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Highly Conductive PEDOT: PSS Flexible Film with Secondary Doping and Spray Pyrolysis Method

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Abstract

Conductive polymers are become widely known amongst researches for practical application. Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) or PEDOT:PSS is one of the most successful and widely known conducting polymer for practical application. But, PEDOT:PSS has an issue because its low electrical conductivity. In order to developed a continuous process for industrial scale and high electrical conductivity, we have proposed a spray pyrolysis and secondary doping method to synthesis a flexible conductive film of PEDOT:PSS on poly(ethylene terephthalate) (PET) with dimethyl sulfoxide (DMSO) as dopant. The optimum condition that resulting a best morphology PEDOT:PSS film was anneal at 90ºC and 20 cm distance with electrical conductivity 4.5 S/cm. Solvent addition method (SAM) also prove that the conductivity can increased up to 770 S/cm with 75% DMSO. It was found that annealing at temperature higher than 90ºC will resulting a stress to a film and formed crack due to a different thermal expansion, while at the distance higher than 20 cm resulting a loss of PEDOT:PSS droplets. Also, solvent vapor method (SVM) and post spray rinsing method (PSRM) was fail to make a good film morphology. IR spectra shows that there is no any sign of PEDOT:PSS degradation up to 110ºC and a peak shifting related to SO_3H group.

Keywords: PEDOT:PSS, PET, DMSO, Conductive polymer, Spray pyrolysis, secondary doping, flexible film

INTRODUCTION

Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) is one of the most successful conductive polymer for practical application [1][2][3][4][5] and becomes the most promising material due to its high mechanical flexibility [6][7]. However, PEDOT:PSS has a problem of low conductivity, generally is less than 1 S/cm, which is lower than many conducting polymers. Thus, PEDOT:PSS is usually used as a buffer layer than the transparent electrode [8].

To improve the conductivity, addition of dimethyl sulfoxide (DMSO) into PEDOT:PSS can enhanced its conductivity by more then 100 factor [9][10][11][12][13]. Another polar solvent like N,N-dimethylformamide (DMF)[11][12], sorbitol [14][15], and ethylene glycol (EG) [12][13][16] also can be used to enhance PEDOT:PSS conductivity.

There are several methods to enhance the electrical conductivity of PEDOT:PSS, such as co-solvent addition [9][13], change of solvent [11] , solvent vapor treatment [12], and dipped in low concentrated solvent [17][18]. Despite numerous studies on the role of these compounds and methods, the mechanism of the conductivity improvement remains unclear.

In this paper, we present a study of developing a thin, flexible, and strong conductive polymer material using poly(ethylene terephthalate) (PET) to support PEDOT:PSS film with spray pyrolysis method. We also present the effect of secondary doping to enhancing its conductivity using DMSO. As we consider the suitable method to improve the film conductivity are solvent addition (SAM), solvent vapors (SVM), and post spray rinsing method (PSRM).

MATERIALS AND METHODS

Materials

The PEDOT:PSS with concentration of 1.3%wt in water dispersion as conductive polymer and DMSO ReagentPlus® with 99.5% purity as secondary dopant was purchased from Sigma Aldrich. PET sheet was obtained from PT. Asiaplast Industries with 0.32 mm thickness as flexible material substrate.

Preparation of PEDOT:PSS flexible films

PET as the substrate was used without any treatment. To develop PEDOT:PSS flexible film, 5 mL PEDOT:PSS solution was sprayed onto PET as a flexible substrate. Spray pyrolysis method consist with a machine equipped with steel tip and brass nozzle. The distance between the tip and the substrate was set at 20 cm. The solution was injected using 3.5 bar and 3 scfm air flow. After deposition, the film was annealed at 90ºC on a hotplate until its dry completely.

Conductivity enhancement by secondary doping

The conductivity of PEDOT:PSS films was enhanced using DMSO as secondary dopant. There are three methods of secondary doping that will be taken. For the SAM, the mixture of DMSO and PEDOT:PSS was adjusted in a ratio by volume of 1:2, 1:1, 2:1, and 3:1, to give final solutions of 33%, 50%, 67%, and 75% by volume of DMSO, respectively. The solution was stirred for 30 min at room temperature before spraying. For the SVM, The PEDOT:PSS film was place on the Petri dish lid and 5 mL DMSO were evaporated at 80, 90, 100, and 110ºC The process was carried out for minimum 30 min while the current-voltage is measured. For the PSRM, the DMSO was carried out by dropping DMSO on the dried PEDOT:PSS films. The dropped DMSO was varied at 1, 2, 3, 4, 5 mL. The obtained films were dried at 90ºC until its dry completely.

Flexible film characterization.

PEDOT:PSS flexible film conductivity was measured using a standard four-point probe method. Transmittance and absorption spectra of the films were measured using a PerkinElmer Frontier FT-IR 96772 and Shimadzu UVmini-1240 spectrophotometer. Film thickness and topography were obtained using a Phenom ProX SEM instrument at 15 kV energy.

RESULTS AND DISCUSSION

PEDOT:PSS Flexible Film

The most acknowledged method to cast PEDOT:PSS film is electrospinning because its resulting a controllable diameters of fibers and also possess some unique properties [19]. But, in terms of industrial purposes, electrospinning has higher cost than traditional methods [19]. In order to develop an industrial scale and continuous process, spray pyrolysis represents a very simple and relatively cost-effective method. Spray has been used for several decades in the glass industry and in solar cell production to deposit electrically conducting electrodes [20].

The most abundance compound in PEDOT:PSS solution is water, with a simple approach, we take water boiling point as PEDOT:PSS bubble point. The main problem to developed a thin flexible film is a crack that cause by intrinsic stress that arise during deposition process.

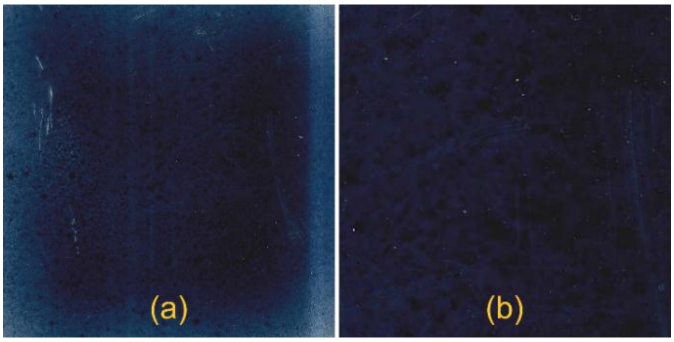

Figure 1. Pristine PEDOT:PSS Flexible Films (a) 1x Zoom (b) 3x Zoom

In order to develop a good morphology, the operation condition is set to a best suitable condition at spray distance 20 cm and annealed temperature 90ºC. The mechanisms of intrinsic stress are not well quantified and most estimates of intrinsic stress levels are obtained by experimental measurement [21]. Due to a difference in thermal expansion of PEDOT:PSS ($49.92x10^{-6}$ K^{-1} [22]) and PET ($80x10^{-6}$ K^{-1} [23]), slow rate deposition will be use in spray pyrolysis method so the expanded annealed film of PEDOT:PSS and PET substrate can be controlled. Spray distance also become important because we also need a good distribution of PEDOT:PSS droplets in order to get a dense film. The closer the spray distance will lead to the droplet splash and resulting poor distribution, also the farther the spray distance will cause the droplets fly away as the result of thermophoretic force. With this operation condition, PEDOT:PSS has a great morphology as shown in Figure 1 and resulting the electrical conductivity 4.5 S/cm. It is noted that the electrical conductivity of PEDOT:PSS solution is 1 S/cm.

Effect of Secondary Doping

In this study, three methods of secondary doping was performed to enhance the conductivity of PEDOT:PSS film. The condition used are at 90ºC annealed temperature and 20 cm spray distance. The difference look very clear as shown in Figure 2, pristine PEDOT:PSS film looks glossy while with the addition of DMSO in solvent addition method (SAM), the SAM PEDOT:PSS film, looks opaque. The process took a long time because DMSO boiling point, 189ºC, is too far apart from annealing temperature. Although the process is very long and the film looks opaque, there is no crack formed in the doped PEDOT:PSS film which the morphology still can be accepted.

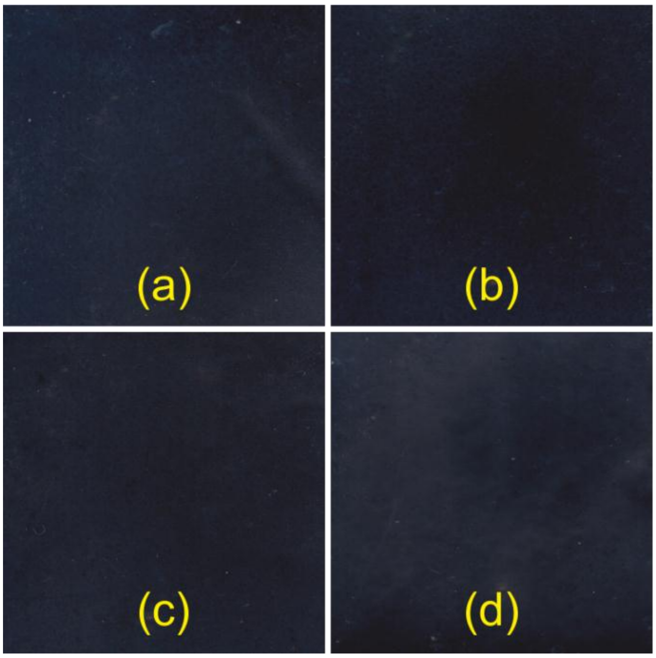

Figure 2. SAM PEDOT:PSS Flexible Films (a) 33% (b) 50% (c) 67% and (d) 75%

Another doping method, SVM and PSRM have failed to prove an increasing of film conductivity because PEDOT:PSS film was dissolved by DMSO before it completely evaporated. It shows that evaporating DMSO at 90ºC annealed temperature which is far below the boiling point cannot be done.

A scheme is proposed due to the failing of SVM and PSRM. When PEDOT:PSS film was exposed to DMSO liquid and DMSO vapor at slow rate evaporation, it attached to the film and interacted with PEDOT:PSS. At certain point, the accumulation of DMSO vapor at PEDOT:PSS film is getting higher, while the vapor that attached to the film cannot evaporate faster and make the rate of accumulation is not equal to zero, thus with DMSO thermal expansion, 880×10^{-6} K^{-1}, show a great difference with thermal expansion of PET cannot be ignored and make the PEDOT:PSS film cracked, as shown in Figure 3, due to thermal stress as mentioned above.

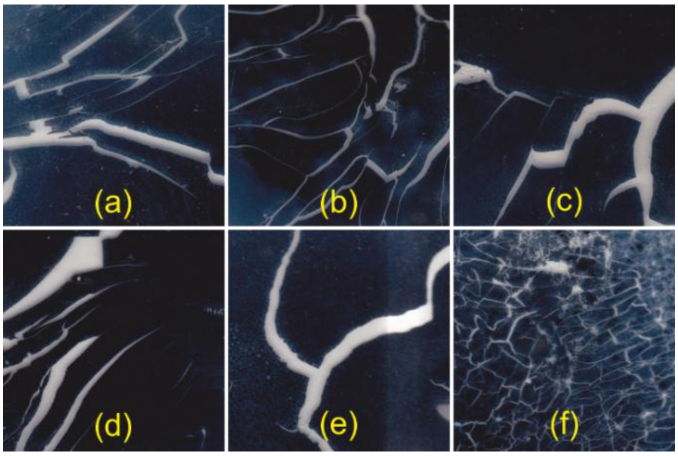

Figure 3. PSRM PEDOT:PSS Films (a) 1 mL, (b) 2 mL, (c) 3 mL, (d) 4 mL, (e) 5 mL, and (f) SVM for 30 min

We tried the condition at 110°C and 20 cm spray distance. The result show that doped PEDOT:PSS film formed a good morphology, but PET substrate was failed to hold onto its perfect morphology. The optical clarity of PET substrate is very poor, a haze was shows at certain spots due to some local concentrated area of DMSO. The optical clarity is one of the important characteristic in dye synthetized solar cell (DSSC) because it has to transmit the light as much as possible so the light can be maximized to be absorb by molecular dye [24].

It is also found that stiffness of PET was become very rigid, stiffness parameter can be calculated by Young Modulus. A research proves that change in modulus of PET from 30°C to 100°C is only decreased from 3.9 GPa to 3.2 GPa, while from 100°C to 150°C shows a great decreasing from 3.2 GPa to 1.0 GPa [25]Thus, increasing annealed temperature was not a good option to achieved a good morphology and failed to show an increasing performance.

IR Spectra Characterization

As shown in Figure 4, the IR spectra of the PEDOT:PSS film in different annealing temperature is not having any different. The spectrum obtained for the PEDOT:PSS film is similar to those reported in the literature [26]. Asymmetric stretching mode of C=C was assigned at the band near 1513 cm^{-1} and inter-ring stretching mode of C–C at the band near 1296 cm^{-1}. The band at 1170, 1127, and 1033 cm^{-1} are attributed to the C–O–C bending vibration in ethylenedioxy group. It is also found that at the band near 965, 919, 828, and 670 cm^{-1} are assigned to stretching vibration of C–S–C bond in thiophene ring. The band near 586 cm^{-1} is assigned to oxyethylene ring deformation, while the band near 480 and 428 cm-1 are attributed to C–O–C deformation [27].

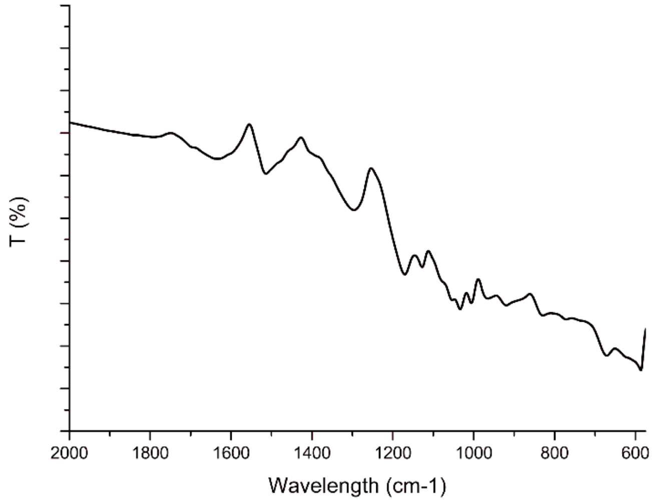

Figure 4. IR Spectra of Pristine PEDOT:PSS Flexible Film

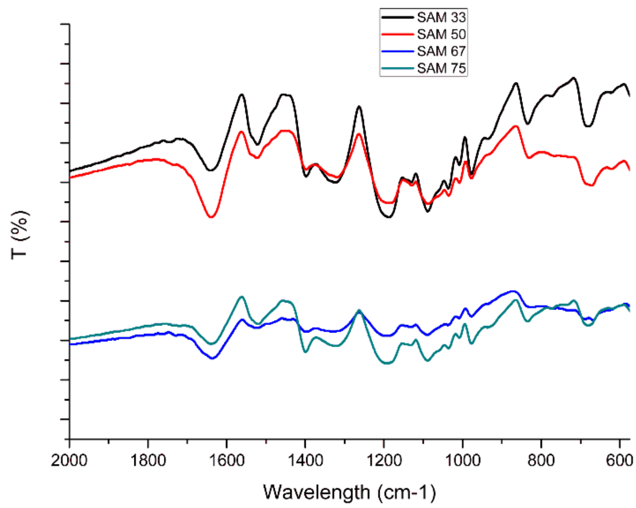

Figure 5. IR Spectra of SAM PEDOT:PSS Flexible Films

As shown in Figure 5 the IR spectra of enhanced SAM PEDOT:PSS film is having a slight change as compared to the pristine PEDOT:PSS film and all the samples of SAM doping have very similar peaks within the wavenumber between 2000 and 575 cm^{-1}. The band near 1397 cm^{-1} asymmetric CH_3 and 1320 cm^{-1} are assigned to asymmetric deformation of CH_3 that attached to S. Another new band also found near 1088 cm^{-1} due to stretching of SO [28]. There is a shifting peak show from pristine film to enhance film corresponding to the SO_3H group of PSS. The pristine PEDOT:PSS have a peak near 1170 cm^{-1} [29]. The addition of DMSO at 33%, 50%, 67%, and 75% concentration lead a shifting peak to 1184 cm^{-1}, 1187 cm^{-1}, 1193cm^{-1}, and 1193 cm^{-1}, respectively, DMSO disrupt the bonding of SO_3H group with the insulating PSS chains and lead the phase separation between the PEDOT and PSS chains [30].

SEM Characterization

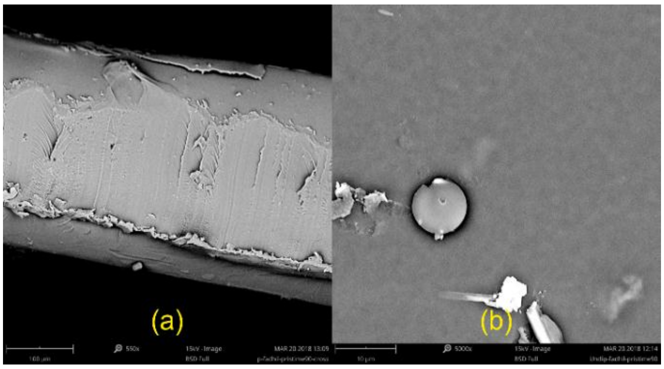

Figure 6. SEM Image of PEDOT:PSS Pristine Flexible Film (a) Cross Section Image (b) Surface Area Image

Figure 6 show the SEM image of PEDOT:PSS pristine flexible film at annealing temperature 90ºC and 20 cm spray distance. The thickness of PEDOT:PSS film has a good distribution with approximately 55 µm

As depicted in Figure 6a, PEDOT:PSS film display that the film thickness has a good distribution with approximately 55 µm thick of PEDOT:PSS. The boundary layer between PET substrate and PEDOT:PSS film is also clearly can be seen. The PEDOT:PSS film also has a smooth surface area (figure 6b) and there is no crack formed which means the operation condition can be acceptable because intrinsic stress is not found. A damage part is also found due to cutting process and show that the film is not a scratch resistance.

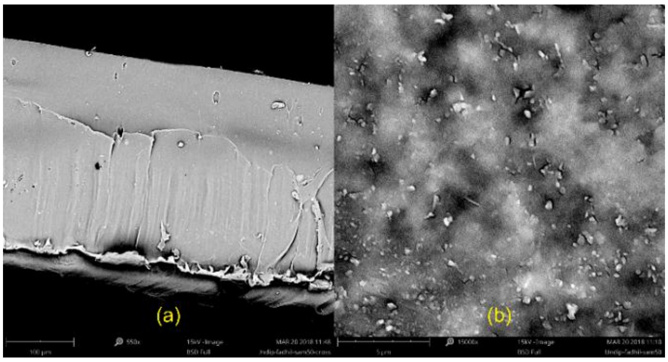

Figure 7. SEM Image of SAM 50 PEDOT:PSS Film (a) Cross Section (b) Surface Area

Figure 7 show the SEM image of SAM with 50% DMSO addition. It is clearly can be seen that there is a micro-sized crack formed, the distribution in not good enough, and creating a haze which resulting opaque look. The distribution is not good enough because the annealed temperature is very low compared to DMSO boiling point and a hydrophobic effect was found on PET substrate. As compared with the pristine PEDOT:PSS film, the haze indicated that the DMSO is not fully evaporated and still attached to the film. This is also has been prove in the result of IR spectra of SAM PEDOT:PSS. Even though a micro-sized crack formed, the electrical conductivity is not affected by it.

Film Electrical Conductivity

The room electrical conductivity of pristine PEDOT:PSS flexible film at annealed temperature 90ºC and spray distance 20 cm is 4.5 S/cm. The addition of polar organic solvent, DMSO, as secondary dopant effectively enhances the conductivity of the PEDOT:PSS film. In this study, the pristine PEDOT:PSS film has a low conductivity below 5 S/cm. SAM prove it can enhance the PEDOT:PSS conductivity with a highest value of 770 S/cm by doping 75% of DMSO in the PEDOT:PSS solution This result is higher than the reported value of 680 S/cm [31]. It is also proved that increasing DMSO concentration in solution can also increase its conductivity. With 33%, 50%, 67%, and 75% DMSO concentration, it can increase to 217, 300, 463, and 770 S/cm.

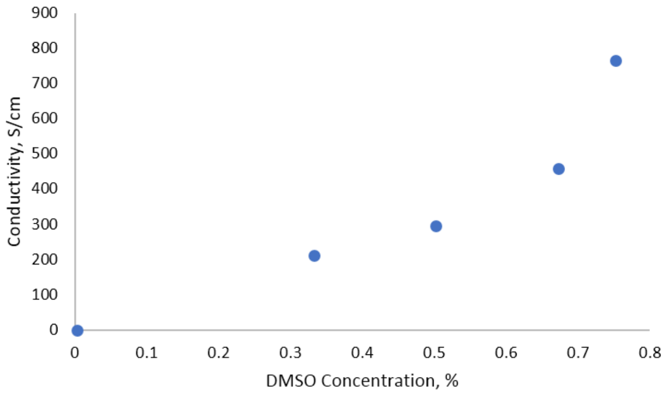

Figure 8. SAM PEDOT:PSS Films Electrical Conductivity

CONCLUSION

Developing a flexible film of PEDOT:PSS can be done using spray pyrolysis method with a suitable condition to anneal PEDOT:PSS film on PET substrate are at annealing temperature 90ºC and 20 cm spray distance with electrical conductivity is 4.5 S/cm. Secondary doping using DMSO proved can increase PEDOT:PSS film. Doping with 75% DMSO using SAM can increase the conductivity up to 770 S/cm, while SVM and PSRM fail due to poor film morphology. According to the IR spectra, annealing up to 110ºC was not found any sign of PEDOT:PSS degradation and there is a shifting of SO_3H group from pristine PEDOT:PSS film to doped PEDOT:PSS film. SEM analysis also found that at pristine PEDOT:PSS film, there is no any sign of crack formed at 90ºC while doped PEDOT:PSS film form micro-sized crack and haze that resulting opaque look in the film.

REFERENCES

[1] J.-M. Nunzi, "Organic photovoltaic materials and devices," *Comptes Rendus Phys.*, vol. 3, no. 4, pp. 523–542, 2002.

[2] U. Lange, N. V. Roznyatovskaya, and V. M. Mirsky, "Conducting polymers in chemical sensors and arrays," *Anal. Chim. Acta*, vol. 614, no. 1, pp. 1–26, 2008.

[3] A. Amiet, S. Nahavandi, and A. Kaynak, "Electromagnetic interference shielding and radiation absorption in thin polypyrrole films," vol. 43, pp. 205–213, 2007.

[4] P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, H. Gerischer, C. W. T. Eds, and J. Wang, *Electrochromism: Fundamentals and Applications*. 1995.

[5] R. J. Mortimer, A. L. Dyer, and J. R. Reynolds, "Electrochromic organic and polymeric materials for display applications," *Displays*, vol. 27, no. 1, pp. 2–18, 2006.

[6] F. Louwet *et al.*, "PEDOT/PSS: synthesis, characterization, properties and applications," vol. 136, pp. 115–117, 2003.

[7] U. Lang, N. Naujoks, and J. Dual, "Mechanical characterization of PEDOT : PSS thin films," vol. 159, pp. 473–479, 2009.

[8] Y. Li, *Organic Optoelectronic Materials*. 2015.

[9] I. Cruz-cruz, M. Reyes-reyes, M. A. Aguilar-frutis, A. G. Rodriguez, and R. López-sandoval, "Study of the effect of DMSO concentration on the thickness of the PSS insulating barrier in PEDOT : PSS thin films," vol. 160, pp. 1501–1506, 2010.

[10] O. P. Dimitriev, D. A. Grinko, Y. V Noskov, N. A. Ogurtsov, and A. A. Pud, "PEDOT : PSS films — Effect of organic solvent additives and annealing on the film conductivity," vol. 159, pp. 2237–2239, 2009.

[11] J. Chen, H. Wei, and K. Ho, "Using modified poly (3 , 4-ethylene dioxythiophene): Poly (styrene sulfonate) film as a counter electrode in dye-sensitized solar cells," vol. 91, pp. 1472–1477, 2007.

[12] M. J. Ikei, T. Y. Amaya, S. U. Ramoto, and K. M. Atsumoto, "Conductivity Enhancement of PEDOT / PSS Films by Solvent Vapor Treatment," *Int. J. Soc. Mater. Eng. Resour.*, vol. 20, no. 2, pp. 158–162, 2014.

[13] J. P. Thomas, L. Zhao, D. McGillivray, and K. T. Leung, "High-efficiency hybrid solar cells by nanostructural modification in PEDOT:PSS with co-solvent addition," *J. Mater. Chem. A*, vol. 2, no. 7, p. 2383, 2014.

[14] A. M. Nardes, M. Kemerink, M. M. de Kok, E. Vinken, K. Maturova, and R. A. J. Janssen, "Conductivity, work function, and environmental stability of PEDOT:PSS thin films treated with sorbitol," *Org. Electron. physics, Mater. Appl.*, vol. 9, no. 5, pp. 727–734, 2008.

[15] S. Park, S. J. Tark, and D. Kim, "Effect of sorbitol doping in PEDOT : PSS on the electrical performance of organic photovoltaic devices," *Curr. Appl. Phys.*, vol. 11, no. 6, pp. 1299–1301, 2011.

[16] T. Wang, Y. Qi, J. Xu, X. Hu, and P. Chen, "Effects of poly (ethylene glycol) on electrical conductivity (styrenesulfonic acid) film," vol. 250, pp. 188–194, 2005.

[17] Y. Xia and J. Ouyang, "Anion effect on salt-induced conductivity enhancement of poly (3 , 4-ethylenedioxythiophene): poly (styrenesulfonate) films," *Org. Electron.*, vol. 11, no. 6, pp. 1129–1135, 2010.

[18] W. Jiantai, "Highly conductive PEDOT : PSS transparent electrode prepared by a post-spin-rinsing method for efficient ITO-free ...," *Sol. Energy Mater. Sol. Cells*, vol. 144, no. January, pp. 143–149, 2016.

[19] X. Shi *et al.*, "Electrospinning of Nanofibers and Their Applications for Energy Devices," *J. Nanomater.*, vol. 2015, 2015.

[20] D. Perednis, "Thin Film Deposition by Spray Pyrolysis and the Application in Solid Oxide Fuel Cells," *Int. J. Thin Film. Sci. Technol.*, no. 15190, 2003.

[21] J. W. Hutchinson and H. M. Jensen, "Stresses and Failure Modes in Thin Films and Multilayers," *Engineering*, vol. 3, no. October, p. 45, 1996.

[22] N. Z. Khan and N. Brunswick, "Modeling and Simulation of Organic MEM Relay for Estimating the Coefficient of Thermal Expansion of PEDOT:PSS," pp. 120–123, 2017.

[23] Goodfellow, "Polyethylene Terephthalate Polyester (PET , PETP) - Properties and Applications - Supplier Data," pp. 1–6, 2003.

[24] H. Wan and H. Wan, "Dye Sensitized Solar Cells," 2004.

[25] M. K. Looney, D. Mackerron, R. Adam, and K. Hashimoto, "Latest advances in substrates for flexible electronics Factors influencing film choice," *J. Soc. Inf. Disp.*, no. December, pp. 1075–1083, 2007.

[26] Q. Zhao, R. Jamal, L. Zhang, M. Wang, and T. Abdiryim, "The structure and properties of PEDOT synthesized by template-free solution method," *Nanoscale Res. Lett.*, vol. 9, no. 1, pp. 1–9, 2014.

[27] S. Garreau, G. Louarn, and J. Buisson, "In situ spectroelectrochemical Raman studies of poly (3, 4-ethylenedioxythiophene)(PEDT)," *Macromolecules*, vol. 32, no. 20, p. 6807, 1999.

[28] N. Mozhzhukhina, L. P. Méndez De Leo, and E. J. Calvo, "Infrared spectroscopy studies on stability of dimethyl sulfoxide for application in a Li-air battery," *J. Phys. Chem. C*, vol. 117, no. 36, pp. 18375–18380, 2013.

[29] E. Liu *et al.*, "Preparation of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate)/silicon dioxide nanoparticles composite films with large thermoelectric power factor," *J. Compos. Mater.*, p. 002199831771257, 2017.

[30] H. Song, C. Liu, J. Xu, Q. Jiang, and H. Shi, "Fabrication of a layered nanostructure PEDOT:PSS/SWCNTs composite and its thermoelectric performance," *RSC Adv.*, vol. 3, no. 44, p. 22065, 2013.

[31] D. Angmo, N. Espinosa, and F. C. Krebs, *Indium TIn Oxide-Free Polymer Solar Cells: Toward Commercial Reality*, no. January. 2014.