Electronic Supplementary Material (ESI) for Analytical Methods.

Determination of the surface coverage at the biosensor surface

The surface coverage of the modified electrodes were quantitatively measured by a previously reported procedure [43]. In this procedure, the electrostatic binding of the cationic redox active $[Ru(NH_3)_6]^{3+}$ to the anionic DNA backbone was used to quantify the amount of probe DNA on the electrode by measuring the charge passed during the reduction of $[Ru(NH_3)_6]^{3+}$ using chronocoulometry, first proposed by Tarlov and co-workers. It can be easily calculated from the following equations:

$$\Gamma_{DNA} = \Gamma_0 (z/m) (N_A) \quad (1)$$

$$\Gamma_0 = Q/(nFA) \quad (2)$$

where Γ_0 is the surface density of $[Ru(NH_3)_6]^{3+}$ (mol cm^{-2}), Γ_{DNA} is the surface density of DNA (mol cm^{-2}), n is the number of electrons in the reaction, A is the area of the working electrode (cm^2), m is the number of nucleotides in the DNA, z is the charge of the redox molecule, F is Faraday constant (C mol^{-1}), and N_A is Avogadro's number. Q is the charge which can be obtained either by integrating the redox peaks in the cyclic voltammograms or by calculating the chronocoulometric intercept at t = 0. The surface densities of probe DNA at the modified electrodes were obtained from the chronocoulometric curves of 100 mmol L^{-1} $[Ru(NH_3)_6]^{3+}$ in 10 mmol L^{-1} phosphate buffer solution with pH 7.0 (Figure 1).

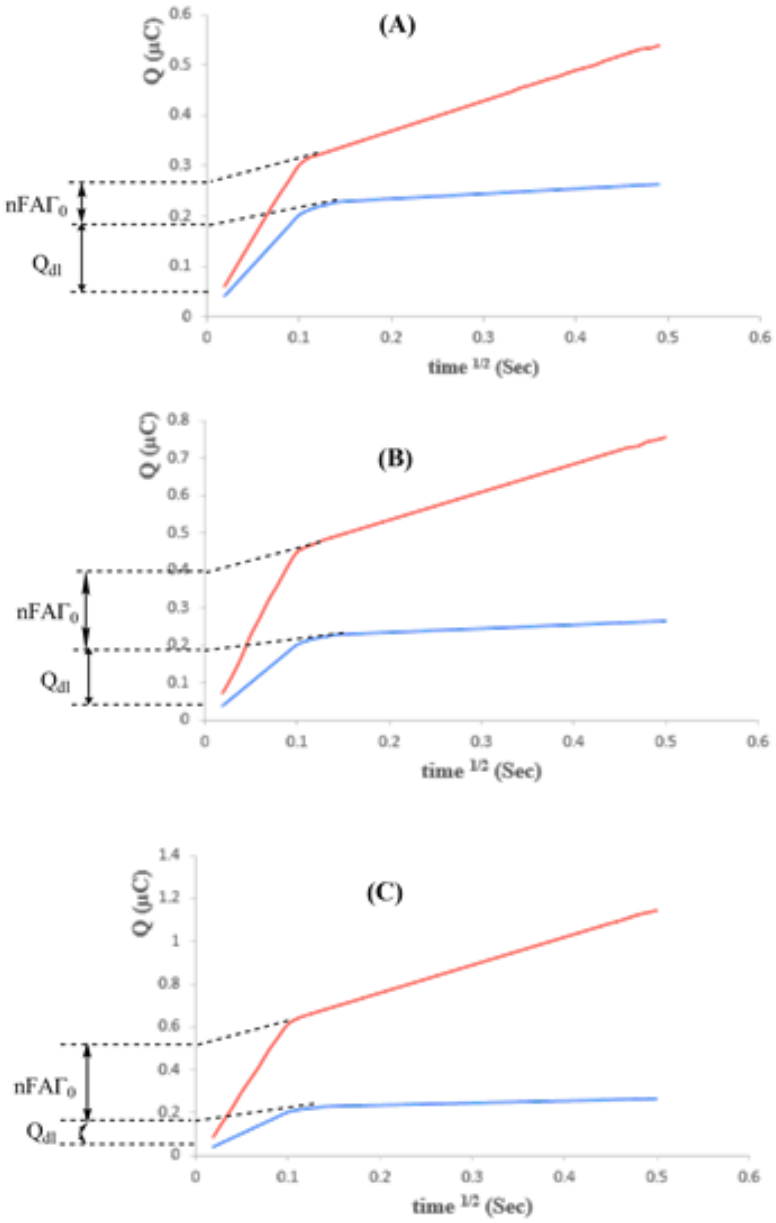

Figure 1. Chronocoulometric curves in the absence (lower curves) and presence (upper curves) of 100 mmol L^{-1} $[Ru(NH_3)_6]^{3+}$ in 10 mmol L^{-1} phosphate buffer solution (pH 7.0) for electrodes modified with different surface densities of probe DNA. The probe concentrations were 0.01 (A), 1 (B), and 5 (C) µmol L^{-1}. The dashed lines represent the linear fit to the data for determination of the intercept at t = 0.