

## Immobilization of Carbon Nanotubes, Cobalt phthalocyanine and Chitosan in Layer-by-Layer Films: A Strategy for Constitutional Dynamic Chemistry Study

R. A. S. Luz<sup>(1)</sup>, M. V. A. Martins<sup>(1)</sup>, J. R. Siqueira Jr.<sup>(2)</sup>, V. Zucolotto<sup>(2)</sup>, O. N. Oliveira Jr.<sup>(2)</sup>, F. N. Crespilho<sup>(3)</sup> and W. C. Silva<sup>(1)\*</sup>

(1) DQ, CCN, Universidade Federal do Piauí, Teresina, PI, Brazil.

(2) IFSC, Universidade de São Paulo, São Carlos, SP, Brazil.

(3) CCNH, Universidade Federal do ABC, Santo André, SP, Brazil

\* welter@ufpi.edu.br.

**Abstract** – This work describes a strategy to explore constitutional dynamic chemistry concepts, where films layer-by-layer nanostructured containing carbon nanotubes, cobalt phthalocyanine and chitosan were utilized. The deposition of thin films for both systems (with and without carbon nanotubes) through quartz crystal microbalance mass measures showed similar behavior, however films containing carbon nanotubes, anchored onto polymeric chitosan matrix, exhibited an increase of the faradaic current probably associated to the interaction between carbon nanotubes and cobalt phthalocyanine at supramolecular level.

Recently [1], we evidence the constitutional dynamic chemistry (CDC) in layer-by-layer (LbL) nanostructured films through interaction between gold nanoparticles (AuNP) and nickel phthalocyanine at supramolecular level. According Lehn [2], the CDC approach allows to control news physic and chemistry properties of hybrid nanostructured systems. In this work cobalt (II) tetrasulfonated phthalocyanine (CoTsPc), chitosan (Ch) and single-walled carbon nanotubes (SWCNT) were utilized to assembly (Ch/CoTsPc)<sub>n</sub> and (Ch-SWCNT/CoTsPc)<sub>n</sub> systems through layer-by-layer approach, where n = number of bilayers. The deposition of the Ch/CoTsPc and Ch-SWCNT/CoTsPc was confirmed by quartz crystal microbalance and voltammetry techniques (Figure 1). The quartz crystal microbalance measures mass for LbL films suggest a similar behavior for material deposition (Figure 1c). The cyclic voltammograms for both systems in physiological medium (NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>PO<sub>4</sub> - PBS, 0.1 mol L<sup>-1</sup> pH 6.8) exhibited well defined one redox process with  $E_{1/2}$  value at -0.65 V (vs SCE) attributed to the [CoTsPc(I)]<sup>5-</sup>/[CoTsPc(II)]<sup>4-</sup>. Moreover, one irreversible oxidation process of CoTsPc(II) to CoTsPc(III) at 0.80 V was observed for Ch/CoTsPc and Ch-SWCNT/CoTsPc systems. For voltammograms of (Ch-SWCNT/CoTsPc)<sub>5</sub> film, which contain SWCNT anchored onto polymeric chitosan matrix, were observed an increase of the faradaic current, probably associated to the supramolecular charge transfer interaction between cobalt phthalocyanine and SWCNT. The electrodes modifieds ITO-(Ch/CoTsPc)<sub>5</sub> and ITO-(Ch-SWCNT/CoTsPc)<sub>5</sub> also showed high electrochemical stability when the cyclic voltammogram was obtained at 20 cycles. The results clearly demonstrate that cited systems can be employed in electrocatalytic test utilizing biological molecules as ibuprofen, H<sub>2</sub>O<sub>2</sub> and cystein.

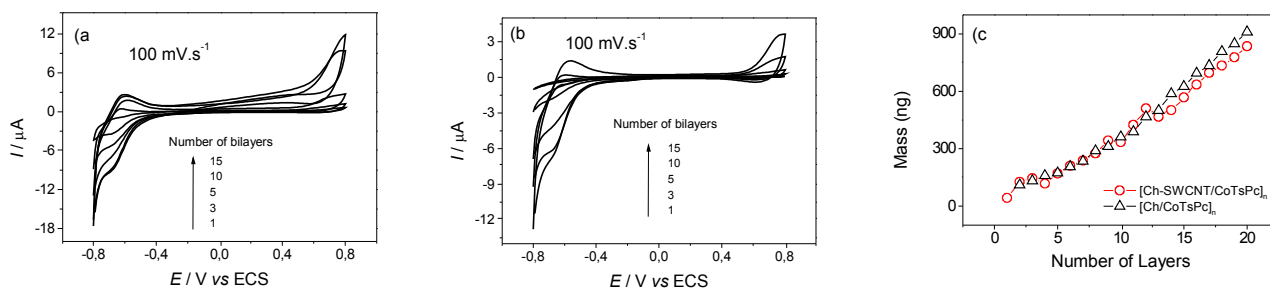


Figure 1. Cyclic voltammograms for: (a) (Ch-SWCNT/CoTsPc) and b) (Ch/CoTsPc) with different number of bilayers. c) Quartz crystal microbalance measures for both systems. Electrolyte: PBS solution 0.1 mol L<sup>-1</sup>, μ = 0.1 mol L<sup>-1</sup>, pH 6.8, T = 25 °C.

### References

- [1] W. S. Alencar, F. N. Crespilho, M. V. A. Martins, V. Zucolotto, O. N. Oliveira Jr., W. C. Silva, Phys. Chem. Chem. Phys. (2009), no prelo, DOI: 10.1039/b821915j  
[2] J. M. Lehn, Chem. Soc. Rev. **36**, 151 (2007).