Supporting Materials

Ionic memory or electrode artefacts? A systematic assessment of nanofluidic memristors

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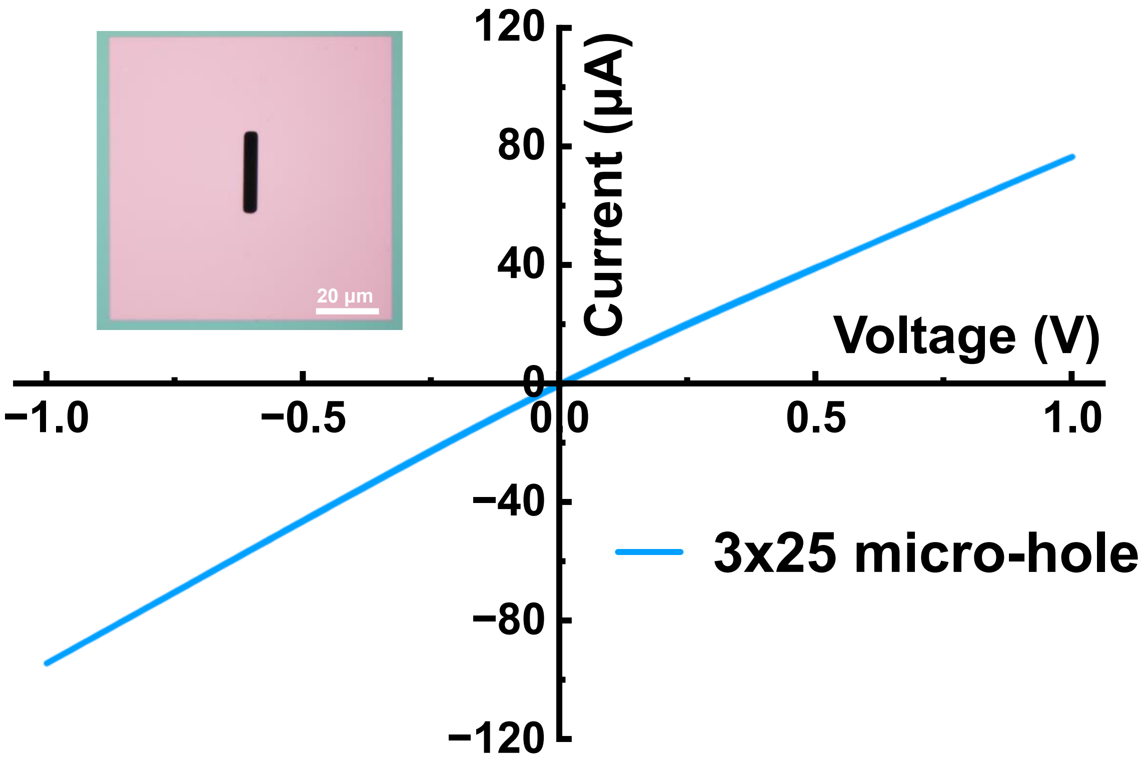
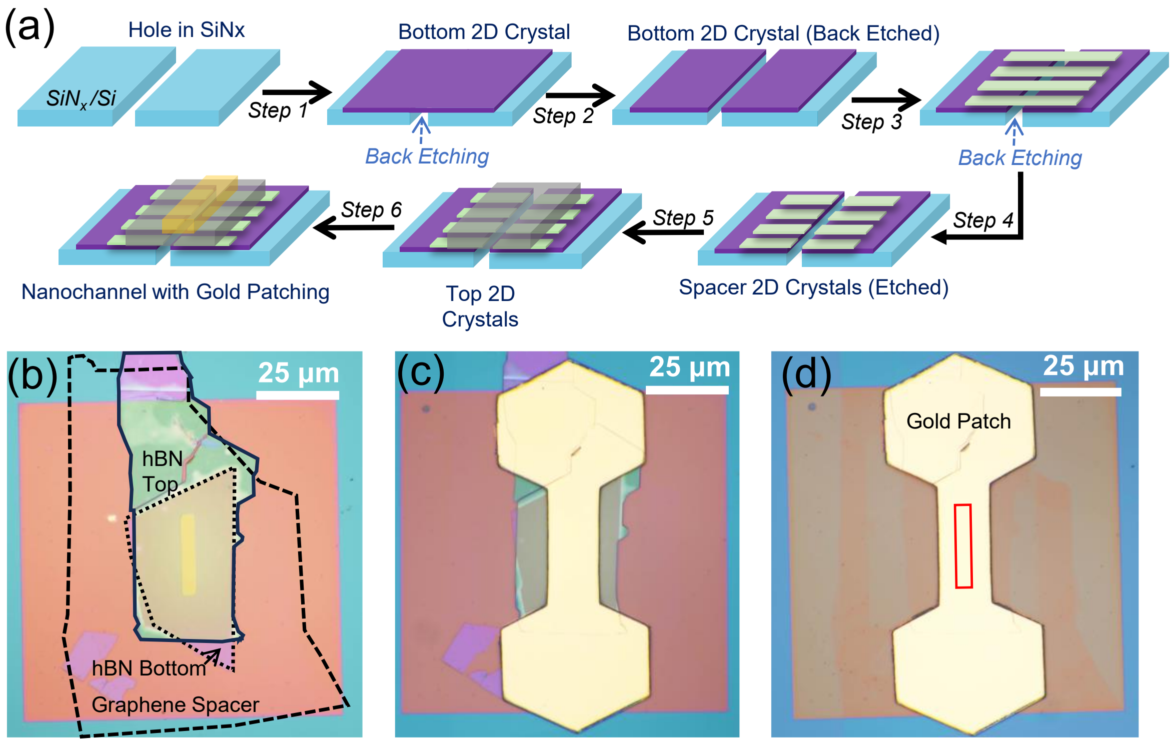
1. Microhole:

We measured ionic currents through a microhole in 1M-KCl solution using Ag/AgCl electrodes, and observed a linear response,without any hysteresis/pinching.



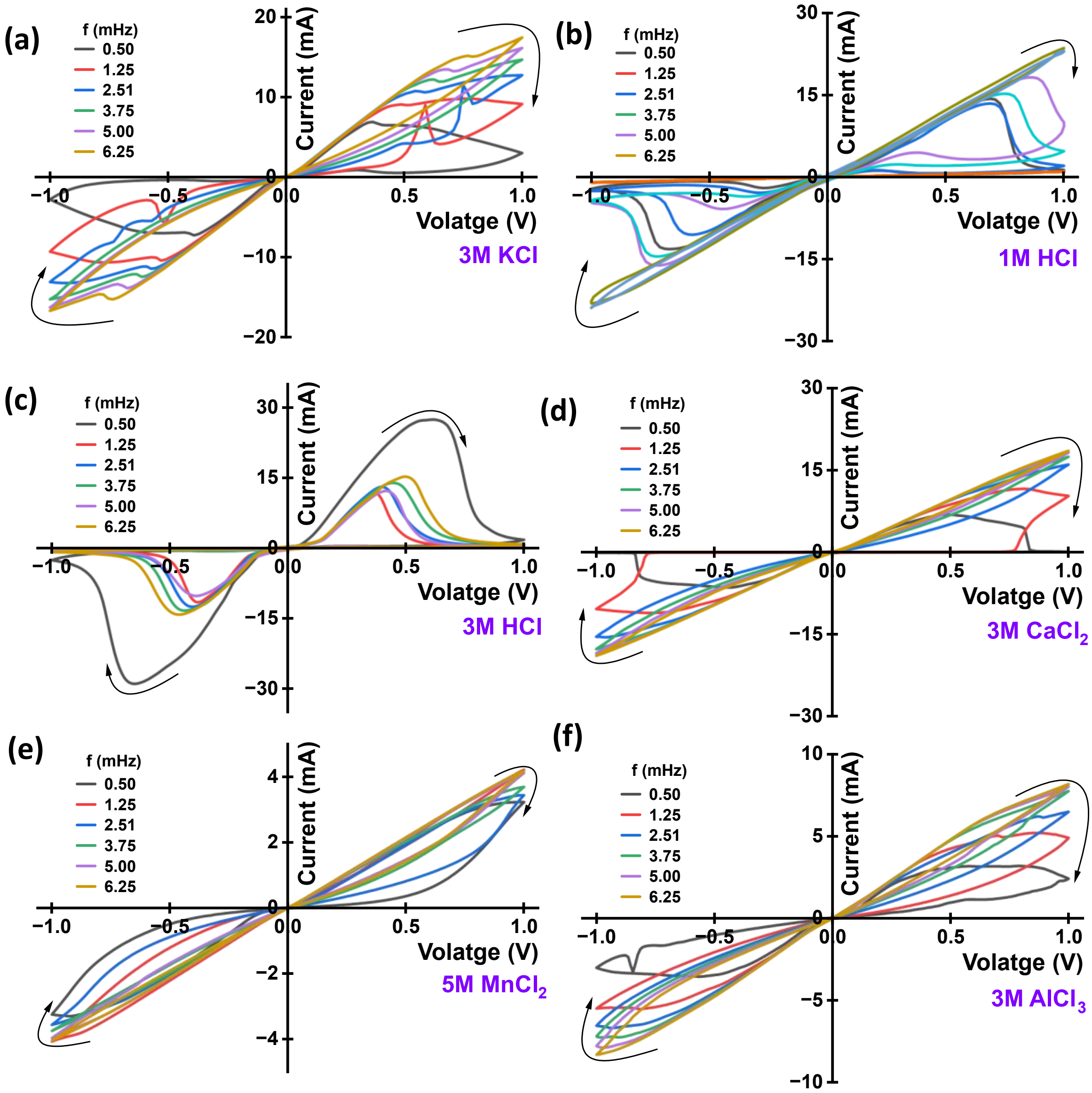
Supplementary Figure 1. I-V characteristics of a 3x25 µm Hole measured measured using a two-electrode Ag/AgCl configuration within a ±1 V potential window in 1 M KCl at a sweep frequency of 3.75 mHz. The inset shows the optical image of the microhole.

2. 2D Nanochannel:



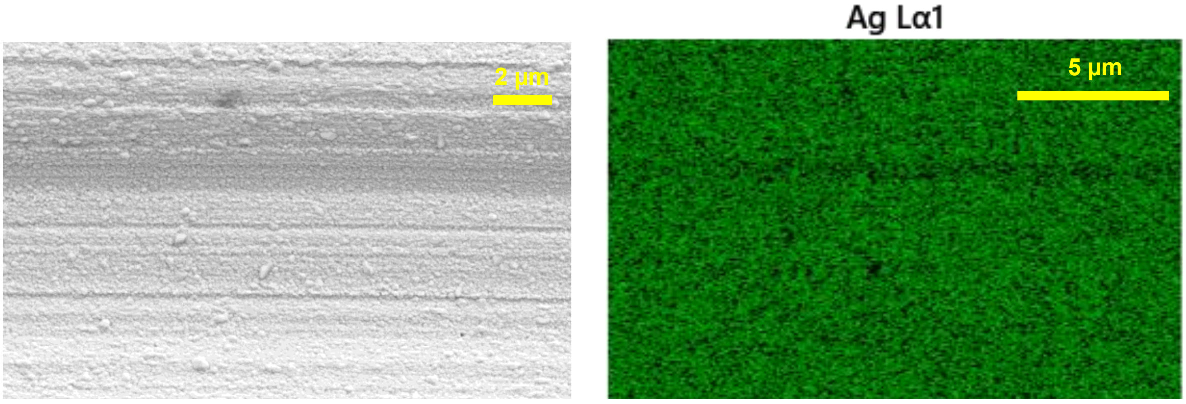
Supplementary Figure 2. Fabrication schematic and optical images of 2D nanochannel device. (a) Schematic process flow of device fabrication. A micro-hole is first defined in a freestanding SiN_x/Si membrane by photolithography and reactive-ion etching. Mechanically exfoliated hBN flakes are then used as bottom and top encapsulation layers, with few-layer graphene in between as the spacer. The graphene is patterned by electron-beam lithography and oxygen plasma etching to define ~130 nm-wide channels, and the hBN/Gr/hBN van der Waals heterostructure is assembled. The stacked heterostructure is annealed in 10% H_2/Ar to remove residues and improve interlayer adhesion, after which a Cr/Au patch is patterned and deposited to define the nanochannel length and protect the covered region during subsequent etching of the exposed trilayer. Optical images: (b) of tri-layer stack (hBN-Gr-hBN) on SiNx free-standing membrane, (c) tri layer stack on SiNx after Cr/Au deposition, and (d) final nanochannel device after etching exposed region of the trilayer stack. The red color in (d) contours the microhole.

3. Variation of salt type, concentration, and frequency:



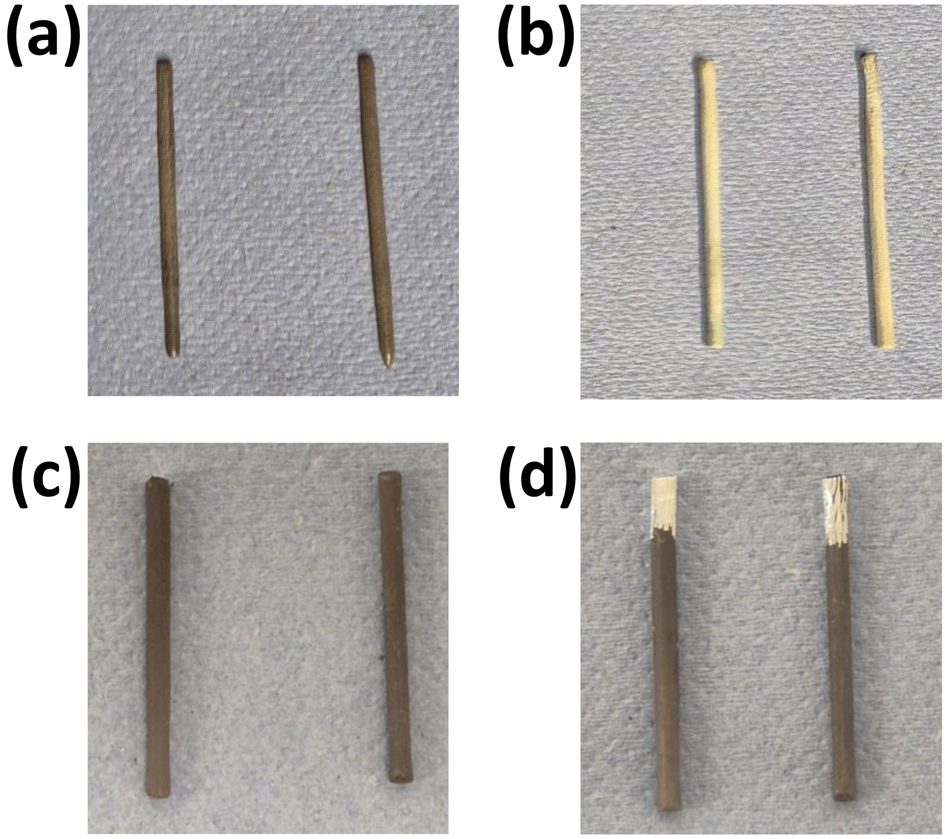
Supplementary Figure 3. I-V characteristics of a 100 nm PVDF membrane measured with Ag/AgCl electrodes in different electrolytes and concentrations. Monovalent salts and acid: (a) 3 M KCl, (b) 1 M HCl, (c) 3 M HCl; bivalent salts: (d) 3 M $CaCl_2$, (e) 5 M $MnCl_2$; trivalent salt: (f) 3 M $AlCl_3$. For each electrolyte, the frequency was varied from 0.50 mHz to 6.25 mHz. We observe pinched I-V loops in all of the above salts, and the hysteresis varies significantly with frequency. This demonstrates the strong dependency of the electrochemical response on the applied voltage frequency.

4. SEM and EDX image of Silver (Ag) Rod:



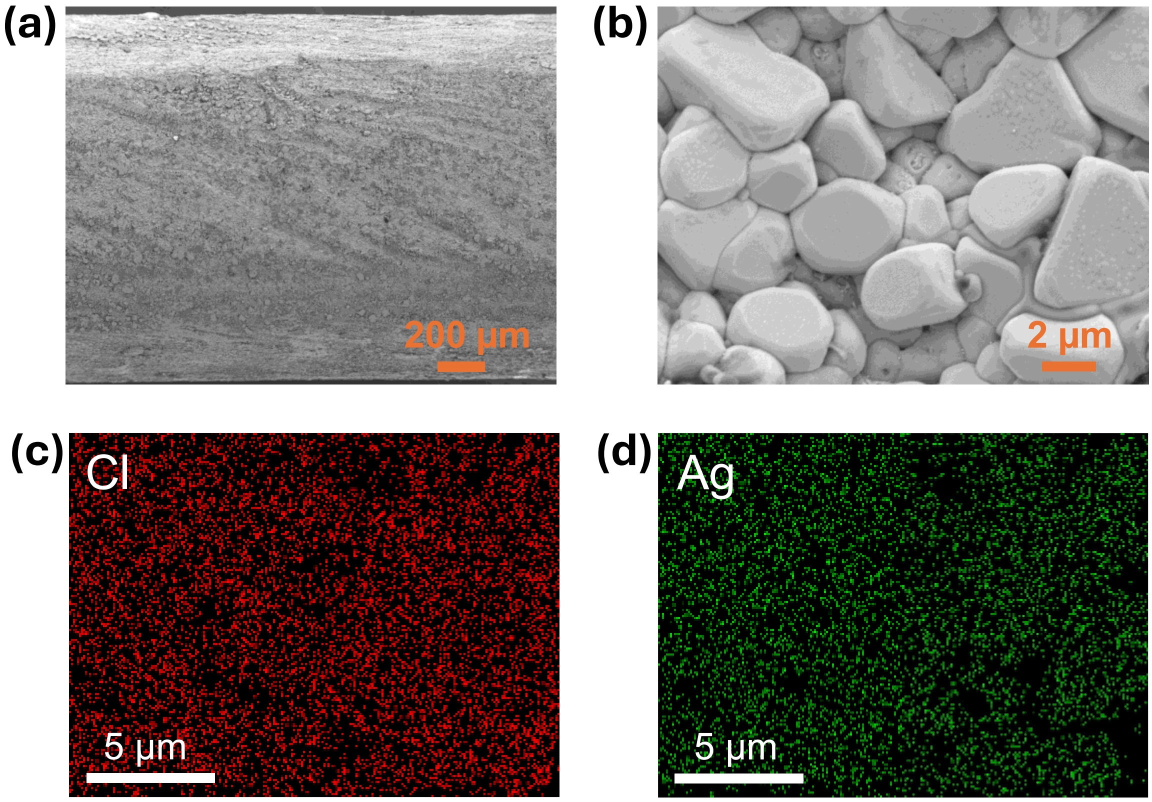
Supplementary Figure 4. Image of Silver (Ag) rod (a) SEM, (b) EDX.

5. Photographs of the electrode before and after 250 cycles:



Supplementary Figure 5. Optical images of Ag/AgCl electrodes. (a) Pristine electrode pair prior to any electrochemical testing. (b) A separate electrode pair after 250 I-V cycles using a PVDF membrane, showing visible colour changes on electrode surface. (c-d) A third electrode pair used for nanochannel I-V measurements: (c) before and (d) after measurements with a bilayer nanochannel device comprising graphene as a spacer and hBN as top and bottom layers. In contrast to (b), no visible surface changes are observed in (d). All measurements were performed in 1 M KCl solution within an applied potential window of 1 V.

6. SEM and EDX images of Ag/AgCl electrode after 250 I-V cycles with nanochannel:



Supplementary Figure 6. SEM and EDX images of electrode after cycling. (a-b) SEM images of electrode surface acquired at an accelerated voltage of 5KV after 250 I-V cycles with nanochannel. (c-d) EDX elemental mapping in corresponding to obtained SEM image in (b). The IV measurements were performed in 1M KCl within an applied potential window of 1V using a nanochannel device comprising a 2 layer thick graphene spacer stacked between the top and bottom hBN flakes.