Ink based on poly(3,4-ethylene dioxythiophene), poly(sulfonostyrene) and silver nanoparticles (PEDOT/PSS/SNP) blends for fabrics printing*)

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Abstract: The influence of co-solvents such as: dimethylsulfoxide (DMSO), isopropyl alcohol (IPA), ethylene glycol (EG), ethanol (EtOH) and deionized water (DI) on the properties of ink based on poly(3,4-ethylene dioxythiophene), poly(sulfonostyrene) and silver nanoparticles (PEDOT/PSS/SNP) blends was investigated. The ink was obtained by the ultrasonic dispersion method by mixing PEDOT, PSS and SNP and then adding co-solvents. The ink was applied to the cotton fabric by printing method. The structure, electrical and functional properties of fabrics were investigated. The increase in electrical conductivity was found as a result of the phase separation between PEDOT and PSS due to the use of co-solvents. SEM micrographs showed good adhesion of the ink to the cotton fiber, which was confirmed by the FTIR method. The developed ink has great application potential, especially in electronic devices for biomedical purposes.

Keywords: poly(3,4-ethylene dioxythiophene), poly(sulfonostyrene), silver nanoparticles, inkjet printing, fabric.

Atrament na bazie mieszaniny poli(3,4-etylenodioksytiofenu), poli(sulfonostyrenu) i nanocząstek srebra (PEDOT/PSS/SNP) do drukowania tkanin

Streszczenie: Zbadano wpływ współrozpuszczalników, takich jak: dimetylosulfotlenek (DMSO), alkohol izopropylowy (IPA), glikol etylenowy (EG), etanol (EtOH) i dejonizowana woda (DI) na właściwości atramentu otrzymanego na bazie mieszaniny poli(3,4-etyleno dioksytiofenu), poli(sulfonostyrenu) i nanocząstek srebra (PEDOT/PSS/SNP). Atrament otrzymano metodą dyspersji ultradźwiękowej poprzez wymieszanie PEDOT, PSS i SNP, a następnie dodanie współrozpuszczalników. Na tkaninę bawełnianą atrament nanoszono metodą druku. Zbadano strukturę, właściwości elektryczne i funkcjonalne tkaniny. Stwierdzono zwiększenie przewodnictwa elektrycznego jako efekt rozdziału faz między PEDOT i PSS na skutek zastosowania współrozpuszczalników. Mikrofotografie SEM wykazały dobrą adhezję atramentu do włókna bawełnianego, co potwierdzono metodą FTIR. Opracowany atrament ma duży potencjał aplikacyjny, zwłaszcza w urządzeniach elektronicznych do celów biomedycznych.

Słowa kluczowe: poli(3,4-etyleno dioksytiofen), poli(sulfonostyren), nanocząstki srebra, druk atramentowy, tkanina.

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Poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) doped silver nanoparticles (SNP) is a promising conductive polymer due to its solubility, electrical conductivity, good thermal stability, and great transparency in the visible wavelength [1]. This conductive polymer is commonly used in the electronic device such as electrodes, sensors, transistors, light emitting diodes, and solar cells [2]. Nonetheless, when compared to good conductors like metals or conductive metal oxides, PEDOT/PSS has a poor conductivity. As a result, it is critical to improve the conductivity of PEDOT/PSS. One of the effective approaches is to dope PEDOT/PSS with metal nanoparticles like SNP as it is claimed by numerous researchers [3–4]. By creating a screening effect, SNP lowers the Coulombic interaction in PEDOT/PSS, allowing charge carriers on PEDOT chains to be transported while balancing the negative PSS counterions [5]. This proved the promising secondary dopants for enhancing electrical conductivity of PEDOT/PSS. With its good conductivity, it can be used as electrodes to stimulate the blood for preventing pressure ulcer in the biomedical devices. These electrodes however, need to be printed on the fabric as its substrate so that the electric current will flow efficiently to serve its purpose. In order to create a biomedical mat embedded with conductive polymer, the inkjet printing method can be used.

The inkjet printing technology has recently gained popularity as a viable deposition process for a wide range of applications, including the manufacture of electrodes for the electronic devices. This technology has been widely used to print low-cost organic electronic devices such as sensors, organic displays, and RFID [6]. This is because the inkjet printing technique can produce drop-on-demand, which a tiny quantity of functional materials can be precisely deposited in well-defined patterns onto a wide range of substrates [7]. As a result, this non-contact technique enables low-cost large-area printing with minimal ink consumption, material waste, and contamination, as well as the possibility of mass production [6–8]. However, one of inkjet printing's challenges is its resolution, which consists in the slightest dot ability to be inkjet-printed without clogging the nozzles. To overcome these obstacles, one method for printing fine details is to prepare an appropriate concentration of ink that is free of insoluble micro or nanoparticles that can agglomerate and precipitate during the printing process.

Inkjet printing formulations made from PEDOT/PSS for printing on flat and rigid or flexible substrates have been established in the literature. According to various studies, a little amount of solvent can be added to the ink composition to improve conductivity [1]. The addition of co-solvents is predicted to involve dielectric screening since the solvent will change the electrical characteristics of PEDOT/PSS/SNP as a result of alterations in the PEDOT chain's conformation or morphological modifications [9]. Xiong *et al.* (2013) developed PEDOT/PSS/SNP ink that was suitable for inkjet printing with a print head model Spectra SE-128 and the printed film with 300 nm thickness achieved a surface resistivity of 182 Ω Sq^{-1}, corresponding to a conductivity of 183 S cm^{-1}. Recently, Barmpakos *et al*. [10] inkjet-printed a multi-parameter paper sensor corresponding to relative humidity, temperature, compressive and tensile bending based on PEDOT/PSS/SNP ink. The findings suggested that the fabricated multi-domain sensor system design is promising for biomedical applications. Yet, the effect of the ink formulation based on PEDOT/PSS/SNP for inkjet printing using fabric as substrate on its properties in biomedical application, especially pressure ulcer prevention is rarely discussed in the literature. Moreover, in comparison to the previous studies, this study presents the preparation of ink formulations of PEDOT/PSS/SNP with the addition of co-solvents and its effects were investigated.

Our earlier work has preliminarily evaluated the effect of the SNP content on the electrical properties of PEDOT/PSS for its potential use as an electrode for electronic devices, especially for biomedical application [5]. This work was aimed to investigate the appropriate formulation of PEDOT/PSS/SNP ink with the incorporation of co-solvents like dimethyl sulfoxide (DMSO), ethylene glycol (EG), ethanol (EtOH), isopropyl alcohol (IPA), and deionized (DI) water to be used during printing on cotton fabric. It was expected that using various types of co-solvents on PEDOT/PSS and SNP in the ink formulations leads to different mechanisms for the changes in conductivity.

EXPERIMENTAL PART

Materials and methods

The materials used in this work were poly (3,4-ethylene dioxythiophene): poly (styrene sulfonate) (PEDOT/PSS) (0.5 wt.%: 0.8 wt.%) containing 1.3 wt.% dispersion in H_2O (1 S cm^{-1}) (conductive grade, Sigma Aldrich, Malaysia) and silver nanoparticles (SNP) colloidal solutions with 5000 parts per million (ppm) concentration (99.99% pure silver, with an average particles diameter of 10–50 nm, SilverSol®, Nanosilver Manufacturing Sdn. Bhd., Malaysia); the various co-solvents such as ethylene glycol ($HOCH_2CH_2OH$, molarity of 62.07 g mol^{-1}), ethyl alcohol (C_2H_5OH, 95% v/v, molarity of 46.07 g mol^{-1}), dimethyl sulfoxide (DMSO) (C_2H_6OS, 99%, molarity of 78.13 g mol^{-1}), and isopropyl alcohol (IPA) (C_3H_8OH, 99%, molarity of 60.1 g mol^{-1}) and all other related substances used in this work were chosen from analytical reagent grade as received from Merck Company (Germany). Plain woven fabric of 100% cotton with a GSM of 180 supplied by the local manufacturer (Malaysia) was used as the substrate.

Table 1 shows the PEDOT/PSS ink formulations consisting similar amount of PEDOT/PSS, SNP, deionized water, isopropyl alcohol but containing different types of co-solvents. These formulations were prepared according to the previous works [5, 9] with minor modifications. Initially, PEDOT/PSS was mixed with SNP and ultrasoni-

T a b l e 1. PEDOT/ PSS ink formulations

Ink composition	Ink 1 wt%	Ink 2 wt%	Ink 3 wt%
PEDOT/PSS	5	5	5
Deionized water	10	10	10
Isopropanol	2	2	2
SNP	–	10	10
DMSO	–	1	1
Ethanol	–	–	0.1
EG	–	–	2

cated in the water bath for 10 min, then homogenously mixed using homogenizer for 5 min and later magnetically stirred on the magnetic plate for 15 min. The prepared inks were filtered through 0.45 μm and 0.22 μm syringes to remove the particles that had agglomerated during the ink formulation procedure.

The inkjet printing was made using a Canon Pixma MP145 printer set to 1200 dpi. Prior to printing, the ink cartridge was cleaned using deionized water to ensure that the cartridge was free from contamination or any ink residues. Then, the cartridge was dried at 37°C in a laboratory dryer overnight to remove moisture from the components. Later, the printer was flushed with PEDOT/PSS ink to remove any pollutant from the preceding print. To eliminate surface contaminants and provide a clean fabric surface to improve ink adhesion onto its surface, all substrates must be cleaned by the lint remover. The testing structure of rectangular shapes with dimension 3 × 3 cm was acquired to assess the quality and the resolution of the print related to the assessing of the printer capability to print the full print areas objects. Various printing parameters were carried out with increasing number of printing layers from 1, 3, 5, 10 and 15 layers. After each layer of printing, the samples were dried at room temperature for 2 min and then the additional layers were printed on top of the samples. Finally, the samples were dried under ambient atmosphere for 24 h.

The changes of the prepared inks were observed for its stability prior printing. The pH of the prepared inks was obtained using pH paper universal indicator. The surface morphology of printed PEDOT/PSS ink on the fabric substrate was observed through scanning electron microscope (SEM) (JEOL, JSM-IT100 InTouchScope™, Japan). The functional groups existed in the samples were determined using Fourier Transformed Infra-red (FT-IR) spectrophotometer (Bruker INVENIO-S, United States) within the range from 4000 cm^{-1} to 600 cm^{-1} with resolution of 4 cm^{-1}. The electrical resistivity was measured using two-probe apparatus (Prostat PRS-801 Resistance Meter, United States). The resistivity values were calculated by distinguishing between two orientations of the printed pattern on the samples: parallel direction to the movement of the printhead and perpendicular direction to the movement of the printhead.

RESULTS AND DISCUSSION

Characterization of Prepared PEDOT/PSS/SNP inks

The physical properties of the prepared composite inks based on PEDOT/PSS/SNP were evaluated. After 24 h, no sedimentation was observed in the inks. However, after more than a week of standing, a few micro-scale black particles could be found on the bottom and sides of the container, indicating that the inks' stability needed to be improved further. The observation was similar to the finding reported previously [2]. As a result, the printing works in this study were accomplished within a week of the ink formulation. The pH of the prepared inks ranged between 6 to 8. The range is acceptable since the pH is vital to prevent any damage to printhead and cartridge [9].

Characterization of Inkjet Printed PEDOT/PSS/SNP Film on Fabrics

The resistivity of five different locations on each ink-jet printed sample was measured for each orientation, and an average of the measured values was analyzed and shown in Fig. 1. The results indicated the effect of the co-solvents in the PEDOT/PSS/SNP ink formulation printed onto the fabrics on its electrical properties. The cotton fabric possesses 4.63×10^8 Ω cm attributed to its insulator properties of the threads. Printing with Ink 1 at 1 layer decreases the resistivity to 2.27×10^8 Ω cm which is about 50%. Increasing the number of layers to 15 during printing gradually decreases the resistivity 1.83×10^7 Ω cm that is about one order of magnitudes. Adding SNP and DMSO to the ink (Ink 2) gives an opposing effect when printing 3 layers, while printing to 10 layers is reducing resistivity due to the increasing PEDOT and SNP interaction and DMSO reorientation of the PEDOT chains arrangement [5], [11]. On the other hand, the Ink 3 reduces resistivity when printing up to 10 layers due to the phase separation between PEDOT and PSS caused by the reduction of Coulombic interaction between them since screening effect between positively charged PEDOT chains and negatively charged PSS chains occurs when adding ethanol and EG in the Ink 2 formulation [12–13]. At 15 layers, the resistivity of Ink 2 and Ink 3 increases in comparison to Ink 1 because of the charge carrier mobility limits between the dried particles in an ink-jet printed film caused by the interaction between the PEDOT/PSS, SNP and co-solvents. It is worth noting that the electrical resistivity (ϱ) is the multiplicative inverse of electrical conductivity (σ). The findings can be concluded with the best printing at 15 layers, where the resistivity of each ink formulation decreases while the conductivity increases due to the uniformity of the pattern by building up a higher concentration of the conductive PEDOT/PSS on the substrate.

The surface morphology of the fabric and PEDOT/PSS--based fabric printed with 15 layers was examined

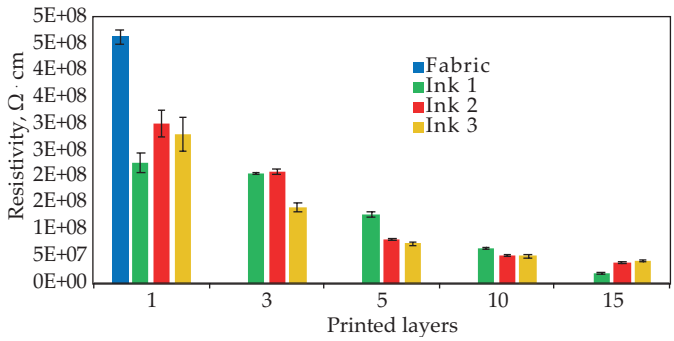

Fig. 1. Resistivity of printed PEDOT/PSS on fabrics

and displayed in Figs. 2a) to 2d). It was revealed that the PEDOT/PSS ink (Ink 1) was well-dispersed on the threads of the fabrics with the presence of coagulation of PEDOT/PSS at certain areas, similar to observation made by Tadesse *et al*. [12]. This implied good interaction between the cotton fiber and PEDOT/PSS, what is promising for developing conductive fabrics. The observation was also confirmed by the low resistivity of the samples since it covered the fabric's surface. Embedment of Ink 2 on the fabric showed the presence of few numbers of SNP particles and agglomerated particles. The surface of Ink 3-based fabric presented SNP particles and was free from agglomeration of any particles. This indicated the improvement in homogeneity of Ink 3 which was obtained with the addition of ethanol and EG in the ink formulation compared to Ink 2.

The functional groups existed in the cotton fabric and Ink 3-based fabric were presented in the FT-IR spectra in Fig. 3. The prominent peaks of the cotton fabric were observed at 3322, 2904, 1630, and 1025 cm^{-1} which is attributed to the -OH stretching, C-H stretching, -OH bending, and C-O stretching, respectively (Fig. 3a). Similar peaks were also displayed when embedding I3 on the fabric by inkjet printing method shown in Fig. 3b. It is noticeable that there was displacement of peaks due to the hydrogen bonding interactions between the cotton fiber and PEDOT/PSS/SNP-based ink. The intensity of the peaks was also decreasing, which is associated with the existence of some other components present in the sample similar to those findings reported by Tadesse *et al*. [12]. As a result, the findings confirmed the successful introduction of co-solvents like DMSO, ethanol and EG as conductive enhancers to the PEDOT/PSS/SNP via inkjet printing.

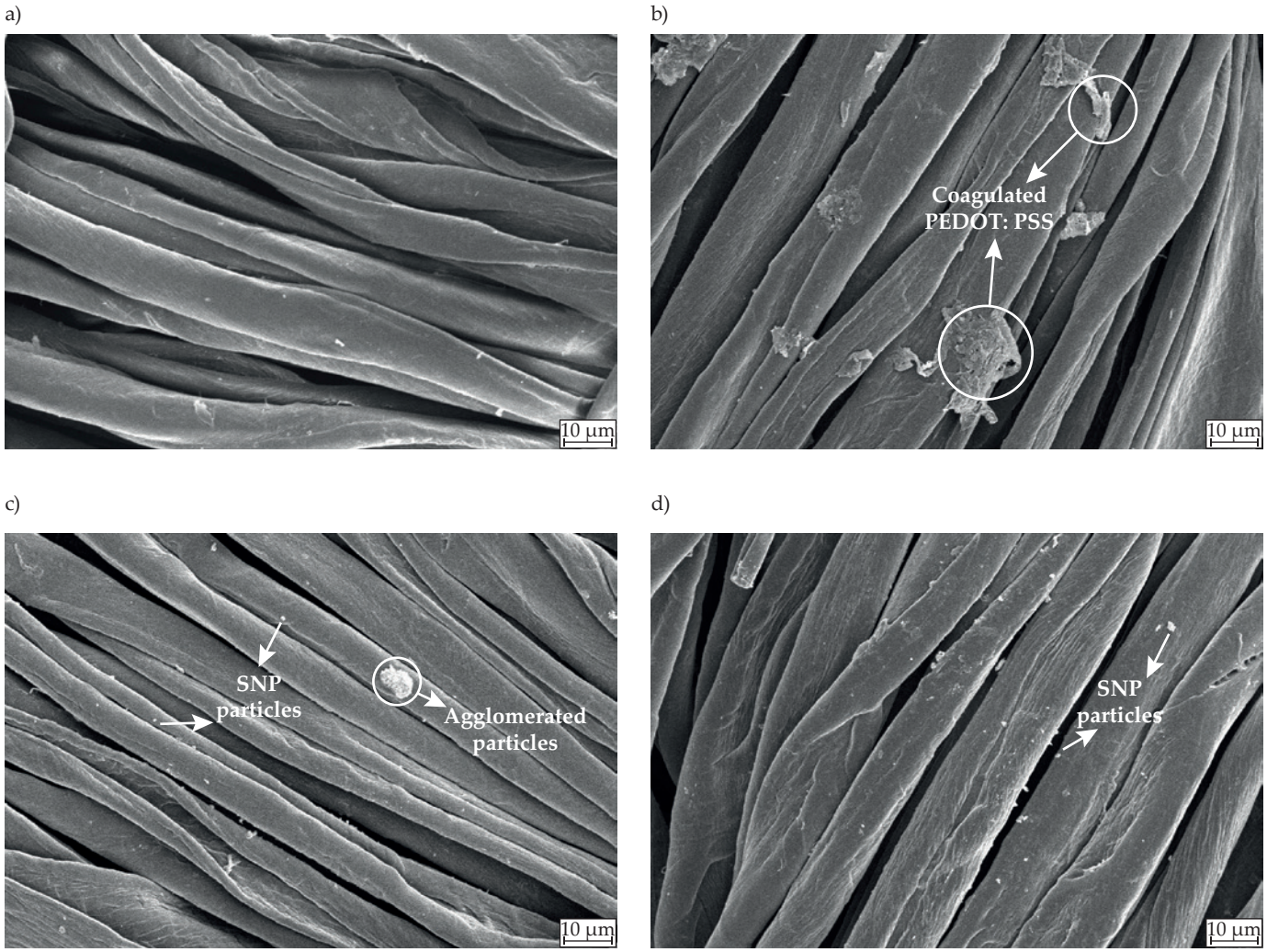

Fig. 2. SEM micrographs of: a) cotton fabric and PEDOT/PSS-based fabric printed with: b) ink 1, c) ink 2, and d) ink 3 at 1000X magnifications

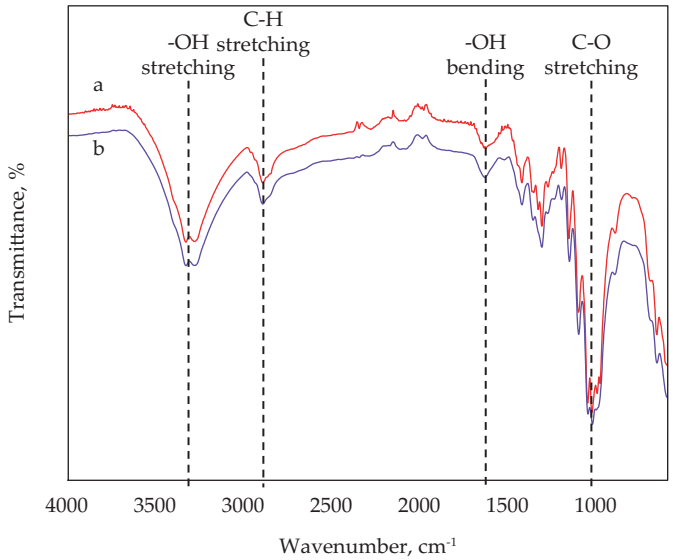

Fig. 3. FT-IR spectra of: a) cotton fabric, and b) ink 3-based fabric

The mechanisms of the conductivity enhancement of the inkjet-printed embedment of PEDOT/PSS ink at 10 layers could be proposed. Soleimani-gorgani [9] stated that reduced Coulomb interaction between PEDOT and PSS due to the co-solvents addition resulted in the separation of PSS from PEDOT chains. Tadesse *et al*. [12] supported the findings by demonstrating the partial reduction of PSS chain in PEDOT/PSS grains are causing the connectivity improvement, hence, its conductivity. Rwei *et al*. [14] reported the conformational changes in PEDOT/PSS chain. When treated with solvents due to the increasing interchain and intrachain charge carrier mobility, the enhancement of conductivity occurs. The change from a coil to a linear structure in PEDOT/PSS is suggested from the outcome. In this work, the possible structural changes of PEDOT/PSS film after the addition of SNP, DMSO, ethanol and EG can be expressed in Fig. 4. The addition of co-solvents in PEDOT/PSS/SNP screens the ionic interaction between PEDOT film and PSS ion by creating hydrogen bonding with PSS, preceding to phase separation between PEDOT film and PSS and linearly oriented PEDOT chains, what leads to the conductivity enhancement of PEDOT/PSS.

CONCLUSIONS

Ink formulations based on PEDOT/PSS doped with SNP and blended with DMSO, EG and ethanol for inkjet printing on the cotton fabric was demonstrated in this work. The findings showed the effect of the co-solvents' addition on the electrical, morphological and functional properties of PEDOT/PSS/SNP-based fabric. The addition of the co-solvents as the conductivity enhancers has been confirmed with the decreasing value of resistivity at 10 printing layers, which suggests that the increasing number of printed layers resulted in lowering the resistivity of each ink formulations. The morphological properties of the PEDOT/PSS-based fabric revealed a well-dispersed ink and was supported with the successful adhesion on the cotton fiber evidenced by the FT-IR spectra. The mechanism of the conductivity enhancement for PEDOT/PSS has been also explained basing on the findings. Nonetheless, future works are recommended to confirm the suggested mechanism which includes further characterization on the PEDOT/PSS/SNP ink formulations and the inkjet-printed embedment of PEDOT/PSS/SNP on the cotton fabric as electrodes. It is also suggested to improve the conductivity by making minor modifications on the methods for preparing the PEDOT/PSS/SNP-based fabric like post-treatment technique. Overall, the ink based on PEDOT/PSS/SNP shows great potential usage in wide applications especially in electronic devices for biomedical purposes.

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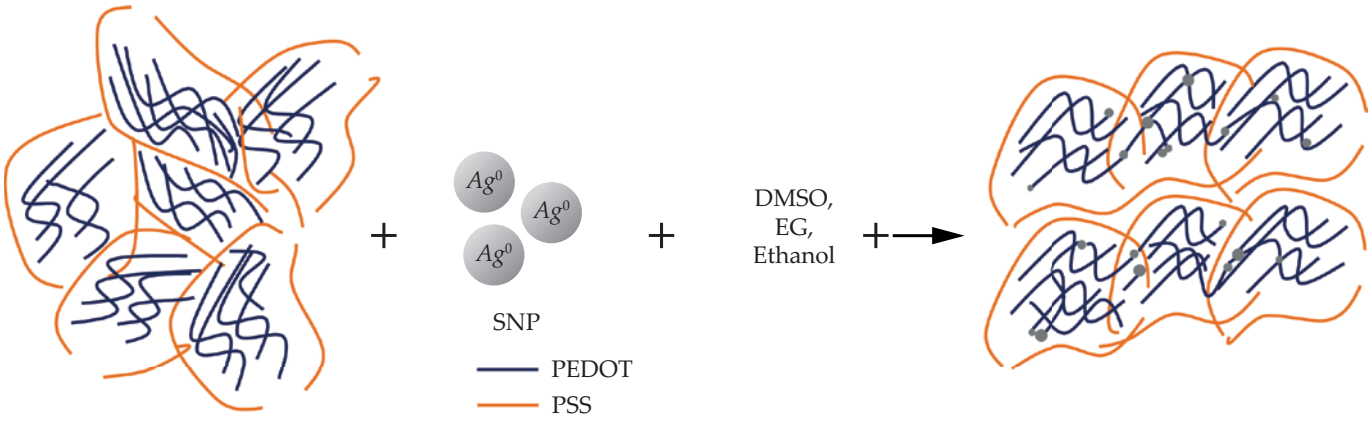

Fig. 4. Schematic mechanism for PEDOT/PSS's conductivity enhancement

REFERENCES

[1] Sain M., Ummartyotin S., Juntaro J. *et al.*: *Journal of Nanomaterials* **2011**, *2011*, 1. https://doi.org/10.1155/2011/606714
[2] Xiong Z., Dong C., Cai H. *et al.*: *Materials Chemistry and Physics* **2013**, *141*, 416. https://doi.org/10.1016/j.matchemphys.2013.05.035
[3] Patil D.S., Pawar S.A. Hwang J.J. *et al.*: *Journal of Industrial and Engineering Chemistry* **2016**, *42*, 113. https://doi.org/10.1016/j.jiec.2016.07.034
[4] Bhowal A.C., Talukdar H., Kundu S.: *Polymer Bulletin* **2018**, *76*, 5233. https://doi.org/10.1007/s00289-018-2652-z
[5] Azmy U., Ahmad Z., Ahmad Shahrim N. *et al.*: *TEST Engineering and Management* **2020**, *83*, 1008. http://www.testmagzine.biz/index.php/testmagzine/article/view/7385/5605
[6] Singh A., Mandal S., Singh V. *et al.*: *16th International Workshop on Physics of Semiconductor Devices* **2012**, *8549*, 854936. https://doi.org/ 10.1117/12.928190
[7] Nguyen P.Q.M., Yeo L.P., Lok B.K. *et al.*: *ACS Applied Materials and Interfaces* **2014**, *6*, 4011. https://doi.org/ 10.1021/am4054546
[8] Srichan C., Saikrajang T., Lomas T. *et al.*: *2009 6th International Conference on Electrical Engineering/ Electronics, Computer, Telecommunications and Information Technology* **2009**, *1*, 465. https://doi.org/ 10.1109/ECTICON.2009.5137049
[9] Soleimani-gorgani A.: *Advances in Natural Sciences: Nanoscience and Nanotechnology* **2018**, *9*, 025009. https://doi.org/10.1088/2043-6254/aac2a0
[10] Barmpakos D., Tsamis C., Kaltsas G.: *Microelectronic Engineering* **2020**, *225*, 111266. https://doi.org/ 10.1016/j.mee.2020.111266
[11] Nevrela J., Micjan M., Novota M. *et al.*: *Journal of Polymer Science, Part B: Polymer Physics* **2015**, *53*, 1139. https://doi.org/ 10.1002/polb.23754
[12] Tadesse M.G., Nierstrasz V., Loghin C. *et al.*: *Smart Materials and Structures* **2017**, *26*, 065016. https://doi.org/ 10.1088/1361-665X/aa6f25
[13] Yildirim E., Wu G., Yong X. *et al.*: *Journal of Materials Chemistry C* **2018,** *6*, 5122. https://doi.org/ 10.1039/c8tc00917a
[14] Rwei S.P., Lee Y.H., Shiu J.W. *et al.*: *Polymers (Basel)* **2019**, *11*, 134. https://doi.org/10.3390/polym11010134

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