

Supporting information

DNAzyme Tunable Lead (II) Gating Based on Ion-Track Etched Conical Nanochannels

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Materials

Poly(ethylene terephthalate) (PET) membranes were irradiated with heavy ion (Au) of energy 11.4 MeV/nucleon at UNILAC linear accelerator by Institute of Modern Physics, Chinese Academy of Sciences.

The primers, 5'-(SH)-(CH₂)₆-ACTCACTATrAGGAAGAGATG-3' (17-DS, DNAzyme 1), 5'-CATCTCTTCTCCGAGCCGGTCGAAATAGTGAGT-3' (17-E, DNAzyme 2), and 5'-(SH)-(CH₂)₆-ACTCACTATGGAAGAGATG-3' (17-D, DNAzyme 3) were synthesized by Takara Biotechnology (Dalian) Co., Ltd.

Sodium hydroxide (NaOH), potassium chloride (KCl), and formic acid (HCOOH) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (SCRC, China).

Potassium perchlorate (KClO₄); Nickel (II) perchlorate hexahydrate (Ni(ClO₄)₂·6H₂O); Zinc perchlorate, Reagent Grade (Zn(ClO₄)₂·6H₂O); Copper (II) perchlorate hexahydrate, Reagent Grade (Cu(ClO₄)₂·6H₂O); Lithium perchlorate, anhydrous, ACS, 95.0% min (LiClO₄); Cobalt (II) perchlorate hexahydrate, Reagent Grade (Co(ClO₄)₂·6H₂O); Lead (II) perchlorate trihydrate, Reagent Grade, 97.0% min (Pb(ClO₄)₂·3H₂O). The above chemicals were purchased from Sigma-Aldrich.

All solutions were prepared by using inactivated water (Sigma-Aldrich) as the dissolvent.

Nanochannel fabrication

First, both sides of the PET membrane were irradiated with UV light for 1 h, respectively; then the multi-nanochannels were prepared using the reported tracks chemical etching technique.¹ The PET membrane was embedded between two chambers of a conductivity cell which had been preheated for 3 hours at the temperature of 30 °C. In the next step, one chamber was filled with etching solution (9 M NaOH), while stopping solution (1 M KCl + 1 M HCOOH) was added in the other chamber. A DC voltage of 1 V was applied across the membrane by the picoammeter,

and the conical multi-nanochannels with a desired diameter could be obtained by monitoring the transmembrane current. At last, the membrane was taken out and washed by MilliQ water (18.2 MΩ) to remove residual salts. Then immerse the etched membrane in MilliQ water for 5 hours.

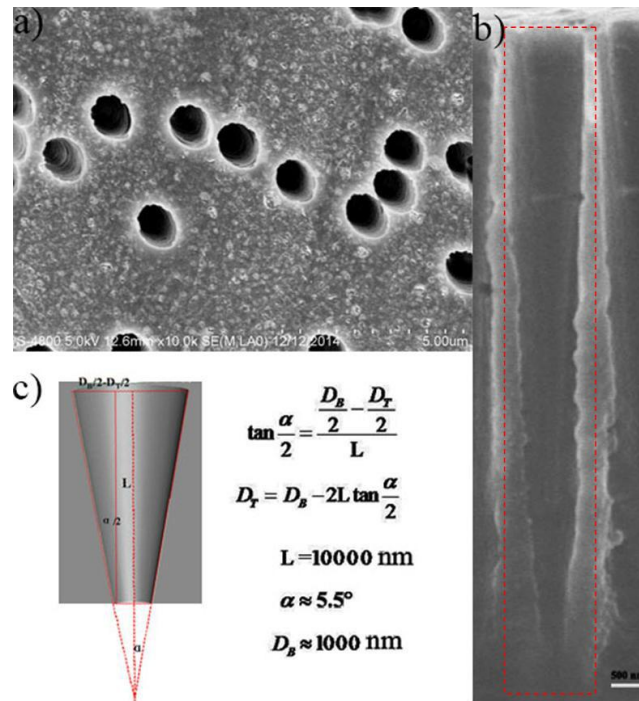


Figure S1. SEM image of the base side of ion-track chemical etching PET film.

Nanochannel functionalization

1. We fabricated the conical nanochannel using an asymmetric track-etched technique with the PET membrane;
2. Then, the gold was deposited on the inner walls of the nanochannel by the gold sputtering from the base side;
3. The modification of DNAzyme was accomplished by forming Au-thiol bond on the inner surface of the nanochannel.

Current-Voltage Recordings

The sensing properties were studied by measuring the ionic current under the condition of absence and presence of Pb^{2+} . The ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). The functionalized multi-nanochannel membrane was mounted between two halves of a conductivity cell; and each half cell was filled with 0.1 M KCl (Figure S2). The Ag/AgCl electrodes were used to apply a transmembrane potential, and the scanning voltage varied from -2 V to +2 V with its period of 40 seconds. Two kinds of nanochannels systems had been measured, namely, the gold-sputtered nanochannels, and the Pb^{2+} -responsive DNAzymes modified nanochannels. The process and conditions of all the measurements mentioned in this communication were the same. If no particular instructions were added on, each test was repeated more than 10 times to obtain the average current value at uniform voltage.

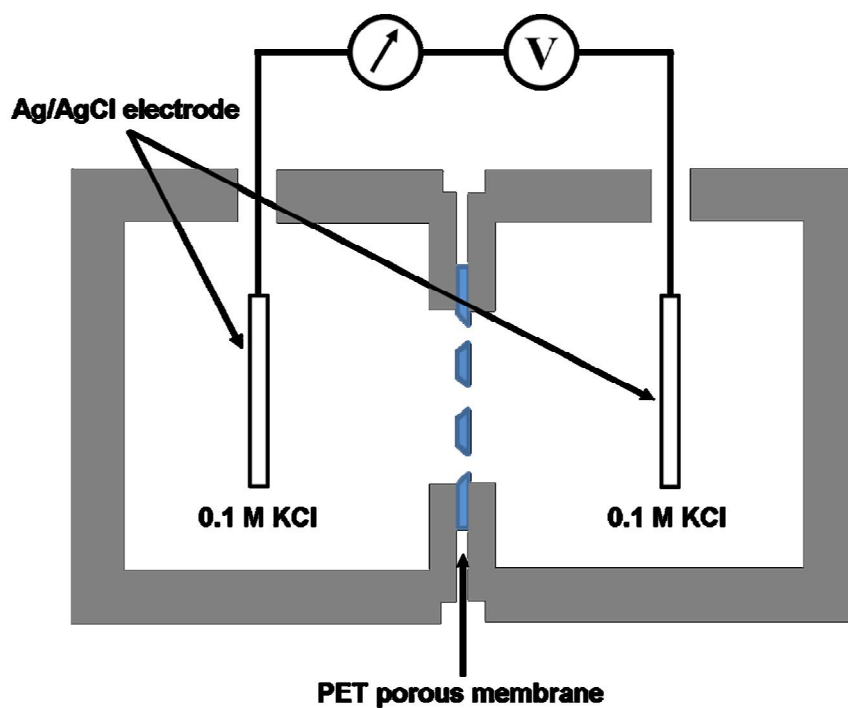


Figure S2. Schematic of a conductivity cell which can be used to record the current-voltage properties.

X-ray photoelectron spectra characterization

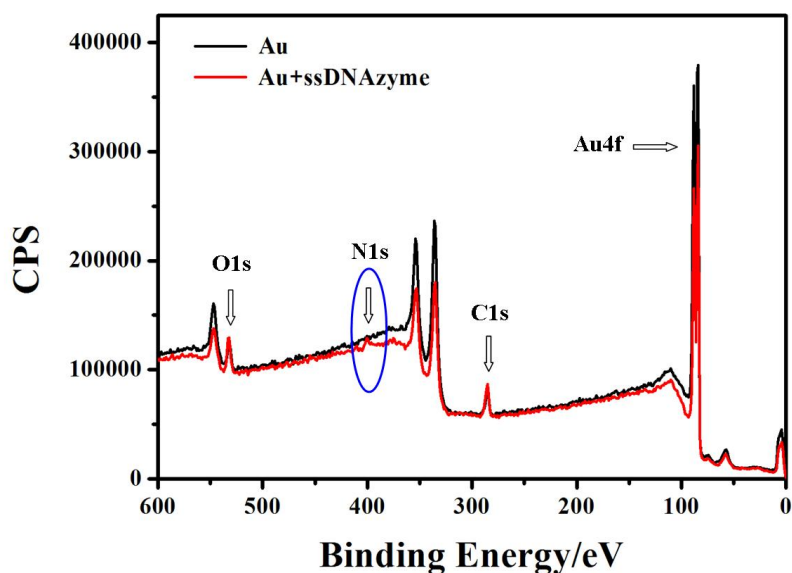


Figure S3. XPS spectra of the Pb^{2+} responsive DNAzyme immobilized PET films. The different colour lines corresponding to the Au sputtering PET film (black), after Pb^{2+} responsive ssDNAzyme grafted (red). The nitrogen element exists in all the residues of the Pb^{2+} responsive ssDNAzyme.

The successfully grafting the ssDNAzyme onto the Au-coating nanopore can also be characterized by the X-ray photoelectron spectroscopy measurement before and after modifying the ssDNAzyme onto the surfaces. The different colour lines in the Fig S3 correspond to the Au sputtering PET film (black) and ssDNAzyme grafted film (red), respectively. The carbon element, aurum element and oxygen element exist in all the samples, and the existence of nitrogen element in the red line indicates that the thiol-terminated ssDNAzyme were covalently attached onto the gold surfaces successfully.

Table S1. The percentage of the elements obtained by X-ray photoelectron spectra (XPS).

Before ssDNAzyme grafted

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area(N) TPP-2M	Atomic%
Au4f	92.77	84.46	80.57	150617.34	0.87	286823.06	0.17	41.73
C1s	292.72	284.87	282.25	5732.17	1.51	12401.31	0.16	39.45
N1s	402.54	398.38	396.52	460.07	0.03	970.25	0.01	1.91
O1s	536.34	531.94	527.86	4920.26	2.35	14078.57	0.07	16.92

After ssDNAzyme grafted

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area(N) TPP-2M	Atomic%
Au4f	92.09	84.12	80.27	110212.29	0.84	204184.45	0.12	22.65
C1s	292.52	284.81	281.07	7775.62	1.49	19914.68	0.25	48.3
N1s	405.79	399.94	396.07	1925.01	3.1	6532.8	0.05	9.8
O1s	536.35	532.76	527.68	7122.75	2.94	21002.17	0.1	19.25

XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al K α radiation. All peaks were referenced to C 1s (CH_x) at 284.8 eV in the deconvoluted high resolution C 1s spectra, and the analysis software used was provided by the manufacturer.

Contact angle measurements of the Pb²⁺-responsive surfaces

Contact angles were measured by using an OCA20 machine (DataPhysics, Germany) contact-angle system at ambient temperature and saturated humidity. To each sample, an about 3 μL water droplet was dispensed onto the substrates. The average contact angle value was obtained at five different positions of the same sample. The flat PET membrane for contact angle measurement was treated with 9 M NaOH for 30 minutes. Then remove the sample from the etching solution and treated it with a stopping solution (1 M KCl and 1 M HCOOH) for 30 min. Finally, immerse the sample into deionized water overnight. Before the contact angle test, the sample was blown dry with N₂. For the flat PET substrate, the mean water contact angle was $72.4 \pm 1.0^\circ$ (Figure S4a). After the PET membrane was sputtered with Au, the sample membrane exhibited a little hydrophilic property, and the mean water contact angle decreased to $68.0 \pm 1.2^\circ$ (Figure S4b). When the gold sputtered PET membrane was modified with thiol-terminated ssDNAzyme through Au-thiol chemistry, its contact angle would decrease again, and the mean contact angle was $38.5 \pm 3.5^\circ$ (Figure S4c), for that the ssDNAzyme were more hydrophilic than the gold surfaces. After introducing Pb²⁺ on the system, the ssDNAzyme would be cleaved, which increased its mean contact angle to $53.4 \pm 2.5^\circ$ (Figure S4d). These results further confirmed that the ssDNAzyme were successfully grafted onto the gold surface and

could be worked as a Pb^{2+} -responsive gate.

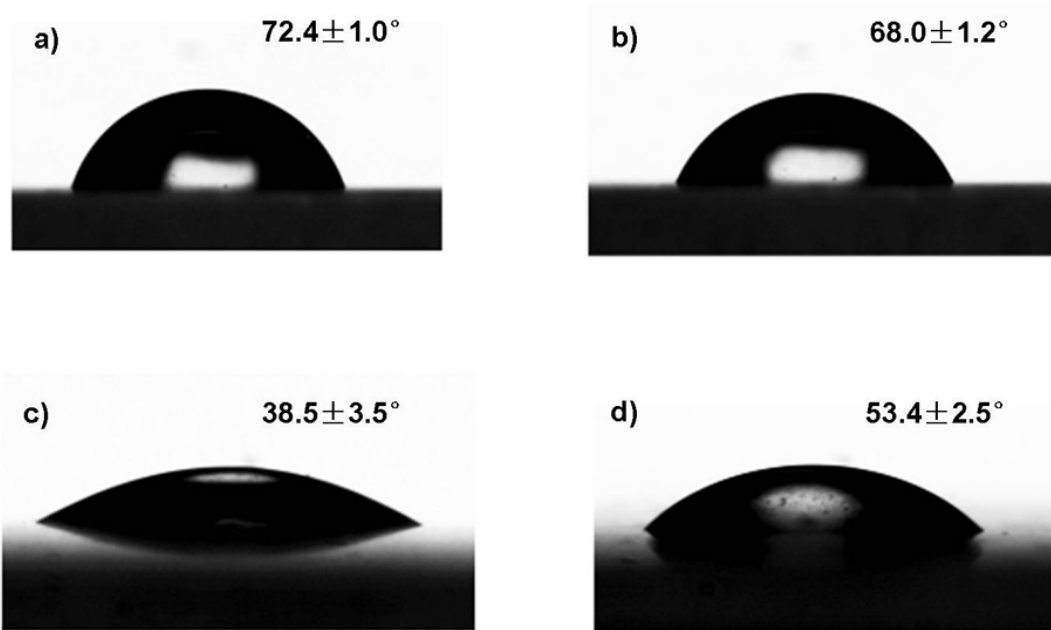


Figure S4. Pb^{2+} -responsive wettability for a PET membrane surface: a) treated with 9 M NaOH, b) Sputtered with gold nanoparticle, c) Modified with ssDNAzyme, d) And interacted with Pb^{2+} . The water contact angles are $72.4 \pm 1.0^\circ$, $68 \pm 1.2^\circ$, $38.5 \pm 3.5^\circ$ and $53.4 \pm 2.5^\circ$, respectively.

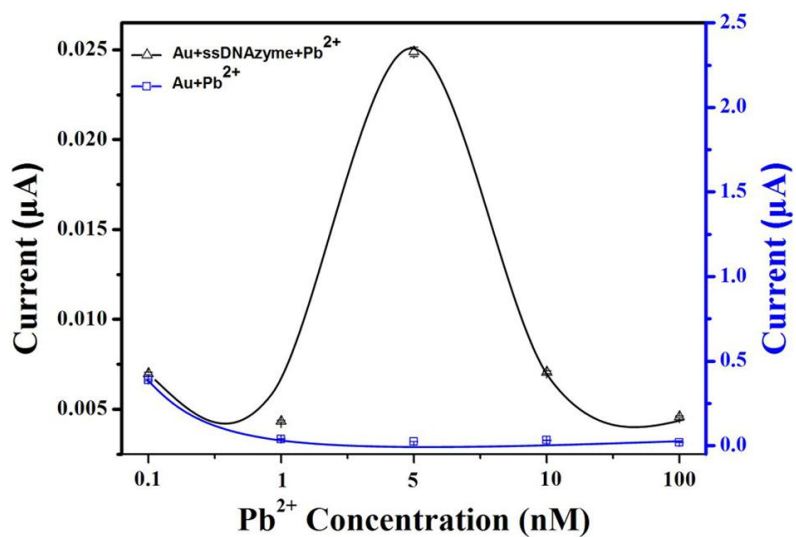


Fig. S5 At the voltage of +2 V, curves measured in 0.1 M KCl on conical gold-coated nanochannels before (blue) and after (black) ssDNAzyme modification with the different Pb²⁺ concentrations.

- [1] Apel, P. Y.; Korchev, Y. E.; Siwy, Z.; Spohr, R.; Yoshida, M. *Nucl. Instrum. Methods B* **2001**, *184*, 337.