Supplementary Information for

Transporting ionic-liquid/water mixture in a conical nanochannel: a nanofluidic memristor

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S1. Fabrication and characterization of the conical nanochannel.

A 12 μm polyethylene terephthalate (PET) foil was irradiated by a single swift heavy ion (Ar) with an energy of 6.17 MeV per nucleon to generate a single latent track and then the foil was irradiated under ultraviolet (4.2×10^3 μW cm^{-2}) for 1 h on both sides. Then, the irradiated foil was mounted on a custom-designed system for asymmetric track-etching, where the foil isolated the two chambers containing the etchant of 9 M NaOH and the stop medium consisting of 1 M HCOOH and 1 M KCl, respectively. A picoammeter (Keithley 6487) with platinum electrodes was used to monitor the breakthrough current across the foil, while applied voltage was 1 V on the etchant side. (The electrode placed at stop medium side was grounded.) Once the etchant penetrated through the foil, the current would suddenly increase, and the stop medium would immediately neutralize the etchant of NaOH from further etching. Lastly, based on the asymmetric etching method, a single conical nanochannel was produced. By electrical measurement of conductance in 1 M KCl solution and estimation of nanochannel size in the larger opening (D_{base}) by etching rate, the diameter of the smaller, D_{tip} was estimated *via* the following equation:

$$D_{\text{tip}} = \frac{4LI}{\pi \kappa U D_{\text{base}}}$$

where L is the nanochannel length, and I, U, and κ are the ion current, applied voltage, and the conductivity of 1 M KCl aqueous solution, respectively.

S2. More detailed information about experimental results.

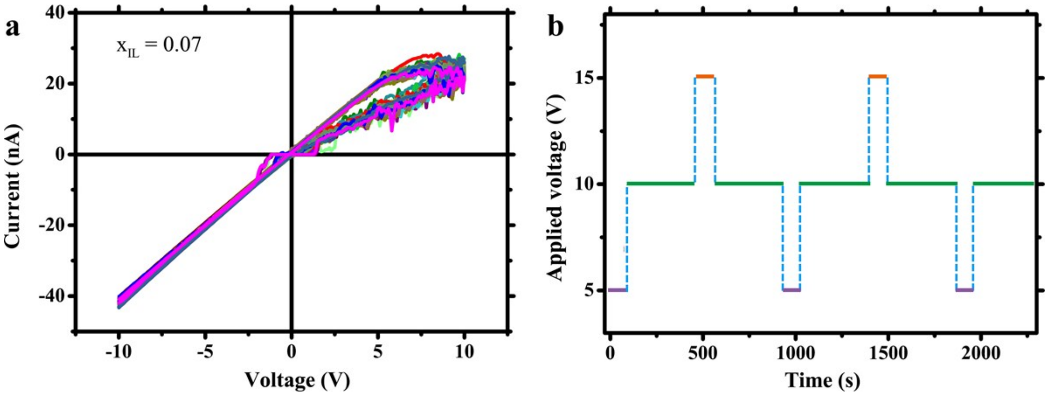

Figure S1. (a) The original *I-V* curves to calculate the resistance of ON/OFF states in Figure 2(c); (b) The applied voltage sequence with time for retention capability measurement in Figure 2(d).

S3. Effect of cations adsorption on the shape of *I-V* curves.

Surface charge is known to have a significant effect on the ion conductance through a nanochannel.[1] A surface-charged conical nanochannel can induce asymmetric ion conductance with enhanced or suppressed ion current under voltage bias. The inner surface of the nanochannels used in this work is negatively charged as prepared, because the surface contains a fair amount of carboxylic groups.[2,3] Many previous studies have shown that the negative surface charge can enhance (or suppress) the ion current under negative (or positive) bias due to the ion enrichment (or depletion) occurred inside the nanochannel.[1] If the polarity of the surface charge is switched to positive, the current enhancement and suppression will accordingly switch with each other, i.e. enhancement (or suppression) of ion current under positive (or negative) bias for positively charged nanochannels. Also, this current rectification phenomenon is mainly determined by the surface charge density near the tip region of the conical nanochannel.

Adsorption of cations can possibly switch the polarity of the surface charge in the nanochannel. If the adsorption is reversible, and the adsorption/desorption process needs a threshold voltage to activate, a hysteresis loop would then appear in the *I-V* curves (Schematically illustrated in Figure S2). Considering that the cations used in this work, i.e. [BMIM]$^+$, were fairly bulky and less mobile, the adsorption/desorption were likely to occur during the cyclic voltammetry scans, thereby resulting in the hysteresis of the *I-V* curves. The reversible adsorption/desorption process of charged species has been suggested by researchers[4-6] in quite a few similar nanochannel systems, and the focused electric field (also, focused ion flux and osmosis flow) near the conical tip could serve to enhance any phenomena which are related to the field strength (e.g. electric-field induced adsorption/desorption). Additionally, the adsorption was also suggested by post *I-V* measurements in aqueous KCl solution after the measurements involving IL. As shown in

Figure S4, the polarity of the asymmetry in the ion conductance was in accordance with the case for positively charged surface, suggesting that the surface of the nanochannel indeed contained a fair amount of adsorbed cations.

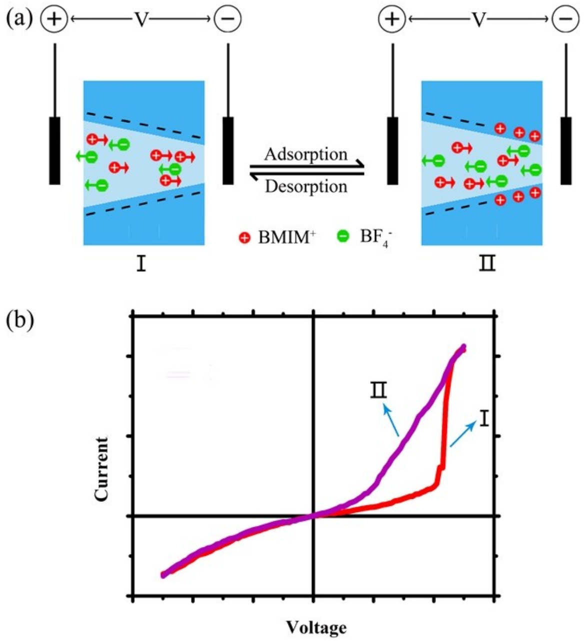

Figure S2. Schematic illustration of the effect of cations adsorption on the shape of the *I*-*V* curve.

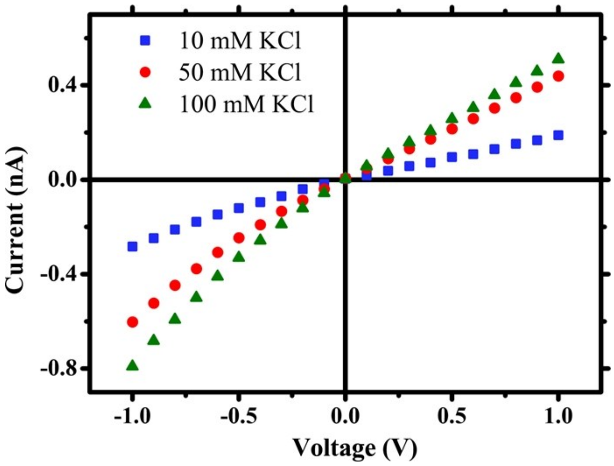

Figure S3. *I*-*V* curves for a conical nanochannel measured in 10, 50, and 100 mM KCl aqueous solutions, showing asymmetric ion conductance (lower conductance under positive bias) as commonly observed for a negatively charged conical nanochannel[1]. The tip diameter for this nanochannel was 6 nm.

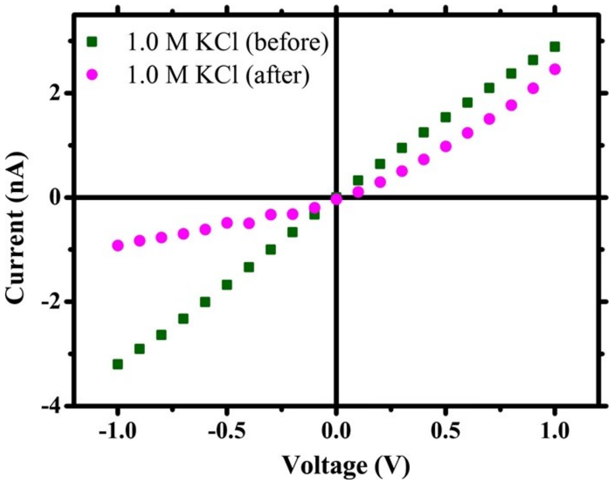

Figure S4. Comparison of the *I-V* curves for the conical nanochannel measured before and after the experiments involving IL/water as described in the main text. The electrolyte was 1M KCl aqueous solution. The *I-V* curve measured after IL experiments also showed asymmetric ion conductance but with an inversed polarity as compared to Figure S3, possibly implying that the surface charge polarity on the nanochannel wall near the tip was inversed from negative to positive[1].

S4. Representative *I-V* curves for using an alternative IL of [BMIM][SCN] showing similar hysteresis loops.

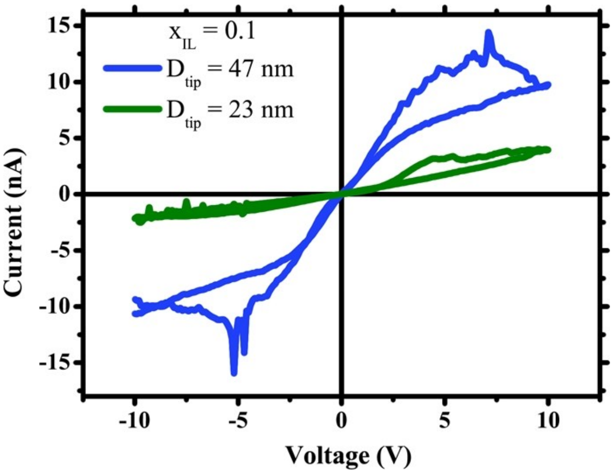

Figure S5. Representative *I-V* curves for two conical nanochannels (23 and 47 nm for tip diameters, respectively) using [BMIM][SCN]/water mixture as the electrolyte. [BMIM][SCN] is 1-butyl-3-methylimidazolium thiocyanate. The molar fraction (x_{IL}) of [BMIM][SCN] was 0.1.

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