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Electropolymerization vs. electrocrystallization: Electrosynthesis of poly(3,4-ethylenedioxythiophene) in the presence of 2,2′-azino-bis(3-ethylbenzothiaxoline-6-sulfonic acid)

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ABSTRACT

Investigating the effect of synthetic conditions on the properties of conducting polymers (CPs) is a prerequisite to the success of using these materials in new technologies. In this study, films of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with 2,2′-azino-bis(3-ethylbenzothiaxoline-6-sulfonic acid) (ABTS) were electrosynthesized over a range of potentials to determine the effect that polymerization potential has on the properties of PEDOT[ABTS] films. It was found that increasing the polymerization potential from 1.2 V to 1.8 V prevented electrocrystallization of the ABTS dopant, which resulted in better quality films with respect to adhesion, interconnected morphology, electroactivity and conductivity. This study demonstrates the important role that dopants and polymerization conditions have on the properties of electrosynthesized CPs, especially when dopants with added functionality (i.e., redox, biological, or catalytic activity) are used.

1. Introduction

Since their discovery by Heeger et al. in 1977 [1], interest in conducting polymers (CPs) has only increased because their conductive properties can be exploited for use in energy conversion [2] and storage devices [3], biomedical devices [4], electrochromic devices [5], sensors[6] and actuators [7,8]. Controlling the materials properties of CPs such as morphology, electroactivity, conductivity, and porosity), which are strongly dependent on how CPs are synthesized, is required for the successful implementation of CPs in devices [9]. Electropolymerization of CPs is often the preferred method of synthesis because reaction conditions such as the polymerization potential, solvent, supporting electrolyte, temperature and substrate materials can be adjusted to tailor the resulting CPs with desired properties [9,10]. The polymerization potential used during the electrosynthesis of CPs is a key parameter used to change the kinetics of the polymerization process. Consequently, polymerization potential impacts chain length and structural disorder of the resulting polymer, which ultimately alters the morphology, electroactivity, and conductivity of the polymer [11–14].

The conductivity of CPs depends, in part, on the extent to which the polymer backbone is oxidized to a polycation and subsequently charge compensated with anionic dopants. Typical dopants include Cl^-, BF_4^- and dodecylbenzenesufonate anions as well as polyanions such as polystyrenesulfonate [15–17]. All of these dopants function solely to balance the charge of the polycationic CP backbone. Recently, dopants such as redox-active molecules (e.g., metallophthalocyanine, anthraquinone analogs) [18,19], biomolecules (e.g., peptides, proteins and cells) [20–22] and inorganic compounds (e.g., TiO_2, SnO_2 and Prussian blue) [23], have been used to add new function or enhance the intrinsic properties of CPs. In our laboratory, the redox active molecule, ABTS, has been used as a dopant in films of pPy and PEDOT to improve the rate of charge transfer between enzymes and electrodes in biofuel cells [24], the electrochromic properties of CPs [25], and the energy density of CP-based batteries [26,27].

Many studies have examined how properties of CPs are affected by the conditions used during electrosynthesis [11,13,14]. These studies, however, have been limited to dopants that have no other function except charge compensation to the polymer backbone. The incorporation of dopants with other functions (i.e., redox or biological activity) creates many challenges to the synthesis of CP films due to their structural complexity, charge distribution, size or effect on cellular viability. For example, when polyglutamic acid (pGlu) is used as a dopant, films only 50 nm thick or less can be electrodeposited [20]. This limitation in film thickness likely is due to

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the structure, charge distribution, and size of pGlu. To overcome these challenges, knowledge of the physicochemical or biological properties of the dopant is essential so that the conditions of CP synthesis can be modified accordingly [22,28,29]. For example, positively charged ruthenium complexes or neutral inorganic oxides were incorporated into CP films by adding polyanionic host-molecules or adjusting the pH of the solution to impart anionic nature to the dopants [28,29]. To insure cellular viability, neurons were incorporated into films of conducting polymers by adjusting the concentration of the monomer, polymerization time and current during electrosynthesis [22].

In this paper, we show that the properties of PEDOT films doped with the redox-active dopant, ABTS, change dramatically depending on the potential applied during electropolymerization. Increasing the potential from 1.2 V to 1.8 V improved the adhesion, electroactivity and conductivity of the films, which contrasts what is found when dopants of PEDOT or pPy are not redox active (i.e., lower voltages result in CP films with better conductivity and electroactivity) [14]. This contrast in findings is attributed to the electrocrystallization of ABTS at oxidative potentials $\leq$1.2 V (i.e., electrocrystallization of ABTS radical or ABTS$^{\bullet}$). Depending on the amount of electrocrystallized ABTS$^{\bullet}$ at the electrode surface, films with poor adhesion, disconnected morphology, low electroactivity and conductivity are electrodeposited.

2. Experimental

2.1. Solvent for electrosynthesis

The solvent used to electrodeposit films of doped PEDOT consisted of a 6:3:8 volumetric mixture of water:ethanol:propylene carbonate (WEPC). This composition of solvent was selected on the basis of the solubility of ABTS in water, 3,4-ethylenedioxythiophene (EDOT) in PC, and the immiscibility of water and PC (ethanol makes water and PC miscible) ensuring enhanced solubility of both hydrophobic EDOT and hydrophilic ABTS. The solubility of EDOT in WEPC was found to be approximately 310 mM, which was 30 times higher than its solubility in water (~10 mM). The solubility of ABTS in WEPC (~150 mM) also was higher than its solubility in water (~125 mM), although the solubility of ABTS in both ethanol and propylene carbonate was low (<5 mM). The total solubility of ABTS in WEPC (S_{WEPC}) can be calculated from the linear relationship that relates the solubility of ABTS in each solvent (S_{solvent}) and the volume fraction of the solvent in WEPC (ϕ_{solvent}):

$$S_{\mathrm{WEPC}} = S_{\mathrm{Water}} \times \phi_{\mathrm{Water}} + S_{\mathrm{EtOH}} \times \phi_{\mathrm{EtOH}} + S_{\mathrm{PC}} \times \phi_{\mathrm{PC}}$$

Substituting the appropriate values yields S_{WEPC} ~50 mM, which is considerably lower than the experimentally determined solubility of ABTS in WEPC of ~150 mM. The unexpected high solubility of ABTS in WEPC is likely due to the mixed hydrophobic and hydrophilic properties of WEPC and solvent ordering.

Shown in Fig. 1 are the absorbance spectra of EDOT ($\lambda_{\max}$ = 257 nm) and ABTS ($\lambda_{\max}$ = 347 nm) in WEPC. A mixture of EDOT (0.1 mM) and ABTS (25 μM) in WEPC yielded a spectrum equivalent to the sum of the spectra of each individual species, indicating no chemical reaction occurs between these two molecules.

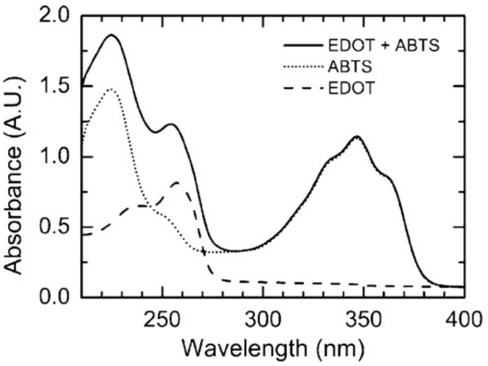

Fig. 1. Absorption spectra of EDOT(100 μM), ABTS(25 μM) and EDOT (100 μM) plus ABTS (25 μM), all in WEPC.

2.2. Electrochemical experiments

A three-electrode configuration in a single compartment cell was used for electrochemical synthesis and characterization: the working electrode was a gold-coated glass slide (Au/Ti/glass), the counter electrode was Pt mesh, and the reference electrode was Ag/AgCl. An EG&G potentiostat/galvanostat (Model 273A) was used for all experiments. Films of PEDOT[ABTS] were electrosynthesized from WEPC containing 0.1 M EDOT and 25 mM ABTS using either cyclic voltammetry (CV) or chronoamperometry (CA). When the films were electrosynthesized by CV, the potential of the working electrode was swept between 0 and 1.8 V (vs. Ag/AgCl) for 10 cycles at a scan rate of 100 mV/s (CV). When the films were electrosynthesized by CA, the potential of the working electrode was poised at 1.2, 1.5 or 1.8 V (vs. Ag/AgCl) for 200 s, or until 2 C of charge passed.

2.3. UV–vis spectroscopy of EDOT and ABTS

Absorbance spectra were obtained by scanning from 200 nm to 600 nm at 600 nm/min with full slit height using a double beam UV–vis spectrometer (Cary 500).

2.4. Conductivity measurements

A two-electrode thin-layer cell reported in the literature [30] was adopted to measure the electrical conductivity of solvent-wetted PEDOT films using a bipotentiostat (Pine Instrument, AFCBP1). The upper gold electrode (area = 3.14 mm^2) was held at a fixed position. The lower gold electrode (area = 50 mm^2) was coated with a thin film of doped PEDOT and subsequently mounted on a micrometer to control its position relative to the upper electrode. The conductivity cell (two gold electrodes), along with counter and reference electrodes, were immersed in electrolyte (0.2 M HCl/aq.) during each measurement. The bipotentiostat enabled the measurement of current flow through the PEDOT film by maintaining a 10 mV offset between the two gold electrodes. The conductivity of the film can be determined by substituting the measured current into the following equation:

$$\sigma = \frac{dI}{AV}$$

where σ is the conductivity of the film in S cm^{-1}, d is the film thickness in cm, I is the current between two electrodes in amperes, A is the area of the upper electrode in cm^2, and V is the potential difference between the two electrodes in volts (i.e. 0.01 V). To measure the potential-dependent conductivity of the film, the potential of the lower gold electrode was fixed at a constant potential of −0.4 V, −0.2 V, 0 V, 0.2 V, and 0.4 V.

3. Results and discussion

3.1. Electrosynthesis of PEDOT[ABTS] films

Films of PEDOT[ABTS] were synthesized via cyclic voltammetry to first obtain qualitative information about the redox processes involved in the electropolymerization. Shown in Fig. 2a are cyclic voltammograms (CVs) measured at the working electrode