Spectral and electrochemical characterization of Immobilization of DNA onto the self-assembling polyelectrolyte film on the gold surface

J.Z. Zhou, L.L. Wu, L.Q. Dong, Z.Y. Lin, J.W. Yan, Z.H. Lin
State key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, Institute of Physical Chemistry, Xiamen University, Xiamen 361005, CHINA

In this work, the characterization of the DNA immobilization onto the gold surface via self-assembling adlayer of cationic polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA), is presented using spectra of Diffuse Reflectance FT-IR and X-ray Photoelectron and voltammograms of the transition metal chelate $[Co(phen)_3]^{3+/2+}$

Diffuse Reflectance FT-IR spectra of dsDNA/PDDA and ssDNA/PDDA films are shown in Fig. 1. The bands at 1240 cm-1 and 1084 cm-1 are assigned to the anti-symmetric and symmetric stretching vibrations of phosphate, respectively. The band at 1666 cm-1 results from double bond stretching vibrations of DNA bases. The IR spectra of dsDNA/PDDA and ssDNA/PDDA are similar. The P2p XPS spectra of P of dsDNA/PDDA, ssDNA/PDDA and PDDA films in Fig. 2 show that there are a lot of P on PDDA modified by dsDNA and ssDNA, while no P is found on PDDA films. The cyclic voltammograms of $[Co(phen)_3]^{3+/2+}$ at dsDNA/PDDA, DNA/PDDA and PDDA electrodes are shown in Fig. 3. The peak current Ipa attributed to $[Co(phen)_3]^{3+/2+}$ oxidation at dsDNA/PDDA/Au electrode is proportional to the sweep rate υ (as shown in Fig. 4), which is characteristic of a surface process. Whereas at ssDNA/PDDA/Au electrode plots of both Ipa ~ υ and Ipa~ υ 1/2 are not linear fit, indicating that it's a composite process including surface process and diffusion process. The difference of peak current and potentials of $[Co(phen)_3]^{3+/2+}$ redox at ssDNA/PDDA and dsDNA/PDDA also indicates different interactions of dsDNA and ssDNA with $[Co(phen)_3]^{3+/2+}$. As a result, the different signal of current of $[Co(phen)_3]^{3+/2+}$ redox at specified potential at the PDDA/DNA self-assembled electrodes can be used to label the hybridization of DNA.

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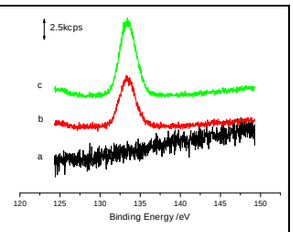

Fig.1 Diffuse Reflectance Infrared spectra of (a) dsDNA/PDDA/Au (b) ssDNA-PDDA/Au

Fig. 2 P2p XPS spectra of (a) PDDA/Au (b) dsDNA/PDDA/Au (c) ssDNA/PDDA/Au

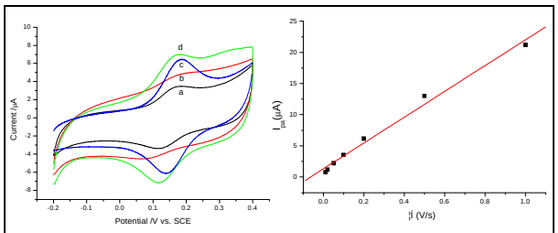

Fig. 3. Cyclic voltammograms of [Co(phen)3]3+/2+ (50μM) at (a) bare Au electrode (b)PDDA/Au (c) ssDNA/PDDA/ Au (d) dsDNA/PDDA/ Au, 5mM pH 7.3 Tris-HCl buffer containing 50mM NaCl, scan rate:100mV/s

Fig. 4 Plot of Ipa~ υ of $[Co(phen)_3]^{2+}$ oxidation at dsDNA/PDDA/Au, solid line is linear fits, R=0.9945