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Vapor phase polymerization and mechanical testing of highly electrically conductive poly(3,4-ethylenedioxythiophene) for flexible devices

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ABSTRACT

Flexible electronic device applications such as organic light emitting diodes, organic solar cells, and touch screen devices require the use of transparent conductive films that maintain their electrical stability under strain. This paper demonstrates a method for polymerizing poly(3,4-ethylenedioxythiophene) (PEDOT) films with an electrical conductivity >1000 S/cm by using the presented vapor phase polymerization (VPP). Conductive atomic force microscopy shows that the high conductivity of these polymer films is concurrent with the presence of large, closely-packed conductive domains. We observe that the choice of cationic oxidant initiator and anionic dopant has a significant effect on film morphology, optical absorption, and conductivity. VPP PEDOT films show stable electrical performance during mechanical strain tests compared to indium tin oxide and spin coated poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) transparent thin film conductors.

1. Introduction

The electronics market has a need for low-cost and flexible conductive films with simplified processing for applications such as organic photovoltaics, organic light emitting diodes, and touch screen devices [1–3]. Indium tin oxide (ITO), the commercial standard for transparent conductive thin film electrodes, is limited by its brittle structure, the necessity for high vacuum fabrication, and the high cost of indium [4–8]. Inherently conducting polymers (ICPs) have been proposed as transparent conducting films that are low cost, flexible and highly conductive [9–12]. However, there is a need to develop new approaches that offer both higher conductivities and easier processing conditions.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is an ICP formed as a co-polymer with a polyelectrolyte, which is used widely in thin film technologies as a water soluble dispersion for many types of solution processing. PEDOT alone is insoluble, so PSS is added to make it soluble in polar solvents. PSS, however, acts as an insulator, limiting the conductivity of PEDOT:PSS by increasing the hopping barrier for charge transport [13–15]. Conductivities greater than 2000 S/cm have been achieved by using post treatments with concentrated acids [16–18]. There have also been efforts to replace the insulating PSS with a counter ion that enhances the conductivity.

There are several alternative ways to process PEDOT films without the use of PSS, including electrochemical deposition, oxidant initiated *in situ* chemical polymerization, chemical vapor deposition (CVD) and vapor phase polymerization (VPP) [19]. The highest performance PEDOT films have been achieved using either CVD or VPP in which 3,4-ethylenedioxythiophene (EDOT) is introduced as a vapor and subsequently polymerized on a substrate [19]. CVD and VPP differ in how the oxidant is applied. For CVD, sublimed oxidant is carried by argon flow into a reaction vessel filled with EDOT monomer [20]. This leads to PEDOT deposition on all surfaces inside the chamber [19]. Moreover, while the CVD method produces highly conductive films, it typically requires complex experimental setups [20]. The VPP method involves coating a substrate with oxidant and then exposing the oxidant-coated substrate to EDOT vapor, resulting in PEDOT growth only on the substrate [19]. The VPP method produces an oxidized p-doped polymer film which shows higher conductivities than solution-based PEDOT:PSS films [21].

The conductive nature of VPP PEDOT thin films varies depending on factors like choice of oxidant, vapor pressure, and

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environmental conditions, such as temperature, which can alter the conductivity by a factor of 3 or more [20–22]. When using the oxidant Fe(III) p-toluenesulfonate hexahydrate ($Fe(PTS)_3$) as the initiator, the VPP method has been shown to produce highly conductive films, with conductivities greater than 1000 S/cm [23,24]. The high conductivities have been attributed to the dopant anion which induces a postive charge on the polymer and increases the overall order and crystallinity of the film compared to solution processing methods [25]. PEDOT polymerization has also been done utilizing different oxidants, such as Cu(II) chloride, though the obtained conductivities are lower [22].

Here, a procedure is demonstrated for depositing PEDOT onto flexible or rigid substrates, using a VPP approach without the use of post processing. This process can be done using a simple experimental setup to achieve high performance: conductivity, mechanical stability, and reproducibility. The resulting molecular and mechanical properties of PEDOT films are tested using different cation and anion dopants and compared to solution-processed PEDOT:PSS thin films. These results could have implications for the future preparation of transparent electrodes, flexible electronics and sensors.

2. Methods

2.1. Materials

ITO (60 Ω/□) coated poly(ethylene terephthalate) (PET) purchased from Aldrich was used as received. PET substrates were washed in deionized water (DI) and acetone and dried under N_2 gas prior to PEDOT deposition. PEDOT:PSS was purchased from H.C. Starck (Clevios S V3). EDOT monomer was purchased from Sigma–Aldrich and used as received. All solvents were purchased from Sigma–Aldrich and used as received.

2.2. PEDOT:PSS film preparation

Solutions of PEDOT:PSS and 2-propanol were mixed in a 1:1 ratio by volume for 24 h. The solution was spin-coated onto a clean PET substrate at 3000 RPM for 15 s. Films were then heated at 90 °C for ten minutes to evaporate solvent, and then stored in a sealed container purged with nitrogen gas.

2.3. Vapor phase polymerization of PEDOT film preparation

Solutions of 0.1 M hydrated Cu(II) and Fe(III) oxidant were prepared in 1-butanol. Pyridine (7.45×10^{-4} M) was added to the iron solutions to act as a base. Pyridine was not added to the copper solution due to solid precipitation and neutralization of the oxidizing properties. The oxidant solution was spin coated onto a clean PET substrate, sonicated in ethanol for 30 min, (3 cm × 6 cm) at 750 RPM for 15 s. The film was then dried in a sealed desiccator for 10 min, to evaporate the solvent, and transferred to another desiccator (Precision Scientific Heated Vacuum Desiccator, volume 3912.6 cm^3) containing a petri dish with 100 μL of EDOT vapor, as shown in Fig. 1A. The film rested on top of the dish with the oxidant side facing down toward the EDOT. A small negative pressure was applied using a sink aspirator, in order to seal the chamber. The chamber was kept at 50 °C which has been shown to promote the formation of highly conductive PEDOT films [26]. The film was removed after 45 min, washed thoroughly with ethanol, dried under nitrogen gas and then heated at 100 °C for 5 min. The resulting film can be seen in Fig. 2B.

2.4. Sample characterization

Conductivity measurements were performed using a custom fabricated 4 point probe, equipped with gold coated tips mounted on springs to maintain constant contact on the material. Voltage measurements were taken using a Keithley 182 Voltmeter coupled with a Keithley 220 programmable current source. Resistivity during bending was measured using a 2 point probe, where each probe was attached to opposite ends of the film by applying layers of copper and carbon tape to ensure contact during flexing.

Thickness values were taken using a Dektak profilometer and cross-sectional scanning electron microscopy (SEM). SEM images were taken on a Zeiss Supra 55VP field-emission SEM. Cross sections were prepared using a JEOL SM-09010 cross section polisher. UV–vis absorption measurements were taken with a PerkinElmer Lambda 2S UV–vis spectrometer using a clean sample of PET as reference.

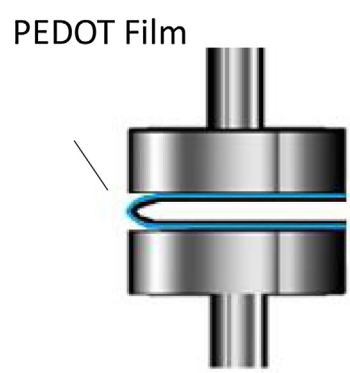

Fig. 2. Schematic of Instron bending experiment. PEDOT is shown facing out.

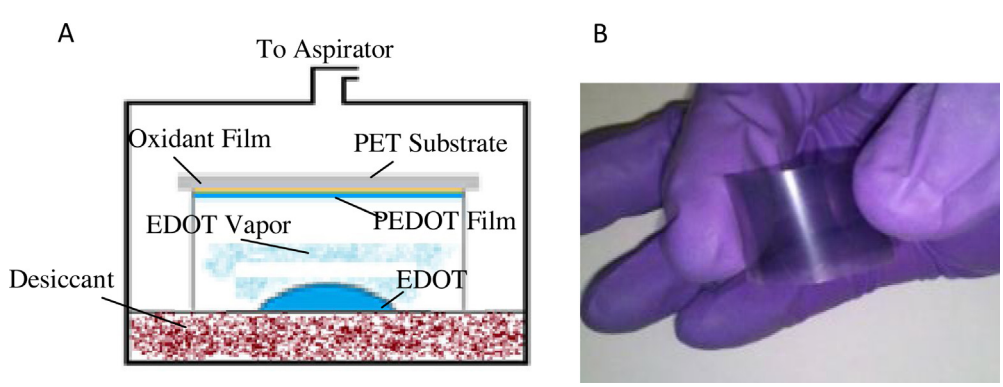

Fig. 1. (A) Schematic of the chamber used for VPP of PEDOT: the PET substrate is suspended on a petri dish which is filled with EDOT vapor. The chamber is sealed and partial vacuum is applied using an aspirator. (B) Picture of a flexed VPP PEDOT film on PET.