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A Versatile Technique for the Fabrication of PEDOT: PSS Films for Organic Solar Cells

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Abstract

Organic solar cells hold the potential of low-cost production as compared to inorganic solar cells, as well as the increase in efficiency. To realize these possibilities, the key is to fabricate most of the functional films in requisite structures via ambient solution-processed techniques. The PEDOT: PSS films, which are commonly used as an anode layer in organic electronic devices, were deposited on large-area ITO glass substrates under optimized conditions. The spin, spray, brush and brush+spray-coating techniques were utilized to examine their suitability in the fabrication of organic solar cells (OSCs). The films were characterized for their morphology, molecular structure, optical and electrical properties and results are compared with the existing data. A smooth and thin films of PEDOT: PSS were obtained by "Spray+Brush" coating method with attractive sheet-conductivity having potential in fabricating OSCs with different architectures.

Key words: Organic solar cells; PEDOT: PSS films; Solution-processed techniques

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INTRODUCTION

The Organic Photovoltaics (OPVs) has seen unprecedented growth during the past decade because of its lower-cost, durability, flexibility, and adaptable substitute for rigid silicon solar cells (Vasselinka, Rudolf, & Adolf, 2009; Zheng & Xue, 2010; Liang & Yu, 2010). Silicon-based solar cells fabrication processes are expensive and complicated involving clean rooms, lithography, and vacuum chambers. Efforts have been made, in the recent past, to improve organic solar cell performance using new materials, novel architectures, and new techniques for mass production. Solution processed techniques like ink-jet printing; spin coating, spray depositing etc, hold greater potential and prove cost-effectiveness in fabricating the OPV's (Na *et al*., 2010; Green *et al*., 2008; Ouyang *et al*., 2004). High efficiencies can be gained, by performing the fabrication steps inside a nitrogen glove box. Additionally, the widely used OPVs geometry utilizes aluminium or calcium metal contacts. Since, the performance of the films deteriorate over time, the cells cannot be operated without encapsulation. In this geometry, it is possible to use noble metals at top electrodes and avoid performance losses due to top contact oxidation. Other approach is the insertion of a thin layer of poly (3, 4-ethylenedioxythiophene): poly(styrene-sulfonate), hereafter referred to as PEDOT: PSS, underneath the top contact. The PEDOT: PSS layer can lower or raise the work functions of the cathode or anode, or enhance the cohesion, and thus lower the interfacial series resistance. Moreover, it is commonly used in non-inverting organic solar cells to enhance the hole-collection and thus improve the efficiency of organic solar cells (Vasselinka *et al*., 2009). Thus, importance of PEDOT: PSS film warrants fabrication of low cost OPV's via low low cost solution processing techniques such as spray and brush coating.

In the present study, several film-depositing techniques of PEDOT: PSS on ITO glass substrates, namely spin-coating, spray-coating, brush-painting and spray+brush (both together) were explored. It was demonstrated that coating technique "S*pray+Brush*", without the use of special machine such as a spin-coater, is a viable alternative.

In order to examine the usability of PEDOT: PSS in solar cells, ITO/PEDOT: PSS/Ag device structures were designed, fabricated and characterized for morphological, molecular-structural, optical and electrical properties.

1. EXPERIMENTAL DETAILS

1.1 Materials

PEDOT: PSS with 2.2-2.6% H_2O [#655201-25G; high conductivity grade], N, N-Dimethylformamide (DMF) [#270547-1L; chromasolv plus grade], deionized water and the Indium Tin Oxide (ITO) supported on glass substrate [#C1737-0107] with sheet resistance of 20 ohm/sq were obtained from Sigma Aldrich.

1.2 Instruments and Characterization Techniques

The ITO substrates were ultrasonicated using an Ultranet Sonic Cleaner. The Spin-Coater utilized was Laurel Technologies [model P6250]. The brush-coatings were performed by artistic brushes. The task of spray-coat on the films was undertaken by a Central Pneumatic Spray Pump (1/8″- 28 NPS). The morphology of films was recorded microscopically by an Aigo Digital Microscope [model EV5610; 10X]. The molecular structure of the PEPOT: PSS films on ITO were determined using a Raman microscope (Optronics Raman-785 Spectrometer) with the excitation wavelength of 785 nm. An incident laser beam was normal to the surface of the glass substrate. The electronic absorption spectra were obtained with a Cary UV-Vis Spectrophotometer in the range of 350-800 nm. The J-V and surface conductivity of films was determined using a well-known 2-terminal configuration via a Keithley 617 Programmable Electrometer.

1.3 Fabrication Methodology

The ITO-glass substrates were subjected to ultrasonic cleaning in acetone for 20 minutes and were rinsed multiple times with deionized water to remove any traces of unwanted sediments. The glass substrates were then set to dry in an oven in air for an hour. For the fabrication of PEDOT: PSS films (also designated as films) via different techniques with enhanced conductivity, DMF solvent was used**.** In order to achieve perfect homogeneity of solution, 1:2 proportions of PEDOT: PSS solution and DMF (designated as PEDOT: PSS-sol) were stirred for about 18 hours. The films were then annealed at 120 ºC for few minutes on hotplate and then it was turned off to cool to room temperature.

1.3.1 Fabrication of Films via Spin-coating (S)

The PEDOT: PSS layer was spin coated on the ITO substrate with a spin rate of 1000 rpm for 20 s.

1.3.2 Fabrication of Films via Brushing (B)

Films was brush coated on a horizontal plane and is allowed to dry in an oven for 5 minutes.

1.3.3 Fabrication of Films via Spraying (Spr)

The spray-coated substrates on a horizontal plane would leave sediments and inhibit defects, like water edges, which eventually affect the conductivity patterns. Thus, the films were spray coated at an angle of 45º on a hotplate at 120 ºC. This adopted unique approach allowed the water molecules trapped under the spray layer to evaporate as well.

1.3.4 Fabrication of Films via Coalesced Brushing and Spraying (B-S)

Films using PEDOT: PSS solution was brush coated on a horizontal plane and is allowed to dry in a closed chamber for 5 min. The semi-wet films are then spray coated at a certain angle as stated above. It is worth mentioning that the PEDOT: PSS solution was not highly viscous, and hence the pressure of the spray makes it hard to adhere to the brush layer. The spray angles and distance from the substrate were optimized in order to avoid the water edges and striations.

1.3.5 Fabrication of the Device for Testing

A schematic diagram of the device (ITO/PEDOT: PSS/Ag) designed and fabricated for investigation of electrical properties is depicted in Figure 1.

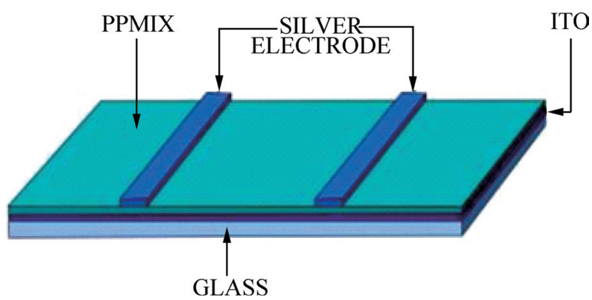


Figure 1
A Schematic Structure of the Device (Ag/PEDOT: PSS/ITO)

2. RESULTS AND DISCUSSION

2.1 Morphological and Structural Characterization

Table 2 demonstrates the surface morphology of PEDOT: PSS films fabricated via various techniques. The optical microscope image of spray-coated film is not smooth but shows pancake boundaries and sediments. It is evident in the brush deposited film, pancake boundaries vanished with appearances of undesirable brush markings such as striations. As anticipated, the surface of spin-coated film was quite uniform. However, some defects such as striations, chuck-marks, and water-edge effects were noticed. The morphological studies of optical microscope image in Table 1 exhibits, the proposed optimized "S*pray+Brush*" coating technique has two fold advantages: smooth and uniform film; and cost-effective as compared with expensive spin coating technique. Thus, cost of fabricating OPVs could be drastically reduced. It is worth mentioning, coalescence of macroscopic pancakes occurred to give smooth film due to methodology adapted: PEDOT: PSS films were brush coated and allowed to dry in oven for 5 minutes; and then semi-wet films spray coated at pre-determined angle on a hot plate (120 ºC) with a velocity of 2 to 3 m/sec, which inhibit defects by allowing water molecules trapped under the sprayed layer to evaporate. Thus, yielding a homogeneous layer of PEDOT: PSS via sufficient wetting as well. The spray coating on the substrate placed horizontally would leave sediments and create defects. The above-mentioned defects will eventually affect surface conductivity patterns, which will degrade the performance of organic solar cells.

Table 1
Summary of Various Techniques Utilized for the Fabrication of PEDOT: PSS Films

Parameters technique	n	E_{OG}	OD	OC	Reference #
S-pp	1.59	3.58	0.102	1.76	Present work
B-pp	1.58	3.61	0.092	0.67	Present work
Spr-pp	1.68	3.57	0.127	0.098	Present work
S-B-pp	1.58	3.59	0.098	1.41	Present work
Spin-pp	1.65	--	--	--	8

n - Refractive Index, E_{OG} - Optical bandgap, OD - Optical density, and OC - Optical conductivity

The molecular structural characteristics of as-prepared PEDOT: PSS films on ITO substrate fabricated utilizing spin and "Spray+*Brush*" techniques can be deduced by Raman spectra shown in Figure 2. The attribution of the main bands has been made considering the data reported in the literature (Ouyang *et al*., 2004). The spectra are mainly characterized by intense band centered at about 1400 cm^{-1} and ascribed to symmetrical $C_\alpha = C_\beta$ (-O) stretching mode (Ouyang *et al*., 2004). No bands of PSS were observed. However, there is a slight upward shift in the band between spin and "S*pray+Brush*" coated films indicating quality of both the films is same.

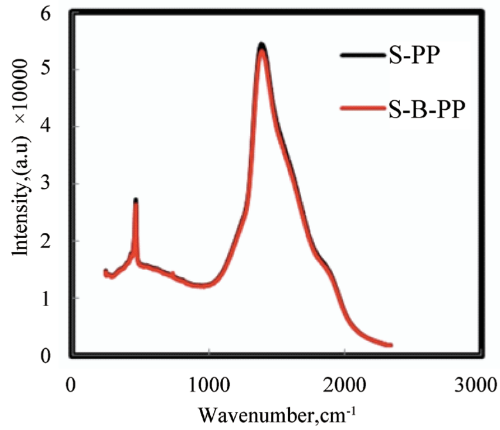
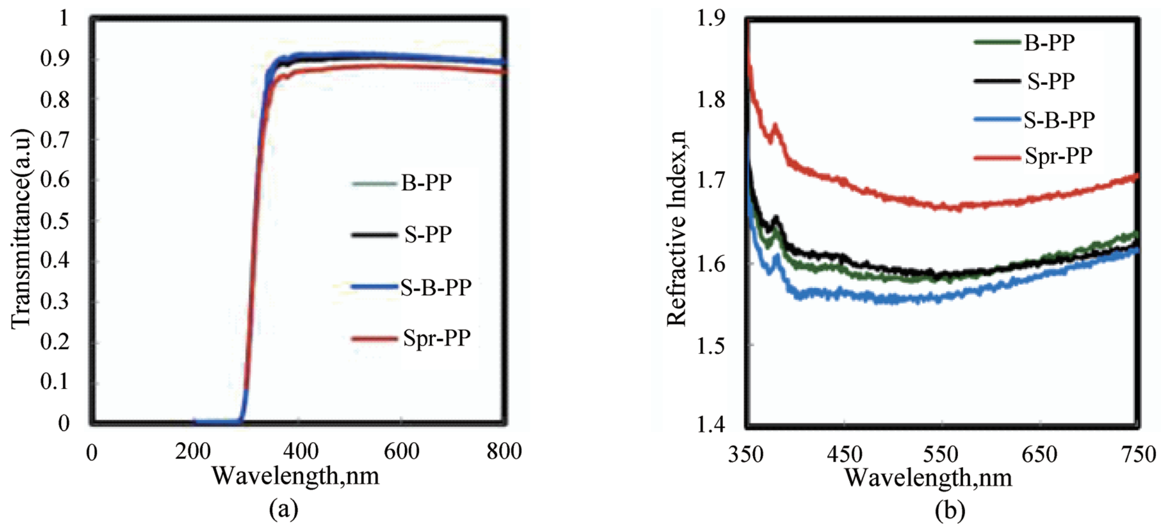


Figure 2
Raman Spectra of PEDOT: PSS Film on ITO Coated Glass

2.2 Optical Characterization

The films produced with various techniques were characterized by UV-visible transmittance spectra, refractive index, absorption intensity (optical density) and optical conductivity as shown in Figures 3(a), (b), (c) and (d) respectively.



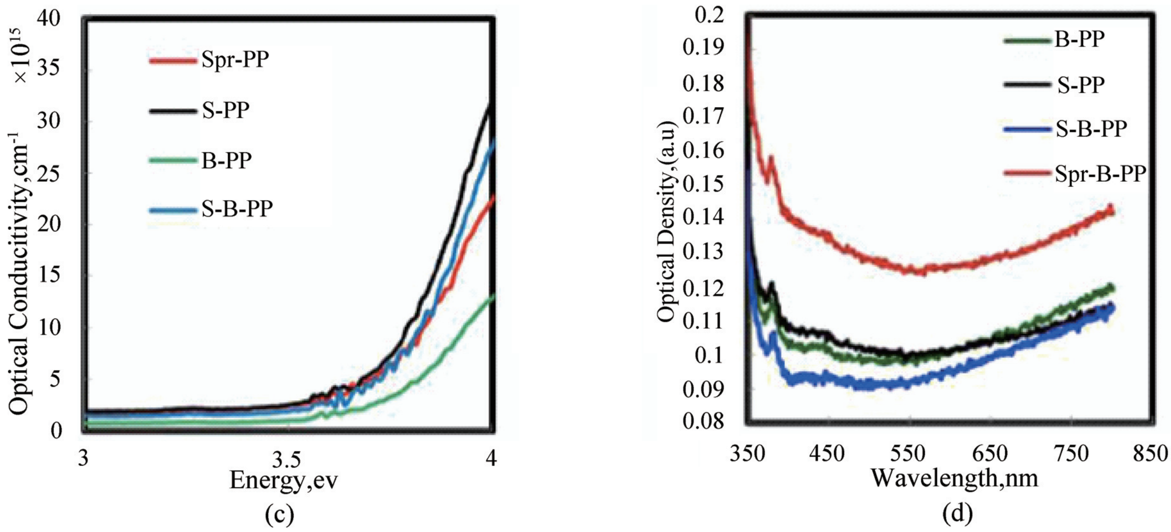


Figure 3
Optical Spectra of PEDOT: PSS Films on ITO Glass Fabricated (a) Transmittance, (b) Refractive Index, (c) Optical Conducitivty, (d) Optical Density

All the PEDOT: PSS films fabricated were highly transparent in the visible region (Lee, Lee, Kim, Lee, & Kim, 2010), as shown in Figure 3(a) all the films exhibited similar transmittance spectra (while the strong absorption below ~350 nm is due to the ITO-glass substrates). It was found that the transmittance of spray coated PEDOT: PSS film was slightly decreased due to non-uniform deposition. The spin and "*Spray+Brush*" coated films have identical transmittance,further confirming quality of films. Interestingly, the optical density and refractive index became higher for spray-coated film. This can be attributed to the influence of light scattering in the grain (pancake) boundary regions and/or possible pinholes. The above-cited optical parameters are tabulated in Table 2 for brevity and comparison with literature values (Dexi Zhu, Weidong Shen, Hui Ye, 2008; Mauger & Moule, 2011). The optical band gap (E_{og}) was determined by analyzing the optical data with the expression for optical absorption coefficient (α) and the incident photon energy (hν) using the relation (Dolakia, Solanki, Patel, & Agarwal, 2003):

$$\alpha h\nu = A(h\nu - E_{og})^{n/2} \quad (1)$$

Where A is a constant, the value of n is eqaul to one for a direct-gap material, and four for an indirect-gap material. The plots of $(\alpha h\nu)^2$ versus $h\nu$ were drawn using the above equation. Extrapolation of the linier portion of the plot to photon energy axis yielded the direct band gap as shown in Figure 4 for various PEDOT: PSS films fabricated and are also listed in Table 2.

Table 2
Conductivities of PEDOT: PSS Films Fabricated via Different Methods

Solvent	Technique	Film	Surface area (cm×cm)	Conductivity (S/cm)
-	-	ITO	2 × 2	3600
-	Spin	PEDOT: PSS	2 × 2	0.031
DMF	Spin	PEDOT: PSS	2 × 2	102.04
DMF	Spray	PEDOT: PSS	2 × 2	91.45
DMF	Brush	PEDOT: PSS	2 × 2	77.28
DMF	Brush+Spray	PEDOT: PSS	2 × 2	98.87

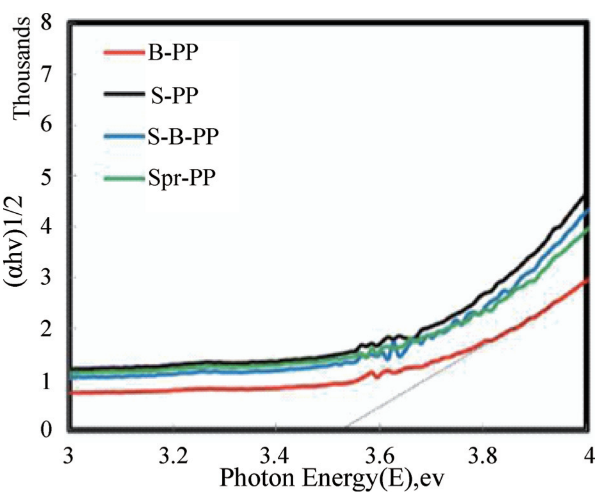


Figure 4
A Plot of $(\alpha h\nu)^2$ Versus Incident Photon Energy of PEDOT: PSS Films

2.3 Electrical Characterization Through J-V and Surface Conductivity Measurements

The dark current density-voltage (J-V) characteristics of the device (Figure 1), measured at room temperature are shown in Figure 5. A linear response up to ~ 2.0 volts confirms that PEDOT: PSS contact with silver electrode is indeed ohmic due their approximately equal work functions [PEDOT: PSS (4.8-5.3eV); Ag (4.73eV)](Tsang, Tse, Tong, & So, 2006). The slight higher leakage current observed at higher voltage in spin coated film might be due to uneven surface. However, concrete explanation can be given by testing via atomic force microscopy. The results of surface conductivity are illustrated in Figure 6 for films fabricated utilizing variety of techniques. Table 3 summarizes the surface conductivity parameters of PEDOT: PSS films fabricated via different techniques including with and without the solvent. The maximum conductivity was observed in the film fabricated by "*Spray+Brush*" among unconventional methods investigated such as spray and brush coating. The lowest conductivity was observed in Brush coated films. The electrical properties of films fabricated are strongly dependent on their morphology and chemical and physical structure (Mantovani, Janssen, & Kemerink, 2008). Thus, change in-conductivity will depend on the technique used affecting long-range hopping transport.

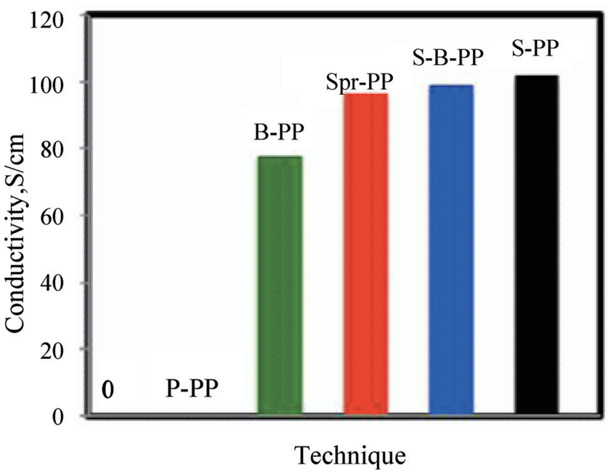


Figure 5
Surface Conductivity of PEDOT: PSS Films

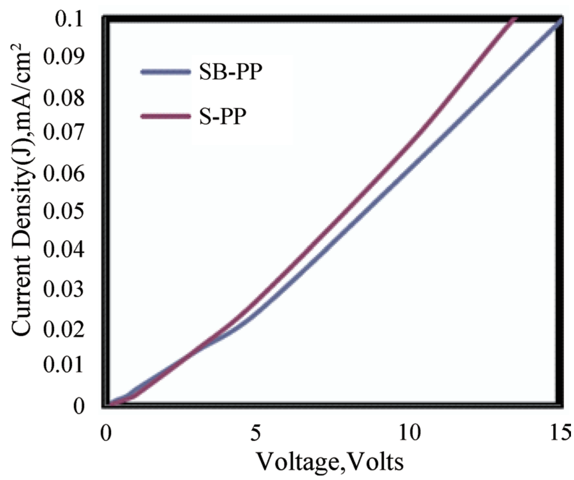


Figure 6
The Dark Current Density Versus Voltage of PEDOT: PSS Films

CONCLUSIONS

In summary, highly cost-effective fabrication of conductive PEDOT: PSS anode films using simple "*Spray+Brush*" deposition method were demonstrated. In this article, we assert on the method employed in fabrication of films modifies the morphological, optical, and electrical properties. However, The promising performance of PEPOT: PSS via "*Spray+Brush*" in terms of conductivity close to spin-coated film and also simplicity and low cost of their fabrication would make it possible to integrate not only in OPVs and also into more complicated electronic structures to build future disposable electronic devices on mechanically flexible substrates. Further work is in progress to fabricate submicron thickness films under optimized conditions.

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The concept and design was given by Dr. A. K. Batra. The execution of the experiments and characterization of films was performed by graduate student A. K. Chilvery, Drs. A.K. Batra, Raja Surabhi and P. Guggilla analysed the results and wrote the manuscript. Dr. R. B. Lal critically reviewed the manuscript.

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