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Influence of Polyelectrolyte on the Electrochemical Response of Single-Walled Carbon Nanotubes-Modified Electrodes for Biosensing

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Abstract – Nanotechnological concepts have fostered the development of highly efficient biosensors. For example, sensitivity and selectivity of enzymatic biosensors can be improved upon using nanomaterials, viz., nanoparticles and nanotubes, in conjunction with immobilized enzymes [1-3]. In this study we investigate the influence of the three types of polyelectrolytes employed in conjunction with single walled carbon nanotubes (SWCNT) in LbL films on the electrochemical properties of modified electrodes. Different film architectures have been investigated as templates for enzyme immobilization.

Three types of polyelectrolytes including chitosan, polyamidoamine G4 dendrimer (PAMAM) and polyaniline (PANI) were employed as cationic building blocks for layer-by-layer (LbL) film fabrication in conjunction with SWCNTs. Chitosan (DG = 14 and MW = 73,000 g mol⁻¹) from Polymar do Brasil, was used at concentration of 0.5 mgmL⁻¹. The PAMAM and PANI solutions were prepared at concentrations of 1.0 mgmL⁻¹ and 0.5 mgmL⁻¹, respectively. The polyanionic solutions of poly(styrene sulfonate) (PSS) (Aldrich) and SWCNTS-COOH (Aldrich) were prepared at a concentration of 1.0 mgmL⁻¹. The pH of all solutions employed was set at 4.0. LbL films of polycations alternated with PSS or SWCNTs were obtained via alternate immersion of a substrate (quartz, glass and ITO-covered glass plates) in the polycationic and polyanionic solutions for 5 min. Film growth was monitored by UV-VIS absorption spectroscopy upon collecting the UV-Vis spectra after deposition of each bilayer. Electrochemical measurements were performed in an 283 EG&G PARC potentiostat/galvanostat with modified ITO as working electrode, Pt plate as the auxiliary electrode and all potentials given with reference to an Ag/AgCl electrode. Cyclic voltammograms (CVs) were performed by using a phosphate buffer solution (pH=7.0) at 23°C.

The electrochemical response of the LbL films containing PSS or SWCNTs as polyanions are shown in figures 1A and 1B, respectively. As it can be observed, the presence SWCNTS-COOH improved the electrochemical response of the modified electrodes, displaying the characteristic semi-reversible redox peaks of the polyelectrolyte/SWCNT with an increasing oxidation/reduction current observed in the sequence: PANI>CH>PAMAM (peak cathodic potentials (E_{pc}) ranging from 100 to 190 mV).

Structural characterization of the modified electrodes was carried out via micro-Raman spectroscopy upon using a 633 nm laser line and the spectra are shown in figure 2. Raman peaks from SWCNTs D and G bands are present in all spectra. In addition, occurrence of specific interactions between SWCNTs and the polyelectrolytes may be inferred only for PANI/SWCNTs films, mostly due to the changes in the D band of the nanotubes, which shifted from 1332 cm⁻¹ (in the SWCNTs cast film) to 1217 cm⁻¹ in the PANI/SWCNTs films. The well defined electroactivity of the films, as well as the fine control over film thickness and architecture allow the use SWCNTs incorporating LbL films in sensing.

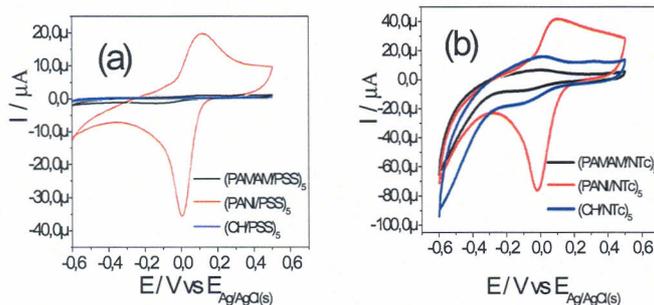


Figure 1: Cyclic voltammograms for LbL films containing PSS (a), and single walled carbon nanotubes (b) as polyanions.

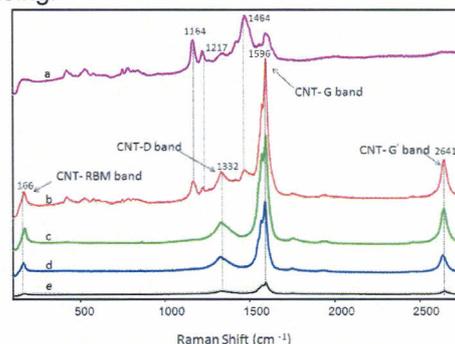


Figure 2: Raman spectra from films of PANI-cast (a), (PANI/SWNT)₅ (b), SWNT-cast (c), (Chitosan/SWNT)₅ (d), and (PAMAM/SWNT)₅ (e).

References

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