Supporting Information

Electrochemical aptasensor based on a potassium ion-triggered DNA conformation transition and self-assembly on an electrode

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Experimental

Materials and chemicals

DL-dithiothreitol (DTT), mercaptohexanol (MCH), sodiumacetate (NaAc), bovine serum albumin (BSA), human serum albumin (HSA), potassium chloride were purchased from Sigma-Aldrich (USA) and used as received. All solutions were prepared with ultra-pure water obtained from a Millli Q water purification system (USA) with the resistivity of 18.2 MΩ cm. The DNA probe used in this work was synthesized and purified by Sangon Biotechnology Co. LTD. (Shanghai, China). The sequence was as follows (from 5' to 3'):

MB-CAGGCTACTAAT*GGTTGGTGTGGTTGG*ATTAGTA-(HS-SH)

DTT reduction

Disulfide bond at the 3' end of DNA probe was opened by DTT reduction to achieve thiol group. Briefly, DNA powder was firstly dissolved in 100 μL of water. Next, 3.5 mg of DTT was dissolved in 300 μL of 0.1 M Tris-HCl (pH 7.45) buffer. After that, the above two solutions were well mixed for 1 h at room temperature. Then, the obtained solution was blended with 50 μL of 3 M NaAc and 1.5 mL of ethanol, which was then placed at -20°C for 15 min. Subsequently, the solution was centrifuged for 1 min (14000 rpm). The supernatant was discarded and DNA product was resuspended with Tris-HCl buffer solution (10 mM, 1 mM EDTA, 10 mM TCEP, and 0.1 M NaCl, pH 7.4).

Preparation of DNA modified gold electrode

The substrate gold electrode was firstly immersed in piranha solution (*Caution: piranha solution was highly corrosive*) for 15 min to eliminate the organic macromolecules and rinsed with plenty of pure water. Then, the electrode was mechanically abraded with silicon carbide paper (P3000 and

P5000), followed by polishing carefully with alumina powders of various sizes (1.0, 0.3, 0.05 μm). After a mirror-like surface was obtained, the electrode was sonicated with ethanol and then ultrapure water for 10 min to remove excess polishing vestigial alumina. The gold electrode was further cleaned by electrochemical scanning in 0.5 M H_2SO_4. After that, it was incubated with a mixed solution of 1 μM DNA probe and different concentrations of K^+ for 16 h. Finally, the electrode was treated with 1 mM MCH for 1 h.

Electrochemistry measurement

All electrochemical measurements were performed by using a CHI660D workstation (CH Instruments, Shanghai, China). The three-electrode system consists of a DNA modified gold working electrode, a saturated calomel reference electrode (SCE) and a platinum auxiliary electrode. SWV experiments were performed in 20 mM Tris-HCl (pH 7.45). EIS measurements were carried out in 5 mM $Fe(CN)_6^{3-/4-}$ with 1 M KCl. Experimental parameters were as follows. SWV: amplitude signal of 25 mV, frequency of 50 Hz, scan range from 0 to -0.5 V; EIS: bias potential of 0.182 V, amplitude of 5 mV, frequency range from 0.1-100000Hz.

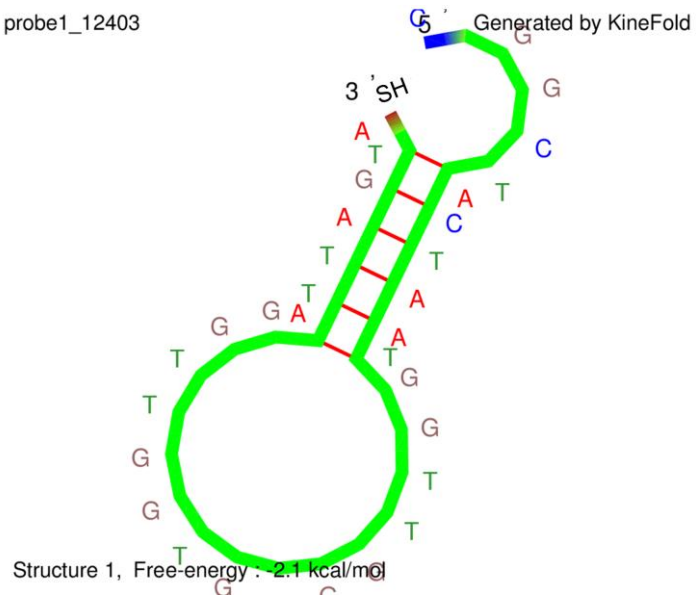

Fig. S1. Secondary structure of the DNA probe predicted by Kinefold web server (http://kinefold.curie.fr/).

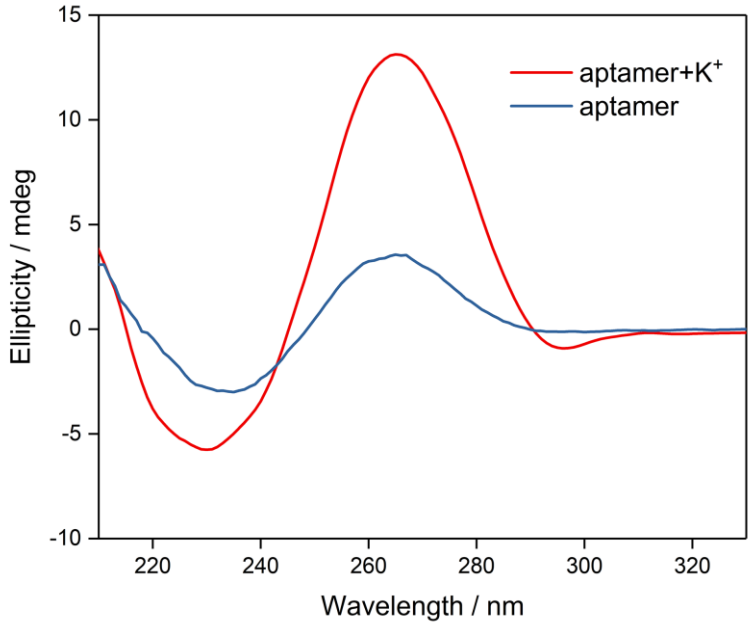

Fig. S2. CD spectra of aptamer (10 μM) before and after the addition of K^+ (50 μM) overnight.

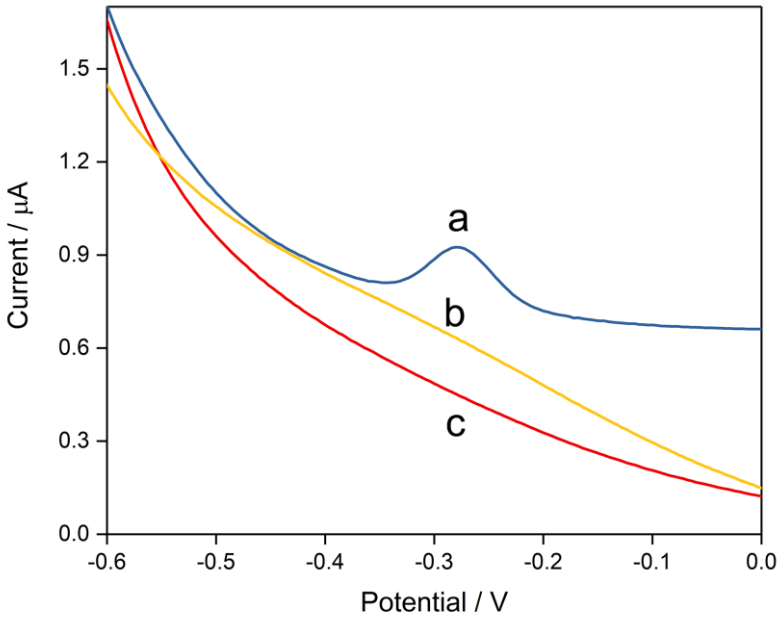

Fig. S3. Square wave voltammograms for the analysis of (a) K^+, (b) BSA, (c) HSA.