Supplementary Information

Rapid assembly of ss-DNAs on gold electrode surface at low pH and high salt concentration conditions

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DNA area percentage and Langmuir adsorption isotherm

The DNA area percentage (θ) was obtained from EIS by fitting the experimental results with the Randles circuit. We calculated the DNA area percentage on the gold electrode surface for the monolayers by using eqn (1): [1]

$$\theta = 1 - (\frac{R_{ct}^{Au}}{R_{ct}^{SAM}}) \quad (1)$$

where R_{ct}^{Au} was charge transfer resistance values for bare gold electrode and R_{ct}^{SAM} was charge transfer resistance values for DNA-modified gold electrode.

As shown in Fig. S1, we found that the relationship between the DNA area percentage and the DNA concentration obeys the Langmuir adsorption isotherm quite well, and the correlation coefficient was 0.9820. In this case, the electrode surface state can be determined by using the Langmuir adsorption isotherm according to the following equation: [2]

$$KC = \theta/(1-\theta) \quad (2)$$

where K is the adsorption–desorption equilibrium constant, and C is the DNA concentration. The standard free-energy of adsorption (ΔG°_{ads}) was calculated from this isotherm using the following relation: [3]

$$K = (1/55.5)\exp(-\Delta G^{\circ}_{ads}/RT) \quad (3)$$

where 55.5 is the water concentration, R is the universal gas constant and T is the thermodynamic temperature. The magnitude of ΔG°_{ads} is consistent with ssDNA adsorption behavior. Generally, values of ΔG°_{ads} up to −20 kJ mol^{-1} are associated with electrostatic interaction between gold surface and ssDNA probe, which indicates physical adsorption. ΔG°_{ads} values more negative than −40 kJ mol^{-1} signify covalent bond. As shown in Table S1, values of ΔG°_{ads} at different pHs on ss-DNA assembly were all more negative than −40 kJ mol^{-1}. This probably suggests that the mechanism related to the adsorption of ssDNA onto the gold surface under different pH

conditions is a chemically absorbed process and involves covalent bond. The absolute value of $\Delta G°_{ads}$ increases with decreasing pH value, indicating that chemisorption on the gold surface was increased in lower pH environment. In our assay, the larger ΔG°_{ads} value means increased number of ssDNA attached to gold surface. Thus, the electrochemical impedance value increased with decreasing pH value as shown in Fig. 4 in the manuscript.

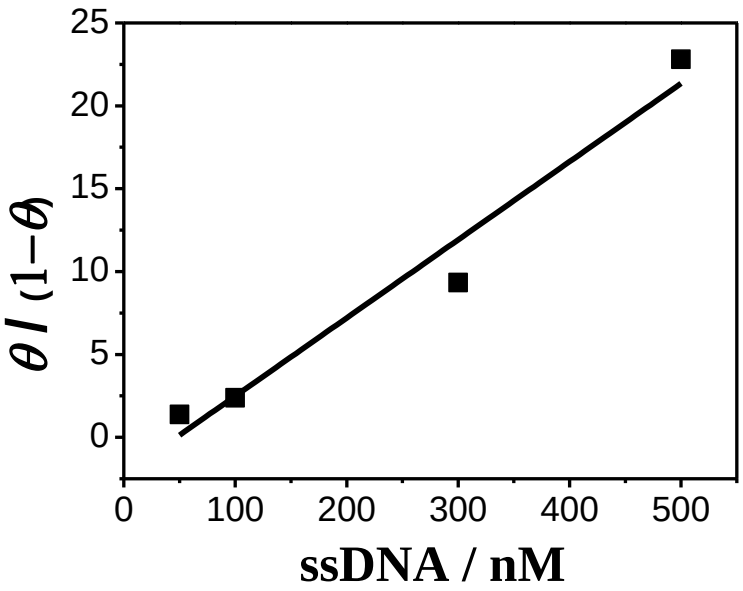

Fig. S1 The graph of Langmuir adsorption isotherm for the adsorption of ssDNA onto the surface of gold.

Table S1 Thermodynamic parameters for different pHs on ssDNA assembly.

pH	$\theta/(1-\theta)$	K ($\times 10^6$ M)	ΔG°_{ads} (KJ mol^{-1})
3.4	9.38	18.76	–51.44
4.4	7.76	15.55	–50.98
5.4	2.34	4.68	–48.01
6.4	0.61	1.21	–44.65
7.4	0.27	0.54	–42.65
8.4	0.11	0.21	–40.31

Table S2 Main parameters obtained from EIS results showing the effect of the salt concentration.[a]

Concentration of NaCl (mol/L)	Rs (Ω)		Rct (Ω)		θ	
	pH 3.4	pH 7.4	pH 3.4	pH 7.4	pH 3.4	pH 7.4
Bare	150.8	150.8	89.23	89.23	\	\
0.1	180.4	173.2	6223	2208	0.986	0.959
0.5	166.9	168.5	19300	8841	0.995	0.989
1.0	168.3	176.6	28610	16020	0.997	0.994

[a] The solution resistance (Rs), the charge transfer resistance (Rct), and the DNA area percentage (θ) were obtained by fitting the experimental results with the Randles circuit. The parameters of the bare Au electrode were obtained in 5 mM $[Fe(CN)_6]^{3-/4-}$–phosphate buffered saline (PBS) (5 mM phosphate, 50 mM NaCl, pH 7.0) solution after electrochemical cleaning.

Table S3 Main parameters obtained from EIS results showing the effect of the immobilization time.[a]

Time (min)	Rs (Ω)		Rct (Ω)		θ	
	pH 3.4	pH 7.4	pH 3.4	pH 7.4	pH 3.4	pH 7.4
Bare	150.8	150.8	89.23	89.23	\	\
10	133	180.7	7388	5480	0.988	0.984
30	166.9	168.5	17300	6841	0.994	0.987
60	173.7	176.9	21010	9376	0.996	0.990
150	175.2	183.6	23979	12260	0.996	0.993
720	\	174.9	\	21490	\	0.996

[a] The solution resistance (Rs), the charge transfer resistance (Rct), and the DNA area percentage (θ) were obtained by fitting the experimental results with the Randles circuit. The parameters of the bare Au electrode were obtained in 5 mM $[Fe(CN)_6]^{3-/4-}$–phosphate buffered saline (PBS) (5 mM phosphate, 50 mM NaCl, pH 7.0) solution after electrochemical cleaning.

References

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