

Peer Review File

In Situ Generation of (Sub)Nanometer Pores in MoS₂ Membranes for Ion Selective Transport



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Liu et al. reported an electrochemical etching method to create subnano-to-nanometer pores on MoS₂ films. The pore density could be controlled by altering the etching voltage pulses. The pore sizes and morphology were well characterized and the ion transport properties of the pores were investigated under monovalent and divalent metal chloride electrolytes. The subnanometer pores showed a weak monovalent over divalent metal ion selectivity. Overall, it is very interesting to see the advance of this work to achieve controllable pore creation on 2D nanosheet materials. Some comments about the pore stability and feasibility of the etching method are given as follows.

1. The authors claim the method generates pores in MoS₂ membranes. However, it is unclear what area of the membrane that this method could be applied. The membrane usually means it has a large area. It would be better to give some data to verify that large-size porous membranes can be fabricated by this method.
2. As the electrochemical etching method for creating pores on MoS₂ nanosheet has been reported previously, the authors should clearly demonstrate the conceptual advances of this work in the introduction part.
3. How about the mechanical properties of the etched MoS₂ membranes? Especially, when it has a high pore density.
4. In Figures 3a-c, the I-V curve shown in 3b indicates a much lower selectivity than the conductance ratios in 3a, and normalized conductance values of the three devices showed very different and low KCl/MgCl₂ selectivity. It would be better to give I-V curves of the devices in supporting information and explain these differences in the manuscript.
5. How about the pore stability? Can it be enlarged during ion current measurement? It would be better to do the cyclic test of the pore conductance under different electrolyte solutions.

Reviewer #2 (Remarks to the Author):

This work reports nanoporous membranes using polycrystalline MoS₂ which exhibit 'remarkable' selectivity for small monovalent and divalent cations. The paper has demonstrated some interesting results. However, the novelty of the work is limited as the pore creation method is not new and the selectivity is not a surprising finding. I cannot recommend its publication in Nature Communications.

I have the following comments:

1. (page 2) the selectivity (the higher permeance of one ion relative to all others) of nanoporous 2D material membranes for monovalent ions (K⁺, Li⁺, Na⁺ and Cs⁺) has remained around two (after accounting for trends in bulk mobility). This work compares K⁺, Li⁺ and Na⁺, and Cs⁺ is not found. Is there any interesting phenomenon with Cs⁺?

2. (page 2) Here we develop a new in situ fabrication method to generate (sub)nm pores with tunable pore size and density by applying a transverse electric field across polycrystalline membranes. This method has been put forward in 2015 (Nano Lett. 15, 3431–3438, 2015). Please show the difference between them.
 3. (page 3) For CVD-MoS₂, as the bias voltage exceeds the threshold value of 0.4-0.5 V, the ionic current through polycrystalline MoS₂ increases rapidly and irreversibly. Usually, MoS₂ is stable under 0.5 V, why the ionic current through polycrystalline MoS₂ increases rapidly for CVD-MoS₂?
 4. (page 6) In figure 2a/2d, there are lots of nanopores, but in Supplementary Table 1, why the conductance is only about 2-228nS?
 5. (page 7) The mechanism of this qualitative shift is elucidated by observing that the presence of Mg²⁺ in a mixed KCl/MgCl₂ solution suppresses the conductance of K⁺ (Fig. 3 f), indicating that Mg²⁺ is adsorbed on or is stuck inside the MoS₂ membrane. Mg²⁺/Ca²⁺ may block the MoS₂ nanopore, how did this problem solve? If nanopore is blocked, the selectivity cannot be compared. And the discussion of Ca²⁺ is not mentioned in the main text.
 6. Are there any results for the Ion Transport experiment with single nanopore? Because the pores in one device varies a lot, maybe single pore will be clearer to demonstrate the results.
 7. Similar to point 5, why the discussion of Ca²⁺ is not mentioned in MD simulation?
 8. The data of Mg and K in 15 devices are showed in Supplementary Table 1. Other reproduced results of other cations should be showed as well.
 9. Does thickness of Mo seed thickness effect the selectivity?
- Other details:
1. Please check the units. For example, in Supplementary Table 1, there is no unit for thickness and voltage.
 2. The conclusion part can be fleshed out.

Reviewer #3 (Remarks to the Author):

General points:

The paper is extremely well organised and written, in fact this is one of the better written manuscripts I have had the pleasure of reviewing. My congratulations (and thanks) to the authors.

The authors present a method for the in situ fabrication of a high-density array of nanopores in the range of 5Å to a few nm. The pores in the resulting membranes can subsequently be tuned in a controllable fashion.

The authors go on to explore conductivity and selectivity of the membranes produced here. Their membranes (in particular those with lower conductances/smaller pores) show a very high degree of selectivity. This high degree of selectivity, combined with the high flux (conductivity) arising from the density of the nanopore array, puts these membranes in a very interesting position. The authors

then use MD simulations (outside my expertise, but it all seems very reasonable) to explore the mechanism of this ion selectivity.

I think that this is an extremely thorough study. The data presented within the main text is sufficient to support the authors' main points/arguments. The supplementary info covers/provides an additional level of detail.

I would be happy for the manuscript to be published as is, the points below are simply minor suggestions that slightly improve the work.

Given the in situ pore formation methodology described here, I find it slightly surprising that the authors do not acknowledge the work of Vincent Tabard-Cossa's lab in developing, and first reporting, the CBD methodology (pore formation and expansion), in particular "Nanopore Fabrication by Controlled Dielectric Breakdown" (Kwok et al, 2014). Because of the multiple pores formed and the in situ methodology, I feel that "Fabrication of multiple nanopores in a SiNx membrane via controlled breakdown" (Wang et al, 2018) is also a relevant reference. Reference 46 should possibly be given more prominence too.

Specific points:

- In Fig 3a - I suggest that you number the devices in the plot. It is possible to work it out which is which from the data in SI table 1, so why not make it easier?

- The legend to Fig 4 contains a typo (the only one I found). "A single pore (c) is drilled in the center of the all MoS₂ films" should (presumably) read "A single pore (c) is drilled in the center of all the MoS₂ films".

Reviewer Comments for:
In Situ Generation of (Sub)Nanometer Pores in MoS₂ Membranes for Ion
Selective Transport

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REVIEWER COMMENTS AND AUTHOR RESPONSE

Reviewer #1 (Remarks to the Author):

0. Reviewer comment

Liu et al. reported an electrochemical etching method to create subnano-to-nanometer pores on MoS₂ films. The pore density could be controlled by altering the etching voltage pulses. The pore sizes and morphology were well characterized and the ion transport properties of the pores were investigated under monovalent and divalent metal chloride electrolytes. The subnanometer pores showed a weak monovalent over divalent metal ion selectivity. Overall, it is very interesting to see the advance of this work to achieve controllable pore creation on 2D nanosheet materials. Some comments about the pore stability and feasibility of the etching method are given as follows.

0. Author response

We thank the reviewer for the positive assessment of our work, and the detailed comments and questions. We have found them very helpful in improving our work, revising the text as well as performing additional experiments to supplement our findings.

1. Reviewer comment

The authors claim the method generates pores in MoS₂ membranes. However, it is unclear what area of the membrane that this method could be applied. The membrane usually means it has a large area. It would be better to give some data to verify that large-size porous membranes can be fabricated by this method.

1. Author response

The feasibility of scale-up for the polycrystalline MoS₂ membranes investigated here is one positive attribute of our system. We are able to grow films on the centimeter scale, limited only by the CVD-furnace in our lab; with larger growth chambers even larger films can be made⁸².

These films can, furthermore, be transferred to porous polymer films; not only can we grow these films, but they can also be transferred easily to arbitrary substrates. To demonstrate, we have added additional data demonstrating the transfer of the as-grown films to track-etched polycarbonate membranes. In **Supplementary Fig. 3**, we include newly acquired data demonstrating the scale-up potential of the CVD-MoS₂ membranes. In **Supplementary Fig. 3 a-b**, we show optical microscope images of a ~1 cm x ~1 cm CVD-MoS₂ film suspended over the porous polymer.

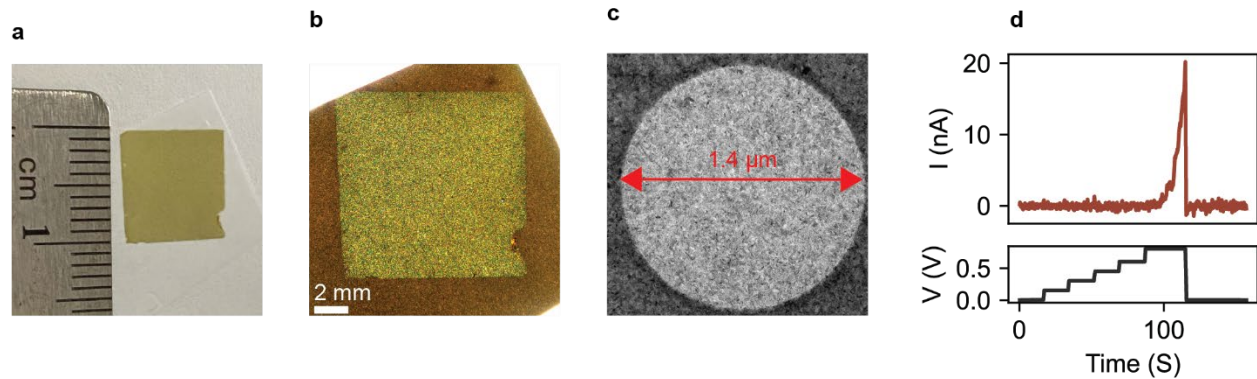
The ionic and molecular transport properties of porous 2D material membranes are commonly tested over nanometer-scale areas, due to the frequent presence of defects such as uncommonly large pores, cracks, and wrinkles^{7,32,83}. However, we show that the polycrystalline films can be tested over large-scale apertures (**Supplementary Fig. 3 c-d**), for which the films display similar pore-creation behavior. As the grain size (~5 nm) is much smaller than the aperture size employed in most of our tests (~300 nm), similarity between devices with different apertures is expected. In future tests we could test the transport properties of even larger films suspended over large areas, like the membranes shown in **Supplementary Fig. 3 a-b**, but to do so we would need to implement defect-sealing techniques⁸⁴.

1. Text revision

The following is added to the main text on page 3.

We choose sub-micron apertures for all experiments below, but we note that the transfer method and pore fabrication methods reported here are scalable to significantly larger areas. The CVD-MoS₂ films, despite the large density of grain boundaries, can be suspended over large-scale apertures (**Supplementary Fig. 3**).

The following is added to the supplementary materials.



Supplementary Fig. 3. Demonstration of large-area transfer of CVD-MoS₂. MoS₂ is grown on cm-scale SiO₂ coupons; the entirety of these films can be transferred to arbitrary substrates, and pores can be fabricated over micron-scale apertures. (a) cm-scale CVD-MoS₂ on track etched polycarbonate films, with ruler for scale. (b) Optical microscope image of the same film, to show continuity. (c) TEM image of CVD-MoS₂ film, after electrochemical pore creation, suspended over a micron-scale aperture. 15 nm Mo seed thickness is chosen to enhance the contrast of pores (d) IV trace of pore in c, showing typical pore creation behavior in CVD-MoS₂ films.

2. Reviewer comment

As the electrochemical etching method for creating pores on MoS₂ nanosheet has been reported previously, the authors should clearly demonstrate the conceptual advances of this work in the introduction part.

2. Author response

The reviewer is correct in identifying that a more explicit differentiation of our work from that done previously is needed in our text. We have added such a discussion to our introduction, copied below. In essence the novelty of our work is premised on a few key components:

1. The fabrication of a dense array of pores with (sub)nanometer sizes require an applied electric field, but also grain boundaries. Our method highlights the potential of designing materials with precisely controlled nanoscale topography for manipulating pore generation, as opposed to the single nanopores in pristine single crystals of the two-dimensional material.

2. The use of polycrystalline MoS₂ with nanoscale topography allows for the fabrication of pores in few-layer films (past a critical thickness to enhance ion selectivity), which we find is not feasible in their single-crystal counterparts. In CVD-MoS₂, pores are formed gradually at relatively low voltages (~0.5 V).

For multilayer, single-crystals, pore creation happens at high voltages (nearly 2 V) rapidly and uncontrollably.

3. The discovery that few-layer MoS₂ is ion selective, whereas monolayer MoS₂ fails to differentiate both mono and divalent ions from each other (MD simulation results in our paper). The monovalent and divalent ion selectivity in this work is among the highest for two-dimensional materials to date.

4. The elucidation of the ion selectivity mechanism, being closely tied to the sluggishness of the water confined to the MoS₂ nanopore. This is an additional novel point to our work that we provide with MD simulations to explain the mechanism behind the selective ion transport, which is important to guide future membrane design.

2. Text revision

Main text page 2

Previous work has shown that nanometer-scale pores can be formed electrochemically in two-dimensional materials, such as MoS₂ and graphene^{38,39}. Single pores, as well as porous membranes, can also be formed electrochemically in thin films such as SiN, although the mechanism in this case differs from that in two-dimensional materials such as MoS₂^{40–42}. For SiN, the application of large voltages leads to a sudden *controlled dielectric breakdown*, resulting in localized heating and subsequent material degradation. In MoS₂, the application of order-of-magnitude smaller voltages leads to a gradual localized electrochemical etching at specific hot-spots, likely grain boundaries or sulfur vacancies³⁸.

In all previous accounts with two-dimensional materials, the pores are formed one at a time, which is beneficial for certain sensing applications⁴³, but could be a shortcoming for ion-separation membrane fabrication. Here, we demonstrate for the first time that, with the nanoscale features of polycrystalline MoS₂, densely porous membranes can be fabricated *in situ* with sub-nanometer control. Furthermore, we demonstrate that pores in multi-layer films can be formed electrochemically, whereas in previous studies only monolayers were used. We show that pore creation in single-crystal, few-layer MoS₂ is significantly more difficult to control.

4. Reviewer Comment

How about the mechanical properties of the etched MoS₂ membranes? Especially, when it has a high pore density.

4. Author response

Two-dimensional materials are well-known for their excellent mechanical properties⁸⁵, but the reviewer is correct in identifying that these mechanical properties change upon the introduction of defects such as grain boundaries, vacancies and cracks⁸⁶. A thorough and quantitative investigation of the mechanical properties of porous, polycrystalline MoS₂ is beyond the scope of the present study. One qualitative test, however, of the strength of the CVD-MoS₂ films is their ability to freely suspend over large-area apertures.

Here, we have made apertures of various sizes (from 3 to 21 μm) and found that the MoS₂ films can be freely suspended over all these apertures, despite their nm-scale thickness. Based on the wrinkling and bending observed in the scanning electron microscopy images, the films behave qualitatively similarly to pristine two-dimensional materials, retaining some of their flexibility and sheet-like behavior⁸⁷. We have

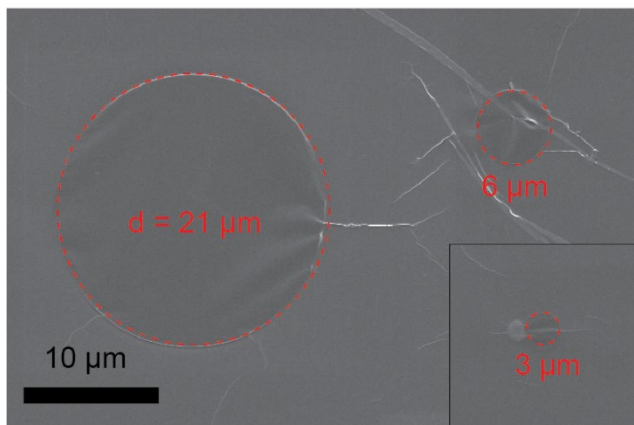
included a brief note on the mechanical properties of the MoS₂ films in the Supplementary Information, including the data for suspended MoS₂ over large apertures, copied below.

5. Text revision

Main text page 3

The CVD-MoS₂ films, despite the large density of grain boundaries, can be suspended over large-scale apertures (**Supplementary Fig. 3**).

Supplementary information



Supplementary Fig. 3 (continued) CVD-MoS₂ films transferred to SiN substrates with a variety of apertures. Due to the superiority of the mechanical properties of 2D materials, CVD-MoS₂, despite its nanometer-scale thickness and high density of grain boundaries, can be suspended freely over apertures from < 1 to at least 20 μm.

4. Reviewer Comment

In Figures 3a-c, the I-V curve shown in 3b indicates a much lower selectivity than the conductance ratios in 3a, and normalized conductance values of the three devices showed very different and low KCl/MgCl₂ selectivity. It would be better to give I-V curves of the devices in supporting information and explain these differences in the manuscript.

4. Author response

We appreciate the note that the data could be presented in a clearer form, and that the presentation of the I-V curves for all devices tested would be beneficial. The data shown in **Fig. 3 a** display a range of selectivity for KCl/MgCl₂ (from at least 20 down to ~1). The data presented in **Fig. 3 b** and **Fig. 3 c**, a subset of the devices in **Fig. 3 a**, display a narrower range (from 8 down to 2). The data presented are consistent with each other, although we agree with the reviewer the spread needs to be addressed, and the entirety of the data shown.

We have addressed these points as follows, following the reviewer's suggestions. First, we have added all the I-V curves for **Fig. 3 a** in **Supplementary Fig. 8**, and copied below. Second, we have added a brief note about the variation in selectivity in the main text. Finally, we have included **Supplementary Table 2** that includes data on all devices tested, not just those in **Fig. 3 a**. This table is copied below.

4. Text Revision

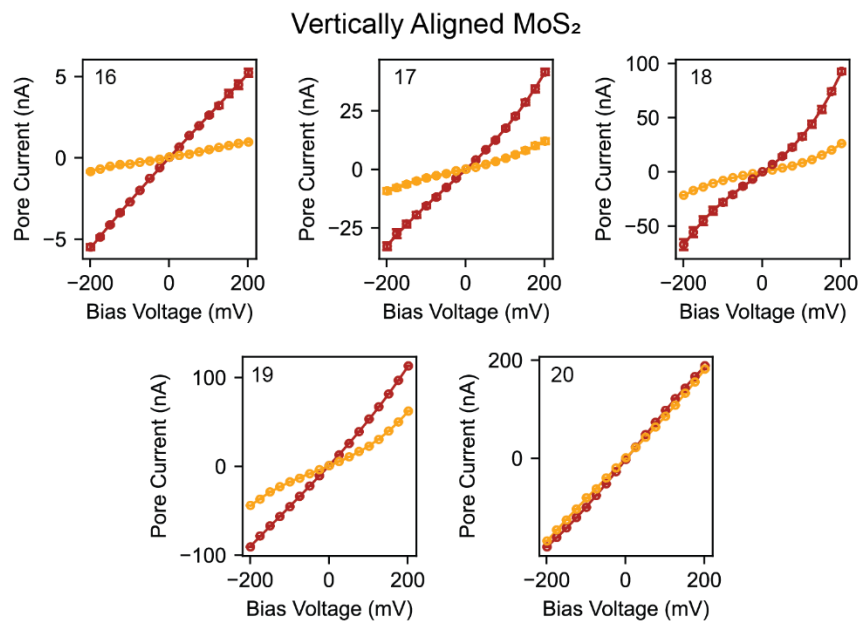
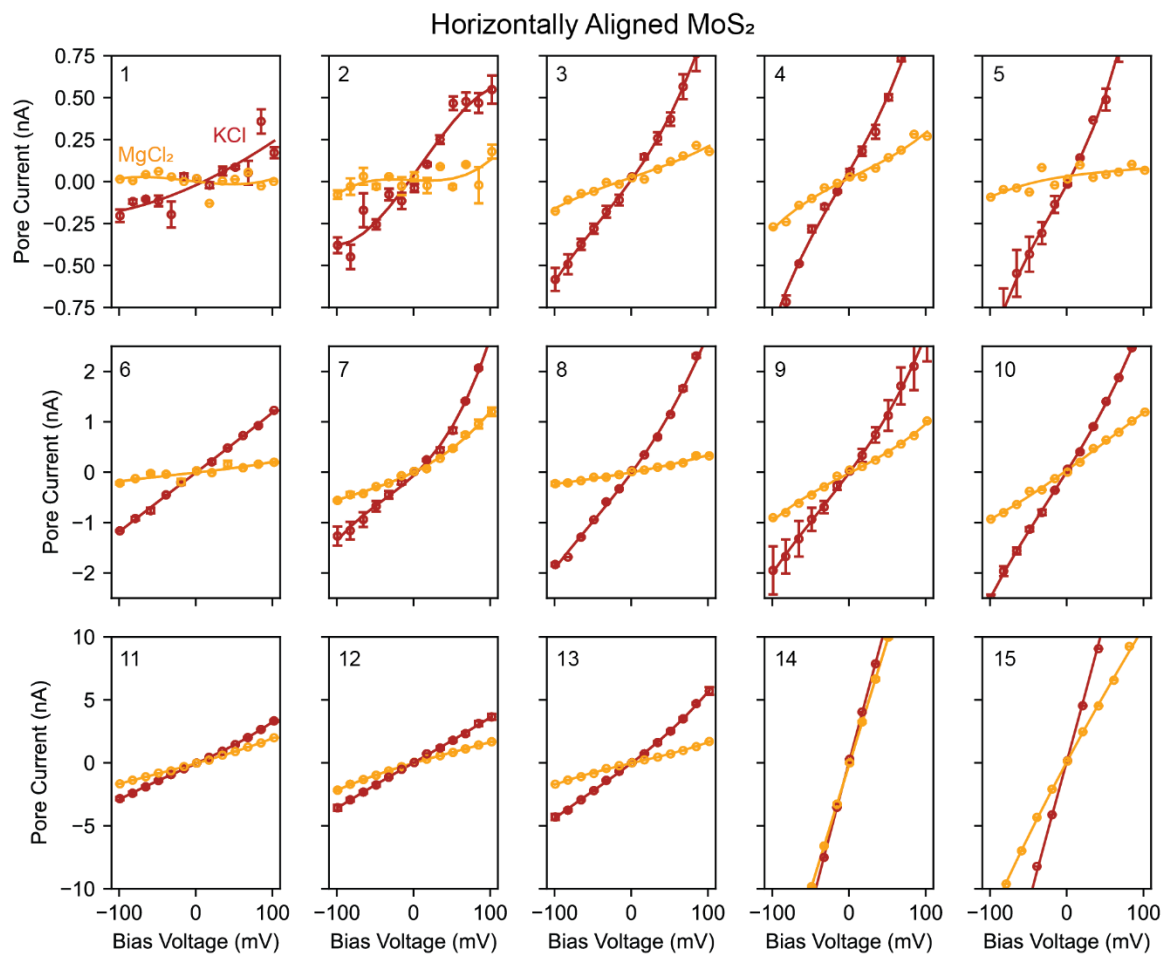
Main text page 2

Variation between devices generally can be ascribed to differences in pore size distributions as a result of the electrochemical etching process, which could be improved by controlling the domain uniformity of the CVD grown MoS₂ film. After pore generation, smaller pore sizes lead to both lower conductivities and higher selectivity, as discussed above in **Fig. 2**. Each device tested has a slightly different pore size distribution, and thus slightly different ion transport characteristics. I-V curves for all devices can be found in **Supplementary Fig. 8**, **Supplementary Fig. 10** and **Supplementary Fig. 11**.

Supplementary Information

	Ion transport data							Pore generation conditions		
	G _{KCl} (nS)	G _{NaCl} (nS)	G _{LiCl} (nS)	G _{CaCl₂} (nS)	G _{MgCl₂} (nS)	G _{CsCl} (nS)	G _{RbCl} (nS)	Pulse Voltage (V)	Pulse Time (mS)	Pulse Number
Device 8	23.4 (1.0)	15.3 (1.0)	6.6 (0.6)	4.6 (0.3)	3.15 (0.2)	-	-	1.5	10	1
Device 7	21.8 (2.0)	16.7 (1.6)	8.42 (0.9)	9.21 (0.9)	9.68 (0.7)	-	-	1.5	10	2
Device 12	37.1 (2.6)	26.4 (1.0)	15.8 (1.5)	25.3 (1.0)	19.23 (0.7)	-	-	1.5	10	2
-	80.0 (3.0)	-	-	-	-	48.0 (2.0)	86.0 (1.0)	2	10	2

Supplementary Table 2. Three horizontally aligned MoS₂ devices, of the 20 total devices tested for both divalent *and* monovalent salt selectivity. Another device is tested with KCl, CsCl and RbCl salts. Test conditions and results for these different devices, used to measure the selectivity of KCl, NaCl, LiCl, CaCl₂ and MgCl₂; or KCl, CsCl and RbCl. Standard errors for a given element in the table are included in parentheses. All Mo seed film thicknesses were 1.75 nm, and the salt concentration is 1 M. Current-voltage curves for these data are shown in **Supplementary Fig. 10** and **Supplementary Fig. 11**.



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Supplementary Fig. 1. I-V traces of KCl and MgCl₂ salts in CVD- MoS₂ nanopores. These data correspond to the 15 devices shown in **Fig. 3 a** (all horizontally aligned MoS₂ films tested for KCl and MgCl₂ selectivity), as well as the 5 vertically aligned devices (> 10 nm Mo seed thickness), displayed, along with the 15 horizontally aligned MoS₂, in **Supplementary Fig. 9**. Details for each device are tabulated in **Supplementary Table 1**. Data are collected using 1 M salts, except for devices 16, 18, 19 and 20, which were collected with 0.1 M salts. The pore current shown for these devices has been scaled by a factor of 10 to correct for this difference.

5. Reviewer comment

How about the pore stability? Can it be enlarged during ion current measurement? It would be better to do the cyclic test of the pore conductance under different electrolyte solutions.

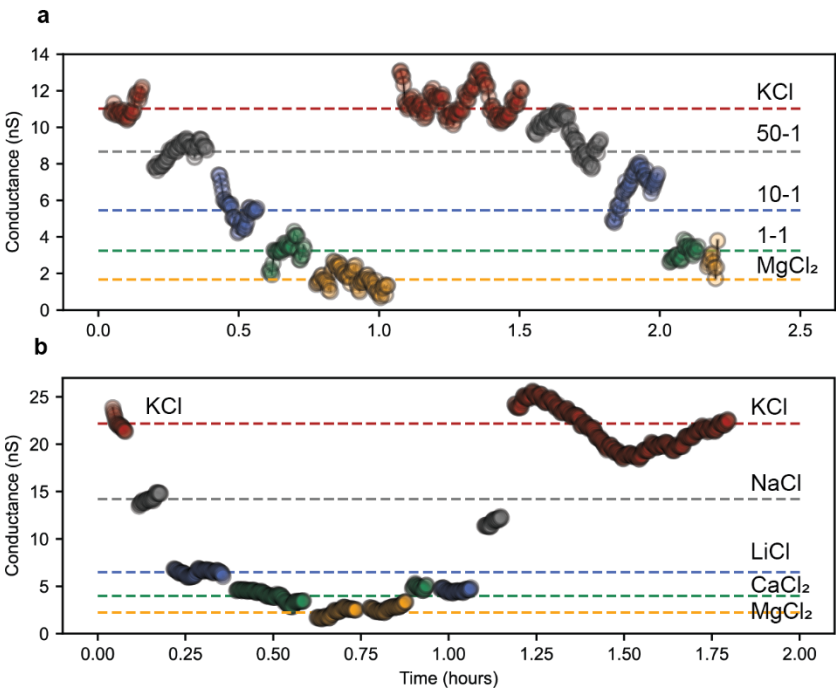
5. Author response

This is an excellent question; improving the stability of nanopores in two-dimensional materials is an active area of research⁸⁸. We find that during the time-scales relevant for our measurements (1-3 hours), the ionic conductance remains quite steady, although there are short timescale fluctuations. We have displayed these results as we cycled through different electrolyte solutions, in Supplementary Fig. 12, and below.

To improve stability, we restrict the voltage bias to low values (within 100 mV) to prevent degradation. We find, furthermore, extended tests with these membranes to be challenging due to pore fouling (sudden decrease in conductance) or rapid pore expansion (due to oxidation or mechanical stress).

5. Text revision

Supplementary Information



Supplementary Fig. 12. Time series for electrolyte cycling. Data shown over hour timescales, demonstrating pore stability. (a) Time series for cycling through electrolyte mixtures with different KCl/MgCl₂ molar ratios, corresponding to the data shown in Fig. 3 f, in the main text. (b) Time series for cycling through electrolyte mixtures for device 3 in Fig. 3 c, the device with the highest ion selectivity. Dotted lines represent average values for the first cycle.

Reviewer #2 (Remarks to the Author):

0. Reviewer comment

This work reports nanoporous membranes using polycrystalline MoS₂ which exhibit 'remarkable' selectivity for small monovalent and divalent cations. The paper has demonstrated some interesting results. However, the novelty of the work is limited as the pore creation method is not new and the selectivity is not a surprising finding. I cannot recommend its publication in Nature Communications. I have the following comments:

0. Author response

We thank the reviewer for their careful reading of our work, and for acknowledging the components they find interesting. We concur that a more direct exposition of the novelty of the work is needed, which we have added to the introduction and copy below for easier reference. In essence the novelty of our work is premised on a few key components (this discussion is also used to respond to Reviewer 1 above):

1. The fabrication of a dense array of pores with (sub)nanometer sizes require an applied electric field, but also grain boundaries. Our method highlights the potential of designing materials with precisely controlled nanoscale topography for manipulating pore generation, as opposed to the single nanopores in pristine single crystals of the two-dimensional material.

2. The use of polycrystalline MoS₂ with nanoscale topography allows for the fabrication of pores in few-layer films (past a critical thickness to enhance ion selectivity), which we find is not feasible in their single-crystal counterparts. In CVD-MoS₂, pores are formed gradually at relatively low voltages (~0.5 V). For multilayer, single-crystals, pore creation happens at high voltages (nearly 2 V) rapidly and uncontrollably.

3. The discovery that few-layer MoS₂ is ion selective, whereas monolayer MoS₂ fails to differentiate both mono and divalent ions from each other (MD simulation results in our paper). The monovalent and divalent ion selectivity in this work is among the highest for two-dimensional materials to date.

4. The elucidation of the ion selectivity mechanism, being closely tied to the sluggishness of the water confined to the MoS₂ nanopore. This is an additional novel point to our work that we provide with MD simulations to explain the mechanism behind the selective ion transport, which is important to guide future membrane design. We hope that our improvements to the text, along with the additional experiments and data analysis we add to the manuscript, can improve their judgement of our work.

0. Text revision

Main text page 1

Previous work has shown that nanometer-scale pores can be formed electrochemically in two-dimensional materials, such as MoS₂ and graphene^{38,39}. Single pores, as well as porous membranes, can also be formed electrochemically in thin films such as SiN, although the mechanism in this case differs from that in two-dimensional materials such as MoS₂^{40–42}. For SiN, the application of large voltages leads to a sudden *controlled dielectric breakdown*, resulting in localized heating and subsequent material degradation. In MoS₂, the application of order-of-magnitude smaller voltages leads to a gradual localized electrochemical etching at specific hot-spots, likely grain boundaries or sulfur vacancies³⁸.

In all previous accounts with two-dimensional materials, the pores are formed one at a time, which is beneficial for certain sensing applications⁴³, but could be a shortcoming for ion-separation membrane fabrication. Here, we demonstrate for the first time that, with the nanoscale features of polycrystalline MoS₂, densely porous membranes can be fabricated *in situ* with sub-nanometer control. Furthermore, we demonstrate that pores in multi-layer films can be formed electrochemically, whereas in previous studies only monolayers were used. We show that pore creation in single-crystal, few-layer MoS₂ is significantly more difficult to control.

1. Reviewer comment

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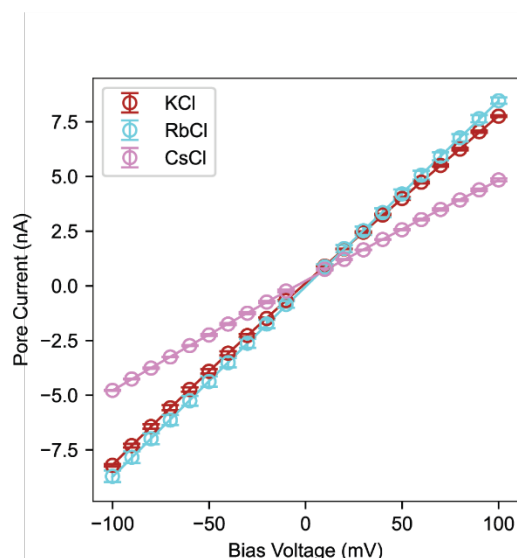
1. Author response

K⁺, Li⁺ and Na⁺ are the most common monovalent ions tested for nanoporous membrane experiments, with Cs⁺ being tested infrequently^{21,32,35,59}. We thank the reviewer for drawing our attention to the absence of a discussion of Cs⁺ in our text, and in response we completed measurements with both Cs⁺ and Rb⁺, to form a complete suite of monovalent ion selectivity (Supplementary Fig. 11) and revised the main text to include a brief note on this inclusion. Cs⁺ has a reduced conductance relative to K⁺, and Rb⁺ has a similar conductance to K⁺. These results are in line with previous studies on ion transport through nanoporous graphene membranes^{32,35}. The selectivity of Cs⁺ is off the trend of relative hydration energies for Cs⁺, Rb⁺, K⁺, Na⁺, Li⁺ as is commonly understood by the Hofmeister series. However, as reported by Fu *et al.*,³⁵ the real trend may be more complicated. Although our results are in line with previous work, we believe this result deserves additional study. Certainly, for more quantitative comparisons, further studies are warranted.

1. Text revision

Main text

We also test the relative conductance Cs⁺ and Rb⁺ in a separate device and find that the trend (reduced conductance for increased hydration radius) continues for Rb⁺ and matches previous work^{32,35} for Cs⁺ (**Supplementary Fig. 11**).



292

293 **Supplementary Fig. 2.** I-V traces for CsCl and RbCl salts. Curves shown for 1 M KCl, CsCl and RbCl
 294 through porous CVD-MoS₂. Test conditions are documented in **Supplementary Table 2.**

295 2. Reviewer comment

296 (page 2) Here we develop a new in situ fabrication method to generate (sub)nm pores with tunable pore
 297 size and density by applying a transverse electric field across polycrystalline membranes. This method
 298 has been put forward in 2015 (Nano Lett. 15, 3431–3438, 2015). Please show the difference between
 299 them.

300 2. Author response

301 We thank the reviewer for pointing out that additional explication of the novelty of our work is needed.
 302 We have responded to this point in above (0. Author response) and added additional explanation in the
 303 introduction to our text, also copied above.

304 3. Reviewer comment

305 (page 3) For CVD-MoS₂, as the bias voltage exceeds the threshold value of 0.4-0.5 V, the ionic current
 306 through polycrystalline MoS₂ increases rapidly and irreversibly. Usually, MoS₂ is stable under 0.5 V, why
 307 the ionic current through polycrystalline MoS₂ increases rapidly for CVD-MoS₂?

308 3. Author response

309 This is a good question, and one we attempt to address in the main text. We find that the breakdown
 310 threshold for CVD grown, polycrystalline MoS₂ is lower than that of mechanically exfoliated MoS₂. The
 311 threshold for single crystal MoS₂ is approximately 0.7 V, whereas for our samples we find it to be just
 312 under 0.5 V, with small variations between samples³⁸. We attribute this difference to the high density of
 313 grain boundaries in the polycrystalline samples. The etching rate at these grain boundaries is
 314 accelerated, as evidenced by transmission electron microscopy of vertically aligned films

315 (Supplementary Fig. 5). This interpretation is in agreement with studies on the morphological-
316 dependent oxidation of MoS₂^{88,89}.

317 4. Reviewer comment

318 (page 6) In figure 2a/2d, there are lots of nanopores, but in Supplementary Table 1, why the
319 conductance is only about 2-228nS?

320 4. Author response

321 Some of the darker regions in **Fig. 2 d** are thinner regions of MoS₂, as opposed to through-pores; and
322 some pores may appear larger due to thinner regions of MoS₂ surrounding the pore. High-resolution
323 STEM is used to calibrate the images to determine the real pore size distribution, as detailed in
324 Supplementary Section 3. According to our approximations, spelled out in **Supplementary Fig. 7**, the
325 ionic conductance of the nanoporous membranes tested here aligns well with the pore size distributions
326 measured *via* transmission electron microscopy. We also note that the MoS₂ membranes are multilayer,
327 and the ionic conductance decays dramatically with thickness, as reported in previous studies^{7,90}.

328 5. Reviewer comment

329 (page 7) The mechanism of this qualitative shift is elucidated by observing that the presence of Mg²⁺ in
330 a mixed KCl/MgCl₂ solution suppresses the conductance of K⁺ (Fig. 3 f), indicating that Mg²⁺ is adsorbed
331 on or is stuck inside the MoS₂ membrane. Mg²⁺/Ca²⁺ may block the MoS₂ nanopore, how did this
332 problem solve? If nanopore is blocked, the selectivity cannot be compared. And the discussion of Ca²⁺ is
333 not mentioned in the main text.

334 5. Author response

335 The reviewer brings up an interesting question, whether the selectivity can be compared between Mg²⁺
336 and K⁺, if the transport of one ion affects the other. We define selectivity in this work as single species
337 selectivity, that is the relative transport speeds of different ions in isolation, following the precedent of
338 previous works^{21,32}. This test format allows us to isolate the dynamics of individual ions, controlling their
339 interactions with other species.

340 The presence of inter-species coupling complicates the picture, as the reviewer mentions. Our data
341 shown in **Fig. 3** does indicate that the selectivity recorded in this work would not be identical to the
342 selectivity in a mixed-species solution. We addressed this point in the main text for the sake of
343 completeness, but also because it potentially enables new and directions of research, such as in-situ
344 tuning of nanopore selectivity^{91,92}. A full survey of the gating effects of all ions, monovalent, divalent and
345 trivalent is a worthy endeavor and is part of a follow-up campaign in our group but is beyond the scope
346 of this particular work. The ion transport behavior of the two divalent cations Ca²⁺ and Mg²⁺ is similar, as
347 shown in the ion selectivity data (**Fig. 3 b**) and newly acquired MD simulation data, discussed in Author
348 response 7, below.

349 6. Reviewer comment

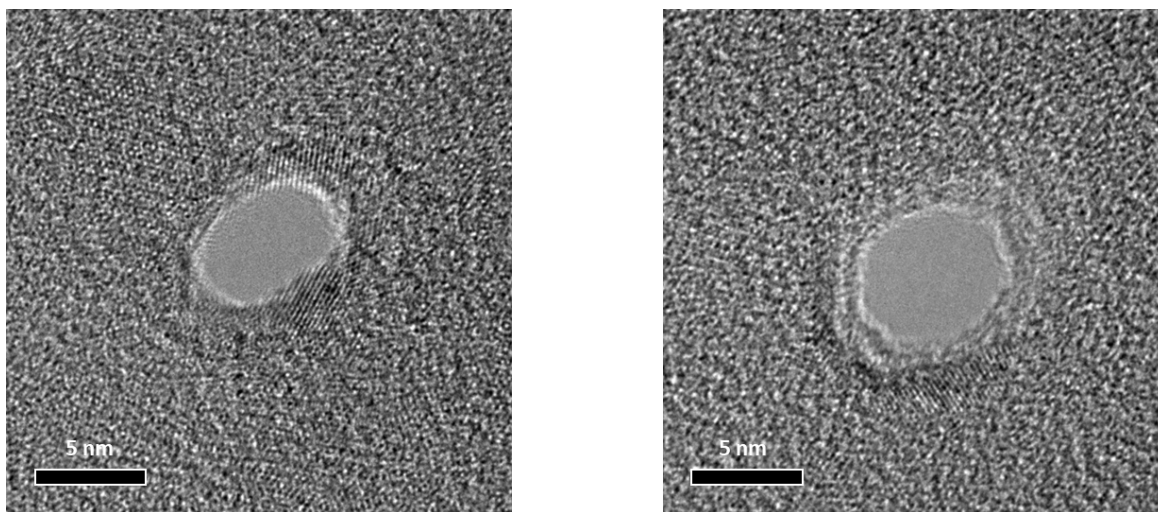
350 Are there any results for the Ion Transport experiment with single nanopore? Because the pores in one
351 device varies a lot, maybe single pore will be clearer to demonstrate the results.

6. Author response

The measurements we conduct here are particularly suitable for porous membranes, rather than single nanopores. We acknowledge that tests with single nanoporous allow for precise characterization of the nanofluidic system under investigation, as well as a more immediate comparison with our molecular dynamics simulations. However, for multilayer MoS₂ membranes, the conductance will be significantly suppressed due to the exponentially lower ion permeation rates in multilayer membranes than their monolayer counterparts.

There are other issues with single pore measurements in multilayer films, however, that caused us to avoid this path. First, we note that electrochemical pore generation in multilayer, single crystals (where we would expect to see the formation of single pores) is challenging to control, as the breakdown happened suddenly and rapidly at high voltages (**Fig. 1 a**).

For comparison, we also attempt TEM drilling of single pores in polycrystalline CVD-MoS₂. This technique is challenging, and we found that the pore edge was disrupted by the electron beam, with the sputtering of material and accumulation of carbon contamination⁹³ (see figures below). This challenge is less relevant for single layer systems, as there is simply less material to sputter from the film, which can then accumulate at the pore edges. For both cases, it is challenging to fabricate single pore with diameters < 1nm on multilayer MoS₂ films.



Author Response Fig. 1. Transmission electron microscopy images of pores drilled *via* a 300 kV focused electron beam. Material accumulation at the pore edges is present for both pores, evidenced by the darker or distorted regions.

7. Reviewer comment

Similar to point 5, why the discussion of Ca²⁺ is not mentioned in MD simulation?

7. Author response

We thank the reviewer for bringing up the absence of Ca²⁺ simulations. In response, we performed additional simulations of Ca²⁺ transport, which we include in the Supplementary Information. We did not originally include simulations of Ca²⁺ in our simulations, as our main focus was on the origins of

monovalent ion selectivity. In addition, subtleties in the transport profiles between Ca^{2+} and Mg^{2+} are not readily apparent in all-classical MD simulations.

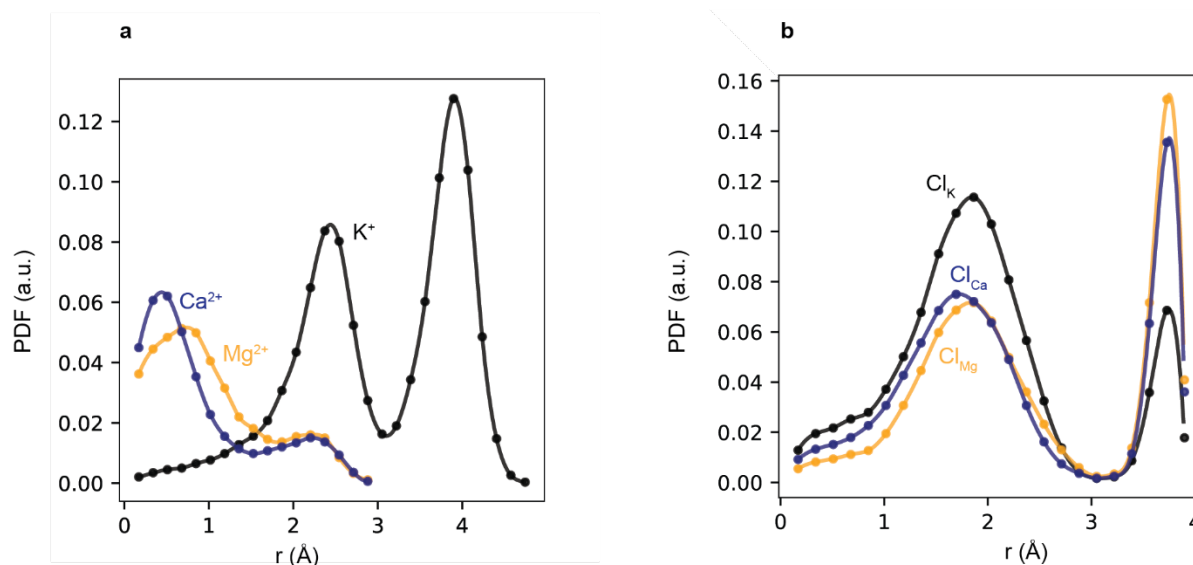
We agree, however, that inclusion of these simulations is important for the sake of rigor and completeness. The concentration profiles of CaCl_2 and MgCl_2 salts are nearly identical, although there are subtle shifts, as expected due to their differing hydration energies (**Supplementary Fig. 18**, copied below). The overall conductance of CaCl_2 is slightly lower than that of MgCl_2 , although relative to the other salts this difference is small (**Supplementary Table 4**). We can conclude, therefore, that, as far as our simulations can discern, Ca^{2+} and Mg^{2+} display similar transport behavior.

7. Text revision

Main text

We also perform simulations with CaCl_2 and find that the behavior of this salt is nearly identical to that of MgCl_2 (**Supplementary Fig. 18**).

Supplementary information



Supplementary Fig. 18. Probability density functions for CaCl_2 . As in **Fig. 4 g** in the main text the data are normalized to K^+ , for each ion inside the 6L-1nm pore. As in **Fig. 4 g**, three distinct regions are apparent, corresponding to different hydration levels. Ca^{2+} and Mg^{2+} show similar profiles, but differ dramatically from that of K^+ , due to their much larger hydration energies.

8. Reviewer comment

The data of Mg and K in 15 devices are showed in Supplementary Table 1. Other reproduced results of other cations should be showed as well.

8. Author response

We thank the reviewer for this suggestion and have provided an additional table with conditions and results of other reproduced cations, which can be found in **Supplementary Table 2**.

403 8. Text revision

404 *Supplementary information*

	Ion transport data							Pore generation conditions		
	G _{KCl} (nS)	G _{NaCl} (nS)	G _{LiCl} (nS)	G _{CaCl₂} (nS)	G _{MgCl₂} (nS)	G _{CsCl} (nS)	G _{RbCl} (nS)	Pulse Voltage (V)	Pulse Time (mS)	Pulse Number
Device 8	23.4 (1.0)	15.3 (1.0)	6.6 (0.6)	4.6 (0.3)	3.15 (0.2)	-	-	1.5	10	1
Device 7	21.8 (2.0)	16.7 (1.6)	8.42 (0.9)	9.21 (0.9)	9.68 (0.7)	-	-	1.5	10	2
Device 12	37.1 (2.6)	26.4 (1.0)	15.8 (1.5)	25.3 (1.0)	19.23 (0.7)	-	-	1.5	10	2
-	80.0 (3.0)	-	-	-	-	48.0 (2.0)	86.0 (1.0)	2	10	2

405

406 **Supplementary Table 2.** Three horizontally aligned MoS₂ devices, of the 20 total devices tested for both
407 divalent *and* monovalent salt selectivity. Another device is tested with KCl, CsCl and RbCl salts. Test
408 conditions and results for these different devices, used to measure the selectivity of KCl, NaCl, LiCl, CaCl₂
409 and MgCl₂; or KCl, CsCl and RbCl. Standard errors for a given element in the table are included in
410 parentheses. All Mo seed film thicknesses were 1.75 nm, and the salt concentration is 1 M. Current-
411 voltage curves for these data are shown in **Supplementary Fig. 10** and **Supplementary Fig. 11**.

412 9. Reviewer comment

413 Does thickness of Mo seed thickness effect the selectivity?

414 9. Author response

415 We thank the reviewer for this question. We think maintaining the same pore size while increasing the
416 MoS₂ thickness will increase the ion selectivity. However, the orientation of the MoS₂ layers changes
417 from horizontally to vertically aligned as the thickness of the Mo seed layer increases, as mentioned in
418 the main text. We have performed additional measurements on our vertically aligned films, past a
419 certain seed thickness. We find that, relative to the thinner membranes of the same conductance, the
420 K⁺/Mg²⁺ selectivity is similar. The same conductance in a thicker vertically aligned film could mean larger
421 pore size distribution. However more investigation is needed to understand the difference between
422 horizontal and vertically aligned MoS₂ which we will pursue in our future work.

423 9. Text revision

424 *Main text page 8*

425 This trend holds for thicker, vertically aligned MoS₂ films (**Supplementary Fig. 9**).

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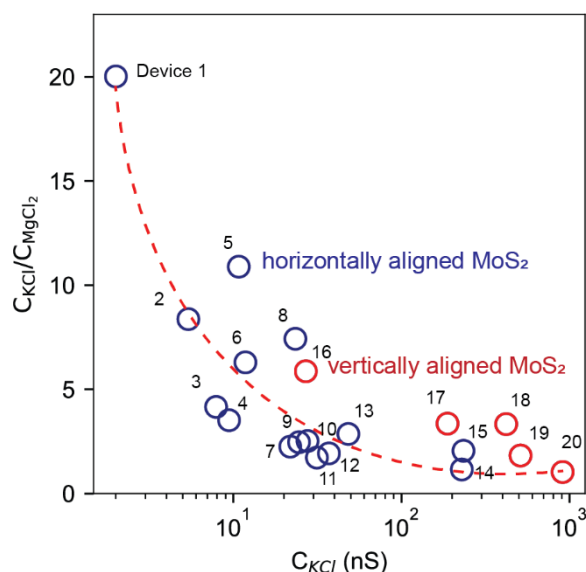
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434 **Supplementary Fig. 9.** KCl/MgCl₂ selectivity. Data shown for all 20 devices tested with KCl and MgCl₂
 435 salts, plotted against membrane resistance to KCl. Red circles are vertically aligned MoS₂ films, blue
 436 circles are horizontally aligned MoS₂ (also plotted in **Fig. 3 a** in the main text). The dotted red curve is a
 437 guideline. Test conditions are provided in **Supplementary Table 1**.

438

439 Reviewer comment (other details)

440 1. Please check the units. For example, in Supplementary Table 1, there is no unit for thickness and
 441 voltage.

442 2. The conclusion part can be fleshed out.

443 Author response (other details)

444 In response to this comment, and the previous comments about device novelty, we have added a brief
 445 discussion in the conclusion about the novelty of our work. As mentioned above, we also added content
 446 to clarify the novelty in the introduction. We thank the reviewer for their attention to detail. We have
 447 corrected their findings and have looked for and revised other such omissions.

448 **Reviewer #3 (Remarks to the Author):**

449

450 0. General points

451

452 The paper is extremely well organised and written, in fact this is one of the better written manuscripts I
 453 have had the pleasure of reviewing. My congratulations (and thanks) to the authors.

454 The authors present a method for the in situ fabrication of a high-density array of nanopores in the
 455 range of 5A to a few nm. The pores in the resulting membranes can subsequently be tuned in a
 456 controllable fashion.

457

The authors go on to explore conductivity and selectivity of the membranes produced here. Their membranes (in particular those with lower conductance/smaller pores) show a very high degree of selectivity. This high degree of selectivity, combined with the high flux (conductivity) arising from the density of the nanopore array, puts these membranes in a very interesting position. The authors then use MD simulations (outside my expertise, but it all seems very reasonable) to explore the mechanism of this ion selectivity.

I think that this is an extremely thorough study. The data presented within the main text is sufficient to support the authors' main points/Discussions. The supplementary info covers/provides an additional level of detail.

I would be happy for the manuscript to be published as is, the points below are simply minor suggestions that slightly improve the work.

0. Author response

We thank the reviewer for their positive review. We have dedicated significant time to this work, both collecting data but also organizing and writing, and are glad that that was apparent. We hope that the following revisions can even further increase the paper in the reviewer's esteem.

1. Reviewer comment

Given the in-situ pore formation methodology described here, I find it slightly surprising that the authors do not acknowledge the work of Vincent Tabard-Cossa's lab in developing, and first reporting, the CBD methodology (pore formation and expansion), in particular "Nanopore Fabrication by Controlled Dielectric Breakdown" (Kwok et al, 2014). Because of the multiple pores formed and the in situ methodology, I feel that "Fabrication of multiple nanopores in a SiNx membrane via controlled breakdown" (Wang et al, 2018) is also a relevant reference. Reference 46 should possibly be given more prominence too.

1. Author response

We appreciate the reviewer's point that a greater emphasis should be placed on the controlled dielectric breakdown (CBD) methodology. We have added additional references and discussion of this work in the introduction (see below), paired with a note on the novelty of this work relative to that mentioned. In this additional discussion, we have also placed additional emphasis on Wang *et al.*, which we agree deserves additional discussion.

1. Text revision

Main text page 2

Previous work has shown that nanometer-scale pores can be formed electrochemically in two-dimensional materials, such as MoS₂ and graphene^{38,39}. Single pores, as well as porous membranes, can also be formed electrochemically in thin films such as SiN, although the mechanism in this case differs from that in two-dimensional materials such as MoS₂⁴⁰⁻⁴². For SiN, the application of large voltages leads to a sudden *controlled dielectric breakdown*, resulting in localized heating and subsequent material degradation. In MoS₂, the application of order-of-magnitude smaller voltages leads to a gradual localized electrochemical etching at specific hot-spots, likely grain boundaries or sulfur vacancies³⁸.

In all previous accounts with two-dimensional materials, the pores are formed one at a time, which is beneficial for certain sensing applications⁴³, but could be a shortcoming for ion-separation membrane fabrication. Here, we demonstrate for the first time that, with the nanoscale features of polycrystalline MoS₂, densely porous membranes can be fabricated *in situ* with sub-nanometer control. Furthermore, we demonstrate that pores in multi-layer films can be formed electrochemically, whereas in previous studies only monolayers were used. We show that pore creation in single-crystal, few-layer MoS₂ is significantly more difficult to control.

2. Reviewer comment

Specific points:

- In Fig 3a - I suggest that you number the devices in the plot. It is possible to work it out which is which from the data in SI table 1, so why not make it easier?

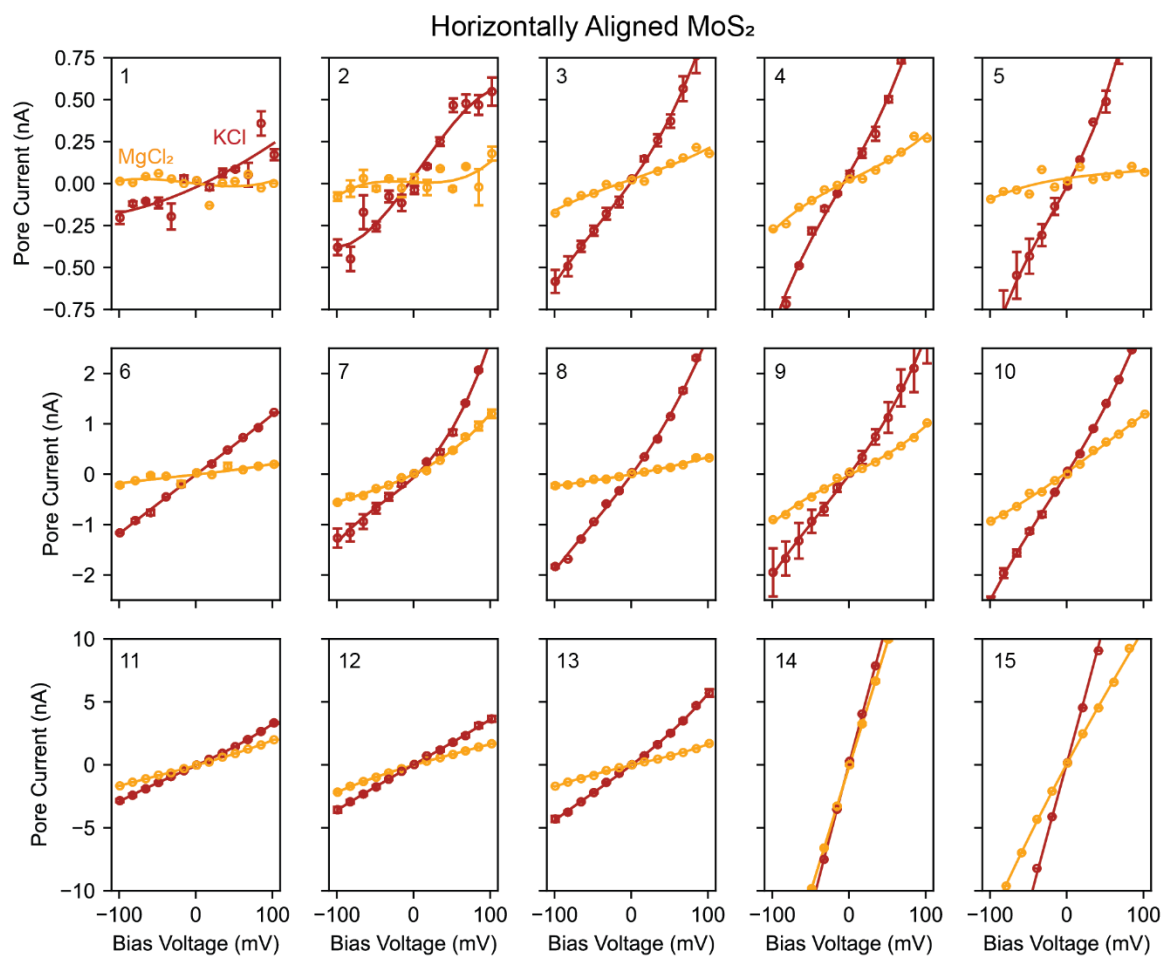
- The legend to Fig 4 contains a typo (the only one I found). "A single pore (c) is drilled in the center of the all MoS₂ films" should (presumably) read "A single pore (c) is drilled in the center of all the MoS₂ films".

2. Author response

We appreciate your attention to detail and have corrected the typo in **Fig. 4**. We also appreciate the suggestion to number the devices in the plot, which we have done. Furthermore, we order the devices in **Supplementary Table 1**, and in newly added **Supplementary Fig. 8**, in order of conductance, making it straightforward to pair a given point in the plot with the device number. Please see below for **Supplementary Table 1** and **Supplementary Fig. 8**. Hopefully this will make it as straightforward as possible to link up all the information for a given device.

Sample	G _{KCl} (nS)	G _{MgCl₂} (nS)	Pulse Voltage (V)	Pulse Time (ms)	Pulse Number	Mo Seed Thickness (nm)
1	2.0	0.1	1.5	5	1	1.75
2	5.4	0.6	1.5	5	1	1.75
3	7.9	1.9	1.5	5	1	1.75
4	9.4	2.7	0.4-0.5	NA	NA	1.75
5	10.8	1.0	1.5	5	1	1.75
6	11.8	1.9	0.4-0.5	NA	NA	1.75
7	21.8	9.7	1.5	10	2	1.75
8	23.4	3.2	1.5	10	1	1.75
9	24.6	10.0	1.5	5	1	1.75
10	27.6	11.0	1.5	25	1	2.0
11	31.4	18.2	1.5	10	1	2.0
12	37.1	19.2	1.5	10	2	1.75
13	48.3	16.9	1.5	5	1	1.75
14	228.5	197.6	1.5	50	2	2.0
15	234.0	114.0	0.4-0.5	NA	NA	1.75
16*	18.8	5.6	0.4-0.5	NA	NA	15.0
17	27.0	4.6	1.5	5	4	15.0
18*	42.0	12.6	0.4-0.5	NA	NA	15.0
19*	51.1	28.0	0.4-0.5	NA	NA	15.0
20*	91.0	88.0	0.4-0.5	NA	NA	10.0

Supplementary Table 1. Devices tested for KCl/MgCl₂ selectivity. Test conditions and results for 20 different devices, used to measure the selectivity of KCl and MgCl₂. Samples were collected over the course of one year. Different film thickness and pulse frequencies were used, although in the ranges tested here there was little effect on the results. The concentration of salts is 1 M, except for those rows marked with a *, which were measured with 0.1 M salts. Current-voltage curves for these data are shown in **Supplementary Fig. 8**.



542

543

Supplementary Fig. 3. I-V traces of KCl and MgCl₂ salts in CVD- MoS₂ nanopores. These data correspond to the 15 devices shown in **Fig. 3 a** (all horizontally aligned MoS₂ films tested for KCl and MgCl₂ selectivity), as well as the 5 vertically aligned devices (> 10 nm Mo seed thickness), displayed, along with the 15 horizontally aligned MoS₂, in **Supplementary Fig. 9**. Details for each device are tabulated in **Supplementary Table 1**. Data are collected using 1 M salts, except for devices 16, 18, 19 and 20, which were collected with 0.1 M salts. The pore current shown for these devices has been scaled by a factor of 10 to correct for this difference.

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571 solid-state nanopores using the poly-Si sacrificial layer process. *Scientific reports* **5**, 14656 (2015).
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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript reports an electrochemical etching method to create nanopores on MoS₂ nanosheets for selective ion transport. The method was developed in 2016 and published in Nature Materials, so it is not new. The ion selectivity of the MoS₂ film is low compared to other 2D nanosheet membranes. In addition, there are so many format mistakes in the manuscript and it is hard to read. The authors should prepare the manuscript carefully. It is unbelievable this kind of manuscript can be sent out for review.

Reviewer #2 (Remarks to the Author):

The authors have responded to most of my original comments. One additional comment: As the point is the porous membrane, it is known that such dense pore array can have huge variations in their structures and lack control over pore sizes/distributions. Can the ion selectivity be generally reproduced?

Reviewer #3 (Remarks to the Author):

I was happy for this to be published in the first instance and this view has not changed with the revision(s).

My (slight) concerns were addressed. The authors appear to have done a good job in adjusting their manuscript to meet the demands of the other reviewers.

Please note - the pdf version of the manuscript that was provided is a horrendous mess. The formatting is wrong in many places, figures have been repeated (particularly figure 3) and the reference system breaks down completely at some point. I don't know if this is an author mistake or a journal issue (or even mine - but I have tried more than one pdf viewer).

Thankfully the word version appears to be as intended and allowed me to see exactly where the changes were made in the manuscript.

Reviewer Comments and Author Response

Reviewer #1 (Remarks to the Author):

The manuscript reports an electrochemical etching method to create nanopores on MoS₂ nanosheets for selective ion transport. The method was developed in 2016 and published in Nature Materials, so it is not new. The ion selectivity of the MoS₂ film is low compared to other 2D nanosheet membranes. In addition, there are so many format mistakes in the manuscript and it is hard to read. The authors should prepare the manuscript carefully. It is unbelievable this kind of manuscript can be sent out for review.

Author response

We thank the reviewer for taking the time to read our updated manuscript. We sincerely apologize and are similarly frustrated with the formatting mistakes in the PDF version of the document, which seem to have occurred during the conversion from the source document on the web application.

The reviewer brings up two important questions concerning the novelty of the pore generation method, as well as the degree of ion selectivity in the resulting membranes relative to existing work. We addressed the former, the novelty of the pore generation method, in our previous response, and had updated the original main text to include a more detailed explanation. We have copied that response and the updated main text, below.

Previous author response regarding method novelty

The reviewer is correct in identifying that a more explicit differentiation of our work from that done previously is needed in our text. We have added such a discussion to our introduction, copied below. In essence the novelty of our work is premised on a few key components:

1. The fabrication of a dense array of pores with (sub)nanometer sizes requires an applied electric field, but also grain boundaries. Our method highlights the potential of designing materials with precisely controlled nanoscale topography for manipulating pore generation, as opposed to the single nanopores in pristine single crystals of the two-dimensional material.
2. The use of polycrystalline MoS₂ with nanoscale topography allows for the fabrication of pores in few-layer films (past a critical thickness to enhance ion selectivity), which we find is not feasible in their single-crystal counterparts. In CVD-MoS₂, pores are formed gradually at relatively low voltages (~0.5 V). For multilayer, single-crystals, pore creation happens at high voltages (nearly 2 V) rapidly and uncontrollably.
3. The discovery that few-layer MoS₂ is ion selective, whereas monolayer MoS₂ fails to differentiate both mono and divalent ions from each other (MD simulation results in our paper). The monovalent and divalent ion selectivity in this work is among the highest for two-dimensional materials to date.
4. The elucidation of the ion selectivity mechanism, being closely tied to the sluggishness of the water confined to the MoS₂ nanopore. This is an additional novel point to our work that we

provide with MD simulations to explain the mechanism behind the selective ion transport, which is important to guide future membrane design.

Previous update to the main text regarding method novelty

Previous work has shown that nanometer-scale pores can be formed electrochemically in two-dimensional materials, such as MoS₂ and graphene^{1,2}. Single pores, as well as porous membranes, can also be formed electrochemically in thin films such as SiN, although the mechanism in this case differs from that in two-dimensional materials such as MoS₂^{3–5}. For SiN, the application of large voltages leads to a sudden *controlled dielectric breakdown*, resulting in localized heating and subsequent material degradation. In MoS₂, the application of order-of-magnitude smaller voltages leads to a gradual localized electrochemical etching at specific hot-spots, likely grain boundaries or sulfur vacancies¹.

In all previous accounts with two-dimensional materials, the pores are formed one at a time, which is beneficial for certain sensing applications⁶, but could be a shortcoming for ion-separation membrane fabrication. Here, we demonstrate for the first time that, with the nanoscale features of polycrystalline MoS₂, densely porous membranes can be fabricated *in situ* with sub-nanometer control. Furthermore, we demonstrate that pores in multi-layer films can be formed electrochemically, whereas in previous studies only monolayers were used. We show that pore creation in single-crystal, few-layer MoS₂ is significantly more difficult to control.

Ion Selectivity Comparison

The ion selectivity measured here is among the highest for nanoporous membranes in two-dimensional materials to date, as shown in **Fig. 3 e** of the main text (copied below). We note, in particular, the significantly higher selectivity of these nanoporous membranes relative to the monolayer MoS₂ films, which the reviewer references⁷. There are other classes of membranes, such as restacked graphene oxide, MoS₂ laminates, and metal organic frameworks, which outstrip the nanoporous membranes when looking at ion selectivity alone, which we list in **Supplementary Fig. 13**. Many related factors, however, have made the field of transport in nanoporous 2D material membranes intriguing for a wide array of researchers, including the high permeance, atom-scale thickness, feasibility of direct characterization with electron microscopy, and relevance to molecular sensing^{8,9}.

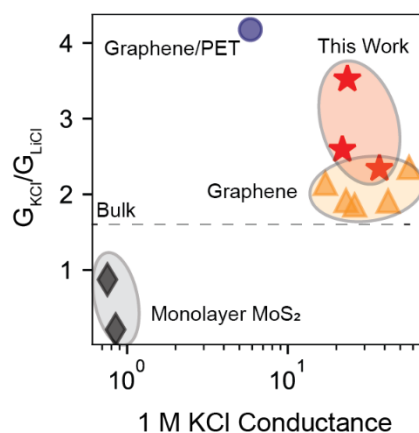


Fig. 3 e. Unnormalized conductance ratio of KCl and LiCl plotted against conductance of 1 M KCl through existing nanoporous 2D material membranes (see **Supplementary Table 3**).

Update to Main Text

The ion selectivity of thicker, layered membranes with angstrom-scale 2D channels, such as those made from liquid-phase exfoliation of graphene and MoS₂, tends to be higher (**Supplementary Fig. 13**).

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1. Feng, J. *et al.* Electrochemical reaction in single layer MoS₂: nanopores opened atom by atom. *Nano Lett.* **15**, 3431–3438 (2015).
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4. Wang, Y. *et al.* Fabrication of multiple nanopores in a SiNx membrane via controlled breakdown. *Scientific reports* **8**, 1234 (2018).

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Reviewer #2 (Remarks to the Author):

The authors have responded to most of my original comments. One additional comment: As the point is the porous membrane, it is known that such dense pore array can have huge variations in their structures and lack control over pore sizes/distributions. Can the ion selectivity be generally reproduced?

Author response

The reviewer brings up an important point about the reproducibility of our pore generation method. The method differs significantly, for example, from electron beam drilling in which single pores are created under the guidance of direct imaging. The ion selectivity reported in our paper, however, can certainly be reproduced, as evidenced by the results of the many devices tested. The degree of ion selectivity for a given device depends on many factors, such as material thickness, crystallite grain size, applied bias. Given all these factors, the ion selectivity varies among the 15 devices tested, although all fall along a clear selectivity vs. conductance trend (**Fig. 3 a**). The K^+ conductance for the three devices tested for monovalent ion selectivity, while not identical, are within a factor of two of each other (**Fig. 3 c**). The reproducibility could be further improved by precisely controlling the grain size and thickness of MoS_2 films and using low voltages to further reduce the speed of pore generation, which are all in our plan for future work.

Reviewer #3 (Remarks to the Author):

I was happy for this to be published in the first instance and this view has not changed with the revision(s).

My (slight) concerns were addressed. The authors appear to have done a good job in adjusting their manuscript to meet the demands of the other reviewers.

Please note - the pdf version of the manuscript that was provided is a horrendous mess. The formatting is wrong in many places, figures have been repeated (particularly figure 3) and the reference system breaks down completely at some point. I don't know if this is an author mistake or a journal issue (or even mine - but I have tried more than one pdf viewer).

Thankfully the word version appears to be as intended and allowed me to see exactly where the changes were made in the manuscript.

Author response

We thank the reviewer for the positive comments. We also appreciate their comment about the formatting. A new PDF document has been uploaded that does not have these issues.

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

The authors have addressed my comments.