Supporting Information

A nanofluidic device for ultrasensitive and label-free detection of tetracycline in association with γ-cyclodextrin and GO

Jiaxi Cheng [a], Fenghua Jiang [a], Siqi Zhang [b]*

[a] School of Civil Engineering & Architecture, Taizhou University, Jiaojiang, 318000, China

[b] School of Pharmaceutical and Materials Engineering, Taizhou University, Jiaojiang, 318000, China

*Corresponding author

E-mail: siqiz@tzc.edu.cn

Tel.: 86-576-88660353

Table of contents

ng/L to 10 ng/L.

Table S1: The detection limits and linearity range of various sensing platforms for TC.

1.1 Instruments

The nanochannel diameter was determined by FE-SEM (S800, Hitachi, Japan). High resolution transmission electron micrograph (HRTEM) measurements were performed on FEI TECNAI G20 (FEI, USA). UV–vis absorption measurements were performed on a Cary 50 Scan UV/Vis Spectrophotometer (Varian, USA). Fluorescence measurements were carried out on a Cary Eclipse Spectrofluorometer (Varian, USA). A Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH, USA) was employed to measure the ion current. The ultrapure water used in this work was purified by a Millipore system.

1.2 Selectivity

Employing analogs in the sensing platform, the specificity of the proposed strategy was assessed. Other interfering antibiotics were used, including metacycline(MTC), doxycycline (DOX), chlorotetracycline (CTC) and oxytetracycline (OTC) to examine the selectivity of the strategy at a concentration of 1 mg/L, going through the same experimental process as the one shown for TC detection.

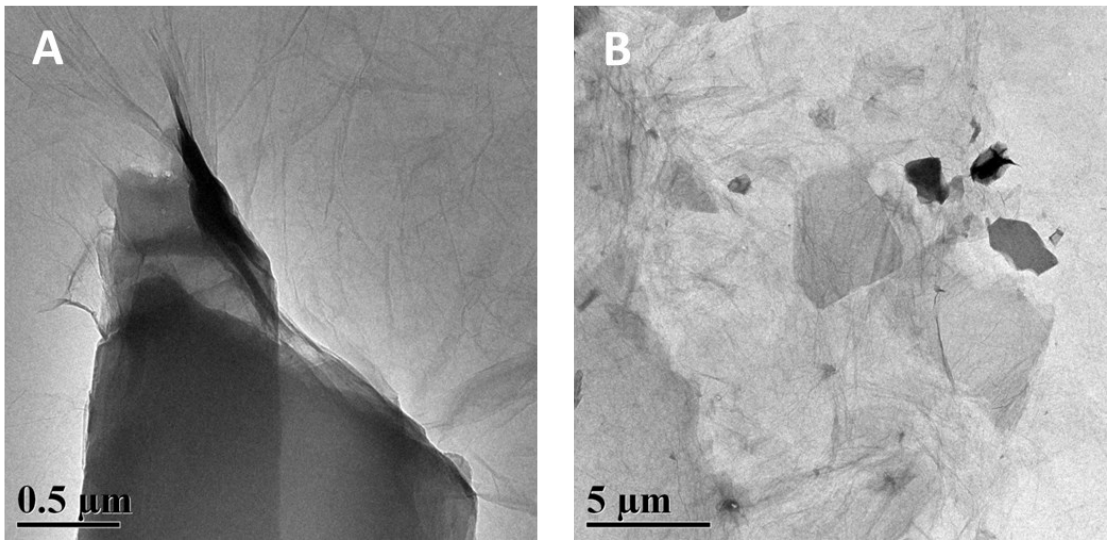

Fig. S1. Transmission electron micrograph (TEM) of GO.

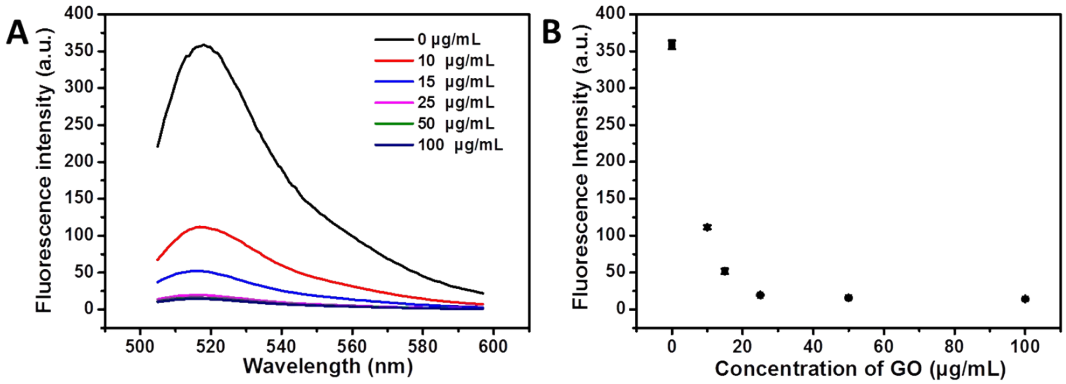

Fig. S2. (A)Fluorescence emission spectra of FAM-modified aptamer (200 nM) in the presence of various concentrate of graphene oxide (GO). (B) The plot of fluorescence emission intensity at 518 nm of FAM-modified aptamer versus the concentration of GO. The optimum concentration of GO is 25 μg/mL.

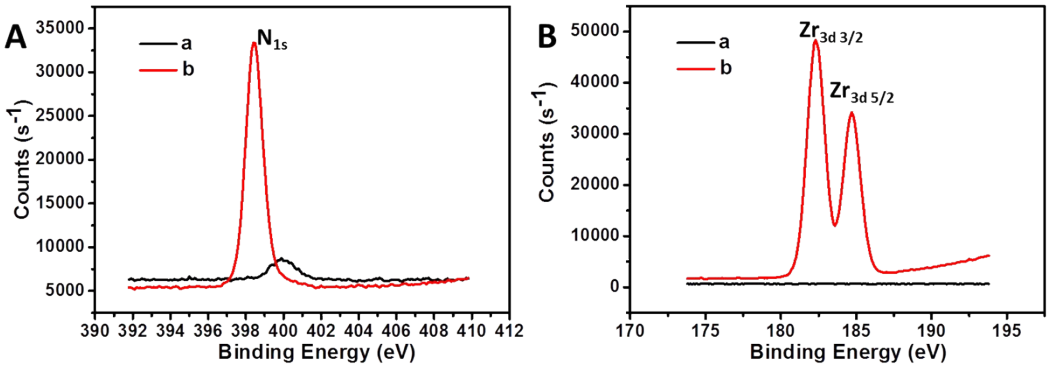

Fig. S3 The N_{1s} and Zr_{3d} data of XPS spectra for PET membrane. (A) (a) the N_{1s} data of XPS spectra for the PET membrane without modification, (b) the N_{1s} data of XPS spectra for the PET surface modified with PEI. (B) (a) Zr_{3d} data of XPS spectra for the PET membrane without modification, (b) Zr_{3d} data of XPS spectra for the PET membrane modified with PEI and Zr^{4+}. The peak at 398.4 eV are attributed to N_{1s}; the peak of $Zr_{3d3/2}$ and $Zr_{3d5/2}$ are occurred at 182.3 eV and 184.7 eV, respectively.

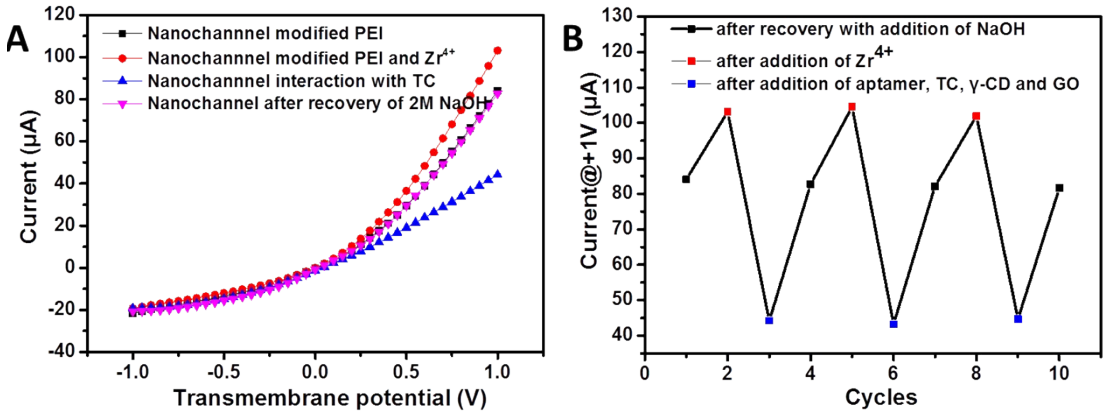

Fig. S4 Regeneration of biomimetic nanochannel through 2M NaOH etching. (A) Current-voltage curves for (a) nanochannel modified with polyethyleneimine, (b) nanochannel coated with PEI and Zr^{4+}, (c) nanochannel after interaction with 1 mg/L TC, 200 nM aptamer, 25 μg/mL GO and 1 mM γ-CD, (d) nanochannel after recovery of 2M NaOH. (B) 3 cycles of modification and regeneration of the nanochannel and each point corresponding to the value measured at +1V.

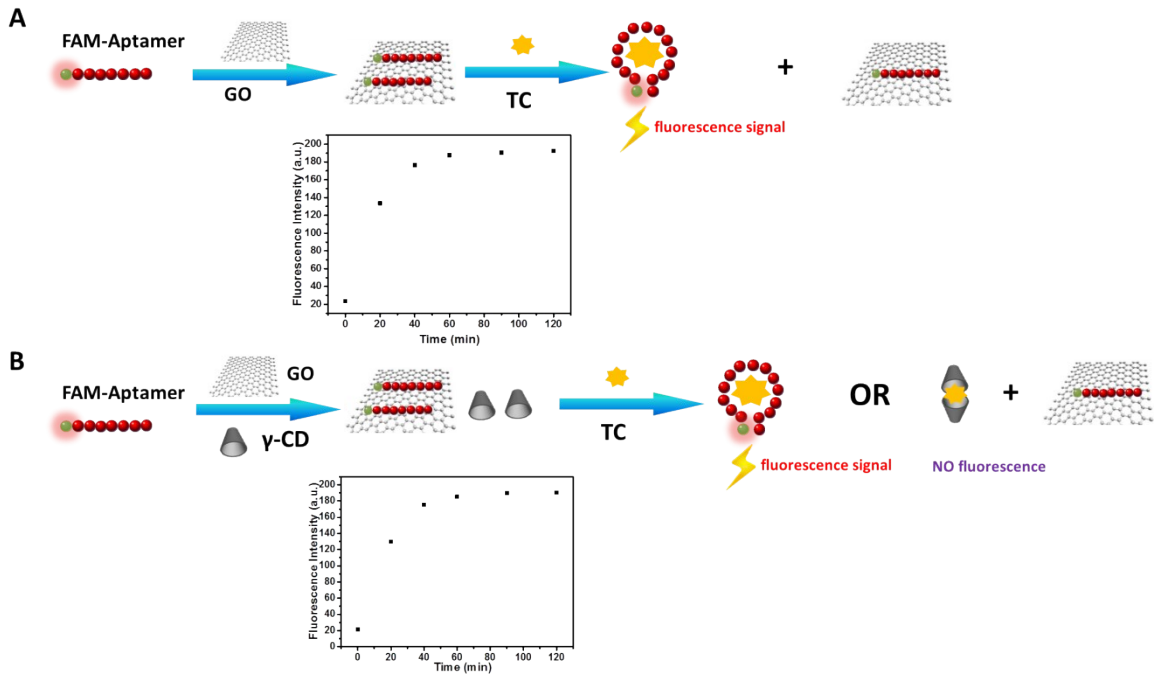

Fig. S5 (A) The plot of fluorescence emission intensity at 518 nm for different reaction time. Experimental conditions: 10 μg/L TC, 200 nM FAM labeled aptamer and 25 μg/mL GO. (B) The plot of fluorescence emission intensity at 518 nm for different reaction time. Experimental conditions: 10 μg/L TC, 200 nM FAM labeled aptamer, 25 μg/mL GO and 1 mM γ-CD.

To investigate the competition binding force between the γ-CD and aptamer with TC, a fluorescence assay was conducted. As shown in Fig. S5, a FAM labeled aptamer was introduced in the system. The system A was composed of FAM labeled aptamer, GO and TC without γ-CD, While the system B contained FAM labeled aptamer, GO, TC and γ-CD. The results showed the fluorescence signal was almost unchanged upon addition of TC, indicating TC preferred to integrate with the aptamer rather than integrate with the γ-CD. Acoording to the results, there is no competition between the CD and aptamer.

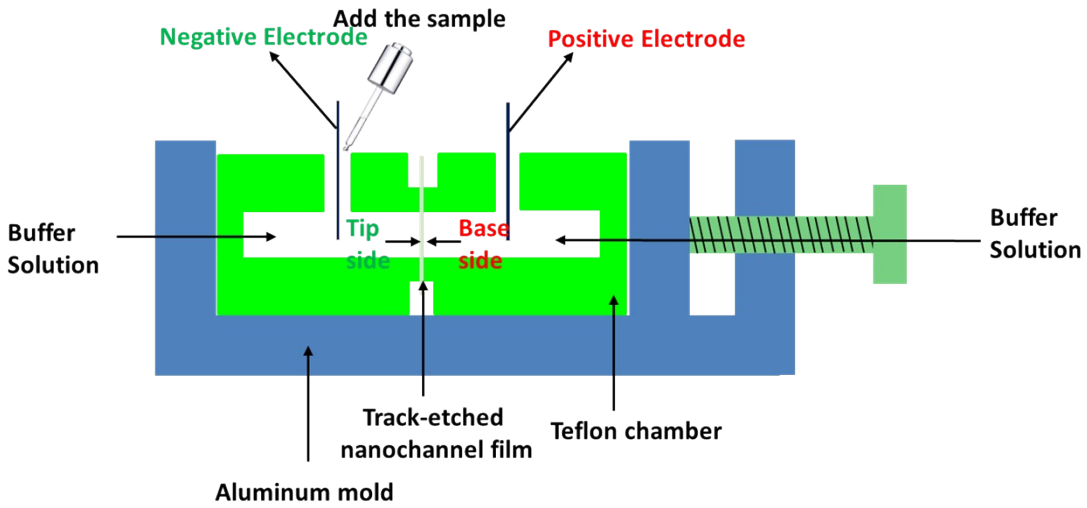

Fig. S6 Figure illustration of the experimental setup with the conductivity cell.

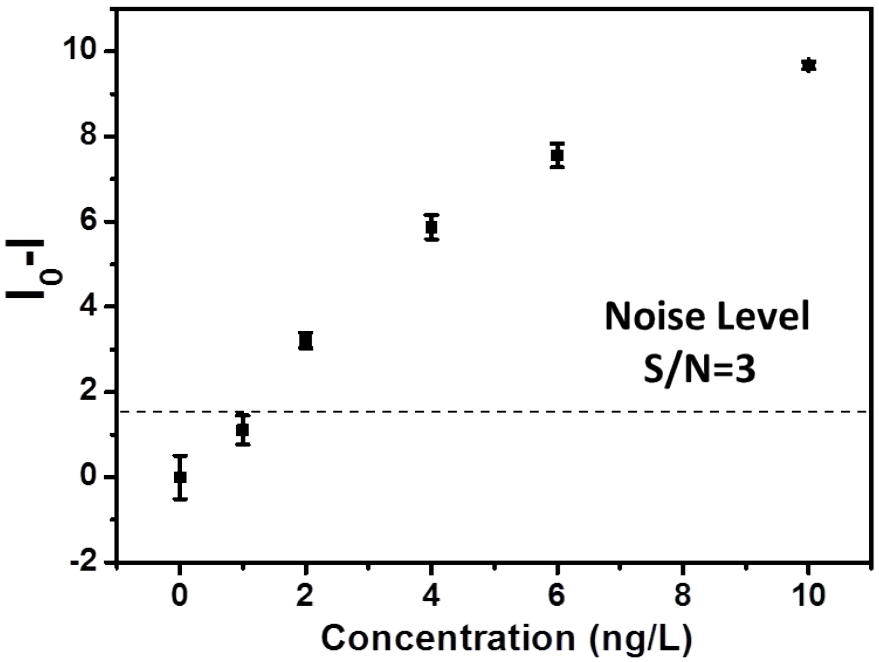

Fig.S7 The ion current change versus various low concentrations ranging from 0 ng/L to 10 ng/L.

Table S1. The detection limits of sensing platform for TC.

Sensing method	Sensing range (ng/L)	Limit of Detection (ng/L)	Reference
Enzyme-linked aptamer assay	1×10^{2}–1×10^{6}	97.8	[1]
Fluorescence Sensor	8.88×10^{4}–8.88×10^{6}	1.332×10^{3}	[2]
Photoelectrochemical Sensor	2×10^{2}–1×10^{6}	10	[3]
Electrochemical Sensor	44.4–4.44×10^{5}	27	[4]
Colorimetric Sensor	4.44×10^{5}–7.10×10^{6}	2.0424×10^{4}	[5]
Photonic crystal sensors	0-6.67×10^{4}	888.9	[6]
Nanochannel Sensor	10–1×10^{4}	2	This work

Reference:

1. S. Wang, J. Liu, W. Yong, Q. Chen, L. Zhang, Y. Dong, H. Su and T. Tan, *Talanta*, 2015, **131**, 562-569.
2. W. Wei, J. He, Y. Wang and M. Kong, *Talanta*, 2019, **204**, 491-498.
3. Q. Han, R. Wang, B. Xing, H. Chi, D. Wu and Q. Wei, *Biosens. Bioelectron.*, 2018, **106**, 7-13.
4. L. Zhou, D.-J. Li, L. Gai, J.-P. Wang and Y.-B. Li, *Sensor. Actuat. B-Chem.*, 2012, **162**, 201-208.
5. Z. Zhang, Y. Tian, P. Huang and F.-Y. Wu, *Talanta*, 2020, **208**, 120342.
6. J. Hou, H. Zhang, Q. Yang, M. Li, L. Jiang and Y. Song, *Small*, 2015, **11**, 2738-2742.