# Understanding the Aqueous Stability and Filtration Capability of **MoS<sub>2</sub>** Membranes

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Supporting Information

ABSTRACT: Membranes made of layer-stacked two-dimensional molybdenum disulfide (MoS<sub>2</sub>) nanosheets have recently shown great promise for water filtration. At present, the reported water fluxes vary significantly, while the accountable structure and properties of MoS<sub>2</sub> nanochannels are largely unknown. This paper aims to mechanistically relate the performance of MoS<sub>2</sub> membranes to the size of their nanochannels in different hydration states. We discovered that fully hydrated MoS<sub>2</sub> membranes retained a 1.2 nm interlayer spacing (or 0.9 nm free spacing), leading to high water permeability and moderate-to-high ionic and molecular rejection. In comparison, completely dry MoS<sub>2</sub> membranes



had a 0.62 nm interlayer spacing (or 0.3 nm free spacing) due to irreversible nanosheet restacking and were almost impermeable to water. Furthermore, we revealed that the interlayer spacing of  $MoS_2$  membranes in aqueous solution is maintained by comparable van der Waals and hydration forces, thereby ensuring the aqueous stability of  $MoS_2$  membranes without the need of cross-linking. In addition, we attributed the high water flux  $(30-250 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1})$  of MoS<sub>2</sub> membranes to the low hydraulic resistance of smooth, rigid MoS<sub>2</sub> nanochannels. We also concluded that compaction of MoS<sub>2</sub> membranes with a high pressure helps create a more neatly stacked nanostructure with minimum voids or looseness, leading to stable water flux and separation performance. Besides, this paper systematically compares MoS<sub>2</sub> membranes with the widely studied graphene oxide membranes to highlight the uniqueness and advantages of MoS<sub>2</sub> membranes for water-filtration applications.

**KEYWORDS:** Molybdenum disulfide, layer-stacked membrane, interlayer spacing, aqueous stability, water filtration, membrane separation

N ovel restacking of two-dimensional (2D) nanosheets produced via the exfoliation of bulk inorganic layered materials can lead to laminar membranes that have excellent mechanical and physicochemical properties.<sup>1-5</sup> By fine-tuning the interlayer spacing between neighboring nanosheets, it is possible to achieve high water permeance while rejecting unwanted species.<sup>6</sup> For example, the widely studied layerstacked graphene oxide (GO) membranes have shown a potential for desalination,<sup>7</sup> water purification,<sup>8–11</sup> oil and water separation,<sup>12,13</sup> and antifouling coating.<sup>14–16</sup> The unoxidized regions of GO nanosheets provide a nearly frictionless surface for water to flow, promising high water permeability.<sup>17</sup> However, the complete recovery of graphitic regions by removing the oxygenated functional groups unavoidably decreases the interlayer spacing of GO membranes to as low as 0.36 nm, which is close to that in bulk graphite and thus undermines water permeability.<sup>18</sup> Besides, the presence of oxygenated functional groups in GO causes several problems. First, the hydrophilicity of functional groups leads to membrane instability in aqueous environment,  $^{19,20}$  demanding cross-linking<sup>21</sup> or reduction<sup>8,22</sup> to ensure membrane integrity but

inevitably increasing the fabrication complexity and structural heterogeneity. Second, the hydration of functional groups increases the interlayer spacing and thus deceases membrane selectivity.<sup>23,24</sup> Third, the existence of surface functional groups could impede the water transport due to their interactions with water molecules via hydrogen bond.<sup>25</sup>

The above problems facing the membranes made by layerstacking GO nanosheets using the weak electrostatic interaction can be potentially circumvented by membranes made by layerstacking MoS<sub>2</sub> nanosheets using the strong van der Waals structure. First, because MoS<sub>2</sub> does not have any hydrophilic functional groups extruding from its surface, the van der Waals (vdW) force between MoS<sub>2</sub> nanosheets could potentially dominate and prevent the layer-stacked MoS<sub>2</sub> nanosheets from redispersion in water.<sup>26</sup> Second, the high surface smoothness (due to the lack of cross-linkers or functional groups) of MoS<sub>2</sub>

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**Figure 1.** Schematic illustration of the  $MoS_2$  membrane preparation process and characterization of chemically exfoliated  $MoS_2$  nanosheets. The process includes three steps: Li intercalation of (a) bulk  $MoS_2$  to obtain (b)  $Li_xMoS_2$ , followed by (c) the exfoliation of  $Li_xMOS_2$  into dispersed  $MoS_2$  nanosheets, and, finally, (d) the deposition of restacked  $MoS_2$  membrane on top of a poly(ether sulfone) (PES) substrate by pressure-assisted filtration. (e) The obtained  $MoS_2$  nanosheets were primarily monolayers with a thickness of ~1.1 nm, as measured by AFM. (f) XPS spectra of exfoliated  $MoS_2$  nanosheets indicate that the phase conversion resulted in the metallic 1T phase as a dominant phase.

nanosheets may lead to low hydraulic resistance and thus potentially high water flux. Third, the  $MoS_2$  nanosheet is much more rigid out-of-plane than the GO nanosheet thanks to the existence of three atomic layers,<sup>27</sup> leading to a nanostructure that is less likely to be further compacted under pressure,<sup>26</sup> in contrast to the often observed elastic deformation of GO nanochannels.<sup>23</sup> Besides, the chemical and mechanical stability,<sup>28</sup> nontoxicity,<sup>29,30</sup> high surface area,<sup>31</sup> and versatile physicochemical properties<sup>32,33</sup> of MoS<sub>2</sub> nanosheets may enable novel multifunctional membranes with advanced reactivities.<sup>34</sup>

To date, research on layer-stacked MoS<sub>2</sub> membranes for water filtration is just emerging, with exciting behaviors reported but many fundamental questions unanswered.<sup>26,35,36</sup> For example, MoS<sub>2</sub> membrane has demonstrated a water flux of around 245 L  $h^{-1}$  m<sup>-2</sup> bar<sup>-1</sup> (LMH/bar) in one study,<sup>26</sup> much higher than ~45 LMH/bar of a GO membrane with comparable thickness and dye rejection.<sup>37</sup> Additionally, extraordinary stability of MoS2 membrane in aqueous environment and size-dependent selectivity of ions have been reported.35 However, contradictory observations from other studies, including low water flux in osmotic processes<sup>36</sup> and potential application of MoS<sub>2</sub>-layered structure as nonpermeable film for corrosion control,<sup>38,39</sup> suggest that it is important to comprehensively characterize the nanostructure of MoS<sub>2</sub> membranes and fundamentally understand their separation performance. In addition, so far there has been a lack of mechanistic insights into the swelling behavior of MoS<sub>2</sub> membranes in aqueous environment as well as the ionic and molecular transport through MoS<sub>2</sub> nanochannels.

In the present study, we systematically elucidated the mechanisms for the nanostructural stability and water filtration capability of layer-stacked  $MoS_2$  membranes in aqueous environment. To achieve this goal, the stability (i.e., antiswelling) of  $MoS_2$  membranes in water was investigated by measuring the changes in the membrane mass and interlayer spacing as well as by analyzing the interaction forces between  $MoS_2$  nanosheets. In addition, both experimental character-

ization and molecular dynamics (MD) simulation were performed to thoroughly study the water transport inside  $MoS_2$  nanochannels. The separation capability of  $MoS_2$  membranes was evaluated using representative ionic species and organic dyes.

Properties of MoS<sub>2</sub> Nanosheets. MoS<sub>2</sub> nanosheets were prepared by an established chemical exfoliation method (i.e., organolithium intercalation followed by forced hydration).<sup>40,41</sup> As schematically illustrated in Figure 1a-c, the lithium intercalation weakens the original attractions between neighboring MoS<sub>2</sub> layers within a bulk and further expands the interlayer spacing by generating hydrogen gas once lithium reacts with water. A dispersion of chemically exfoliated MoS<sub>2</sub>  $(ce-MoS_2)$  was thus generated with the assistance of sonication and used to make layer-stacked membranes via pressureassisted filtration (Figure 1d). The obtained MoS<sub>2</sub> nanosheets were mostly in monolayer form, as shown in the atomic force microscopy (AFM) image (Figure 1e), and the hydrodynamic size was determined by dynamic light scattering as 304 nm (Figure S1a). X-ray photoelectron spectroscopy (XPS) analyses in Figures 1f and S1b reveal that the ce-MoS<sub>2</sub> was a mixture of metallic 1T phase (dominant component) and semiconducting 2H phase, unlike the pure 2H phase in the bulk counterpart. Furthermore, UV-vis spectra (Figure S1c) also confirm the predominance of the 1T phase in the as-prepared MoS<sub>2</sub>. In addition to phase transformation during the intercalation process, electrons are believed to transfer from the organolithium reagent to  $MoS_2$ <sup>42</sup> leading to a high negative charge density with a  $\zeta$  potential of -55 mV in neutral pH conditions (Figure S1d) and thus good water dispersibility.

**Properties of MoS<sub>2</sub> Membrane.** The layer-stacked MoS<sub>2</sub> membrane was prepared with the as-synthesized ce-MoS<sub>2</sub> nanosheets by pressure (0.7 bar or 10 psi)-assisted filtration onto a poly(ether sulfone) (PES) ultrafiltration substrate. As shown in Figure S2a, it typically took ~30 min to filter 10 mL of MoS<sub>2</sub> solution (0.5 mg/mL) to make a membrane with a thickness of ~1  $\mu$ m, while it took almost a day to make a GO membrane with similar thickness. The faster filtration process



**Figure 2.** Irreversible restacking of completely dried  $MoS_2$  nanosheets. (a) XRD patterns of  $MoS_2$  membranes showed the evolution of characteristic peaks during a drying and rewetting process, implying that the dry  $MoS_2$  membrane had an interlayer spacing of 0.62 nm similar to that of bulk  $MoS_2$ , and this interlayer spacing remained unchanged after the dry  $MoS_2$  membrane was rewetted for 1 day. (b) The mass and thickness of the dry  $MoS_2$  membrane, as measured by a quartz crystal microbalance with dissipation monitoring coupled with ellipsometry, remained unchanged during 2 days of soaking in water.



**Figure 3.** Comparison of the stability of wet  $MoS_2$  and GO membranes. (a) Cross-sectional SEM image of the laminar structure of a dry  $MoS_2$  membrane. As the membrane-containing bulk was mildly stirred at 200 rpm on a shaking table, the (b) freshly prepared ~1  $\mu$ m thick GO membrane readily disintegrated in water after (c) 1 min, (d) 30 min, and (e) 1 h, whereas the wet  $MoS_2$  membrane having similar thickness remained intact. (f) At 1 h, the GO membrane-containing solution showed the characteristic absorption peak of GO nanosheets, while no  $MoS_2$  nanosheets were found to be released into the corresponding solution. (g) The interlayer spacing of wet  $MoS_2$  and GO membranes (measured by ellipsometry) as a function of soaking time. (h) Comparison of van der Waals, electrostatic repulsion, and hydration forces, as a function of free spacing, in the  $MoS_2$  and GO membranes. The electrostatic repulsion is estimated considering nanosheets with a surface potential of -55 mV in 1 to 200 mM NaCl solutions.

indicates that a  $MoS_2$  membrane most likely has much higher water permeability than a comparable GO membrane. Furthermore, we discovered that the prepared  $MoS_2$  membrane must be kept in wet/hydrated condition to maintain its filtration capability, as the oven-dried (at 60 °C for 2 h)  $MoS_2$ membrane almost entirely lost its water permeability. As shown in Figure S2b, the dry  $MoS_2$  membrane was impermeable to water for at least 6 h under a pressure up to 4.1 bar (60 psi). This observation is consistent with the results from a recent study that reported ultralow permeance of water and small ionic species through  $MoS_2$  membranes even under a high osmotic pressure (1 M NaCl)<sup>35</sup> as well as from other studies that used  $MoS_2$  membranes as anticorrosion coatings.<sup>38,39</sup> Consistently, the X-ray diffraction (XRD) characterization (Figure 2a) shows that the intensity peak (002) of the dry  $MoS_2$  membrane was located at  $2\theta$  of  $16.4^\circ$ , corresponding to an interlayer spacing of merely 0.62 nm (or 0.3 nm free spacing), which is essentially the same as that of bulk  $MoS_2$  and too narrow for water molecules to pass through.<sup>31</sup> In contrast, the XRD signal of the hydrated  $MoS_2$  membrane was significantly weakened not only due to the X-ray absorption by the water molecules within  $MoS_2$  nanochannels but also due to the less-ordered long-range structure as a result of water layer fluctuation.<sup>43,44</sup> Note that a peak started to appear halfway through the drying process, indicating that the interlayer spacing was reduced and became measurable as the  $MoS_2$ 

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membrane was gradually dried. To confirm that the enlarged spacing between hydrated  $MoS_2$  nanosheets was caused by the intercalation of water molecules, the wet  $MoS_2$  membrane was treated by freeze-drying with liquid nitrogen, creating an apparently more porous structure (Figure S3) due to the crystallization and evaporation of water molecules during the freeze-drying process. In addition, the restacking of  $MoS_2$  nanosheets caused by drying was irreversible, as evidenced by the unchanged XRD peak position after the dry  $MoS_2$  membrane was soaked in water for 1 day (referred to as the rewetted sample in Figure 2a). Another evidence is that the mass and thickness of the dry  $MoS_2$  membrane in water remained unchanged for at least 2 days (Figure 2b), as measured by a quartz crystal microbalance with dissipation monitoring (QCM-D) coupled with ellipsometry.

Structure and Stability of  $MoS_2$  Membranes without Cross-Linking. The cross-sectional SEM images of the dry  $MoS_2$  membrane exhibit a typical layered structure (Figure 3a) with a long-range uniform thickness (Figure S4a). The energy dispersive X-ray spectroscopy (EDS) analysis (Figure S4b) showed a uniform distribution of molybdenum and sulfur with an approximate ratio of 1:2, while such elements were not obviously observed in the PES substrate after the removal of the  $MoS_2$  film, indicating the absence of  $MoS_2$  penetration into the PES substrate.

The stability of fully hydrated MoS<sub>2</sub> membranes in aqueous solution was compared with that of GO membranes. GO and MoS<sub>2</sub> membranes with similar thickness were freshly prepared under the same filtration conditions (Figure 3b), and the wet and fully hydrated membranes thus synthesized were subsequently soaked in water with mild agitation at 200 rpm using a shaking table. It was observed that the GO membrane quickly disintegrated into pieces after 1 min (Figure 3c), small particles after 30 min (Figure 3d), and very fine powders after 1 h, clearly evidencing the redispersion of GO nanosheets because the solution turned brownish (Figure 3e). In contrast, the MoS<sub>2</sub> membrane remained intact throughout a similar soaking and agitation process, although the GO and MoS<sub>2</sub> nanosheets have similar charge properties and hydrophilicity (Figures S1d and S5).<sup>45</sup> The supernatants from the soaking solutions were then measured by UV-vis absorption. As shown in Figure 3f, the presence of a characteristic peak of GO at ~250 nm confirmed the existence of redispersed GO nanosheets, whereas the absence of any characteristic peak of MoS<sub>2</sub> verified that no MoS<sub>2</sub> nanosheets were released from the membrane. The above comparison implies that the MoS<sub>2</sub> membrane, even in its fully hydrated state with an enlarged interlayer spacing, still possesses excellent stability in water without the assistance of any cross-linker between individual lavers.

**Nonswelling MoS**<sub>2</sub> vs Swelling GO. Because the accuracy of XRD in measuring a relatively large interlayer spacing is lowered by weakened signals, ellipsometry was used instead to obtain the interlayer spacing of a MoS<sub>2</sub> membrane. To do so, we measured  $h_d$  and  $h_w$ , the thicknesses of oven-dried and wet MoS<sub>2</sub> membranes, respectively. Taken 0.62 nm as the interlayer spacing of an oven-dried MoS<sub>2</sub> membrane (Figure 2a), the interlayer spacing  $d_w$  of a wet MoS<sub>2</sub> membrane can be calculated as  $0.62 \cdot h_w/h_d$ . Figure 3g shows that the interlayer spacing of a wet MoS<sub>2</sub> membrane did not change over 3 days of soaking, indicating the MoS<sub>2</sub> membrane did not further swell over time after it was hydrated at the beginning. Based on three repeated measurements, we calculated the interlayer spacing of

a wet MoS<sub>2</sub> membrane to be 1.2  $\pm$  0.1 nm. This relatively constant interlayer spacing would lead to stable separation performance of MoS<sub>2</sub> membranes in aqueous environment. Deducting the thickness (0.3 nm) of a MoS<sub>2</sub> layer<sup>31</sup> from the calculated interlayer spacing, we estimate the free spacing of a wet MoS<sub>2</sub> nanochannel to be 0.9  $\pm$  0.1 nm, which is capable of separating multivalent ions and many organic molecules from water. In comparison, the interlayer spacing of a GO membrane in a same soaking experiment gradually increased from 0.8 to 5.2 nm (Figure 3g), indicating that the GO membrane swelled significantly in water.

The above membrane behavior can be explained by analyzing the interaction forces between nanosheets. Based on the extended DLVO theory,<sup>46</sup> the equilibrium interlayer spacing is most likely controlled by the balance among the electrostatic repulsion, hydration, and vdW attraction forces. Because  $MoS_2$ and GO nanosheets have similar hydrophilicity and carry almost the same amount of negative charge, their electrostatic repulsion and hydration forces can both be estimated using eqs S1-6. As shown in Figure 3h, the electrostatic repulsion is almost negligible, and the hydration force is the predominant repulsive force considering less than 2 nm free spacing in the present study.

The vdW attraction between two nanosheets is estimated using a simplified parallel surface model:<sup>47</sup>

$$P_{\rm vdW} = \frac{A_{131}}{6\pi D^3}$$
(1)

where *D* is the free spacing (i.e., interlayer spacing excluding a nanosheet thickness) between two nanosheets, and  $A_{131}$  is the Hamaker constant of two identical phase 1 interacting across medium 3, which is defined by:

$$A_{131} = \frac{3kT}{4} \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3h\omega}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}}$$
(2)

where *k* is the Boltzmann constant,  $1.38 \times 10^{-23}$  J/K; *T* is the absolute temperature, 293 K;  $\varepsilon_1$  is the dielectric constant of MoS<sub>2</sub> (3.7) or GO (3.0);<sup>48,49</sup>  $\varepsilon_3$  is the static dielectric constant of water, 80.1; *h* is the Planck's constant,  $6.63 \times 10^{-34}$  J·s;  $\omega$  is the absorption frequency,  $4.73 \times 10^{14}$  s<sup>-1</sup>;  $n_1$  is the refractive index of MoS<sub>2</sub> (2.7) or GO (1.6); and  $n_3$  is the refractive index of water, 1.33 in visible light regime, as determined by ellipsometry. Therefore, the Hamaker constants of MoS<sub>2</sub> and GO nanosheets in water are calculated to be  $48.9 \times 10^{-21}$  and  $5.47 \times 10^{-21}$  J, respectively.

As exhibited in Figure 3h, the MoS<sub>2</sub> nanochannel has a much stronger vdW attraction force than the GO nanochannel. In addition, the vdW attraction between neighboring GO nanosheets falls below the estimated range of hydration force (denoted as the dash-hatched area in Figure 3h), implying that the hydration force can overcome the relatively weak vdW attraction to initiate the GO membrane swelling. As a result, the long-range electrostatic force starts to play a role and eventually becomes the dominating force in the fully swelled GO membrane. In contrast, the strong vdW force of the MoS<sub>2</sub> membrane provides sufficient attraction to prevent its interlayer spacing from increasing. In particular, the vdW force associated with the dry MoS<sub>2</sub> membrane is so large that its interlayer spacing of 0.62 nm remains unchanged even after being soaked in water for 2 days (Figure 2), thereby explaining the irreversible restacking of MoS<sub>2</sub> nanosheets by drying. Besides, as the free spacing between the nanosheets of a wet MoS<sub>2</sub>



Figure 4. Understanding the fast water filtration through  $MoS_2$  membranes. (a) Experimental measurements revealing the thickness-dependent water flux of  $MoS_2$  membranes, in comparison with the data of GO-based membranes (measured in a pressure-driven system) from literature.<sup>8,9,21,23,50-60</sup> (b) The velocity profiles of GO,  $MoS_2$ , and pristine graphene nanochannels by MD simulations. Side and top views of single-layer water molecules in the (c)  $MoS_2$  nanochannel and (d) graphene nanochannel, each showing the alignment of water molecules in a rhombus-shaped network.

membrane increases, the vdW force decreases significantly. At a free spacing of ~0.9 nm, the vdW force becomes equal in magnitude to the average hydration force (Figure 3h), reaching an equilibrium (stable) state of the  $MoS_2$  nanochannel.

Water Flux of MoS<sub>2</sub> Membranes. Fast compaction of freshly prepared MoS<sub>2</sub> membranes under transverse pressure was implied from the water permeability test. As shown in Figure S6a, a  $\sim$ 500 nm thick MoS<sub>2</sub> membrane initially exhibited a constant water flux of 140 LMH when tested at 0.7 bar (10 psi), or 200 LMH/bar, which is in the same range as the reported ~245 LMH/bar for a micrometer-thick membrane.<sup>26</sup> However, upon the increasing of pressure with an increment of 0.7 bar, the water flux promptly increased (due to higher driving force) but then quickly decreased and reached a muchlower, nearly steady-state level (due to membrane compaction). After a pressure of 4.1 bar (60 psi) was applied, the pressure was gradually decreased by 0.7 bar at a time. At each lowered pressure level, the water flux dropped proportionally and became steady immediately. At the end of the test, the pressure was removed from the membrane, which was tested again on the next day using an identical procedure. It is observed in Figure S6b that the day 2 water flux was immediately steady at each pressure level, irrespective of an increasing or decreasing pressure phase, indicating that the compaction of the MoS<sub>2</sub> membrane during day 1 was irreversible.

Such behavior of the  $MoS_2$  membrane under a varying pressure is completely different from that of a GO membrane tested using a very similar procedure with a pressure varying from 0.7 to 4.8 bar.<sup>23</sup> In contrast to the steady flux versus

applied pressure relationships of the MoS<sub>2</sub> membrane over the 2 day test, as summarized in Figure S6c, almost indistinguishable nonlinear flux-pressure relationships of the GO membrane were reported,<sup>23</sup> indicating elastic (and hence reversible) deformation of the GO membrane. Considering the aqueous stability of the MoS<sub>2</sub> membrane, we hypothesize that the applied pressure, which was generally higher than that used in membrane preparation (0.7 bar), further organized the layered structure of the MoS<sub>2</sub> membrane by reducing and eliminating the larger pores and channels caused by random restacking, as schematically illustrated in Figure S7. To confirm such a compressed structure, direct morphological and structural characterizations are necessary and planned as future work. The resulting MoS<sub>2</sub> membrane with mostly rigid nanochannels contributed to the linear flux-pressure relationship (Figure S6C). Therefore, it is beneficial to apply a relatively high pressure during MoS<sub>2</sub> membrane preparation to form a neatly stacked structure with minimum voids or looseness, leading to both consistent and improved selectivity. In the following discussion, MoS<sub>2</sub> membranes were first compacted with a high pressure of 4.1 bar to eliminate any loose structure prior to permeability and separation tests.

The water flux data of  $MoS_2$  membranes obtained from the present study are compared in Figure 4a with those of GO membranes available in the literature, with detailed information on their properties and performance provided in Table S1. Depending on membrane thickness, the water flux of  $MoS_2$  membranes varies between 30 and 250 LMH/bar, which is in general much higher (2–10 times) than that of GO membranes

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Figure 5. Performance and mechanism of  $MoS_2$  membranes in rejection of ionic species and organic dyes. (a) The steady water permeance of a 500 nm thick  $MoS_2$  membrane in filtering water and salt solutions (20 and 200 mM NaCl). (b) Effects of solute charge and ionic strength of solutions on the rejection of ionic species. (c) The concentrations of organic dye (rhodamine-WT) in permeate, feed, and retentate, as evidenced by the absorption spectra. The inset optical image shows the nearly colorless permeate and concentrated retentate, as compared to the feed solution. (d) Dependency of organic dye rejection on  $MoS_2$  membrane thickness. (e) The proposed mechanisms of  $MoS_2$  membranes include both size exclusion and electrostatic repulsion.

prepared by vacuum filtration (blue symbols) or layer-by-layer/ LbL assembly (green symbols), while inserting large spacers between GO layers could increase the water flux of GO membranes (red symbols with dots) at the cost of sacrificing their capability in rejecting small ionic and organic species.

It is important to note that the  $MoS_2$  membranes in fully dried versus hydrated states exhibit dramatically different water transport behaviors, which can be explained by considering the interlayer spacing of  $MoS_2$  membranes in different hydration states. When a  $MoS_2$  membrane is fully hydrated, its interlayer spacing is maintained at 1.2 nm to allow fast water transport through the  $MoS_2$  nanochannel. However, once a  $MoS_2$ membrane is dried during fabrication or storage, its interlayer spacing decreases to 0.62 nm. As discussed earlier, the corresponding restacking of  $MoS_2$  membrane is unable to be hydrated and rewetted in water, and thus, it is nearly impermeable to water.

To fundamentally understand the fast water flux of MoS<sub>2</sub> membranes, we used MD simulation to investigate water transport in the MoS<sub>2</sub> nanochannel under different pressures (25, 50, and 100 bar, respectively) and compared it with those in GO and graphene nanochannels, respectively. Note that both MoS<sub>2</sub> and graphene have well-defined single-layer crystalline structures, while GO has a chemically irregular morphology due to the uncertain distribution of different functional groups. A detailed description of the modeling of all three materials can be found in the Supporting Information. As shown in Figure 4b, the velocity profile in the MoS<sub>2</sub> nanochannel at each pressure level takes a parabolic shape. A slip velocity can be obtained by averaging the velocity values of all water molecules within the first water layer, which is ~0.32 nm away from the nanochannel wall. The slip velocity in the MoS<sub>2</sub> nanochannel increases with increasing pressure (i.e., 1.2, 3.3, and 7.2 m/s under 25, 50, and 100 bar, respectively) and is about 3-4 times

the slip velocity in the GO nanochannel (i.e., 0.34, 0.9, and 1.9 m/s under 25, 50, and 100 bar, respectively). Note that a fast slip velocity in general amounts to a high water flux in the nanochannel, consistent with the observation in Figure 4a that the water flux of  $MoS_2$  membranes is higher than that of GO membranes. Such a flux difference is most likely attributed to the lower hydraulic resistance of the smoother, more-rigid  $MoS_2$  nanochannel as well as the higher hydraulic resistance of the GO nanochannel due to the extrusion of oxygenated functional groups from the GO basal plane.

Particularly, our MD simulation revealed that the single-layer water molecules confined in both MoS<sub>2</sub> and graphene nanochannels exhibit a well-aligned, rhombus-shaped network (Figure 4c,d), which has been confirmed experimentally in graphene nanocapillaries.<sup>61</sup> Such water alignment is attributed to the lack of hydrogen bonding at the water-surface interface and has been associated with the fast water permeation through the nanocapillaries in carbon nanotube and graphene membranes.<sup>61,62</sup> The well-aligned water structure in our MoS<sub>2</sub> nanochannels is also consistent with the finding from a recent MD study, which revealed that such an aligned pattern is mainly caused by the H-bonds within the water network.<sup>63</sup> As shown in Figure 4b, under the same pressure, the velocity in the pristine graphene nanochannel is the highest and has a horizontal profile, which differs remarkably from the parabolic shape for GO and MoS<sub>2</sub> nanochannels. This is because significant boundary slip exists in the pristine graphene nanochannel due to the diminishing friction at the liquidsolid interface.<sup>17</sup> For the graphene nanochannel, the water velocity is uniform over the cross-section of the nanochannel and thus equal to the slip velocity, which are 3.2, 7.9, and 15.8 m/s under 25, 50, and 100 bar, respectively.

MD simulation also enabled us to theoretically verify the water flux data obtained experimentally. Considering the computational cost, we built a simplified multilayer MoS<sub>2</sub>

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model (section 4 of the Supporting Information) instead of a model with a thickness of hundreds of nanometers. Simulation results in Figure S9 indicate that the overall water flux of a  $MoS_2$  membrane may be approximately inversely proportional to the membrane thickness. Thus, for a 500 nm thick  $MoS_2$  membrane (the one used in the separation tests as discussed below), the water flux should be approximately 50 LMH/bar, matching the experimental result very well (Figure 4a).

Note that, in addition to interlayer spacing and watermembrane interface interactions, other specific microstructural features of the restacked nanosheets may also influence the water flux of  $MoS_2$  and GO membranes. For example, smaller lateral dimensions of nanosheets and the presence of pores and defects on nanosheets are expected to shorten the pathway for water molecules and, thus, increase water flux. However, to understand such effects on the flux behaviors of  $MoS_2$  and GO membranes, the membrane microstructure should be experimentally tuned and characterized, followed by systematic investigation of the corresponding membrane performance.

Separation Performance of MoS<sub>2</sub> Membranes. The separation capability of layer-stacked MoS<sub>2</sub> membranes was evaluated using representative ionic species and organic dyes. During the rejection experiments with a 500 nm thick MoS<sub>2</sub> membrane, constant water permeability was observed (Figure 5a) as the test solutions were switched between deionized water and NaCl solutions (20 and 200 mM), confirming the rigidity and stability of MoS<sub>2</sub> nanochannels under different ionic strength conditions. This observation is also consistent with the analysis in Figure 3h that the vdW force is dominant in the MoS<sub>2</sub> nanochannel and, thus, the change in the electrostatic repulsion due to the change in ionic strength cannot vary the net interactions or interlayer spacing. Furthermore, the effect of ionic strength on the interlayer spacing was studied using ellipsometry measurements, which confirmed that the interlayer spacing of MoS<sub>2</sub> nanochannels stays almost the same in different ionic strength conditions (Figure S10). In comparison, the GO nanochannel is relatively elastic and, as a result, it becomes narrower and thus water permeation decreases in higher ionic strength solutions due to the compression of electric double layers.<sup>23</sup>

Rejection experiments were carried out using sodium-based ionic species with mono-, di-, or trivalent anions (chloride, acetate, sulfate, and citrate). As shown in Figure 5b, the 500 nm thick MoS<sub>2</sub> membrane exhibited high rejection (~55–70%) of all ionic species when the ionic strength was low (<2 mM). However, the rejection of ionic species decreased noticeably with the increasing ionic strength of the solution, most likely due to the compression of double layers and the decrease of surface  $\zeta$  potential (Figure S11). In addition, the MoS<sub>2</sub> membrane showed better rejection of di- and multivalent anions (sulfate and citrate), again demonstrating that the rejection mechanism is dominated by electrostatic repulsion between the negatively charged MoS<sub>2</sub> membrane and anions.

MoS<sub>2</sub> membranes were also tested for the removal of organic dyes using model compounds, including negatively charged rhodamine-WT and positively charged methylene blue. The dye concentrations in the permeate and retentate solutions were monitored by UV–vis analysis. As shown in Figure 5c, the retentate solution was concentrated with the absorbance twice as much as that of the feed solution after the same volume of permeate solution was collected, implying insignificant physical adsorption of negatively charged rhodamine-WT. Typically, the removal of rhodamine-WT by the 500 nm thick MoS<sub>2</sub> membrane was as high as 90%. The increase in  $MoS_2$  membrane thickness (from 200 to 900 nm) did not improve the rejection significantly (Figure 5d), further confirming the negligible role of adsorption in the separation of rhodamine-WT molecules. The rejection of rhodamine-WT by our  $MoS_2$  membrane is similar to the rejection of Evans blue obtained in a previous study,<sup>26</sup> although rhodamine-WT has a smaller molecular weight (487 versus 961)<sup>21</sup> and a smaller Stokes radius (1.1–1.2 nm, as calculated using eq S8, versus 2.8 nm).<sup>64,65</sup> The capability of removing smaller molecules was possibly due to the compaction of loose  $MoS_2$  structure by high pressure after membrane preparation in our study.

The rejection of positively charged methylene blue by the 500 nm thick  $MoS_2$  membrane was initially 100% but decreased to a stable level of ~40% (Figure S12). The initial high rejection was due to physical adsorption on the anionic  $MoS_2$  nanosheets. At the end of the test, methylene blue was also concentrated in the retentate, indicating a size exclusion mechanism after the saturation of membrane adsorption capacity. We believe that the overall separation mechanisms for organic dye separation by a  $MoS_2$  membrane include both size exclusion and electrostatic repulsion (Figure Se).

In conclusion, we have shown that, unlike layer-stacked GO membranes that tend to disintegrate in aqueous environment, layer-stacked MoS<sub>2</sub> membranes possess an excellent antiswelling property with a stable 1.2 nm interlayer spacing (or 0.9 nm free spacing) for hydrated nanochannels. We have attributed this aqueous stability to the equilibrium between the shortrange attractive van der Waals and repulsive hydration forces. As a result, cross-linking of restacked MoS<sub>2</sub> nanosheets is not needed, an advantage that simplifies the synthesis procedure, reduces the production cost, and potentially improves the membrane performance due to the absence of cross-linkers that impede water flow within the membrane. We have also demonstrated that the water flux of MoS<sub>2</sub> membranes is much higher than that of GO membranes having similar thickness, and we have attributed this high water permeability to the low hydraulic resistance of the smooth, rigid MoS<sub>2</sub> nanochannels. Besides, we have fundamentally elucidated the remarkably different, water-impermeable behavior of the dry MoS<sub>2</sub> nanochannel, which has a 0.62 nm interlayer spacing (or 0.3 nm free spacing), caused by the irreversible nanosheet restacking during a drying process. It is emphasized that, despite the promise of MoS<sub>2</sub> membranes as demonstrated in the present study, much needs to be done to gain a complete knowledge of their nanostructure and various properties toward enhanced water filtration and separation performance. Finally, it is worth noting that the methods that integrate experiments and simulation for the present MoS<sub>2</sub> study should prove useful for the performance evaluation and mechanistic understanding of other 2D nanomaterials for potential membrane-based applications.

Methods for Preparing 2D Nanomaterials and Layer-Stacked Membranes. A dispersion of GO nanosheets was prepared from graphite using the modified Hummers' method.<sup>66,67</sup> MoS<sub>2</sub> nanosheets were prepared by a chemical exfoliation method.<sup>40</sup> Typically, in a nitrogen-filled glovebox, 300 mg of MoS<sub>2</sub> powder (Sigma-Aldrich, Saint Louis, MO) was dispersed in 3 mL of 1.6 M *n*-butyllithium hexane solution (Sigma-Aldrich, Saint Louis, MO) under moderate stirring for lithium intercalation. After reaction for 2 days, the resulting lithium-intercalated product was rinsed twice with hexane to remove the excess organolithium reagent and organic byproducts, and then immediately exfoliated into nanosheets by reaction with deionized water in an ultrasonic bath for 1 h. Unexfoliated MoS<sub>2</sub> was removed by centrifugation at 500 rpm for 10 min. The supernatant was subjected to dialysis (3.5K MWCO Tubing, Thermo Scientific, Saint Louis, MO) in water to remove the inorganic byproducts (e.g., LiOH). Dispersions of chemically exfoliated MoS<sub>2</sub> samples were stored in a glovebox. The layer-stacked GO membrane and MoS<sub>2</sub> membrane were each assembled by pressure-assisted filtration in a stirred cell (50 mL, Amicon, Billerica, MA) on a porous PES substrate (Sterlitech, Kent, WA) with a nominal pore size of around 30 nm. The membrane thickness was controlled by the volume and concentration of the dispersion. In a typical experiment, 5 mL of 0.5 mg/mL MoS<sub>2</sub> solution led to a membrane thickness of about 500 nm, and a GO membrane of the same thickness was prepared with 10 mL of 0.1 mg/mL GO dispersion.

Method for Integrated QCM-D and Ellipsometry Measurement. The swelling of MoS<sub>2</sub> and GO membranes in aqueous environment was each characterized by using an integrated system of QCM-D and ellipsometry.<sup>68</sup> As illustrated in Figure S13, this system was set up by mounting an ellipsometry-specified QCM-D module (E-1, Biolin, Sweden) on the sample stage of a multiwavelength ellipsometer (FS-1Multi-wavelength, Film Sense, Lincoln, NE). The QCM-D module has a glass lens on each side, through which the incident light from the light source shines on the sample and reflects back to the detector. As the first step, a bare gold sensor was characterized in a dry state and then in an aqueous environment by the integrated system to collect the oscillation frequency and energy dissipation (for QCM-D analysis) as well as the complex refractive index (for ellipsometry analysis) of the gold sensor.

Preparation of the tested  $MoS_2$  and GO thin films was each based on a transplanting method, which was elaborated in our previous study<sup>68</sup> and is briefly described here. The thin film was assembled on a PES support by filtration, and subsequently, a clean gold sensor was attached onto the surface of the thin film with its topside facing the thin film. The thin film was then transplanted to the gold sensor after peeling the sensor off from the polymer support. Changes in the mass and thickness of the thin film in aqueous environment were simultaneously monitored by the integrated system. The dynamic mass change was model-fitted using the Voigt model,<sup>69</sup> and the thickness change was fitted by a three-layer (Au—thin film—water) optical model.

**Membrane Characterization Techniques.** The top-view and cross-sectional images as well as the elemental analyses of a layer-stacked membrane were recorded and analyzed by a field emission SEM (Zeiss Gemini Ultra-55, Jena, Germany). Powder XRD was performed by using graphite-monochromated Co Ka radiation ( $\lambda = 0.179$  nm) on a D8 Discover GADDS system (Bruker, Madison, WI). XPS analysis of samples was carried out using PHI 5400 XPS spectrometer (PerkinElmer, Waltham, MA). The UV–vis absorbance spectra were collected from Genesys 10S UV–vis (Thermo Scientific, Fremont, CA). The  $\zeta$  potential measurements were conducted on a Zetasizer Nano-ZSP analyzer (Malvern, Westborough, MA).

**Protocols of Membrane Flux and Rejection Tests.** Water flux and rejection performance were tested in a cross-flow configuration for dry  $MoS_2$  membranes and in a stirred cell (50 mL, Amicon), where the tested membranes were prepared, for wet MoS<sub>2</sub> membranes at a stirring rate of 500 rpm. The hydraulic pressure was varied to study its effects on the water permeability of MoS<sub>2</sub> membranes. To test the permeance and rejection of various solutes, the MoS<sub>2</sub> membrane was first stabilized under a high compressive pressure of 4.1 bar (60 psi) to achieve steady permeance. The concentrations of organic dyes in feed, permeate, and retentate solutions were measured by using a UV-vis spectrophotometer. The concentration of an ionic aqueous solution was calculated according to its ionic conductivity. The rejection *R* of markers was calculated as R =  $(1 - C_p/C_R) \cdot 100\%$ , where  $C_p$  and  $C_R$  are the concentrations of markers in the permeate and retentate solutions, respectively.

Method for MD Simulations. MD simulations were performed using GROMACS,<sup>70,71</sup> and the simulation results were processed and visualized by VMD.<sup>72</sup> The OPLS force fields,<sup>73</sup> which are well-optimized for simulating fluid problems, were used to model the MoS<sub>2</sub> membrane as well as ions and water molecules. The extended simple point charge model<sup>74</sup> was employed to describe water molecules. The simulation was carried out with a time step of 2 fs. Each system was simulated for 5 ns followed by an equilibration under the NVT ensemble (constant number of atoms, fixed volume, and constant temperature of 298 K). The Nose-Hoover thermostat<sup>75</sup> was used to maintain the temperature at 298 K, and then the nonequilibrium MD simulation was performed<sup>76</sup> by adding constant acceleration in one direction to each atom. The particle-mesh Ewald method was employed to accurately account for the long-range electrostatic interactions of the charges or ions and their periodic images. The cutoff of the Lennard-Jones interactions was set at 1.2 nm in all three directions. Additional details are provided in the Supporting Information.

# ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.7b02804.

Additional figures, detailed calculations of electrostatic repulsion and hydration force between nanosheets, detailed information on MD simulation of  $MoS_2$  membranes, and a table summarizing the separation performance of GO-based membranes. (PDF)

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## Notes

The authors declare no competing financial interest.

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