

ELECTROSPUN NETWORK STRUCTURE FOR ORGANIC PHOTOVOLTAIC DEVICE

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ABSTRACT

In this paper, the enhancements in the light harvesting of photoactive materials by fabricating hierarchical structures were examined using electrospinning. Electrospinning due to ease of processing, has become an attractive technique for fabrication of polymer fibers ranging from sub-microns to few nanometers. Here we present a uniform network structure obtained by electrospinning of a conducting polymer blend; poly (3 hexyl thiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM). The study was carried out by varying the processing parameters like voltage applied, flow rate, tip-to-collector distance while solution concentrations, needle gauge, fabricating time were kept constant. Scanning electron microscopy and optical microscopy were used to evaluate the morphology changes with respect to varying processing conditions. The dictating parameters on the evolving structure were high voltage, tip to collector distance and solvent used. It was observed that there was an upper and lower limit to the voltage applied, and flow rate used, to get uniform network. Moving away from either of the limits leads to irregular deposition. Optical properties due to structured architecture showed enhancement in the internal reflection and in turn leading to higher light absorption. Opto-electrical characteristics of these devices showed higher order of response in comparison to standard film devices. This structure was evaluated for better light harvesting, and enhanced pathways for charge transportation as active layer architecture in an organic photovoltaic devices. Hence a step towards better light and charge management is possible by tuning the morphological structures of photoactive materials with optimized process parameters by electrospinning.

INTRODUCTION

Organic photovoltaic (OPVs) are an interesting class of devices and are explored widely due to their inherent properties of low-energy fabrication, and ease of processability compared to inorganic solar cells. Also organic conducting materials have an advantage over other material devices for collection of photons even in diffuse sunlight. With extensively studied donor acceptor combination being poly (3-hexylthiophene):

phenyl C61-butyric acid methyl ester (P3HT: PCBM) blend, used as active layers in bulk heterojunction (BHJ) devices.

Commonly employed processes of fabricating the active layers are spincoating, doctor blade method,[1] whereas more sophisticated methods utilized are template assembly and devices on patterned substrates. However, all these techniques creates a thin film surface with nearly no morphology. On other hand two dimensional nanostructures like fibers could be a better alternate from the fact that continuous long distance charge transport can be efficiently attained due to the directionality for the charge species given by the nanofibers compared to thin film active layers.

Electrospinning (ES) is a relatively simple technique to generate micro-to nanofibers and significantly valuable in controlling the morphology. In ES, high voltage potential is applied between syringe containing polymer solution and a grounded collector. It has various process parameters like applied voltage, flow rate, tip to collector distance, needle gauge and fabrication time to regulate the size and shape of the final fiber and also materials parameters like solvent employed, solution concentration, to modify the morphology. Therefore ES has become quite a popular technique in aspects of customized morphology and has numerous applications as in bioengineering like tissue scaffolds, in filtration membranes via nano porous fibers. Furthermore it is also gaining acceptance in energy related field like in supercapacitor, Li batteries, field effect transistors (FETs), fuel cells and OPVs due to its straight-forward nature of processability.

Electrospinning has been reported in fabrication of organic field effect transistors (OFETs) with P3HT: polystyrene fibers and P3HT: polycaprolactone fibers [2-4] While in the area of OPVs, studies such as electrospun solar cloth of P3HT:PCBM: poly (vinyl pyrrolidone) [5] P3HT:PCBM: polycaprolactone as sheath material in coaxial electrospinning have been illustrated.[6] Furthermore, electrospraying of P3HT:PCBM using additives like diiodooctane have been described.[7] Hence several studies using electrospinning for organic devices as OFETs and OPVs have been examined. However process parametric centered study with respect to electrospinning and its morphology on OPVs has not been explored. Process

parametric studies for OPVs for other fabrication processes have been reported. [8,9]

In this study electrospinning has been carried out by varying solution parameters such as solvent, polymer blend concentration and process parameters such as applied voltage, tip to collector distance, flow rate and deposition time. Morphological and optical studies were analyzed to evaluate the influence of electrospinning parameters and opto-electrical characterization were carried out by fabricating a OPV device with optimized parameters and obtained enhancement in device efficiency.

EXPERIMENTAL

Materials: Regioregular P3HT from Rieke metals, Inc. PCBM from Nano-C, and chloroform, analytical grade from S D fine chem. Ltd all were used as received. Indium tin oxide (ITO) coated glasses were purchased from Delta Tech. with sheet resistance of 70-100 Ω .

Electrospinning. A horizontal set-up consisting of high voltage source (Gamma RR50) with maximum capacity of 50 kV and syringe pump (Holmarc SPL-2D) was used to perform the optimization and fabrication. Chloroform was the choice of solvent. P3HT:PCBM ratio of 1:0.8 was kept constant throughout whereas overall polymer blend concentration was 54 mg ml⁻¹. Applied voltage range was 25 kV, flow rate was 6 ml/hr, tip to collector distance (TCD) was 8 cm, deposition duration was 30 sec. All the experiments were carried out in ambient conditions.

Device fabrication. ITO coated glass were etched selectively with HCl, HNO₃ and DI water in the ratio of 1:1:5. Etched ITO's were thoroughly rinsed using soap solution water and acetone and sonicated using water, acetone and isopropanol for 5 min each and subsequently cleaned the substrate surface using UV-Ozone chamber for 10 min. Poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) PEDOT:PSS from Baytron Clevis with a drop of Triton-X®, as surfactant was sonicated for 5 min and filtered using 0.45 μm syringe filter. A layer of PEDOT:PSS of thickness about 50 nm was spincoated (SC) on substrates at 4000 rpm and annealed at 130°C for 15 min. After annealing substrates were allowed to cool down to room temperature on the same hot plate. Glass substrates were stuck to aluminium foil collector using double sided tape and electrospinning was performed at optimized conditions of 25 kV-8 cm-50 $\mu\text{l min}^{-1}$ for 30 sec. The substrates were further divided into two batches marked as ES and ESSC. For ESSC batch a layer of P3HT:PCBM were spincoated after ES, at 1000 rpm to fill the area between the network structure. Another batch of substrates marked as SC, were also spincoated at 1000 rpm. All three batches (Figure 1) were annealed at 110°C for 15 min. P3HT:PCBM solution for ES and SC had difference in concentration with ratio of (ES:SC) 1.5:1. Aluminium electrodes of thickness ~100 nm were deposited on the substrates with active area of 1 mm². Subsequent to electrospinning further fabrication and characterization of devices were carried out in glove box.

Schematic representation of three types of active layer are shown in figure 1, as can be seen device architecture remains the same, just an active layer morphology changes due to various fabrication steps; spincoating produces a uniform layer, while electrospinning generates much uneven surfaces, and furthermore electrospinning and spincoating will have a network structure and spincoated matrix to prevent rough surfaces.

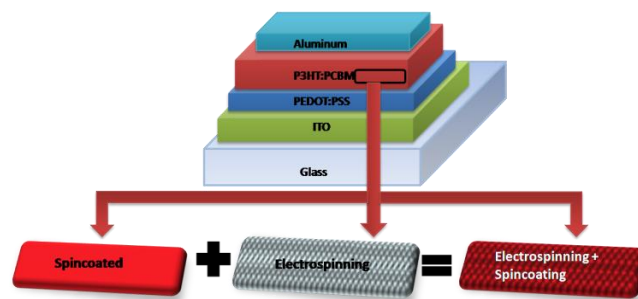


Figure1. Schematic representation of three types of active layer: electrospinning, electrospinning and spincoating and spincoating.

Characterization. Morphological studies, were performed using SEM (ESEM Quanta 200 FEI) and FESEM (Carl Zeiss Ultra 55), samples were sputtered with gold before imaging. For optical properties, aluminum coated glass were used as substrates to fabricated ES, ESSC and SC batches and characterization was carried out with integrating sphere (lampsphere) diffuse reflectance spectroscopy using Lambda 35 UV/Vis spectrophotometer to determine percent reflectance (%R). Current – voltage (I-V) characterization was performed under AM 1.5 solar radiation with power density of 100 mWcm⁻² using Newport Oriel full spectrum. I-V characteristics were obtained using Keithley 4200 semiconductor parametric analyzer.

RESULTS AND DISCUSSIONS

Morphological analysis as shown in figure 2(a), suggests electrospinning of P3HT: PCBM blend forms a 3-D network structure that has penetrated across several layers and exhibits a porous nature. Figure 2b shows the network structure obtained on larger scale with more than 300 μm coverage area. Fiber morphology was governed by parameters like type of solvent, due to its evaporation rate and depending on flow rate that is the rate of volume dispensing for controlling the size.

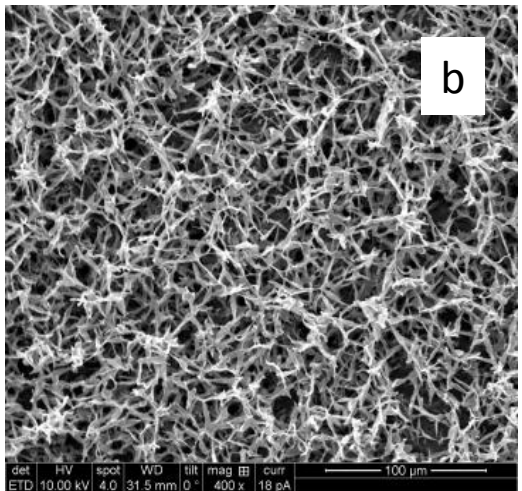
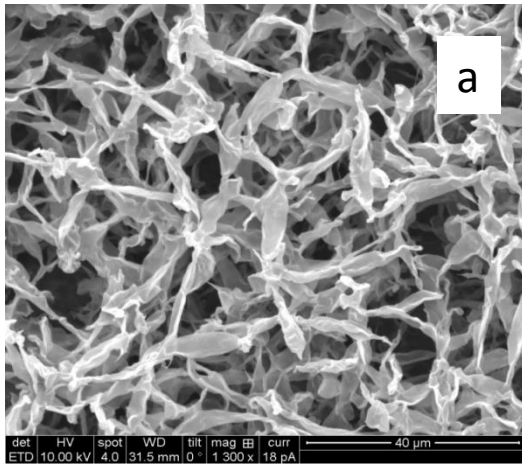


Figure 2: Scanning electron micrographs of electrospun P3HT:PCBM blend.

Optical Characterization: As observed through the scanning electron micrographs, electrospinning has changed the morphology; hence this morphology assists in increase in surface area, in turn increases in light absorption by enhanced scattering inside the matrix. To quantify this, diffuse reflectance spectroscopy was carried out at absorption range of 400-550 nm and as can be observed from the figure 3 there is a decrease in reflectivity for electrospun and spincoated sample than spincoated sample and electrospun sample. The decrease in reflectivity was found to be ~ 6-10 %. This result suggests that morphology can be used as a parameter for light management in these types of devices. Aluminium (Al) was used as standard as it has higher reflectivity.

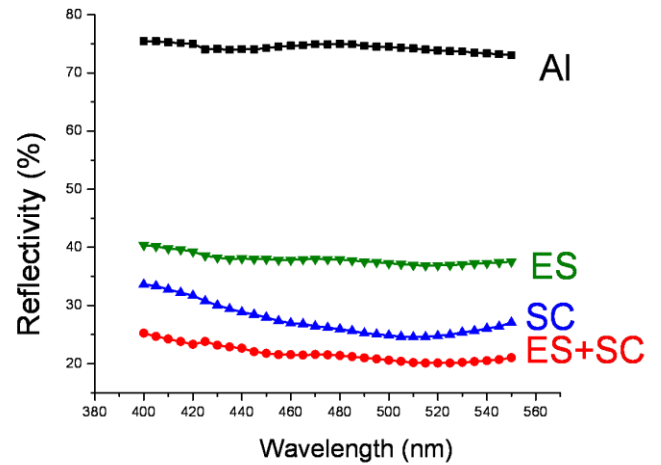


Figure 3: Optical graph of P3HT:PCBM blend using diffuse reflectance spectroscopy.

Opto-electrical Characterization: I-V characterization showed electrospun (ES) device gives an efficiency of mere 0.13%, that may be due to the uneven interfaces between active layer and cathode and also as electrospinning was performed outside glove box, this would have resulted in partial oxidation of P3HT. However, a considerable increase in efficiency from 2.18% to 3.66%, from SC to ESSC architecture was observed in figure 4. With short circuit current I_{SC} , open circuit voltage V_{OC} fill factor FF and photon conversion efficiency (PCE) details given in table 1. As can be observed, change in V_{OC} of ESSC and SC, is marginal; 0.01V, although I_{SC} has increased significantly. This suggests that network and porous structure due to higher surface area, absorbs more light by imparting more torturous pathway for light before exiting the active layer as reflected light. In addition network structure facilitates charge transportation in the active layer matrix.

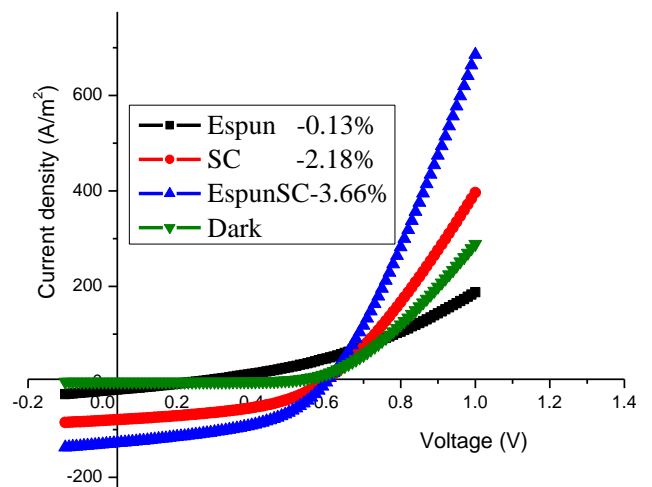


Figure 4. Current density versus voltage characteristics for electrospinning, electrospinning spincoating and spincoating devices.

	J_{SC} (A/m ²)	V_{oc} (V)	FF	Eff (%)
Espun	190	0.25	0.27	0.13
SC	812	0.59	0.45	2.18
Espun+SC	1310	0.60	0.47	3.66
Dark	1.28E-02	0.23	0.41	0.00

Table 1: I-V characteristics data for electrospinning, electrospinning spincoating and spincoating devices

CONCLUSION

For better light and charge transportation management, optimized electrospinning was carried out to fabricate electrospinning (ES), electrospinning and spincoating (ESSC) and spincoating (SC) devices to obtain a network structure of active layer (P3HT:PCBM). These structures in the matrix appear to decrease the reflectivity for ESSC samples compare to SC samples by 6-10%. Enhanced increased in short circuit current by an order of magnitude suggest that these structures impart better pathways for efficient charge transportation. Furthermore this electrospinning spin coating architecture can be explored for various other organic photovoltaic materials to study the effect of change in morphology on I-V characteristics.

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