

Research Article

Performance of Bulk Heterojunction Solar Cells Fabricated Using Spray-Deposited Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]/[6,6]-Phenyl C71 Butyric Acid Methyl Ester Blend Active Layers

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The Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothia diazole-4,7-diyl-2,5-thiophenediyl]/[6,6]-phenyl C71 butyric acid methyl ester blend active layers were prepared by spray deposition method with different preparative conditions. The active layers were prepared with and without TiO_x layer in order to study the property changes. The absorption and surface morphology of the active layers were analyzed using UV-visible spectral and atomic force microscopic studies. The photovoltaic cells were fabricated using the spray-coated active layers with and without TiO_x layer. The results were compared with the cells fabricated using the conventional spin-coated active layers.

1. Introduction

Organic solar cells (OSCs) are the best alternate for inorganic solar cells because of their low cost roll-to-roll production, and large area processability on flexible substrates. Therefore, organic solar cell (OSC) devices are of increasing interest as new materials for future light-activated energy sources. During the last two decades, the research activities and reports on OSC-based devices have been increased [1–3]. In the recent years, a number of photoactive polymers, fullerene, and the bulk heterojunction concept has been put forth to increase the efficiency of OSC devices. Among them, conjugated low band gap polymers-based active layers yielded high PCE of 5–7% [4–7]. Especially, poly(2,7-carbazole) derivatives are potential materials for solar cell applications [8–11]. There are several reports on the fabrication of organic photovoltaic cells using low-cost solution processes such as spin-coating, inkjet printing,

screen printing, and spray coating [12–14]. Spin coating is the most widely used method to prepare active layers and also most efficient devices still adopt this process. However, the spin-coating process cannot be used in large area devices. Spray deposition is widely used for painting in commercial production and is one of the cheapest processes for coating of polymer solutions. Spray-coating method has become important in the fabrication of large area polymer: fullerene based bulk heterojunction solar cells [15, 16]. Different approaches have been adopted to achieve high power conversion efficiency from spray deposited active layers by various research groups [17–20]. In the present work, we report the bulk heterojunction solar cell devices fabricated using the spray-deposited active layers of polymer blend materials of poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM). The effect

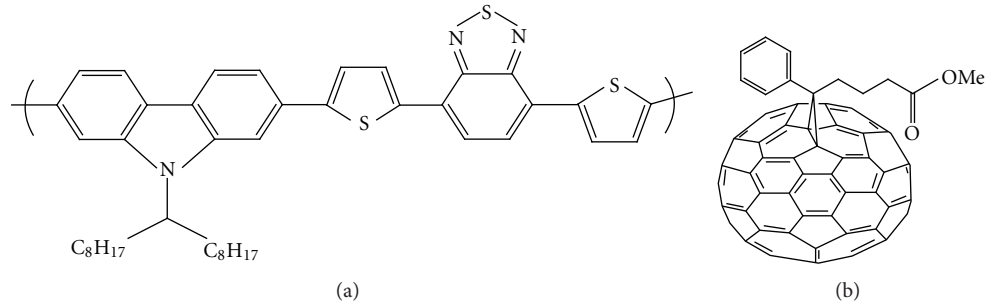


FIGURE 1: Molecular structure of (a) PCDTBT and (b) $PC_{71}BM$.

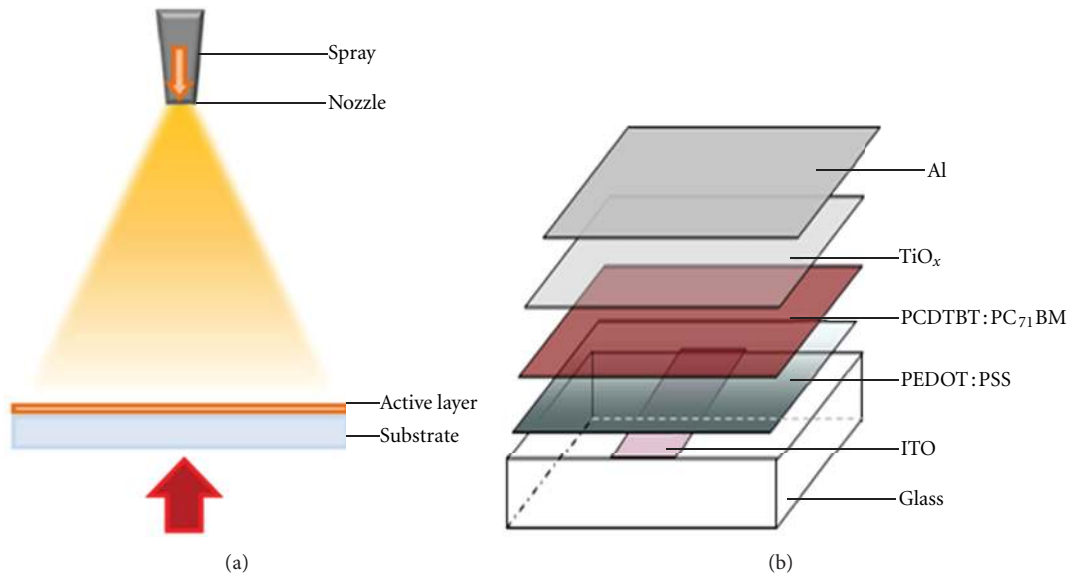


FIGURE 2: (a) Schematic of spray deposition and (b) structure of BHJ device.

of various deposition parameters such as spraying time, substrate temperature, and substrate-nozzle distance has been investigated. TiO_x layer redistributes the light intensity within the bulk heterojunction by changing the optical interference between the incident light and the light reflected from the metal electrode and thus enhances the power conversion efficiency of the solar cells [21]. Therefore, in the present study, we have introduced TiO_x layer in between the active layer and metal electrode in order to improve the power conversion efficiency of the photovoltaic device.

2. Experimental Details

Figures 1(a) and 1(b) show the molecular structures of PCDTBT and $PC_{71}BM$, respectively. Figure 2(a) shows the schematic of the spray deposition unit consisting of spray gun, spray nozzle, and substrate holder used to deposit the active layers. In the present work, the parameters such as spraying time, substrate temperature, and substrate-nozzle distance were varied to coat the active layers of PCDTBT: $PC_{71}BM$ by spray method. Figure 2(b) shows

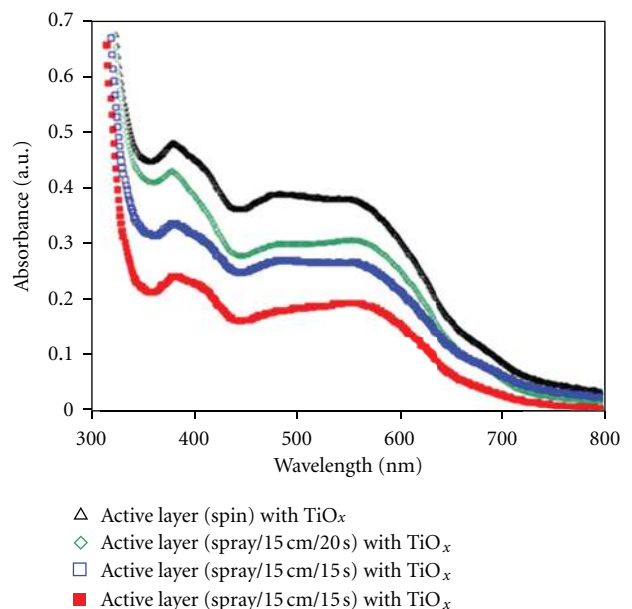


FIGURE 3: Absorption spectrum of PCDTBT : $PC_{71}BM$ active layers.

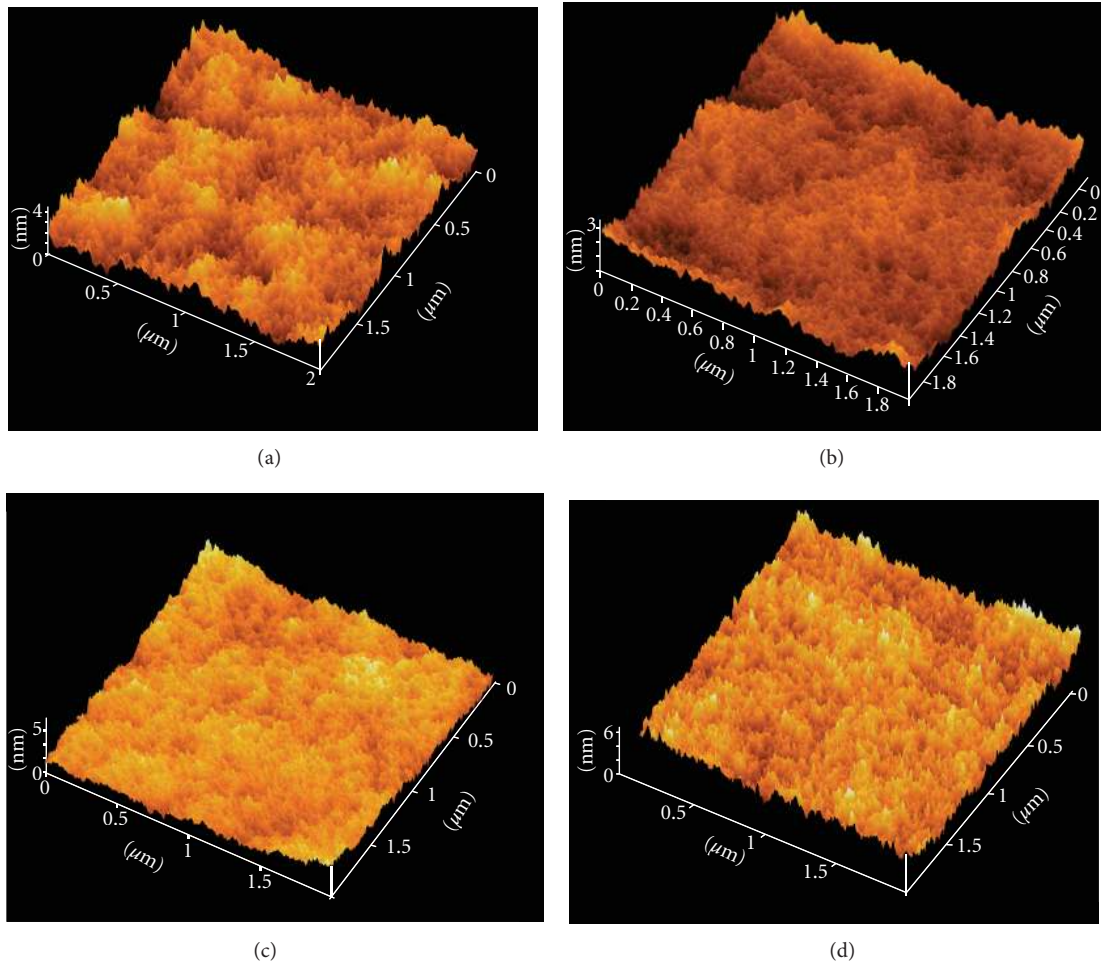


FIGURE 4: Surface morphology of PCDTBT : PC₇₁BM active layers.

the schematic of the fabricated photovoltaic cell structure (ITO/PEDOT : PSS/PCDTBT : PC₇₁BM/TiO_x/Al).

To fabricate the bulk heterojunction solar cells indium-tin-oxide-(ITO-) coated glass substrates were cleaned with detergent, water, acetone, and ethanol and then treated with UV/ozone for 10 min. Then the PEDOT : PSS layer was coated on the top of ITO electrode by spin coating at a rotation speed of 5000 rpm for 30 s followed by drying at 100°C for 10 min in air. An active layer of PCDTBT : PC₇₁BM was deposited by spray coating on the top of the coated PEDOT : PSS layer. For active layers-coating, the precursor solution was prepared in 1 : 4 ratio of PCDTBT : PC₇₁BM using chloroform as solvent. The blend PCDTBT : PC₇₁BM solution was sprayed on the PEDOT : PSS layer. By introducing the nitrogen gas with the pressure of 7.85×10^4 Pa into the spray apparatus the solution was sprayed on the PEDOT : PSS layer. The blend films were prepared for 15 and 20 s and with the substrate-nozzle distance of 15 cm. The active layers with thickness from ~100 to 110 nm were obtained. The active layers were prepared at room temperature as well as 60°C to study the effect of substrate temperature. In order to increase the photocurrent, an optical spacer (TiO_x layer) between the photoactive layer and the top

electrode has been introduced. The maximum light intensity is redistributed to be within the active charge separating bulk heterojunction layer while using the optical spacer. Therefore, titanium suboxide (titanium isopropoxide in ethanol) layer was deposited on the active layer by spin coating at a rotation speed of 5000 rpm for 30 s followed by drying at 60°C for 10 min in air. Finally, Al electrode was evaporated on the active layer through a shadow mask at 10^{-6} Torr. The absorption spectra of the spray-coated blend layers were recorded using a Shimadzu UV2450 UV-vis. spectrometer. The surface morphology of the blend layers was examined by atomic force microscopy using a Seiko Instrument SPA400-SPI4000. All AFM images were taken in dynamic force mode at optimal force. Silicon cantilevers (Tip radius: ~10 nm; SI-DF20; Seiko Instruments Inc.), with spring constant of 14 N/m and resonance frequency of 136 kHz, was used to record AFM images. For comparison, the solar cells were fabricated using conventional spin-coated active layers. For that, the precursor solution was prepared in 1 : 4 ratio of PCDTBT : PC₇₁BM using the solvent of 5 mL chloroform. The active layers with ~100 nm thickness were achieved with a spin speed of 1000 rpm by conventional spin coating method. The current-voltage characteristics of the fabricated

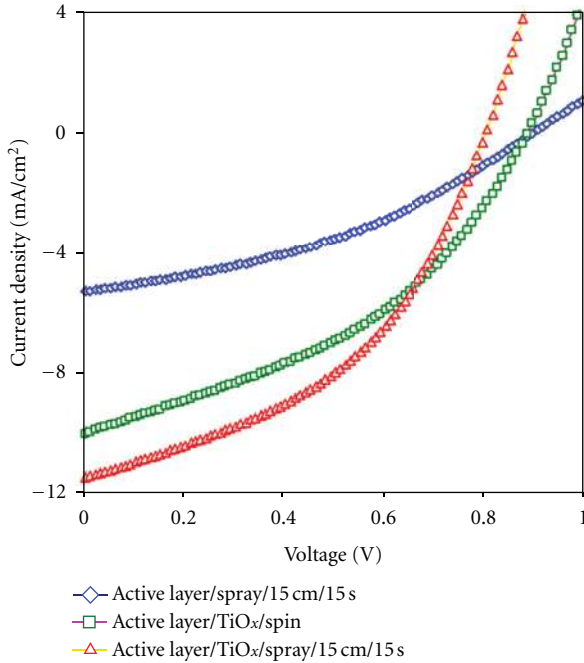


FIGURE 5: Current-voltage characteristics of PCDTBT:PC₇₁BM active layers-based solar cells.

solar cells were measured by employing the Advantest-R-6441A.C. meter and a 100 mW solar simulator with an air mass 1.5 G (AM 1.5 G) filter.

3. Results and Discussion

3.1. Absorption Spectral Studies. The absorption spectra of spray-coated active layers of PCDTBT:PC₇₁BM from 1:4 ratio with and without TiO_x layer and spin-coated active layers with TiO_x layer are shown in Figure 3. The spin-coated active layers show better absorption than the spray-coated active layers. The active layers with TiO_x layer possess relatively better optical absorption. This is because the optical spacer is a nonabsorbing layer that redistributes the maximum light intensity to be within the charge-separating bulk heterojunction layer. In that, the active layer prepared using 15 cm substrate-nozzle distance and the spray time of 20 s shows better absorption than the active layer prepared from the spray time of 15 s. It is observed from the results that the blend molecules are more aggregated on the substrate when increasing the coating time to 20 s and hence the films formed were less uniform. The active layers with uniform thickness were observed when the substrate to nozzle distance was 15 cm and the spray time of 15 s.

3.2. Atomic Force Microscopy Study. Figures 4(a)–4(d) show the AFM images of PCDTBT:PC₇₁BM active layers prepared in 1:4 ratio at different preparative conditions. The images were recorded on a film area of 2000 × 2000 nm. Figures 4(a) and 4(b) show the surface morphology of the active layer without TiO_x layer prepared at room temperature and at 60°C with a spray-nozzle distance of 15 cm and spray

TABLE 1: Root means square, peak-valley value of active layers, and power conversion efficiency of photovoltaic devices fabricated using the active layers with and without TiO_x layer.

Method of preparation	Active layer	RMS (nm)	Peak-valley value (nm)	PCE (%)
Spray coating	Without TiO _x	0.56	4.32	1.76
	With TiO _x	0.47	5.47	4.01
Spin coating	With TiO _x	0.69	7.08	3.56

time of 15 s, respectively. Blended films without TiO_x layer and prepared at room temperature show more roughness than the surface of the active layer prepared at 60°C. The surface of the active layer with TiO_x layer prepared at 60°C with the spray-nozzle distance of 15 cm for 15 s shows smooth and better morphology (Figure 4(c)). The surface of the active layers prepared using spin coating (Figure 4(d)) also shows smooth morphology when compared to spray-deposited active layer prepared at room temperature. From this analysis, we have observed that the active layers prepared with TiO_x for 15 s with substrate-nozzle distance of 15 cm show flat morphologies and specifically the active layer prepared at 60°C shows well flattened morphology (Figure 4(c)). The photovoltaic cells were fabricated using the spray- and spin-deposited PCDTBT:PC₇₁BM active layers with and without TiO_x layer.

3.3. Current-Voltage Characteristics. The spray- and spin-coated PCDTBT:PC₇₁BM active layers with and without TiO_x layer were used to fabricate the photovoltaic cells. The fabricated photovoltaic cells were characterized by *J-V* studies under illumination of AM 1.5 G (100 mW/cm²). Figure 5 shows the current-voltage characteristics of photovoltaic cells fabricated using spray-deposited PCDTBT:PC₇₁BM active layers. The effective area of devices is 5 mm². From this analysis, it is observed that the devices fabricated using active layers with TiO_x layer prepared for 15 s with substrate-nozzle distance of 15 cm at the substrate temperature of 60°C exhibit the power conversion efficiency of 4.01%. Table 1 gives the comparison data of root mean square value, peak to valley value, and power conversion efficiency of solar cells prepared using spray- and spin-coated active layers at different conditions. It is observed that the short circuit current and PCE of solar cells fabricated using spray-coated active layer are higher than those of photovoltaic cells fabricated using the conventional spin coated active layers. The devices fabricated using the spray-coated active layers with TiO_x show higher open circuit voltage, short-circuit current, fill factor, and power conversion efficiency.

4. Conclusions

Organic photovoltaic cell devices were fabricated using spin- and spray-deposited PCDTBT:PC₇₁BM active layers with and without TiO_x layer. The effect of spray time and substrate temperature was investigated. Atomic force microscopic analysis shows that the active layers prepared in 1:4 ratio

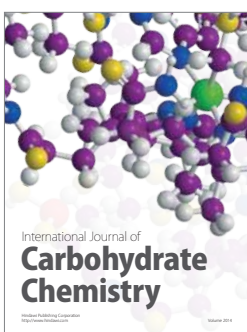
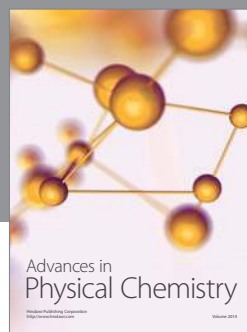
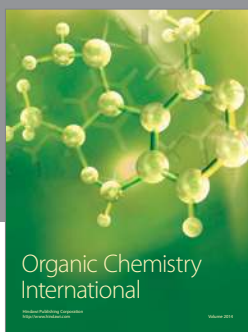
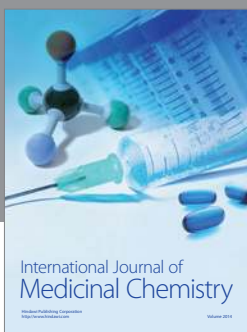
with the substrate-nozzle distance 15 cm and for 15 s possess well-flattened and smooth morphology. The cells fabricated using the PCDTBT:PC₇₁BM active layers prepared at 60°C with TiO_x layer show the power conversion efficiency (PCE) of 4.01%. The PCE of solar cells fabricated using the active layers coated by spray coating is relatively larger than that of the spin coated active layer. From this analysis, we observed that the device fabricated with TiO_x layer shows better power conversion efficiency than that of the device without TiO_x layer.

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