

COUNTERION EFFECT ON THE MORPHOLOGY AND ELECTRICAL PROPERTIES OF POLY(3,4-ETHYLENEDIOTHIPHENE) DEPOSITIONS.

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Abstract

In this work, electropolymerizations of PEDOT in aqueous solution were carried out. Nanometric graphite layers (NGL) deposited on glass were used as the electrodes. Counterions such as dodecyl sulfuric acid (DSA) [2], 4-dodecylbenzenesulfonic acid (DBSA) [3] or polystyrene sulfonic acid (PSS) [3] were evaluated to study their effect on PEDOT morphology and electrical conductivity. PEDOTs' morphology was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM), and electrical properties by electrochemical impedance spectroscopy (EIS). Microscopy techniques showed that the longer the counterion alkyl chain, the greater the particle size and the greater film thickness. According to this, PEDOT:DBSA films presented the largest particle size and thickest films and also the best conduction in comparison with PEDOT:PSS or PEDOT:DSA.

Introduction

Morphology is a very important characteristic of polymers and largely determines their properties. Of course, morphology is intimately related to the synthesis conditions [4]. The choice of a synthetic method depends on the type of CP and the macroscopic form of it. A chemical bulk method produces the polymer as powder and the electrochemical polymerization produces the material as a thin film [5].

The electrochemical polymerization involves the oxidation of monomers such as 3,4-ethylenedioxythiophene (EDOT) (Figure 1). In this process, the polymerization initiates at the electrode/electrolyte interface that promotes the formation of a polymeric film that adheres to the electrode surface [6]. Polymerizations at constant current are more convenient for controlling the thickness of the deposited films [7].

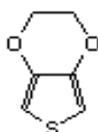


Figure 1. 3,4-Ethylenedioxythiophene (EDOT) monomer.

EDOT monomer has very poor solubility in water (2.1 g/L). Furthermore, electrochemical polymerization of EDOT is inhibited by water molecules interacting with thienyl cation radical, the polymerization intermediate. To solve these problems, it was recently proposed to add significant amounts of anionic surfactants to aqueous solutions of EDOT. The use of a surfactant for electropolymerization of heteroaromatic compounds has several important effects. The presence of micelles provides an

interesting solvent system for solubilization of these water insoluble compounds. Moreover, the addition of surfactants to the electrolyte can stabilize charged species such as anions or cation radicals, and can also improve the properties of conducting polymers [8].

The aim of this work was to evaluate the effect of the three evaluated counterions on morphology and electrical properties of PEDOT salts electropolymerized, in aqueous medium, by a potentiostatic mode electropolymerization.

PEDOT salts electropolymerization.

In oxidative polymerization the monomer is oxidized at the electrode surface, releasing an electron to become a radical cation. Two radical cations react to form a dimer, which immediately splits off two protons. The neutral dimer is then readily oxidized to generate a radical cation, which continues the process of chain growth, eventually producing a polymer [9].

Films of PEDOT salts were electrochemically deposited on top of NGL working electrode, a Sigma Aldrich Ag/AgCl electrode as reference electrode, and a Pt wire counter electrode, using a three-electrode electrochemical cell in a Solartron Instrument.

The monomer (EDOT) (0.001 moles), the counterion (PSS, SDS or DBSA) (0.001 moles) and distilled water (200 mL) were mixed in a three-necked round bottom flask. This mixture was sonicated in a Branson sonicator at 25 °C, for 30 min, time enough to form a stable emulsion. Once the emulsion was obtained the three electrodes were immersed to perform polymerization. Solartron Analyzer equipment was used as the power source.

The reactor was perfectly closed to prevent monomer evaporation. The emulsion was de-oxygenated by bubbling N₂ for 20 min prior to all electropolymerizations. The experiments were performed at room temperature under N₂ atmosphere. The electropolymerization and deposition of PEDOT were carried out using the potentiostatic mode, applying a 1.5 V for 2,400 s. At the end, the NGL electrode with the deposited polymer was removed of the reactor and washed with distilled water (10 mL).

Characterization

The topography, morphology and thickness of the deposits were analyzed by: SEM using a JEOL JSM-7401F Field Emission microscopy, with ultra high vacuum and 1 nm resolution. AFM characterization was carried out in tapping mode, with a VEECO SPM MultiMode AFM system, using a 225 μm probe.

EIS analyses were carried out with a Solartron Analyzer, model 1260 and 1287. The interface software used was Z-Plot, in which the AC voltage (100 mV and 50 mV) and the frequency (1E⁶ Hz to 0.1 Hz) were set. The configuration was a three-electrode electrochemical cell, used to carry out the electrochemical polymerization and as electrolyte the aqueous micellar solution.

Results and Discussions

PEDOT synthesized is in its conductive form, the oxidized form. In this state PEDOT contains positive charge carriers, which were offset by incorporating anions (PSS, DSA or DBSA) from the electrolyte (aqueous micellar solution), or counterions, with the aim of maintain the electroneutrality and improve the polymer stability in an aqueous medium.

The type of counterion affects PEDOT properties in different ways. First of all, both the size and shape of ions, which have a considerable effect on the diffusion rates inside the polymer matrix, limiting the oxidation and reduction rates of the polymer, and second, determine the morphology and conductivity of the polymer.

The nanometric graphite deposition used as electrode in the electrochemical polymerization is showed in Figure 2(?). This film was deposited onto the glass slide; it is ~200 nm thick and is conductive enough to carried out the CP deposition. The Figure 2 (a) shows the spheroidal morphology of PEDOT:PSS microstructure, this spherical particles are ~1 μm diameter according to Figure 2(b) graph. Looking at the 3-D graphic (Figure 2(c)) it is possible to conclude that this film has a low rough surface, with ~500nm thick.

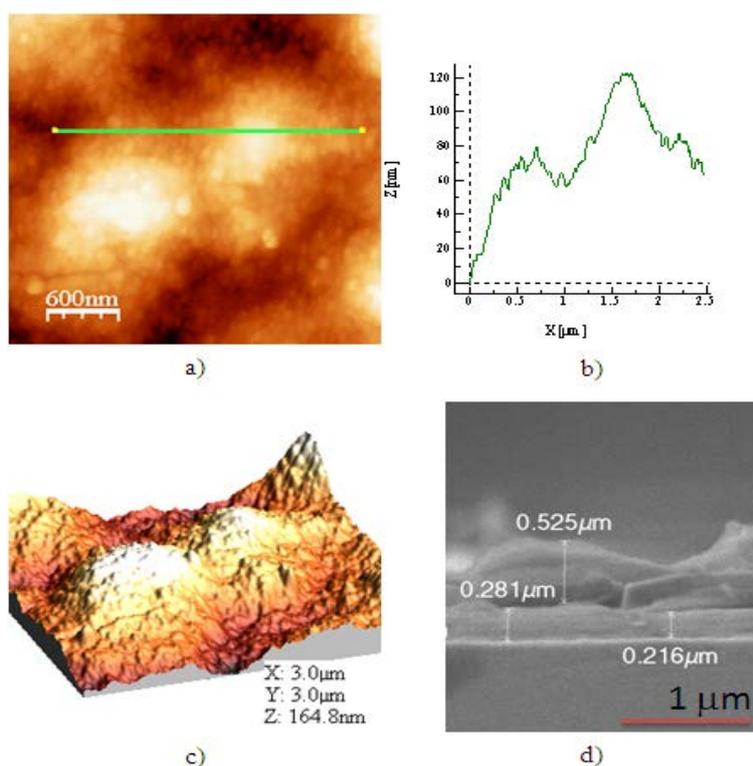


Figure 2. a) AFM tapping mode image of PEDOT:PSS deposition, b) the height and particle size evaluation, c) 3-D visualization of the film topography, d) SEM image of film thickness and e) PSS counterion.

The topography of the deposited PEDOT:DSA film is illustrated in Figure 3. As it is observed, the surface is clearly rough as shown in the 3-D graphic, and the microstructure or the polymer particles shape is also spherical, but these have larger diameters than PEDOT:PSS ($\sim 1.5 \mu\text{m}$). The PEDOT:DBSA salts deposited is the thicker one, with $\sim 4 \mu\text{m}$ height (Figure 4(d)), this is due the DBSA is the larger counterion used. And as the Figure 4(b) shows the particle diameter is $2 \mu\text{m}$, and also the microstructure is spheroidal.

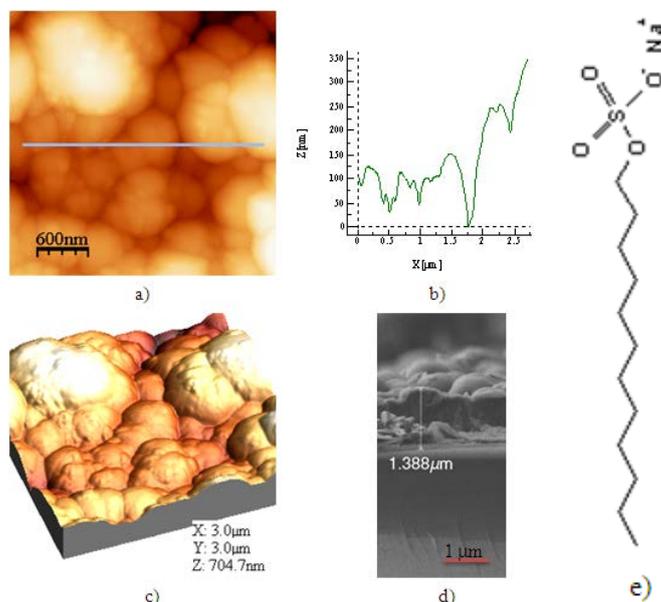


Figure 3. a) AFM tapping mode image of PEDOT:DSA deposition, b) height and particle size evaluation, c) 3-D visualization of the film topography, d) SEM image of film thickness, and e) DSA counterion.

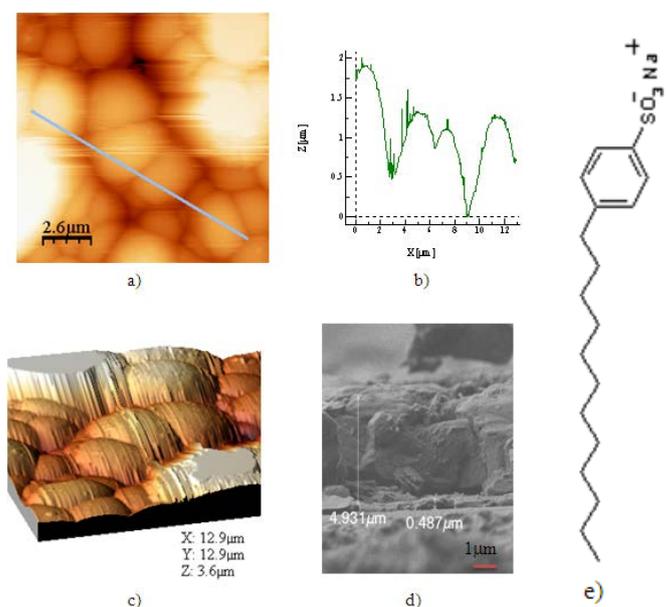


Figure 4. a) AFM tapping mode image of PEDOT:DBSA deposition, also b) the height and particle size evaluation, the c) 3-D visualization of the film topography, d) SEM image of film thickness, and e) DBSA.

As mentioned, morphology has an important effect on conductivity; the values of conductivity in S/cm are shown in Table 1. These values were obtained by EIS of the deposited films, the high value is 2.4E-8 S/cm, and is for PEDOT:DBSA film. The lowest conductivity value was for the PEDOT:PSS deposit, with 1.02E-8 S/cm.

Table 1. Resistance and Capacitance of PEDOT salts deposited, measured by EIS.

PEDOT:	PSS	DSA	DBSA
Resistance (Ω)	1,290.10	1186.8	437.2
Capacitance (F)	5.77E-10	5.09E-10	9.73E-10
Film thickness (cm)	4.0E+06	1.0E+06	5.0E+05
Conductivity (S/cm)	1.02E-09	4.42E-09	2.40E-08

Conclusions

SEM and AFM showed that anions chain length has a determining effect on the polymer morphology, the larger the counterion, the thicker the film deposited. EIS measurements let us to determine resistance and capacitance, allowing calculating conductivity. These values showed that conductivity was also importantly affected by counterion length, indicating that the larger the counterion, the higher the conductivity.

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