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Film formation, surface character, and relative density for electrochromic PEI/(PSS:PEDOT) multilayered thin films

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Abstract

Thin films of alternating layer composition were constructed from the polyelectrolyte complex PEDOT:PSS and the polycation PEI, using ionic self assembly (ISA). The PEI/PEDOT:PSS system displays a consistent trend in film growth, as evidenced by UV–visible spectroscopy and ellipsometry. We find that the overall density of PEDOT increases with increasing number of layers. The density of PSS during multilayer deposition differs from PEDOT, with a sharp drop in density between the 3rd and 6th bilayers. Combining film deposition estimates with contact angle measurement, we distinguish three regions of growth, separated by the 3rd and 6th layers. We ascertain that a constant level of interpenetration between PEI and PEDOT:PSS is reached by the 6th layer. Results from kinetics experiments and pH variation reveal a local increase in pH for the PEDOT species as it comes into contact with the PEI surface. Electrochemical characterization indicates that our films have an interpenetrated PEDOT network and a relatively hydrophilic surface. We demonstrate that ISA can be used to generate robust thin films, stable over a large pH range, whose coloration and conductivity may be manipulated on a large scale using applied voltage, and may be fine-tuned by changing the pH. The films exhibit electrochromic properties similar to other PEDOT derivatives, with a change in transmittance of 51% for 16 bilayers at 643 nm.

Keywords: Polyelectrolyte; Electrochromic; Self-assembly

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1. Introduction

Conducting polymer thin films have shown great promise in the field of optical electronics, demonstrating applications over a wide range of technologies including light detection [1], microcavity lasing [2], electrochromic display [3], light emitting diodes [4], optical switching [5], and optical computing [6]. Specifically, the ability for many polymeric materials to undergo coupled alterations in optoelectronic properties due to chemical or electrical perturbations of redox state lend to them unique advantages within the field of functional materials engineering [7–9]. Polymeric materials possess substantial tensile strength, may be inexpensively processed, and may retain their optoelectronic stability over a long period of time. Furthermore, many such materials have considerable water solubility, facilitating assembly into multilayered architectures [10,11]. Well known examples of polymers with such diverse function include polyaniline [12], poly(3,4-ethylenedioxythiophene) (PEDOT) [13–16], and poly(*p*-phenylene vinylene) [17,18].

PEDOT has been well studied within the field of conducting polymers over the past decade [19–23]. PEDOT is stable, easily oxidized, and has a structure lacking undesired α,β- and β,β-couplings within the polymer backbone. PEDOT films have a very high conductivity (>200 S/cm) [24], and display switchable optical absorbance when converted from the reduced to the oxidized state. By introducing the water soluble polyelectrolyte poly(styrene sulfonate) (PSS) as a counterion dopant during polymerization, a PEDOT:PSS complex has been

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generated, showing high water solubility. This dual-polymer complex formed a highly stable dispersion in water, with substantial conductivity (∼10 S/cm), high visible light transmissivity, and robust film formation properties [25,26]. Since PEDOT:PSS can switch color (opaqueness) through changes of oxidation potential, polyelectrolyte thin films incorporating PEDOT:PSS show promise for electrochromic and optoelectronic technologies such as flexible displays and smart windows [27,28].

Popular thin film deposition methods for polyelectrolytes include electropolymerization [29], spin-assembly [30–32], ionic self-assembly [33–35] and surface polymerization by chemical means [36]. Ionic self-assembly (ISA) is an ideal technique for the adsorption of electroactive polyelectrolytes, as it allows substantial control over film design and resulting molecular architecture [33,37–40]. A charged substrate is alternately dipped into dilute aqueous solutions of polycation and polyanion, depositing layers with specific thickness and composition. Homogeneous, electronically conductive ISA films have been fabricated, including assembly schemes containing the PEDOT:PSS composite [27,28].

In this work, we assemble thin films in a scheme of alternating charge using a PEDOT:PSS colloidal dispersion (Baytron P) as the polyanion and poly(ethylenimine) (PEI) as the polycation (Fig. 1). The challenge we faced in working with this system is that PEI is insulating and once it was used as a binder between PEDOT:PSS layers, it prevented electrochemical accessibility throughout the films. This presents a serous limitation of using PEDOT:PSS/PEI for the development of optoelectronic devices. A natural solution to this problem is to reduce the thickness of the PEI layer by lower the PEI concentration used for thin film deposition. By doing so, we have demonstrated a way to prepare PEDOT:PSS/PEI thin films with full electrochemical accessibility throughout the films. We can rationalize the above results as interpenetration between layers is responsible for establishing connection between PEDOT:PSS layers. The effects of interpenetration/film formation can be realized through the study of surface character, morphology, and relative layer density. Overall, we have achieved a greater understanding of film deposition using the self-assembly method that would allow further development of functional thin films, not limited to one single material or device.

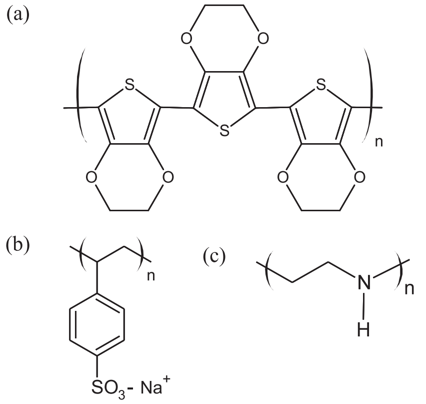

Fig. 1. Molecular structure for (a) PEDOT, (b) PSS, and (c) PEI.

2. Experimental section

2.1. Materials

The branched polycation, poly(ethylenimine) (PEI; average molecular weight 25,000) and the polyanion poly(acrylic acid) (PAA; average molecular weight 90, 000) were purchased from Aldrich and Acros, respectively, and used as received. The polymer composite Baytron P, consisting of 3,4-poly(ethylenedioxythiophene) (PEDOT) and poly(styrenesulfonate) (PSS) was purchased from Starck. PEDOT is partially oxidized to allow complex with PSS, however, the exact oxidation state of DEDOP is unknown. PEI was diluted to 1 mM concentrations using ultrapure distilled water (resistivity ≥ 18 MΩ/cm). The pH value of PEI solution is ∼8.0. The PEDOT:PSS solution was diluted to 50, 5 and 0.5 mM, respectively, using ultrapure water and the pH values 2.5, 3.5 and 4.2, respectively.

2.2. Substrate preparation

Substrates for polyelectrolyte deposition included Fisherfinest glass microscope slides, 2 in. round single-side polished silicon wafers (Silicon Sense, Inc.), 3 in. Fused Silica plates (Sierra Precision Optics), and ITO (indium tin oxide) coated glass slides with 8–12 MΩ/cm resistance (Aldrich). Prior to film formation, fresh substrates were sonicated for 10 min in ethanol or acetone, Ar plasma cleaned (Harrick model PDC-32G.) for 5 min to expose an oxide surface, and stored in ultrapure water.

2.3. Film assembly

Multilayered thin films were constructed by ionic self-assembly (ISA), alternately immersing a substrate in polyelectrolyte solutions of opposite charge for 5 min each. After deposition of each layer, the substrate was washed four times with water. Prior to measurement, substrates were dried with a stream of N_2.

Ex situ deposition kinetics experiments for PEDOT:PSS were performed by immersing the substrate in PEDOT:PSS solution for specified time intervals, and characterizing the thin film after each period of deposition. Prior to investigation of kinetics at a given layer, a number of underlying layers were constructed, also by ISA.