Supporting Information

A Biomimetic Mercury(II)-gated Single Nanochannel

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Nanochannel Preparation and Modification with T-rich ssDNA: The single conical nanochannel was prepared with polyimide (PI, 12 μm thick) membrane which was irradiated with single swift heavy ion (Au) of energy 11.4 MeV per nucleon at the UNILAC linear accelerator (GSI, Darmstadt, Germany). Then the ion track polymer membrane was chemical etched at 60 degrees (about 333 K) from one side with 9 % NaClO, whereas the other side of the cell contains 1M KI which can neutralize the etchant as soon as the pore opens (Figure S 1A). The diameters of the base side of the nanochannel were determined by scanning electron microscopy. The tip diameter was evaluated by an electrochemical measurement of the ionic conductance with 1M KCl solution as electrolyte via the following equation:

$$d_{tip} = \frac{4LI}{\pi k(c)UD} \qquad (1)$$

Where d_{tip} is the tip diameter, D is the base diameter; k(c) is the special conductivity of the electrolyte. For 1M KCl solution at 25 °C is 0.11173 Ω-1cm-1. L is the length of the channel, which could be approximated to the thickness of the membrane after chemical etching. U and I are the applied voltage and measured ionic current in the pore conductivity measurement respectively. In this work, the base diameter was usually around 1.5 μm (Figure S 1B). Ion sputtered flux was employed to deposit gold onto the base side pore wall. The thiol-terminated T-rich ssDNA were covalently attached onto the gold surfaces through Au-thiol chemistry.

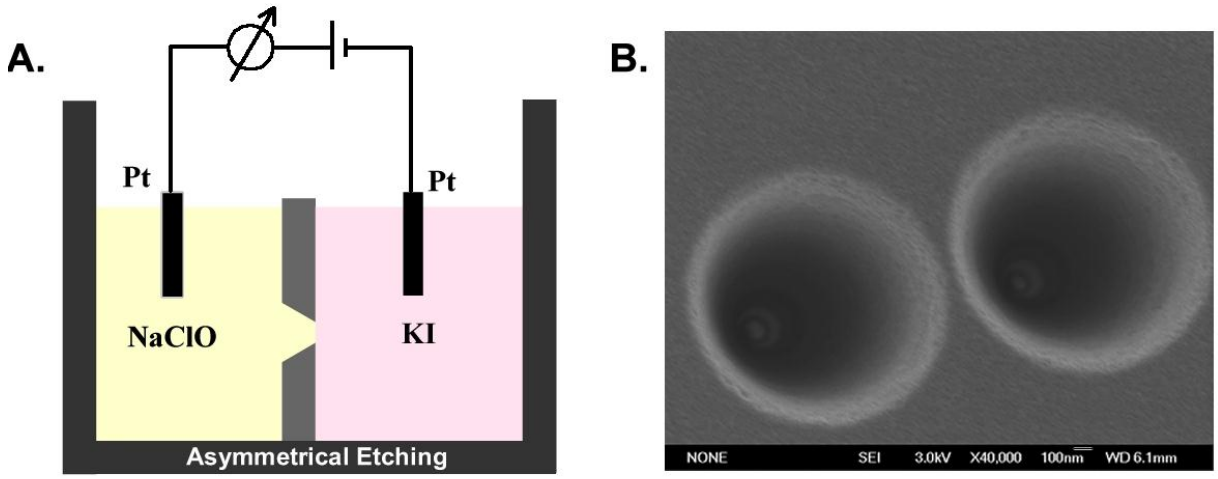

Figure S1. Schematic of an etching and characterizing conductivity cell (A), and a SEM image of nanochannel in track-etch PI membrane (B).

Current-Voltage Recordings: The sensing properties were studied by measuring the ionic current under the condition of absence and presence of Hg^{2+} ions. The ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). The single functional nanochannel-membrane was mounted between two halves of a conductivity cell; and each half cell was filled with 1 M KCl. (Figure S 2) Ag/AgCl electrodes were used to apply a transmembrane potential, and the scanning voltage varied from –1.5 V to +1.5 V with its period of 30 seconds. Two kinds of nanochannel systems have been measured, namely, the gold nanoparticle-sputtered nanochannels, and T-rich ssDNA modified nanochannels. The process and conditions of all the measurements mentioned in this article are of the same, if no particular instructions were added on, and each test was repeated 10 times to obtain the average current value at uniform voltage.

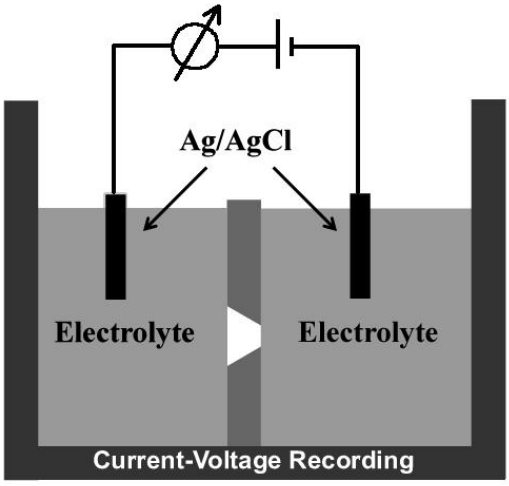

Figure S2. Schematic of a conductivity cell which can be used to record the current-voltage properties

Contact angle measurements of the mercury (II) responsive surfaces.

Contact angles were measured using an OCA20 machine (DataPhysics, Germany) contact-angle system at ambient temperature and saturated humidity. In each measurement, an about 2 μL droplet of water was dispensed onto the substrates under investigation. The average contact angel value was obtained at five different positions of the same sample. The original PI membrane for contact angle measurement was treated with NaClO (9 %) for 3 hours. The sample was then removed from the etching solution and treated with a stopping solution (1 M KI) for 30 min. After that, the sample was treated with deionized water overnight. Before the contact angle test, the sample was blown dry with N_2. For the flat PI substrate, the mean water contact angle was 76 ± 2.2 ºC (Figure S 3A). Once the PI membrane was sputtered with Au, the sample membrane exhibited hydrophilic property, and the mean water contact angle increased to 85 ± 1.5° (Figure S 3B). If the gold sputtered PI membrane was modified with thiol-terminated ssDNA through Au–thiol chemistry, its contact angel will decrease again, and the mean contact angel was 65 ± 1.8 ºC, since the ssDNA are more hydrophilic than the gold surfaces (Figure S 3C). After adding mercury (II) on the system, the ssDNA will seize mercury (II) via thymine bases and form strong and stable thymine-Hg^{2+}-thymine complexes (T-Hg^{2+}-T), then increase its contact angel to 70 ± 2.5 ºC (Figure S 3D). Hence, the results further confirmed that the ssDNA were successfully attached onto the gold surface and worked properly as a mercury-responsive detector.

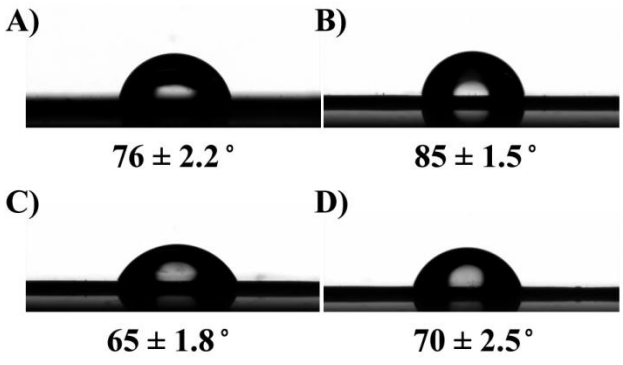

Figure S3. Mercury-responsive wettability for a flat ssDNA-modified gold-coated PI surface: Changes of water drop profile when the PI membrane (A) were sputtered with gold nanoparticle (B), modified with ssDNA (C) and interact with mercury ions (D) with water contact angles of 76 ± 2.2°, 85 ± 1.5°, 65 ± 1.8° and 70 ± 2.5°, respectively.

Fluoroscopy of the mercury (II) responsive surfaces.

The optical and fluorescent micrographs of naked and modified PI membrane were investigated through an optical microscope (Vision Engineering Co., UK), which was coupled to a CCD camera and connected to a desktop computer.

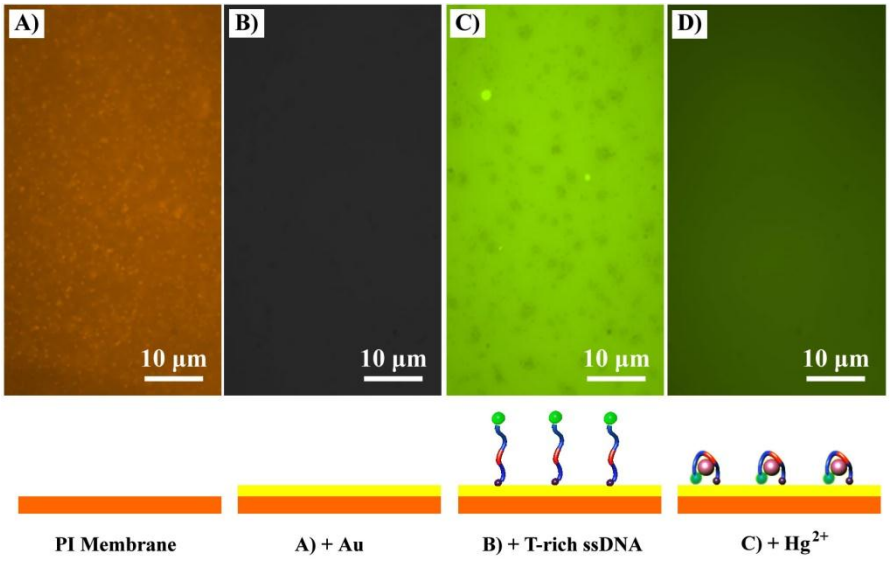

Figure S4. Optical image of PI membrane (A), PI membrane sputtered with gold nanoparticle (B), The sputtered PI membrane was modified with thiol-terminated ssDNA (C) and which interact with mercury ions (D).

CD spectra of ssDNA in the presence of mercury (II) ions and cysteine alternately

The conformational change of ssDNA was determined by circular dichroism (CD) spectra measurements. CD spectra were measured at 296 K maintained by the temperature-control units affiliated to the spectrometers and collected on a JASCO J-810 CD spectrometer. Wavelength scans were performed between 250 and 400 nm. Quartz cells with a path length of 1 mm were used for ssDNA and cysteine solutions. As shown in Fig. S5, when the system is in contact with mercury (II), the positive peak near 283 nm disappeared, indicating a typical T-Hg^{2+}-T conformation (black). An obvious change in the CD spectra could be observed after adding cysteine, which indicates the deformation of the T-Hg^{2+}-T structure (red). Therefore, the CD spectra showed the multi-cycle of the ssDNA between a T-Hg^{2+}-T structure and a random single-stranded structure.

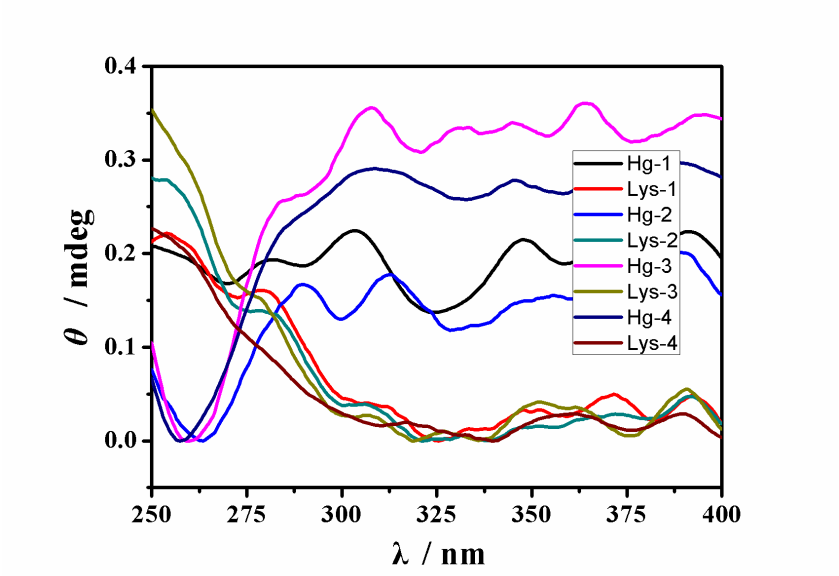

Figure S5. Monitoring of the cycles of the conformational switch of mercury-responsive ssDNA (5′(SH)-$(CH_2)_6$-CCTCTCTTTCTCCCCTGTTTgTgT(Rhodamine Green)3′) through measurement of the circular dichroism. When some cysteines (Lys) were added to the ssDNA system, it can pull out the Hg^{2+} from the T-Hg^{2+}-T complexes then the ssDNA can also react with Hg^{2+} ions again which means such a system recover the function for sensing Hg^{2+}.