Fabrication of Stable Single Nanochannels with Controllable Ionic Rectification

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The single conical nanochannel investigated here was produced in polymer films using the ion track-etching technique. Before the chemical etching process, the samples of PET were exposed to the UV light for 1 h from each side. To produce a conical nanochannel, etching was performed only from one side, the other side of the cell contains a solution that is able to neutralize the etchant as soon as the channel opens, thus slowing down the further etching process. To additionally stop the etching, the voltage (1 V) used to monitor the etching process was applied in such a way that the negatively charged ions of the etchant were drawn out of the channel tip. The following are the etching and stopping solutions for the etching of PET: NaOH (9 M) for etching, KCl (1 M) + HCOOH (1 M) for stopping. The large opening of the conical nanochannel was called base, while the small opening was called tip. The diameter of the base and tip were estimated from the multitrack membranes etch rate measured in the parallel etching experiments by AFM (see Fig. S1), due to the difficulty of locating both the tip and base opening in AFM. In this work, its base is usually controlled from ~400 to ~2500 nm, and its tip is from ~2 to ~700 nm.
The Pt films were deposited on the samples by ion sputtering with Pt target (99.99%) by an ion sputtering system (SBC-12, KYKY Technology Development LTD., China) in vacuum. Vacuum before switching on the ion source was 4 Pa and the working temperature was 25°C. In our experiment setup, the sputtering current was kept constant (2 mA) and the deposited amount of Pt was adjusted by modifying the sputtering time. The photos of the sputtering mask and the sample before and after ion sputtering are given in Figure S2.

The ion transport properties of the nanochannel were studied by measuring ion current through the nanochannels before and after the ion sputtering. Ion current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). A single-channel PET membrane was mounted between two chambers of the etching cell mentioned above. Ag/AgCl electrodes were used to apply a transmembrane potential across the film. Forward voltage was the potential applied on the base side. The main transmembrane potential used in
this work was evaluated (see Fig. S3) and a scanning voltage varied from -2 to +2 V with a 40 s period was selected. The concentration and the pH of the electrolyte in this work were also evaluated (see Fig. S4 and S5), and we finally chose 1 M potassium chloride solution as electrolyte. In this work, each test was repeated 5 times to obtain the average current value at different voltages. The testing temperature was 20°C.

**Figure S3.** The different current measurement conditions of the transmembrane potential across the single nanochannel (Sample4). 

- **a**, The different scanning voltages varied from 1 to 10 V with a 40 s period, the voltage is 0 V at 20th s.
- **b**, The different step time of the scanning voltage (2 V).
- **c**, The different directions of the scanning voltage (2 V).
Figure S4. The different concentrations of KCl solutions for the current measurements of the single nanochannel (Sample4). a, I-V curves of the different KCl concentrations. b, The current ratio in the single nanochannel with different KCl concentrations at a potential of 2 V.

Figure S5. The different pH influence for the current measurements of the single nanochannel (Sample4, KCl 1 M). a, I-V curves of the different pH conditions. b, The current ratio in the single nanochannel with different pH at a potential of 2 V.
Contact angles were measured using an OCA20 (DataPhysics, Germany) contact-angle system at ambient temperature and saturated humidity. The original sample was treated with NaOH (9 M) for 1h. The sample was then taken out from the etching solution and treated with the stopping solution (1 M KCl + 1 M HCOOH) for half an hour. After that, the sample was treated with the deionized water, and had been stored for one day in the deionized water before further experiments. Before the CA test, the sample was blown dry by N₂. Deionized water droplets (about 2 µl) were then dropped carefully onto the surfaces. The average contact angel value was obtained at five different positions of the same sample. Finally, the results were summarized.

Figure S6. The CA of the PET film surfaces before and after ion sputtering. a, Before ion sputtering. b, After ion sputtering (Iₛ = 2 mA, t = 60 s).

The contact angles of the PET film surfaces (PET, Hostaphan RN12 Hoechst, 12 µm thick) after ion sputtering (Fig. S6b) were larger than the one before ion sputtering (Fig. S6a). The CA results indicate that the ion sputtering deposition could lead to a remarkable change of the wettability of the surface (from 68.1°±1.6° to 88.2°±1.2°) which means the change of the chemical composition. These results may potentially spark further experimental approach to study the relationship between the wettability and the ion transport property on confined space in nano scale.
Figure S7. XPS spectra of PET films before and after ion sputtering deposition. a, Before ion sputtering deposition. b and c, After ion sputtering deposition (I_s = 2 mA, t = 60 s).

XPS measurements were performed to validate the chemical identity of the PET films (PET, Hostaphan RN12 Hoechst, 12 μm thick) before and after ion sputtering deposition. XPS data were obtained by an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation, and the base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. We observe the reduction of the C1s-O1s ratio after ion sputtering deposition (Fig. S7a and S7b). This shows that the increasing oxygen may come from the oxygen bonding with platinum to form metallic oxide compounds, used to stabilize the chemical/structure asymmetric artificial single nanochannel materials. Figure S7c shows that the binding energy of the Pt4f7/2 is 72.7 eV. According to standard data of XPS spectroscopy\(^{[S3]}\), the binding energy of the nonvalent Pt4f7/2 is 70.9 eV. This may explain the state of Pt of nanochannel materials are the oxidation state. Moreover, as we know the ray depth of XPS is generally 2 - 10 nm, according to the
XPS results (Table S1- S4), it shows that the tip side of the depth ($I_s = 2 \text{ mA, } t = 60 \text{ s}$) is less than 10 nm.

**Table S1.** Before ion sputtering, the angle of incidence is 90°.

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<th>Name</th>
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**Table S2.** After ion sputtering, the angle of incidence is 15°.

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**Table S3.** After ion sputtering, the angle of incidence is 45°.

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**Table S4.** After ion sputtering, the angle of incidence is 90°.

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References

