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Self-Assembled Redox Polyelectrolyte-Surfactant Complexes: Nanostructure and Electron Transfer Characteristics of Supramolecular Films with Built-In Electroactive Chemical Functions

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ABSTRACT

The mesostructural and electrochemical characterization of a redox-active polyelectrolyte-surfactant complex formed by polyallylamine tagged with an osmium complex and dodecylsulfate is presented. X-ray reflectivity (XRR), grazing-incidence small-angle X-ray scattering (GISAXS), X-ray photoelectron spectroscopy (XPS), contact angle goniometry (CA) and cyclic voltammetry (CV), including the numerical simulation of the voltammetric response, were employed to analyze the structure, stability and the electrochemical response of these supramolecular films. In contrast to redox-active polyelectrolyte multilayers (PEMs), the self-assembled system presented here shows a mesoscopic order yielding a film of layered structure very stable to an aqueous environment where the hydrophilic moieties (amino and sulfate groups) are not exposed to the solution since a contact angle of 95° is observed upon exposure to water. However, the film shows a self-exchange electron transfer mechanism with an apparent diffusion coefficient of 2×10^{-9} cm^2 s^{-1} for a film of 300 nm of thickness. This behavior shows that the film exposed to an aqueous solution undergoes a fast electron transfer process to/from the electrode surface and ions to/from the electrolyte solution.

1. Introduction

Ionic self assembly (ISA) has opened doors to the facile creation of supramolecular materials. This approach offers new strategies for the bottom-up assembly of integrated supramolecular systems displaying concerted functions. This construction strategy was pioneered by Decher assembling layer by layer oppositely charged water-soluble polyelectrolytes generating a polyelectrolyte multilayer system (PEM).[1] The technique has since been used to construct highly ordered three-dimensional, multifunctional, reactive thin films. Polyelectrolyte systems fabricated through PEM are currently incorporating different building blocks sensitive to specific stimuli to obtain responsive films, which have found different application as lens coatings, drug-delivery systems, biosensors, light emitting and nonlinear optical devices, among others.[2]

In particular, electroactive PEMs contain building blocks that can efficiently exchange electrons. They have been applied in fundamental studies,[3–7] sensors,[8,9] microelectronics,[10] photovoltaics,[11–13] biofuel cells[14] and battery design.[15] For all these applications it is necessary to ensure a stable structure that guarantee an efficient charge transport between the redox-sites in the multilayer and the electrode for a certain period of time. The electron transfer mechanism in all the electroactive PEMs investigated up to now can be explained by electron hopping, this transfer mechanism can be described by a diffusive behavior characterized by an apparent electron diffusion coefficient (D_{app}), typically ranging between 10^{-8} to 10^{-12} cm^2 s^{-1}. The PEMs with higher D_{app} corresponds to systems of linearly grown multilayers where the polyelectrolyte interdiffusion plays an important role in the electron hopping process.[7]

An alternative method for the modification of electrode surfaces can be carried out using polyelectrolyte-surfactant complexes. These complexes combine in unique ways the properties of polyelectrolyte with those of low molecular weight amphiphiles. The polyelectrolyte components can provide, for instance, mechanical strength and thermal stability, while the surfactants retain their

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tendency to assemble in layered structures.[16,17] They can be completely dissolved in organic solvent[18] and to be applied as a paint on practically any surface, yielding an spontaneous self-assembled system.[19]

We have recently presented results regarding the formation of self-assembled system using a polyelectrolyte (polyallylamine, PA) containing a polypyridyl osmium complex (OsPA) and a surfactant (sodium dodecylsulfate, SDS). The osmium modified polyelectrolyte in presence of SDS precipitates, generating a product that is readily soluble in DMF. This organic solution applied on graphite or gold substrates forms an extremely stable and resistant film after solvent evaporation, showing a quasi-reversible electrochemical behavior.[20]

In this work our investigation was aimed at characterizing the mesostructural features and the electron transfer mechanism taking place in this redox-active polyelectrolyte-surfactant complex. Also, new surfaces (glassy carbon, ITO and silicon) were explored to show the universality of the construction process. To this end we drew upon a set of techniques including x-ray reflectivity (XRR), grazing-incidence small-angle X-ray scattering (GISAXS), X-ray photoelectron spectroscopy (XPS), contact angle goniometry (CA) and cyclic voltammetry (CV) including the numerical simulation of the voltammetric response. The use of a surfactant instead of a polyelectrolyte as counter ion in the construction of the self-assembled system with a redox-active polyelectrolyte generates a system with a mesoscopic order randomly oriented on the surface electrode where the electron hopping process is taking place with a D_{app} higher than 10^{-9} cm^2 s^{-1} for films of different thickness. The combination of a stable ordered structure with an efficient electron transfer process is a remarkable difference with respect to electroactive PEMs where the interdiffusion of the polyelectrolytes plays a relevant role.[7] Here, the surfactant is able to maintain a tight structure but, at the same time, the redox centers are close enough to efficiently allow the electron transfer process.

2. Experimental

2.1. Reagents and Materials

The synthesis of poly(allylamine) containing a pyridine based osmium complex (OsPA) is described elsewhere,[21] the stoichiometry ratio between of osmium complex and allylamine monomer was: 1:35. All other reagents were analytical grade. Glassy carbon electrodes were from Tokay; ITO electrodes were from Delta technologies and silicon substrates (single side polished, <100>, N-type, P as dopant, resistivity: 560-840 ohm-cm) were supplied by UniversityWafer Inc.

2.2. Polyelectrolyte-surfactant composite material

200 μL of SDS 1% in Milli-Q water were added to a 100 μL of OsPA (0.2 mM). The mixture immediately generated a precipitate (OsPA-DS), which was easily separated by centrifugation. The OsPA-DS complex was analyzed by elemental microanalysis showing a ratio ca. 1:1 between allylamine monomer and dodecylsulfate (N:S ratio).

2.3. Modified electrodes

ITO and glassy carbon were employed as working electrodes. The precipitated complex is dissolved in 250 μL of DMF yielding 3 mM solution in osmium complex. This solution was applied on ITO by spin coating. Glassy carbon electrodes were modified by drop coating.

2.4. Equipment

2.4.1. Electrochemical Measurements

Electrochemical experiments were carried out using a purpose-built potentiostat (TEQ-02) using a three-electrode Teflon electrochemical cell equipped with a platinum mesh counter electrode and an Ag|AgCl reference electrode. Cyclic voltammetry experiments were carried in a 20 mM Tris-HCl buffer (pH = 7.4, 0.1 M KNO_3).

2.4.2. Surface Profilometry

Film thicknesses were determined using a Dektak 150 Stylus Surface Profiler with a stylus of 12.5 μm and an applied force of 29 μN.

2.4.3. Contact Angle Measurements

A KSV Cam200 equipment was used for contact angle measurements. Distilled water was used as liquid probe in all assays.

2.4.4. X-ray reflectometry (XRR) and grazing-incidence small-angle X-ray scattering (GISAXS)

XRR and GISAXS measurements were performed at the D10A-XRD2 line of Laboratório Nacional de Luz Síncrotron (LNLS, Campinas, Brazil). A monochromatic beam of 7709 eV ($\lambda = 1.608$ Å) was used to perform both, XRR and GISAXS, experiments. XPS measurements were performed at D04A-SXS beamline of LNLS, using photon incident energy l = 1840 eV with a 45° detection angle. Quoted binding energies were referenced to the adventitious C 1s emission at 285 eV. Si (100) wafers were used as support substrates and were pretreated before coating. They were rinsed with acetone and dried with argon blowing before coating. Thin polymer films were prepared by spin-coating a 50 μL portion of OsPA-DS dispersion using a commercial spin coater (Laurell WS-400B).

2.5. Numerical model

Finite-element software (Comsol Multiphysics 3.4) was used to simulate the cyclic voltammetry experiments and the concentration profiles. Further details are given in Supplementary information.

3. Results and Discussion

3.1. Mesostructural organization of the polyelectrolyte-surfactant complex

The structure of the film was characterized by specular X-ray reflectivity analysis and grazing incidence small-angle X-ray scattering measurements. They were carried out with synchrotron radiation sources to investigate the mesostructural organization of the OsPA-DS film formed on solid surfaces, Si(100). Fig. 1 shows the X-ray reflectivity data corresponding to the PA-DS thin film as a reference system[19] and the OsPA-DS thin film studied in this work. The presence of sharp Bragg peaks up to the third order indicates highly oriented lamellar structures for both films. From the Bragg peak positions, it can be deduced a lamellar spacing (d) of 3.96 and 4.15 nm for the PA-DS and OsPA-DS systems, respectively. The simplest lamellar nanostructure of a polyelectrolyte–surfactant complex is a microphase-separated model consisting of an ionic phase and a non-ionic phase.[22] The ionic phase contains the polyelectrolyte chains and the ionic head groups of the surfactants, where the non-ionic phase contains the hydrophobic moieties such as alkyl chains (see Fig. 2, left). The repeating unit of the lamellar system presents a thickness values close to those observed in self-assembled systems built by layer by layer deposition; for instance, 5 nm was reported for a layer of poly(vinylsulfonate)-ferrocene