

Stability, Molecular Sieving, and Ion Diffusion Selectivity of a Lamellar Membrane from Two-Dimensional Molybdenum Disulfide

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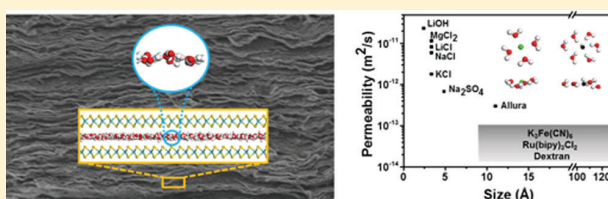
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Supporting Information

ABSTRACT: Two-dimensional (2D) subnanometer channels allow unique mass transport promising for molecular sieving. New 2D channels of MoS₂ nanosheets allow one to understand molecular transmission and separation, unlike the graphene oxide counterpart containing various defects and cationic metal contaminants. Membranes from layered MoS₂ platelets show extraordinary stability in an aqueous environment and compatibility with polymer filters, both beneficial to efficient manufacturing. Sharing gas-tightness and unimpeded water vapor permeation with a graphene oxide membrane, our lamellar MoS₂ membrane demonstrates a molecular sieving property for organic vapor for the first time. The MoS₂ membrane also reveals diffusion selectivity of aqueous ions, attributable to the energy penalty in bulk-to-2D dimensional transition. These newly revealed properties of the lamellar membrane full of angstrom-sized 2D channels point to membrane technology applications for energy and environment.

KEYWORDS: 2D material, 2D channel, molybdenum disulfide, stability, molecular sieving



Lamellar architecture of two-dimensional (2D) materials including graphene and its derivatives offers unique transport properties that originate from the dimension and tight confinement.^{1–5} Subnanometer-scale 2D channels of the graphene oxide (GO) interlamellar space have demonstrated gastight yet water-selective permeation, as well as sieving of hydrated ions.^{6–11} It is the continuous layered configuration of the narrow 2D channels^{12–14} that provides a potential mechanism and adaptability for aqueous molecular sieving.^{10,11,15,16}

Despite the unique molecular transport and clear-cut sieving properties, there are challenges around the graphene derivatives. For instance, stability of GO in aqueous solutions is of concern.¹⁷ A stable GO membrane could be obtained with the insertion of multivalent cations and the use of a porous alumina support^{13,17} at the expense of purity, cost, and the versatility of support material. Use of reduced GO (rGO) may partly resolve the stability issue, though the nanometer-scale thickness necessary for permeation through the rGO lamella could easily compromise the mechanical strength. Other concerns are the varying height of the nanochannels and the chemically defective regions of graphitic 2D channels, obscuring the transport mechanism. Today, transition metal dichalcogenides are considered as one of the 2D materials beyond graphene. According to a recent report, stacked WS₂ platelets with a nanostrand intermediary in between lamellas have blocked the penetration of a large dye (>3 nm) yet allowed water permeation. Still, a systematical understanding is

missing of the detailed aspects of mass transport through such 2D channels or across lamellar membranes.¹⁸ Altogether, they hamper an unambiguous understanding of molecular transport and separation through the lamellar connection of 2D channels. Alternative material is desired to rule out these concerns from the laminated membrane architecture in order to elucidate the transport phenomenon under angstrom-scale 2D confinement.

Molybdenum disulfide (MoS₂) can offer clean 2D channels with limited undesirable chemical defects or inherent intercalation.^{19,20} The mass production of MoS₂ nanoplatelets is possible, and the lamellar stacking method is known just as the graphene derivatives via chemical exfoliation and vacuum filtration.^{12,21} Despite bringing out the manufacturing route, these initial investigations, however, have merely shown a size exclusion of few-nanometer-thick particles instead of a potential for separation of chemical species that these 2D subnanometer channels pose. A nanometers-thin stack of MoS₂ nanoplatelets has been fabricated for gas separation, though insufficient stacking followed by potential membrane defects has limited the observation of gas transport other than Knudsen diffusion and selectivity.²² Hence, there exists a lack of clear understanding of the transport in the angstrom-scale 2D channels formed between MoS₂ planes. Moreover, both mechanical strength and chemical stability of the MoS₂ lamellar membrane

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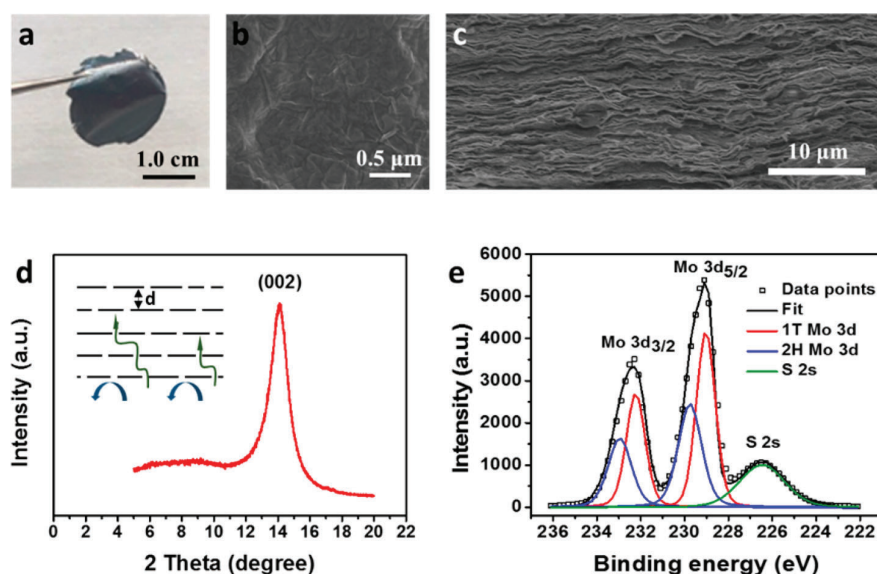


Figure 1. (a) Optical image of an as-prepared membrane of stacked MoS₂ platelets. (b) Scanning electron micrograph (SEM) of the exposed membrane surface. (c) SEM image of the membrane cross section showing the lamellar texture of the MoS₂ platelets. (d) XRD spectrum of an as-prepared stack of MoS₂ platelets (inset: schema of the laminated mixture of 2D platelets). (e) XPS spectra highlighting Mo_{3d} and S_{2s} (green) peaks from the stacked MoS₂ platelets, indicating 1T and 2H phases of Mo_{3d} in red and blue, respectively. (A wide spectrum is provided in Figure S1b.)

have not been characterized yet. Here, we demonstrate that there is no disintegration concern of a stack of MoS₂ platelets in an aqueous environment in a wide range of pH. In order to better understand the effect of these stable 2D channels on molecular transport, we carry out a systematic investigation of selective molecular transport of gases, vapors, ions, and dye molecules using membranes of the stacked MoS₂ platelets. Other than confirming the gas tightness and the unimpeded water vapor permeation, 2D channels of MoS₂ claim molecular sieving toward small organic vapor molecules for the first time. We also learn of prominent diffusion selectivity of aqueous ions through the lamellar membranes from the 2D MoS₂ platelets, possibly attributable to energy penalty in 3D–2D transition.

A membrane of stacked MoS₂ platelets is constructed via chemical exfoliation, centrifugation, and vacuum filtration (Figure 1a). The exposed surface of the membrane reveals wrinkles, indicative of a lateral nest of the 2D platelets providing entrance paths to the permeating molecules (Figure 1b). Cross sections of the membrane sample manifest clearly the lamellar texture of the stacked 2D platelets (Figure 1c). An X-ray diffraction (XRD) spectrum (Figure 1d) identifies an intensive peak (002) located at 2θ of 14.1° corresponding to an interplanar distance of 6.28 Å. There is a broad peak located between 5° and 10°, likely attributable to randomly distributed mismatch yet negligibly small in population. Hence, our MoS₂-platelet lamella is largely composed of an interconnected layered configuration of 2D channels of approximately 6.3 Å in height, including a tiny population of mismatched platelets possibly serving as voids amid and entrances atop the lamellar membrane. Altogether, this laminated configuration offers continuous 2D channels for the molecular transport and separation.

An X-ray photoelectron spectrum (XPS, Figure 1e) verifies Mo_{3d} and S_{2s} components of the membrane sample and distinguishes between two polymorphs of MoS₂, that is, 1T and 2H phases. Deconvolution of the Mo_{3d} peak differentiates 1T and 2H phases, which are in good agreement with a previous

work.¹² From the peak intensity ratio, the relative fractions of the 1T- and 2H-phase MoS₂ are ~56% and ~44%, respectively. The 1T-phase composition is smaller than the previously reported value of ~70%, ascribable to the absence of a reflux step during the chemical exfoliation.²⁰

The 2D channels out of the layered GO platelets are known to have stability concern in an aqueous environment, for GO likely turns to a negatively charged hydrophilic surface upon hydration.¹¹ GO membranes stable in water could be obtained if vacuum filtration uses an anodic aluminum oxide (AAO) filter and an acidic GO solution (e.g., pH ~ 3), figuring out the cross-linking effect of Al³⁺ toward the otherwise repellent, negatively charged GO platelets.¹⁷ Because AAO membranes are costly and the use of acidic solution will add additional process steps, there is a strong need to develop a lamellar membrane that sustains long in an aqueous environment without the need of expensive material and additional steps.

Unlike the GO counterpart,¹⁷ the MoS₂ lamellas turn out to be remarkably stable in an aqueous environment. We established the aqueous stability of the stacked MoS₂-platelet membrane by a test using AAO and Polysulfone (PSf) filters. In our test, the MoS₂ lamellas prepared by vacuum filtration were all stable in water for 12 h of soaking (Figure 2a), hinting that the need for cationic binders is not critical. XRD spectra also remained similar after the 12 h long soaking in water (Figure S4b), indicating that water expands these 2D channels less severely than GO; wetted GO shows interspace as wide as ~13 Å compared with ~5 Å for the dried one.^{6,7} Retention of the original 2D channels in an aqueous environment is strong evidence for the integrity and stability of the MoS₂ platelet lamellas.

Compatibility of the lamellas at various pH values were further verified by immersing the PSf-filtered, stacked MoS₂ membranes in aqueous solutions of pH ranging from 0.6 to 13.2. No disintegration was observed during the long soaking (Figure 2b), which confirms the stability in a harsh chemical environment. According to XRD spectra (Figure 2c), there is

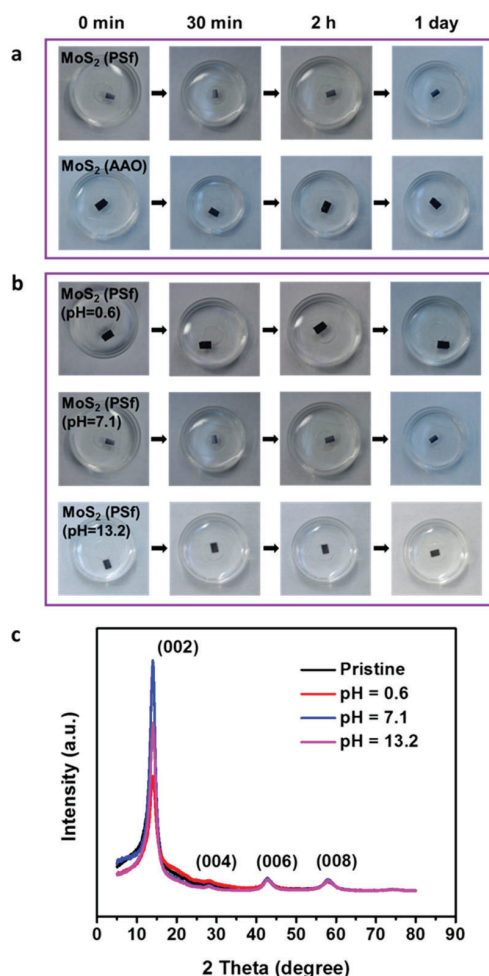


Figure 2. Effects of (a) a filter and (b) pH on the stability of the MoS₂ platelet lamellas in an aqueous environment. (c) XRD spectra from MoS₂ lamellar samples soaked in aqueous solution with different pH after 12 h of soaking.

also no significant difference observed between the pristine MoS₂ membrane and other samples after 12 h of soaking, suggesting a well-maintained lamellar configuration. A wide XPS (Figure S1b) exhibits no sign of multivalent ions in agreement with a previous report.^{20,22} Relief from the requirement for cationic binders effectively prevents the

insertion of contaminants into the MoS₂ channels and allows the use of a cheap commercial polymeric filter.

The stability of the membrane is surprising considering that the single sheets of MoS₂ are stable in the supernatant solution. Both MoS₂ and GO lamellas share a favoring mechanism (van der Waals interaction) required for their stacking, as well as a mildly hydrophilic nature supported by the contact angle (66.5°, Figure S1a) of the MoS₂ lamella in agreement with the literature.²³ What is missing in the MoS₂ lamella is a strong electrostatic repulsion mechanism that the GO counterpart has because of oxygen-containing moieties stemming from (uncontrolled) chemical functionalization of the graphene basal plane. To achieve a stable GO membrane, a cross-linker (multivalent cation metal) should be introduced to shield this strong electrostatic repulsion. It is the chemical functional heterogeneity and the electrostatic repulsion that we speculate could disengage the GO platelets to unstack the GO lamellar membrane for certain conditions. Without such a strong disengaging mechanism, the MoS₂ lamella could stably maintain its van der Waals binding.

Sharing much in common with the GO membranes, the membrane of stacked MoS₂ platelets bears its own unique mass transport properties clearly. For example, membranes of both GO- and MoS₂-platelet stacks are impermeable to gases yet unimpededly permeable to water vapor. When we measured gas permeability of our MoS₂ membrane, a mass flow meter (MKS Instruments MF1) detected no hint of permeation, even for He, across the membrane (Figure S2). The upper bound estimate for the permeability of N₂, CO₂, H₂, and He is 10⁻⁸ mm·g/cm²·s·bar (Figure 3a), suggesting that our micrometers-thick, lamellar MoS₂ membranes are impermeable to gases in agreement with the GO counterpart,⁷ which underpins our assumption that the Knudsen diffusion of the ultrathin MoS₂ layers²¹ likely results from a defect or tiny unsealed crack. On the other hand, water vapor is transmitted across our MoS₂ membranes at a permeability comparable to that of the GO counterpart.⁷

For organic vapors, 1-propanol, 2-propanol, and 1-pentanol did not show any weight loss even after 12 h and more (Figure S3b) with the estimated upper bound of ~10⁻⁸ mm·g/cm²·s·bar, similar to GO's impermeability to organic vapors. Unlike the GO membrane, the lamellar MoS₂ membrane can permeate light organic vapors such as methanol, ethanol, cyclohexane, and acetone. When the sizes of molecules are assumed by a long-axis dimension of an ellipsoid, we observe a molecular sieving behavior (Figure 3b) along with permeability decrease

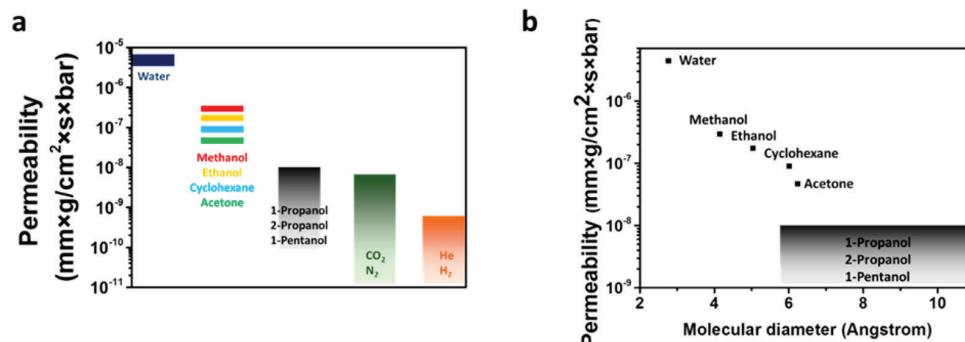


Figure 3. (a) Permeability of various gases and vapors through the stacked MoS₂ membrane (with gradient ramps indicating the estimated permeability). (b) Dependence of the permeability on the molecular size.

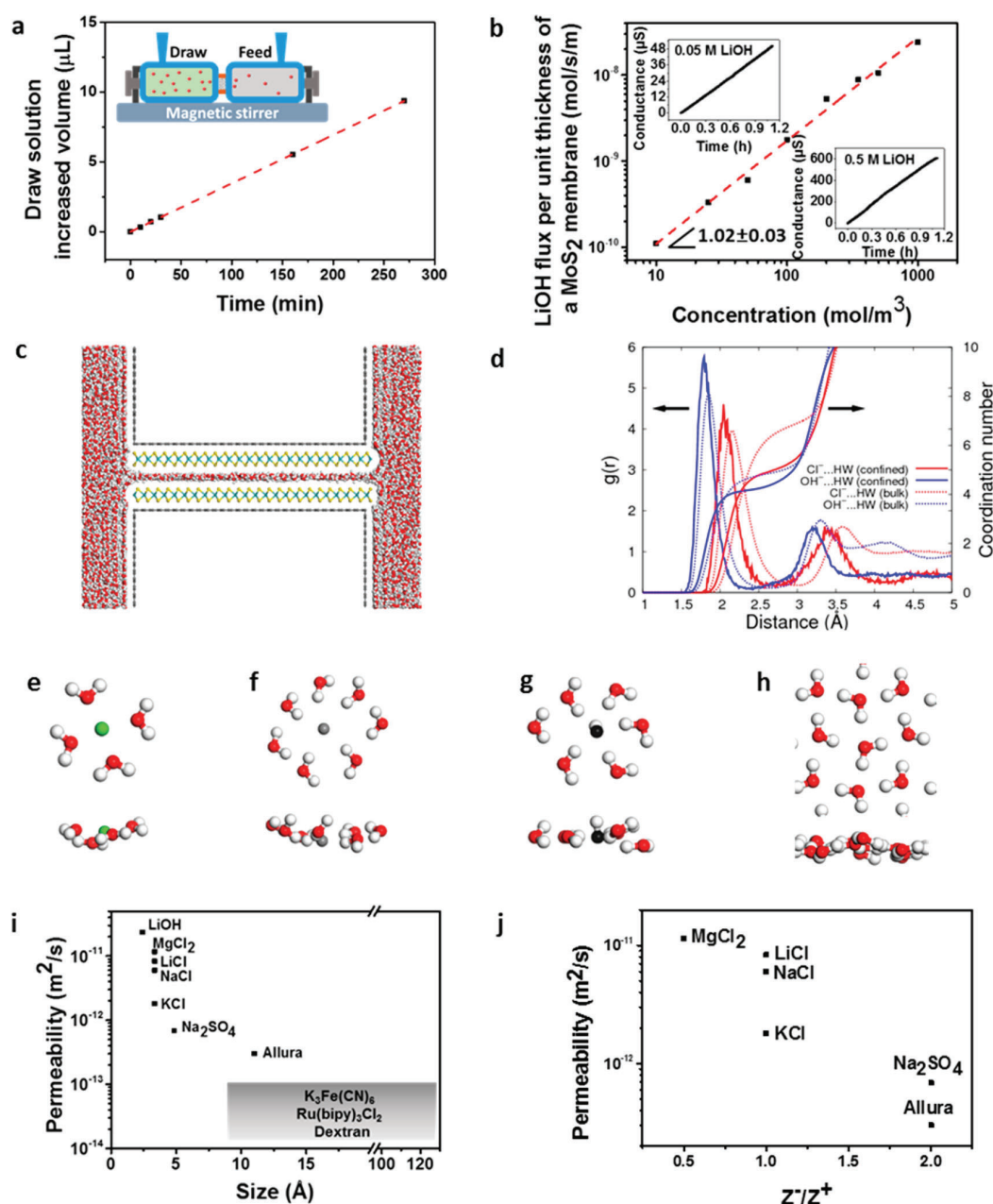


Figure 4. (a) Liquid volume change on the draw side (1 M NaCl) and conductance change on the feed side (DI water). Inset: a schematic of a setup for the ion transmission measurement. (b) Transmembrane diffusion rate of LiOH per unit membrane thickness at various draw concentrations (inset: temporal change of conductance at 0.05 and 0.5 M of aqueous solutions of LiOH on the feed side). (c) Simulation domain comprised of right-angled graphene sheets, two MoS₂ layers between the graphene sheets, and an ionic solution of LiCl or LiOH (1 M). (d) The radial distribution and coordination number of H atom in water (W) around OH[−] (blue) or Cl[−] (red) ions in bulk (dotted) and in between (solid) the MoS₂ sheets. Solvation structure taken from the MD simulation for (e) Li⁺, (f) Cl[−], (g) OH[−] ion, and (h) H₂O: O (water), red; H (water or hydroxide), white; Li⁺, green; O (hydroxide), black; Cl[−], gray color. (i) Size-dependent permeability of ions and dyes (diffusion of the molecules within the gradient area could not be detected and ion size reflects the size of the larger ion). (j) Permeability variation of strong electrolyte salts with respect to the ion valence ratio.

with the sizes. Consequently, when the molecular diameter exceeds the interspatial distance of ~ 6.3 Å, no weight change was measured implying that 1-propanol and 1-pentanol are hardly permeable through the stacked MoS₂ membrane. Nevertheless, an exception was found that 2-propanol having the estimated size of 5.76 Å is unlikely to penetrate the MoS₂ lamellar membrane, either.

Apparently, molecular sieving alone would not offer a perfect explanation, necessitating consideration of other physical mechanisms. In order to penetrate the lamellar membrane, molecules of an organic species should first successfully reach the MoS₂ lamella driven by the vapor pressure. Among those tested, all the permeated organic species pose higher vapor pressure at room temperature than the blocked ones. Considering the driving force only, 1-propanol, 2-propanol,

and 1-pentanol may not be able to as effectively reach the MoS₂ lamella as others. When approaching the MoS₂ lamella entrance, size-dependent steric hindrance would sieve out the organic molecules at the membrane entrance. Once entering the lamellar channel, the tight 2D confinement could possibly induce capillary condensation to the vapor molecules to form an ordered configuration. Because the directional transport from one 2D channel to another would be disfavored by an isotropic molecular motion,⁹ the condensed phase with less isotropic motion is presumed to favor the 2D permeation more than the gas phase. Meanwhile, molecular transmission from one lamella to the next will incorporate the exit-and-entrance event. The impedance associated with the event would be largely determined by steric hindrance such as size exclusion and entrance energy penalty. These three hypothetical mechanisms, transport driving by vapor pressure, facilitation by capillary condensation, and impedance from steric hindrance, would cooperate to determine the cross-lamella permeation and explain our transport data. The proof of this hypothesis deserves future investigation.

Interestingly, water vapor permeates at least one order of magnitude faster than the other vapor molecules do, possibly owing to the 2D hydrogen bonding network over the entire MoS₂ platelet. It shares the similarity of GO that ordered 2D water layer has been simulated and proposed to be crucial to realize the water permeation.^{9,24} The reason why MoS₂ is found permeable toward light organic vapors may be that the clean, angstrom-sized 2D channels of MoS₂ provide the continuous transport path. For GO, lots of randomly distributed defects and metal contaminants might completely block the pathway for organic vapor molecules, although water molecules can still pass through the intact graphene channels⁷ or by the slip-and-hopping mechanism among islands of graphene channels.

In order to understand aqueous ion transport in the 2D channels, we characterized diffusion of ions and dye molecules of various valences and sizes across the lamellar MoS₂ membrane. First, we observed that by using 1 M NaCl as a draw solution, the liquid meniscus on the draw side continued to rise (Figure 4a) confirming osmosis through the lamellar membrane of 2D material platelets. The corresponding water permeance of $\sim 2.2 \times 10^{-3}$ LMH/bar agrees with osmosis across a GO membrane ($\sim 8 \times 10^{-3}$ LMH/bar) driven by a 1 M sucrose solution.⁶ It follows that water molecules can transport under the 2D confinement of MoS₂, be it vapor or liquid.

Next, we characterized the diffusive ion permeability by monitoring conductance change at the DI water (feed) side (Figure 4a, inset). Each reservoir was stirred continuously to alleviate concentration polarization during the measurement. LiOH diffusion characterization is measurable at various concentrations of LiOH. As shown in Figure 4b insets, conductance of the DI water side increases linearly with time as the result of ion diffusion. The rate of the transmembrane ion diffusion is inversely proportional to the membrane thickness within micrometers range, according to our measurement for 0.1 M LiOH (Figure S5). The measured LiOH flux across a unit thickness of the lamellar MoS₂ membrane increases linearly with the concentration difference (Figure 4b, Figure S7), likely suggesting a Fickian diffusion characteristic.

How ions adapt themselves into an environment of the 2D hydrogen bonding network plays a crucial role in the ion transport in the 2D aqueous channel and across the lamellar membrane. Although, when Cl⁻ replaces OH⁻, LiCl apparently follows the Fickian diffusion as well (Figure S4a), the

corresponding permeability value of 8.21×10^{-12} m²/s is smaller than the LiOH permeability of 2.31×10^{-11} m²/s. A first-order disparity between LiCl and LiOH is the smaller size of OH⁻ and its compatibility to the hydrogen bonding network of water, possibly rendering the entry and diffusion of OH⁻ in the aqueous 2D channel energetically more favorable and dynamically less frictional than those of Cl⁻. For electro-neutrality constraint, cations and anions would move along the MoS₂ channels nearly in a stoichiometric ratio, resulting in fast LiOH diffusion.

In order to obtain a molecular level understanding of the ion diffusion behavior under the 2D aqueous confinement, we carried out equilibrium molecular dynamics (MD) simulations for 1 M aqueous solutions of LiOH and LiCl in between two MoS₂ layers separated by 6.5 Å (Figure 4c). Water molecules form a single 2D layer of square hydrogen bonding network, sporadically perturbed by hydrated ions. Detailed MD snapshots of the 2D hydration of ions (Figure 4e–h) provide insight for the entrance energetics and transport dynamics. In both LiOH and LiCl cases, the Li⁺ ions retain the similar coordination numbers both at the bulk state and in a flat configuration in the 2D aqueous channel (Figure 4d,e). On the other hand, for anions the coordination numbers for OH⁻ and Cl⁻ decrease by 0.7 and 1.6–2.1 (Figure 4d, Tables S3 and S4), respectively, in the 2D channel with reference to the bulk solution. In moving from bulk to the 2D confined space, isotropically hydrated Cl⁻ and OH⁻ both have to adapt themselves to the tight 2D confinement by partial dehydration. In this process, Cl⁻ has to lose water molecules more than OH⁻ does, favoring the entrance of OH⁻ to the aqueous 2D channel with less energy penalty in comparison to Cl⁻. Once inside, the hydrogen atom of OH⁻ tends to orient perpendicular to the 2D water plane toward electronegative S atoms of the MoS₂ layers. Such a tighter configuration of the hydration of OH⁻, however, perturbs less the 2D hydrogen bonding network nearby beyond the first hydration shell, leading to energetically favorable 2D hydration of OH⁻ within the channel. Regarding the coexistence of 2H-1T phases, our MD simulations for 2H versus 1T phases (Tables S3 and S4) yielded qualitatively the same interpretations for relative permeation of Cl⁻ versus OH⁻. That is, for both isomorphs, a noticeable reduction in the coordination number of H (water) around Cl⁻ ions in MoS₂ confinements relative to in bulk water was consistently observed (2.05 for 2H and 1.61 1T), while that around OH⁻ ions was much smaller for both isomorphs (0.65 for 2H and 0.74 for 1T). Thus, the relative population of 2H versus 1T may not be the critical factor to qualitatively change the trend in the permeation results observed.

The energetically favorable entrance of OH⁻ is manifested by ion intercalation to the MoS₂ lamella. Upon soaking into aqueous solutions, the MoS₂ lamella is intercalated with ions. Our interlamellar distance investigation based on XRD reveals that there is a significant rise of a peak corresponding to a gap of ~ 11.28 Å upon immersion of the stacked MoS₂ sample in 0.1 M LiOH (Figure S4b). However, there is no conspicuous peak observed for the sample soaked in 0.1 M LiCl. The newly appeared peak agrees with a previous report on the Li⁺ intercalation in MoS₂ lamellas,²⁰ supporting that LiOH can get in the interlamellar space of MoS₂ much easier than LiCl can do. The increased concentration of LiOH in the lamellar MoS₂ membrane could lead to large membrane permeability.

Ions and dye molecules in aqueous solutions exhibit various permeation characteristics depending on their size, valence, and

compatibility with the 2D hydrogen bonding network of water. All ion sizes in Figure 4i are presented with the size of larger ions. Ions smaller than the average interlamellar distance are allowed to enter the 2D channels (Figure 4i). As discussed above, the salt permeation behavior is determined primarily by the dehydration energy penalty and compatibility with the 2D hydrogen bonding network of water. Ions and dye molecules larger than the channel dimension (Figure 4i) find it hard to enter and diffuse along the aqueous 2D channel. Obviously, our membranes of MoS₂ lamellas tend to block ions and dye molecules larger than the nominal channel width (6.3 Å) and to usher in smaller ones, presenting prominent diffusion selectivity. Those ions entering the membrane show different permeability values to one another (Figure 4i,j). This phenomenon can be explained by electrostatic screening caused by the negative polarization of sulfur on the MoS₂ channel. In this mechanism, counterions are attracted to the (electro-negative) 2D MoS₂ channel and diffuse along with co-ions for electroneutrality, whereas co-ions are rather repelled with carrying an equivalent charge amount of counterions.^{10,25} The higher the valence, the stronger this tendency. When balanced, ion permeability is determined sensitively to the valence ratio, Z^-/Z^+ . Among the penetrable small salts we tested, MgCl₂ having the smallest Z^-/Z^+ value indeed shows the highest permeability, followed by LiCl, NaCl, and KCl ($Z^-/Z^+ = 1$). Na₂SO₄ and Allura with their Z^-/Z^+ ratio of 2 show meager permeability. Because Allura is larger in size than Na₂SO₄ (SO₄²⁻), its permeability is smaller. Therefore, it is not surprising that K₃Fe(CN)₆, having the size of Fe(CN)₆³⁻ larger than the average 2D channel width but smaller than that of Allura, shows permeability even lower than the permeability of Allura; it should be because of the collaborative effect of steric hindrance (9.5 Å for Fe(CN)₆³⁻) and strong anionic valence ($Z^-/Z^+ = 3$), leading to repulsion from the membrane. Nevertheless, the lamellar MoS₂ membrane does not follow exactly the Donnan exclusion theory, for its salt permeability shows no dependence on the concentration (Figure S7). As a consequence, a synergistic effect of steric hindrance, energy penalty concerning dimensional transition, and charge exclusion determines the extent of the trans-membrane ion diffusion, manifested by prominent diffusion selectivity observed for the first time. Large molecules find it hard to pass through the lamellar MoS₂ membrane due to steric hindrance, whereas small ones can permeate depending on their valence and compatibility with the 2D hydrogen bonding network.

In conclusion, without significantly expanding the inter-lamellar distance, the lamellar MoS₂ membrane is far more stable in an aqueous environment than the GO membrane. The lack of additional operation step and expensive filter material endows an environmentally friendly and cost-efficient way of massive fabrication of the angstrom-sized 2D channels. Sharing the 2D channel configuration with its GO counterpart, the stacked MoS₂-platelet membrane shows gas tightness and unimpeded water vapor transmission. Remarkably, it is the first time revealing molecular sieving toward small organic vapor molecules through the 2D channels, keeping larger ones from permeating through it. The first observation of the selective diffusion of aqueous ions in the MoS₂ 2D channels and the lamellar membrane thereof is explainable with mechanistic interplay of steric hindrance (or dehydration energy penalty), compatibility with the 2D hydrogen bonding network of water and electrostatic interaction. We believe that this new 2D

channel will further our understanding of the molecular transport phenomena at the subnanometer scale, lending the 2D material-based lamellar membranes potential adaptability to membrane technology applications such as organic species separation, desalination, and electrochemical energy conversion and storage.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b05238.

Methods section and additional data from gas permeation, vapor and ion transmission (PDF)

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Notes

The authors declare no competing financial interest.

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