

Supporting Information

Selective Electrodeposition of inorganic ions/DNA multilayer film for tunable DNA release

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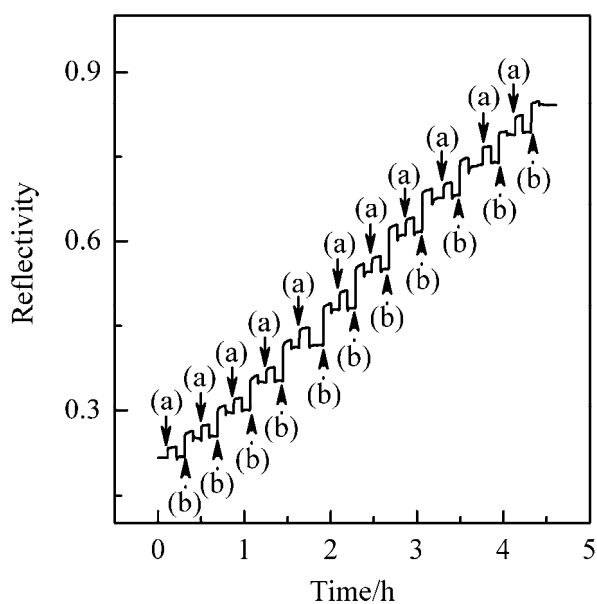


Fig. S1 In situ SPR R-t mode monitoring the construction of $(\text{Zr}^{4+}/\text{DNA})_{11}$ LbL films. SPR angle was fixed at 62° and kept unchanged. During the preparation of the LbL film, the film was rinsed in the water between the alternated assemblies of Zr^{4+} (a) and DNA (b) on MUA modified SPR gold thin film.

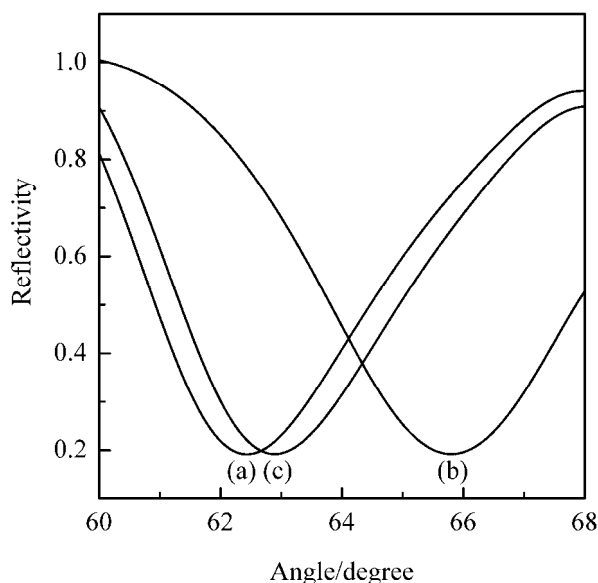


Fig. S2 In situ scanning SPR curves of the $(\text{Zr}^{4+}/\text{DNA})_{11}$ films before (b) and after (c) the selective electrodisassembly on the MUA modified SPR gold thin film (a). All curves were recorded in pure water after washing.

Figure S2 shows the scanning SPR spectra of the MUA-modified, negatively charged gold thin film, curve a, after assembly of $(\text{Zr}^{4+}/\text{DNA})_{11}$ LbL film, curve b, and after complete electrodisassembly for 2 h, curve c. After formation of $(\text{Zr}^{4+}/\text{DNA})_{11}$ LbL film, the reflectance minimum is right-shifted by ca. 3.36° in comparison to the basal surface. Upon electrochemical disassembly of the films, the reflectance minimum is left-shift by 2.92° , indicating that 86.9% of the original film has been released from the surface. This is consistent with SPR R-t mode measurement.

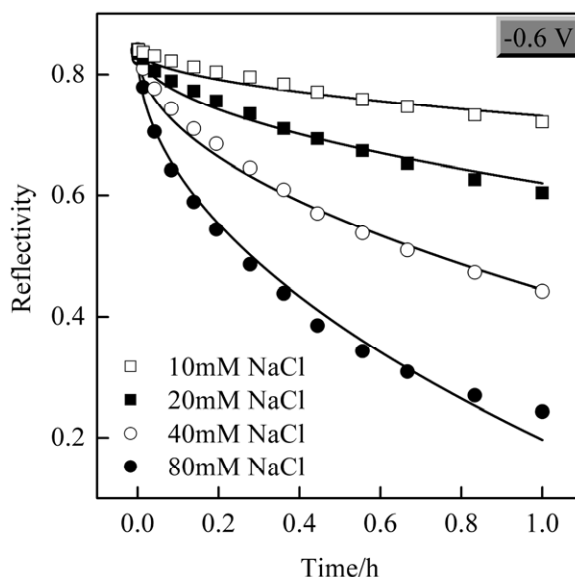


Fig. S3 In situ SPR R–t monitoring DNA release kinetics from $(\text{Zr}^{4+}/\text{DNA})_{11}$ film by the application of electric potential (-0.6 V vs Ag/AgCl) in 10 (\square), 20 (\blacksquare), 40 (\circ), and 80 mM (\bullet) sodium chloride solution (pH 7.0). Only several points of SPR R–t monitoring curve are shown in this figure. A mathematical fitting of the disassembly curve is drawn as a solid line. The fixed angle is 62° and the angle position holds unchanged. A relative reflectivity of 100% represents the existence of original $(\text{Zr}^{4+}/\text{DNA})_{11}$ film, while 0% designates the SPR gold thin films.

Table 1. Parameters of the mathematical fitting that was used to fit the disassembly profiles (measured by SPR) of the $\text{Zr}^{4+}/\text{DNA}$ multilayer film shown in **Figure S3**.¹

Concentration of NaCl [mM]	Mathematical fitting parameters	
	$R=R_0-R_s t^{1/2}$, $R_s=2k\pi^{1/2}D_z^{1/2}\Delta R_z^*$	
	$100\times R_0$	$100\times R_s$
10	84.2	0.194
20	84.2	0.389
40	84.2	0.698
80	84.2	1.14

¹ The coefficient of determination (R^2) was higher than 0.95 for all fitted curves.

The mathematical fitting the electrodisassembly kinetics of DNA-containing multilayer films was based on the following deduction:

Assuming that the disassembly rate is proportional to the concentration of Zr^{4+} (degree of the disrupted films electroneutrality) at the electrode surface, the time differential of SPR reflectance ($\partial R/\partial t$, a symbol of the disassembly rate) can be correlated with the concentration of surface-confined Zr^{4+} , as shown by eq 1,

$$\frac{\partial R}{\partial t} = -kC_z(t) \frac{\Delta R_z^*}{C_z^*} \dots\dots\dots (1)$$

where k is a positive constant, $C_z(t)$ is the concentration of Zr^{4+} at the electrode surface at time t , C_z^* is the bulk concentration of Zr^{4+} and ΔR_z^* is the SPR reflectance variation of the multilayer films. As a constant, $\Delta R_z^*/C_z^*$ is also used to simplify k and the following deduction.

According to Cottrell equation¹ (eq 2),

$$C_z(t) = \frac{i(t)}{nFA} = \frac{D_z^{1/2} C_z^*}{\pi^{1/2} t^{1/2}} \dots\dots\dots (2)$$

where D_z is the diffusion coefficient of Zr^{4+} . The depletion of Zr^{4+} near the surface shows an inverse $t^{1/2}$ function in potential-step experiments under diffusion control. It is a mark of diffusive control over the rate of electrolysis.²⁻⁴ Combining this result and eq 1, then we have

$$\frac{\partial R}{\partial t} = -k \frac{D_z^{1/2} \Delta R_z^*}{\pi^{1/2} t^{1/2}} \dots\dots\dots (3)$$

Thus,

$$R = R_0 - 2k\pi^{-1/2} D_z^{1/2} \Delta R_z^* t^{1/2} = R_0 - R_s \sqrt{t} \dots\dots\dots (4)$$

$$R_s = 2k\pi^{-1/2} D_z^{1/2} \Delta R_z^* \dots\dots\dots (5)$$

where R_0 and R_s are constants. As is clearly shown in eq 5, R_s is proportional to the diffusion coefficient of Zr^{4+} (D_z).

It must be note that the above deduced equation was based on two assumptions: one is the disassembly rate is proportional to the concentration of Zr^{4+} at the electrode surface. The other is the diffuse layer thickness of the electroactive species is far thicker than that of the electroactive species-containing films.⁵ During the selective electrodisassembly, the Zr^{4+} /DNA multilayer film is not steady and the distribution of Zr^{4+} is more complex. So the proposed equation can only provide a

semiquantitative analysis of the diffusion coefficient of Zr^{4+} (D_z). In addition, SPR reflectance (R) should have an inverse $t^{1/2}$ function in the present mathematical fitting procedure while the experimental SPR reflectance shows an exponential-like decay with time. It is appropriate to fit the experimental SPR reflectance curves at a short time at the beginning of electrodisassembly.

Then we carried out mathematical fitting of the disassembly curves by using the above deduced equation. As shown in **Fig. 3S** and **Table 1**, R_s is increasing with the concentration of NaCl. As the diffusion coefficient of Zr^{4+} (D_z) is proportional to R_s , it is demonstrated that the ion diffusion coefficient value increased in high concentration of sodium chloride electrolyte. In other words, the electrochemical accumulation rate of Zr^{4+} to gold thin film could be faster when the multilayer film was immersed in high concentrations of sodium chloride.

Reference

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