



Characterization of ultrathin electroactive films synthesized via the self-limiting electropolymerization of *o*-methoxyaniline

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ABSTRACT

The electropolymerization of *o*-methoxyaniline under self-limiting deposition conditions yields ultrathin (<20 nm) coatings of an insoluble, low-molecular-weight polymer on planar indium-tin-oxide electrode substrates. The self-limiting nature of the electropolymerization is achieved by using citrate-buffered aqueous electrolytes (pH 4.7) in which the developing polymer that deposits at the electrified interface is neither conductive nor permeable to monomer. Although non-conductive as electrodeposited, the resulting poly(*o*-methoxyaniline) coating becomes electroactive when transferred to acidic aqueous electrolytes. The morphology and chemical structure of the poly(*o*-methoxyaniline) coatings are characterized by surface-sensitive methods including atomic force microscopy, specular-reflectance infrared spectroscopy, X-ray photoelectron spectroscopy, and electrochemistry. Fundamental understanding of the structure/property relationships derived from these investigations on planar substrates will ultimately be applied to three-dimensional electrode nanoarchitectures that incorporate such electroactive coatings for enhanced charge-storage functionality.

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1. Introduction

Electrochemically deposited conjugated polymers [1,2] have been intensively investigated for more than two decades, and have demonstrated promising performance for such varied applications as sensing [3–7], corrosion-protection [8,9], electrocatalysis [10], and energy storage [11–14]. For electrochemical applications where fast kinetics are critical to performance (e.g., for rapid electrocatalytic turnover or high charge-discharge rates), fabricating the desired polymer as a nanoscopic coating on the current collector is essential. The desirable charge-storage and molecular-transport properties of nanoscale forms of polymers can further be exploited when they are incorporated into more complex nanostructured substrates (e.g., aerogels, nanofoams, or nanotube assemblies) to form multifunctional electrode architectures [15–17]. In these systems, the electrochemical interface is projected in three dimensions (3D) to realize technologically relevant energy-storage capacities or electrocatalytic reactivity. For energy-storage applications, distributing the electroactive polymer component as a nanoscale coating on a 3D conductive support should also mitigate the effects of the potential-dependent conductivity that characterizes many

conducting polymers, which may vary over several orders of magnitude as the polymer is cycled between the doped and de-doped states [18].

Electropolymerization provides some degree of control with respect to the morphology, thickness, and conductivity of the polymer coatings that are generated directly on planar electrode substrates, but electrodeposition on non-planar, 3D electrode substrates is complicated by inhomogeneous monomer flux and non-uniform current-potential distributions at the interior electrified interfaces. Self-limiting electrodeposition allows for the extension of electropolymerization methods to porous 3D substrates, and if present, preserves the through-connected pore network inherent to the initial electrode nanoarchitecture throughout the deposition process.

Researchers in the field of amperometric biosensors have previously demonstrated the effectiveness of self-limiting electropolymerization as a simple approach to deposit ultrathin (10–100 nm), electrically insulating polymer films on planar electrodes [19–22] and on 3D substrates, such as reticulated vitreous carbon and carbon nanotube assemblies [23–25]. We have adapted related self-limiting electropolymerization protocols to functionalize ultraporous, electrically conducting manganese oxide [26–28] and carbon [29,30] aerogel substrates with ultrathin (<20 nm) polymer coatings en route to multifunctional electrode structures for batteries and electrochemical capacitors.

The arylamine-based ultrathin polymers that were previously exploited for biosensor applications exhibit a key property for charge-storage functionality—although electrodeposited under

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conditions where the growing polymer film is electrically insulating (typically from monomer solutions with $\text{pH} > 1$), the resulting ultrathin films are readily converted to electroactive forms when transferred to acidic aqueous electrolytes. Self-limiting polymerization of related aniline monomers such as *o*-phenylenediamine [26,31–36] and *o*-aminophenol [21–23,29,30] has been reported, but important aspects of structure and electrochemical properties of relevance for charge-storage applications have not yet been fully addressed.

In this report we describe the electrodeposition of self-limiting, ultrathin poly(*o*-methoxyaniline), POMA, coatings on indium-tin-oxide (ITO) substrates, evaluate the physical and chemical structures of the resulting polymer coatings by such surface-sensitive techniques as specular-reflectance Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM), and examine their electrochemical properties in aqueous electrolytes. The findings of this investigation on planar electrode substrates will ultimately be exploited to design and optimize hybrid electrode nanoarchitectures comprising 3D, porous, electrically conducting carbon substrates with ultrathin, conformal, electroactive polymer coatings.

2. Experimental

2.1. Chemicals

Sulfuric acid (J.T. Baker), hydrochloric acid (Fisher), citric acid (Sigma), sodium citrate (Alpha Aesar), sodium sulfate (Aldrich), potassium ferricyanide (Alpha Aesar), and *o*-phenylenediamine (Aldrich) were used without additional purification. Ortho-methoxyaniline (Aldrich, also denoted as *o*-anisidine) was purified immediately prior to use by passing small aliquots through an activated alumina column. All solutions were prepared with ultrapure water ($>18 \text{ M}\Omega \text{ cm}$) from a Barnstead NANOpure™ water purification system.

2.2. Electrochemical methods

Electrochemical measurements were made in a three-electrode electrochemical cell with a VoltaLab 40 potentiostat/galvanostat (Radiometer Analytical). Indium-tin-oxide-coated (ITO) glass slides (Delta Technologies, Ltd., $7 \text{ mm} \times 50 \text{ mm} \times 0.7 \text{ mm}$, $R_s = 4\text{--}8 \Omega$) were masked with Fluorglas tape to expose a 1-cm^2 electrode area. A Pt mesh counter electrode and Ag/AgCl (Bioanalytical Systems, Inc.) or saturated calomel (SCE, Radiometer Analytical, Inc.) reference electrode were used. All solutions were degassed with N_2 prior to electrochemical measurements and blanketed with the gas during the experiments.

Self-limiting electropolymerization of *o*-methoxyaniline (OMA) and *o*-phenylenediamine at ITO electrodes (POMA-ITO and PPD-ITO) was achieved by cyclic voltammetric (CV) or potential-pulse in 10 mM OMA and 50 mM citrate buffer ($\text{pH} 4.7$)+0.2 M Na_2SO_4 . For voltammetric deposition, the potential was cycled five times from 0 to +1.0 V at 10 mV/s. Potential-pulse deposition methods consisted of 50 pulse cycles with an oxidizing potential of +1.0 V (15 s duration) and a rest potential of 0 V (60 s duration) per cycle. Thick, electrically conducting POMA films were electrochemically deposited (CV or pulse) from 0.1 M OMA in 1 M H_2SO_4 . After electrodeposition, POMA-ITO electrodes were removed from the deposition solution, rinsed thoroughly with ultrapure water, and dried under vacuum before subsequent electrochemical measurements. Select POMA-ITO electrodes were heated overnight under vacuum ($100\text{--}200^\circ\text{C}$) to study the effect of heat treatment on polymer stability.

2.3. Materials characterization

Atomic force microscopy was carried out using a Digital Instruments Dimension 3000 microscope equipped with a Nanoscope IIIa controller. Surface images of electrochemically deposited POMA films on ITO-coated glass substrates were obtained in TappingMode® using BS-Multi 75, springboard style, low force constant tapping tips (Budget Sensors, resonance frequency $\sim 75 \text{ kHz}$ and force constant $\sim 3 \text{ N/m}$). All images were acquired at scan rates ranging from 0.3 to 0.5 Hz. To determine the film thickness, the film was first carefully scored with a razor blade followed by measurement of the step height with the AFM. The thickness was calculated using the bearing analysis algorithm within the vendor supplied software. Prior to calculation of film thickness and root-mean-square (RMS) roughness, each image was treated with a zero-order flatten to remove the vertical offset between scan lines.

Infrared spectroscopy (Nicolet Magna 750 FTIR Spectrometer with an N_2 -cooled MCT-B detector and a Harrick reflection module at 80°) was used to investigate the chemical structure of the electrodeposited POMA films on ITO substrates. Spectra were collected after purging the reflection accessory for 15 min with N_2 using 512 scans with a 4-cm^{-1} resolution. Prior to analysis of the POMA films, a background spectrum of clean, bare ITO was collected.

The chemical composition and oxidation state of the POMA films were investigated using X-ray photoelectron spectroscopy (XPS, Fissons 220iXL) with a monochromatic Al-K α X-ray source gun at 20 mA and 10 kV with a $250 \mu\text{m} \times 1000 \mu\text{m}$ spot size. The average chain length for POMA films was determined by exposing the electrodes to vapors of 4-trifluoromethylbenzaldehyde (TFMBA, Aldrich) for 1 h, and subsequent analysis of the N 1s and F 1s regions by XPS [33].

3. Results and discussion

3.1. Self-limiting electropolymerization

Polymer films derived from aniline and related monomers are typically prepared by electrodeposition from acidic aqueous electrolytes, where the deposition charge is monitored to achieve the desired film thickness and micrometers-thick films can develop [37–42]. However, that form of deposition control is not readily adaptable to complex 3D electrode structures. The challenges associated with electrodeposition on nanostructured 3D substrates can be mitigated by selecting conditions in which the electropolymerization process is self-limiting. An example of a self-limiting electropolymerization on a 2D electrode substrate (ITO) is shown in Fig. 1a, for the voltammetric deposition of POMA from a citrate-buffered ($\text{pH} 4.7$) aqueous electrolyte. The first voltammetric cycle exhibits a large anodic wave commencing at $\sim +0.4 \text{ V}$, which corresponds to oxidation of the unprotonated OMA monomer ($\text{pK}_a = 4.5$). On successive cycles the oxidation current decreases by more than an order of magnitude, indicating that the ITO electrode is rapidly passivated against further monomer oxidation.

We also explored potential-pulse electrodeposition methods, which are known to yield higher quality polymer films than voltammetric techniques for co-polymerization of two different monomers, or in cases where mass transport of monomer to the electrode surface is limited [43]. The current-time trace for a potential-pulse deposition of an ultrathin, self-limiting POMA film on ITO from citrate-buffered electrolyte is shown in Fig. 1b. The decrease in magnitude of anodic current with each successive pulse cycle indicates passivation of the electrode, as expected for a self-limiting electropolymerization.

Self-limiting electropolymerization occurs if: (i) the growing polymer coating is non-conducting or minimally conducting, which

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