

# Bifunctional electroactive nanostructured membranes

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## Abstract

The advent of techniques based upon the spontaneous assembly of different materials with control over molecular architecture has afforded the fabrication of composite thin films for many nanotechnological applications. The layer-by-layer technique (LbL), in particular, has largely been used in the molecular level processing of nanohybrid systems in the form of multilayers, owing to its low cost and experimental simplicity. In this study we describe the fabrication of a novel, bifunctional film containing platinum nanoparticles/polyamidoamine (PAMAM) dendrimers. Pt nanoparticles were chemically synthesized/stabilized in the presence of PAMAM dendrimers and incorporated in LbL films in conjunction with nickel tetrasulfonated phthalocyanine (NiTsPc). A metallophthalocyanine was chosen because of its well-defined redox activity. Indium tin oxide (ITO)-covered glass plates were used as substrates for film deposition. The nanocomposites displayed high electrocatalytic activity toward dopamine and hydrogen peroxide molecules, two compounds with dissimilar chemical properties.

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## 1. Introduction

The search for new materials with tailored properties has been at the heart of nanoscience and nanotechnology [1–16]. For nanostructured films, in particular, the layer-by-layer [1–4] (LbL) technique is now widely used due to the possible control of film architecture at the molecular level, in which synergy between distinct materials may be achieved [5–18]. We proposed recently a new concept to prepare electroactive nanostructured membranes (ENMs) with high electrochemical performance [13,16,18]. These membranes were obtained by supramolecular manipulation of metallic nanoparticles encapsulated within polyamidoamine dendrimers (PAMAM), using the procedures developed by Crooks and collaborators [19,20], which were assembled in LbL films onto conducting substrates. The latter could be employed as working electrodes in metha-

nol-tolerant cathodes for direct-methanol fuel cells [18], biosensing [13], sensing and catalysis [16]. PAMAM is particularly advantageous as a template material for nanoparticle growth [18], functioning as a nanoreactor with effective nanoparticle stabilization [18–21]. Further advantages of PAMAM include high density of active groups to form LbL films with polycationic compounds, good structural homogeneity, internal porosity and biocompatibility [16].

In this communication we describe the fabrication of a novel, bifunctional ENM (Bi-ENM), which displayed high electrocatalytic activity toward dopamine and hydrogen peroxide molecules, two compounds with dissimilar chemical properties. Within the same ENM, layers of nickel tetrasulfonated phthalocyanine (NiTsPc) and PAMAM incorporating platinum nanoparticles (PAMAM-Pt) were adsorbed onto ITO substrates (indium tin oxide). The choice of a metallophthalocyanine as building block of the LbL films was based on its well-defined redox activity [22].

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## 2. Experimental

### 2.1. Reagents and solutions

Ni(II)TsPc, G4 PAMAM dendrimer and chloroplatinic acid hydrate ( $\text{H}_2\text{PtCl}_6$ ) were purchased from Aldrich Co. and used without further purification. The aqueous solutions of NiTsPc and PAMAM were used at a concentration of  $0.5 \text{ g L}^{-1}$  and  $1.0 \text{ g L}^{-1}$ , respectively. Both solutions were prepared at pH 4 and room temperature. The PAMAM-Pt solution with Pt 20 wt% was prepared by adding  $53 \mu\text{L}$  of  $\text{H}_2\text{PtCl}_6$  and 2.7 mL of formic acid in 5 mL of PAMAM solution under stirring in the dark during 7 h.

### 2.2. LbL film fabrication

LbL films were fabricated by immersing the substrates alternately into the polycationic PAMAM or PAMAM-Pt and anionic NiTsPc solutions for 5 min. After deposition of each layer, the films were rinsed in a washing solution at pH 4, and dried under a  $\text{N}_2$  flow. Scheme 1 shows the idealized architecture of a PAMAM-Pt/NiTsPc LbL film.

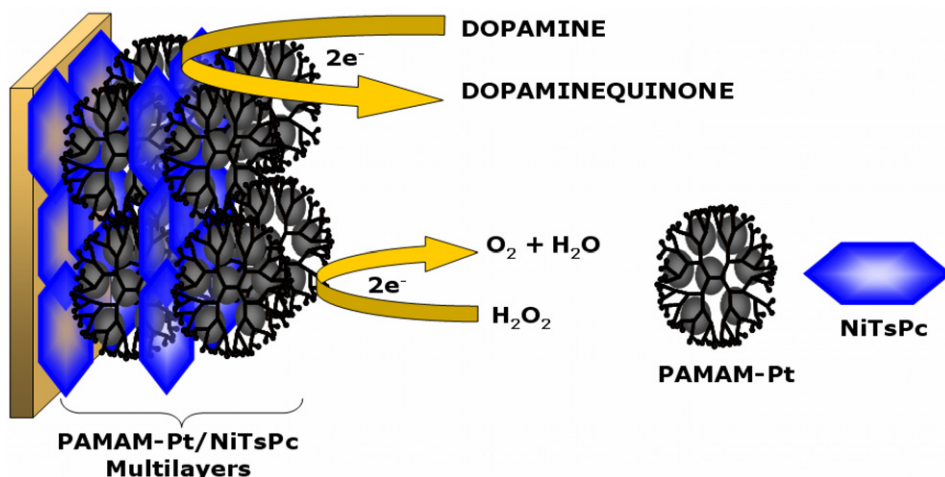
### 2.3. Apparatus

The Pt nanoparticles formed (3 nm) were imaged with a 200 kV transmission electron microscope (TEM) (Philips CM200). The multilayer growth was monitored by measuring the UV–vis spectra after every two bilayers were deposited on a hydrophilic quartz substrate, using a Hitachi U-2001 spectrophotometer. Fourier transform infrared spectroscopy (FTIR) experiments were carried out in LbL films containing 10 bilayers onto silicon substrates in the transmission mode, using a Nicolet 470 Nexus spectrometer. Neat NiTsPc, PAMAM and PAMAM-Pt were analyzed as cast films. The film morphology was studied with 5-bilayer LbL films deposited onto glass substrates, using an atomic force

microscope (AFM) Nanoscope III (Digital Instruments). Cyclic voltammograms were taken with an EG&G PAR M280 potentiostat in LbL films with 2, 5, 7 and 10 bilayers on ITO as working electrode. An Ag/AgCl electrode was used as reference electrode and a  $1.0 \text{ cm}^2$  platinum foil was employed as the counter electrode. The electrochemical measurements were carried out at room temperature using a  $0.1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution as supporting electrolyte. For the electrocatalytic studies, solutions of  $5.0 \times 10^{-3} \text{ mol L}^{-1}$  dopamine (DA) (3-Hydroxytyramine hydrochloride,  $\text{C}_8\text{H}_{11}\text{NO}_2 \cdot \text{HCl}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were used. Before each measurement,  $\text{N}_2$  was bubbled in the electrolytic solution to eliminate dissolved  $\text{O}_2$ .

## 3. Results and discussion

The multilayer growth was monitored by measuring the optical absorption of the Q-band of NiTsPc. For the 20-bilayer LbL films of PAMAM/NiTsPc and PAMAM-Pt/NiTsPc deposited onto quartz substrates, the spectra in Fig. 1a shows the Q-band of NiTsPc due to dimeric species [22] blue shifted to 615 nm from 625 nm for NiTsPc in an aqueous solution. This shift is attributed to the formation of H-aggregates in the films, indicating strong interactions among NiTsPc molecules [15]. The shoulder at 660 nm, associated with monomeric species, only appears in the solution spectrum. Interestingly, the absorbance at 615 nm increased exponentially with the number of bilayers (inset, Fig. 1a), unlike other polyelectrolytes for which the growth was linear [15,17]. The PAMAM/NiTsPc and PAMAM-Pt/NiTsPc films exhibited morphology with low roughness, 4.5 and 5.0 nm, respectively, for a scanned area of  $1.0 \times 1.0 \mu\text{m}$  as shown in Fig. 2. The latter film displayed a globular morphology on the surface, which can be ascribed to the presence of Pt-nanoparticles. This reflects the high degree of organization of the multilayers, which is consequence of the strong interaction via ionic bonds between  $-\text{NH}_3^+$  terminal groups from PAMAM and  $-$



Scheme 1. Idealized representation of the architecture for a PAMAM-Pt/NiTsPc LbL film and schematic representation of reaction of dopamine and hydrogen peroxides at PAMAM-Pt/NiTsPc LbL film modified electrode.

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