Electronic Supplementary Material (ESI) for Analyst

Supplementary Information

Scanning Positional Variations in Single-Nucleotide Mismatch of DNA: An Electrochemical Study

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Table S1. Values of the electrical components obtained by fitting the EIS data with the equivalent circuit. Data were taken from fully complementary (FC) and 25 mismatch positions (from M1 to M25) in ds-DNA films.

	Zn present/absent	R_s $\Omega\cdot cm^2$	C_{dl} $\mu F\cdot cm^{-2}$	R_{ct} $\Omega\cdot cm^2$	CPE (Yo)x10^{-6}	n	R_x $\Omega\cdot cm^2$	ΔR_{ct} $\Omega\cdot cm^2$
FC	absent	0.03	3.5 (3.1)	1089 (130)	2.4 (2.1)	0.91 (0.02)	1.5 (0.7)	905 (130)
	present	0.04	2.9 (0.5)	184 (40)	3.0 (0.4)	0.92 (0.02)	1.0 (0.1)	
M1	absent	0.10	3.0 (2.9)	916 (150)	2.3 (0.9)	0.91 (0.02)	2.5 (2.1)	749 (175)
	present	0.10	1.8 (0.2)	167 (45)	1.6 (0.5)	0.93 (0.03)	1.7 (0.1)	
M2	absent	0.01	2.4 (0.9)	771 (80)	2.3 (1.2)	0.91 (0.03)	1.9 (0.8)	560 (110)
	present	0.01	2.2 (0.3)	211 (110)	1.9 (0.9)	0.91 (0.02)	2.4 (0.7)	
M3	absent	0.02	1.7 (0.1)	428 (60)	2.7 (0.7)	0.90 (0.01)	1.6 (0.1)	263 (70)
	present	0.02	1.9 (0.3)	165 (25)	2.1 (0.4)	0.92 (0.02)	1.7 (0.1)	
M4	absent	0.02	1.7 (0.1)	519 (90)	2.7 (0.7)	0.90 (0.01)	1.6 (0.1)	309 (145)
	present	0.02	1.9 (0.3)	210 (50)	2.1 (0.4)	0.92 (0.02)	1.7 (0.1)	
M5	absent	0.07	2.2 (0.6)	334 (45)	2.9 (0.8)	0.90 (0.02)	1.6 (0.4)	218 (20)
	present	0.07	2.3 (0.7)	116 (45)	2.6 (0.8)	0.90 (0.03)	1.5 (0.1)	
M6	absent	0.07	2.4 (0.8)	463 (75)	3.1 (0.6)	0.92 (0.01)	1.2 (0.1)	246 (35)
	present	0.07	3.2 (1.5)	217 (55)	2.4 (0.4)	0.92 (0.01)	1.2 (0.1)	
M7	absent	0.10	2.6 (0.8)	730 (80)	5.9 (4.5)	0.93 (0.02)	1.6 (0.9)	398 (50)
	present	0.10	2.6 (1.0)	332 (45)	4.8 (2.0)	0.89 (0.06)	1.2 (0.2)	
M8	absent	0.11	3.1 (1.6)	607 (75)	2.8 (1.0)	0.89 (0.05)	1.7 (0.5)	401 (40)
	present	0.06	2.3 (1.8)	206 (65)	4.1 (1.2)	0.91 (0.02)	1.3 (0.1)	
M9	absent	0.08	2.9 (1.4)	613 (75)	2.2 (0.8)	0.92 (0.02)	2.2 (0.8)	452 (50)
	present	0.05	5.3 (0.7)	161 (70)	2.3 (0.7)	0.89 (0.01)	1.8 (0.3)	
M10	absent	0.06	2.1 (0.5)	725(75)	2.8 (0.6)	0.90 (0.05)	1.2 (0.1)	619 (30)
	present	0.05	1.6 (0.5)	106 (45)	3.2 (2.5)	0.93 (0.04)	1.3 (0.1)	
M11	absent	0.01	1.7 (0.4)	925 (120)	2.2 (0.3)	0.93 (0.02)	1.8 (0.2)	488 (130)
	present	0.02	1.8 (0.4)	437 (15)	2.2 (0.6)	0.94 (0.02)	1.6 (0.1)	
M12	absent	0.03	2.0 (0.3)	1102 (310)	1.9 (0.5)	0.94 (0.03)	1.8 (0.1)	793 (150)
	present	0.02	2.0 (0.3)	309 (190)	2.1 (0.3)	0.93 (0.02)	1.7 (0.1)	
M13	absent	0.05	4.2 (2.9)	821 (35)	3.4 (1.8)	0.91 (0.02)	1.7 (0.5)	713 (60)
	present	0.05	2.8 (2.2)	108 (35)	2.3 (0.7)	0.92 (0.03)	1.4 (0.2)	
M14	absent	0.01	2.7 (1.7)	702 (80)	2.2 (1.7)	0.91 (0.02)	1.7 (0.7)	594 (95)
	present	0.01	1.3 (0.5)	108 (25)	1.7 (0.5)	0.89 (0.04)	1.9 (0.3)	
M15	absent	0.01	3.2 (1.6)	578 (150)	2.5 (1.1)	0.91 (0.06)	2.4 (1.2)	548 (80)
	present	0.02	1.7 (0.3)	120 (80)	2.6 (1.5)	0.89 (0.05)	1.6 (0.3)	
M16	absent	0.01	1.9 (0.3)	606 (90)	2.3 (0.8)	0.90 (0.02)	1.8 (0.3)	375 (80)
	present	0.01	2.1 (0.4)	231 (40)	1.3 (0.9)	0.91 (0.03)	1.7 (0.5)	
M17	absent	0.02	1.8 (0.2)	845 (165)	2.5 (1.2)	0.95 (0.04)	2.1 (0.6)	429 (60)
	present	0.01	2.2 (0.3)	416 (125)	2.7 (0.7)	0.92 (0.04)	1.9 (0.8)	

Table 2. Continued.

	Zn present/absent	R_s $\Omega \cdot cm^2$	C_{dl} $\mu F \cdot cm^{-2}$	R_{ct} $\Omega \cdot cm^2$	CPE $(Yo) \times 10^{-6}$	n	R_x $\Omega \cdot cm^2$	ΔR_{ct} $\Omega \cdot cm^2$
M18	absent	0.01	2.3 (0.1)	772 (130)	2.3 (1.1)	0.93 (0.05)	2.3 (1.1)	387 (90)
	present	0.01	1.9 (0.1)	385 (65)	2.1 (1.7)	0.91 (0.04)	2.2 (1.0)	
M19	absent	0.09	3.1 (1.1)	454 (70)	2.2 (1.1)	0.90 (0.03)	3.7 (1.9)	301 (70)
	present	0.10	2.8 (1.1)	153 (25)	2.5 (0.6)	0.89 (0.04)	3.9 (3.1)	
M20	absent	0.07	3.3 (0.9)	560 (125)	3.2 (1.0)	0.91 (0.02)	2.5 (1.4)	334 (100)
	present	0.07	3.0 (1.2)	226 (80)	2.1 (0.6)	0.91 (0.03)	1.6 (1.2)	
M21	absent	0.02	2.9 (1.1)	758 (95)	1.9 (0.4)	0.92 (0.05)	1.8 (0.9)	541 (120)
	present	0.03	2.7 (0.9)	217 (60)	1.8 (0.2)	0.91 (0.03)	2.1 (0.5)	
M22	absent	0.03	3.7 (2.3)	968 (140)	1.7(0.5)	0.90 (0.04)	3.6 (1.5)	745 (170)
	present	0.01	4.6 (1.3)	223 (80)	2.8 (3.5)	0.89 (0.25)	3.5 (2.1)	
M23	absent	0.03	2.5 (0.7)	975 (215)	3.6 (1.6)	0.94 (0.04)	4.3 (2.5)	764 (145)
	present	0.04	1.8 (0.7)	211 (100)	2.7 (1.7)	0.91 (0.04)	4.1 (1.9)	
M24	absent	0.01	3.3 (2.7)	840 (130)	2.6 (0.9)	0.95 (0.1)	4.2 (1.9)	632 (120)
	present	0.03	3.5 (1.8)	208 (65)	3.4 (3.5)	0.91 (0.07)	3.7 (1.9)	
M25	absent	0.01	2.6(0.6)	1024 (140)	1.8 (1.0)	0.93 (0.02)	4.7 (1.1)	714 (155)
	present	0.01	4.6 (0.1)	310 (85)	3.8 (0.8)	0.91 (0.15)	3.9 (0.5)	

The solution resistance, R_s, remains constant at 0.01-0.05 $\Omega \cdot cm^2$ for both before and after Zn^{2+} addition, as would expected for measurements under identical conditions of electrolyte concentration and temperature. Moreover, the distance between the Pt counter electrode and the gold electrode was kept approximately constant in order to minimize variations in the solution resistance R_s. There are minor variations in the C_{dl} values among the ds-DNA films. This irregular change was in the order of the measuring error. Since the exponential modifier, n, is greater than 0.9, the CPE can be considered as a capacitor according to the previous report.[1] The charge transfer resistance, R_{ct}, was found to decrease significantly once the metal ion is added. The values of R_x are similar for almost all of the ds-DNA films before addition of Zn^{2+}. This indicates that the number and size of the assumed pinholes are almost same in all of the films. However, a slight but random decrease in R_x was observed in most of the films after addition of Zn^{2+}.

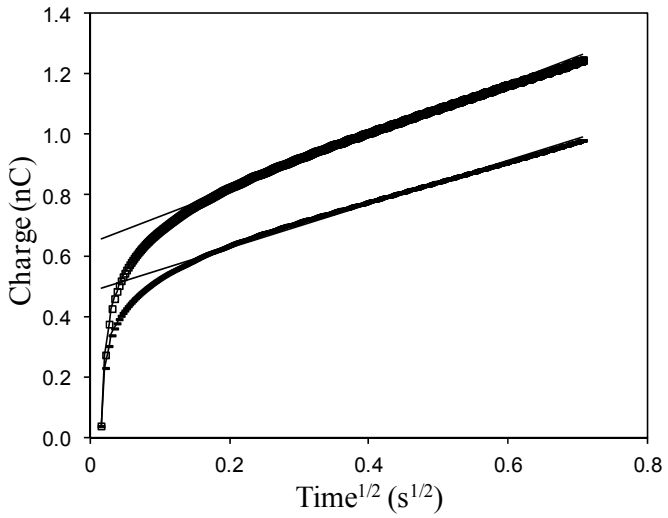

Figure S1. Typical chronocoulometric curves for ds-DNA modified electrode in the absence of (-) and presence of (□) RuHex. The lines are the fits to the data to determine the intercepts at $t = 0$. The intercepts of the plot of charge (Q) versus $t^{1/2}$ was the measured value of charges on the modified electrodes.

Chronocoulometric measurements were performed on DNA modified electrodes in 10 mM Tris in absence and presence of 5 μM $Ru(NH_3)_6^{3+}$. Regression lines show the value of charge on Y-axis in absence and presence of $Ru(NH_3)_6^{3+}$.

The total charge passing through the electrode is given by the integrated Cottrell equation[1]:

$$Q = 2nFAC(D/\pi)T^{1/2} + Q_{dl} + nFA\Gamma_{Ru} \qquad (1)$$

where n is the number of electrons per molecule for reduction, F the Faraday constant (96500 C/mol), A the electrode area (cm^2), D the diffusion coefficient ($cm^2 \cdot s^{-1}$), C the bulk concentration ($mol \cdot cm^{-3}$), Q_{dl} the capacitive charge (C), and $nFA\Gamma_{Ru}$ the charge from the reduction of Γ_{Ru} ($mol \cdot cm^{-2}$). The Chronocoulometry intercept of the Q *vs.* $T^{1/2}$ plot at t = 0 represents the sum of the charges of double-layer capacitance and the surface-confined species, $[Ru(NH_3)_6]^{3+}$ in this

[1] Electrochemical Methods: Fundamentals and Applications, ed. By A.J. Bard, L.R. Faulkner, (Wiley, New York, 2001)

case. By subtracting the capacitive charge (intercept at $T = 0$ in the absence of redox cation), the total charge of surface-confined $[Ru(NH_3)_6]^{3+}$ were evaluated using following formulae.

$$Q_{sum} = Q_{dl} + nFA\Gamma_{Ru} \quad (2)$$

and

$$\Gamma_{Ru} = (Q_{sum} - Q_{dl}) / nFA \quad (3)$$

where Γ_{Ru} is surface density of surface-confined $[Ru(NH_3)_6]^{3+}$ and Q_{sum} is a sum of charges. Then, surface coverage of the DNA was evaluated by following formula.

$$\Gamma_{DNA} = \Gamma_{Ru} (z/m) N_A \quad (3)$$

where Γ_{DNA} is the DNA surface density in molecules·cm^{-2}, m is the number of nucleotides in the probe DNA, z is the charge of the redox molecule, and N_A is Avogadro's number.

1. S. E. Creager, T. T. Wooster, *Anal.Chem.*, 1998, **70**, 4257-4263.