

Supporting Information

Effect of monovalent cations (Li^+ , Na^+ , K^+ , Cs^+) on self-assembly of thiol-modified double-stranded and single-stranded DNA on gold electrode

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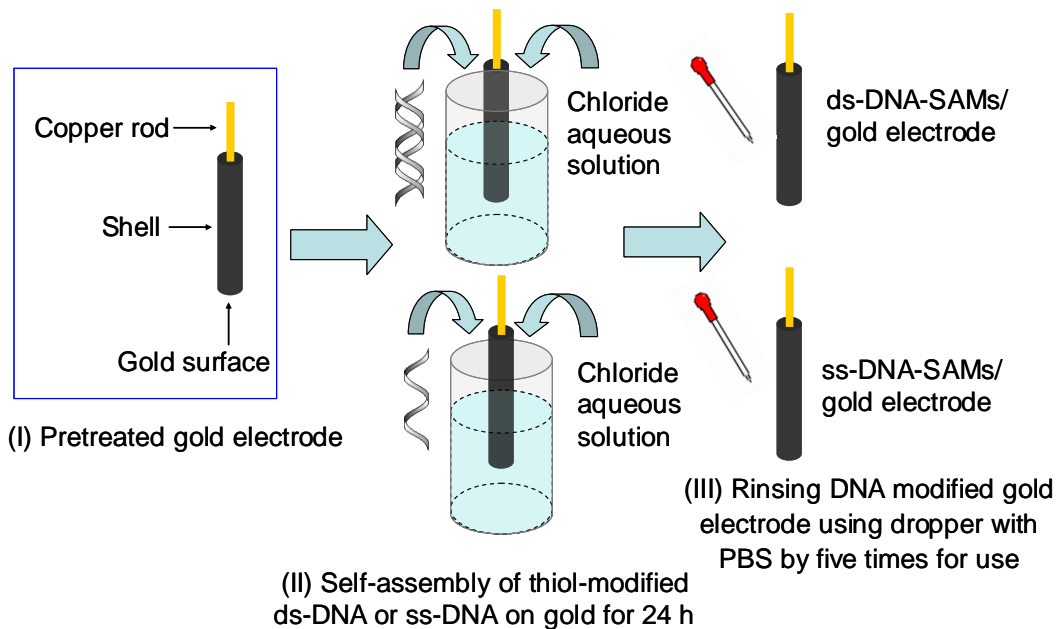
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Contents

- [1. Scheme for self-assembly process of thiol-modified ds-DNA or ss-DNA on gold.](#)
2. Interfacial parameters for characterizing ds-DNA-SAMs on gold assembled in 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions.
3. Interfacial parameters for characterizing ss-DNA-SAMs on gold assembled in 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions.
4. Confirmation of our experimental results (Γ_m , C , R_{it}^* , Δi , R_{ct})
5. References

1. Scheme for self-assembly process of thiol-modified ds-DNA or ss-DNA on gold.



Scheme S1. Self-assembly process of thiol-modified ds-DNA or ss-DNA on gold. (Chloride aqueous solution is 0.1 M or 1 M LiCl, NaCl, KCl, CsCl aqueous solution; PBS is 5 mM phosphate-50 mM NaCl, pH 7.0).

2. Interfacial parameters for characterizing ds-DNA-SAMs on gold assembled in 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions

Table S1. Parameters for characterizing ds-DNA-SAMs on gold assembled in 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions

Assembly electrolytes	Surface coverage		Ions penetration (5 mM phosphate-50 mM NaCl, pH 7.0)						Charge transfer (2 mM Fe(CN) ₆ ^{3-/4-})			
	<i>CC</i>		<i>CV</i>				<i>EIS</i>		<i>CV</i>	<i>EIS</i>		
	Γ_m (10 ⁻¹¹ mol cm ⁻²)		<i>C</i> (μF cm ⁻²)				$\Phi_{1\text{Hz}}$ (°)	R_{it}^* (Ω cm ²)	Δj (μA cm ⁻²)	R_{ct} (Ω cm ²)		
			0.1 V s ⁻¹	0.5 V s ⁻¹	1 V s ⁻¹	5 V s ⁻¹	20 V s ⁻¹	50 V s ⁻¹				
0.1 M LiCl	0.5		19.4	12.8	10.6	6.8	4.8	3.9	70	1.7 × 10 ⁴	129	7.6 × 10 ³
0.1 M NaCl	0.7		17.0	12.4	11.0	8.7	7.1	6.3	76	1.6 × 10 ⁴	320	2.2 × 10 ³
0.1 M KCl	0.6		24.6	17.7	15.3	10.5	7.7	6.4	74	1.2 × 10 ⁴	183	5.4 × 10 ³
0.1 M CsCl	0.6		22.6	16.1	13.8	9.9	7.5	6.4	74	1.3 × 10 ⁴	266	2.0 × 10 ³
1 M LiCl	1.4		16.7	11.8	10.3	7.7	6.3	5.7	75	1.7 × 10 ⁴	23	5.2 × 10 ⁴
1 M NaCl	1.8		21.2	15.1	12.9	9.4	7.7	7.0	75	1.4 × 10 ⁴	30	4.5 × 10 ⁴
1 M KCl	1.4		22.0	15.6	13.7	10.4	8.4	7.3	76	1.3 × 10 ⁴	80	1.3 × 10 ⁴
1 M CsCl	1.1		22.4	14.8	12.4	8.5	6.6	5.8	72	1.4 × 10 ⁴	60	1.7 × 10 ⁴

3. The parameters for characterizing ss-DNA-SAMs on gold assembled in 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions

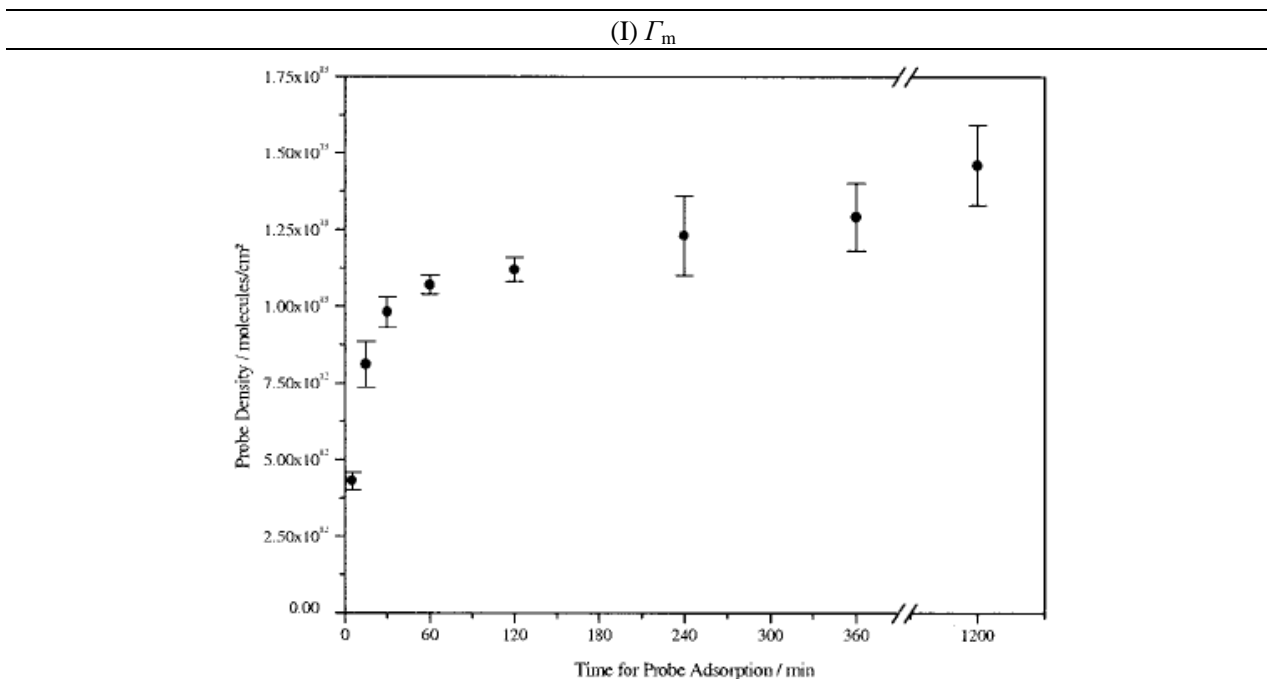
Table S2. Parameters for characterizing ss-DNA-SAMs on gold assembled in 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions

Assembly electrolytes	Surface coverage		Ions penetration (5 mM phosphate-50 mM NaCl, pH 7.0)						Charge transfer (2 mM Fe(CN) ₆ ^{3-/4-})			
	<i>CC</i>		<i>CV</i>				<i>EIS</i>		<i>CV</i>	<i>EIS</i>		
	Γ_m (10 ⁻¹¹ mol cm ⁻²)		<i>C</i> (μF cm ⁻²)				$\Phi_{1\text{Hz}}$ (°)	R_{it}^* (Ω cm ²)	Δj (μA cm ⁻²)	R_{ct} (Ω cm ²)		
			0.1 V s ⁻¹	0.5 V s ⁻¹	1 V s ⁻¹	5 V s ⁻¹	20 V s ⁻¹	50 V s ⁻¹				
0.1 M LiCl	1.9		11.7	7.4	6.4	4.8	4.1	3.8	73	2.8 × 10 ⁴	48	3.7 × 10 ⁴
0.1 M NaCl	2.0		20.8	14.8	12.4	9.1	7.2	6.4	73	1.5 × 10 ⁴	109	7.8 × 10 ³
0.1 M KCl	2.2		16.7	11.4	9.9	7.4	5.9	5.4	75	1.9 × 10 ⁴	36	5.6 × 10 ⁴
0.1 M CsCl	2.3		15.4	10.5	9.1	7.0	5.9	5.3	75	2.0 × 10 ⁴	32	6.5 × 10 ⁴
1 M LiCl	4.9		30.0	20.6	17.2	12.3	9.6	8.2	74	1.1 × 10 ⁴	15	2.4 × 10 ⁵
1 M NaCl	5.1		23.3	15.9	13.8	10.6	9.0	8.3	75	1.3 × 10 ⁴	19	1.1 × 10 ⁵
1 M KCl	3.9		44.2	29.7	24.8	16.6	12.1	10.1	72	7.9 × 10 ³	20	2.2 × 10 ⁵
1 M CsCl	4.0		22.2	15.0	13.0	9.2	6.9	6.0	75	1.4 × 10 ⁴	35	9.1 × 10 ⁴

4. Confirmation of our experimental results (Γ_m , C , R_{it}^* , Δi , R_{ct})

(a) Relative standard deviation (RSD) of experimental data (Γ_m , C , R_{it}^* , Δi , R_{ct}) from literature reports

Table S3. Relative standard deviation (RSD) of experimental data (Γ_m , C , R_{it}^* , Δi , R_{ct}) from literature reports



(a) Surface density of 5' thiol-modified 16mer oligonucleotide on gold after 6-mercapto-1-hexanol (MCH) treatment as a function of deposition period. Probe densities were determined electrochemically. The probe, sequence 5'-thiol-ACT-GAC-TGA-CTG-ACT-G-3', was deposited from a 1 mM solution for the indicated time, followed by exposure to 1 mM MCH for 1 h.¹

(II) C and R_{it}^*

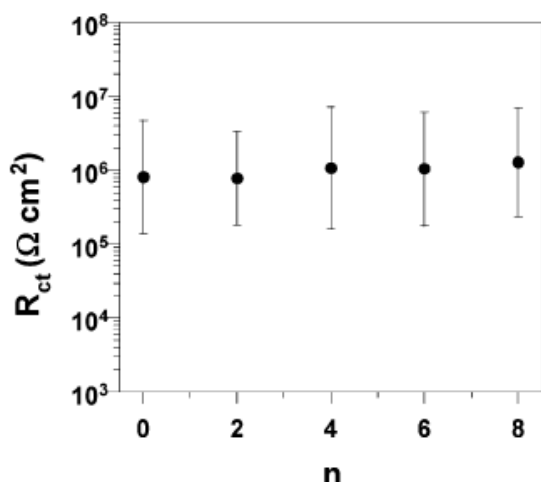
Table 1. Capacitance of DNA-Modified Electrodes

monolayer	capacitance ($\mu\text{F}/\text{cm}^2$)	n^a
bare Au	43 ± 15	6
MCH	3.9 ± 0.1	10
P1	25 ± 8	4
P2	33 ± 7	4
P1/MCH	4.8 ± 0.2	8
P2/MCH	4.9 ± 0.2	8

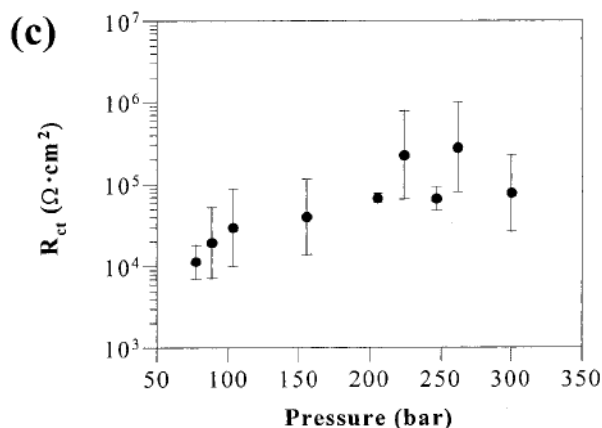
^a The number of independent measurements on different monolayer preparations.

(b) Capacitance of 5' thiol-modified 25mer DNA-SAMs on gold was determined in 10 mM Tris buffer (pH 7.4).²

(III) Δi and R_{ct}



(c) Influence of fluorocarbon chain length (n) on the charge transfer resistance (R_{ct}) of SAMs prepared by exposure of gold to 0.2 mM $F_nH_{(16-n)}SH$ in CH_2Cl_2 for 48 h.³



(d) Effect of pressure on the properties of C_{12} SAMs formed on gold after 30 min in CO_2 at 35 °C, as determined by measuring the charge-transfer resistance. Electrochemical impedance measurements were performed in an aqueous solution containing 0.1 M Na_2SO_4 , 1 mM $K_3Fe(CN)_6$, and 1 mM $K_4Fe(CN)_6 \cdot 3H_2O$.⁴

Table 1. Results of the CNLS Fitting of the Impedance Response for Different Deposition Times of the n -Dodecyl Selenide on a Au(111) Single Crystal Electrode^a

deposition time, s	R_s, Ω	$R_{ct}, \Omega \times 10^{-6}$	CPE (C_{dl}) $\times 10^7, {}^b F cm^{-2}$	φ
5	179.3 (1.10)	0.11 (0.50)	2.00 (1.50)	0.9795
10	177.1 (1.03)	1.17 (0.44)	1.11 (0.57)	0.9929
60	179.0 (1.28)	2.34 (0.69)	1.17 (0.64)	0.9902
300	147.6 (1.02)	4.41 (0.56)	1.23 (0.39)	0.9850
54 000	148.2 (2.37)	7.52 (1.91)	1.34 (0.95)	0.9567
86 400	171.2 (0.74)	11.7 (0.72)	1.15 (0.27)	0.9928

^a The percent errors from the fit for each element are given in parentheses. ^b The area of the electrode was equal to 0.0856 cm^{-2}

(e) Impedance spectra for the Au/ n -Dodecyl performed in solutions containing 0.5 mM $Fe(CN)_6^{3-/4-}$ with 0.1 M $NaClO_4$. Au/ n -Dodecyl was prepared by dipping the Au(111) electrodes into ~3 mM n -Dodecyl in ethyl alcohol for different time.⁵

* The *RSD* of parameters (R_{it}^* and Δj) for ds-DNA-SAMs and ss-DNA-SAMs on gold had been shown in our recently published papers,^{6,7} The *RSD* of Γ_m was smaller than 10%,¹ *RSD* of C , Φ_{1Hz} and R_{it}^* was generally smaller than 20%,^{2,8} whereas *RSD* of Δj and R_{ct} was much bigger and even >100%.^{3-5,9}

(b) Experimentally cross-checked the experimental data (C values) for ds-DNA-SAMs and ss-DNA-SAMs on gold assembled in 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions by CV and EIS

We calculated the C of ds-DNA-SAMs and ss-DNA-SAMs by EIS and drew the plots of C with frequency f_m . The aim was to further validate the data of C by CV in Figure 3C and Figure 5C in the manuscript. C calculated by EIS (Figure S1) was close to that by CV (Figure 3C and Figure 5C). Furthermore, C calculated by EIS decreased with the increase of f_m (Figure S1), consistent with the decrease of C calculated by CV with the increase of scan rate ν (Figure 3C and Figure 5C).

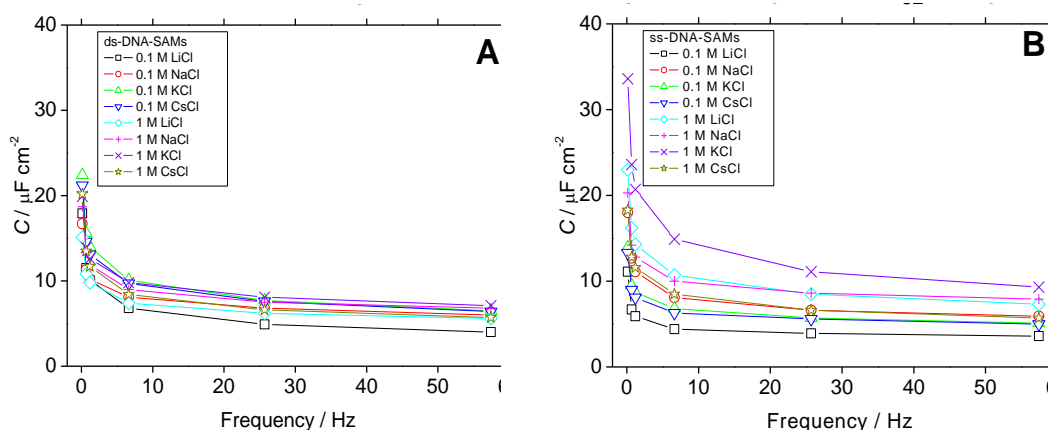


Figure S1. The plot of C obtained from EIS ($C = \frac{1}{2\pi f_m AZ''}$, Z'' was the imaginary parts of impedance at the frequency f_m , A was the real area of electrode)¹⁰ with frequency f_m for ds-DNA-SAMs (A) and ss-DNA-SAMs (B) on gold assembled under 0.1 M or 1 M LiCl, NaCl, KCl, CsCl solutions. In order to compare the C obtained from EIS with CV, f_m was designated close to

$f_m = \frac{\nu}{2\Delta E_m} = \frac{\nu}{2(E_{\max} - E_{\min})}$ based on the potential zone ($2\Delta E_m = 2(E_{\max} - E_{\min}) = 0.8\text{V}$) of a CV scan period from -0.2 (E_{\min}) to $+0.2$ V (E_{\max}) and scan rate ν (0.1, 0.5, 1, 5, 20, 50 V s^{-1}). f_m was calculated to be 0.12, 0.66, 1.18, 6.64, 25.7, 57.4 Hz.

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