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Electrospun Nanofiber Poly (3,4-ethylenedioxytriophene): poly (styrene sulfonate) / poly (vinyl alcohol) as Strain Sensor Application

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Abstract: A strain sensor based on poly (3,4-ethylenedioxytriophene): poly (styrene sulfonate)/poly (vinyl alcohol) (PEDOT: PSS/PVA) nanofiber has been successfully fabricated by electrospinning technique. Patterned copper wires were deposited on the mica flexible substrate with the distance of 1 mm. The sensor then characterized with various strain by one side bending. The conductivity of as-spun nanofiber mats can be adjusted from 0.03 to 1.2 µS cm^{-1} with various concentration of PVA and depends on its structure and its nanofiber diameter. The sensing mechanism of nanofiber-based strain sensor is due to the common piezoelectric effect of PEDOT:PSS polymer and unique nanostructure of nanofiber mats. When the sensor stretched, the length of nanofiber increase affecting the geometrical change and lead the increasing in resistance. This sensor shows good repeatability with gauge factor of 17. The performance of PEDOT:PSS/PVA nanofiber based strain sensor make nanofiber mats as promising alternative materials for strain sensor application.

Keywords: *nanofiber, PEDOT: PSS, PVA, strain sensor, conductivity*

Introduction

The development of nanofiber technology has been increased significantly in the last two decades. Many researchers begin to have more interest on nanofiber than the regular thin film. One of the reasons is that a nanofiber can be easily produced by electrospinning technique through certain conditions. Compared to other techniques, like drawing, self-assembly, polymerization in nanopores templates, and dip-pen nanolithography, electrospinning offers advantages of being a conventional simple method, low production cost and the most potential technique to produce nanofiber on an industrial scale [1–5]. Nanofiber has a large surface area for a given volume. Its textures enhance the transport of ions or other electrical charges [6]. The mechanical, electrical and biocompatibility properties of electrospun nanofiber can also be modified by changing polymer solution and process parameters.

Application of electrospun nanofiber varies in many fields including membrane technology [7], medical application [8–10] and electronic devices [11–14]. The electronic device applications, especially sensors devices, become an interesting topic for future research because of its huge applications. There are many sensors based on nanofiber structure, such as a gas sensor, strain sensor, biomimetic sensors, and real-time radiation sensor [15–20]. Moreover, the nanofiber-based sensor exhibits high sensitivity and fast response [21]. Recently, the demand on strain sensor is relatively high.

There are a lot of flexible strain sensors based on inorganic materials have been developed [22–25]. All these materials require a flexible polymer for the substrate because the inorganic materials are unable to get high repeatability as high as flexible polymers [21]. If the electrical properties of inorganic materials could be replaced by the properties of the organic materials (flexible polymer), that means we can improve the flexibility and electricity at once in nanofiber-based strain sensor. Poly (3,4-ethylenedioxytriophene): poly (styrene sulfonate) (PEDOT: PSS) polymer becomes common organic materials used as materials in strain sensor application because of its piezoelectric effect [26,27]. PEDOT: PSS polymer commonly cast on indium tin oxide (ITO) substrate using spin-coating technique [28,29]. Electrospinning is another technique to cast PEDOT: PSS with the addition of poly (vinyl alcohol) or PVA as a flexible thin film[30–33]. In this study, we proposed a simple and low cost method to fabricate strain sening elements of strain sensor using PEDOT: PSS mixed PVA. The sensing performance of the as-prepared sensor is reported.

Materials and Experimental

Materials

The PVA polymer PVA (M_w = 85.000 – 124.000) powder was purchased from Sigma-Aldrich, while the PEDOT: PSS (PH1000) with a concentration of 1.3 wt% and the PEDOT: PSS ratio was 2:5 v/v was purchased from Heraeus C Stark. All these materials were applied without any further purification.

Electrospinning

The solution used for electrospinning technique were prepared by dissolving (9-13) wt % PVA polymers into distilled water at a temperature of 95 °C and stirred for 2 hours to obtain a homogeneous solution. The PEDOT:PSS/PVA solutions were produces by adding the PEDOT:PSS aqueous dispersion into the PVA solutions with a ratio of 40:60 (v/v). The mixing then stirred at ambient temperature for 45 min. The schematic of electrospinning process used to fabricate PEDOT: PSS/PVA nanofiber reported previously [34]. The electrospinning parameter used during the process was 15 kV voltage, with tip-to-collector distance set at 10 cm. The process took place about 30 minutes and further dried for 15 min.

Strain sensor performance testing

The stretch process and the magnitude of the strain were calculated as reported in the literature [35]. We used mica flexible paper for substrate and copper wire as electrodes. The length and the distance between electrodes were 2 cm and 1 mm, respectively. One end of the strain sensor was fixed on a sample holder, and the other free end of the strain sensor was derived by a mechanical stage, which brings a tensile strain.

Sample Characterization

The electrical response (current-voltage) of the sensor with various strain was measured with Keithley 2400-SMU connected to a computer using a graphical programming language of LabVIEW. All of the measurements were carried out at room temperature in ambient condition. The nanofiber morphology of the samples with a various concentration of PVA was characterized using scanning electron microscope (SEM) JEOL JSM-6510. The samples were mounted on metal stubs and sputter-coated with platinum for 70 s with JEOL fine-coater before SEM characterization. The average nanofiber dimensions and standard deviations were determined by measuring the diameters of about 100 fibers using ImageJ software.

Results and Discussion

The nanofiber mats have been successfully fabricated with uniform diameter and morphology as shown in Figure 1. In this study, we used a different concentration of PVA as listed in Table 1. The viscosity of solution has been known as the most importance parameter during electrospinning process [21,36]. The solution with lower viscosity tends to form beaded nanofiber. Oppositely, a solution with too high viscosity tends to make the syringe plugged by condensation droplet of the solution (observed by the solution with PVA concentration of 13 wt%).

Table 1. Sample composition and nanofiber form used in this study.

PVA concentration (%)	Mixing ratio (v/v) (mL)		Fiber Form
	PVA	PEDOT: PSS	
9	60	40	More beaded
10	60	40	Beaded
11	60	40	Less beaded
12	60	40	Smooth
13	60	40	Not form

The higher PVA concentration increases the viscosity of the solution. With increased viscosity, the diameter of nanofiber is also increased. This is probably due to the greater resistance of the solution to be stretched by the charges on the jet [37]. Moreover, the solution conductivity and surface tension also influence the formation of beads along the fiber surface [37].

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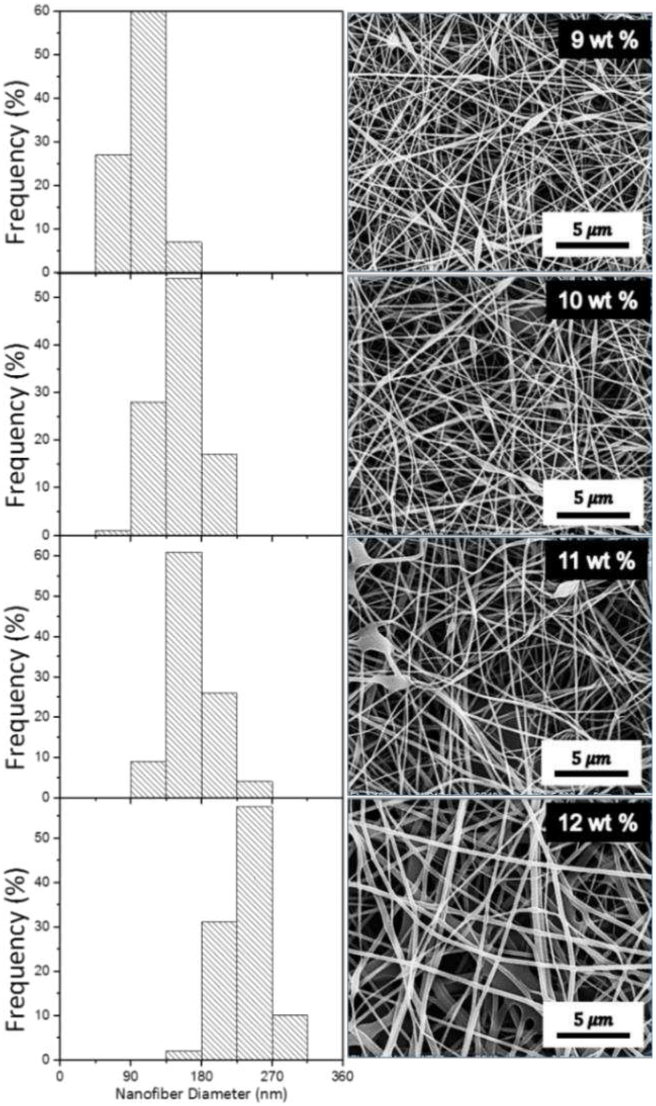

Figure 1. SEM images and nanofiber diameter distribution of sample PEDOT: PSS/PVA nanofiber with various PVA concentration.

Figure 2(a) shows the cross-section SEM image of PEDOT:PSS/PVA nanofiber with a thickness about $\sim 6\mu m$ and physical appearance of the sample. The colour of PEDOT:PSS/PVA was light blue (inset Figure 2(a)), indicating the incorporation of PEDOT:PSS into the nanofibers, while the colour of the as-spun pure PVA nanofibers was white. The electrical conductivity and diameter of nanofiber with various concentration of PVA are shown in Figure 2(b). It shows that as the concentration increased the nanofiber diameter was also increased. From Figure 2(b) we can also see that, as the nanofiber diameter increased the conductivity of nanofiber was also increased. The fiber electrical conductivity increases with increasing nanofiber diameter [38]. A polymer with low concentration would tend to form beaded nanofiber instead of the smooth nanofiber. The presence of beads would cause decreasing on the conductivity of nanofiber. With the increasing of solution concentration, the conductivity of nanofiber mat was increase from 0.03 µS cm^{-1} to 1.2 µS cm^{-1}. For further treatment, we focused on nanofiber with 12 wt% PVA concentration because of the lowest resistance (highest conductivity).

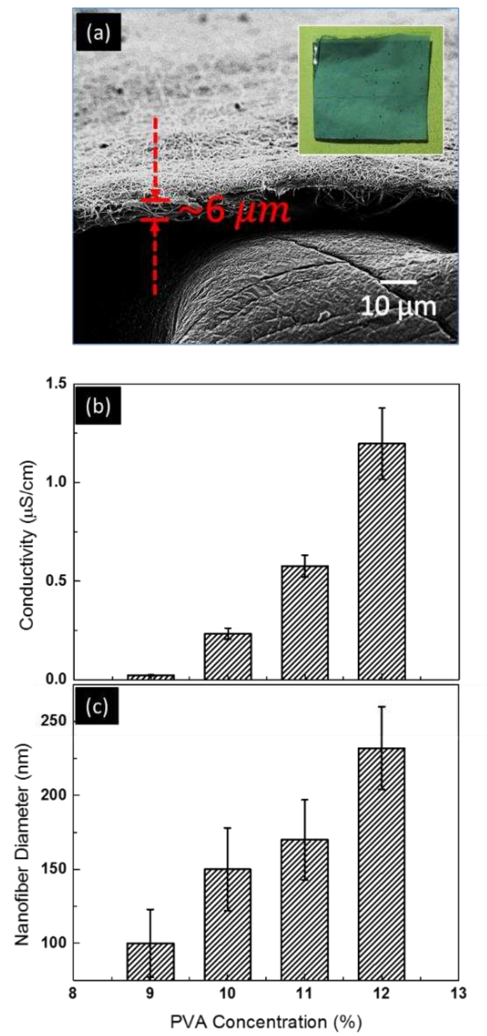

Figure 2. (a) cross-section SEM image of nanofiber with physical appearance of nanofiber mat (inset), (b) conductivity, and (c) diameter of nanofibers mats with various PVA concentration.

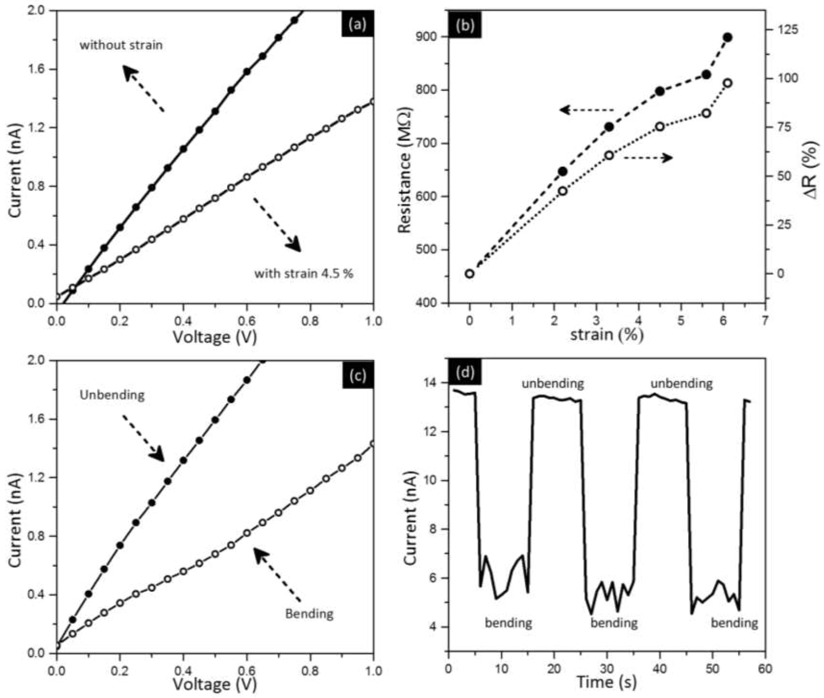

Figure 3. (a) Current-Voltage characteristic of device with and without strain, (b) resistance and change in resistance of nanofiber sensor with various strain (c) bending- unbending current-voltage measurement of sample (d) Current value of bending-unbending at 5V.

Figure 3(a) shows the current-voltage characteristic of nanofiber with and without strain. It clearly observes that the resistance of nanofiber increases after stretch (strain) indicating good response as strain sensor application. Figure 3(b) shows resistance and change in resistance of nanofiber sensor with various strain. The resistance of the sample increased from 455 to 899 MΩ as the strain increased. We also calculated the gauge factor of the sensor using the data of the relative change in resistance (ΔR) from Figure 4(b). The gauge factor can be calculated by Eq. (1).

$$GF = \frac{\Delta R}{R}\frac{1}{\Delta \varepsilon} \qquad (1)$$

where GF is gauge factor, R is resistance (Ω), ΔR is changing in resistance (Ω), and $\Delta\boldsymbol{\varepsilon}$ is a strain (%).

The gauge factor of our sensor is about 17 (0.0 % - 6.1 %) which is smaller than that of reported by Liu et. al (2011) (55 and 369) [21]. The different gauge factor compared to their result is due to the smaller ratio of PEDOT:PSS in solution. The ratio of PEDOT:PSS and PVA in our study are 1:15 meanwhile in their study is 1:5. The amount of PEDOT:PSS in solution will affect the gauge factor as the presence of PEDOT:PSS which known have a piezoelectric effect [26,27].

The two aspects affecting on the strain sensor device are the common piezoelectric effect of PEDOT:PSS polymer and the unique nanostructure of nanofiber mats [21]. The unique nanostructure of nanofiber PEDOT:PSS/PVA gives the sensor significant change in resistance after stretch. We believe that the resistance measured on our sensor is following simple equation on sheet resistance measurement as shown in Eq. (2)

$$R = \frac{\rho}{d}\frac{l}{w} \qquad (2)$$

where, R is resistance (Ω), ρ is resistivity (Ωm), d is the thickness of nanofiber (m), l is the distance between electrodes (m) and w is the length of contact (m). With the resistivity and the thickness of nanofiber is unchange, it is clear that the change in resistance is effect of the geometrical change of sensors.

We also investigated the stability and response of our sensor. We measured the current of the sensor with bending and unbending treatment for every 10 s, alternately. Figure 3(c) and 3(d) show the current-voltage and current-time response of our sensor with bending and unbending treatment, respectively. The sensor shows high repeatability and stability after treatment. We suggest the mechanism process of the increase of the resistance as the effect of strain process shown in Figure 4. When the sensor stretches, the nanofiber length will increase and affect the increase in distance between electrodes.

The increasing of the distance of electrodes and assuming there is no change on other parameter will make the resistance measured increased following the Eq. (2). It is clear that the distance of electrode is linearly dependent with resistance. It means that if the distance

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of electrode increased then the resistance also increased [21].

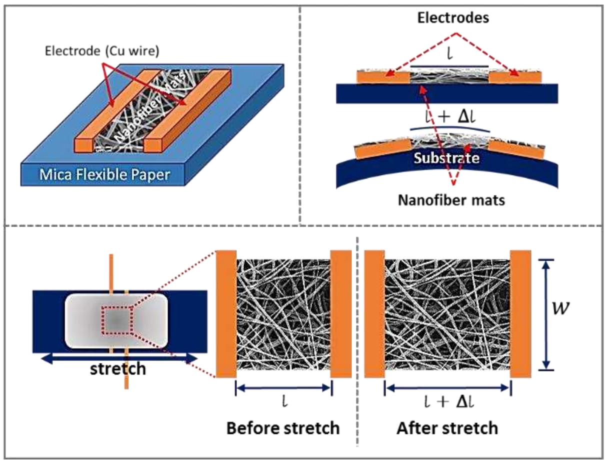

Figure 4. schematic illustration of stretching process on nanofiber mats.

Conclusions

The Electrospun PEDOT: PSS/PVA nanofiber mats has been successfully fabricated as a strain sensor. The conductivity of as-spun nanofiber mats can be adjusted from 0.03 to 1.2 µScm-1 with various concentration of PVA solution. The PEDOT: PSS/PVA nanofiber network strain sensors have good stability, and gauge factor about 17. The performance of PEDOT:PSS/PVA nanofiber based strain sensor make nanofiber mats as promising materials for strain sensor application. For further investigation, we suggest substituting PVA with other more conducting polymer to improve the gauge factor.

Conflicts of interest

There are no conflicts to declare.

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References

[1] Y. Liu, M. Hao, Z. Chen, L. Liu, Y. Liu, W. Yang, S. Ramakrishna, A review on recent advances in application of electrospun nanofiber materials as biosensors, Curr. Opin. Biomed. Eng. 13 (2020) 174–189. doi:10.1016/j.cobme.2020.02.001.

[2] H. Chen, M. Huang, Y. Liu, L. Meng, M. Ma, Functionalized electrospun nanofiber membranes for water treatment: A review, Sci. Total Environ. 739 (2020) 139944. doi:10.1016/j.scitotenv.2020.139944.

[3] F.E. Ahmed, B.S. Lalia, R. Hashaikeh, A review on electrospinning for membrane fabrication: Challenges and applications, Desalination. 356 (2015) 15–30. doi:10.1016/j.desal.2014.09.033.

[4] G. Panthi, M. Park, H.-Y. Kim, S.-J. Park, Electrospun polymeric nanofibers encapsulated with nanostructured materials and their applications: A review, J. Ind. Eng. Chem. 24 (2015) 1–13. doi:10.1016/j.jiec.2014.09.011.

[5] A. Refino, H.T. Yudistira, D.H.T. Nugroho, D.L. Puspitarum, Numerical Investigation of Electrospray Working Performance on Ethanol, J. Sci. Appl. Technol. 3 (2019) 51. doi:10.35472/jsat.v3i2.196.

[6] M. Yan lmaz, a. S. Sarac, A review: effect of conductive polymers on the conductivities of electrospun mats, Text. Res. J. 84 (2014) 1325–1342. doi:10.1177/0040517513495943.

[7] X. Wang, B.S. Hsiao, Electrospun nanofiber membranes, Curr. Opin. Chem. Eng. 12 (2016) 62–81. doi:10.1016/j.coche.2016.03.001.

[8] S.F. Chou, D. Carson, K.A. Woodrow, Current strategies for sustaining drug release from electrospun nanofibers, J. Control. Release. 220 (2015) 584–591. doi:10.1016/j.jconrel.2015.09.008.

[9] M. Cheng, Y. Qin, P. Qian, Z. Qin, Electrospun Cellulose Acetate Nanofibrous Mat as the Tissue Scaffold, in: Int. Conf. Adv. Energy, Environ. Chem. Eng., 2015: pp. 801–804.

[10] D. Serbezeanu, A.M. Popa, T. Stelzig, I. Sava, R.M. Rossi, G. Fortunato, Preparation and characterization of thermally stable polyimide membranes by electrospinning for protective clothing applications, Text. Res. J. 85 (2015) 1763–1775. doi:10.1177/0040517515576326.

[11] L. Persano, A. Camposeo, D. Pisignano, Active polymer nanofibers for photonics, electronics, energy generation and micromechanics, Prog. Polym. Sci. 43 (2014) 48–95. doi:10.1016/j.progpolymsci.2014.10.001.

[12] J. Yao, G. Li, C.W.M. Bastiaansen, T. Peijs, High performance co-polyimide nanofiber reinforced composites, Polym. (United Kingdom). 76 (2015) 46–51. doi:10.1016/j.polymer.2015.08.054.

[13] L. Nulhakim, M. Rozana, B. Yuliarto, H. Makino, Electrical and optical properties of Ga-doped ZnO thin films deposited by DC magnetron sputtering, J. Sci. Appl. Technol. 4 (2020) 15. doi:10.35472/jsat.v4i1.264.

[14] D.D. Yanti, E. Maryanti, Green Synthesis ZnO Nanoparticles Using Rinds Extract of Sapindus rarak DC, J. Sci. Appl. Technol. 5 (2021) 198–201. doi:10.35472/jsat.v5i1.372.

[15] T. Julian, S.N. Hidayat, A. Rianjanu, A.B. Dharmawan, H.S. Wasisto, K. Triyana, Intelligent Mobile Electronic Nose System Comprising a Hybrid Polymer-Functionalized Quartz Crystal Microbalance Sensor Array, ACS Omega. 5 (2020) 29492–29503. doi:10.1021/acsomega.0c04433.

[16] A. Rianjanu, E. Nurfani, M.F. Arif, K. Triyana, H.S. Wasisto, Stability evaluation of quartz crystal microbalances coated

with polyvinyl acetate nanofibrous mats as butanol vapor sensors, Mater. Today Commun. 26 (2021) 101770. doi:10.1016/j.mtcomm.2020.101770.

[17] A. Rianjanu, T. Julian, S.N. Hidayat, N. Yulianto, N. Majid, I. Syamsu, H.S. Wasisto, K. Triyana, Quartz crystal microbalance humidity sensors integrated with hydrophilic polyethyleneimine-grafted polyacrylonitrile nanofibers, Sensors Actuators B Chem. 319 (2020) 128286. doi:10.1016/j.snb.2020.128286.

[18] H. Di Zhang, X. Yan, Z.H. Zhang, G.F. Yu, W.P. Han, J.C. Zhang, Y.Z. Long, Electrospun PEDOT:PSS/PVP Nanofibers for CO Gas Sensing with Quartz Crystal Microbalance Technique, Int. J. Polym. Sci. 2016 (2016) 1–6. doi:10.1155/2016/3021353.

[19] A. Rianjanu, R. Aflaha, N.I. Khamidy, M. Djamal, K. Triyana, H.S. Wasisto, Room-temperature ppb-level trimethylamine gas sensors functionalized with citric acid-doped polyvinyl acetate nanofibrous mats, Mater. Adv. 2 (2021) 3705–3714. doi:10.1039/D1MA00152C.

[20] R. Roto, A. Rianjanu, A. Rahmawati, I.A. Fatyadi, N. Yulianto, N. Majid, I. Syamsu, H.S. Wasisto, K. Triyana, Quartz Crystal Microbalances Functionalized with Citric Acid-Doped Polyvinyl Acetate Nanofibers for Ammonia Sensing, ACS Appl. Nano Mater. 3 (2020) 5687–5697. doi:10.1021/acsanm.0c00896.

[21] N. Liu, G. Fang, J. Wan, H. Zhou, H. Long, X. Zhao, Electrospun PEDOT:PSS–PVA nanofiber based ultrahigh-strain sensors with controllable electrical conductivity, J. Mater. Chem. 21 (2011) 18962. doi:10.1039/c1jm14491j.

[22] S. Zhang, H. Zhang, G. Yao, F. Liao, M. Gao, Z. Huang, K. Li, Y. Lin, Highly stretchable, sensitive, and flexible strain sensors based on silver nanoparticles/carbon nanotubes composites, J. Alloys Compd. 652 (2015) 48–54. doi:10.1016/j.jallcom.2015.08.187.

[23] E. Roh, B.U. Hwang, D. Kim, B.Y. Kim, N.E. Lee, Stretchable, Transparent, Ultrasensitive, and Patchable Strain Sensor for Human-Machine Interfaces Comprising a Nanohybrid of Carbon Nanotubes and Conductive Elastomers, ACS Nano. 9 (2015) 6252–6261. doi:10.1021/acsnano.5b01613.

[24] J. Seo, T.J. Lee, C. Lim, S. Lee, C. Rui, D. Ann, S.B. Lee, H. Lee, A Highly Sensitive and Reliable Strain Sensor Using a Hierarchical 3D and Ordered Network of Carbon Nanotubes, Small. 11 (2015) 2990–2994. doi:10.1002/smll.201401812.

[25] K.K. Kim, S. Hong, H.M. Cho, J. Lee, Y.D. Suh, J. Ham, S.H. Ko, Highly Sensitive and Stretchable Multidimensional Strain Sensor with Prestrained Anisotropic Metal Nanowire Percolation Networks, Nano Lett. 15 (2015) 5240–5247. doi:10.1021/acs.nanolett.5b01505.

[26] U. Lang, P. Rust, B. Schoberle, J. Dual, Piezoresistive properties of PEDOT:PSS, Microelectron. Eng. 86 (2009) 330–334. doi:10.1016/j.mee.2008.10.024.

[27] G. Latessa, F. Brunetti, A. Reale, G. Saggio, A. Di Carlo, Piezoresistive behaviour of flexible PEDOT:PSS based sensors, Sensors Actuators, B Chem. 139 (2009) 304–309. doi:10.1016/j.snb.2009.03.063.

[28] W.A. Daoud, J.H. Xin, Y.S. Szeto, Polyethylenedioxythiophene coatings for humidity, temperature and strain sensing polyamide fibers, Sensors Actuators, B Chem. 109 (2005) 329–333. doi:10.1016/j.snb.2004.12.067.

[29] J.C. Wang, R.S. ubhra Karmakar, Y.J. Lu, C.Y. Huang, K.C. Wei, Characterization of piezoresistive PEDOT:PSS pressure sensors with inter-digitated and cross-point electrode structures, Sensors (Basel). 15 (2015) 818–831. doi:10.3390/s150100818.

[30] T. Julian, A. Rianjanu, S.N. Hidayat, A. Kusumaatmaja, R. Roto, K. Triyana, Quartz crystal microbalance coated with PEDOT–PSS/PVA nanofiber for a high-performance humidity sensor, J. Sensors Sens. Syst. 8 (2019) 243–250. doi:10.5194/jsss-8-243-2019.

[31] S.N. Hidayat, T. Julian, A. Rianjanu, A. Kusumaatmadja, K. Triyana, Roto, Quartz crystal microbalance coated by PAN nanofibers and PEDOT:PSS for humidity sensor, in: 2017 Int. Semin. Sensors, Instrumentation, Meas. Metrol., IEEE, 2017: pp. 119–123. doi:10.1109/ISSIMM.2017.8124274.

[32] Chotimah, B. Winandianto, M. Munir, I. Kartini, A. Kusumaatmaja, K. Triyana, The electrical properties of PEDOT:PSS nanofibers, AIP Conf. Proc. 1755 (2016) 150013. doi:10.1063/1.4958586.

[33] D. Cho, N. Hoepker, M.W. Frey, Fabrication and characterization of conducting polyvinyl alcohol nanofibers, Mater. Lett. 68 (2012) 293–295. doi:10.1016/j.matlet.2011.10.109.

[34] - Chotimah, A. Rianjanu, B. Winardianto, M. Munir, I. Kartini, K. Triyana, Electrical Conductivity Improvement of Polyvinyl Alcohol Nanofiber by Solvent Vapour Treatment, Int. J. Adv. Sci. Eng. Inf. Technol. 6 (2016) 675. doi:10.18517/ijaseit.6.5.1055.

[35] N. Liu, G. Fang, W. Zeng, H. Long, L. Yuan, X. Zhao, 11 Novel ZnO Nanorod Flexible Strain Sensor and Strain Driving Transistor with an Ultrahigh 107 Scale "On" -"Off" Ratio Fabricated by a Single-Step Hydrothermal Reaction.pdf, (2011) 570–575.

[36] J.. Deitzel, J. Kleinmeyer, D. Harris, N.. Beck Tan, The effect of processing variables on the morphology of electrospun nanofibers and textiles, Polymer (Guildf). 42 (2001) 261–272. doi:10.1016/S0032-3861(00)00250-0.

[37] S. Ramakrishna, K. Fujihara, W.E. Teo, Z. Ma, T.C. Lim, An Introduction to Electrospinning and Nanofibers, World Scientific, Singapore, 2005.

[38] J.L. Duvail, P. Rétho, S. Garreau, G. Louarn, C. Godon, S. Demoustier-Champagne, Transport and vibrational properties of poly(3,4-ethylenedioxythiophene) nanofibers, Synth. Met. 131 (2002) 123–128. doi:10.1016/S0379-6779(02)00195-9.

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