Supporting Information

Experimental details

Reagents

Aldehyde-functionalized Ru-SiNPs were prepared according to the procedure reported in S1 (Santra et al., 2001). The TEM (Transmission electron microscopy) image of nanoparticles (Fig.S1, Tecnai G2 F20 S-TWIN 200KV) showed that the prepared aldehyde-functionalized Ru-SiNPs solution was similar to that of the published assay (S1, Santra et al., 2001). ATP and its analogue compounds, cytidine triphosphate (CTP), guanosine triphosphate (GTP), uridine triphosphate (UTP), and 2-(Dibutyl-amino) ethanol (DBAE)，were purchased from Sigma (St. Louis, MO) and used without further purifying. Other chemicals were of analytical reagent grade. Double-distilled water was used throughout. Phosphate buffer solution (PBS, pH 7.4) was used as the DNA buffer solution.

The DNA oligonudeotides were synthesized by Sangon Inc. (Shanghai, China). And their sequences were shown as follows：

Capture probe (ss-DNA1)

5’-HS-$(CH_2)_6$-ACCTGGGGGAGTAT-3’

Detection probe (ss-DNA2)

5’-TGCGGAGGAAGGT-NH_2-3’

A single ATP aptamer was synthesized, and its sequence is characterized as the combination of the former two fragments.

Apparatus

The measurement of ECL was performed using a BPCL ultra-weak luminescence analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China) and a CHI 660a electrochemical system (Shanghai Chenhua Equipments, China). Gold electrodes (diameter: 3.0 mm, surface area: 7.07 mm^2, CH Instruments, Shanghai, China) were used as the working electrodes. Platinum wire and Ag/AgCl (saturated with KCl) were used as counter and reference electrodes, respectively. The electrochemical cell was placed directly in front of a photomultiplier (PMT, operated at -800 V).

Preparation of the sensor and detection procedures

The ECL probe was fabricated by adding freshly prepared aldehyde-functionalized Ru-SiNPs into the buffer solution containing ss-DNA2 with amido in the 3'end to interact with each other in 37^{o}C water bath for 2 h. Then, the above Ru-SiNPs-modified-ssDNA2 was washed, centrifuged and suspended in PBS and kept at 4 ^{o}C for later use.

A lot of literatures reported the procedure for sensor fabrication (eg., S2, Zhu et al, 2010; S3, Chen et al, 2010). In brief, the gold electrode was polished with 1.0, 0.3 and 0.05 μm α-Al_2O_3 powders in sequence before each experiment; then, it was rinsed with double-distilled water and ultrasonically cleaned in ethanol and water for a short time. Finally, the electrode was electrochemically activated in 0.5 mol/L H_2SO_4.

A 10 μL ssDNA1 solution was dropped onto the previously activated gold electrode surface and kept it for 2 h to form an Au-thiol monolayer. Then the

modified electrode was immersed in MCH solution for 1 h to cover the nonspecific sites. Eventually, the electrode was immersed into the solution which contains Ru-SiNPs-modified-ssDNA2 and various concentrations of ATP at room temperature and held for for 2 h. After these procedures, the electrode was washed with buffer solution to remove the excrescent matter. The obtained biosensor is immersed in 2.0 mL PBS (Phosphate Buffered Solution, pH 7.4) containing 5.0×10^{-3} mol/L DBAE for ECL detection..

Characterization of the sensor

Faradic electrochemical impedance spectroscopy (EIS) was employed to monitor the process of the electrode modification. The spectra consists of a semicircle part at higher frequency and a linear one at lower frequency, referring to the electron transfer-limited and diffusion process which can directly described by Nyquist plots. The increase of the diameter of the semicircle indicates an increase of the interfacial charge-transfer resistance (R_{ct}). The electrolyte solution with electroactive ions $Fe(CN)_6^{3-/4-}$ and with 0.5 mol/L KCL was used. Some substances with negative charge can prevent redox probe $Fe(CN)_6^{3-/4-}$ from transferring on the electrode surface.

As shown in Fig.S2, the R_{ct} value for the bare gold electrode (curve *a*) is about 100Ω, indicating the electroactive ions of $Fe(CN)_6^{3-/4-}$ transfer well on the electrode interface. Since its surface is immobilized by thiol-modified ssDNA1, the value of impedance (curve *b*) increases owing to the negatively charged phosphate backbone of the oligonudeotides, which increases the electron-transfer distance (S4, Huang et al, 2010). The ssDNA1 modified electrode was immobilized into the solutions of

ssDNA2 with or without ATP for about 2 h. In the case of ssDNA2 solution with ATP, little amount of ssDNA2 could interacts with ssDNA1 through physical adsorption and only partial ssDNA2 is captured on the electrode surface, which results in larger R_{ct} of curve *c*. Compared with the former one, a larger value (curve *d*) was observed attributing to the stable complex formed by the ATP-induced split aptamer chips combination. This would produce a nearly insulating layer on the electrode surface, and deter the electro-active species in the solution from transferring to the electrode surface.

Serum samples detection procedure

Human serum samples were provided by the Hospital of Fuzhou University (Fujian, China). Prior to each test, the samples were treated with EDTA for holding back the blood clotting. Then, the solutions were centrifuged to gather total blood cells. The obtained samples were diluted 10^3 times with PBS. Subsequently, cell lysis was performed under iterative freezing (at -77^{o}C) and melt (at 37^{o}C) according to the literature (S5, Zuo et al, 2007). Then Ru-SiNPs-modified-ssDNA2 was added into the sample solution. The ssDNA1 modified electrode was immersed into the mix solution for 2 h. After these procedures, the electrodes were washed with buffer solution to remove the excrescent matter, and the ECL intensity from the sensor was tested. The ATP was added into the serum samples for testing the biosensor.

Reference

S1. S. Santra, P. Zhang, K. M. Wang, R. Tapec, W. Tan, Anal. Chem. 2001, 73, 4988.

S2. X. Zhu, Z. Y. Lin, L. F. Chen, B. Qiu, G. N.Chen, Chem. Commun. 2010, 46, 3149-3151.

S3. L. F. Chen, Q. H. Cai, F. Luo, X. Chen, X. Zhu, B. Qiu, Z. Y. Lin, G.. N. Chen, Chem. Commun. 2010, 46,7751-7753

S4. H. P. Huang, Y. L. Tan, J. J. Shi, G. X. Lian, J. J. Zhu, Nanoscale 2010, 2, 606.

S5. X. L. Zuo, Y. Xiao, K. W. Plaxco, J. Am. Chem. Soc. 2009, 131, 6944.

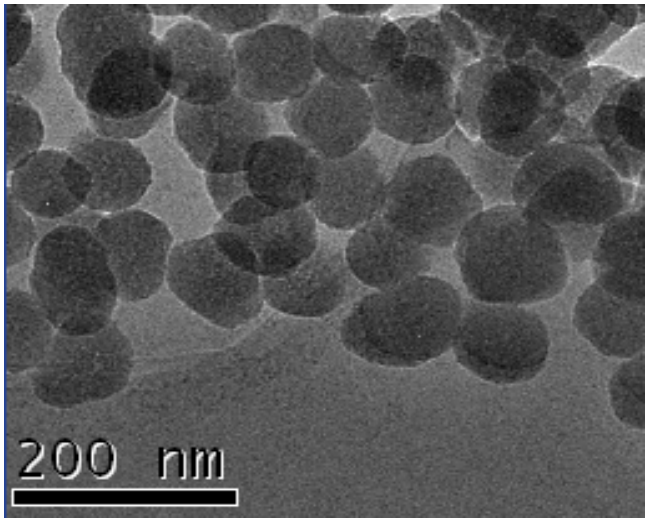

Fig.S1 The TEM image of Ru-SiNPs

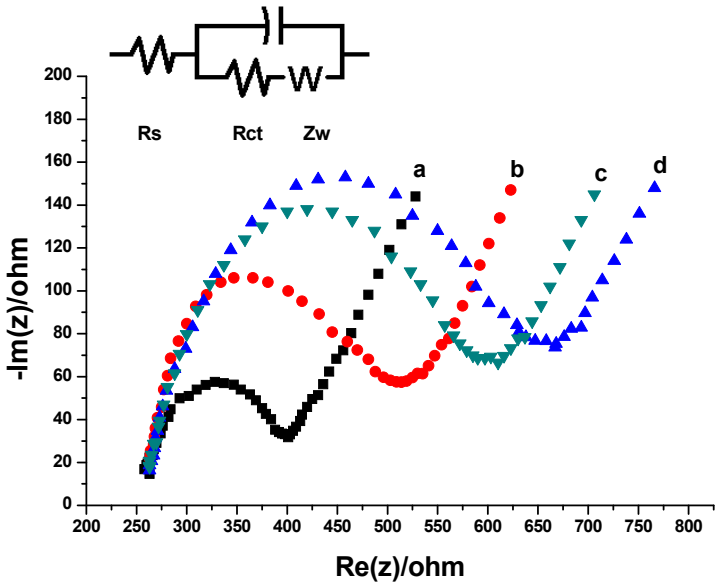

Fig. S2 Faradic electrochemical impedance spectroscopy of different modified electrodes in 5.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ containing 0.5 mol/L KCL (a) bare Au electrode (b) ssDNA1 modified electrode (c) dsDNA electrode (d) dsDNA-ATP electrode. The data were received based on the biasing potential 0.218V and 5 mV alternative voltages in the frequency range of 1 Hz-10 kHz.

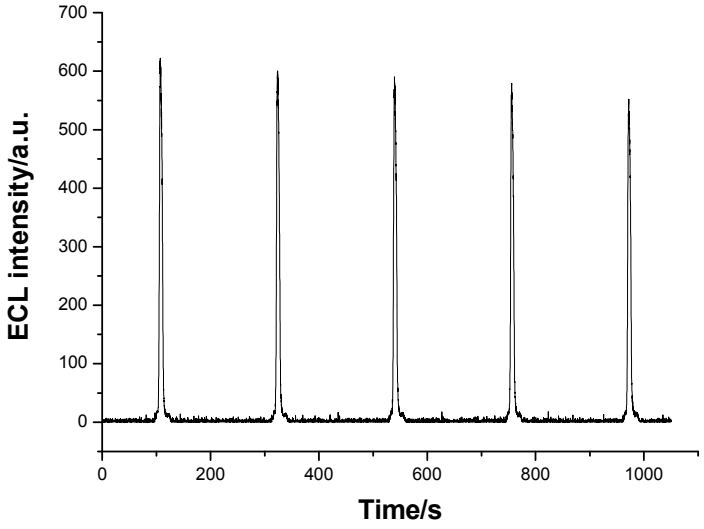

Fig. S3 Stability of the aptamer-sensor after reacting with 1.0×10^{-11} mol/L ATP.