

A chronocoulometric aptamer sensor for adenosine mono- phosphate

**Li Shen, Zhong Chen, Yihan Li, Ping Jing, Shubao Xie, Shali He, Pingli He* and
Yuanhua Shao***

Supplementary information

Supplementary information

Materials. DNA oligonucleotides were synthesized and purified by Sangon Inc. (Shanghai, China). The sequences of the oligomers employed are given below:

5'-HS-(CH₂)₆-

AGAGAACCTGGGGGAGTATTGCGGAGGAAGGT-3' (1)

3'-TCTCTTGGACCC-5' (2)

Tris(2-carboxyethyl) phosphine hydrochloride (TCEP), hexaamineruthenium(III) chloride (RuHex), tris(hydroxymethyl)aminomethane and 6-mercaptohexanol (MCH) were purchased from Sigma. Adenosine monophosphate (AMP) was from Fluka. Cytidine monophosphate (CMP) was obtained from Shanghai Chemical Reagent Company. All other chemicals were analytical grade.

DNA buffers involved in this work were comprised of 300 mM NaCl, 50 μM TCPE and 25 mM tris-acetate (pH 8.2). Buffers for electrochemistry were 10 mM Tris-acetate buffers (pH 7.4). Deionized water was used to prepare solutions.

Sensor preparation. Solutions of oligonucleotide (1) and (2) were mixed in the buffers with equal mole. The samples were stored at 4 °C for more than 90 min for creating half-duplex before used.

Gold electrodes (2 mm in diameter, CH Instruments Inc.) were polished with alumina and sonicated in water for 5 min. They were then cleaned in "piranha" solution (1: 3 volume ratio of 30% H₂O₂ and concentrated H₂SO₄) for about 1 h, and rinsed thoroughly with water. The cleaned gold electrodes were held upside down, covered with a plastic cap, and 20 μL of 2.5 μM DNA solutions was dropped onto the electrode surfaces for more than 16 h. The electrodes were then passivated with 2 mM MCH for 1 h.

Apparatus. Cyclic voltammetry (CV) and chronocoulometry (CC) were performed with a CHI 910B electrochemical workstation (CH

Instruments). The experiments were carried out in a three-electrode cell with a Ag/AgCl electrode as reference electrode, a Pt wire as counter electrode, and a DNA modified gold electrode as working electrode. Buffers were purged with highly purified nitrogen for at least 15 min prior to a series of electrochemical experiments. A nitrogen environment was then kept in the cell during the whole experiment. All experiments were performed at ambient temperature (20 ± 2 °C).

Characterization of the DNA probes. The density of grafted DNA probes is usually estimated electrochemically by the Cottrell's experiment. It can be easily calculated from equations (1) and (2),

$$\Gamma_{\text{Ru}} = \frac{Q_{\text{ds}} - Q_{\text{dl}}}{nFA} \quad (1)$$

$$\Gamma_{\text{DNA}} = \Gamma_{\text{Ru}} (z/m)(N_A) \quad (2)$$

where Γ_{Ru} is the amount of the redox marker confined near the electrode surface, Q_{ds} and Q_{dl} are surface charges (Fig. S1), n is the number of electrons in the reaction, F is the Faraday constant, A is the area of the working electrode, Γ_{DNA} is the surface density of grafted DNA, z is the charge of the redox marker, m is the numbers of the bases in DNA, and N_A is Avogadro's number.

Figures.

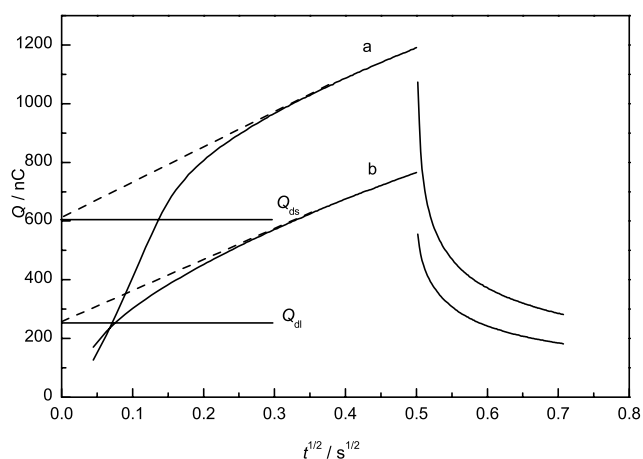


Fig. S1 Chronocoulometric curves for (a) half-duplex/MCH and (b) MCH modified electrodes in the presence of 50 μM RuHex. The chronocoulometric intercept at $t = 0$ represents the charges of the redox marker confined near the electrode surface.

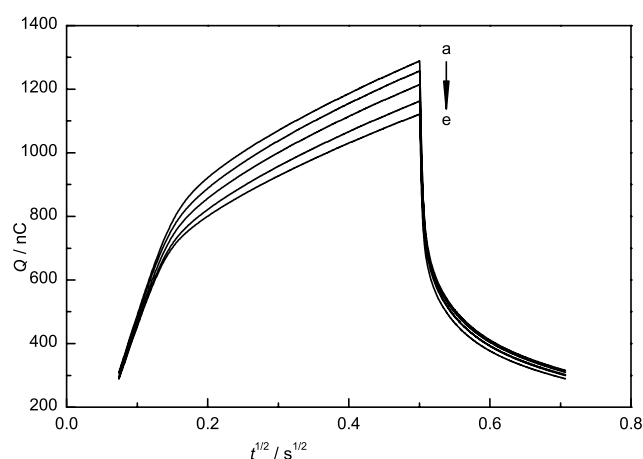


Fig. S2 Chronocoulometric curves for half-duplex modified electrodes upon different concentrations of K⁺ (a) 0 M, (b) 10⁻⁴ M, (c) 10⁻³ M, (d) 10⁻² M and (e) 10⁻¹ M. The solution is 10 mM Tris buffer (pH7.4) containing 50 μM RuHex.

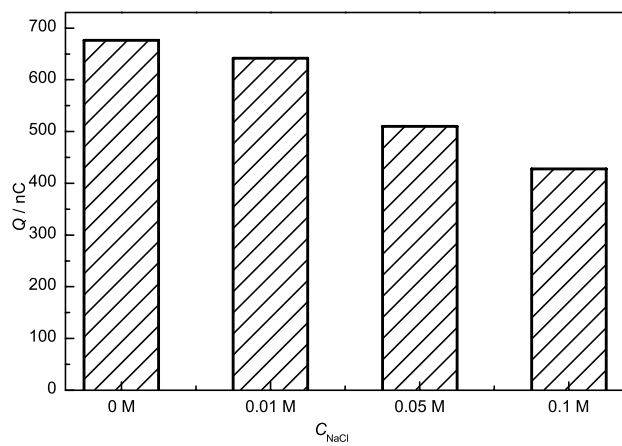


Fig. S3 Effect of NaCl concentrations on CC signals of the half-duplex modified electrode.