International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.6, pp 3415-3418, Aug-Sep 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Evolution of nanomorphology, conductivity and improved power conversion efficiency of polymer solar cells using modified PEDOT:PSS films

Kannappan Santhakumar[1]*, P. Induja[1], M. Shivashankar[2] and G.Chandramohan[3]

[1]Environmental & Analytical Chemistry Division, VIT University, Vellore-632 014, Tamilnadu, India.
[2]Pharmaceutical Chemistry Division, VIT University, Vellore-632 014, Tamilnadu, India.
[3]Department of Chemistry,A.V.V.M.Sri Pushpam College ,Poondi- 613503, Thanjavur, Tamilnadu, India.

*Corres. author: ksanthakumar@vit.ac.in

Abstract: The introduction of donor–acceptor heterojunctions made small molecules and conjugated polymers attractive candidates for the fabrication of cost-efficient and flexible power sources. Polymer conductivity is key factor to improve the performance of the electronic and photonic devices. Poly(3,4-ethylenedioxy thiophene): poly(styrenesulfonate) (PEDOT:PSS) is promising to be the next-generation transparent electrode of optoelectronic devices. In this research, we investigated the high efficiency of an OPV for which PEDOT:PSS and active layers were fabricated by spray deposition using the air brush coating method using various solvents like methanol, ethanol, acetone, acetonitrile, hydrochloric acid and sulphuric acid to form a hole transport layer (HTL). The surface morphology of the films deposited was examined using Atomic Force Microscopy (AFM). The current density(*J*)-voltage(*V*) characteristics were measured under the illumination of simulated solar light with 100 mW/cm^2 (AM 1.5 G) by an oriel 1000 W soalr simulator. The obtained results show a considerable impact and bright future for organic polymer solar cells.
Keywords: Organic photovoltaic device, bulk heterojunction, PEDOT:PSS, PTB7, $PC_{70}BM$.

Introduction and Experimental

Organic solar cells have attracted a significant amount of attention due to the need to develop an inexpensive clean and sustainable renewable energy source. During the past decade, there have been intensive researches on cost-effective organic solar cells based on conjugated polymers [1,2]. PEDOT:PSS is composed of PEDOT, which is hydrophobic and conductive, and PSS, which is hydrophilic and insulating; the conductivity of the thin-film is directly related to the way in which the PEDOT is formed. It is used as a hole transport layer on transparent conducting oxides serving to control the interfacial properties, both as a transparent conductor and as a planarizing layer. In this study, we discuss the high efficiency of an OPV for which PEDOT:PSS and active layers were fabricated by spray deposition using the air brush coating method.

In order to improve the conductivity of spray-deposited PEDOT:PSS, we modified the PEDOT:PSS films by UV irradiation and UV irradiated solvent modified PEDOT:PSS using various solvents like methanol, ethanol, acetone, acetonitrile, hydrochloric acid and sulphuric acid to form a hole transport layer (HTL). Then we observed the morphology of each PEDOT:PSS film and investigated the performance of the OPV′s.

An aqueous dispersion of the conductive polymer blend PEDOT and PSS (PEDOT:PSS, Clevios^{TM} PH 1000) was purchased from H.C. Strack (Germany) and passed through a 0.45 μm filter before use. Active materials include thieno(3,4-b)thiophene-alt-benzodithiophene copolymer (PTB7) and [6,6]-phenyl-C70-butyric acid methyl ester ($PC_{70}BM$) were purchased from 1-material (Quebec, Canada). These chemicals act as an electron donor (D) and acceptor (A) materials, respectively. Pre-patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 12 Ω/ square were cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol for 15 min, and dried in an oven at 120°C. UV-ozone treatment was used to treat the ITO surface for 10 min to increase further the surface energy of the ITO anode for a uniformly coated PEDOT: PSS. The photovoltaic cells were fabricated with an anode first layer consisting of PEDOT: PSS with or without UV irradiation on ITO-coated glass substrates. The PEDOT: PSS solution was irradiated with UV light (emission centered at 365 nm and power density of 300 μ W cm^{-2}) in the dark glove box for 15, 30, 45 and 60 min. The pristine PEDOT:PSS and UV irradiated PEDOT:PSS solution were then transferred to a handheld airbrush and sprayed. The second layer, a bulk heterojunction film composed of interconnected networks of electron-donor and -acceptor materials, were prepared by mixing the polymer and $PC_{70}BM$ in different blend ratios of 1:1; 1:1.5, 1:2, 1:3 and 1:4 (w/w) in chlorobenzene solution was sprayed at a pressure of 0.1 MPa and at a nozzle-to substrate distance of 20 cm, for 30 s in argon, which formed the active layer with a thickness of ~120 nm. Then the samples were transferred into a vacuum chamber to deposit Al. The active surface area of the device was 0.12 cm^2.

Result and Discussion

Fig. 1 shows the molecular vibrational spectra of the pristine, UV irradiated and UV irradiated solvent modified PEDOT:PSS films. Noticeable differences were observed for the strongest atomic vibration band between 1420 cm^{-1} and 1520 cm^{-1}, which was assigned to the stretching vibration of $C_\alpha = C_\beta$ on the five-membered thiophene ring and to the out-of-plane bending of the ethylenedioxy ring of PEDOT chains [2-4]. As the UV exposure time of the PEDOT:PSS increased, $C_\alpha = C_\beta$ stretching band red shifted and the peak intensity at high-vibration frequencies (1450 cm^{-1} to 1500 cm^{-1}) decreased. These findings indicate that the resonant structure of the PEDOT chain changes domination from a benzoid structure to a quinoid structure [5-7]. Both the benzoid structure and the quinoid structure exist simultaneously in the pristine PEDOT:PSS film [8-10]. The surface morphology of pristine, UV irradiated and UV irradiated solvent modified PEDOT:PSS films were characterized by dynamic mode AFM.

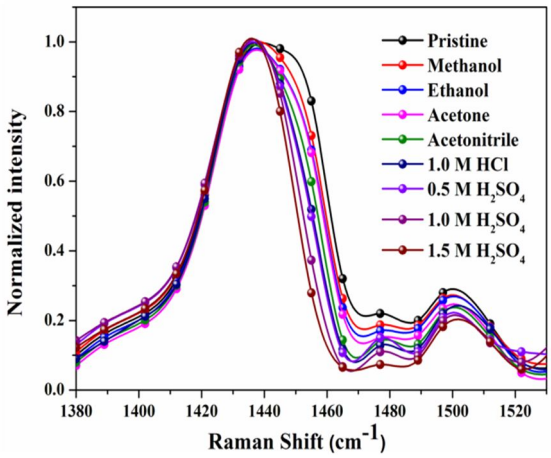

Fig. 1. Raman spectra of solvent modified PEDOT: PSS films formed by irradiating the PEDOT:PSS aqueous solution for 60 min.

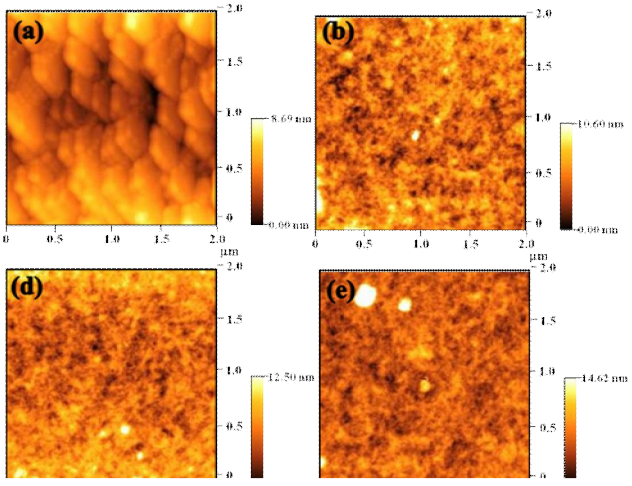

Fig.2 AFM images (2 μm x 2 μm) of (a) pristine (b) UV irradiated 15 min (c) UV irradiated 30 min (d) UV irradiated 60 min

Table 1 Thickness, Conductivities, Photovoltaic parameters and Efficiencies BHJ solar cells based on PTB7: $PC_{70}BM$ composite under AM 1

PEDOT:PSS anode	Thickness	Conductivity (S cm^{-1})	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	PCE (%)
Pristine	30 ± 4	0.32 ± 0.2	9.7 ± 0.2	0.727 ± 0.02	0.504 ± 0.01	3.55 ± 0.1
Methanol	44 ± 2	104 ± 8	11.4 ± 0.1	0.738 ± 0.03	0.553 ± 0.01	4.65 ± 0.1
Ethanol	48 ± 3	125 ± 4	11.9 ± 0.2	0.747 ± 0.01	0.568 ± 0.02	5.04 ± 0.1
Acetone	42 ± 3	169 ± 10	12.3 ± 0.1	0.753 ± 0.04	0.572 ± 0.01	5.28 ± 0.1
Acetonitrile	40 ± 2	199 ± 7	12.5 ± 0.1	0.762 ± 0.03	0.574 ± 0.02	5.45 ± 0.1
1.0 M HCl	42 ± 2	1821 ± 4	12.8 ± 0.1	0.769 ± 0.02	0.592 ± 0.03	5.83 ± 0.1
0.5 M H_2SO_4	43 ± 2	2432 ± 3	11.4 ± 0.2	0.736 ± 0.01	0.574 ± 0.03	4.84 ± 0.1
1.0 M H_2SO_4	37 ± 3	3066 ± 5	13.0 ± 0.1	0.761 ± 0.04	0.601 ± 0.01	5.94 ± 0.1
1.5 M H_2SO_4	35 ± 3	2615 ± 3	12.1 ± 0.2	0.752 ± 0.02	0.582 ± 0.02	5.28 ± 0.1

Fig.2 presents the topography images of a 2 μm x 2 μm area of PEDOT:PSS films under various conditions. The pristine PEDOT:PSS film was quite smooth with an rms of 1.42 nm. When the PEDOT:PSS solution was exposed to UV irradiation with different timing, the porosity and surface roughness decreased with increasing UV irradiation time. The rms roughness is 1.33 nm, 1.24 nm, 1.20 nm and 1.17 nm respectively, for 15 min, 30 min, 45 min and 60 min UV irradiation. To analyze the power conversion efficiency (PCE) on the pristine, UV irradiated and UV irradiated solvent modified PEDOT:PSS films, were fabricated with the conventional device architecture of Glass/ITO/PEDOT:PSS/PTB7:$PC_{70}BM$/Al The *J-V* curves of the PTB7:$PC_{70}BM$ in chlorobenzene based solar cells are shown in Table 1.

4. Conclusion

We investigated the effect of pristine, UV irradiated and UV irradiated solvent modified PEDOT: PSS films and monitored the changes in the efficiency of OPV′s when those thin-films were used as the HTL. The highest conductivity of 3066 S cm^{-1} has been obtained for a single layer PEDOT: PSS film with a power conversion efficiency of 5.94 %. These results will help in better understanding the underlying relationship between the polymer morphology and the device performance and will subsequently help in enhancing the efficiencies of plastic solar cells to a level of practical applications.

References

1. Green, M.A. Emery, K. Hishikawa, Y. and Warta, W. “Solar cell efficiency tables”, Progress in Photovoltaics, vol. 15, no.5, pp. 425- 430, 2007.
2. Green, M.A. Emery, K. Hishikawa, Y. and Warta, W “Solar cell efficiency tables”, Progress in Photovoltaics, vol. 19, no.1, pp. 84-92, (2011).
3. Voigt, M. Macjenzie, R.C, King, S.P., Yau, C.P., tienzar, P., Dane, J., Keivanidis, P.E., Zadrazil, I., Bradley, D.D, and Nelson, J. “Gravure printing inverted solar cells: The influence of ink properties on film quality and device performance”, Solar Energy Materials and Solar Cells, vol. 105, pp. 77-85, 2012.
4. Santhakumar, K., Kumar, P. Tatsugi, J. Shin P.K. and Ochiai, S. “Fabrication and characterizations of PCDTBT:PC71BM bulk heterojunction solar cell using air brush coating method”, Journal of Material Science, vol. 48, no.6, pp. 2308-2317, 2013.
5. Na, S.I. Kim, S.S., Jo J.J. and Kim, D.Y. “Efficient and Flexible ITO-Free Organic Solar Cells Using Highly Conductive Polymer Anodes”, Advanced Materials, vol. 20 no. 21, pp. 4061-4067, 2008.
6. Emmott, C.J. Urbina, A. and Nelson, J. “Environmental and economic assessment of ITO-free electrodes for organic solar cells, Solar Energy Materials and Solar Cells, vol. 97, pp. 14-21, 2012.
7. Kim, Y.H. Sachse, C., Machala, M.L., May, C., Meskamp, L.M. and Leo, K., “Highly conductive PEDOT:PSS Electrode with Optimized Solvent and Thermal Post-Treatment for ITO-Free Organic Solar Cells, Advanced Functional Materials, vol. 21, no. 6, pp.1076-1081, 2011.

8. Reyes, M.R., Cruz , I.C., and Sandoval, R.L., "Enhancement of the Electrical Conductivity in PEDOT:PSS Films by the Addition of Dimethyl Sulfate", Journal of Physical Chemistry C, vol.114, no. 47, pp. 20220-20224, 2010.
9. Ouyang, J., Chu, C.W., Chen, F.C., Xu, Q., and Yang, Y. "High-Conductivity Poly(3,4- ethylene dioxy thiophene):Poly(styrene sulfonate) Film and Its Application in Polymer Optoelectronic Devices", Advanced Functional Materials, vol.15, no.2, pp. 203-208, 2005.
10. Xia, Y., Sun, K., and Ouyang, J., "Solution-Processed Metallic Conducting Polymer Films as Transparent Electrode of Optoelectronic Devices", Advanced Materials, vol. 24, no. 18, pp. 2436-2440, 2012.

*****