unit of L/m²/h/bar (LMH/bar), $\Delta V$ is the total volume of solution in permeate side, $A$ is the effective area of GOM ($A=1.77$ cm²), $t$ is the permeation time ($t=5$ hours), and $P$ is the applied pressure in vacuum filtration ($P=0.9$ bar).

**Computational details.** Molecular dynamic (MD) simulations have been performed using the CP2K suite of programs. A double-zeta-valence plus polarization (DZVP) MOLOPT basis set is used to expand the Kohn-Sham orbitals, while the electronic structure is described within the Gaussian and Plane Waves framework (GPW). Exchange and correlation are considered through the Perdew-Burke-Ernzerhof (PBE) functional, while Goedecker type (GTH) pseudopotentials have been used to model the interaction of valence electrons with the atomic cores.
The metals absorbed on the graphene/GO structures were first relaxed using DFT through the Quickstep\textsuperscript{36} module of CP2K, until forces were inferior to 1.0E-03 a.u. Later, \textit{ab-initio} MD simulations, based on the propagation of the equations of motion with Langevin dynamics, were performed in the canonical ensemble at 310 K. The graphene/GO structures have been kept fixed, while water has been allowed to move freely. Each simulation ran for 4 ps, using a timestep of 1 fs.

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**Competing interests**

The authors declare no competing interests.

**References**

1. Joshi, R. K. \textit{et al.} Precise and Ultrafast Molecular Sieving Through Graphene Oxide Membranes. \textit{Science (1979)} \textbf{343}, 752–754 (2014).

2. Nair, R. R., Wu, H. A., Jayaram, P. N., Grigorieva, I. v & Geim, A. K. Unimpeded permeation of water through helium-leak–tight graphene-based membranes. \textit{Science (1979)} \textbf{335}, 442–444 (2012).

3. Abraham, J. \textit{et al.} Tunable sieving of ions using graphene oxide membranes. \textit{Nat Nanotechnol} \textbf{12}, 546–550 (2017).

4. Foller, T. \textit{et al.} Mass Transport via In-Plane Nanopores in Graphene Oxide Membranes. \textit{Nano Letters} \textbf{22}, 4941–4948 (2022).

5. Joseph, P. & Tabeling, P. Direct measurement of the apparent slip length. \textit{Physical Review E} \textbf{71}, 35303 (2005).

6. Wei, N., Peng, X. & Xu, Z. Understanding water permeation in graphene oxide membranes. \textit{ACS Appl Mater Interfaces} \textbf{6}, 5877–5883 (2014).

7. Kavokine, N., Bocquet, M. L. & Bocquet, L. Fluctuation-induced quantum friction in nanoscale water flows. \textit{Nature 2022} 602:7895 \textbf{602}, 84–90 (2022).

8. Mouhat, F., Coudert, F. X. & Bocquet, M. L. Structure and chemistry of graphene oxide in liquid water from first principles. \textit{Nature Communications 2020} 11:1 \textbf{11}, 1–9 (2020).

9. Faucher, S. \textit{et al.} Critical Knowledge Gaps in Mass Transport through Single-Digit Nanopores: A Review and Perspective. \textit{Journal of Physical Chemistry C} \textbf{123}, 21309–21326 (2019).
10. Joly, L., Tocci, G., Merabia, S. & Michaelides, A. Strong Coupling between Nanofluidic Transport and Interfacial Chemistry: How Defect Reactivity Controls Liquid–Solid Friction through Hydrogen Bonding. *J. Phys. Chem. Lett* **7**, 34 (2016).

11. Müller, E. A., Rull, L. F., Vega, L. F. & Gubbins, K. E. Adsorption of water on activated carbons: a molecular simulation study. *The Journal of Physical Chemistry* **100**, 1189–1196 (1996).

12. Mi, B. Graphene oxide membranes for ionic and molecular sieving. *Science (1979)* **343**, 740–742 (2014).

13. Foller, T., Wang, H. & Joshi, R. Rise of 2D materials-based membranes for desalination. *Desalination* **536**, 115851 (2022).

14. Jin, X. *et al*. Effective separation of CO2 using metal-incorporated rGO membranes. *Advanced Materials* **32**, 1907580 (2020).

15. Yeh, C.-N., Raidongia, K., Shao, J., Yang, Q.-H. & Huang, J. On the origin of the stability of graphene oxide membranes in water. *Nat Chem* **7**, 166–170 (2015).

16. Chen, L. *et al*. Ion sieving in graphene oxide membranes via cationic control of interlayer spacing. *Nature* **550**, 380–383 (2017).

17. Wang, S. *et al*. Effects of cationic concentration on controlling the interlayer spacings for highly effective ion rejection via graphene oxide membranes. *Chemical Communications* **56**, 2743–2746 (2020).

18. Gogoi, A., Reddy, K. A. & Mondal, P. K. Influence of the presence of cations on the water and salt dynamics inside layered graphene oxide (GO) membranes. *Nanoscale* **12**, 7273–7283 (2020).

19. Liu, T., Yang, B., Graham, N., Yu, W. & Sun, K. Trivalent metal cation cross-linked graphene oxide membranes for NOM removal in water treatment. *Journal of Membrane Science* **542**, 31–40 (2017).

20. Foller, T. *et al*. Enhanced graphitic domains of unreduced graphene oxide and the interplay of hydration behaviour and catalytic activity. *Materials Today* **50**, 44–54 (2021).

21. Nie, L. *et al*. Realizing small-flake graphene oxide membranes for ultrafast size-dependent organic solvent nanofiltration. *Sci Adv* **6**, eaaz9184 (2020).

22. Huang, L., Li, Y., Zhou, Q., Yuan, W. & Shi, G. Graphene oxide membranes with tunable semipermeability in organic solvents. *Advanced Materials* **27**, 3797–3802 (2015).

23. Long, Y. *et al*. Molecule Channels Directed by Cation-Decorated Graphene Oxide Nanosheets and Their Application as Membrane Reactors. *Advanced Materials* **29**, 1606093 (2017).

24. Yuan, S., Li, Y., Xia, Y., Selomulya, C. & Zhang, X. Stable cation-controlled reduced graphene oxide membranes for improved NaCl rejection. *Journal of Membrane Science* **621**, 118995 (2021).

25. Lv, X.-B. *et al*. A Novel Strategy to Fabricate Cation-Cross-linked Graphene Oxide Membrane with High Aqueous Stability and High Separation Performance. *ACS Applied Materials & Interfaces* (2020).
26. Myers, T. G. Why are slip lengths so large in carbon nanotubes? *Microfluidics and Nanofluidics* **2010** 10:5 10, 1141–1145 (2010).

27. Radha, B. *et al.* Molecular transport through capillaries made with atomic-scale precision. *Nature* **538**, 222–225 (2016).

28. Keerthi, A. *et al.* Water friction in nanofluidic channels made from two-dimensional crystals. *Nature Communications* **2021** 12:12, 1–8 (2021).

29. Keerthi, A. *et al.* Ballistic molecular transport through two-dimensional channels. *Nature* **558**, 420–424 (2018).

30. Chong, J. Y., Wang, B., Mattevi, C. & Li, K. Dynamic microstructure of graphene oxide membranes and the permeation flux. *Journal of Membrane Science* **549**, 385–392 (2018).

31. Sun, P. *et al.* Selective trans-membrane transport of alkali and alkaline earth cations through graphene oxide membranes based on cation–π interactions. *Acs Nano* **8**, 850–859 (2014).

32. Sun, P. *et al.* Selective ion penetration of graphene oxide membranes. *ACS Nano* **7**, 428–437 (2013).

33. Nightingale Jr, E. R. Phenomenological theory of ion solvation. Effective radii of hydrated ions. *The Journal of Physical Chemistry* **63**, 1381–1387 (1959).

34. Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. cp2k: atomistic simulations of condensed matter systems. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **4**, 15–25 (2014).

35. VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J Chem Phys* **127**, 114105 (2007).

36. VandeVondele, J. *et al.* Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Computer Physics Communications* **167**, 103–128 (2005).

37. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys Rev Lett* **77**, 3865 (1996).

38. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Physical Review B* **54**, 1703 (1996).
Supporting Information

1. Interlayer space of cation intercalated GOMs

Figure S1: Interlayer space of cation intercalated GOMs in dry state. Here X stands for corresponding cation, and M and S indicate that the intercalation occurs with GOM and GO solution, respectively. The short-dashed line corresponds to the interlayer space of pure GOMs. Error bars are standard deviations of interlayer spaces from three membranes.

In this work, we prepared cation intercalated GOMs with two methods, membrane intercalation (X-M-GO) and solution intercalation (X-S-GO). The two preparation methods for the GO membrane led to a similar trend in the interlayer spacing when altering the intercalated cation (Figure S1). For both X-M-GO and X-S-GO, the interlayer space increases with the increased hydrated diameter of intercalated cations. In the case of X-M-GO, the interlayer space of K⁺-M-GO (red column) is lower than pure GOM (short-dashed line), whereas Na⁺-, Mg²⁺-, and Ca²⁺-M-GO show larger interlayer space. This unique behaviour of K⁺-M-GO is in close agreement with the previous research, attributing the reduced interlayer space to a squeezed hydration structure of intercalated cations. However, the interlayer space of all X-S-GO showed reduced interlayer space compared to pure GO (blue columns), suggesting the structural distortion occurs to not only K⁺ but also Na⁺, Mg²⁺, and Ca²⁺ cations. This distortion could result from severely squeezed hydration structure during vacuum filtration and consequently the decreased interlayer space for X-S-GO.

2. Water transport through nanochannels
**Figure S2: Schematic illustration of water transport through tunnels.** Black and white arrows correspond to the unimpeded and impeded velocity of water transport, respectively. We calculated the slip length ($l_s$) to explain the water transport mechanism through cation intercalated GOMs. The slip length is often used to characterize the friction interaction between water molecules and channel walls\(^2\). As shown in Figure S2A, when the water molecules transport through the channel, the channel wall interacts with the neighboured water molecules. The velocity of water molecules that interact with channel wall are impeded (white arrows in Figure S2A) while the water molecules in the middle of tunnel are unimpeded (black arrows in Figure S2A). Here, we plot a dashed straight line in Figure S2A on the left that corresponds to the plane of zero-velocity and dashed curve on the right indicating the plane of real-velocity. The tangential extension of the curve intercept with the straight line. This intercept is the extrapolated zero-velocity point. According to the physical definition, the slip length ($l_s$) is the distance from the channel wall to the extrapolated zero velocity point\(^3\)^4. If the water molecules move frictionless through the channel (Figure S2B), the zero-velocity plane is parallel to the real velocity plane, resulting in infinitive slip length ($l_s = \infty$). Moreover, if the friction between water molecules and tunnel walls increased to maximum, the velocity of water molecules that are close to the tunnel walls approaches to zero (Figure S2C). The intercept point is located on the surface of the tunnel wall leading to a non-slip condition ($l_s = 0$).
2.1 Calculation of slip length. According to Nair et al\textsuperscript{5}, the water transport through GO laminates fits the above illustration in Figure S2. Here we analysed the friction behaviour on water-GO flakes interface by calculating the slip length ($l_s$) of water transport through different cation intercalated GOMs. We first calculate the ‘empty’ space ($\delta$) for water transport (Figure S3),

\begin{equation}
\delta = d - 2a
\end{equation}

where $d$ is the interlayer space derived from XRD measurements of the respective GO membrane after water immersion and $a$ is electronic cloud around graphene sheets ($a\approx1.75$ Å)\textsuperscript{5}.

The total length (Figure S4) of water transport ($l$) is

\begin{equation}
l = \frac{hL}{d}
\end{equation}

where $h$ is the thickness of the membrane ($h\approx200$ nm) and $L$ is GO flake size ($L\approx480$ nm)\textsuperscript{5}.

The theoretical water flux ($Q$) is
\[ Q \approx \delta^3 \times \frac{1}{12\eta} \times \frac{1}{L} \times \frac{\Delta P}{l} \times \rho \tag{4} \]

where \( \eta \) is viscosity of bulk water (\( \eta = 1 \text{ mPa} \cdot \text{s} \)), \( \rho \) is density of water (\( \rho = 1 \text{ g/mL} \)) and \( \Delta P \) is driving pressure (\( \Delta P = 10^3 \text{ bar} \)).

Considering the experimental flux \( (J) \), the theoretical flux \( (Q) \) is enhanced by a factor \( (\theta) \) of

\[ \theta = \frac{J}{Q} \tag{5} \]

The slip length \( (l_s) \) is calculated from

\[ l_s \approx \frac{\theta \times \delta}{8} \tag{6} \]

**2.2 Carbon/cation ratio.** The carbon-cation ratio was calculated as follows. According to our XPS results showing the C/O atomic ratio is 2.97 (Figure 1G), we could estimate the number of moles of carbon in the 0.5 mg of GOM is

\[ 12 \text{ mg/mmol} \times n(C) + 16 \text{ mg/mmol} \times n(O) \approx 0.5 \text{ mg} \tag{7} \]

\[ n(C)/n(O) = 2.97 \tag{8} \]

where \( n(C) \approx 28.7 \mu\text{mol} \) (here we made assumption that the contribution of H element to mass of GOM is negligible). Compared with the intercalated cations (0.2 \( \mu\text{mol} \)), the number of carbon atoms are \(~144\) times more than cations. This means that very limited number of cations existed in the nanochannels, indicating weak the steric hindrance of cations.

![Figure S5: Steric hindrance affecting the water transport through 0.2 \( \mu\text{mol} \) of cation intercalated GOMs. (A) Variation of water flux of cation intercalated X-S-GO\( \backslash \) against ionic](image-url)
diameter of cations. (B) Variation of slip length with ionic diameter of cations. Error bars indicate the standard deviation from three tested membranes.

2.3 Steric hindrance. The steric hindrance of intercalated cations refers to the physical presence of the cations in between the free space of GO layers. It may slow down the water transport through the GO nanochannels. The steric hindrance caused by intercalated cations is related to the structure of non-hydrated cations, i.e., the ionic diameter. We plot the flux of X-S-GOMs with 0.2 µmol cation against the ionic diameter ($D_I$) as shown in Figure S5A. The largest $K^+$ (i.e., highest steric hindrance) shows highest water flux. This is irrational that more hindrance to water transport results in higher water flux. Similar trend of slip length is shown in Figure S5B, where $K^+$ ions result in largest slip length (i.e., lowest water transport hinderance). Therefore, we exclude the effect of steric hindrance of cations to reduced water flux and slip length.

3. Cation intercalation stability test

![Image](image.png)

Figure S6: Visual presentation of cation intercalated GOM for integrity check after 7 days and 14 days. The membrane pieces were ~0.5 cm$^2$ in triangle shape. After 7 days and 14 days water soaking, the membranes were ultrasonicated for 0.5 h.

To exclude differences in cation intercalation stability, we examined the integrity of GOMs and the stability of intercalated cations. The cation intercalated GOMs were cut into ~0.5 cm$^2$ triangle shape pieces and immersed into 5 mL of deionized water in small centrifuge tubes. The membranes were ultrasonicated for 0.5 h after immersion for 7 and 14 days. Photographs of GOMs pieces after ultrasonication were taken to examine whether they were peeled off from substrate or any cracks were created. As shown in Figure S6, these GOMs showed excellent attachment to PVDF substrate after soaking in water for 7 days and 14 days. No visible cracks were found on the membrane surface.
We also performed pressure driven filtration to study the intercalation stability. Deionized water was filtered through intercalated GOMs under ~0.9 bar of vacuum pressure for 5 h. Every 1 hour, we collected the water samples from permeate side. The volumes of these samples were measured for subsequent flux calculation. Concentrations of cations in the permeate solutions were measured by ICP-OES to calculate masses of eluted salt (NaCl, KCl, MgCl$_2$ and CaCl$_2$). As shown in Figure S7 for the volumes of permeate samples in each hour, pure GOMs had highest volume of permeation compared with intercalated GOMs in every single hour.

![Figure S7: Volume of deionized water filtration through pure GOMs and cation intercalated GOMs in each hour. (A) X-M-GO and (B) X-S-GO. Error bars were the standard deviation from three independent samples.](image)

The ICP-OES results of each water samples were listed in Table S1 for X-M-GO and Table S2 for X-S-GO. The detection limit of ICP-OES instrument is 10 µg/L. We found the elution of cations were highest in the first hour of filtration and rapidly fell in the second hour. The cation concentrations were undetectable in the 5th hour for all samples.

| Time (h) | Na$^+$ Concentration (µg/L) | K$^+$ Concentration (µg/L) | Mg$^{2+}$ Concentration (µg/L) | Ca$^{2+}$ Concentration (µg/L) |
|---------|-----------------------------|-----------------------------|--------------------------------|-------------------------------|
| 1       | 11.7                        | 73.4                        | 29.9                           | 41.5                          |
| 2       | 10.0                        | 12.0                        | 21.5                           | 19.1                          |
| 3       | N/A*                        | 10.0                        | 10.0                           | 10.0                          |
| 4       | N/A                         | N/A                         | N/A                            | N/A                           |

Table S1: Concentration of eluted cations in each hour from X-M-GO
Table S2: Concentration of eluted cations in each hour from X-S-GO

| Time (h) | Na⁺ Concentration (µg/L) | K⁺ Concentration (µg/L) | Mg²⁺ Concentration (µg/L) | Ca²⁺ Concentration (µg/L) |
|----------|--------------------------|-------------------------|---------------------------|---------------------------|
| 1        | 56.1                     | 94.4                    | 30.5                      | 44.4                      |
| 2        | 10.0                     | 29.8                    | 21.9                      | 20.3                      |
| 3        | N/A                      | 10.9                    | 10.0                      | 10.0                      |
| 4        | N/A                      | 10.0                    | N/A                       | N/A                       |
| 5        | N/A                      | N/A                     | N/A                       | N/A                       |

*N/A corresponds to the concentration is lower than the detection limit of ICP-OES.

Based on the above results, we could calculate the masses of eluted NaCl, KCl, MgCl₂ and CaCl₂. For example, the permeate volume of Na-GOM is 14.4 mL (from Figure S7A first hour) and the concentration of eluted Na⁺ is 11.7 µg/L (from Table S1 first hour). We could calculate the mass of eluted Na⁺ is 11.7 µg/L * 14.4 mL / 1000 = 0.17 µg. Considering the mass ratio of Na⁺ in NaCl is 23.0 g mol⁻¹ / 58.4 g mol⁻¹ = 0.39, the eluted mass of NaCl is 0.17 µg / 0.39 = 0.4 µg. We calculated the masses of eluted NaCl, KCl, MgCl₂ and CaCl₂ and listed in Table S3.

Table S3: Eluted salts mass in each hour and total 5 h from intercalated GOMs

| Time (h) | Eluted NaCl (µg) | Eluted KCl (µg) | Eluted MgCl₂ (µg) | Eluted CaCl₂ (µg) |
|----------|------------------|-----------------|-------------------|-------------------|
| X-M-GO   | X-S-GO           | X-M-GO          | X-S-GO            | X-M-GO            | X-S-GO           | X-M-GO            | X-S-GO            |
| 1        | 0.4              | 2.3             | 2.5               | 3.6               | 1.6              | 1.5              | 1.8               | 1.8               |
| 2        | 0.4              | 0.4             | 0.4               | 1.1               | 1.0              | 1.0              | 0.8               | 0.7               |
| 3        | N/A              | N/A             | 0.3               | 0.4               | 0.5              | 0.4              | 0.4               | 0.4               |
| 4        | N/A              | N/A             | N/A               | 0.4               | N/A              | N/A              | N/A               | N/A               |
| 5        | N/A              | N/A             | N/A               | N/A               | N/A              | N/A              | N/A               | N/A               |
| Total    | ~0.8             | ~2.6            | ~3.2              | ~5.5              | ~3.1             | ~3.0             | ~3.0              | ~2.8              |

Furthermore, we also tested the residue solution after solution intercalated GOMs preparation. We found the concentration of all residue solution were lower than the detection limit of ICP-OES, indicating adequate reaction of cations with GO suspension.
4. Simulation study on water affinity towards cation intercalation at functionalized graphene

**Figure S8: Simulation study on the water affinity towards cation intercalation at graphene functionalised with hydroxy group.** (A) Schematic diagram of the simulation cell at initial state (0 ps). The supercell consists of a graphene sheet (grey spheres) functionalised with hydroxy groups intercalated with a cation (violet and red spheres correspond to cations and oxygen atoms from hydroxy groups). The supercell is filled with water molecules (red and white spheres are oxygen and hydrogen atoms, respectively). The periodic boundary conditions ensure the nanoconfinement. (B) Distribution of water molecules at the initial state. Violet circles are the position of cations. X is a placeholder for different types of cations. The Blue area represents a water-free area, while from cyan to red corresponded to an increased number of water molecules accumulated. (C-E) Distribution of water molecules after 4 ps for functionalized graphitic sheets intercalated with K⁺, Na⁺ and Ca²⁺, respectively.

Previous studies suggest that cations intercalate GO mainly via cation-π interaction. It may also occur at sp³ carbon areas, where the epoxy, hydroxy and carboxy groups exist. Such intercalation may affect the slip length when water molecules transport through GO membranes. The carboxy groups, located at the edges of GO sheets, have limited contribution to the morphology of the GO nanochannels. Therefore, the cation intercalation with carboxy groups may not affect the slip length. On the other hand, hydroxy and epoxy groups are located at basal plane of GO sheets which may affect the slip length. To investigate
this, we performed further simulation study using cation-hydroxy intercalation. As shown in Figure S8A, the simulation cell was chosen to emulate the cation-hydroxy interaction. Two cations were attached to the hydroxy groups on the graphene basal plane. Periodic boundary conditions were applied for bilayer configuration. The simulation cell was filled with water molecules. The projection of water molecules on the plane was examined at initial state (Figure S8B) and final state (Figure S8C-E) after relaxing the cell for 4 ps. Mg atom failed to bind with hydroxy groups similar as the case for graphitic areas.

We observed that the water molecules are rearranged and become denser due to the attraction of positively charged cations. However, unlike the case of cation-π interaction (Figure 4C-E), the density of water molecules around the Na+, K+ and Ca2+ ions show no obvious difference in water affinities (Figure S8C-E). Based on that we believe that the cation intercalation with sp3 carbon area cannot explain the trend of the slip length observed in Figure 2D. As the water affinity shows a matching trend if the cations interact with the sp2 carbon (Figure 4C-E), it suggests that the cation-pi interaction is the more dominant case for governing the slip length.

References

1. Chen, L. et al. Ion sieving in graphene oxide membranes via cationic control of interlayer spacing. Nature 550, 380–383 (2017).
2. Qin, X., Yuan, Q., Zhao, Y., Xie, S. & Liu, Z. Measurement of the rate of water translocation through carbon nanotubes. Nano Lett 11, 2173–2177 (2011).
3. Myers, T. G. Why are slip lengths so large in carbon nanotubes? Microfluidics and Nanofluidics 2010 10:5 10, 1141–1145 (2010).
4. Radha, B. et al. Molecular transport through capillaries made with atomic-scale precision. Nature 538, 222–225 (2016).
5. Nair, R. R., Wu, H. A., Jayaram, P. N., Grigorieva, I. v & Geim, A. K. Unimpeded permeation of water through helium-leak–tight graphene-based membranes. Science (1979) 335, 442–444 (2012).
6. Sun, P. et al. Selective ion penetration of graphene oxide membranes. ACS Nano 7, 428–437 (2013).
7. Sun, P. et al. Selective trans-membrane transport of alkali and alkaline earth cations through graphene oxide membranes based on cation–π interactions. Acs Nano 8, 850–859 (2014).
8. Lerf, A., He, H., Forster, M. & Klinowski, J. Structure of graphite oxide revisited. The Journal of Physical Chemistry B 102, 4477–4482 (1998).