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Research Article

Electrospun Polymer-Fiber Solar Cell

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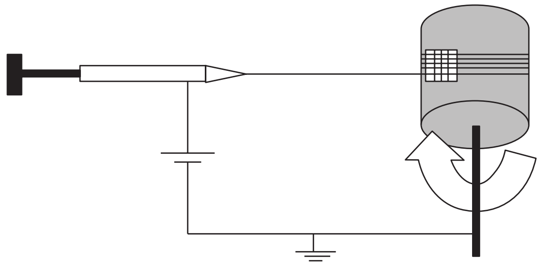
A novel electrospun polymer-fiber solar cell was synthesized by electrospinning a 1 : 2.5 weight% ratio mixture of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) resulting in bulk heterojunctions. Electrospinning is introduced as a technique that may increase polymer solar cell efficiency, and a list of advantages of the technique applied to solar cells is discussed. The device achieved a power conversion efficiency of $\eta = 3.08 \times 10^{-7}\%$. The absorption and photoluminescence of MEH-PPV nanofibers are compared to thin films of the same material. Electrospun nanofibers are discussed as a favorable structure for application in polymer solar cells.

1. Introduction

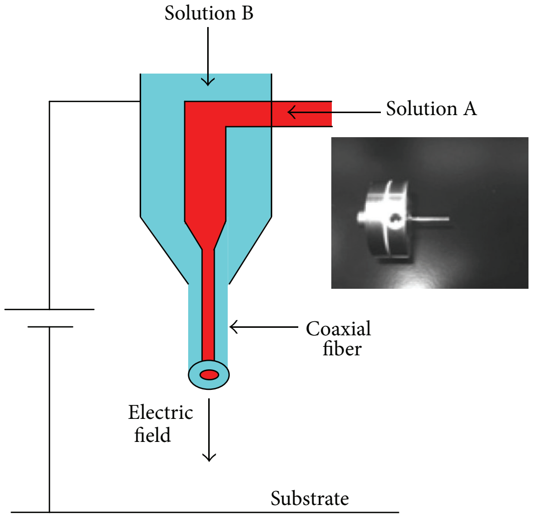
While the efficiencies of inorganic photovoltaics continue to improve, market penetration is still limited due to their high cost in comparison to nonrenewable energy sources. Studies have shown that the long lifetime of photovoltaic systems is often overlooked when calculating the cost of solar energy [1]. Nonetheless, the cost per kilowatt-hour for electricity from Si-based solar cells is as high as \$0.15–0.65/kWh [1, 2]. This is roughly 3 times more than the price of electricity produced using fossil fuels. In addition to the high cost of inorganic solar cells, the potential increase in demand for Si crystals can lead to even higher costs for the devices. By one estimate, the amount of silicon needed to supply electricity for a family consuming 20 kWh/day using 15% efficient solar cells is approximately 10,000 times more than the amount of silicon in a computer [3]. Clearly, a low cost alternative to inorganic solar cells is needed.

Polymer-based solar cells are being widely investigated as a potential low cost alternative to silicon because, in principle, they can be produced on a large scale using inexpensive solution-based processes such as spraying, painting, and roll-to-roll printing [4–6]. For example, it has been shown that the manufacturing cost of polymer solar cells can be reduced very quickly (from 35 to 8 Euros/W in one year) [4]. On the other hand, the lifetime of polymer solar cells is still too short to allow comparisons with crystalline silicon [4]. In addition to their lower cost, polymeric materials are lighter, have much greater mechanical flexibility, and are capable of being directly fabricated on to most surfaces including plastics [7].

Bulk heterojunction polymer solar cells convert light into electricity using a straightforward process. Photons are absorbed by an organic semiconductor (the polymer) resulting in the creation of mobile electron-hole bound pairs known as Frenkel excitons [8]. The electron-hole pairs are then separated at a polymer/electron-acceptor interface. Typical acceptors include titanium dioxide and carbon fullerenes. The holes travel through the polymer to the anode, and the electrons travel through the electron acceptor toward the cathode resulting in an externally measurable current. The device efficiency depends on a number of important design parameters. For example, electron-hole separation requires a symmetry breaking condition such as using electrode materials with different work functions to provide a preferred direction to the internal electric fields [9].



(a)



(b)

FIGURE 1: (a) Electrospinning with a grounded rotating drum. (b) Coaxial electrospinning.

2. Application of Electrospinning to Solar Cells

Electrospinning is a well-established technique that uses electrical rather than mechanical forces to draw polymer fibers from a solution. A typical electrospinning apparatus is shown schematically in Figure 1(a). An electrically conducting polymer solution, normally contained within a hypodermic syringe, is biased with respect to a counter electrode. The electric force on the solution produces a jet of liquid containing the dissolved polymer and solid fibers are formed and deposited onto the counter electrode as the volatile solvent evaporates. The electrospinning technique has been used to produce micro- and nanoscale fibers from various polymers as well as more advanced structures such as coaxial and even triaxial composites (Figure 1(b)). By creating core/shell structures with a "spinnable" polymer on the outside, coaxial electrospinning allows the formation of fibers from polymers that do not readily form electrospin on their own.

Applications of electrospun fibers are numerous and include filtration, tissue engineering, superhydrophobic coatings, protective clothing, and electrical and optical devices [10]. Because the structures produced by electrospinning can be produced at the nanoscale, there is an opportunity to apply this technique toward the development of organic photovoltaics. Small device lengths have the potential to result in improved charge collection without sacrificing collection efficiency. Increasing charge collection efficiency could lead to improved device efficiency and the simple fabrication method could result in lower cost and ease of scale-up.

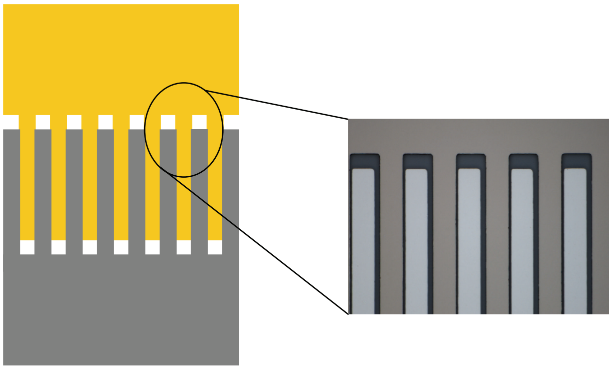
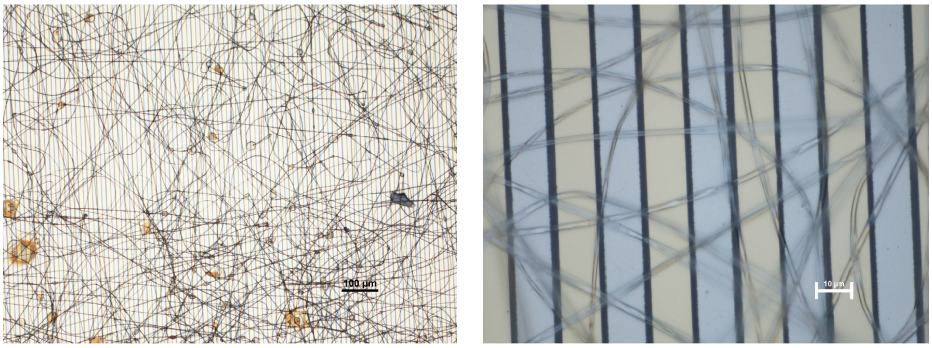


FIGURE 2: Interdigitated bimetal electrode.

Sundarrajan et al. recently reported photovoltaic cells from conjugated polymer nanofibers [11]. A coaxial electrospinning technique was utilized with a blended solution of poly(3-hexylthiophene-2,5-diyl) and [6, 6]-phenyl C61-butyric acid methyl ester (P3HT/PCBM) in chloroform/toluene (3.5/1 wt.-%) for the core and 10 wt.% Polyvinylpyrrolidone (PVP) in chloroform/ethanol (1/1 wt.-%) for the shell. The coaxial fibers were collected on fluorine-doped tin oxide (FTO) plate. After etching away the PVP shell by soaking in an ethanol solution for ~20 min, the nanofiber mat was then covered with an aluminum (Al) sputtered FTO substrate and clamped using binder clips. However, even with a structurally increased light harvesting ability, the electrospun P3HT/PCBM nanofiber yielded a relatively low photovoltaic efficiency of 8.7×10^{-8}.

A significant drawback in Sundarrajan's electrospun solar cell comes from its device structure, where the P3HT/PCBM nanofibers serving as the active layer of the device actually form a thick mat of ~5 μm. Because of low charge carrier mobility of P3HT/PCBM, a 5 μm active layer sandwiched between aluminum and FTO electrodes is far too thick for efficient charge transfer. For better implementation of nanofibers to solar cells, different device structures need to be considered.

In this paper, we report on the development and testing of electrospun polymer-fiber solar cells using coplanar interdigitated electrodes of dissimilar materials (Figure 2) [12]. This device structure offers some potential advantages in comparison to previously reported configurations. For example, coplanar interdigitated electrodes in electrospun polymer-fiber solar cells can utilize fibers with diameters <1 μm allowing for complete charge separation and collection. In addition, the interdigitated structure has an inherent reliability due to the incorporation of multiple junctions for charge collection. Finally, the use of nontransparent electrode materials may be advantageous.



(a) (b)

Figure 3: Optical microscope image of the collected coaxial nanofibers on coplanar bimetallic interdigitated electrode substrate at 10x (a) and 100x (b).

3. Experimental Procedure

An electrospun polymer-fiber solar cell was fabricated using a 2.28% weight concentration of poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] MEH-PPV : PCBM solution (1 : 2.5 weight ratio) prepared in chlorobenzene. All materials were obtained from Sigma-Aldrich. To prepare the MEH-PPV : PCBM solution, a base solution of 0.9% by weight of MEH-PPV in chlorobenzene was first prepared and stirred for 10 days. Then 24.8 mg of PCBM was added to 1 mL of the 0.9% MEH-PPV base solution. The prepared solution was directed through the inner core syringe, and a 10% by weight concentration of PVP in 8.5 parts ethanol and 1.5 parts DI water was directed through the outer shell syringe for coaxial electrospinning. The infusion rate for the inner core was 4 μL/min, and the infusion rate of outer shell was 25 μL/min. The needle to substrate distance was maintained at 11 cm, and the humidity was measured to be 16.9%.

The electrospun fibers were collected on a gold and aluminum coplanar bimetallic interdigitated electrode [12], and the electrode separation between the two gold and aluminum junctions was measured using an optical microscope and alternated between 1.61 μm and 2.34 μm. The electrodes were approximately 10 μm in width and the total area of the device was approximately 0.11 cm^2. However, only the area between the electrodes is expected to contribute to the photocurrent. For our device, the area between the electrode metal surfaces was approximately 15% of the total illuminated area (or approximately 0.017 cm^2). The separation between electrodes was limited by the available photolithographic equipment. Making narrower electrodes with a smaller separation between them would likely increase the output of the device. The actual area of the fibers is discussed below.

The collected fibers were immediately dipped in ethanol to remove the PVP shell and were dried on a 130°C hot plate. During deposition, the electrode substrate was mounted on a grounded rotating drum using copper tape. This leads to some degree of alignment of the collected fibers. However, the process of washing the fibers does cause some movement of the fibers and causes them to lose their alignment and agglomerate slightly.

To insure good contact with the measurement equipment, any residual PVP coating was removed from the external contacts by scratching the surface with a wooden stick, and silver paste was added prior to testing of the electrospun polymer-fiber solar cell device. The current-voltage (J-V) characteristics were measured using a Keithley 236 source generator by varying the applied voltage from –1 to 1 V in 0.0222 V steps across gold and aluminum electrode.

4. Results and Discussion

In order to most accurately characterize the photovoltaic performance of the electrospun polymer fibers, the number of fibers collected was kept relatively low. This allowed a countable amount of fibers for total active area calculation, while maintaining the device functionality. Figure 3 is an optical microscope image of the collected coaxial nanofibers at 10x and 100x magnification. The average fiber diameter before washing was approximately 1.8 μm and after washing was approximately 0.8 μm indicating that the PVP outer shell has been successfully washed away. Before washing, the devices were tested for photovoltaic characteristics and were found to be complete insulators. After washing, the devices displayed the current-voltage characteristics associated with photovoltaic devices (described below), further indicating that most of the PVP has been washed away.

5. Characterization of Electrospun Fibers

5.1. Absorption. The electrospun polymer fibers were tested by a series of optical characterization methods. A Perkin Elmer model Lambda 40 UV-Vis spectrophotometer was used to study the change in absorption of electrospun MEH-PPV nanofibers. These fibers did not contain PCBM. Various concentrations of MEH-PPV with 0.24, 0.35, 0.47, and 0.7 weight % in chloroform were coaxially electrospun, and their absorptions were measured after PVP extraction with ethanol. Results of these absorption measurements are presented below in Figure 4.

The absorption peak of the MEH-PPV thin film was measured at 514 nm. A significant red shift was observed for all concentrations of MEH-PPV nanofibers. The nanofiber made using a 0.7% concentration solution was the highest recorded red shift. The absorption bands also show broadening with

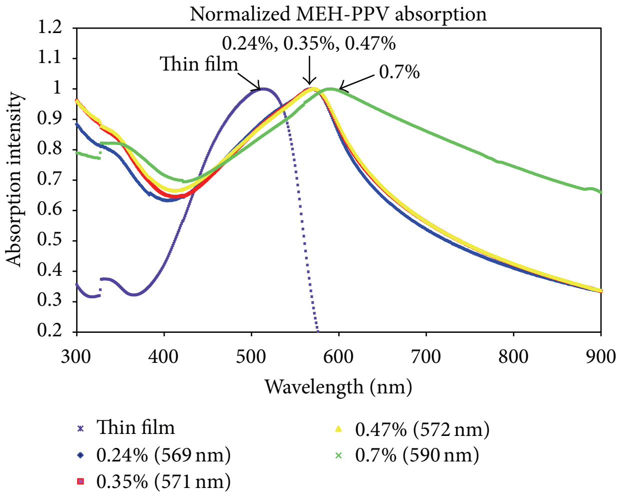


FIGURE 4: MEH-PPV absorption of 0.24%, 0.35%, 0.45%, and 0.7% concentrations in chloroform. All curves were normalized to their maximum value.

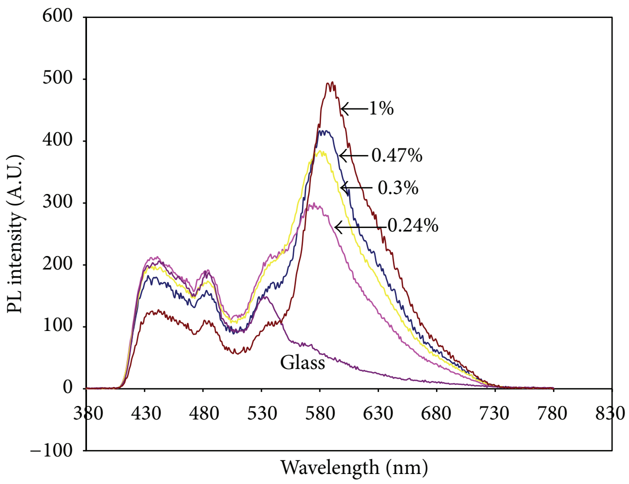


FIGURE 5: Photoluminescence of MEH-PPV nanofibers made from varying concentrations of MEH-PPV solutions. Excitation wavelength was 365 nm.

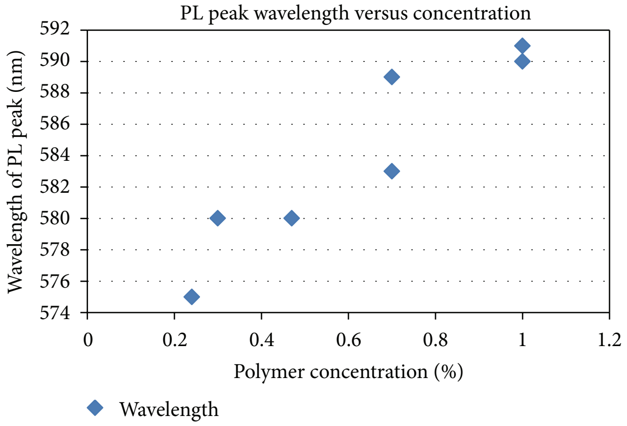


FIGURE 6: Photoluminescence peak wavelength of nanofibers as a function of the polymer concentration used to form the fibers.

increased concentration. Similar broadening and red shifts have been reported previously and attributed to extension of the polymer chains in the fibers resulting in an increase in the π-conjugation length [13]. Recently, Balderas et al. produced a similar absorption red shift in fibers electrospun from a blend of MEH-PPV and poly(9-vinylcarbazole) (PVK) [14]. They attribute the red shift to changes in the interaction between the polymer chains and in their interconnectivity. This may imply the presence of residual PVP in the MEH-PPV fibers in our experiments.

Regardless of the source, the red shift can potentially increase the optical absorption of the device and therefore increase the efficiency.

5.2. Photoluminescence. Photoluminescence (PL) measurements were performed using a QM-3 Quanta-Master luminescence spectrofluorometer on MEH-PPV nanofibers (again, no PCBM) and Figure 5 shows a series of measured PL spectra.

To make these plots, the collected coaxial fibers on glass microscope slides were soaked in ethanol for 2 hours to remove the PVP shell followed by PL measurement of the MEH-PPV nanofibers. In general, as the concentration of the solution increased, a consistent increase in PL intensity was observed. The main peak around 580 nm is known to be strongly influenced by the degree of polymer interchain interactions and aggregate states where the PL intensity has been shown to be lower for interactive aggregate states [15]. Typically, higher concentration solutions will deposit more material on the surface potentially explaining the higher PL intensity.

Figure 6 shows the wavelength for the PL peak as a function of polymer concentration. As with the absorption spectra, the peak is red shifted with increasing polymer concentration and supports the idea of an extension of the polymer chains in the fibers resulting in an increase in the π-conjugation length [13].

The electrospun polymer-fiber solar cell (MEH-PPV: PCBM) was further evaluated by measuring its J-V curve as shown in Figure 7.

The J-V curve shows a photovoltaic response with an open-circuit voltage V_{oc} of 0.11 V and a short-circuit current I_{sc} of 3×10^{-7} mA. When the *total* area of the device is considered ($0.11\,\text{cm}^2$), the short-circuit current density is $J_{\text{sc}} = 2.73 \times 10^{-3}\,\mu\text{A/cm}^2$. The fill factor was ff = 0.43 while the power conversion efficiency is calculated to be $7.92 \times 10^{-10}\%$ based on the *total* area of the coplanar bimetallic interdigitated electrode. However, to determine the efficiency of the fibers alone, the area can also be estimated from the number of gold-nanofiber-aluminum junctions using the diameter of electrospun nanofibers. The diameter of the nanofibers was measured to be around 1 μm from optical microscope. By estimating the number of potential devices and using the area of the fibers that lies in between two electrodes (diameter × electrode separation × number of fibers), the short circuit current density is increased to

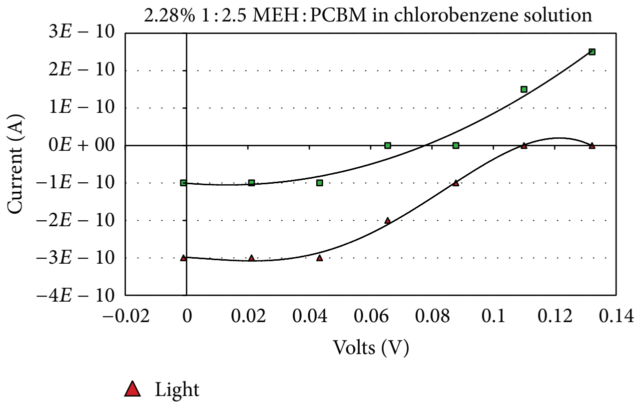


Figure 7: *J-V* curve measured for MEH-PPV : PCBM nanofibers on coplanar bimetallic interdigitated electrode. Red triangles are the device response with AM1.5 illumination of 80 mW/cm^2, and green squares show the response with the device placed in the dark. The curves are polynomial fits to guide the eye.

$J_{sc} = 0.525\,\mu\text{A/cm}^2$ and the power conversion efficiency for the electrospun polymer-fiber solar cell is estimated to be 3.08×10^{-7}% or better. By counting the number of fibers, the efficiency calculation becomes independent of the number of fibers and therefore more reproducible.

6. Conclusion

An electrospun polymer-fiber solar cell was synthesized from an MEH-PPV : PCBM mixture in chlorobenzene solution using coaxial electrospinning. From a careful estimate of the active area of the polymer fibers, the device achieved a power conversion efficiency of $\eta = 3.08 \times 10^{-7}$%, a short circuit current density of $J_{sc} = 0.525\,\mu\text{A/cm}^2$, an open circuit voltage of $V_{oc} = 0.11$ V, and a fill factor of ff = 0.43. The measured red shift in the absorption and photoluminescence for the MEH-PPV polymer fibers may offer promise for increased device efficiency compared to thin films. Taking advantage of these optical effects, electrospinning of polymer solar cells onto interdigitated electrodes may prove useful for integration into MEMS/NEMS devices or for increased efficiency for larger scale power generation.

Although the efficiency of this device is low in comparison to typical MEH-PPV thin-film devices (e.g., 2.9% by [16]), it is an order of magnitude higher than that reported by Sundarrajan et al. [11] for an electrospun fiber mat and demonstrates the potential benefits of the reported structure. The fibers provide a red shift in absorption which can lead to an increase in generated current. In addition, the orientation of the fibers may lead to improved mobility and better charge transfer. Several factors could further improve the efficiency of the devices. If the initial alignment of the fibers across the electrode gap can be maintained such that the fibers are perpendicular to the electrodes, then the active length of the fibers will be reduced and lead to improved charge transfer to the electrodes. The device performance would likely also improve with a smaller electrode separation. Depositing more aligned fibers will also generate more current and therefore increase the overall efficiency of the system provided that these fibers are in good contact with the electrodes. While the use of interdigitated electrodes allows the use of nontransparent materials, one deficiency with this design is the difficulty in establishing contact between the fibers and the electrodes. The efficiency could certainly be increased by improving this contact. With proper adjustments made for electrospun polymer-fiber solar cells, this device structure may bring significant impact in the field of organic photovoltaics.

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