Supporting Information

Heterostructured Nanochannels with Modulated Ionic Current Rectification for Ultrasensitive Detection of Hg^{2+}

Wenrui Ma [a, b], Lulu Liu [c], Xu Zhang [d], Xingfei Liu [d], Yi Xu [a, b], Shunbo Li [a, b, *] and Muling Zeng [d, *]

[a] Key Laboratory of Optoelectronic Technology and Systems, Ministry of Education & Key Disciplines Laboratory of Novel Micro-Nano Devices and System Technology, College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, China.

[b] International R & D center of Micro-nano Systems and New Materials Technology, Chongqing University, Chongqing 400044, China.

[c] College of Chemistry and Chemical Engineering, Chongqing University of Science and Technology, Chongqing 400044, China.

[d] School of Biotechnology and Health Sciences, Wuyi University, Jiangmen 529020, China.

Corresponding authors. E-mail addresses: shunbo.li@cqu.edu.cn (S. Li) and mulingzeng@163.com (M. Zeng)

Section S1. Surface charge distribution of the Nafion/AAO hybrid nanochannels before and after the recognition reaction

In this work, the surface charge density on the Nafion side is constant after the Nafion membrane with a certain thickness is anchored on AAO membrane, which does not change with the occurrence of the recognition reaction. Due to the permselectivity of Nafion for cations, the surface of channels is negatively charged. In addition, because the pore diameter of Nafion side is smaller than that of AAO side, it is assumed that the number of Nafion nanochannels contained in a single AAO nanochannel is N and the surface charge density of a single Nafion nanochannel is σ_0. The surface charge density of Nafion side (σ_N) is,

$$\sigma_N = N \cdot \sigma_0 \tag{1}$$

When the DNA probes are immobilized on the AAO side, the surface charge density of AAO side σ_A is equal to the surface charge density σ_1 generated from the negatively charged phosphate backbone of DNA. In the presence of Hg^{2+}, the recognition reaction of Hg^{2+} with DNA will neutralize and decrease the negative surface charge density of DNA. Assuming that the change in surface charge density on the AAO side caused by this recognition reaction is σ_2, and the proportion of the number of binding sites caused by the recognition reaction to the total number of active sites of DNA is θ (θ is only a function of Hg^{2+} concentration). The surface charge density on the AAO side can be described as follows:

In the absence of Hg^{2+},

$$\sigma_A = \sigma_1 \tag{2}$$

In the presence of Hg^{2+},

$$\sigma_A = \sigma_1(1 - \theta) - \sigma_2 \cdot \theta \tag{3}$$

Compared with AAO nanochannels, Nafion membrane has smaller pore diameter (usually several nanometers), so the surface charge density on the Nafion side is higher than that on the AAO side, namely $\sigma_N \geq \sigma_A$. The coordinate system is established as shown in Fig.S1.
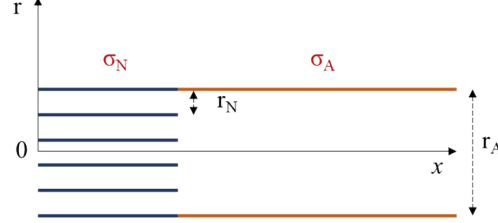

Fig. S1 A sketch of the profile of the Nafion/AAO hybrid nanochannels. The walls inside the Nafion and AAO nanochannels have the surface charge density σ_N and σ_A respectively.

It is assumed that the surface charge density has an exponential decay from the Nafion side to the AAO side. The asymmetric surface charge distributions ($\sigma(x)$) of hybrid nanochannels can be described by the following equations.

In the absence of Hg^{2+},

$$\sigma(x) = N \cdot \sigma_0 + (\sigma_1 - N \cdot \sigma_0)/\left\{1 + exp\left[-k\left(\frac{x}{L} - \lambda\right)\right]\right\} \tag{4}$$

In the presence of Hg^{2+},

$$\sigma(x) = N \cdot \sigma_0 + [\sigma_1(1 - \theta) - \sigma_2 \cdot \theta - N \cdot \sigma_0]/\left\{1 + exp\left[-k\left(\frac{x}{L} - \lambda\right)\right]\right\} \tag{5}$$

Where k denotes the coupling constant of surface charge interaction between Nafion and AAO nanochannels; λ represents the position of heterojunction between Nafion and AAO nanochannels, namely $\lambda = L_N/L$; L is the length of whole hybrid nanochannels, $L = L_N + L_A$ (L_N and L_A are the length of Nafion and AAO nanochannels, respectively).

Equation (4) and (5) describe the surface charge distribution of the Nafion/AAO hybrid nanochannels before and after the recognition reaction, respectively. Generally, in the DNA modified Nafion/AAO nanochannels, values of N, σ_0, σ_1, σ_2, L and λ are set as: N=5~15, σ_0=-0.088 C/m², σ_1=-0.088 C/m², σ_2=0.015 C/m², L=50~60 μm and λ=0.01~0.1. The value of k is strongly dependent on the geometry of the nanochannels, which is varied from 1 to 200. The calculated results are shown in Fig.S2. As the

recognition reaction goes on, the θ value increases, resulting in a significance difference in surface charge distribution on the AAO side.
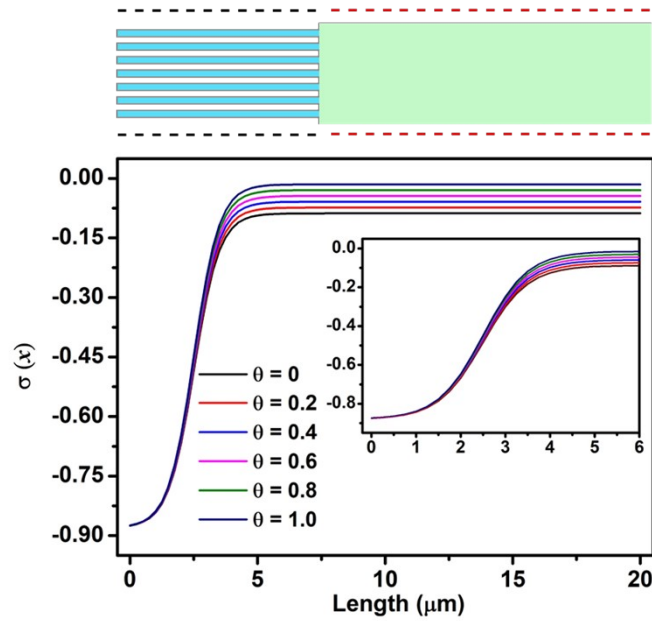

Fig. S2 Surface charge distributions in the absence and present of Hg^{2+} (k=100, N=10, L=50, λ=0.05).

Section S2. Numerical Simulation for Ion Transport in Nafion/AAO Hybrid Nanochannels

A theoretical model based on coupled Poisson and Nernst-Planck (PNP) equations is established to simulate and analyze the ion concentration distribution and ionic current rectification property in detail under appropriate boundary conditions [1].

$$\nabla^2 \varphi = -\frac{F}{\varepsilon_0 \varepsilon_r} \sum_{i=1}^{2} z_i c_i$$

(6)

$$j_i = D_i \cdot \left(\nabla c_i + \frac{z_i F c_i}{RT} \nabla \varphi \right)$$

(7)

$$\nabla \cdot j_i = 0$$

(8)

Where z_i, c_i, j_i and D_i are the charge, the concentration, the flux and the diffusion coefficient of ion species i (i=1 or 2, 1 and 2 represent positive ions and negative ions), respectively; φ is the electrical potential; ε_0 and ε_r are the vacuum dielectric constant and the relative dielectric constant of fluid; F, R and T are the Faraday constant, the ideal gas constant and the Kelvin temperature, respectively.

Based on the above equations, a 2D model that consists of some small cylindrical nanochannels on single large cylindrical nanochannel is established by using the

software of Comsol 5.3a, corresponding to the Nafion/AAO heterostructured nanochannels, as shown in Fig.S3 [2, 3]. It is assumed that the prepared Nafion/AAO nanochannels have uniform structure and surface property, and the heterojunction is just the change of diameter of hybrid nanochannels. For simplicity, the width of small cylindrical nanochannels representing Nafion and single cylindrical nanochannels representing AAO is designed to be 4 nm and 60 nm, respectively. A center to center distance on Nafion side is 4 nm. The length of Nafion and AAO side are set to 100 nm and 2000 nm.

The boundary condition for potential φ on the wall of nanochannels is,

$$\vec{n} \cdot \nabla \varphi = - \sigma/\varepsilon \tag{9}$$

Where σ is the surface charge density. In our case, σ_N and σ_A are the surface charge density of Nafion and AAO, respectively. The σ_N is set to a constant of -0.088 C/m^2 due to the cationic selectivity of Nafion. Based on this hypothesis that the surface charge density of AAO side will change due to the recognition of target Hg^{2+} by DNA, the σ_A is used as a variate from negative to positive.

The ion flux has the zero normal components at boundaries,

$$\vec{n} \cdot j = 0 \tag{10}$$

Then, the ionic current is calculated by integrating the ion flux on the boundary h1 or h2.

$$i = - F \cdot \int \left(J_{K^+} - J_{Cl^-} \right) ds \tag{11}$$

For rectification calculations, the electric potentials of the AAO and Nafion are set to ground and a sweep from -1.0 to +1.0 V, respectively. The relative permittivity of water is set to 80. The diffusion coefficients of K$^+$ and Cl$^-$ are 1.957×10^{-9} and 2.032×10^{-9} m^2/s. And the KCl concentration in both reservoirs is 0.1 M. The ionic current at -1 V and +1 V bias are calculated and the rectification ratio (f) is obtained by $f = I_{+1V}/I_{-1V}$.
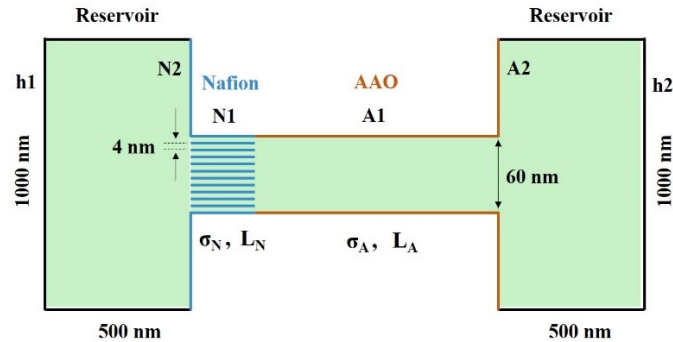

Fig. S3 Calculation model of the Nafion/AAO heterostructured nanochannels.

Table S1 Comparisons of the linear range and the limit of detection (LOD) for the detection of Hg^{2+} using different electrochemical technologies

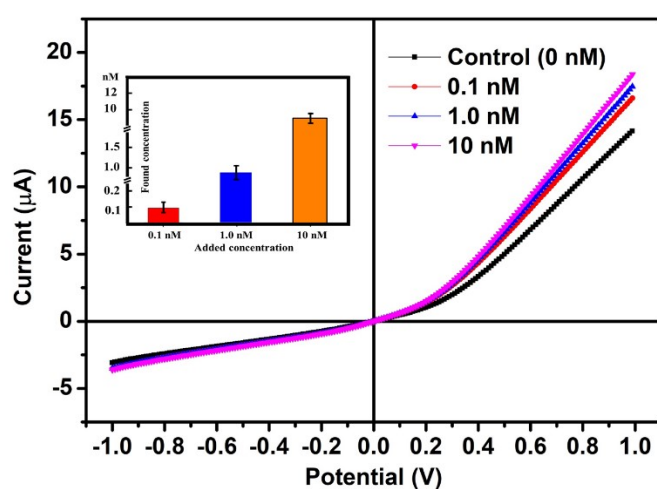| Sensitive surface	Detection technique	Linear range (nM)	LOD (pM)	Ref.
DNA-modified Au electrode	EIS	10~500	30	[4]
MWCNTs and AuNPs	DPV	0.1~20	30	[5]
DNA-modified rGO/chitosan	EIS	0.1~10	16	[6]
N-rGO/MnO_2	SWSV	10~200	41.4	[7]
3D-rGO@PANI	EIS	0.01~100	35	[8]
Glass nanopore	LSV	0.001~1000	1	[9]
DNA-modified GO/AAO	LSV	10^{-6}~10^3	0.07	[10]
This work	LSV	0.001~1000	1	—

Fig. S4 I-V curves of the sensor for determination of Hg^{2+} in real samples.

Table S2 Determination of Hg^{2+} concentrations in real samples (n=3).

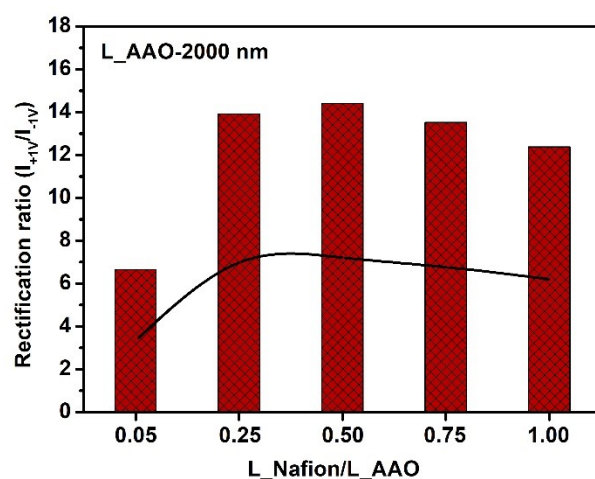| Sample	prepared (nM)	detected (nM)	Recovery (%)
Tap water	0.1	0.0885	88.51
	1.0	0.9027	90.27
	10	8.7490	87.49

Fig. S5 The influence of Nafion thickness on the ion rectification ratio.

References

[1] C. Y. Li, Z. Q. Wu, C. G. Yuan, K. Wang and X. H. Xia, *Anal. Chem*., 2015, **87**, 8194-8202.

[2] J. Jung, J. Kim, H. S. Lee, I. S. Kang and K. Choi, *ACS Nano*, 2019, **13**, 10761-10767.

[3] J. Gao, W. Guo, D. Feng, H. Wang, D. Zhao and L. Jiang, *J. Am. Chem. Soc.*, 2014, **136**, 12265-12272.

[4] L. Chen and Z. N. Chen, *Talanta*, 2015, **132**, 664-668.

[5] X. Lu, X. Dong, K. Zhang and Y. Zhang, *Anal. Methods,* 2012, **4**, 3326-3331.

[6] Z. Zhang, X. Fu, K. Li, R. Liu, D. Peng, L. He, M. Wang, H. Zhang and L. Zhou, *Sens. Actuators, B*., 2016, **225**, 453-462.

[7] G.-L. Wen, W. Zhao, X. Chen, J.-Q. Liu, Y. Wang, Y. Zhang, Z.-J. Huang and Y.-C. Wu, *Electrochim. Acta*, 2018, **291**, 95-102.

[8] Y. Yang, M. Kang, S. Fang, M. Wang, L. He, J. Zhao, H. Zhang and Z. Zhang, *Sens. Actuators, B*., 2015, **214**, 63-69.

[9] S. Chen, H. Chen, J. Zhang, H. Dong, K. Zhan and Y. Tang, *RSC Adv*, 2020, **10**, 21615-21620.

[10] L. Shi, F. Jia, L. Wang, M. Jalalah, M. S. Al-Assiri, T. Gao, F. A. Harraz and G. Li, *Sens. Actuators, B*., 2021, **326**, 128976.