Stochastic Ionic Transport in Single Atomic Zero-Dimensional Pores

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ABSTRACT: We report on single atomic zero-dimensional (0D) pores fabricated using aberration-corrected scanning transmission electron microscopy (AC-STEM) in monolayer MoS₂. Pores are comprised of a few atoms missing in the two-dimensional (2D) lattice (1−5 Mo atoms) of characteristic sizes from ∼0.8 to 1.2 nm, and pore edges directly probed by AC-STEM to map the atomic structure. We categorize them into ∼30 geometrically possible zigzag, armchair, and mixed configurations. While theoretical studies predict that transport properties of 2D pores in this size range depend strongly on pore size and their atomic configuration, 0D pores show an average conductance in the range from ∼0.6−1 nS (bias up to 0.1 V), similar to biological pores. In some devices, the current was immeasurably small and/or pores could not be wet. Furthermore, current−voltage (I−V) characteristics are largely independent of bulk molarity (10 mM to 3 M KCl) and the type of cation (K⁺, Li⁺, Mg²⁺). This work lays the experimental foundation for understanding of the confinement effects possible in atomic-scale 2D material pores and the realization of solid-state analogues of ion channels in biology.

KEYWORDS: zero-dimensional pore, atomic pore, angstrom-size pore, sub-nm pore, nanopore, two-dimensional material, transition metal dichalcogenides

In recent years, biological proteins such as Na⁺ channels, K⁺ channels, and aquaporins are being revered as touchstones for their water molecule and ionic transport properties. Studies have shown unique nonlinear current−voltage (I−V) characteristics in sub-nm solid-state pores fabricated and tuned under a variety of operating conditions.1−5 These observations constitute a breakthrough in understanding water purification and ionic selectivity with low-dimensional materials. Among reports on fabrication using solid-state materials, there have been a few innovative device architectures that mimic biological protein ion channels such as K⁺ channels. For example, carbon nanotubes (CNTs) with 0.8−1.5 nm diameters,6−8 nanocapillaries with 0.6 nm heights,9,9 and nanopores in graphene, MoS₂, and WS₂ with ∼0.2 nm to few-nm diameters,4,10,11 have shown cation selectivity. Arrays of pores with diameters comparable to the hydrated ion sizes have been demonstrated in two-dimensional (2D) materials, opening a regime of transport studies at the atomic scale.4,11,12 A few notable experimental studies were conducted on single sub-1 nm diameter 2D pores.5,12 They used theoretical fits of conductance vs pore diameter to quote the “experimental” 2D pore diameter in the sub-nm regime from measured currents,5 rather than measure it directly, assuming that models are correct in the sub-nm regime. These pore diameter values were then used as important ingredients to obtain, what could be considered, a “by design” match with theories5 such as claiming evidence for “Coulomb blockade”5 and “atom-by-atom” pore formation phenomena.13 However, the fabrication and ionic transport properties of individual atomically engineered pores in 2D membranes have yet to be experimentally established.5,12 Effects arising from ion confinement such as quantized ionic conductance vs pore diameter, Coulomb blockade, and steric hindrance, where the drop in conductance as successive hydration shells are prevented from passing through the small pores, have been anticipated.4,5,14−17 Other competing effects may include hydrophobicity of pores.18,19 Understanding ionic conduction phenomena in these confined geometries will expand their applications in drug delivery, biomedical devices, water filtration, nanopower generation, and energy harvesting.4,10,20,21
In this study, we create single atomic (sub-nm) pores in a monolayer 2D material, obtain their single-atom resolution structural images, and probe the correlated current−voltage behavior in salt solutions. We fabricate devices with individual atomically precise MoS₂ pores using aberration-corrected scanning transmission electron microscopy (AC-STEM). The resulting pores contain 1−5 missing Mo atoms with effective diameters (dTEM, see Methods for definition and discussion) ranging from ∼0.53 to 0.87 nm. Using atomic resolution images, we also present a library of predicted MoS₂ pores with discretized sub-nm diameters and zigzag−armchair edge configurations. These pores constitute quasi-zero-dimensional (0D) channels with feature sizes comparable to the dimensions of water molecules (∼0.28 nm), hydrated ions (∼0.7−1 nm) and Debye screening lengths (∼0.1−3 nm in 3 M to 10 mM KCl, respectively).

Using ionic transport measurements, the wetting properties, ion current noise, and conductivity properties of individual 0D MoS₂ pores are characterized. We present a methodology for inducing a conducting ion channel in a sub-nm 2D pore using ethanol solutions and probe different ionic states (unwet, partially wet, and fully wet) through current−voltage and noise power spectral density measurements. Due to their similar effective sizes, the measured conductance (G) range for 0D pores (0.6−1 nS) in monolayer MoS₂ is similar to the conductance in biological ion channels. In the low-bias regime (±100 mV), we also observe that the ionic conductivity of 0D MoS₂ pores is largely independent of the bulk conductivity of different salt solutions and concentrations, making the pore almost equally conducting in 0.01 M KCl as in 3 M KCl. This is in contrast to larger diameter pores in the same material where pore and bulk conductivity are approximately the same.24,25

These experimental findings are overall consistent with molecular dynamics (MD) simulations of sub-5 nm diameter MoS₂ nanopores for 1 M KCl26 and provide opportunities for further studies on low-dimensional ionic transport in solid-state materials.

RESULTS AND DISCUSSION
Pore fabrication in 2D materials has been realized using several methods including electron28,29 and ion irradiation,30 electro-poration,13,31 polymer patterning,32,33 annealing/healing,34 in situ transmission electron microscopy (TEM),35 and plasma etching.10,27,36 Electron beam drilling with sub-nm size probes enables the formation of individual pores while offering control over pore size and geometry. With the growing use of aberration-corrected electron optics, transmission electron beams can be focused to diameters of <0.1 nm and have enabled studies of 2D materials down to a resolution of ∼39 pm.37 Recent advances in electron microscopy also open possibilities for precise nanopore device engineering in 2D materials to controllably

Figure 1. Selected area AC-STEM drilling for individual sub-nm MoS₂ pores. (a) Optical image of a 3 mm-diameter SiNₓ/Si circular chip platform (gray) for the TEM-beam fabrication of sub-nm pores with transferred MoS₂ flakes. (b) A monolayer MoS₂ flake (outlined by the purple dashed lines) transferred over a ∼150−200 nm diameter FIB hole on a SiNₓ/Si chip (inside the blue square) and annealed to form a seal with the supporting chip.44 Inset: Enlarged TEM image of the FIB hole with suspended MoS₂ flake. (c) Atomic resolution image of pristine (as-grown and transferred) monolayer MoS₂ suspended on a SiNₓ/Si chip and (d) the lattice with a pore of effective diameter (dTEM, see Methods for definition) ∼1.1 nm. Z contrast is indicative of Mo and S atoms. (e) Schematic showing imaging of suspended monolayer MoS₂ under an AC-STEM beam (light blue) with a dose of 3.2 × 10⁶ e⁻/nm². Mo and S atoms are shown in dark blue and yellow, respectively, while the electron exposure area is shown in orange. (f) Illustration of the sub-nm pore drilling using STEM selected area exposure technique with a dose of 9.7 × 10⁸ e⁻/nm² and (inset) a completely drilled 0D pore.

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make single and few atom-sized pores and to atomically engineer the pore edges. Defect and pore creation in 2D materials has been studied in vacuum inside the TEM,\textsuperscript{38,43} where 2D flakes typically hang off the supporting substrate or TEM grid and the chip is not designed for ex situ nanofluidics. Correlating advanced microscopy (AC-TEM) insights with transport properties from the same 2D devices measured ex situ has been challenging due to device requirements, such as having a single nanopore within an otherwise continuous membrane that does not leak and a nanopore that is sufficiently stable in liquid or gas environments.

**Atomic Pore Fabrication.** Figure 1 shows the sub-nm diameter MoS\textsubscript{2} pore fabrication process using AC-STEM selected-area exposure of the 2D membrane. A monolayer MoS\textsubscript{2} flake is transferred onto a 50 μm \times 50 μm window in the center of the 3 nm diameter TEM grid with a 30 nm-thick SiN\textsubscript{x} film on top of a 290 μm-thick Si support substrate (Figure 1a). As indicated in the inset of Figure 1b, the electron transparent SiN\textsubscript{x} window contains a ∼150 nm diameter hole drilled with a focused Ga\textsuperscript{+} ion beam (FIB). The MoS\textsubscript{2} flake ∼50–80 μm in size is positioned such that it is suspended over the FIB hole (Figure 1b) and annealed at 300 °C with Ar:H\textsubscript{2}. The pore drilling process starts by zooming into the suspended MoS\textsubscript{2} region covering the FIB hole to acquire a high-angle annular dark-field (HAADF) image (dose = 3.2 × 10\textsuperscript{6} e\textsuperscript{-} / nm\textsuperscript{2}, time = 8 s) of the pristine (as-grown and transferred) lattice (Figure 1c).

For a 2D material exposed to an electron beam, defect production is mediated by momentum transfer from energetic electrons to lattice atoms (knock-on damage) and in-plane electronic excitations (radiolysis).\textsuperscript{45} Here, we employ a STEM acceleration voltage of 80 kV, in which the maximum knock-on electron energy transfer is lower than the displacement acceleration voltage of 80 kV, in which the maximum knock-on damage in monolayer MoS\textsubscript{2}.\textsuperscript{4,47,39} To drill a sub-nm diameter pore, the STEM instrument is switched from full scan (13 nm \times 13 nm area) to selected area (1 nm \times 1 nm area) exposure, in which the raster area of the electron beam is reduced, thereby increasing the dose to 9.7 × 10\textsuperscript{6} e\textsuperscript{-} / nm\textsuperscript{2} (total exposure time = 10 s). At this exposure dose, radiolysis causes atoms to be sputtered off the lattice within the selected area,\textsuperscript{45,47} thus creating a sub-nm pore (pore 1, Figure 1d). The process is demonstrated schematically in Figure 1e,f. Atomic pores are formed by removing a fixed, small number of Mo and S atoms, with edges that mainly follow the lattice shape.

Compared to other electron exposure techniques such as high-resolution TEM (HRTEM) drilling and electron beam lithography, the use of a highly focused (probe beam with full width at half-maximum (fwhm) ∼ 0.1 nm) STEM beam allows for simultaneous imaging and atom removal while creating pores with atomically precise geometries. The resulting electron micrographs of the 0D pore are crucial in accurately characterizing pore size and atomic structure for subsequent ionic transport measurements.

**Geometric Pore Models and Atomic Structures of Fabricated Pores.** Selected area STEM drilling enables fabrication and investigation of a finite number of pores fabricated with an area below 1 nm\textsuperscript{2}. MD modeling has shown how the pore edge configuration in a 2D material drastically affects its molecular transport.\textsuperscript{1} For example, Heiranian et al.\textsuperscript{13} theoretically predicted that a nanopore with only Mo-terminated edges allows for higher water fluxes compared to pores that are mixed (i.e., edges with Mo and S atoms), S-terminated pores, and C-terminated (i.e., graphene) pores.\textsuperscript{1} We first present a library of 27 geometrically possible combinations of missing atoms to create 0D MoS\textsubscript{2} pores, ≤ 1 nm\textsuperscript{2} in area. These pore model configurations are shown in Chart 1 and correspond to 1–5 Mo atoms missing and up to 12 S atoms missing. Pore areas range from (i) A\textsubscript{model} ≈ 0.26 nm\textsuperscript{2} for missing 1 Mo atom to (xxvii) A\textsubscript{model} ≈ 1.0 nm\textsuperscript{2} for missing 5 Mo and 12 S atoms.
The geometric models provided in Chart 1 are labeled as \((n \text{Mo}, m \text{S})\) and defined by \((n, m)\), where \(n\) and \(m\) are the numbers of missing Mo and S atoms, respectively. These models show ideal pores without lattice distortions around the pore edges that we can occasionally observe in experiments. For example, in the image of pore 1 in Figure 1f, we observe about 3−4 Mo atoms that have been displaced at the upper right side of the pore’s edge. The specific pore models (i), (vii), (xiv), and (xxi) have only Mo atoms missing and are simply labeled as (1 Mo) to (4 Mo). To compute pore sizes, the area of one hexagonal ring, \(A_{\text{ring, model}} = 0.086 \text{ nm}^2\) (Chart 1, top view of the lattice) is estimated from the normal distance from the Mo atom to the line connecting the two out-of-plane S atoms, a distance of 0.182 nm.\(^4,26\) For each model, the pore area is estimated from the number of missing hexagonal rings. For example, for pore (i) (1 Mo), \(A_{(1 \text{Mo}), \text{model}} = n_r \times A_{\text{ring, model}} = 0.26 \text{ nm}^2\), where the number of missing rings is \(n_r = 3\). Since STEM drilling preserves the localized atomic structure of the MoS\(_2\) pore edges are combinations of zigzag and/or armchair paths, which are defined in Chart 1. A few examples of purely zigzag pores are (i) (1 Mo) and (xx) (3 Mo, 12 S), while purely armchair pores include (x) (2 Mo, 4 S) and (xvii) (3 Mo, 6 S). Conventional descriptions of pore diameter applicable for nm-scale pores break down since these pores can no longer be assumed circular (Chart 1). A better way to capture the pore size and anisotropy is using the histogram of pore sizes in different planar directions passing through the pore’s center of mass (see the Supporting Information of ref 4). Here we use the number of missing Mo and S atoms along with a schematics of the most probable pore edge configuration and suggest to generalize this notation for similar 2D nanopore studies in the future.

Figure 2. TEM images of MoS\(_2\) (sub-nm-size) atomic pores and pore geometric models. Zigzag-armchair 0D pores in MoS\(_2\), AC-STEM image (left) and schematic (right) of 0D pores with (a) (2 Mo, 8 S), (b) (1 Mo, 2 S), (c) (5 Mo, 12 S), (d) (2 Mo, 7 S), and (e) (2 Mo, 8 S) atoms missing. (f) The 3D renderings of the intensity from the HAADF images of the pores shown in (b) and (d) are also provided.

While Chart 1 shows the majority of the geometrically possible combinations of 0D pores in a monolayer MoS\(_2\) lattice with an area below 1 nm\(^2\), it explicitly displays a few pore geometries that are likely feasible and can be fabricated through STEM drilling (such as in Figure 1). For example, armchair pores (ix) (2 Mo, 4 S) and (x) (2 Mo, 4 S) contain the same missing atoms of 2 Mo atoms and 4 S atoms, however, they are neither identical in their pore shape nor in area ((ix) 0.52 nm\(^2\) and (x) 0.60 nm\(^2\)). Similarly, (xiv) 3 Mo and (xv) 3 Mo illustrate pores that are a combination of zigzag and armchair pore edges (i.e., mixed) with the same theoretical area of 0.60 nm\(^2\) but differ in their shape as seen in Chart 1.

In this case, we find that the pore in (xv) is difficult to experimentally fabricate, and we attribute this to its highly elongated shape: Under electron irradiation, pores prefer circular expansion due to the reduced displacement energy for atoms on the pore edge.\(^41\) More convoluted and intricate pore edges such as those depicted in (xii) and (xiii) pose a challenging fabrication and detection task even for tools with high controllability such as STEM due to the low displacement threshold and Z-contrast of chalcogen sites.\(^30,38\) Even more importantly, the structural stability of such artistically rendered, intricate pores is far from guaranteed, is likely lattice dependent, and yet to be explored and understood in different environments.
Figure 3. Schematic of single pore STEM drilling, solution treatment, and measurement setup. (a) Fabrication and pore wetting workflow for a suspended monolayer MoS$_2$ 0D pore. (i) Drilling a sub-nm pore on the suspended MoS$_2$ flake. (ii) Wetting of pore with ethanol (50%) for 15−30 min. (iii) Device rinsed in DI water before ionic measurement. (iv) Device flushed with salt solution for ionic measurement. (b) The design of nanopore ionic measurement consisting of a 2D MoS$_2$, nanopore separating two chambers of salt solution with Ag/AgCl electrodes (mounted on a microfluidic platform, not shown). (Inset) A sample HAADF image of a sub-nm MoS$_2$ pore.

Figure 4. Ion current−voltage and noise curves in single pore devices. (a) AC-STEM image of the as-fabricated sub-nm pore 2 (1 Mo, 2 S) in vacuum, prior to any $I−V$ measurements with $d_{\text{TEM}} = 0.53$ nm. (b) Control device and pore device $I−V$ measurements: (black) bare Ag/AgCl electrodes in air, (orange) partially wet pore 2, and (yellow) likely a fully wet pore 2 after exposure to ethanol for 15 min. (c) $I−V$ measurements of pore 3 (5 Mo, 12 S) with $d_{\text{TEM}} = 0.87$ nm in 1 M KCl, pH 8.7 (purple) after 15 min ethanol exposure, (red) de-wetting after an additional 30 min in 1 M KCl, and (blue) again after following the wetting procedure it was found to rewet. For comparison, $I−V$ curves for a pristine MoS$_2$ membrane are shown in green in both (b) and (c). (d) Current noise PSD of samples in various conditions: (green) pristine membrane (no intentional holes), (black) bare Ag/AgCl electrodes in air, (red) a pore before ethanol wetting, and (blue) a pore after ethanol wetting.
Atomic structure, formation, and stability of 2D MoS₂ pores (as in pore configurations in Chart 1) made by the electron beam irradiation in vacuum have been investigated using density functional theory (DFT), for example, by Wang et al. who claimed that it is favorable for the ejected Mo atoms to attach to the 2D sheet as well as by other authors who also modeled the ion conductance through 2D MoS₂ pores. Ironically, many structural DFT stability simulations consider the material in vacuum. While these simulations seem suitable for TEM-only studies, their relevance is lower for nanofluidic devices where additional atoms and ions are present around the pore and can interact with the 2D material to form chemical bonds and even etch the material. Stability of pores in salt solution is therefore a different and more complex problem than stability of pores in vacuum, as evidenced by various electrochemical phenomena observed between salt solutions and 2D materials such as oxidation. There are exceptions of MoS₂ nanopore modeling in fluids, but further work is required. DFT combined with MD simulations may provide further insight, especially if they are in concordance with experimental findings. Our experiments outline several pores that were stable enough to be measured in ionic solutions.

Figure 2 demonstrates five example devices with AC-STEM HAADF images of zigzag and armchair structures successfully drilled and examined using the selected area technique shown in Figure 1c–f. The five pores include: (a) (2 Mo, 8 S), (b) (1 Mo, 2 S), (c) (5 Mo, 12 S), (d) (2 Mo, 7 S), and (e) (2 Mo, 8 S). Overall, the pores in this study range from 1–5 Mo vacancies with a pore area from 0.34 nm² to 1.0 nm². Figure 2f shows three-dimensional (3D) renderings of the intensity from the HAADF images of pores 2 and 4. The STEM beam can be controlled down to a ~0.1 nm probe size, nevertheless, the precision of this technique is limited due to sample drift and the relatively low displacement threshold (~7 eV) for S vacancies. As a result of this, AC-STEM is mainly employed to create defects at Mo sites (Z = 42), while further efforts are needed to precisely control the composition of chalcogen (S) sites.

Pore Contamination. It is likely to have 2D membrane and pore contamination by a carbon/graphitic film partially or completely covering the MoS₂ that cannot be easily observed in our HAADF images, as specifically discussed for similar MoS₂ films by Wen et al., who demonstrated the detection of often-missed, lighter atoms (C, O, N) by 4D STEM imaging. This additional material could alter the pore’s wetting and other properties, reduce its diameter or completely block the pore, and also yield smaller ionic current than predicted since the contaminated pore may be significantly thicker. For larger, nm-diameter MoS₂ pores, a good agreement was found between the ionic conductance models and expected 2D MoS₂ pore thickness in the range of ~0.7–1.6 nm, with the quoted device failure for 2–20 nm diameter MoS₂ pores from membrane leakage (G > 300 nS) or pore clogging (G < 10 nS) of <30%. Future efforts of modeling 2D pores and other ultrathin devices may wish to consider effects of carbon contamination, whose role is becoming increasingly more recognized and could be considered in interpreting behaviors of pores and devices at the atomic scale.

Ionic Transport Measurements and Properties of Single 0D Pores. After drilling in an ultrahigh vacuum (p ~ 1.7 × 10⁻⁵ Pa) in the aberration-corrected STEM, the 0D pore is immediately stored in a vacuum-sealed container prior to experimental measurements to minimize oxidation-induced pore changes and expansion. Figure 3a displays a schematic of the 3 mm diameter SiN/Si device (also pictured in Figure 1a) with a monolayer MoS₂ flake. The single 0D pore that is drilled and imaged is located in the center of this membrane, as explained previously in Figure 1. A number of studies have highlighted the importance of wetting nano-channels and pores prior to ionic measurements. Here, we elaborate on the dedicated pretreatment steps used to facilitate wetting of sub-nm MoS₂ pores while monitoring and examining intermediate responses before a measurable current state. We use a 1:1 mixture of ethanol and DI water to help wet our devices using the process shown schematically in Figure 3a(ii–iv). The process begins by immersing the device in the ethanol–water mixture for 15–30 min (Figure 3a(ii)). The following steps include rinsing with DI water and immersing the chip in salt solution (Figure 3a(iii,iv)). These last two steps take about 1 min each with a total time of a few minutes. This cycle of processes is repeated sequentially a few times (about 3–6 times) until a detectable current (discussed later in Figure 4) is observed. Ionic transport measurements are performed with two-terminal Ag/AgCl electrodes (Figure 3b). The inset of Figure 3b shows an AC-STEM image of a pore that was not electrically measured. During measurements, we limit the applied voltage to ±100 mV to minimize electric-field induced damage to the device.

We observe that the wetting of 0D pore devices is a challenge for ionic measurements, indicating their hydrophobic nature. Figure 4 represents a different sequence of events involved in wetting 0D MoS₂ pores. The HAADF image of pore 2 shown in Figure 4a indicates a structure with a area of ~0.22 nm² (dTEEM = 4A/TEEM × π × 0.53 nm), consisting of 1 Mo and 2 S atoms missing (also shown in Chart 1 as (ii)). The method to extract area from an HAADF images is shown in Supplementary Figure S1. The intensity profile of the dashed yellow line is shown in the inset of Figure 4a and demonstrates the absence of a single Mo atom in the periodic lattice structure. In the linescan across this pore, we also observe residual peaks whose intensity appears consistent with the presence of single S atoms. To better characterize and understand differences in conductance levels observed in a single 0D pore sample (from vacuum to salt solution via ethanol immersion), we empirically categorize its observed transport behavior into three different states:

1. State 1: Negligible conductance (<0.1 nS (~10 pA for V < 0.1 V) with I−V curves similar to those measured in pristine membranes in solution. When pores were immersed in salt solution directly from vacuum, without any ethanol treatment, immeasurable ionic current was obtained (<10 pA in some cases), similar as the noise of the open circuit setup. This means that either (i) the ionic solution did not reach the pores (unwet state) or that (ii) the ion current through these pores is below the detection limit. An example of this state is shown in red in Figure 4c.

2. State 2: Measurable ionic current with pronounced hysteresis in I−V curves. In this case, samples were immersed in ethanol prior to ionic measurements. The I−V curves were characterized by pronounced hysteresis but measurable signals. This is possibly due to incomplete pore wetting and gas molecules dissolved in solution and present on the surface of the microfluidic chip that make their way to the pore region and affect the conductance. Hysteresis in I−V curves were noticed to be temporary in some devices before obtaining a
conducting state (state 3). The orange curve in Figure 4b shows an example of state 2.

(3) State 3: Measurable ionic current with no hysteresis in I−V curves. After immersing the samples for adequate (>15 min) time in ethanol, we observed I−V curves with no hysteresis corresponding to a measurable conductance up to ∼0.8 nS. Such curves are shown in yellow in Figure 4b as well as purple and blue in Figure 4c. Additional examples of all three states can be found in Supplementary Figure S3.

Current−voltage characteristics of samples in this work show different scenarios with various sequences of events. Three of such sequences involving states 1−3 are shown for pore 2 (Figure 4b), pore 3 (Figure 4c), and pore 4 (Figure 5), all successfully resulting in a measurable current and therefore ending in state 3. Figure 4b shows the first scenario where the ionic current−voltage curves obtained for pore 2 go through the following stages in the wetting process: (i) After soaking in an ethanol:water mixture for 15 min (see Methods), we measure an I−V curve (orange) in 1 M KCl with hysteresis behavior where the maximum current is ±10 pA. This value of current is comparable to pristine MoS2 membranes with ethanol wetting (green) but shows a looplike I−V curve characteristic of state 2. (ii) After placing the device into ethanol for 3 h, we measure in 10 mM KCl and observe an I−V curve (yellow) with G ∼0.98 nS (i.e., state 3).

We also have fabricated several pores which led to hysteresis-like I−V behavior and ended in state 2 (pores 1 and 5 shown in Figure 1) or had other issues such as excessive PMMA contamination. Pore/membrane breakage was observed in three devices which exhibited excessive conductance (∼375 nS or higher, see Supplementary Figure S3a) caused likely due to (1) an unstable pore with significant PMMA contamination introduced during the transfer process and (2) device damage during measurements. Out of a total of ∼30 fabricated devices, 41% accounted for devices with drilled pores where ionic measurement was attempted. This also includes devices which had multiple sub-nm pores, for example, pores 6−8 in Supplementary Figure S3. In the case of pore 7 which was measured up to ±0.5 V in 1 M KCl, we observe a nonlinear trend in I−V with a conductance G ∼ 2.2 nS. In order to clearly
distinguish between the background signal and signal dominated by pore conduction, the control I–V curves for bare Ag/AgCl electrodes (black) and pristine MoS$_2$ membranes (green) were also measured (Figure 4b). As expected, the bare electrodes in air show a negligible conductance $G$ ~ 10 pS with a current of $\sim$0.5 pA at $-100$ mV to 1 pA at $+100$ mV, also comparable to pristine membranes, $G$ ~ 10–30 pS.

We do not detect any systematic dependence of conductance on pore size or geometry, but rather a stochastic set of values. For example, pore 2 showed a higher conductance than pore 3 despite a smaller pore size recorded during TEM drilling and measurement at a lower KCl concentration (Figure 4b vs Figure 4c). This may be a real, counterintuitive effect, or it may be an artifact from pores changing during the course of the experiments. Previous non-equilibrium molecular dynamics (NEMD) conductance simulations on selected MoS$_2$ pore geometries (including pores (ii) and (xix) from Chart 1) showed that conductance varies in magnitude ($\sim$0.01 nS to $\sim$1 nS) in this pore size range ($\sim$0.4 to 0.9 nm).

**Sub-nm MoS$_2$ Pore Studies.** It is useful to compare our findings with previous measurements. Single MoS$_2$ monolayer pores with somewhat larger diameters (1.1 and 1.4 nm, directly imaged by AC-TEM) yielded measured $G$ ~ 1.5 nS and 10 nS in 1 M KCl, respectively, and NEMD simulations for pores as in (ii) and (xix) in Chart 1 computed $G$ ~ 0.02 nS and $G$ ~ 0.03 nS, respectively. Feng et al. reported conductance in pores made by electroporation to be $\sim$1 nS (extracted at 100 mV) for quoted diameters of 0.3, 0.6, 0.8, and 1 nm, but failed to explain how pore diameters were obtained given that the pore images were not presented. Salt (bulk) conductivities are not a useful measure for thin-film porosities, and measurements of conductance in pores show a high degree of variability. Moreover, the conductance of single pores is not obtained as a simple measurement of pore diameter directly, but rather as a stochastic set of values.

**Rewetting Behavior.** It is important to note that these conducting states are reversible in a sense that a conducting pore (state 3) can switch to a nonconducting state (state 1) (more discussion on hydrophobicity in pores is below). This implies that the ionic current paths may easily close in 0D pores. We find that if the same pore is treated in ethanol again, it can start to show measurable ionic current and conduct (state 3). Ethanol is therefore critical for ionic measurements in 2D materials and especially for smaller diameter 0D pores here. This is demonstrated in pore 3 (5 Mo, 12 S), which shows the second scenario where the pore was initially measured in state 1 after both 30 s and 5 min of ethanol wetting where we obtained an immeasurable and unstable I–V response. However, after an interval of 15 min in ethanol, the pore was observed to conduct (i.e., state 3) with $G$ ~ 0.73 nS in 1 M KCl (purple curve in Figure 4c). This conductive state ($\sim$0.7 nS) was verified periodically after 10 min but the pore was found to de-wet and reverted to state 1 after about 30 min after measuring in salt solution. This is denoted by the red I–V curve in Figure 4c with a max current of 0.9 pA at $-100$ mV and 0.6 pA at $+100$ mV. By repeating the wetting procedure, the pore was measured after 60 min and was found to return to the conductive state 3 (light blue) with a conductance of 0.72 nS in 1 M KCl. Later, this pore was stored in an ethanol mixture overnight and observed to still conduct after 14 h with similar conductance values of 0.73 nS in 1 M KCl and 0.72 nS in 1 M LiCl.

**Hydrophobic Characteristics of Single Atomic Pores.** We observe that pores can wet and de-wet repeatedly, manifested by the fluctuation in the pore’s conductance “on” and “off” upon successive current—voltage measurements, on the time scales of minutes. This resembles, at least qualitatively, the behavior of biological (K+) ion channels where “hydrophobic gating” is observed, an “on/off” behavior where the voltage is increased, the pore can transition to a conducting state at higher voltage measurements, on the time scales of minutes. This resembles, at least qualitatively, the behavior of biological (K+) ion channels where “hydrophobic gating” is observed, an “on/off” behavior where the channels opens and closes for ion flow due to changes in the degree of pore wetting and presence of “nanobubbles”.

In biological ion channels, the current depends on the degree to which the ion channels are wet with liquid, which, in turn, was found to depend on pore diameter, the hydrophobic nature of atoms lining the pore, and the applied voltage. In our case, transferred 2D materials are largely hydrophobic, and wetting of the surface is a challenge. We explored an alcohol (ethanol) prewetting procedure in the context of sub-nm pores to maximize the amount of electrolyte that flows through the pore and to maximize the measured current.

The hydrophobic nature of transferred 2D material solid-state nanopores has been previously observed, and ethanol-prewetting of MoS$_2$ and WS$_2$ was found to help obtain measurable ion currents consistent with the pore size. Wetting can be probed further by applying external pressure to force the liquid transport through the pore. The general concepts of wetting and de-wetting of pores used here are not new. Difficulty of pore wetting, the “dry”, “wet”, and “partially-wet” states of hydrophobic solid-state (silicon nitride) and polymeric pores with diameters of the order of ~10 nm and ~100 nm, and the corresponding hysteretic behavior observed in I–V curves have been reported a while ago. A hydrophobic pore can transition between the dry (nonconducting) and the wet (conducting) state upon voltage application. As voltage is increased, the pore can transition to a conducting state at higher bias resulting in an apparent nonlinear I–V curve. This phenomenon was referred to as “voltage-induced gating” and “electric-field-induced wetting and de-wetting” of a fabricated hydrophobic pore. Therefore, by applying voltage, a hydrophobic pore can be forced into a partially or fully wet,
conducting state. In this fully conducting state, the pore allows a maximum current possible based on its size, that is, the same current as in a hydrophilic pore of the same size. In addition, MD simulations have shown ionic “memcapacitive effects” and hysteresis loops (I−V measurement in a loop with no crossover) in nanopore systems, that depend on frequency and were proposed to arise from polarizability of ionic solutions.55

Nonlinearities in I−V curves can originate from hydrophobic effects and also from the ion confinement effects in small diameter pores, when their sizes are comparable to sizes of hydrated ions and Debye lengths. In biology, hydrophobicity is an essential property for ion channel behavior and gating, and it can be an inherent property of the pore. For example, stable gas pockets (“bubbles”) can form inside hydrophobic regions of the pore. A sub-nm wide pore region is required to make the bubbles stable long enough to observe relevant biological effects, and when bubbles break, ions and water molecules flow through.53 Analogous effects could be expected in solid-state pores, and, because they are fabricated, these pores could serve as model systems to study such effects further and design artificial pores with specific functions. For example, according to MoS2 pore modeling, water flux can vary depending on whether Mo only, S only, or mixed atoms, Mo and S, are at the edges.1 Another approach to controlling the degree of hydrophobicity would be to coat the 2D pores, for example, by atomic layer deposition of TiO2, as demonstrated on graphene pores, to make them hydrophilic while only slightly increasing the pore thickness.29 It is interesting to note that the nonlinearity in I−V measurements is largely absent in MD simulations,9 and this is yet to be understood.

Pores may be dynamic in shape and change their conformations and edge termination, as in ion channels. This is a possibility for solid-state pores as well, but it is hard to probe directly and more thermodynamic modeling would be beneficial to inform the experiment. It is likely that the pore structure could change over time. Atomic-scale fluctuations at the pore edge could have additional contributions to the degree of hydrophobicity inside of the atomic-scale pores. In biological pores, “nanobubbles” within the pore have been theoretically considered as possibly responsible for ion channel gating.55 The extent to which the different parts of the pore itself are hydrophilic or hydrophobic depends on the ion channel diameter, the applied voltage, and the local properties of pore edges and their interactions with ions and water molecules.51 Future studies can attempt to directly probe effects of these parameters in atomic 2D material pores and the degree to which these effects can be controlled at the atomic scale.

**Noise Characteristics of Single Atomic Pore Chips.** In addition to I−V characteristics, we find that the power spectral density (PSD) of these states yields insights into frequency-dependent properties and can be used to help determine the extent to which a 0D pore is wet. PSD in solid-state nanopores is given as

\[
\text{PSD} = \frac{I^2 A}{f^\alpha} \tag{1}
\]

where I denotes the ionic current, A is the noise coefficient, \(\alpha\) is the low-frequency noise component, and f is the frequency.56 The PSD acquired at different stages of the wetting process for pore 4 is shown in Figure 4d. For the bare electrodes (black), we obtain a noise coefficient of \(A = 2 \times 10^{-7}\) and noise component of \(\alpha = -0.3\), which is representative of instrumentation noise. Additionally, the spectrum for bare electrodes is identical to the PSD for a de-wet, incomplete wet pore (red), suggesting the absence of a conducting ion channel. For pore 4 (2 Mo, 7 S), a completely wet with ethanol (navy blue), we note \(A = 5 \times 10^{-6}\) and \(\alpha = -0.47\), which is similar to that of the pristine MoS2 membrane wet with ethanol (green, \(A = 7 \times 10^{-5}\), \(\alpha = -0.14\)). Crucially, the PSD for both cases exhibits a decrease in the sub-10Hz regime (Figure 4c) compared to the rest of the frequency range and is characteristic of 1/f noise in conducting solid-state pores.4,44,45,58 This is in stark contrast to the flat PSD obtained for both bare electrodes and de-wet pore and suggests that ethanol is essential in creating a conducting ion channel through either intrinsic defects (in the pristine membrane) or STEM-fabricated 0D pores (in pore 4). A combination of I−V and noise analysis can therefore be utilized to better understand these states (states 1−3) to determine whether a sub-nm pore is completely wet.

Another example of such a zigzag–armchair pore (pore 4) is shown in Figure 5. A HAADF image of this pore is shown in Figure 5a, alongside its atomic edge configuration shown in the inset of Figure 5b. Pore 4 has 2 Mo atoms and 7 pairs of S atoms missing, shown as (xii) in Chart 1, corresponding to a geometric area of 0.69 nm². This is, again, confirmed by the Z contrast produced across the pore (yellow line) in the inset of Figure 5a. In the case of pore 5 (which is our third I−V scenario), abiding by the procedure outlined in Figure 3a(i−iv), we obtain the current−voltage measurements for multiple salt solutions and salt concentrations. First, we examine the conductance in the case of different salt concentrations in Figure 5b: 10 mM KCl (yellow), 1 M KCl (blue), and 3 M KCl (green) at pH 8.7. We clearly observe a phenomenon where the 0D pore demonstrates an ionic conductance largely independent of the salt concentration, all three I−V of 10 mM, 1 and 3 M KCl correspond to G ∼ 0.71 nS, 0.69 nS and 0.75 nS, respectively, extracted as slopes of the linear fits to the I−V curves in the voltage ranges ±100 mV.

I−V characteristics acquired for other salt solutions such as 1 M LiCl (orange) and 1 M MgCl2 (pink) from an applied voltage range of ±200 mV are presented in Figure 5c. Given that these salt solutions have a significant difference in bulk conductivity (precisely, 1 M LiCl = 9.5 S/m, 1 M MgCl2 = 12.3 S/m, 10 mM KCl = 0.14 S/m, 1 M KCl = 10.8 S/m, and 3 M KCl = 29.28 S/m), it is noteworthy that we observe a small change in pore conductance value in these salt solutions through the 0D pore in the ±200 mV range, compared to the difference in respective bulk values. In contrast to the typical linear behavior of nm-sized pores, these 0D pores also exhibit somewhat nonlinear current−voltage curves. These nonlinearities are more evident at higher concentrations, all three I−V of 10 mM, 1 and 3 M KCl in 1 M LiCl (these arrays contained on average 240 pores on average were larger than 0.6 nm, the hydrated K⁺ ion diameter), and these samples exhibited a G in a wide range ∼0.5−50 nS in 1 M KCl (these G values are for the dose used for “array 3”), while the particular sample “array 3” in Figure 5c is found to be less conducting than pore 4, the mean conductance of all such measured samples, FIB irradiated at the same dose, was larger than the G of pore 4, with a mean conductance value of ∼20 nS. Additional, slight nonlinearities is also observed in case of multiple pore devices, for example, pore
7, in Supplementary Figure S3e for 1 M KCl. We also plot in Supplementary Figure S2 a bar graph of calculated conductance ranges by fitting a line to $I-V$ curves over several voltage ranges, such as ±30 mV, ±50 mV, ±100 mV, and ±200 mV from 0D pores measured in this work (pores 2–4) in Supplementary Figure S2. We note that there is a difference of ±0.01 to 0.086 nS across different voltage range for a given 0D pore, reflecting the degree of nonlinearity. About 42% of the 0D pores fabricated yielded a conductance of 0.7–0.9 nS across various cation-based chloride salt solutions from 0.1 to 3 M with a slight variation in conductance (±0.1 nS). While the other devices showed hysteretic $I-V$, the current was immeasurably small and/or pores could not be wet.

**Calculation of Pore Conductivities Based on Measured Conduction and Pore Sizes.** We can estimate pore conductivities based on measured conductance $G$ and effective pore diameters from TEM images prior to $I-V$ measurements, $d_{TEM}$, and those obtained from pore models, $d_{MODEL}$, assuming a known pore thickness, $L$, discussed below. Using a continuum model applicable for bulk behavior in nm-size and larger diameter solid-state pores, conductance $G$ can be well-described for solid-state pores:

$$G \approx \sigma \left( \frac{4L}{\pi d^2} + \frac{1}{d} \right)^{-1}$$  

(2)

where $\sigma$ is conductance of the solution that depends on the molarity, $d$ is effective pore diameter (assuming circular pores), and $L$ is the effective pore thickness; $d$ and $L$ correspond to the effective dimensions of the ionic conducting cylindrical channel. As $d$ and $L$ approach zero, ions are confined in spaces of dimensions comparable to ionic radii, and the ion concentrations, mobilities, and hydration are theoretically different from bulk.\(^{12,26,30}\) Perez et al.\(^{26}\) recently proposed an analytical expression similar to eq 2, based on inputs from MD simulations, for small MoS$_2$ pores, but with a modified multiplication prefactor $\sigma$ in eq 2, to reflect the reduced K$^+$ and Cl$^-$ ion concentrations and mobilities compared to bulk (see the equation in SI section 5). In other words, for small pores, the authors proposed that one can consider that a small pore has a modified conductivity compared to bulk, and eq 2 can be modified by replacing $\sigma$ with another function of diameter, $\sigma_{pore}(d) \neq \sigma_{bulk}$. For an effective MoS$_2$ pore diameter of around 1 nm, the ion mobility was computed to be about 60% of bulk mobility, and ion concentration to be about 30% of bulk concentration.\(^{26}\)

In eq 2, the total resistance $R = 1/G = R_{pore} + R_{access}$ where $R_{pore} = (\frac{4L}{\pi d^2})$ is the resistance of the pore, which is modeled as a cylinder. The second term, $R_{access} = (\frac{1}{\sigma_{eff}})$ is the so-called “access” resistance, arising from the solution in the top and bottom hemispheres on the two sides of the membrane.\(^{61,62}\) In our case, the effective pore diameter, $d$, and the effective pore length, $L$, are comparable (both ~1 nm). For $L = 0.7$ nm,\(^{4,13}\) (the geometric thickness of the MoS$_2$ membrane) up to $L = 1.6$ nm estimated from previous MoS$_2$ pore conductance measurements on larger diameter pores.\(^{24}\) For the effective diameter estimates here, we use $A_{TEM} \sim 0.22$ nm$^2$ to 0.59 nm$^2$ and $A_{Model} \sim 0.34$ nm$^2$ to 1 nm$^2$, yielding $d_{TEM}$ from ~0.53 nm to ~0.87 nm and $d_{MODEL}$ from 0.65 to 1.12 nm. The pores could be thicker if there is contamination and have larger diameters if they expanded over time.

From measured conductances, $G_{meas}$, we can estimate the equivalent pore conductivities that would yield these conductances, a perspective proposed by Perez et al.\(^{26}\) to view sub-5 nm diameter MoS$_2$ pores, as

$$\sigma_{pore} = \frac{4L}{\pi d^2} + \frac{1}{d}$$

(3)

where $G_{meas}$ is the measured conductance, $d$ is the diameter, and $L$ is the pore thickness. Using measured conductance from 0D pores, a range of pore diameters from AC-STEM images, from corresponding pore models and $L$ values from 0.7–1.6 nm,\(^{2,24}\) we calculated $\sigma_{pore}$ plotted for various salt solutions and concentrations in Figure 5d.\(^{59,60,61,62}\) Therefore, error bars in Figure 5d reflect uncertainties in $d$ from our analysis. Errors are plotted using the ranges of $d_{TEM}$ and $d_{MODEL}$ for $d$ and the range from 0.7 nm to 1.6 nm for $L$.

For comparison, also plotted in red symbols are the corresponding bulk conductivities for each solution. Our results at 1 M KCl display $\sigma_{pore}/\sigma_{bulk} = 25–65\%$ (for 0.53–0.87 nm diameter pores), which also somewhat agrees with the trend from MD simulations for sub-5 nm MoS$_2$ pores where they reported 8–40% (for 0.7–1.25 nm diameter pores).\(^{26}\)

The conductance values observed are a bit smaller than 1 nS and similar across different concentrations and cations (K$^+$, Li$^+$, Mg$^{2+}$). Furthermore, $I-V$ characteristics are nonlinear, although nonlinearities are mostly pronounced for higher voltages (Figure 5c). While hydrophobicity can lead to such observations as discussed above, another contributing factor in small pores is the spatial confinement and interactions experienced by the salt ions when the pore is of the similar size to the size of the hydrated salt ions. This has also been shown in other MD simulations where dehydration of the first hydration layer and orientation of water dipoles inside and outside the pore dictate the type of nonlinearities observed in these small measurable currents.\(^{3}\) Further, Richards et al.\(^{17}\) showed that ion transport is hindered when pore size is comparable to dimensions of hydrated ion molecules and that partial dehydration is the main factor for energy barriers.\(^{17,63}\) Ion selectivity of pores is another aspect that has been experimentally investigated, such as in cation-selective sub-nm graphene pores.\(^{10}\) but the available body of reproduced experimental work is limited.\(^{12}\)

**Saturation of Conductance vs Molarity.** We observe a saturation in conductance across 3 M to 0.01 M KCl and other salt solutions. For larger, nanometer size solid-state pores, this saturation in KCl solution was previously observed to occur for molarities below ~0.1 M.\(^{21,64}\) This molarity corresponds to Debye length, $\lambda_D \approx 1$ nm for 0.1 M KCl, equivalent to about four water molecule diameters, and $\lambda_D \approx 3$ nm for 10 mM KCl. We see that for a 0D pore ($d < 1$ nm) the saturation of $G$ with decreasing molarity, $M$, occurs at higher molarities than for one order of magnitude larger nm-size pores. This is likely because the characteristic pore size $d$ is now comparable to $\lambda_D$, even at relatively higher molarities such as 1–3 M KCl, where $\lambda_D \approx 0.1–0.3$ nm, explaining why we observe similar conductance for 3 M and 10 mM KCl.

At low molarity ~0.1 M KCl, we observe in Figure 5d that conductance is similar or larger than expected from the corresponding bulk value and assuming an idealized inert transport channel governed by eq 2.\(^{65}\) This is because eq 2 does not take directly into account that pores have charged surfaces (although this is effectively taken into account in eq 3 by assuming some equivalent pore conductivity, $\sigma_{pore}$). For “large”
pores, the pore’s surface charge effect on \( G \) can be negligible given that surface charges are screened within Debye’s length \( \lambda_D \approx 0.3 \text{ nm} \) in \( 1 \text{ M KCl} \). It was previously established that as the system size decreases approximately below micron and nm-scales, the surface charge effects on \( G \) can be noticeable on ionic transport at molarities below \( \sim 0.1 \text{ M} \), and transport can even become fully governed by surface charges in nanofluidic channels in very “small” systems and/or very “low” molarities.\(^{65} \)
The lower the molarity, the larger the size of the channel for which surface charge effects on \( G \) are noticeable.

In nanofluidic channels, as molarity \( M \) decreases, conductance transitions from a regime where \( G \sim M \) to the regime where \( G \) saturates as a function of \( M \) at low molarities.\(^{65} \) This dependence was established experimentally in silicon nitride (see for example SI in ref64) and 2D pores, with negative surface charge densities of the order \( \sim 0.01 \text{ C/m}^2 \) to \( \sim 0.1 \text{ C/m}^2 \) reported\(^{51} \) for MoS\(_2\) pores with diameters \( d > 2 \text{ nm} \) by fitting \( G \) vs \( M \) and dependent on pH. This “low-molarity transport behavior”, where the definition of what is “low” depends on the system size, is explained by electrostatic effects of the channel’s surface charge on the fluid. The smaller the system, the higher the molarity at which this saturation occurs: a charged pore surface attracts oppositely charged counterions from solution while repelling co-ions. This results in a charged layer forming close to the pore walls, called the double layer, and this layer screens the immobile surface charge. To maintain charge neutrality, the number of mobile counterions in a channel can exceed the bulk ion concentration and dominate transport.\(^{65} \)

Low conductance presents an experimental challenge in general and specifically for higher bandwidth measurements, requiring capacitance minimization to reduce noise and current contributions from capacitor charging. Compared to 0D MoS\(_2\) pores supported on Si chips (Figure 1), pores fabricated on low-capacitance glass chips\(^{66,67} \) exhibited a lower noise, but our initial attempts yielded significantly higher polymer contamination (see Supplementary Figures S4 and S5). Future studies will benefit by using low-capacitance platforms combined with low-noise transimpedance amplifiers\(^{64-67} \) to get insight into the short time-scale behavior of both ion channels and 0D solid-state pores, such as to resolve short current events and probe the mechanisms of the channel on/off dynamics.\(^{66} \)

**CONCLUSIONS AND FUTURE DIRECTIONS**

With the help of the state-of-art transmission electron microscopy and advancement of 2D material devices, we report an elaborate device fabrication of single zigzag-armchair 0D pores which have definite pore edges and known initial atomic composition of pore edges. In this regime of sub-nm pores, we observe that the conductance of a 0D pore is largely independent of bulk conductivity and dependent on the applied bias to drive ions through the pores. We observe a quenched ionic conductance (\( \sim 0.8 \text{ nS} \)) compared to nm-scale pores in the case of pores with the diameters similar to the size of hydrated salt ions, and the conductance saturation vs molarity in a wide ion concentration range. This conductance is close to values recently reported in other solid-state atomic-scale systems where ion transport was confined to \( \sim 1 \text{ nm} \) in one or more dimensions, such as in single 0.8 nm and 1.5 nm diameter, 10 nm-long CNTs.\(^{67,12} \)

Blockade of ion passage by small pores and dehydration of solvated ions were hypothesized as mechanisms to explain experimentally observed suppressed ionic current at low voltages and nonlinear \( I-V \) curves as voltage is increased.\(^{2,5} \) We are now able to fabricate 0D pores that mimic the biopores, with good reproducibility and similar ionic conductance (\( \sim 0.6-1 \text{ nS} \)) to that of protein pores that occur naturally.\(^{69,70} \) Another important aspect of these biological pores is their transport mechanisms and selectivity for specific cations or anions. This feature is yet to be studied in 0D, and future experiments can investigate conductance at various pH and attempt to modify the surface charge of these 0D pores. Further, studies can also attempt AC-TEM imaging of the pores after the ionic measurements and examine the extent to which these measurements result in some geometrical and compositional changes of the pore.

Several limitations existed in our study. TEM images correspond to pores before ionic measurements, and we were not able to image the pores after the ionic measurements. Also, because the membrane is contaminated after being in a salt solution, the baseline ionic current was established from pristine membrane samples (with no intentional pores) that are not the same samples used for pore TEM drilling, although all samples came from the nominally identical batch of membranes (from the same CVD growth) and the same fabrication procedures.

Pretreatment with ethanol here is seen to enhance the pore hydrophilicity and enable measurements of small but measurable currents through the pore. Studies have proven that the methanol or ethanol/water solvent mixture changes the dielectric constant of the solution, which could alter the surface charge on the pore in a favorable way to allow ions to translocate.\(^{72} \) This wetting technique aided by an alcohol is being used by several experimental studies already on 2D nanopores and nanochannels.\(^{5,6,24,29,44} \) So far, our experimental investigation leads to the conclusion that wetting the pore is possible through a polar solvent such as ethanol, which is important for translocating ions through the entirety of the zigzag-armchair pore. Future studies may design pore edges to further control ion translocation through the pores and maybe, also guided by MD simulation studies, address pore composition, stability, and transport.

**METHODS**

**CVD Growth.** Monolayer MoS\(_2\) flakes were grown using CVD processes reported in previous works.\(^{30} \) Solutions of 0.2% sodium cholate growth promoter and 18 × 10\(^{-3} \) M ammonium heptamolybdate were spun onto piranha-cleaned Si substrates coated with 300 nm of SiO\(_2\), which were then loaded into the center of a 1 in. tube furnace (Thermo Scientific Lindberg/Blue M). For the MoS\(_2\) growth, samples were heated under \( \text{N}_2 \) gas flow (700 sccm) at a rate of 70 °C min\(^{-1} \) and held at 750 °C for 15 min. Approximately 100 mg of sulfur precursor placed 22 cm from the substrates was kept at 180 °C during the growth procedures. Samples were rapidly cooled to room temperature by opening the furnace.

**Device Fabrication.** MoS\(_2\) crystals were transferred from Si/SiO\(_2\) substrates with a FIB hole (~150–200 nm in diameter) using a wet etch technique. Crystals were first coated with C4 PMMA, while an aqueous 1 M KOH solution was used to etch away the underlying substrate. After being washed in deionized (DI) H\(_2\)O, crystals were scooped onto TEM grids and dried for 30 min. Polymer liftoff and sample cleaning were performed using acetone and rapid thermal annealing in Ar/H\(_2\) gas at 300 °C, respectively. While tears and other failure modes of membranes and pores are possible, we have optimized our procedure to have continuous triangular flakes of MoS\(_2\) that are sealed to the supporting chip by annealing. When there are tears, the measured current is significantly larger, for example, for pores larger than 1 nm in diameter, the current is in the tens of nA’s and for larger tears orders of magnitude more. We had a few samples that clearly broke as evidenced by a sudden surge of current, followed by...
confirmation in microscopy. The small magnitude of current is an indicator of two possible outcomes: either the conducting pore is small or the membrane and/or pore are not fully wetting to allow maximum current flow based on pore size.

**Pore Fabrication and Imaging.** Sub-nm MoS₂ pores were fabricated and imaged using a Cs-corrected JEOL ARM 200CF STEM operating at 80 kV. The spherical aberration coefficients were generally Cs ∼ 100 nm. Pores were drilled by switching the instrument with a 22 pA probe current to selected area (1 × 1 nm) exposure and monitoring the radiolysis process. After approximately 10 s, the instrument was switched back to full scan (13 × 13 nm). Images were obtained using a HAADF detector with a collection angle of 54°–220 mrad and 10 cm camera length. Only one image was acquired after pore drilling to minimize beam-induced knock-on damage.

We note that TEM images provide structural information only for the initial, as-fabricated pores in vacuum, prior to any I–V measurements. This presents a limitation here as well as previous nanopore studies where it was experimentally challenging to locate and image the pores after ionometric measurements. Previous similar individual pore studies have not measured the pore diameter directly. It is possible and likely that once the pores are taken out of vacuum and immersed in solution, their structure can change and these changes can include pore clogging as well as pore etching over time in salt solution. Moreover, these changes could be amplified by the applied electric field to enlarge the pores. Here, we limit the applied voltage to 0.1 V, and we also calibrate our conductance values using results from larger 2D pores as expected upper bounds for our sub-nm pores (<1–10 nS). A conductance larger than 1 nS may strongly indicate that the pores have expanded beyond 1 nm in diameter over the course of handling and measurements.

There can be several complications in device fabrication. While we did not probe the extent of debris, we observed that annealing is critical to seal the membrane to prevent leakage or lift off from the supporting chip in ionometric solution. The amount of measured ionometric current is a guiding indicator of the degree of holes or current paths. We did not observe membranes lifting off, but we observed pore expansions and increases in ionometric current if higher voltages are applied.

**Pore Diameter Determination.** The geometric models (Chart 1 and pore schematic in figures) were carefully created based on the missing atoms observed in TEM images and the 3D view such as in Figure 2f. These models do not consider the electron cloud space or the orbital distance which can perhaps be accounted for through MD (not employed here). Additionally, we assume that the pore edges follow a perfect lattice from which the missing atoms are simply cut out. In the real TEM images, however, we see that there can be lattice distortions and bunching of Mo atoms, such that the distances between atoms along the edge can vary and be slightly shorter or longer than in the perfect lattice. Furthermore, in the real pores, there is a consistent uncertainty in the number of S atoms spatially along the pore edges due to the weaker intensity of S atoms produced, in contrast to heavier Mo atoms that are bunched up on the edges, such as in Figure 1f.

**Ionic Measurements.** EPC-10 HEKA amplifier setup5 with Ag/AgCl electrodes was used to perform ionometric measurements on our devices. One M KCl and other salt solutions (with 10 mM EDTA and 1 mM Tris; measured solution conductivity = 11.18 S/m for 1 M KCl, pH 8.7) were prepared using DI water, and the conductivity and pH were measured with Accumet XL-20 pH conductivity meter. Similar measurements were also conducted for glass chips4,26 but on the Chimera amplifier setup with higher bandwidth (1 MHz). Prior to ionometric measurements, the device was annealed at 300 °C in an Ar:H₂ environment for 90 min. The device was then immersed in a 50% water–ethanol solution typically for 15–30 min, which we empirically found to help wetting and formation ofionic channels through the pores. Some samples were immersed for longer times from 3 to 5 to 12 h. The device in ethanol was intermittently bubbled in the solution with the glass pipet to ensure no air bubbles were left trapped in the device. Voltage (V) was applied across the pore while measuring the ionometric current (I). Voltage bias was kept below ±0.1 V for most pores in this work. A custom-built LabView Software was used to run experiment on a Heka amplifier, and I–V sweeps and time-trace features of this program were utilized. A majority of the I–V measurements involved a sweep rate of 5 mV/s, and a 10 mV/s was used for faster acquisition. All I–V sweeps were offset to start at zero and were averaged in cases of multiple I–V sweeps. “Pristine membranes” (membranes without holes) are control devices and not the same devices used to drill pores. It was challenging for us to measure in a salt solution and then use the same membrane again to drill the pore and remeasure in solution. This is because the membrane is often contaminated from the salt solution and there are additional possible failure modes such as membrane breaking during handling. Therefore, we rely on control samples (membranes without drilling) to establish the baseline current and on samples with drilling to establish the current through the pore, which may include some contribution from any defects in the pristine membrane. Because these are not the same samples, this presents a limitation of the present study.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsnano.0c04716.

Conductance of 0D pores, samples containing multiple (2–3) sub-nm MoS₂ pores, current—voltage and noise characteristics of sub-nm MoS₂ pores on low-capacitance glass chips, image processing to determine the TEM pore area and diameter, MD simulation-based analytical equation26 for sub-5 nm diameter MoS₂ pore conductance in 1 M KCl (PDF)

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Author Contributions
J.P.T., P.M.D., and M.D conceived the project idea. J.P.T. and P.M.D. grew 2D materials, fabricated devices, and performed image analysis. J.P.T. performed ionic measurements and data analysis. P.M.D. conducted the AC-TEM work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare the following competing financial interest(s): M.D. is consultant and founder of Goeppert (www.gppert.com), that is manufacturing nanotechnology-related products including solid-state and TEM chips, and 2D materials.

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