



Aqueous deposition of a semiconducting polymer by electrocoating

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ABSTRACT

An aqueous-based deposition of a semiconducting polymer using an electrolysis-based technique is demonstrated here. Regioregular poly (3-alkylthiophene) with a carboxylic acid group in the side chain was synthesized and dispersed in water with triethylamine to create a quaternary ammonium salt. The dispersion was then successfully electrocoated onto galvanized steel, forming films with good uniformity in just a few seconds. The optoelectronic properties of these new films were compared with that of organic solvent-casted regioregular poly (3-hexylthiophene). Optical and electronic properties of the electrocoated films were similar to that of the organic solvent processed films, indicating that the semiconducting polymer was stable to the voltages and aqueous environment used in the electrocoating process. These results suggest that electrodeposition is a promising deposition method for organic electronic applications including conformal deposition onto complex shaped surfaces for low-cost and environmentally friendly nanoscale film formation.

1. Introduction

Significant progress has been made over the last decade in fabricating thin film organic electronic devices. Polymer semiconductors are particularly interesting for applications where large area, mechanical flexibility and low-cost are important, such as thin film transistor arrays for displays, photovoltaics (OPV), field effect transistors (OFET) and light emitting diodes (OLED) [1–3]. However, these polymers are typically processed from organic solvents with attendant health and environmental hazards [4–7]. New aqueous-based approaches to large area fabrication techniques would open new environmentally-friendly, commercial opportunities.

Water processed π -conjugated polymers are now being synthesized for use in organic electronic devices [8]. This is made possible by attaching a surfactant-like side group to the π -conjugated backbones of the polymers during their synthesis [9,10]. These newly designed and synthesized polymers retain their intrinsic optoelectronic properties due to the presence of the π -conjugated backbones. These can be dissolved in water owing to the side group for solution processing to make thin films by spin coating and/or dip coating. This opens a whole new avenue for the fabrication of optoelectronic organic devices. Processing these films from water makes them more environmentally favorable as compared to the ones made using organic solvents.

Laboratory-scale solvent methods for deposition of π -conjugated

polymers on small, flat substrates include spin coating, doctor blading and drop casting [11–13]. Several high-volume processing techniques are being explored and used in industry. These methods, mostly in OPVs, include screen printing [14,15], ink jet printing [16,17], pad printing [2], slot die coating [18], gravure coating [19], and spray coating [20]. These techniques are suited for high-speed coating at low-cost, but have notable shortcomings including environmental issues associated with organic solvents, considerable waste of precious active materials, and difficulty in making conformal films for certain applications. The electrocoating technique described here promises to overcome these shortcomings [21]. Electrocoating uses water as the solvent and an electrical field to alter the local pH at the electrodes, thereby causing the deposition of dispersed materials. In contrast to other electrodeposition techniques, the scalability of electrocoating has led to its widespread industrial use for coating complex surfaces such as vehicles.

Other approaches to electrodeposition include electropolymerization and electrophoresis. Electropolymerization relies on using an electric field to grow films by polymerizing monomers in solution [22,23]. Electropolymerization can be performed in aqueous solutions [24], however, it is difficult to scale for industrial applications. Electrophoretic deposition uses an electric field to migrate solid polymer particles to the substrate. Similarly, this technique provides most of the benefits of electrocoating as it uses an electric field and substrates of

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any shape can be effectively coated [25]. Recently, electrophoretic deposition has been used to deposit semiconducting organic films over insulators [26]. Electrophoretic deposition can be used to deposit onto insulators since neutral molecules are used. Still, one of the main drawbacks is the use of organic solvents such as toluene, or methanol in electrophoretic deposition [27].

The process of electrocoating was developed in the last century [21] and it is now widely used for coating metal-parts of cars and appliances on the industrial level. This established process quickly produces precise, uniform coatings from water-based dispersions. Electrocoating systems use processes and materials that are environmentally friendly and have high economic efficiency. One of the major advantages of electrocoating is that it gives total coverage of complex parts with high film uniformity in seconds. With the material transfer efficiency ranging from 95 to 99%, it can easily be utilized in a highly automated closed-loop system for larger scale applications. Electrocoating systems have excellent productivity, low operating costs and generate very low air and waste water emissions [28]. Production of conformal organic photovoltaic devices by an electrocoating system would result in the efficient, easy fabrication of functional devices on surfaces with complex geometry. To our knowledge, this technique has never been applied to the deposition of polymer semiconductors.

In the electrocoating process, polymers with weak acid/base groups are ionized with a weak base/acid just enough to disperse the polymer in water [29]. A voltage is then applied between two electrodes to cause electrolysis of water [21,28,30]. The electrolysis of water affects the local pH at the electrodes: at the positive electrode (anode), water is oxidized to O_2 and H^+ and the pH is low whereas at the negative electrode (cathode), water is reduced to form H_2 and OH^- and the pH is high. The ionized polymers migrate towards the oppositely charge electrodes and are neutralized at the electrode surface due to local pH change. Since the neutral polymer is insoluble in water, it precipitates at the surface, forming a dense polymer film. Electrocoating is termed anodic or cathodic if it occurs at the anode or cathode, respectively. Fig. 1 illustrates a typical anodic electrodeposition. This technique is not limited to polymers, and can be applied to any powdered solids that have acid or base moieties capable of forming a stable suspension in water [21,31,32]. Films have been made by electrocoating with a wide range of particle sizes and shapes, from micro-to nanometric particles, including equiaxed particles, nanotubes, nanoplatelets, and nanorods [29,30]. It has also been widely used to deposit polymers having diverse particulate geometries [21,30]. The versatility of this film deposition technique extends to almost any substrate architecture, from

flat or spherical to porous or three-dimensional (3D), as well as a wide range of electrically conductive materials [29,30]. In addition to this, electrocoating offers relatively short processing times and requires relatively simple and low cost equipment to produce uniform films with significant control of the film thickness [21,29–31,33]. Most importantly, electrodeposition offers the possibility of upscaling to large, real world dimensions [21,30].

In this paper, we report a deposition mechanism of nanoscale thickness semiconducting films of functionalized poly (3-alkylthiophene) (P3AT) by electrocoating on metal substrates. Uniform thin films were obtained on galvanized steel by anodic electrodeposition of a P3AT functionalized with carboxylic groups (P1) dispersed in water with triethylamine ($P1^-$). The morphological and electrical properties of the resulting films were measured and compared to solvent-deposited poly (3-hexylthiophene) (P3HT).

2. Theoretical and experimental methods

2.1. Kinetics of anodic potentiostatic electrocoating

The kinetic equation for film growth can be derived from the theory of oxide films on metals [33]. Assuming Ohmic film deposition, the thickness of the deposited film (δ) can be related to applied potential (V) and deposition time (t) per Faraday's laws of electrolysis, given by the following equation:

$$\delta = (2c\sigma_F)^{1/2}(Vt)^{1/2} \quad (1)$$

where c is the coulombic efficiency and σ_F is the film conductivity. This simple kinetic model describing the anodic deposition process is quite accurate and routinely used to fit data in commercial electrocoating systems.

2.2. Preparation of functionalized P3AT

To create a water-dispersible conjugated polymer suitable for anodic electrodeposition, we functionalized P3AT with carboxylic acid groups (P1, Fig. 2). P1 was synthesized using the literature procedures starting from a regioregular poly (3-(6-bromohexyl)thiophene) that has average molecular weight (M_w) of 29.5 kDa and poly dispersity index (PDI) of 2.2 by gel permeation chromatography (GPC) [34–37]. The identity of P1 was confirmed by attenuated total reflectance (ATR) spectroscopy with the appearance of a carbonyl stretch at 1700 cm^{-1} (see Supporting Information). Further characterization by proton nuclear magnetic resonance spectroscopy ($^1\text{H NMR}$) and matrix assisted laser desorption ionization-time of flight (MALDI-TOF) could not be done due to the low solubility of P1. P1 was then ionized and dispersed in water by sonication with triethylamine to give $P1^-$ (Fig. 2). Upon

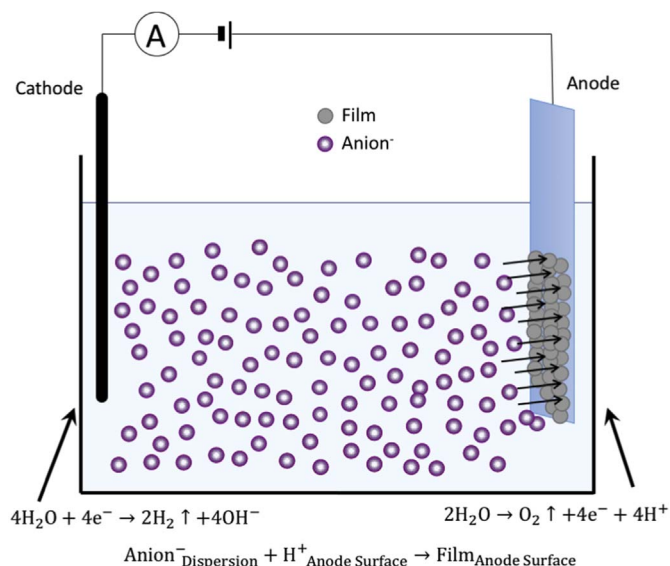


Fig. 1. Schematic diagram of anodic electrocoating.

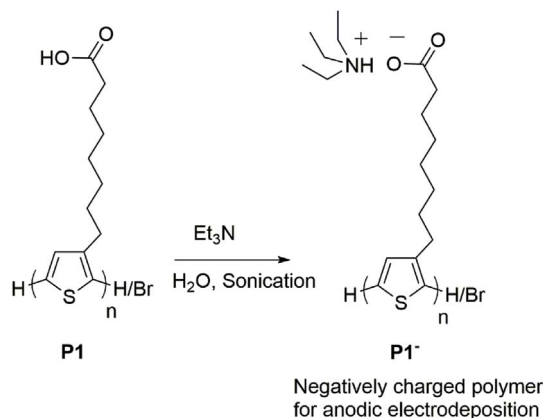


Fig. 2. Chemical structure of P1 and its ionization to form water dispersions of $P1^-$, suitable for anodic electrodeposition.

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