

Supporting Information

Biomimetic nanopore for sensitive and selective detection of Hg (II) in conjunction with single-walled carbon nanotubes

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Detailed Experimental Procedures

Current-versus-Voltage Measurements. The I-V curves of nanopore in sodium phosphate solution (100 mM, 1 M KCl and pH=3.0) was shown in Figure S3. In the case of metal ion sensing measurements, Tris-HCl buffer solution with pH=7.4, 100 mM KCl was employed. The negative electrode was placed at the side of the membrane with the tip opening of the pore. Voltage from -1V to 1V was scanned across the membrane to obtained corresponding current through the pore. PEI-Zr⁴⁺ modified asymmetrical nanopore formed in PET membrane was directly used for determining the concentration of metal ions.

The optimal concentration of T-rich ssDNA and SWNTs. In order to achieve the best experimental results for Hg²⁺ detection, the optimal concentration of T-rich

ssDNA was investigated. The analytical results was shown in Figure S5. It is clearly indicated that the surface coverage (theta) was gradually increased with the concentration of the T-rich ssDNA from 0 to 1 μM . At a concentration of 200 nM, the surface coverage reached saturated. Even higher concentration of ssDNA, the theta was almost no increase. Finally, the concentration of T-rich ssDNA was chosen as 200 nM. According to the reported literature¹, when the concentration of ssDNA was 200 nM, the optimal SWNTs concentration was chosen as 50 μgL^{-1} . And 200 nM T-rich ssDNA and 50 μgL^{-1} SWNTs were used for the whole experimental process.

The data in Figure S3 shows that without the existence of Zr^{4+} on the nanopore surface, the I-V curves showed negligible change in the ion current rectification upon adjusting the concentration of Hg^{2+} from 0 to 3 μM while keeping ssDNA and SWNTs concentration constant. The results indicates that Zr^{4+} plays a very important role in the adsorption of DNA.

In order to further prove the selectivity of the nanopore biosensor towards Hg^{2+} , the measurement for the mixture of Hg^{2+} containing other metal ions has been completed, and the results was shown in Fig S6. It was indicated that the mixture of other metal ions has hardly any effect on the selectivity. From the above, we can draw that the nanopore biosensor has good selectivity for Hg^{2+} detection.

Supplementary Figures

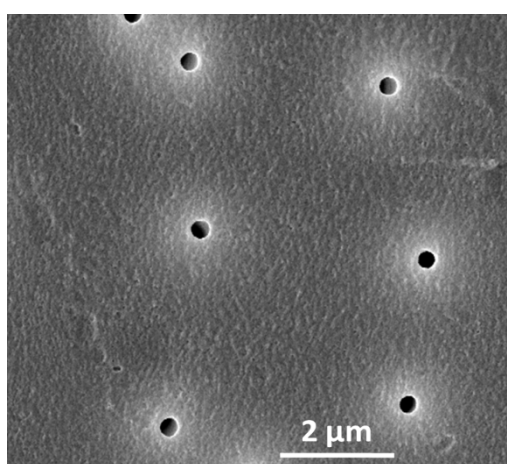


Figure S1. Scanning electron microscopy (SEM) of the multi-nanopore in PET membrane used for the XPS characterization. The diameter of the nanopore is about 300 nm.

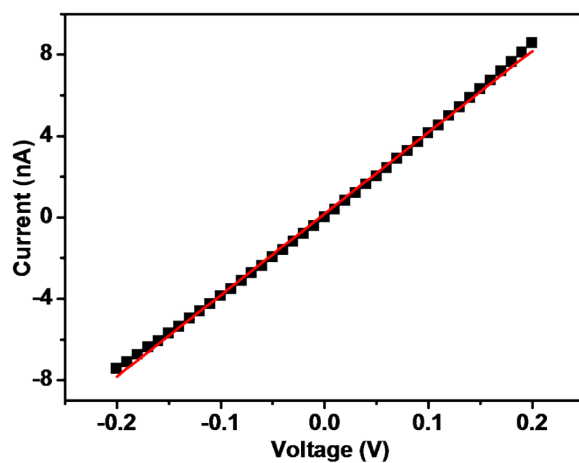


Figure S2. I-V characteristics of the nanopore after wet etching. Measurements were carried out in PBS buffer (100 mM, 1 M KCl and pH=3.0).

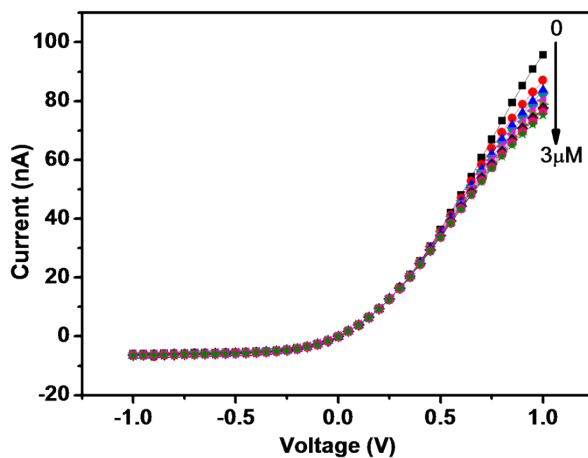


Figure S3. I-V characteristics of PEI modified conically shaped nanopore upon addition of various concentration of Hg^{2+} into 10 mM Tris-HCl buffer (100 mM KCl, pH=7.4, 200 nM ssDNA and 50 μgL^{-1} SWNTs).

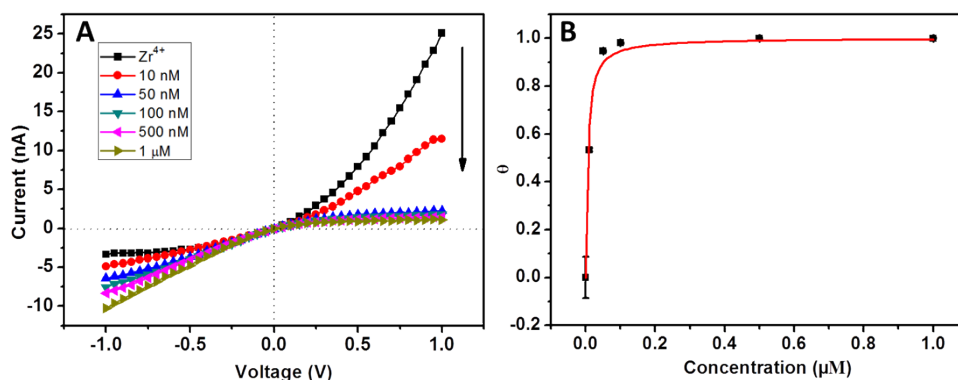


Figure S4. (A) I-V curves for Zr^{4+} -PEI modified conically shaped nanopore in the presence of various concentrations of T-rich ssDNA from 0 to 1 μ M 10 mM Tris-HCl buffer (100 mM KCl, pH=7.4). (B) Plot of surface coverage (θ) versus concentration of T-rich ssDNA. The error bars were obtained from three replicate measurements.

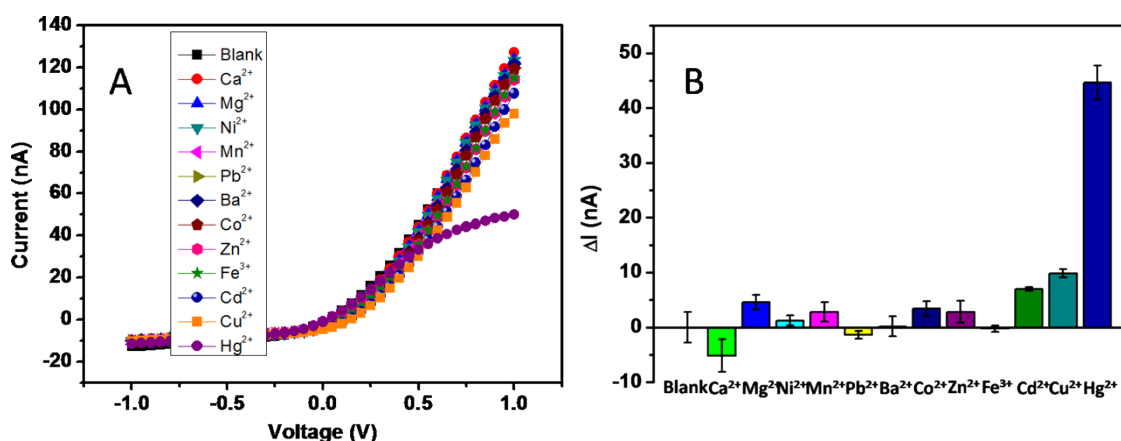


Figure S5. (A) I-V curves of the Zr^{4+} -PEI modified single nanochannel in 10 mM Tris-HCl buffer (100 mM KCl, pH=7.4, 200 nM ssDNA), with the addition of 1 μ M Ca^{2+} , Mg^{2+} , Ni^{2+} , Mn^{2+} , Pb^{2+} , Ba^{2+} , Co^{2+} , Zn^{2+} , Fe^{3+} , Cd^{2+} , Cu^{2+} and Hg^{2+} . (B) Current change (ΔI) measured at +1V in the presence of different metal ions (1 μ M) for the Zr^{4+} -PEI modified nanopore. All measurements were done in 10 mM Tris-HCl buffer (100 mM KCl, pH=7.4, 200 nM ssDNA and 50 μ g L^{-1} SWNTs.).

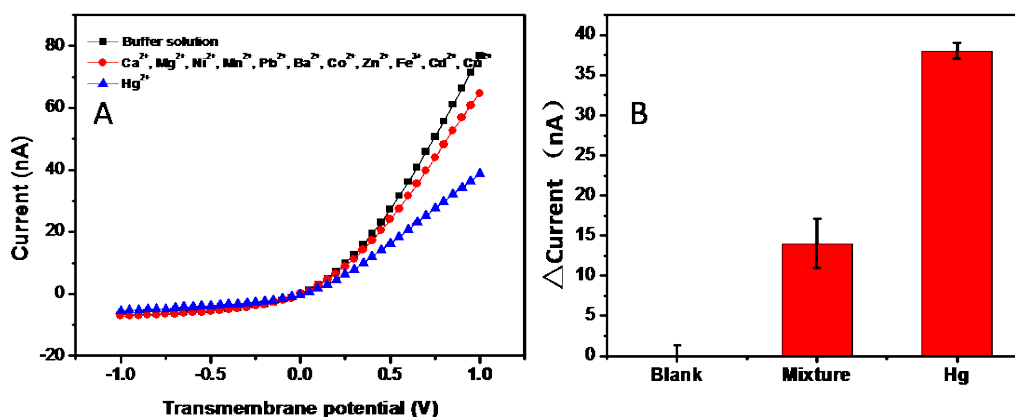


Figure S6. (A) I-V curves of the Zr^{4+} -PEI modified single nanochannel in 10 mM Tris-HCl buffer (100 mM KCl, pH=7.4, 200 nM ssDNA) , with the mixture of other metal ions (the concentration of each metal ion was 1 μ M) and Hg^{2+} . (B) Current change (ΔI) measured at +1V in the presence of other metal ions for the Zr^{4+} -PEI modified nanopore. All measurements were done in 10 mM Tris-HCl buffer (100 mM KCl, pH=7.4, 200 nM ssDNA and 50 μ g L^{-1} SWNTs.).

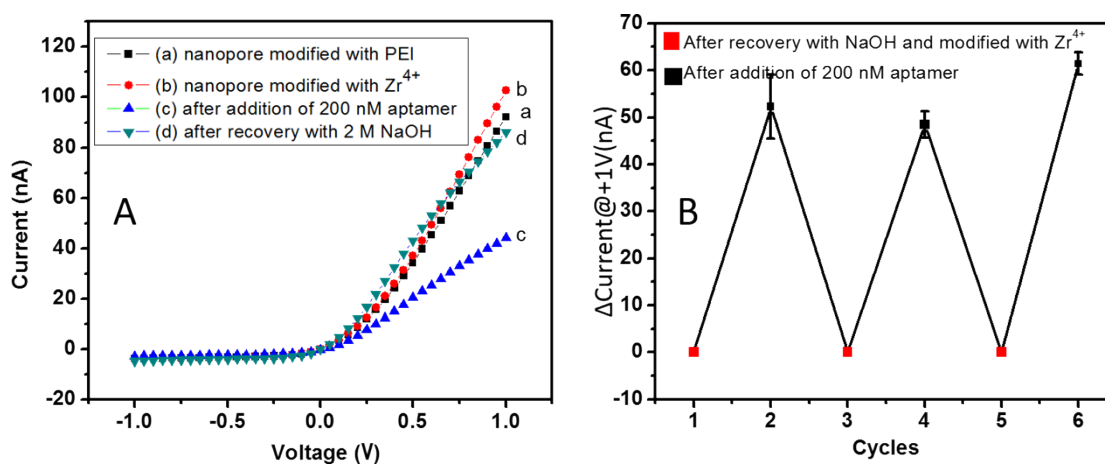


Figure S7. Reusability of biomimetic nanopore through 2 M NaOH etching. (A) (a) I-V curves for nanopore modified with PEI, (b) nanopore coated with PEI and Zr^{4+} , (c) nanopore after interaction with 200 nM aptamer, (d) nanopore after recovery of 2 M NaOH, (B) 3 circles of modification and regeneration of the nanopore and each point corresponding to the value measured at +1 V, where $\Delta current = I_{Zr^{4+}} - I_{aptamer}$,

$I_{Zr^{4+}}$ and I_{aptamer} were the current after modified with Zr^{4+} and after addition of 200 nM aptamer, respectively.

1. Z. Guo, J. Ren, J. Wang and E. Wang, *Talanta*, 2011, **85**, 2517-2521.