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Original Article

Enhancing Poly(3,4-ethylenedioxythiophene) Polystyrene Sulfonate (PEDOT:PSS) Conductivity by Dimethyl Sulfoxide (DMSO) Dopant

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Abstract: Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), a type of conducting polymer has caught lots of attraction from scientists for its excellent properties as low-cost, non-toxic, etc. This also is a potential material for various applications as transparent electrodes, flexible and stretchable devices, thus improving the electrical properties of this polymer plays an important role. Among various methods such as post-treatment, doping with glycerol, and d-sorbitol herein, DMSO was chosen as an additive to enhance the conductivity of PEDOT:PSS. The results, including the increase in the films conductance according to the rise of DMSO dopant ratio from 0 to 2, good transmittance and surface morphology were clearly presented. This will be the platform for the further study of the utilization of PEDOT:PSS in various potential optoelectronic devices in the future.

Keywords: PEDOT:PSS, DMSO, conductivity, dopant, transparent electrodes.

1. Introduction

Nowadays, flexible and stretchable optoelectronic devices (OEDs) have become one of the most attractive research topics among scientists. This is due to the fact that in comparison with conventional

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devices on rigid substrates, flexible and stretchable ones provide more superior advantages. In other words, they can be integrated with cars to reduce the use of combustion energy [1] or stuck onto human skin to monitor their health and surrounding conditions [2]. For this reason, researches about these devices have been thoroughly carried out with several positive results being published. Recently, Lee's group reported a flexible photodetector with high sensitivity to visible illumination [3]. Besides, Bi et al., also presented a solar cell on poly(ethylene terephthalate) with the recorded efficiency up to 18.1 % [4]. Although flexible OEDs' components have been deeply investigated, fabricating them is still facing severe disadvantages. Indeed, the devices electrode, which is mainly based on ITO or deposited silver is one of the factors hindering the development and application of flexible OEDs as these types of electrodes are brittle and thus easily broken under stretching and bending condition [5]. Thus, seeking the new materials that can be used as flexible electrodes play a crucial role.

Nowadays, the mentioned problems could be solved by using conducting polymers for electrodes, for example, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). This polymer is becoming more and more prevalent in fabricating OEDs electrodes due to its noticeable properties such as high transparency in visible region, high conductivity, etc. [6]. Despite its superior properties, PEDOT:PSS is still facing some issues, especially those related to its lower conductivity in comparison with ITO [7]. Thus, scientists are finding ways to enhance the natural properties of PEDOT:PSS under various modification methods. For example, in a paper published by Huang et al., demonstrated that, PEDOT:PSS electrical properties increased significantly when being thermal-treated [8]. Otherwise, as reported by group of Moujoud, illuminating PEDOT:PSS under UV light can boost its conductivity [9]. Another popular method, adding "additives" like ethylene glycol (EG), glycerol, d-sorbitol, methanol, X-triton, and Zonyl fluorosurfactant into PEDOT:PSS solution is also an effective way to modify this polymer electrical quality [10]. However, these methods require complicated fabricating and investigating techniques.

In this work, we investigated the electrical properties of PEDOT:PSS when it was simply modified with dimethyl sulfoxide (DMSO) with different concentrations to enhance the conductivity. The PEDOT:PSS films electrical properties were studied through urrent-voltage (I-V) characteristics, which indicated that their conductivity remarkably increased when being doped with DMSO. Moreover, we also carefully investigated their transmittance in the visible region and ensure that our PEDOT:PSS can be used as transparent electrodes. Finally, surface morphology of the films was evaluated through scanning electron microscope (SEM). Our research will be the platform for further study related to the potential of PEDOT:PSS in OEDs, especially the flexible or stretchable devices.

2. Materials – Methods

2.1. Chemical Materials

The chemical materials utilized in this work included poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (Purity \geq 99%, Sigma Aldrich, United States) and dimethyl sulfoxide (DMSO) (Purity \geq 99%, Xilong Scientific, China).

2.2. Substrate Preparation

A glass substrate was cut into the size of 1×1 inch and then washed with ethanol, acetone and DI water for 10 minutes each turns. Then, the glass pieces were immersed in NaOH 0.5 M solution before being washed again with DI water. In the next step, it was dried and silver was sputtered through a shadow mask, leading to the formation of the electrodes.

2.3. The Coating Process of PEDOT: PSS/DMSO:

Various mixtures consisting of PEDOT:PSS with different DMSO concentrations were prepared in several beakers under sonication condition. Next, the substrates were heated to 95 °C and a spin-coating process with the rate of 700 rpm in 20 s was conducted to create a thin layer of PEDOT:PSS/DMSO. Finally, the as-coated thin films were heated at 95 °C before any further measurements.

2.4. Characterization

The electrical characteristics of the PEDOT:PSS/DMSO films were assessed through the current – voltage (I-V) curves and the time dependence of the current (I-t curves) recorded on the Keithley 2400 system.

3. Results and Discussions

3.1. Electrical Properties of PEDOT: PSS/DMSO Films

After the electrodes sputtering process (Fig. 1a), during the spin-coating step, which is depicted in Fig. 1b, the as-synthesized samples were labeled as x:y where x is the ratio of PEDOT:PSS and y described that of DMSO (for example, in 8:2 sample, the ratios of PEDOT:PSS and DMSO were 8 and 2, respectively).

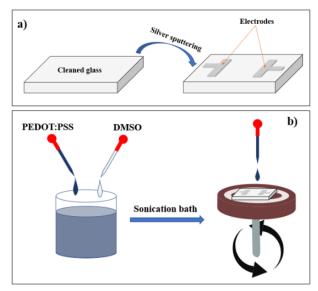


Figure 1. a) The sputtering of electrodes and b) The spin-coating process used to fabricate the samples.

The I-V characteristics of the films were measured and plotted in Fig. 2a. As can be seen, under a bias of 5 V, the films illustrate the linear I-V dependence with the high symmetry under forward and reverse bias, which indicates good Ohmic metal-semiconductor contact [11]. Besides, with the increase from 0 to 2 of DMSO proportion, the current rose significantly. However, a decrease in the current was observed when adding more DMSO concentrations into the mixture, as demonstrated by the results of 7:3 thin films. Then, the recorded currents through the films at the 1 V bias were plotted versus the ratios of DMSO (Fig. 2b). The current gradually increased with the rise of DMSO concentrations and the

highest current was recorded at the ratio of 2. In contrast, at the ratio of 3, the current reduced remarkably. Thus, it is reasonable to conclude that the largest conductivity of PEDOT:PSS was achieved when the ratio of PEDOT:PSS/DMSO is of 8/2.

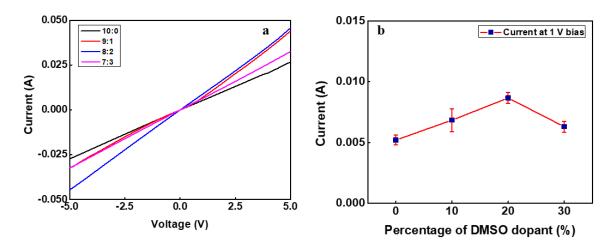


Figure 2. a) I-V characteristics of PEDOT:PSS/DMSO films with different ratios and b) The current through the films at 1 V bias according to the ratio of DMSO dopant with error bars.

Next, to check the stability of the thin films, their I-t properties were assessed under the bias of 1 V in a 120-second duration. From Fig. 3, for all 4 samples, the recorded currents show no remarkable change. Therefore, it is clear that all the samples exhibit relatively good stability during the measured time.

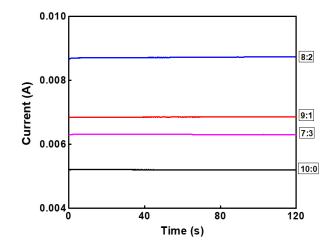


Figure 3. The I-t measurement of PEDOT:PSS/DMSO films.

3.2. Optical Properties and Surface Morphology

Since the sample with the PEDOT:PSS/DMSO ratio of 8/2 possessed a largest conductivity, the optical properties and surface morphology of these samples were chosen for investigation and comparison with the one of the samples without DMSO. Their transmittance spectra in visible region of all these samples are shown in Fig. 4.

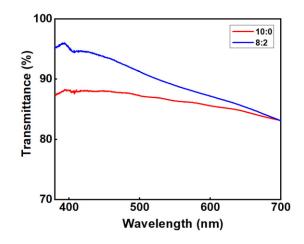


Figure 4. Transmittance spectra in visible region of 10:0 and 8:2 PEDOT:PSS doped DMSO films.

It is easy to recognize that for the undoped and doped samples a transmittance in visible region reached a value larger than 80%. Additionally, in the doped sample (namely the ratio PEDOT:PSS/DMSO is of 8/2), the slight increase in transmittance was observed, which demonstrated the decline of solid content in the PEDOT:PSS solution when it was treated with DMSO. This result is similar to that published by group of Pathak et al., [12].

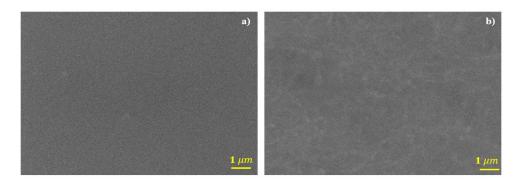


Figure 5. SEM images of a) PEDOT:PSS pristine and b) PEDOT:PSS treated DMSO at 8:2 ratio.

SEM images of the undoped and doped with DMSO samples are shown Figs 5a and 5b. As shown in Fig. 5, with the addition of DMSO, some changes in the surface of the films occurred, including the noticeable formation of the micro grains and they were well interconnected, facilitating the charge transfer in the polymer backbone, which is assumed in the report published by Pasha et al., [13].

4. Conclusion

We have simply modified the conductivity of PEDOT:PSS by embedding of DMSO. As the results indicated, the ratio of DMSO doped in the PEDOT:PSS solution increased, resulting in the increase of the conductivity. The largest value of the conductivity was attained for the 2/8 ratio of DMSO/PEDOT:PSS. This can be explained due to some changes on the morphology of the polymer through the doping process. Beyond 2/8 ratio, adding more DMSO into PEDOT:PSS solution can create

detrimental effects on the electrical properties of the films. Based on the obtained results, we strongly believe that this will be the platform for our other studies in the future, consisting of those on the flexible or stretchable OEDs – one of the most promising fields of research in the world at present.

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References

- X. Li, P. Li, Z. Wu, D. Luo, H. Y. Yu, Z. H. Lu, Review and Perspective of Materials for Flexible Solar Cells, Materials Reports: Energy, Vol. 1, No. 1, 2021, pp. 100001, https://doi.org/10.1016/J.Matre.2020.09.001.
- [2] Y. Liu, M. Pharr, G. A. Salvatore, Lab-on-skin: A Review of Flexible and Stretchable Electronics for Wearable Health Monitoring, Acs Nano, Vol. 11, No. 10, 2017, pp. 9614-9635, https://doi.org/10.1021/Acsnano.7b04898.
- [3] T. Q. Trung, V. Q. Dang, N. E. Lee, A Stretchable Ultraviolet-to-nir Broad Spectral Photodetector using Organic– Inorganic Vertical Multiheterojunctions, Nanoscale, Vol. 14, No. 13, 2022, pp. 5102-5111, https://doi.org/10.1039/D2nr00377e.
- [4] C. Bi, B. Chen, H. Wei, S. Deluca, J. Huang, Efficient Flexible Solar Cell Based on Composition-Tailored Hybrid Perovskite, Adv. Mater., Vol. 29, No. 30, 2017, pp. 1605900, https://doi.org/10.1002/Adma.201605900.
- [5] R. K. L. Tan et al., Graphene as A Flexible Electrode: Review of Fabrication Approaches, J. Mater. Chem. A, Vol. 5, No. 34, 2017, pp. 17777-17803, https://doi.org/10.1039/C7ta05759h.
- [6] K. Sun et al., Review on Application of Pedots and Pedot:Pss in Energy Conversion and Storage Devices, J Mater Sci: Mater Electron, Vol. 26, No. 7, 2015, pp. 4438-4462, https://doi.org/10.1007/S10854-015-2895-5.
- [7] Y. Wen, J. Xu, Scientific Importance of Water-processable Pedot-pss and Preparation, Challenge and New Application in Sensors of Its Film Electrode: A Review, J. Polym. Sci. Part A: Polym. Chem., Vol. 55, No. 7, 2017, pp. 1121-1150, https//doi.org/10.1002/Pola.28482.
- [8] J. Huang, P. F. Miller, J. C. D. Mello, A. J. D. Mello, D. D. C. Bradley, Influence of Thermal Treatment on the Conductivity and Morphology of Pedot/Pss Films, Synthetic Metals, Vol. 139, No. 3, 2003, pp. 569-572, https://doi.org/ 10.1016/S0379-6779(03)00280-7.
- [9] H. Shi, C. Liu, Q. Jiang, J. Xu, Effective Approaches to Improve the Electrical Conductivity of Pedot:Pss: A Review, Adv. Electron. Mater., Vol. 1, No. 4, 2015, pp. 1500017, https//doi.org/10.1002/Aelm.201500017.
- [10] X. Fan et al., Pedot:Pss for Flexible and Stretchable Electronics: Modifications, Strategies, and Applications, Adv. Sci., Vol. 6, No. 19, 2019, pp. 1900813, https://doi.org/10.1002/Advs.201900813.
- [11] M. Salah, S. Azizi, A. Boukhachem, C. Khaldi, M. Amlouk, J. Lamloumi, Structural, Morphological, Optical and Photodetector Properties of Sprayed Li-doped Zno Thin Films, J Mater Sci, Vol. 52, No. 17, 2017, pp. 10439-10454, https//doi.org/10.1007/S10853-017-1218-Z.
- [12] C. S. Pathak, J. P. Singh, R. Singh, Effect of Dimethyl Sulfoxide on the Electrical Properties of Pedot:Pss/N-Si Heterojunction Diodes, Current Applied Physics, Vol. 15, No. 4, 2015, pp. 528-534, https://doi.org/10.1016/J.Cap.2015.01.020.
- [13] A. Pasha, A. S. Roy, M. V. Murugendrappa, O. A. A. Hartomy, S. Khasim, Conductivity and Dielectric Properties of Pedot-pss Doped Dmso Nano Composite Thin Films, J Mater Sci: Mater Electron, Vol. 27, No. 8, 2016, pp. 8332-8339, https://doi.org/10.1007/S10854-016-4842-5.