Supporting Information

pH Gated Glucose Responsive Biomimetic Single Nanochannels

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Materials

Poly(ethylene terephthalate) (PET, 12 μm thick) membranes were irradiated with single heavy ion (Au) of energy 11.4 MeV/nucleon at UNILAC linear accelerator (GSI, Darmatadt, Germany). 1-Ethyl-3-(3-dimethyllaminopropyl) carbodiimide (EDC), N-hydroxysulfosuccinimide (NHSS), 3-aminobenzeneboronic acid were purchased from Sigma-Aldrich. sodium hydroxide (NaOH), formic acid (HCOOH), potassium chloride (KCl), sodium dihydrogen phosphate (NaH_2PO_4), and sodium hydrogen phosphate (Na_2HPO_4) were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. (SCRC, China). All solutions were prepared in MilliQ water (18.2 MΩ).

Fabrication

The single conical nanochannel was prepared in PET films using the ion track-etching technique. Before etching process, each side of the PET membranes were exposed in Uv light (320 nm) for 1h. In order to obtain the conical nanochannel, 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. The PET membrane was embedded between the two chambers of a conductivity cell at 30 ^{o}C, one chamber was filled with etching solution (9 M NaOH), the other chamber was filled with stopping solution (1 M KCl + 1 M HCOOH). Then a voltage of 1 V was applied across the membrane. The etching process was stopped at a desired current value corresponding to a certain tip diameter. The membrane was immerged in MilliQ water (18.2 MΩ) to remove residual salts. The diameter of the

large opening of the conical nanochannel which was called base (D) was determined by scanning electron microscopy (SEM), the diameter of the small opening which was called tip (d_{tip}) was estimated by the following relation:

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

L is the length of the pore; I is the current; U is the applied voltage; d_{tip} and D is the tip diameter and the base diameter respectively; *k(c)* is the specific conductivity of the electrolyte. For 1 M KCl solution at 25 ^{o}C, *k(c)* is 0.11173 $\Omega^{-1}cm^{-1}$. In this work, the base diameters were several hundred nanometers and the tip diameters was from 14 to 21nm.

Modification

As a result of asymmetric chemical etching, carboxyl groups are generated on the nanochannel surface. These can be activated with EDC/NHSS, forming an amine-reactive ester intermediate. Then these reactive esters were further condensed with 3-aminobenzeneboronic acid through the formation of covalent bonds. In this paper NHSS ester was formed by soaking PET film in an aqueous solution of 15 mg EDC and 3 mg NHSS for 1 h. After that washing this film with distilled water and treated it with 1mM 3-aminobenzeneboronic acid solution overnight. Finally, the modified film was washed three times with distilled water.

Ion currents measurement

Ion currents were measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). Ag/AgCl electrodes were used to apply a transmembrane potential across the film. The film was mounted between the two halves of the conductance cell. Both halves of the cell were filled with a 0.1 M KCl solution prepared in 0.1M phosphate saline buffer (PBS pH 7.38). In order to record the I–V curves, a scanning triangle voltage signal from -2V to +2V with a 40s period was

selected. Each test was repeated 5 times to obtain the average current value at different voltage.

Contact angles measurment

Contact angles were measured using an OCA 20 contact angle system (Dataphysics, Germany). at 25 °C. The original PET membrane for contact angle measurement was treated with etching solution (9 M NaOH) for 1h. The membrane was then taken out from the etching solution and treated with a stopping solution (1 M KCl + 1 M HCOOH) for 30 min. After that, the membrane was immerged in deionized water ovenight. Before the contact angle test, the sample was blown dry with N_2. In each measurement, an about 2 μL droplet of water was dispensed onto the surface of PET membrane. The average contact angel value was obtained at five different positions of the same membrane. The 3-aminobenzeneboronic acid modified PET membrane was immerged in deionized water overnight and blown dry by N_2 for contact angle measurements. As shown in Figure S1, after 3-aminobenzeneboronic acid modification a slight change of the wettability of the surface (from $64.6^o \pm 1.2^o$ to $70.1^o \pm 2.5^o$) which means the change of the chemical composition.

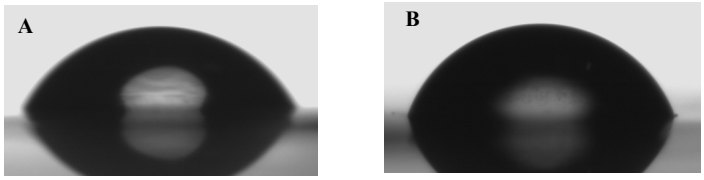

Figure S1 Photographs of water droplet shape on the PET films before (A) and after (B) 3-aminobenzeneboronic acid modification.

XPS

X-ray photoelectron spectra (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation. All peaks were referenced to C 1s (CHx) at 284.8 eV in the deconvoluted high resolution C 1s spectra. The nitrogen and boron element existed in the modified PET film indicates that 3-aminobenzeneboronic acid was modificated on the membrane successfully.

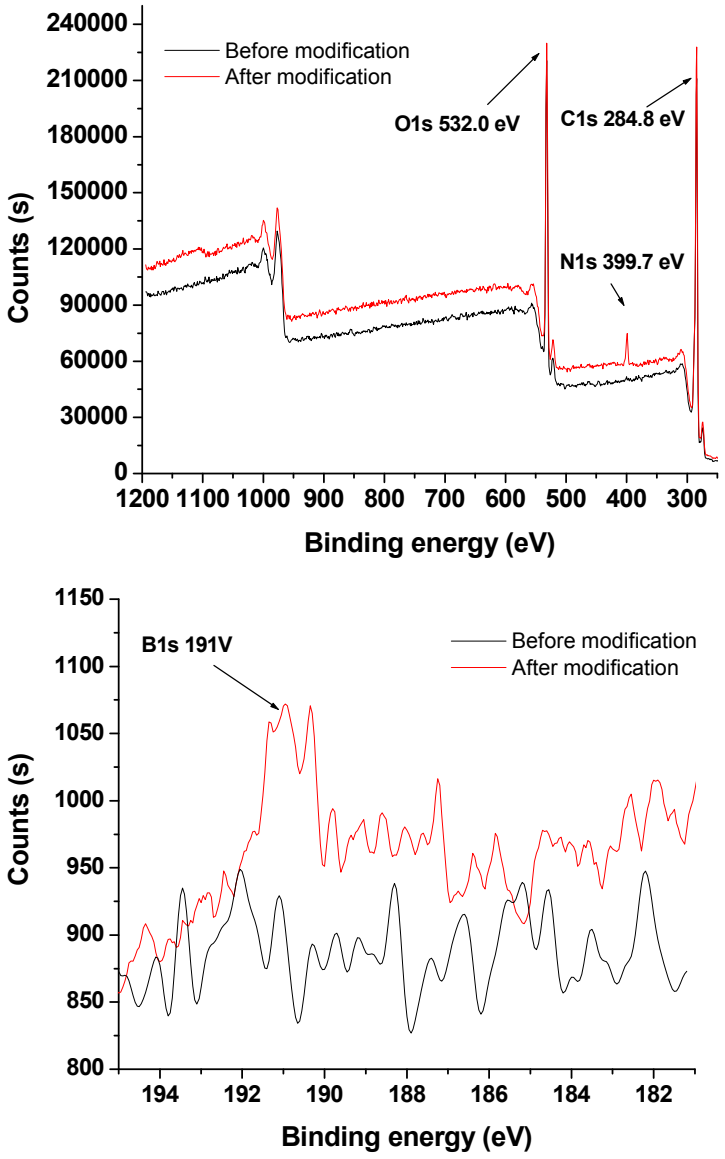

Figure S2 XPS spectra of PET films before and after 3-aminobenzeneboronic acid modification.

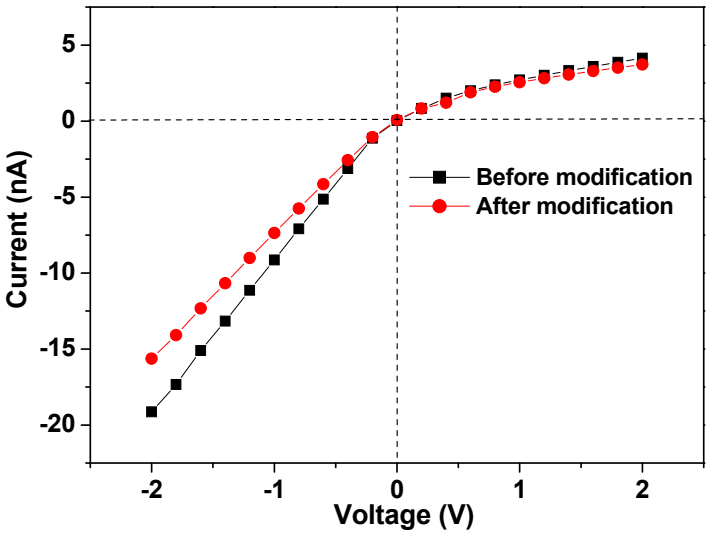

Figure S3 Current-voltage (I-V) properties of the single nanochannel before and after 3-aminobenzeneboronic acid was modified on the film in 0.1 M KCl solution prepared in phosphate saline buffer (PBS pH 7.38). Before modification, the single asymmetric nanochannel rectified the ionic current due to the presence of anionic carboxylate ($-COO^-$) groups. After immobilization of the 3-aminobenzeneboronic acid, the current decreased that because some neutral 3-aminobenzeneboronic acid reacted with $-COO^-$ and decreased the negative charge on the channel surface. Before modification, the diameter of the tip is 21 nm.

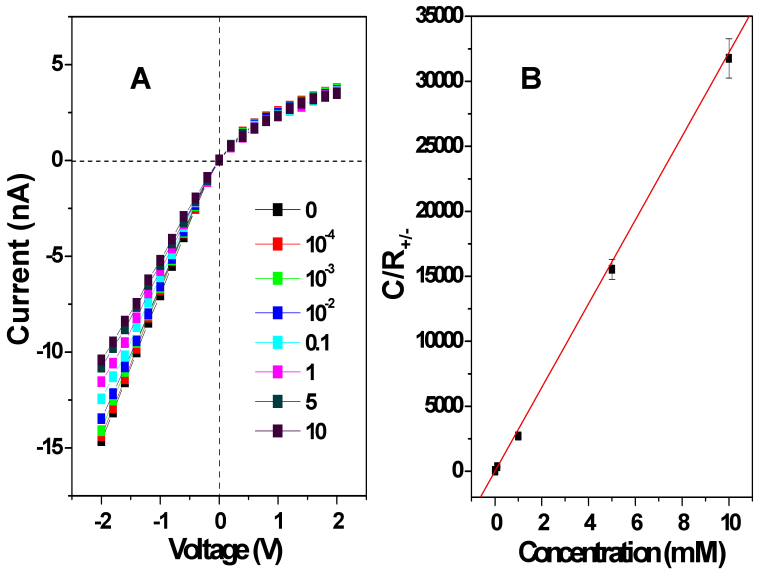

Figure S4 I-V curves A) and Concentration /Rectification ratios-Concentration B) of the 3-aminobenzeneboronic acid modified single nanochannel in 0.1 M KCl (pH 7.38) with the addition of 10^{-4} ～10 mM Glu. The experimental data was found to provide a perfect fit to Langmuir model. Before modification, the diameter of the tip is 21 nm.

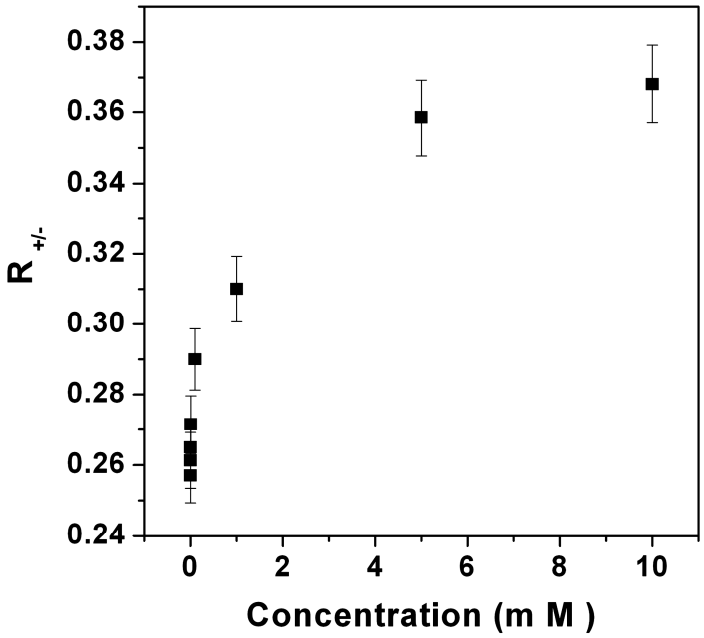

Figure S5 Effect of increasing concentrations of Glu on the rectification ratios of 3-aminobenzeneboronic acid modifided nanochannel.

Switchable property

In this paper electrolytic solution is 0.1 M KCl prepared in 0.1 M phosphate saline buffer (PBS, pH 7.38 and pH 4.49). First, I–V curves of boronic acid modified film were recorded at 0.1 M KCl solution (pH 7.38). Then ion currents were measured after adding 10^{-3} M Glu solutions prepared in 0.1 M KCl at pH 7.38 for 5 min and the current at -2V decreased ("off" state). After that, emerging this membrane in pH 4.45 PBS solution for 15 min, the hydrolysis of the cyclic ester was achieved. Glu break away from channel surface under pH 4.49. And then washed film with water for three times and immerged in water for 10 min. At this time, boronic acid unit exposed on the channel surface, the ionic current at -2V measured in 0.1 M KCl (pH 7.38) increased ("on" state).

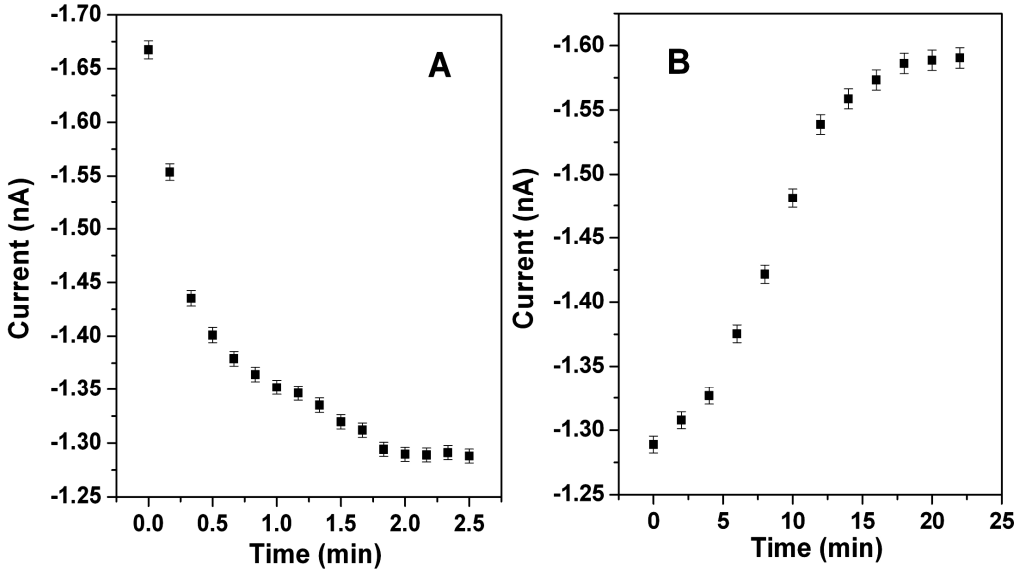

Figure S6 Current-time curves of a single nanochannel with A) formation, B) hydrolysis of the cyclic ester.

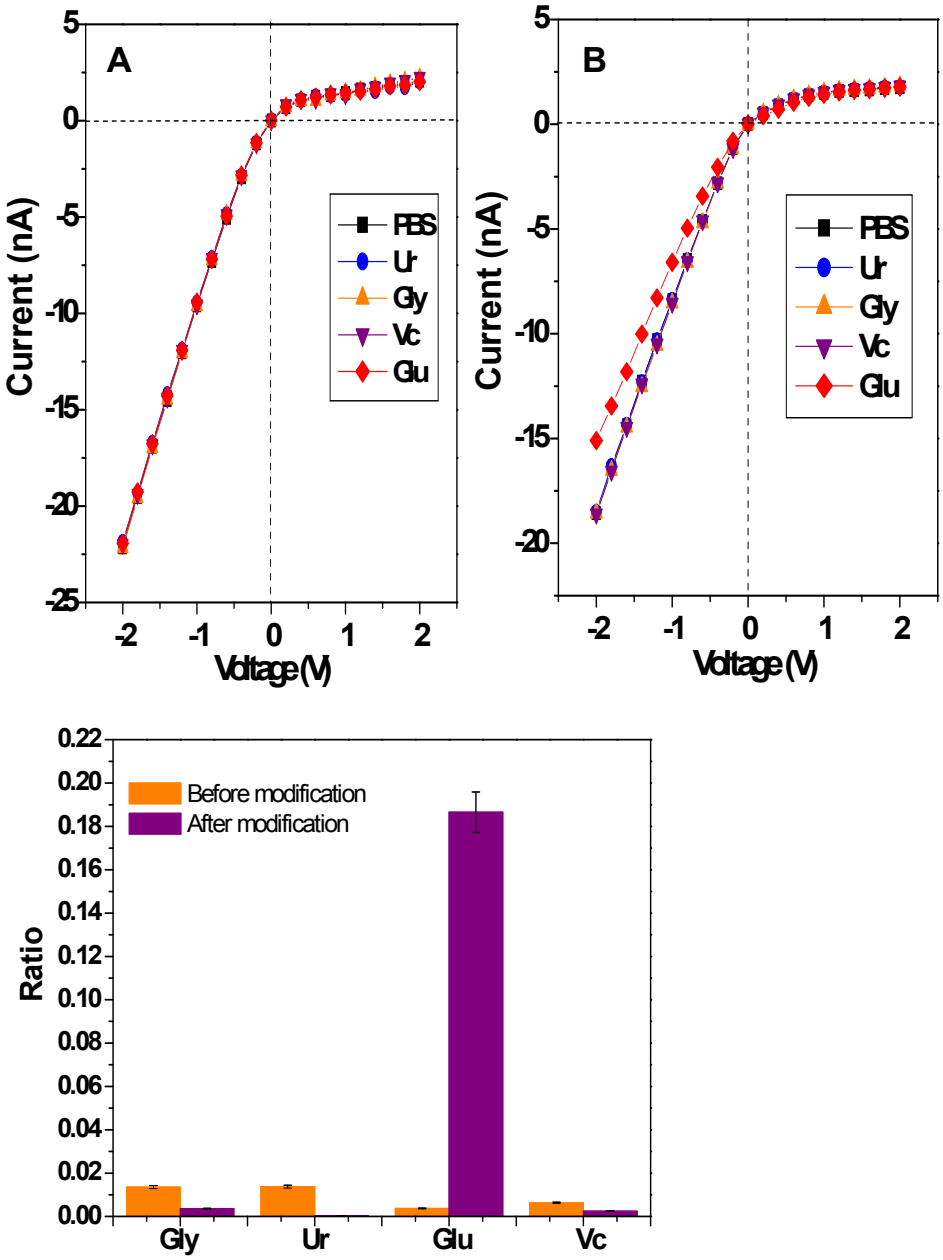

Figure S7 I-V curves of the single nanochannel before A) and after B) 3-aminobenzeneboronic acid modification in 0.1 M KCl PBS (pH 7.38) without or with the addition of 1 mM Gly, Ur, Glu, Vc respectively. C) Current change ratios ($R= I-I_0/I_0$) measured at -2 V of before (orange) and after (purple) 3-aminobenzeneboronic acid modified nanochannel with the addition of 1 mM Gly, Ur, Glu, Vc respectively. This modified nanochannel maintains good response to Glu in the presence of other interferents. Before modification, the diameter of tip is about 23 nm.