Electronic Supplementary Information (ESI) for *Chemical Communications*

Electronic Supplementary Information

Monitoring of trace oxytetracycline using a porphyrin-MOF layer-based electrochemical aptasensor

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Experimental detail

Material and general method. Chemicals and solvents were obtained through commercial purchase. The oxytetracycline (OTC) aptamer (5′-GGA ATT CGC TAG CAC GTT GAC GCT GGT GCC CGG TTG TGG TGC GAG TGT TGT GTG GAT CCG AGC TCC ACG TG-3′) was purchased from Shanghai Sangon Biotechnology Co., Ltd. Fourier transform infrared (FT-IR) spectra were collected on a Bruker ALPHA-T FT-IR spectrometer. Powder X-ray diffraction (PXRD) patterns were measured on a Haoyuan·DX-2700BH. The morphology and microstructure were carried out on a Nova Nano SEM 230 scanning electron microscope (SEM) and Tecnai G^2 F20 S-TWIN transmission electron microscope (TEM). X-ray photoelectron spectra (XPS) were carried out on an AXIS Ultra DLD X-ray photoelectron spectroscopy.

Synthesis

The synthetic procedure was similar with a previous report.[1] The synthetic process of the bulk Cu-TCPP: $Cu(NO_3)_2 \cdot 3H_2O$ (15.0 mg) was dissolved in a mixed solution of *N*,*N*-dimethylformamide (DMF, 9.0 mL) and ethanol (EtOH, 3.0 mL). Then, tetrakis(4-carboxyphenyl)porphyrin (TCPP, 12.0 mg) was added in the above solution and stirred for 10 min. The resultant reaction system was added in to a Teflon-lined autoclave and heated at 80 °C for 24 h. The obtained samples were washed by methanol (MeOH) and dried in air. For the Cu-TCPP nanolayer, the synthetic process was similar with the bulk Cu-TCPP, but PVP (20.0 mg) was introduced in the $Cu(NO_3)_2 \cdot 3H_2O$ mixed solution of DMF and EtOH. The other procedure was same with the bulk Cu-TCPP.

Electrochemical aptasensor

KCl (0.10 g), NaCl (4.00 g), KH_2PO_4 (0.12 g), and Na_2HPO_4 (0.73 g) were dissolved in distilled pure water (0.5 L) with the pH value of ~7.4. $K_3Fe(CN)_6$ (0.83 g) and $K_4Fe(CN)_6$

(1.06 g) were dissolved in the above solution to prepare the used electrolyte. The as-synthesized samples, including bulk Cu-TCPP, Cu-TCPP nanolayer, and CuO, were dispersed in water to obtain a material dispersion (0.5 mg L^{-1}). 1.0 μL suspension was covered on the glassy carbon electrode (GCE), resulting in the formation the functional material-modified electrode (material/GCE). The material/GCE was incubated in an aptamer solution (0.01 pg mL^{-1}) for 5 min to obtain the electrochemical aptasensor (aptamer/material/GCE). The fabricated aptasensor was immersed in the OTC solution at different concentrations for 5 min to collect the electrochemical responsive signal.

Electrochemical measurement

Electrochemical measurements were carried out on ta Shanghai Chenhua CHI760E workstation with GCE as working electrode, Ag/AgCl reference electrode (saturated KCl), and Pt slide as counter electrode. KCl (0.1 M) and $[Fe(CN)_6]^{3-/4-}$ (0.5 M) were prepared as the electrolyte.

Real sample

Tap water was centrifugated for 10 min at 12,000 rpm to collect the supernatant, which was further filtered through filter membrane (0.22 μm). The milk (2.0 mL) was diluted into ultrapure water (8.0 mL), which was treated by a mixture of 10% trichloroacetic acid and chloroform (6.0 mL) for 30 min. The used milk was collected by centrifugation treatment for 10 min at 12,000 rpm.

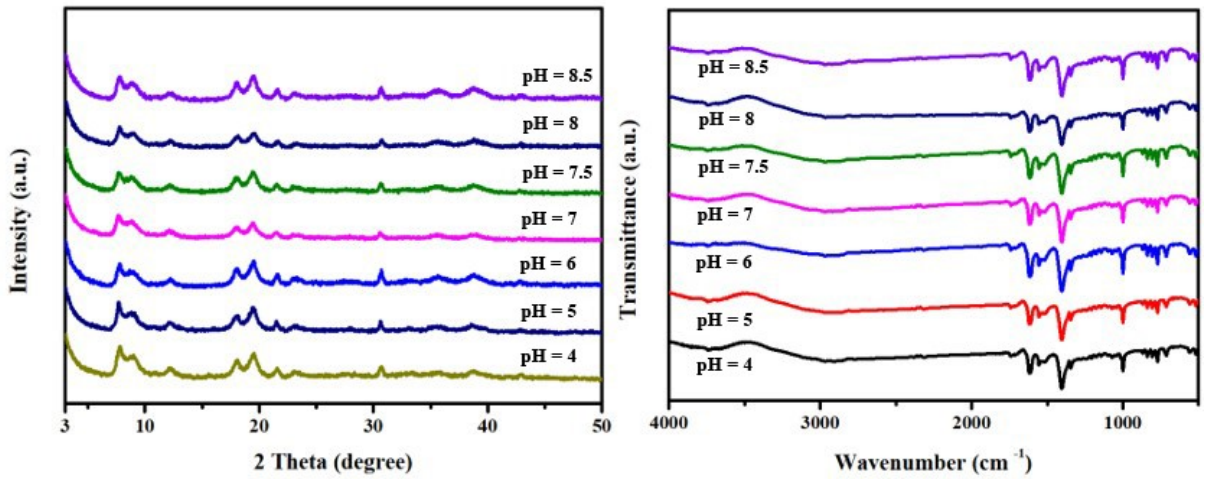

Fig. S1 (a) PXRD patterns and (b) FT-IR spectra of the as-synthesized Cu-TCPP after immersing in different pH aqueous solutions for 30 min.

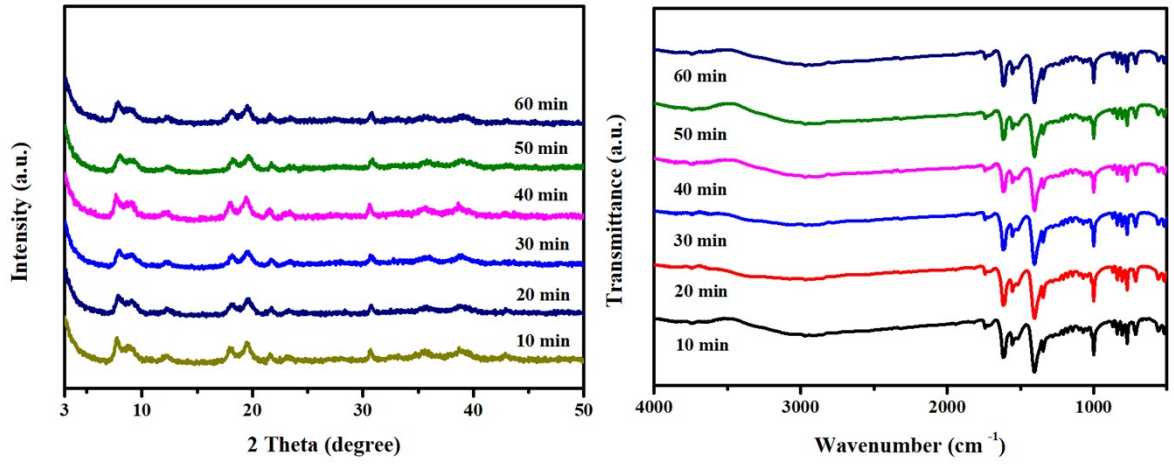

Fig. S2 (a) PXRD patterns and (b) FT-IR spectra of the as-synthesized Cu-TCPP after immersing in phosphate buffer solutions at different times.

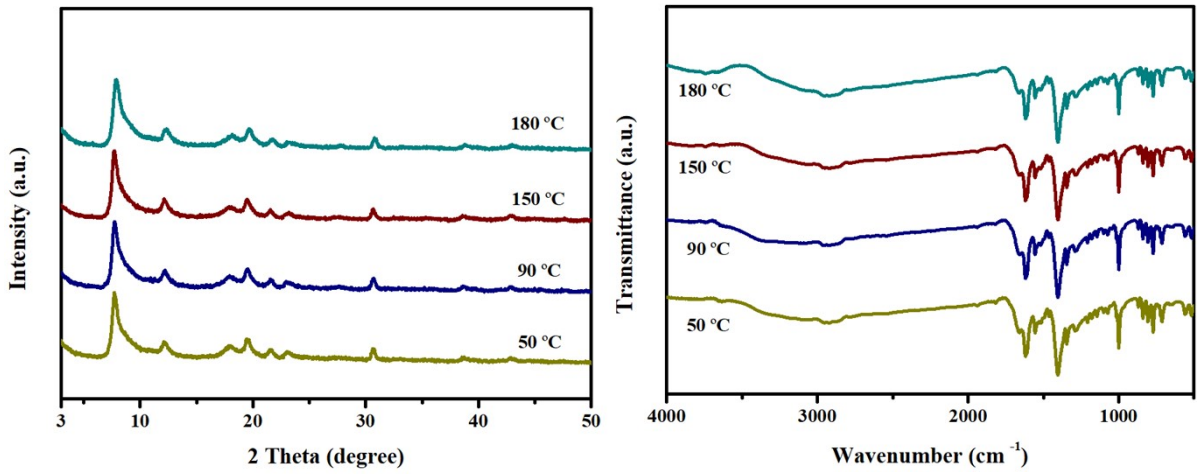

Fig. S3 (a) PXRD patterns and (b) FT-IR spectra of the as-synthesized Cu-TCPP after heating at different temperatures for 30 min.

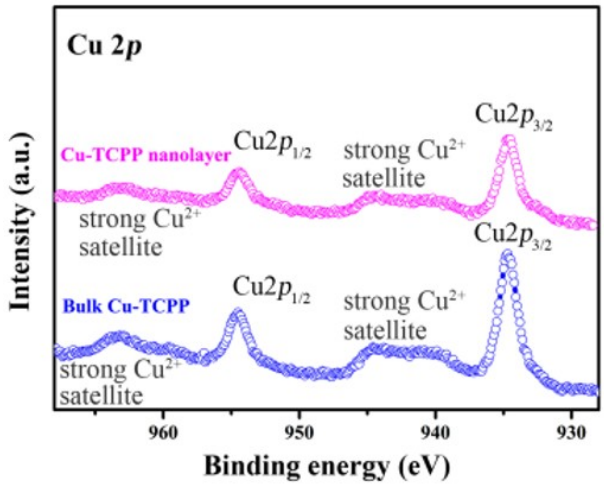

Fig. S4 The high-resolution Cu 2*p* XPS of as-synthesized samples.

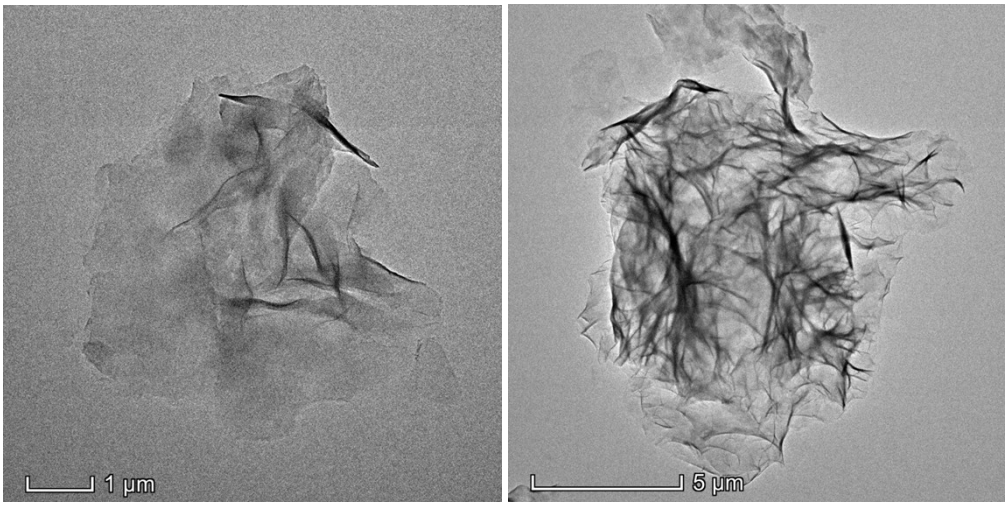

Fig. S5 TEM images of the as-synthesized Cu-TCPP nanolayer.

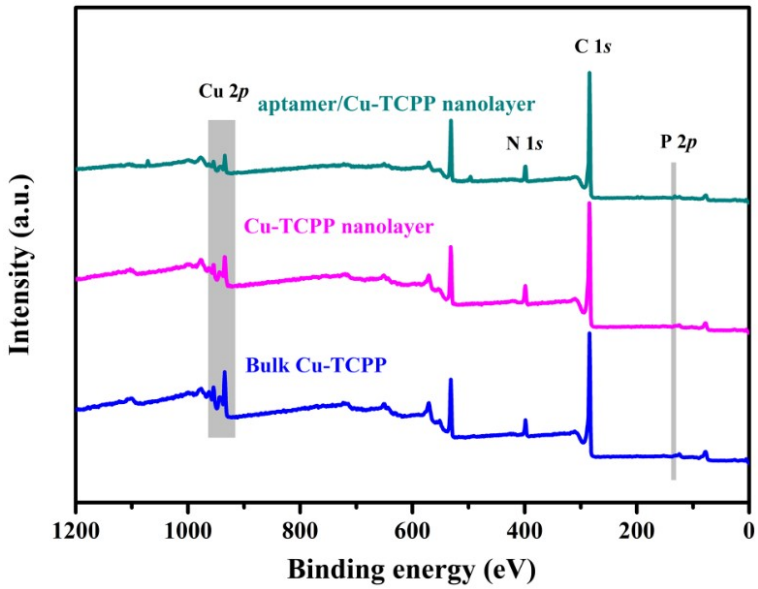

Fig. S6 The full XPS of different samples.

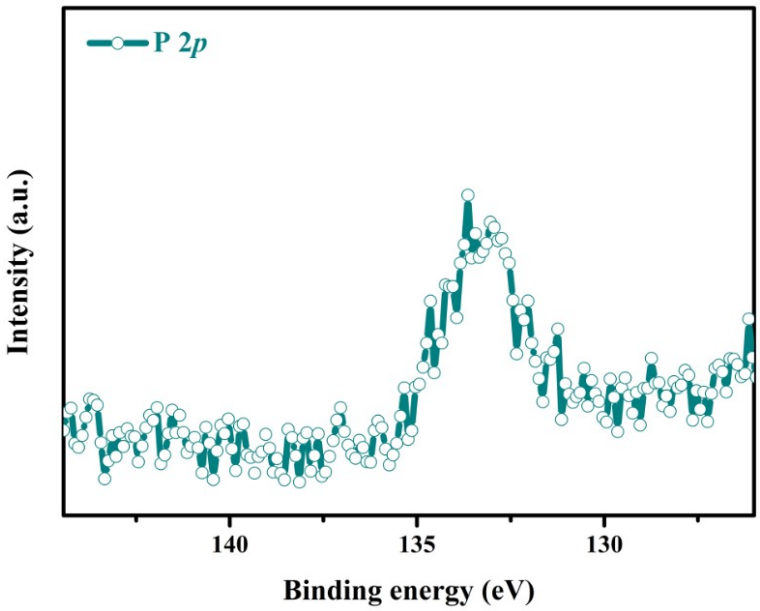

Fig. S7 The P 2*p* XPS of the aptamer/Cu-TCPP nanolayer.

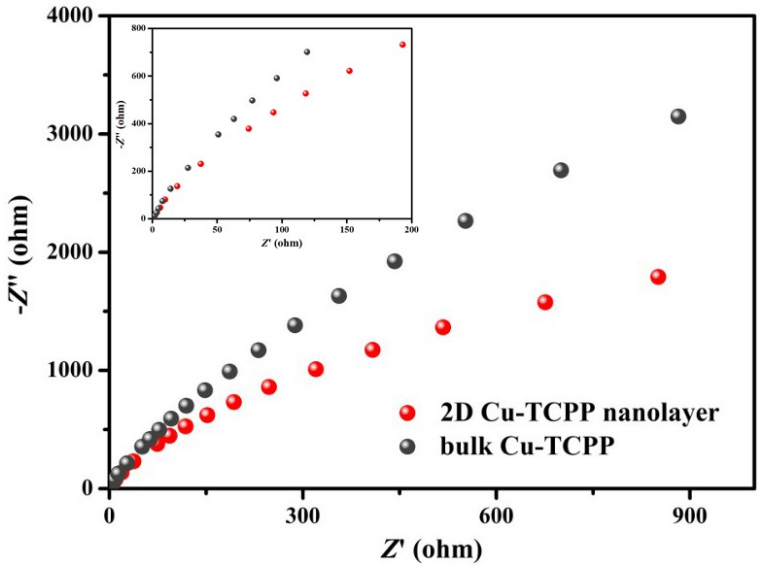

Fig. S8 EIS Nyquist plots of both samples (insert a local magnification figure).

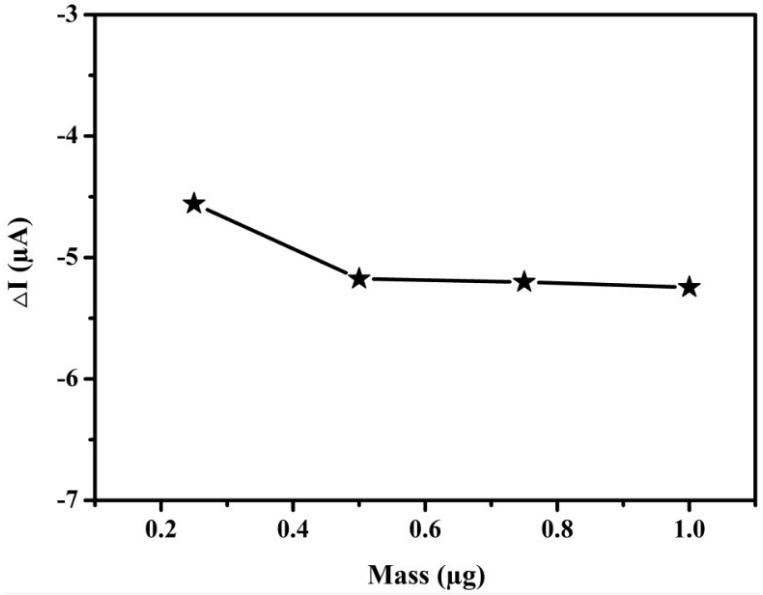

Fig. S9 The ΔI value of the adding mass of the Cu-TCPP nanolayer on the GCE surface.

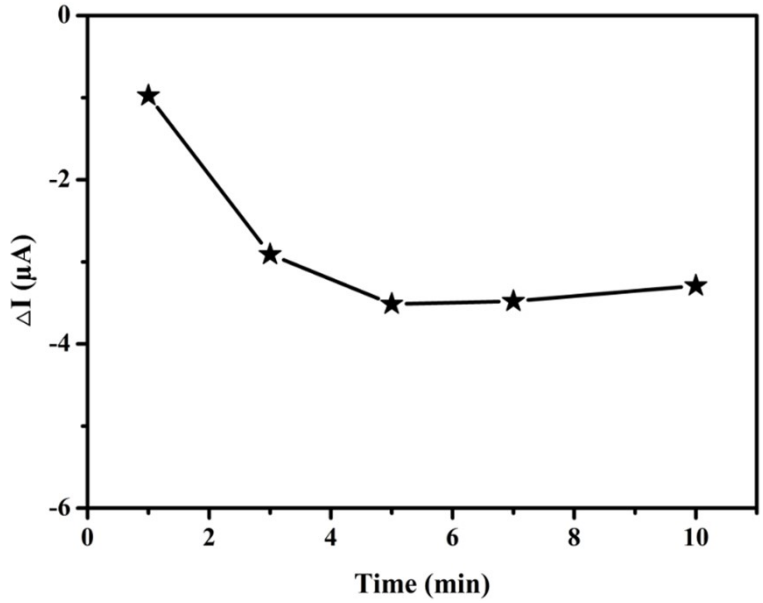

Fig. S10 The relationship between the ΔI value and the immersed time of the fabricated Cu-TCPP nanolayer-based electrochemical aptasensor in the OTC (0.01 pg mL^{-1}) solution.

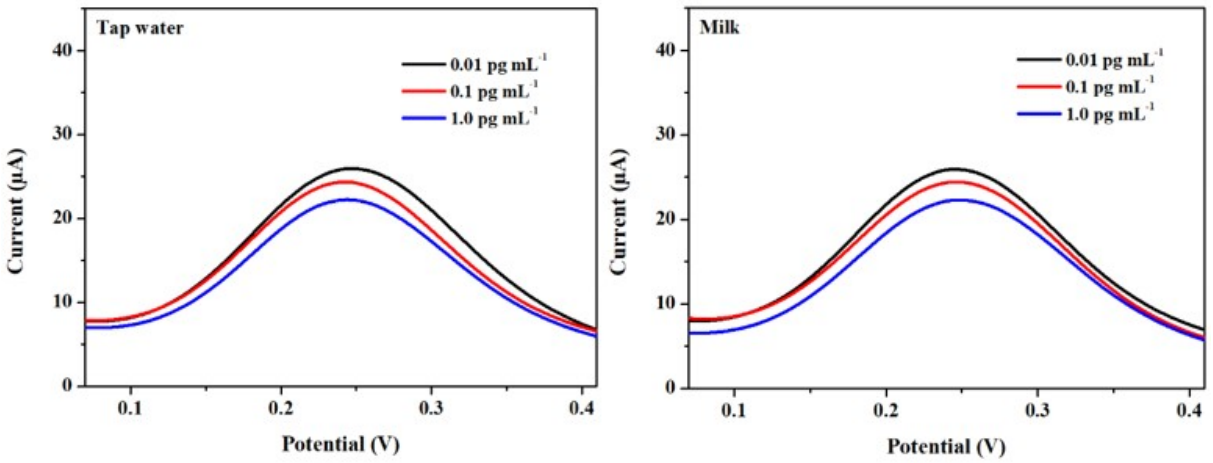

Fig. S11 The DPV curves of the fabricated aptasensor in the tested real samples.

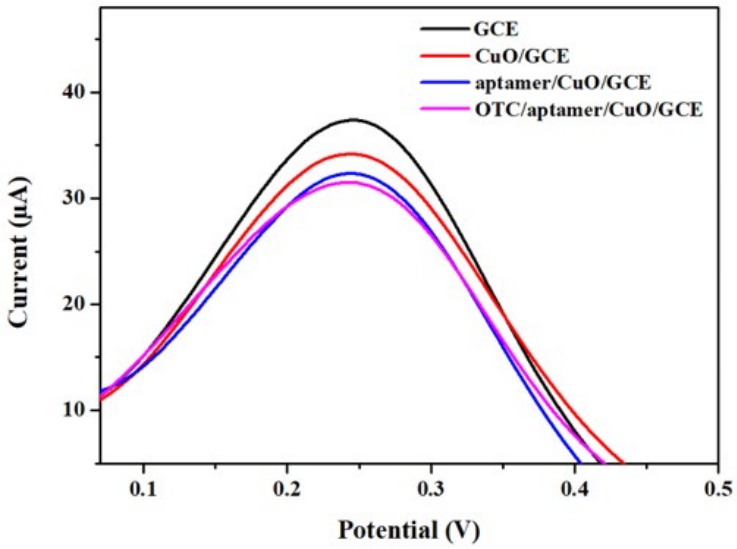

Fig. S12 The DPV curves of the aptasensor based on CuO.

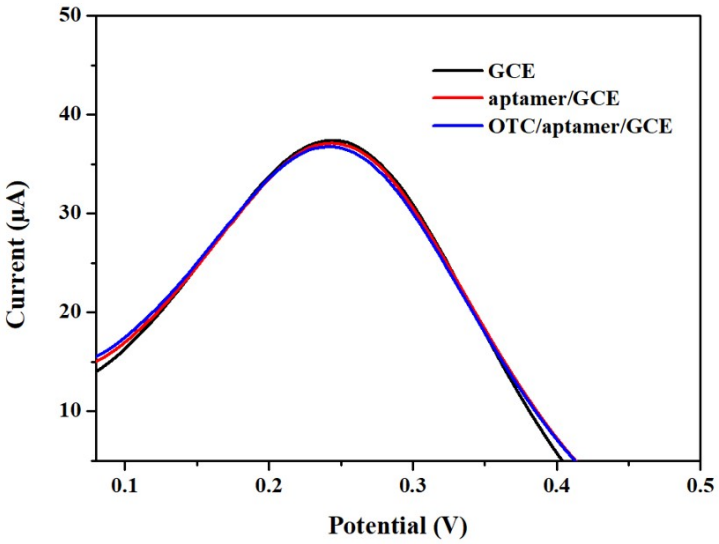

Fig. S13 The DPV curves of the aptasensor based on a blank GCE.

References

1. D. Yang, S. Zuo, H. Yang, Y. Zhou and X. Wang, *Angew. Chem. Int. Ed.*, 2020, **59**, 18954.