



Electrolyte and current density determines the fate of electrodeposited polythiophene from waveguide to photovoltaics

Om Prakash Bajpai^a, Sujit Kumar^b, Subhendu Bhandari^a, Achintya Dhar^b, Dipak Khastgir^a, Santanu Chattopadhyay^{a,*}

^a Rubber Technology Centre, Indian Institute of Technology Kharagpur, 721302, India

^b Department of Physics, Indian Institute of Technology Kharagpur, 721302, India

ARTICLE INFO

Keywords:

Polythiophene
Dendritic growth
Solar cell
Electrochemical synthesis
Boron
Trifluoride diethyl etherate

ABSTRACT

Nucleation and growth process of electrodeposited polymer determine its morphology, thus its function and applicability. In this work, we show how minute changes in polymerization condition, like current density and electrolyte concentration, alter nucleation pattern of polythiophene. Different nucleation patterns in turn give rise to different morphology and functional properties. Polythiophene was electrochemically synthesized on indium tin oxide (ITO) using boron trifluoride diethyl etherate (BF₃.Et₂O) electrolyte. At constant current density (8 μA/cm²), 20 vol% electrolyte gives rise to dendritic structures, while pure electrolyte gives rise to uniform film. Similarly, if current density was increased (0.08–0.4 mA/cm²) in 20 vol% electrolyte, dendritic structures were completely suppressed and again uniform polymer film was obtained. Although electrical properties are compromised in the dendritic sample owing to the higher surface roughness, dendritic structures efficiently guide light and are shown to be a good candidate for photonic and energy applications. On the other hand; uniform polythiophene, obtained at high current density and electrolyte concentration shows enhanced redox capacity and electrical conductivity. Utilizing optical and electrical properties of smooth polythiophene films (without dendrites), basic photovoltaic (PV) device (Glass/ITO/PT/P3HT:PC61BM/Al) was constructed using electrochemically grown polythiophene as Hole-Transporting Layer (HTL). Fabricated device exhibits significant photovoltaic performance with comparable efficiencies of 0.98–1.24%. Such electrochemically grown polythiophene thin films can be a substitute for other HTLs (like PEDOT: PSS) in photovoltaic devices.

1. Introduction

Conducting polymers have been explored extensively since their discovery in the 1970s [1–4]. Conducting polymers are predominantly used in electrochromic rearview mirrors, window sheets, thin-film transistors/displays/sensors, polymer light-emitting diodes, photovoltaics [5] and electrochromic devices [6–10]. These polymers possess various types of micro/nano structures on the surface such as nanospheres, nano-wires, etc. [11–15]. Such structures are made up of carbon, metal oxides or other polymers in diffusion-limited polymerization conditions. However, the growth of such structures needs expensive catalyst, high temperature or complex manufacturing techniques like vapour–liquid–solid growth, vapour–solid growth, etc. Lately, electrochemical polymerization has been employed to overcome these problems and several nano/micro structures have been reported [16–20]. The nano/micro structures on the surface of polymer alter its functional properties. For example, such structures on polymer film

increase capacitive behavior of the film [21]. Particularly, hyper-branched nano-structure decreases energy gap between LUMO and HOMO of the polymers [22]. Thus, nano/micro structures are favorable for energy, organic electronics, photonic and waveguide applications. On the other hand, these nano/micro structures adversely affect the performance of electronic device like OLED, solar cell, etc., and must be suppressed to get significant output from such devices. Hence, nano/micro structures on polymer surface should be differentially modulated for different applications.

Among various conducting polymers, polythiophene is a lightweight, flexible, environmentally stable and degradation resistant polymer [23–27]. This polymer has been widely probed for its fast switching time, outstanding coloration efficiency, stability and high contrast ratio in the visible and NIR regions. Numerous applications have been proposed for the polythiophene such as in transparent electrode, supercapacitors, light emitting diodes, photovoltaic cells [28,29], corrosion protection, thermo-electric and electro-chromic

* Corresponding author.

E-mail addresses: santanu@rtc.iitkgp.ernet.in, santanuchat71@yahoo.com (S. Chattopadhyay).

displays, polymer field effect transistors (FET), etc. [10,26,30–33] Photoluminescence (property of absorbing or emitting light) of polythiophene makes it optimum for optical devices. The polymer has a relatively low band gap (Eg) [27]. Notably, the low band gap is preferred in solar cells and other photovoltaic applications. Moreover, doped polythiophene has sufficient transparency in UV–Vis region that facilitates its use as a Hole Transport Layer (HTL) in organic photovoltaic devices [31]. Polythiophene can be synthesized chemically or electrochemically, where both have their advantages and disadvantages [24,26,34–36]. The electrochemical process has several advantages over chemical method as the former needs lesser amount of precursor monomer, no catalyst, generates smooth thin films and polymer can be selectively grown on patterned ITO.

During electrodeposition, aqueous solvents are reported to decrease the rate of polythiophene deposition due to poor solubility of monomer and higher oxidation potential in water [25]. Therefore, different non-aqueous solvents have been used for electrochemical synthesis, e.g., acetonitrile, benzonitrile, nitrobenzene, etc. [3,10] Among various non-aqueous solvents, acetonitrile has been singularly used [37–39]. It has a high dielectric constant (36 approx.) that ensures good ionic conductivity of the electrolytic medium, low nucleophilicity and good electrochemical stability at high potential. In the 1990s, Shi and Jin first developed a novel method for the electrochemical synthesis in boron trifluoride diethyl etherate (BF₃.Et₂O) complex [40]. The complex worked as a unique solvent-electrolyte system for the polythiophene electro-polymerization and gave rise to high strength and high conductivity of polythiophene [25,41–43]. Most electrolytes require high oxidation potential to electro-oxidize thiophene monomer. High oxidation potential, thus over-oxidation of thiophene, affects the conjugate molecular structure of polythiophene. This gives rise to *polythiophene paradox* where degradation of the polymer may compete with its electrodeposition. However in BF₃.Et₂O electrolyte system, sulfur of thiophene interacts with BF₃ which decreases aromaticity and overall oxidation potential of the thiophene ring. The lower oxidation potential (1.2–1.3 V) of thiophene makes it resistant to over-oxidation in this system. Additionally, polar molecules [(C₂H₅O)₃O⁺]BF₄⁻ make the electrolytic medium more conductive [25,41]. In the course of polymerization, thiophene dimerizes to release protons in solution [35]. This increase in the proton concentration decreases the rate of polymerization significantly. Contrary, BF₃.Et₂O reacts with water and produces H⁺BF₃OH complex by abstracting a proton from solution. Thus, BF₃.Et₂O maintains proton concentration and also the rate of reaction. Since pure BF₃.Et₂O is highly acidic (strong Lewis acid), acetonitrile solvent is used for the dilution according to the requirement [39,44].

Understanding nucleation and growth process of the electrodeposited polymer at controlled potential or current have a crucial impact on final morphology of the product [45,46]. Polythiophenes, polymerized in the different electrolyte, have already been evaluated regarding their morphology and functional properties [47–51]. But the origin and suppression of dendritic structures of the electrodeposited polythiophene have not been studied. Likewise, very little is known about how different polymerization conditions induce differential structure, optical and photovoltaic properties. Here, we have reported the effect of electrolyte-current density on nucleation-growth process, and formation of dendritic structures on the surface of electrodeposited polythiophene. Additionally, we have also studied electrical, optical and photovoltaic properties of these polythiophene films and have correlated altered morphology to functional property variation. For this, four different samples were prepared by varying electrolyte concentration (i.e., BF₃.Et₂O with/without acetonitrile solvent) and current density. Electrodeposition was carried out under very low current density (8 μA/cm²–0.4 mA/cm²) to avoid any side reactions and irregular arrangement of the polymer chain at very high current density [26]. Morphology and functional properties were examined by different analytical techniques for possible optical waveguide and photovoltaic

applications. Photovoltaic property of the polythiophene film (without dendrites) was inspected with basic PV device (Glass/ITO/PT/P3HT:PC₆₁BM/Al). To the best of our knowledge; this type of correlative study of polythiophene, ranging from the waveguide to photovoltaics, has not been reported yet.

2. Experiment

2.1. Materials

Thiophene monomer (> 99%), Poly(3-hexylthiophene-2,5-diyl) (P3HT), [6,6]-Phenyl C₆₁ butyric acid methyl ester (PC₆₁BM > 99.5%) and Indium Tin Oxide (ITO) glass slides (rectangular, surface resistivity 70–100 Ω/sq) were purchased from Sigma-Aldrich, USA. Boron trifluoride diethyl etherate (BF₃.Et₂O) complex, 1, 2-dichlorobenzene and acetonitrile (CH₃CN) solvent were obtained from the Merck Specialties Chemicals Ltd, Mumbai, India. All these materials were used without any further purification. Since BF₃.Et₂O is highly moisture sensitive, corrosive and toxic; proper precautions must be taken while handling.

2.2. Method of sample preparation

Polymerization was performed in one compartment-three electrode system using the Autolab Electrochemical Workstation (302 N) at room temperature (24 ± 2 °C). Rectangular glass slides of ITO were used for both counter and working electrode, while Ag/AgCl as a reference electrode. The size of counter electrode should be large or same as a working electrode to reduce the effect of working electrode polarization. Hence, ITO slides of same dimensions (1.2 × 3.5 cm) were used for both counter and the working electrode. Before polymerization, ITO slides were properly washed with acetone, isopropanol and deionized water. In the electrochemical setup counter and working electrodes were kept 1.2 ± 0.1 cm apart. Electrolyte concentration, electrodeposition time and current densities were optimized separately before the sample preparation (not shown here).

For polymerization, 0.1 M thiophene has been used in the 20 vol% BF₃.Et₂O in acetonitrile (AN) or pure BF₃.Et₂O (without AN). The solution of the thiophene monomer and electrolyte was purged with nitrogen for 10 min before polymerization reaction. To understand the effect of electrolyte concentration on the polymer properties, polymerization was carried out either in pure BF₃.Et₂O or 20 vol% BF₃.Et₂O keeping monomer concentration and current density constant (0.1 M and 8 μA/cm², respectively). Samples were collected at different deposition time points as mentioned (1, 20 & 60 min for pure electrolyte based samples and 13 s, 30 Sections, 1, 3, 5, 10, 20 & 60 min for 20 vol % electrolyte based samples). Similarly, to understand the effect of current density on the properties of polythiophene, some samples have been prepared at high current density 0.08 and 0.4 mA/cm² keeping the monomer concentration (0.1 M) and electrolyte dilution constant (i.e., 20 vol% BF₃.Et₂O in AN) for 40 and 30 min of electrodeposition time respectively. As different thickness may affect properties of the polythiophene films, deposition time was modulated according to current density to avoid differential thickness. The electrodeposition time was increased to 40 min for 0.08 mA/cm² in comparison to 30 min for 0.4 mA/cm² to acquire approximately same film thickness in both the cases. All samples electrodeposited on ITO electrode were washed with acetone, isopropanol and deionized water, and dried in vacuum oven for one day before the characterization. The complete process of samples preparation has been depicted in Fig. 1.

2.3. Device fabrication

We have prepared simple photovoltaic devices- Glass/ITO/PT/P3HT:PC₆₁BM/Al using patterned ITO as substrate (15 Ω sq⁻¹, Sigma). Before device fabrication, ITO surface was cleaned by ultrasonication in acetone and dried under a nitrogen flow. Polythiophene films were

Download English Version:

<https://daneshyari.com/en/article/6534078>

Download Persian Version:

<https://daneshyari.com/article/6534078>

[Daneshyari.com](https://daneshyari.com)