

Electronic Supplementary Information

Photo-induced Current Generation in L-histidine Modified Nanochannel based on Big Charged Photoacid in Solution

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Materials

The fabrication of single nanochannels in 12 μm thick PET films was performed by the track-etching technique. Before the chemical etching process, each side of the sample was independently exposed to the UV light for 1 h. 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 pore opens, thus slowing down the further etching process. Briefly, the PET membrane was embedded between the two chambers of a conductivity cell at 35 °C, one chamber was filled with etching solution (9 M NaOH), while stopping solution (1 M KCl + 1 M HCOOH) was added in the other. A voltage of 1 V was applied across the membrane. The membrane was soaked in MilliQ water (18.2 M Ω) to remove residual salts. The diameter of the large opening of the conical nanochannel was called base (D). In order to observe the base side of the nanochannel, we etched the multi-channel PET membrane under the same condition.

The SEM image of the base side was obtained by a Hitachi S-4300 microscope at an accelerating voltage of 5 kV.

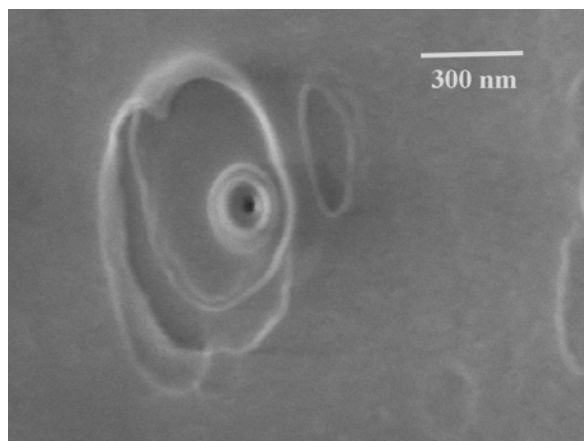


Fig. S1 SEM image of the base of the nanochannel. The diameter was ~400 nm.

The diameter of the small opening which was called tip (d_{tip}) was estimated by the following relation:

$$d_{tip} = \frac{4LI}{\pi k(c)UD}$$

Where L is the length of the channel, I and U is the measured current and the applied voltage, respectively, d_{tip} is the tip diameter, D is the base diameter, $k(c)$ is the special conductivity of the electrolyte. For 1 M KCl solution at 25°C, $k(c)$ is 0.11173 $\Omega^{-1}\text{cm}^{-1}$. In this work, the base diameter was ~400 nm, and the tip diameter was ~10 nm.

Modification

The carboxylic groups generated on the pore surface during the track-etching process were modified by the following procedure. Step 1, these groups were converted into pentafluorophenyl esters by using ethanolic solution of N-(3-dimethylaminopropyl)-N-

ethylcarbodiimide hydrochloride (EDC, 100 mM) and pentafluorophenol (PFP, 200 mM) for 1 h. Step 2, reactive esters were condensed with the amino groups of L-histidine (50 mM) solution prepared in 60 % aqueous ethanol and allowed to react overnight at room temperature. Finally, the functionalized membranes were washed with distilled water several times.

Ion current measurement

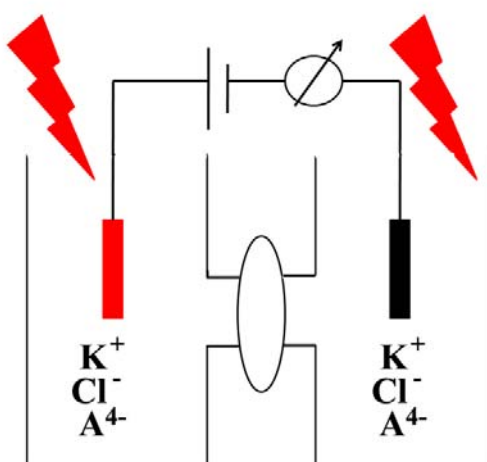


Fig. S2 The experimental cell used in the ion current measurement experiment. The anode faced the base of the nanochannel. Ag/AgCl electrode is unstable under UV light, but it does not influence the current during measurement. We irradiated from the both sides of the solution and then put in the electrode to test the conductance of the nanochannel.

The ionic transport properties of the nanochannel were studied by measuring ionic current through the nanochannel. Ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). A single conical shaped PET membrane was mounted between two chambers of the etching cell. Ag/AgCl electrodes were used to apply a transmembrane potential across the film. A scanning voltage varied from -2 V to +2 V at a scanning rate of 40 s.

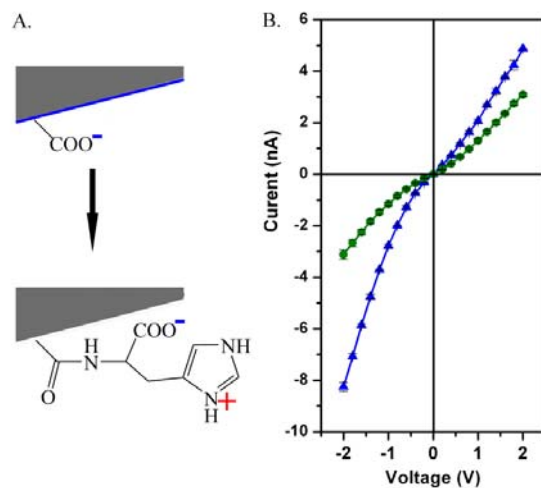


Fig. S3 The process of chemical modification and the current-voltage (I - V) curves during the process of chemical modification. I - V curves were recorded under symmetric electrolyte condition. The electrolyte was 0.1M KCl at pH 4.2. The pristine nanochannel rectifies the current due to the negatively carboxyl groups (▲, blue). After conversion of carboxyl groups into L-histidine, the channel can be either positively charged or negatively charged according to the pH of the solution. At pH 4.2, L-histidine is neutral and the curve became nearly linear (●, olive).

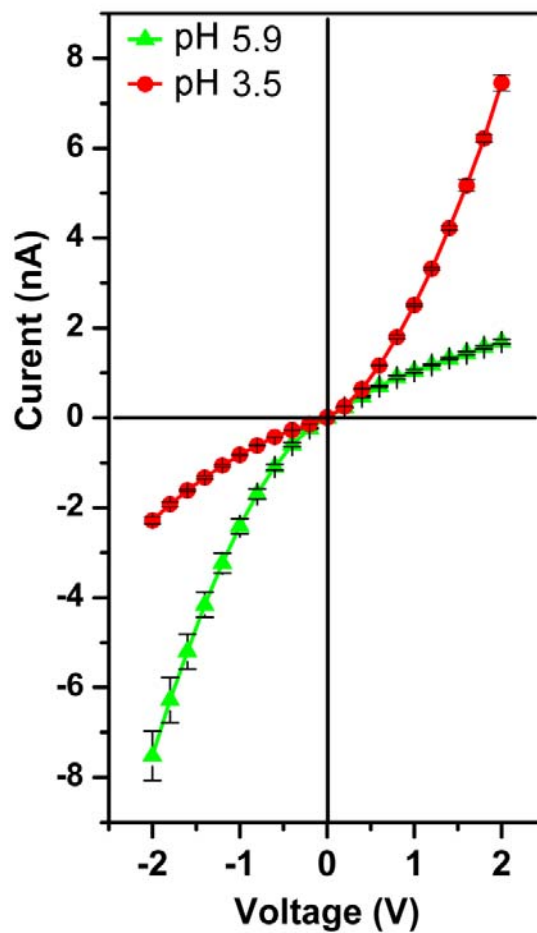


Fig. S4 Current-voltage (I-V) curves at different pH adjusted with HCl. At pH 5.9, the carboxylic groups are responsible for the negatively charged channel surface(▲, green). At pH 3.5, the ionized imidazole group provides a net positive charge(●, red). Therefore, the current rectification direction is reversed.

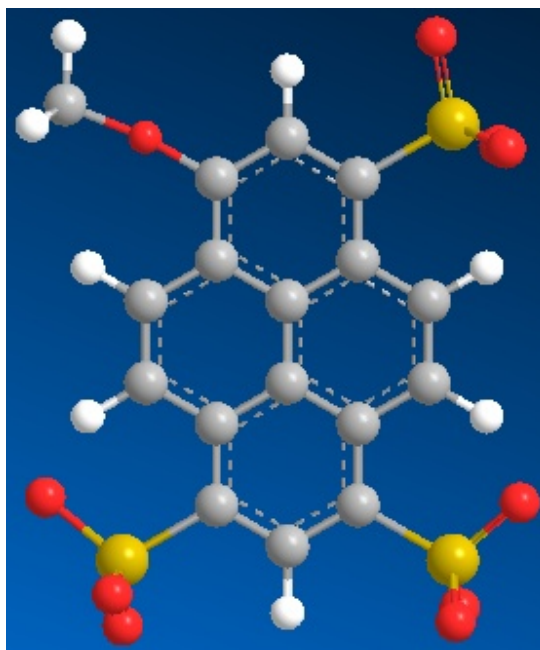


Fig. S5 3D molecular structure of 8-hydroxypyrene-1,3,6-trisulfonate. The diameter is ~1.1 nm.

References:

1. P. Y. Apel, Y. E. Korchev, Z. Siwy, R. Spohr and M. Yoshida, *Nucl. Instrum. Meth. B*, 2001, **184**, 337.
2. M. Ali, P. Ramirez, S. Mafe, R. Neumann and W. Ensinger, *Acs Nano*, 2009, **3**, 603.