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Effects of Silver Nanoparticles Concentration on Resistivity of PEDOT: PSS Thin Conductive Films

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Abstract:

In this study, the effects of silver (Ag) concentration on the electrical resistivity of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) films were investigated. The thin films were prepared by depositing Ag nanoparticles from aqueous dispersion using different concentrations: 2000 and 5000 ppm (parts per million) via syringe deposition method. Based on the results, it was found that, the film's resistance reduced (from 1.49 kΩ to 0.52 kΩ) with the increase in Ag concentration (from 2000 to 5000 ppm). This is supported by the Field Emission Scanning Electron Microscopy (FESEM), in which the 5000 ppm Ag nanoparticles were well dispersed in PEDOT:PSS compared to 2000 ppm Ag nanoparticles. Additionally, the low resistivity of 5000 ppm Ag nanoparticles addition is corroborated with the presence of crystalline peak at 2θ of 38° and 78° evident by X-ray Diffractogram. Low resistivity of film leading to good electrical conductivity, hence, giving promising potential to be utilized in many applications such as in biomedical.

***Keywords:** PEDOT:PSS, silver nanoparticles, resistivity, electrical properties.*

I. INTRODUCTION

During the past years, electrically conductive polymers are of great interest in the field of research because of their tremendous potential for many applications such as biomedical [1]. One of the popular conducting polymers is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) because of its high conductivity, commercially available, good stability and processability [2]. PEDOT is a conjugated polymer which consists of single (σ) bondsalternating with double (π) bonds along its chainand PSS to counterpoise the charge of the charge carriersin form of polarons or radical ions as shown in Fig. 1. The π electrons in their conjugated backbones are easily delocalized since they are weakly bound, hence, able to conduct electricity [3].According to Joy et al. [4], incorporating PEDOT with PSS as a p-type (electron accepting) dopant enhanced the electrical conductivity. This is due to the Coulombic interaction that exist between the polarons on the PEDOT chain that balances the fixed negative charges on the PSS chain. Moreover, through doping with PSS, an insoluble PEDOT can be well-dispersed in water because of the formation of coil-like structure [5].It is believed that, this structure form blobs onthe PEDOT-attached PSS segments to pullthe PEDOT away from water.Consequently, PEDOT:PSSis stabilized and can be easily processed *via* solvent-casting method to produce thin conductive film.

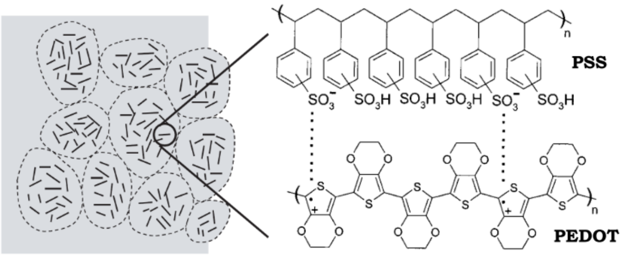

Fig. 1.Schematic illustration on morphology (left) and chemical structure of PEDOT:PSS (right), where the “plus” and“dot” on the PEDOT chain denotes the positive charge and unpaired electron, respectively (adapted from Atabaki et al. [6])

However, PEDOT:PSS has a substantial drawback which is insufficient electrical conductivity ranging from 10^{-6} to 10^{-3} S/cm[7], which makes it inappropriate compare to the commercialized electrodes made from stainless steel for biomedical applications specifically in reducing the risk for acquiring pressure ulcers.It has been stated that, the electrical stimulation can be delivered efficiently to the muscle through electrodes required conductivity about 2×10^{-3} S/cm [8].The insufficient electrical conductivity is due to the insulating PSS shell that limit the charge transmit across thegrains even though conductive PEDOT is rich in the core as illustrated in Fig. 1.In addition, the coiled structure of PEDOT:PSS also leads to the low conductivity due to the localization of positive charges [6]. As such, much effort has been focused to increase the conductivity of PEDOT:PSS by secondary doping. According to Nevrela et al. [7], addition of organic compounds such as sulfoxides, polyols and salts increased the conductivity of PEDOT:PSS. Yet, the mechanism of conductivity improvement by the addition of these secondary dopants is controversial [9]. Thus, the incorporation of metal nanoparticles like silver (Ag) might clearly demonstrate the electrical conductivity improvement in PEDOT:PSS, as claimed by Melendez et al. [9]. Besides, the incorporation of silver nanoparticles with PEDOT:PSS in this study was chosen because it possessesantimicrobial agents’ characteristics, thus it is safeto human body andbeneficial in medicalbackgrounds [10].

Henceforth, in this study, the effect of different concentration of Ag nanoparticles: 2000 and 5000 ppm (parts per million) on the electrical, morphological and structural properties of PEDOT:PSS films are investigated. It is expected that the results could provide deeper understanding of PEDOT:PSS conductivity improvement by the secondary doping, which gives a promising potential for applications.

II. EXPERIMENTAL PROCEDURES

The films containing 1.3 wt. % dispersion PEDOT:PSS (0.5 wt. % : 0.8 wt. %) in H_2O (conductive grade, Sigma Aldrich, Malaysia) incorporated with 2000 and 5000 ppm concentrations of Ag nanoparticles solutions (99.99% pure silver,SilverSol®, Nanosilver Manufacturing Sdn. Bhd., Malaysia) were prepared according to the procedure described by Azman et al. [10] with minor modifications. Initially, 60 ml of Ag nanoparticles solution underwent evaporation process on a hot plate at 100 °C, where the solution saturates to 20 ml. Then, different volumes of evaporated Ag solution, which are 1 ml, 3 ml and 5 ml were mixed with 3 ml of PEDOT:PSS. These solutions were magnetically stirred continuously at room temperature for 12 hrs and later, evaporated at 100 °C for 5 min. Then, each solution was loaded into the syringe for 0.5 ml and dropped onto the glass substrates with 4 × 3 × 1.2 mm dimension. The deposited solution was dried at 60 °C for 24 hrs. Table I lists the materials’ abbreviations and corresponding sample compositions.

Table I: Materials’ abbreviations and corresponding compositions of specimens

Materials’ abbreviations	**Samples (Volume, ml)**		
	PEDOT:PSS	**Ag**	
		2000 ppm	**5000 ppm**
PEDOT:PSS	3		
Ag2		3	
Ag5			3
PEDOT:PSS/Ag2-1	3	1	
PEDOT:PSS/Ag2-3	3	3	
PEDOT:PSS/Ag2-5	3	5	
PEDOT:PSS/Ag5-1	3		1
PEDOT:PSS/Ag5-3	3		3
PEDOT:PSS/Ag5-5	3		5

The samples in form of solution (after completing the evaporation) and film were evaluated for their electrical resistance using a digital multimeter by two-probing method. A Hitachi S-4800 Field Emission Scanning Electron Microscope (FESEM) was used to observe the morphology of the samples at 5000× magnification. In addition, the samples were characterized by Rigaku Ultima IV X-ray Diffractometer (XRD) with Cu- Kα radiation (wavelength (λ) = 1.54056 Å) at 40 kV and 40 mA and the scanning region of the angles (2θ) was from 20° to 80°.

III. RESULTS & DISCUSSION

The resistivity can be defined by how much a material counters the current flow through it. In other words, current simply flowsas the resistance is low. The measured resistivity value of PEDOT:PSS and Ag nanoparticles as well as PEDOT:PSS/Ag are shown in Fig. 3.As expected, doped polymer of PEDOT:PSS shown higher resistivity of 8.25 kΩ resistivity value when compared to both two different concentration Ag nanoparticles used which are 0.76 kΩ and 0.16 kΩ for 2000 and 5000 ppm concentrations, respectively. Coulombic interaction in doped polymer PEDOT:PSS hindered more charges to be transmitted for electrical conductivity thus increasing the resistivity of the materials.Morphological structure illustrated in Fig. 1 also elucidated that the charge carriers on the PEDOT chain are difficult to be transported because of the insulating shell that surrounding the conductive core [6]. Specifically, incorporating PSScreates a hole by removing a π-electron from the PEDOT chain as shown in Fig. 1. Then, an electron jumps from a neighboring position, filling that hole andcreatesa new hole. This electron movement leads to the formation of polarons causingcharge to flow acrossthe polymer chain, hence facilitates the electrical conductivity, as illustrated in Fig. 2.

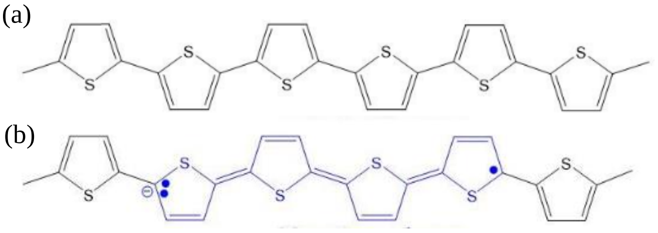

Fig. 2. Chemical structures of polythiophene at (a) undoped state and (b) n-type doping

High resistivity of PEDOT:PSS aqueous solution used in this study are due to the amount of PSS content. It is known that this polyelectrolyte is stable dispersion in water. This can be elucidated with the higher molecular weight of PSS that holds the PEDOT chain segments dissolved in the aqueous form.Unlike PEDOT:PSS, Ag is a material with metallic bonding with clouds of mobile electrons that act as charge carrier leading to lower resistivity. The lower the resistivity, the more readily the material permits the flow of electric charge as evidenced in Fig. 3 for Ag. Results for Ag2 and Ag5 explaining on the increasing of the charge carrier leads to electrical conductivity enhancement and lowering the resistivity.

(b)

As predicted, the resistivity value of PEDOT:PSS decrease with the incorporation of Ag, as evident in Fig. 3(a). Both PEDOT:PSS solution containing 2000 and 5000 ppm of Ag shows a fluctuating trend, when the volume is increasing from 1 to 3 ml, the resistivity value increase (from 1.14 to 1.48 kΩ, and 0.62 to 0.86 kΩ), and further increment of volume to 5 ml results in decreasing resistivity value (1.09 and 0.18 kΩ). This is contradicting with what is expected to be, which has a decline trend of resistivity when adding more amount of Ag in PEDOT:PSS. It is assumed that the resistivity value increases when adding 3 ml of Ag because of the presence of an excess amount of PSS in the solution during the evaporation process after mixing.

On the contrary, the resistivity of the film shows a huge different value compared to those samples in form of solution (Fig. 3(b)). The PEDOT:PSS film exhibits lower resistivity due to the closer arrangement of atoms, thus produce less collision when electrons are moving through the material.Additionally, the Coulombic repulsions between the PSS anions and positive charges on PEDOT are reduced, forming blobs to pull the PEDOT away from water because of the coil-like structure [5,11], as mentioned in previous section (Section I). In the case of Ag, the resistivity value achieved MΩ due to the unstable silver ions (Ag^+) because of the absence of water. Additionally, it might cause by the freestanding Ag thin film could not be obtained due to the deposition of Ag nanoparticles separately on the glass substrate. Hence, the resistivity measured could reflected the resistivity value of the glass substrate, which is an insulating material. Moreover, when adding Ag (from 1 ml to 5 ml) in PEDOT:PSS, the resistivity value decreased from 1.49 to 0.88 kΩ and 9.79 to 0.52 kΩ for 2000 and 5000 ppm, respectively. This is because Ag reduces the Coulombic interaction in PEDOT:PSS by inducing a screening effect, thus allowing the charge carriers on the PEDOT chains to be transported and balancing the negative PSS counterions [12], as illustrated in Fig. 4. These findings are in agreement with the work reported by Melendez et al. [5]. It is worth to note that, the electrical resistivity (ρ) is reciprocal of electrical conductivity (σ). The conductivity can be calculated by the following Equation(1):

$$\sigma = \frac{1}{\rho} \qquad (1)$$

Thus, by increasing the volume of Ag in PEDOT:PSS, the conductivity is enhanced. The trend of the electrical resistivity seems to indicate that larger number of Ag particles promote lower electrical resistivity, which is supported with the FESEM images (Fig. 5).

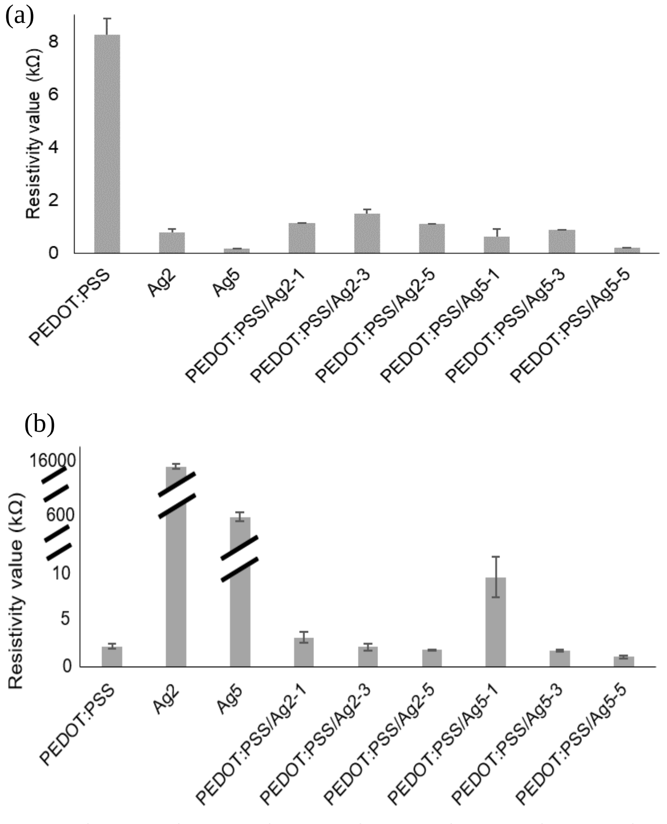

Fig. 3.Resistivity value for pristine PEDOT:PSS, Ag2, Ag5 and PEDOT:PSS/Ag in form of solution (a) and film (b)

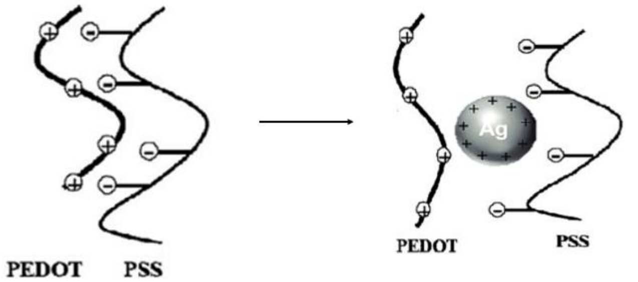

Fig. 4. Schematic illustration of suggested electrical conductivity mechanism of PEDOT:PSS before and after doping withAg nanoparticles

The morphological properties of PEDOT:PSS incorporated with Ag were observed by FESEM, as shown in Fig. 5. It was revealed that the morphology of PEDOT:PSS/Ag is a granular type, similar to that reported by Moreno et al. [13]. It was observed that the dispersed Ag nanoparticles have spherical shape with an average diameter value of 25 nm. Interestingly, the Ag nanoparticles are well distributed within PEDOT:PSS matrix regardless of the Ag concentration.Moreover, it can be seen that, the PEDOT:PSS film with 2000 ppm Ag (Fig. 5(a)) has fewer number of Ag nanoparticles compared to the one with 5000 ppm Ag (Fig. 5(b)). This explained the higher resistivity value of PEDOT:PSS film with lower concentration of Ag, thus, lower electrical conductivity.

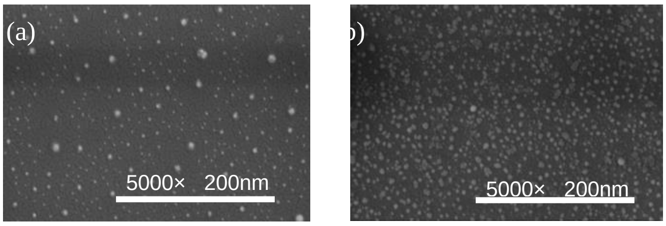

Fig. 5. FESEM image of (a) PEDOT:PSS/Ag2-1 and (b) PEDOT:PSS/Ag5-5 films

The XRD patterns of PEDOT:PSS and PEDOT:PSS/Ag films are illustrated in Fig. 6. It was found that, the PEDOT:PSS film has an amorphous structure since there is no sharp peak in the diffractogram [14]. Addition of 1 ml of 2000 ppm Ag in PEDOT:PSS film shows no crystallinity peak since there is insufficient Ag nanoparticles. On the other hand, the incorporation of 5000 ppm Ag at 5 ml in PEDOT:PSS presented crystalline peak at 2θ of 38° and 78°, which corresponds to the (111) and (311) plane, respectively. This indicates the Ag incorporated has a face centered cubic (FCC) structure [14,15]. In fact, the crystallinity structure in PEDOT:PSS/Ag5-5 film contributes the lower resistivity value, hence, higher electrical conductivity.

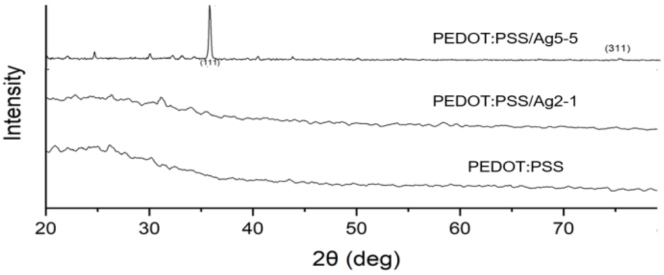

Fig. 6.XRD patterns of pristine (a) PEDOT:PSS, (b) PEDOT:PSS/Ag2-1 and (c) PEDOT:PSS/Ag5-5 films

IV. CONCLUSION

In summary, this study demonstrates the preparation of PEDOT:PSS films incorporated with Ag nanoparticles at different concentration: 2000 and 5000 ppm via syringe deposition method. Specifically, it was found that, the measured resistivity values for samples in form of aqueous dispersion and film were significantly different, yet with similar trend. The addition of Ag in PEDOT:PSS causes the resistivity value decreases to 0.52 kΩ with increasing Ag concentration to 5000 ppm. The FESEM image supports the finding by revealed the larger number of Ag nanoparticles within PEDOT:PSS matrix, which also contributing the low resistivity value. Additionally, the PEDOT:PSS film with 5000 ppm of Ag has a crystallinity structure evident by the x-ray diffractogram. Therefore, it can be said that, the addition of high concentration of Ag in PEDOT:PSS leads to low resistivity value, at the same time, expected to provide good electrical conductivity. Hence, the PEDOT:PSS/Ag gives a promising potential to be utilized in applications including biomedical.

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REFERENCES

[1] G. Kaur, R. Adhikari, P. Cass, M. Bown, and P. Gunatillake, “Electrically conductive polymers and composites for biomedical applications,” *RSC Adv.*, vol. 5, no. 47, pp. 37553–37567, 2015.

[2] D. Mantione, I. del Agua, A. Sanchez-Sanchez, and D. Mecerreyes, “Poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives: Innovative conductive polymers for bioelectronics,” *Polymers (Basel).*, vol. 9, no. 8, 2017.

[3] T. Nezakati, A. Seifalian, A. Tan, and A. M. Seifalian, “Conductive Polymers: Opportunities and Challenges in Biomedical Applications,” *Chem. Rev.*, vol. 118, no. 14, pp. 6766–6843, 2018.

[4] N. Joy, G. P. Gopalan, J. Eldho, and R. Francis, “Conducting Polymers: Biomedical Applications,” *Biomed. Appl. Polym. Mater. Compos.*, pp. 37–89, 2016.

[5] S. P. Rwei, Y. H. Lee, J. W. Shiu, R. Sasikumar, and U. T. Shyr, “Characterization of solvent-treated PEDOT:PSS thin films with enhanced conductivities,” *Polymers (Basel).*, vol. 11, no. 1, 2019.

[6] F. Atabaki, M. H. Yousefi, A. Abdolmaleki, and M. Kalvandi, “Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonic Acid) (PEDOT:PSS) Conductivity Enhancement through Addition of Imidazolium-Ionic Liquid Derivatives,” *Polym. - Plast. Technol. Eng.*, vol. 54, no. 10, pp. 1009–1016, 2015.

[7] J. Nevrela *et al.*, “Secondary doping in poly(3,4-ethylenedioxythiophene):Poly(4-styrene sulfonate) thin films,” *J. Polym. Sci. Part B Polym. Phys.*, vol. 53, no. 16, pp. 1139–1146, 2015.

[8] H. Zhou *et al.*, “Stimulating the comfort of textile electrodes in wearable neuromuscular electrical stimulation,” *Sensors (Switzerland)*, vol. 15, no. 7, pp. 17241–17257, 2015.

[9] R. G. Melendez *et al.*, “On the Influence of Silver Nanoparticles Size in the Electrical Conductivity of PEDOT: PSS,” *Mater. Sci. Forum*, vol. 644, pp. 85–90, 2010.

[10] A. W. Azman *et al.*, “An analysis of a flexible dry surface electrodes,” *Indones. J. Electr. Eng. Comput. Sci.*, vol. 10, no. 1, pp. 74–83, 2018.

[11] A. Giuri *et al.*, “Rheological and physical characterization of PEDOT: PSS/graphene oxide nanocomposites for perovskite solar cells,” *Polym. Eng. Sci.*, vol. 57, no. 6, pp. 546–552, 2017.

[12] X. Crispin *et al.*, “The Origin of the High

Conductivity of (PEDOT-PSS) Plastic Electrodes,” *Chem. Mater.*, no. 18, pp. 4354–4360, 2006.

[13] K. J. Moreno *et al.*, “Silver nanoparticles functionalized in situ with the conjugated polymer (PEDOT:PSS).,” *J. Nanosci. Nanotechnol.*, vol. 9, no. 6, pp. 3987–92, 2009.

[14] C. Gao, J. Li, J. Liu, J. Zhang, and H. Sun, “Influence of MWCNTs doping on the structure and properties of PEDOT:PSS films,” *Int. J. Photoenergy*, 2009.

[15] K. Jyoti, M. Baunthiyal, and A. Singh, “ Characterization of silver nanoparticles synthesized using Urtica dioica Linn. leaves and their synergistic effects with antibiotics ,” *J. Radiat. Res. Appl. Sci.*, 2016.

[16] D. Li, B. Hong, W. Fang, Y. Guo, and R. Lin, “Preparation of well-dispersed silver nanoparticles for oil-based nanofluids,” *Ind. Eng. Chem. Res.*, vol. 49, no. 4, pp. 1697–1702, 2010.

UdaimatunnoorAzmyundergraduate student and works on the conductivity and resistivity of the PEDOT:PSS doped silver nanoparticles of different concentration was done for the final year project.

Zuraida Ahmad Associate professor and recognized with the Ir. title by the Board of Engineer Malaysia (BEM). She has published more than 80 research articles, specifically about biomaterials and composites. Currently, her research interest is focused on the conductive polymers like PEDOT:PSS for biomedical applications.

Nur’Aishah Ahmad Shahrimpostgraduate student and works involved in preparation and characterization of the PEDOT:PSS doped silver nanoparticles for pressure ulcer prevention

Amelia Wong Azman Associate professor and her research works in articles and book has been published in designated platforms. She also has embarked in the conductive polymer research by introducing electrical stimulation for the biomedical application.

FawwazEniolaFajingbesipostgraduate student and work is focused on the electrical stimulation in PEDOT:PSS doped silver nanoparticles for pressure ulcer prevention.