Supporting Information

Chiral Recognition of Arg Based on Label-Free Nanochannel

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1. 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). bovine serum albumin (BSA), D-, L- Arginine (Arg), Aspartic acid (Asp), Glutamate (Glu), Tryptophan (Trp), Tyrosine (Tyr), Leucine (Leu), Threonine (Thr) were purchased from Sigma-Aldrich. sodium hydroxide (NaOH), hydrochloric acid (HCl), 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).

2. 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 $\Omega^{-1}cm^{-1}$. As shown in Figure S1, the large

opening (base) is about 520 nm in diameter and the tip diameter is about 16 nm, as measured with electrochemical methods.

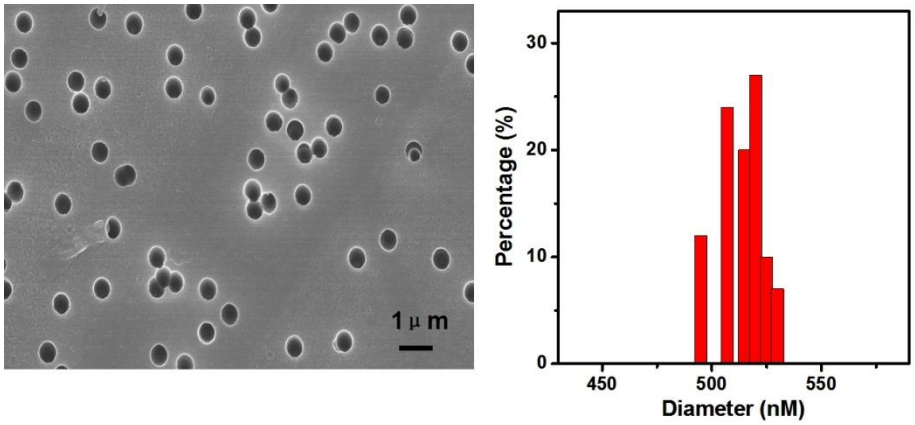

Fig. S1 SEM and size distributions of nanochannel.

3. 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 0.03 M phosphate saline buffer (PBS pH 7.1). 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.

4. Confocal Images.

Confocal images were acquired using a Zeiss confocal laser scanning unit mounted on a LSM710 fixed-stage upright microscope.

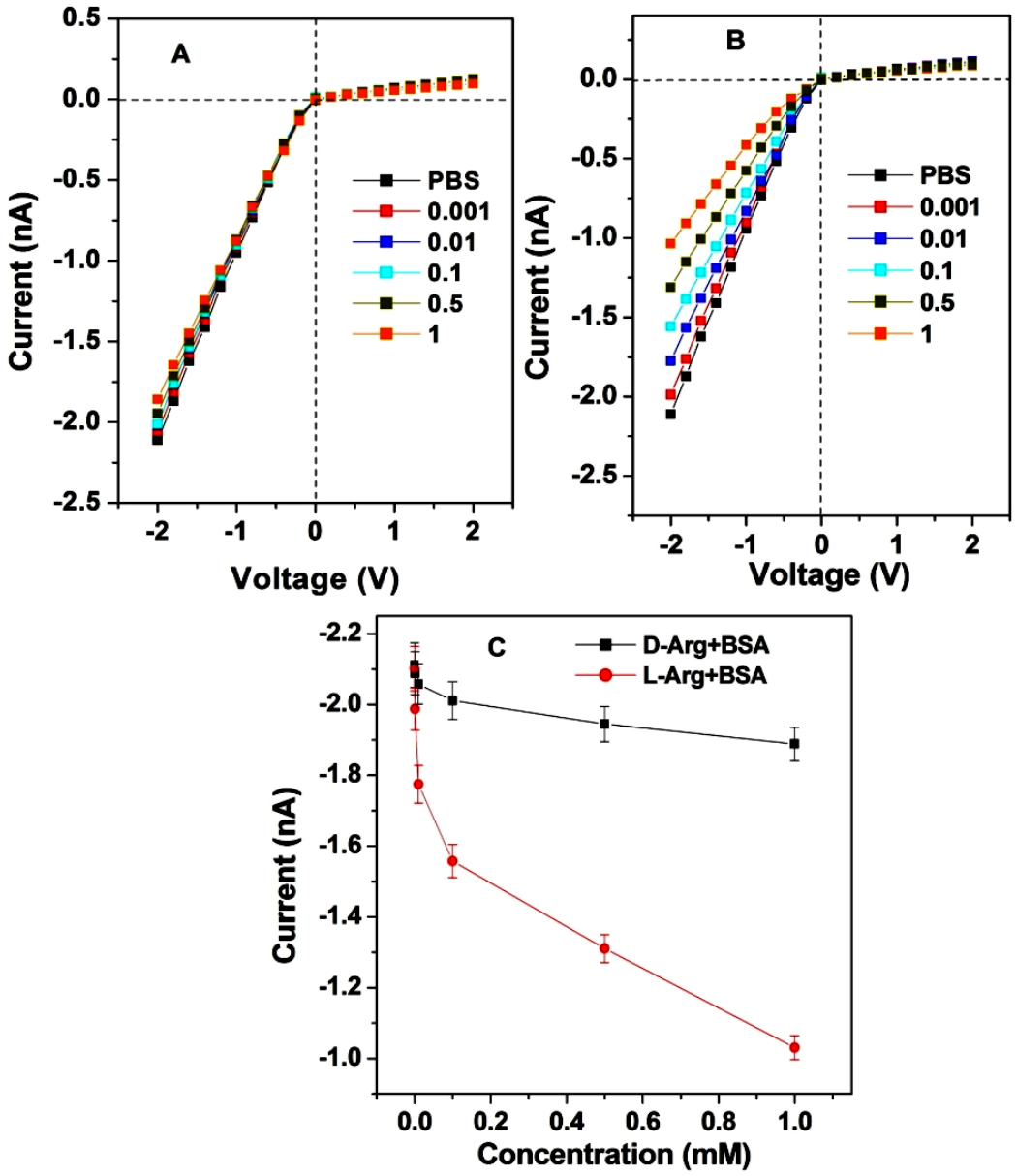

Fig. S2. A) and B) I-V curves of the label-free nanochannel exposed in different concentration of D- and L-Arg (0 to 1 mM) in 0.03 M PBS (pH 7.1) addition of 1 mg/mL BSA. C) Current-concentration (I-C) properties, with concentration increase the difference in the enantiomeric ionic currents became larger and larger. This label-free nanaochannel can enantioselective recognition of L-Arg with the addition of BSA.

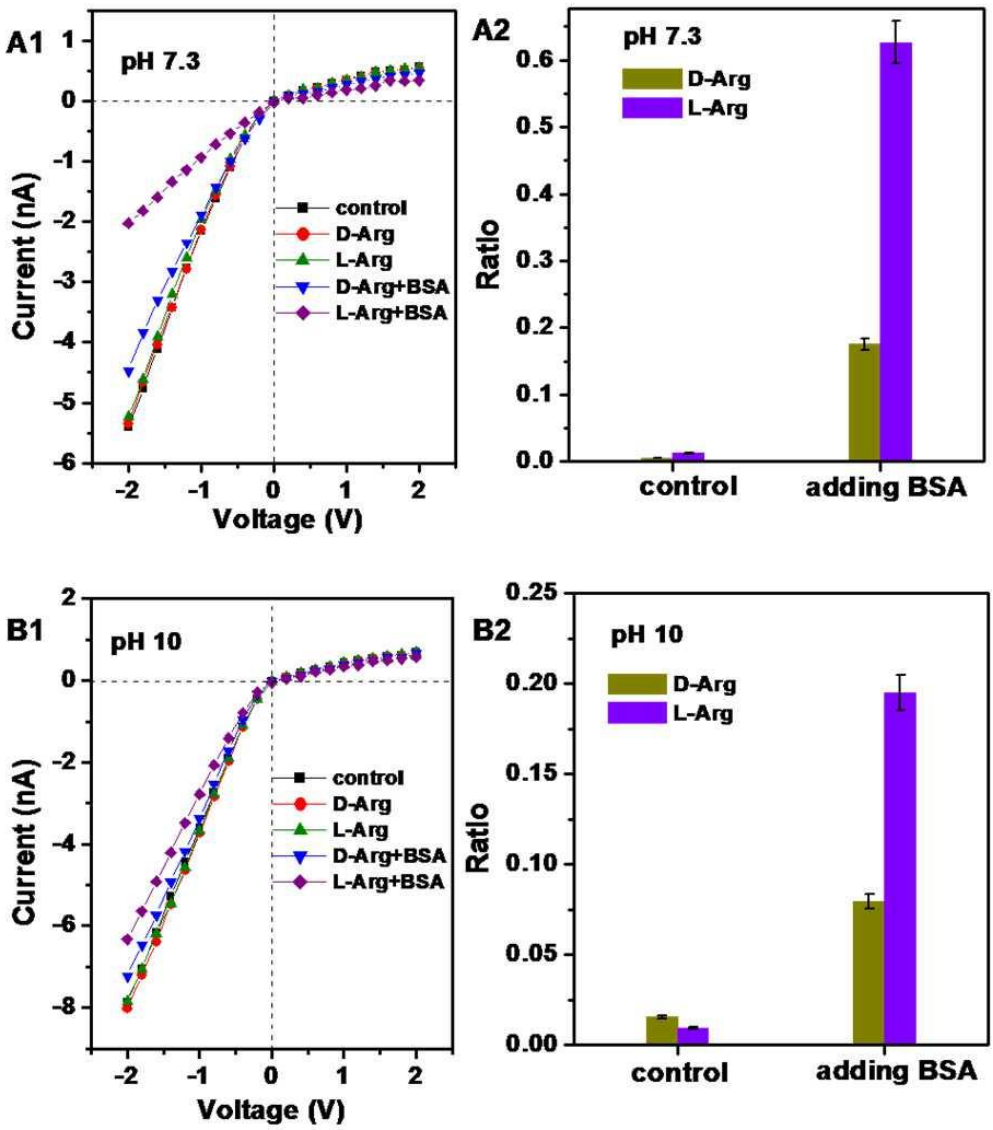

Fig. S3. At pH 7.3, (A1) I – V curves and (A2) current change ratios at -2 V and at pH 10, measured (B1) I – V curves and (B2) current change ratios at -2 V of the single nanochannel before and after addition of 1 mM Arg and Arg/BSA in 0.1 M KCl (pH 7.3 and pH 10) solution. Before modification, the diameter of the tip is about 21 nm.

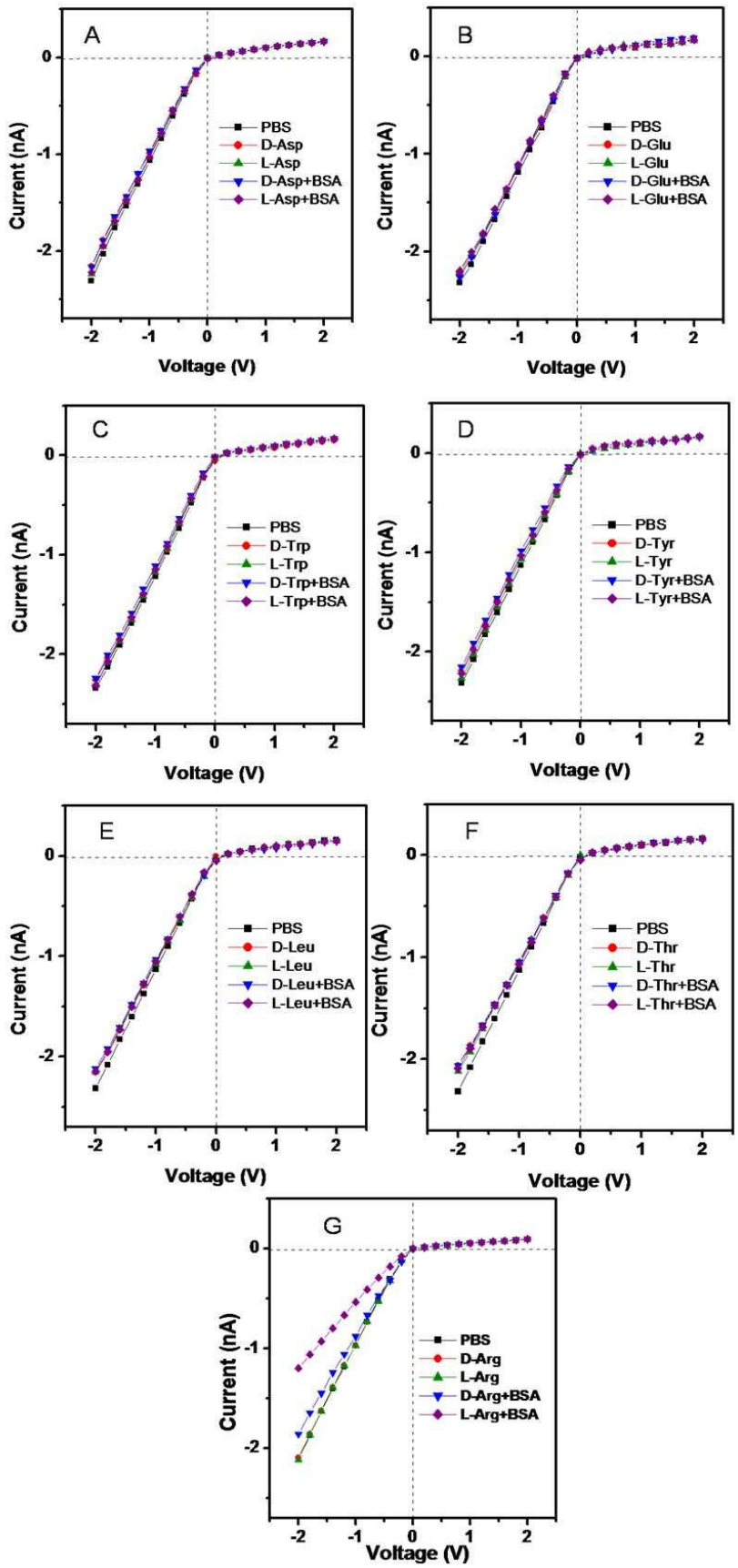

Fig. S4 I-V curves of single nanochannel before and after addition of 1 mg/ml BSA into 1 mM A) Asp, B) Glu, C) Trp, D) Tyr, E) Leu, F) Thr and G) Arg solution respectively in 0.03

M PBS (pH 7.1). This system showed a high selective on chiral recognition for D-, and L-Arg.