Carbon Nanotube/PEDOT: PSS Composite-based Flexible Temperature Sensor with Enhanced Response and Recovery Time

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Abstract— Temperature sensors with good mechanical flexibility, high sensitivity, fast response and recovery time are essential features for real time measurements by electronic Skin (eSkin). This paper presents the fabrication and characterization of a flexible temperature sensor using PEDOT: PSS and carbon nanotube (CNT) at 1:1 mixing ratio. In order to establish the performance enhancement capability of this composition, a comparative study was carried out. This was done by fabricating two flexible temperature sensors each on ~175µm-thick PVC substrate using only CNT and then with **CNT/PEDOT: PSS polymer composite following simple drop** casting technique. Both sensors show good sensitivity ~0.27(%)°C⁻¹)) for CNT and ~0.64(%)°C⁻¹)) for CNT/PEDOT: PSS for temperatures varying from 20°C to 80°C. Although both the sensors, CNT and CNT/PEDOT: PSS composite revealed fast response and recovery time, the latter shows a higher sensitivity (~0.64 (%)°C⁻¹)). Further, a comparison of the sensor made with CNT/PEDOT: PSS with similar works in literature reveals that the presented sensor exhibits relatively faster response (~4.8s) and recovery (~2.5s) time. This response enhancement can provide a biomimetic eSkin with unique feature.

Keywords — Sensors; e-Skin; Temperature Sensor; CNT; PEDOT:PSS

I. INTRODUCTION

Electronic skin (eSkin) with various types of physical sensors is increasingly being explored as the interface allowing efficient interaction of robots and prosthesis with their environment [1-3] and in many other applications such as healthcare, and wearable systems [4-8]. Among various physical parameters needed to be monitored in these applications, temperature is one of most fundamental parameters. A temperature-sensitive eSkin with enhanced temperature response, similar to the Transient Receptor Potential subfamily V member 1(TRPV1) [9] inherent in the human skin, will be advantageous for these applications [10-12]. To this end, a temperature sensor with good mechanical flexibility, high sensitivity, fast response and recovery time is required for efficient real time temperature monitoring [13-17].

In literature, temperature sensors with various response and recovery times have been widely reported for measurement of the temperature variations either through direct contact with the heat source or remotely through radiations [15, 18-20]. Temperature sensors utilizing different

materials and technologies such as thermocouples, resistive, thermistor, infrared, and semiconductor sensors have been previously reported [21-25]. Among them, the resistive type temperature sensor is widely used due to its rapid response, stability and accuracy [26]. The materials including conducting polymers, carbon nanotube (CNT), and graphene are widely used active materials [26, 27]. Majority of these sensors have relatively slow response to temperature, which is undesirable for the application of eSkin in robotics, where fast response is desired. However, by tuning new active temperature sensitive materials, it is possible to address this challenge and enhance the response and recovery time of these sensors. For example, the CNT based sensors demonstrate fast response and recovery time in comparison with poly (3,4ethylenedioxythiophene): poly (styrene sulfonate) polymers-based (PEDOT:PSS) conducting materials. However, the responses of CNT-based temperature sensors are four times lower than the PEDOT: PSS counterparts. A mixture of CNT/PEDOT: PSS could enhance the temperature sensing characteristics and we demonstrate the same here with a mixture of 1:1 ratio. In this work we utilized a mixture of CNT and PEDOT: PSS to realize a flexible temperature sensor on ~175µm Polyvinyl Chloride (PVC) substrate. Two different temperature sensors were fabricated: First temperature sensor is based on CNT alone and the second utilizes a mixture of CNT and PEDOT: PSS as temperature sensing material. To evaluate the enhancement provided by this mixture, the performance of both sensors was compared. The comparison shows an enhancement in response and recovery time for both, but higher percentage change in resistance for the CNT+PEDOT: PSS composite.

The rest of the paper is organised as follows: the materials and methods utilized for the fabrication of sensing devices are presented in Section II. The characterizations carried out and the results are discussed in Section III. Finally, the key findings are summarized in Section IV.

II. MATERIALS AND METHODS

This section presents the method adopted for the fabrication of the flexible temperature sensor (Fig. 1). Two different temperature sensors based on different temperature sensing layers (only CNT and mix of CNT/PEDOT: PSS) were fabricated and their performance compared.

Two samples (1 and 2) were prepared on \sim 175 µm thick Polyvinyl Chloride (PVC) substrate. For each sample, PVCbased hard mask (Fig. 1a) was realized using a computercontrolled blade cutter (Silhouette Cameo). The 2mm-wide opening through the hard mask allows deposition of two

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Fig. 1: (a) Hard mask utilized for deposition of contact electrodes; (b) Metal deposition using Plassys MEB 550S Electron Beam Evaporator system; (c) PVC with the deposited contact electrodes; (d) drop casting of CNT+PEDOT:PSS; (e) Encapsulation of the active sensing region; (f) Fabricated temperature sensor.

contact electrodes (10/80 nm thick Ti/Au). The contact electrodes for both samples were deposited on the PVC using Plassys MEB 550S Electron Beam Evaporator system (Fig. 1b and 1c). Following this, the temperature sensing layer was drop-casted (Fig. 1d) for each of the samples and then encapsulated (Fig. 1e).

A. Dropcasting of temperature sensing layer for Sample 1

The active temperature sensing matrix for sample 1 is composed of CNTs only. A $\sim 25\mu$ L active temperature sensing layer composed of CNTs was drop-casted on the prefabricated electrodes to realize the sample 1 (Fig. 1d). This is followed by annealing of the sample at 80°C in an oven for an hour. Finally, the sensing area was encapsulated with ultra-thin PDMS (<100 μ m) to shield it against possible environmental effect (e.g. humidity).

B. Dropcasting of temperature sensing layer for sample 2

The active temperature sensing layer for sample 2 is composed of a mixture of CNT and PEDOT: PSS composite. First. ~2ml CNT solution was poured into a glass bottle containing an equal volume of PEDOT: PSS. The solution was then thoroughly mixed by constantly stirring for ~2 minutes to allow the realization of a homogenous composition without any CNT precipitation. The composite was then drop-casted along the channel region between the contact electrodes as shown in Fig. 1d. This is followed by annealing of the sample at 80°C in an oven for an hour. Similar to sample 1, the sensing area was encapsulated with ultra-thin PDMS (<100µm) to shield it against possible any possible environmental effect (e.g. humidity)



Fig 2: Temperature sensor characteristics: The relative change in resistance with respect to time for temperature ranging from 20 to 80 °C for (a) CNTbased temperature sensor (sample 1) and (b) CNT/PEDOT: PSS nanocomposite-based temperature sensors (sample 2).



Fig 3: Temperature sensor characteristics: Comparison of response of CNT and CNT + PEDOT: PSS based sensors with respect to change in temperature.

III. CHARACTERISATION AND RESULTS

This section presents the characterization and results for the temperature sensor based on CNT (sample 1), and that of the temperature sensor based on CNT/PEDOT: PSS composite (sample 2). Both temperature sensors were characterized by connecting their contact electrodes to an Agilent 34461A digital multimeter which measures the change in resistance.

The outputs of the sensors were recorded in a PC running a custom-made LabVIEW 2018 Robotics v18.0f2 program (National Instruments, Texas, USA). During the characterization, the sensors were carefully placed on the hot plate and subjected to temperature change from room temperature and up to temperatures above the activation temperature (~43 °C) of TRPV1 receptor of the human skin.

The test temperature ranged from 30°C to 80°C. Fig. 2a and 2b show the relative change in the resistance with respect to the time for various temperature ranges for CNT-based temperature sensor (sample 1) and CNT+PEDOT:PSS-based composite temperature sensor (sample 2) respectively. Both the sensors, sample 1 and sample 2, revealed fast response (~2.5s) and recovery (~4.8s). However, in the CNT-based sensor, the relative change in resistance is much lower (~0.26% per °C) than that PEDOT: PSS+CNT composites (~0.64% per °C) based sensor. Fig. 3 shows the response of sensors with respect to the temperature change. At room temperature, the resistance of the sensor was ~6150 Ω and the resistance value linearly decreased with increasing temperature. Accordingly, the response of the sensor linearly increased with increasing the temperature as shown in Fig. 3.

TABLE I. COMPARISON TABLE FOR EXISTING TEMPERATURE

| Active Material | Sensitivity (°C-1) | Response Time | Recovery Time | Ref. |
|--------------------|-----------------------|--------------------------|--------------------------|--------------|
| GO + PEDOT:PSS | 1.09 | 18 s for ΔT of 75 °C | 32 s for ΔT of 75 °C | [18] |
| Reduced GO | 0.6 | 1.2 s for ΔT of 20 °C | ~ 7 s for ΔT of 20 °C | [28] |
| Silver | 0.2 | - | - | [29] |
| CNT+ PEDOT:PSS | 0.64 | 4.8s | 2.5s | This Work |



Fig 4: Comparison of temperature sensor recovery speed with (a) our previous result (graphene oxide/PEDOT: PSS) vs commercial thermistor and (b) our present work. The recovery speed of current device (4.8s) is much faster than GO/PEDOT: PSS (32s) and commercial thermistor (120s). Figure 4a is reproduced from our previous work ref [15].

The fabricated CNT+PEDOT: PSS sensor exhibited a sensitivity of ~ 0.64 (%)/(°C) with fast response (~4.8s) and recovery time (~2.5s).

Table 1 shows a comparison of the fabricated temperature sensor with other works reported in the literature. This comparison shows that our sensors show faster response and recovery time. In addition, our sensor's recovery time was also evaluated by comparing it with our previous work and a commercialized sensor as shown in Fig 4. These plots clearly show the advantage of our sensors and their potential for the realization of a temperature-sensitive eSkin which could quickly distinguish the hot and cold objects.

IV. CONCLUSION

In this work, two different temperature sensors using CNT and CNT+PEDOT: PSS composite were explored. Although both devices show enhanced response and recovery times, the sensor made with a mixture of CNT+PEDOT: PSS has a higher percentage change in the resistance (~0.64%) per degree rise in the temperature. The sensor exhibited good response below and above the activation temperature (~43°C) of the TRPV1 receptor of the human skin, and thus show their capability for inclusion in a temperature sensitive eSkin with human-like functionalities. Further studies are being conducted to fabricate an array of the integrated temperature with the accompanying readout circuit to realize a biomimetic sensorized e-Skin for humanoid robots.

REFERENCES

- C. Wang, D. Hwang, Z. Yu, K. Takei, J. Park, T. Chen, et al., "Userinteractive electronic skin for instantaneous pressure visualization," *Nature Materials*, vol. 12, pp. 899-904, 2013.
- [2] R. Dahiya, N. Yogeswaran, F. Liu, L. Manjakkal, E. Burdet, V. Hayward, et al., "Large-Area Soft e-Skin: The Challenges Beyond Sensor Designs," *Proceedings of the IEEE*, vol. 107, pp. 2016-2033, 2019.
- [3] C. G. Núñez, L. Manjakkal, and R. Dahiya, "Energy autonomous electronic skin," *npj Flexible Electronics*, vol. 3, p. 1, 2019.
- [4] W. Navaraj, C. Smith, and R. Dahiya, "E-skin and wearable systems for health care," in *Wearable Bioelectronics*, ed: Elsevier, pp. 133-178, 2020.
- [5] O. Ozioko, P. Karipoth, M. Hersh, and r. Dahiya, "Wearable Assistive Tactile Communication Interface based on Integrated Touch Sensors and Actuators," *IEEE Transactions on Neural Systems and Rehabilitation Engineering*, vol. In Press, 2020.
- [6] [6] L. Manjakkal, W. Dang, N. Yogeswaran, and R. Dahiya, "Textile-based potentiometric electrochemical pH sensor for wearable applications," *Biosensors*, vol. 9, p. 14, 2019.
- [7] L. Manjakkal, S. Dervin, and R. Dahiya, "Flexible potentiometric pH sensors for wearable systems," *RSC Advances*, vol. 10, pp. 8594-8617, 2020.
- [8] L. Manjakkal, D. Szwagierczak, and R. Dahiya, "Metal oxides based electrochemical pH sensors: Current progress and future perspectives," *Progress in Materials Science*, p. 100635, 2019.
- [9] [9] J. O. Sosa-Pagán, E. S. Iversen, and J. Grandl, "TRPV1 temperature activation is specifically sensitive to strong decreases in amino acid hydrophobicity," *Scientific Reports*, vol. 7, p. 549, 2017.
- [10] M. Soni and R. Dahiya, "Soft eSkin: distributed touch sensing with harmonized energy and computing," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 378, p. 20190156, 2020.
- [11] R. Dahiya, D. Akinwande, and J. S. Chang, "Flexible Electronic Skin: From Humanoids to Humans [Scanning the Issue]," *Proceedings of the IEEE*, vol. 107, pp. 2011-2015, 2019.
- [12] R. S. Dahiya and M. Valle, *Robotic Tactile Sensing: Technologies and System*: Springer Netherlands, 2013.
- [13] M. Yurddaskal, M. Erol, and E. Celik, "Carbon black and graphite filled conducting nanocomposite films for temperature sensor applications," *J. Mater. Sci.: Mater. Electron.*, vol. 28, pp. 9514-9518, 2017.
- [14] C. Yan, J. Wang, and P. S. Lee, "Stretchable Graphene Thermistor with Tunable Thermal Index," ACS Nano, vol. 9, pp. 2130-2137, 2015.
- [15] S. Y. Hong, Y. H. Lee, H. Park, S. W. Jin, Y. R. Jeong, J. Yun, et al., "Stretchable Active Matrix Temperature Sensor Array of Polyaniline Nanofibers for Electronic Skin," Adv. Mater., vol. 28, pp. 930-935, 2016.
- [16] Q. Liu, H. Tai, Z. Yuan, Y. Zhou, Y. Su, and Y. Jiang, "A High-Performances Flexible Temperature Sensor Composed of

Polyethyleneimine/Reduced Graphene Oxide Bilayer for Real-Time Monitoring," Adv. Mater. Technol., vol. 4, p. 1800594, 2019.

- [17] L. Wu, J. Qian, J. Peng, K. Wang, Z. Liu, T. Ma, et al., "Screenprinted flexible temperature sensor based on FG/CNT/PDMS composite with constant TCR," J. Mater. Sci.: Mater. Electron., vol. 30, pp. 9593-9601, 2019.
- [18] M. Soni, M. Bhattacharjee, M. Ntagios, and R. Dahiya, "Printed Temperature Sensor Based on PEDOT:PSS - Graphene Oxide Composite," *IEEE Sens. J.*, pp. 1-1, 2020.
- [19] G. Liu, Q. Tan, H. Kou, L. Zhang, J. Wang, W. Lv, et al., "A Flexible Temperature Sensor Based on Reduced Graphene Oxide for Robot Skin Used in Internet of Things," Sensors, vol. 18, 2018.
- [20] L. Manjakkal, M. Soni, N. Yogeswaran, and R. Dahiya, "Cloth Based Biocompatiable Temperature Sensor," in 2019 IEEE International Conference on Flexible and Printable Sensors and Systems (FLEPS), pp. 1-3, 2019.
- [21] T. Q. Trung, S. Ramasundaram, B.-U. Hwang, and N.-E. Lee, "An All-Elastomeric Transparent and Stretchable Temperature Sensor for Body-Attachable Wearable Electronics," *Adv. Mater.*, vol. 28, pp. 502-509, 2016.
- [22] C. Lee, S. Lee, Y. Lee, M. Tang, P. Chen, and Y. Chang, "In situ monitoring of temperature using flexible micro temperature sensors inside polymer lithium-ion battery," in 2012 7th IEEE International Conference on Nano/Micro Engineered and Molecular Systems (NEMS), pp. 698-701, 2012.
- [23] P. Tao, W. Shang, C. Song, Q. Shen, F. Zhang, Z. Luo, et al., "Bioinspired Engineering of Thermal Materials," Adv. Mater., vol. 27, pp. 428-463, 2015.
- [24] [24] R. S. Dahiya, D. Cattin, A. Adami, C. Collini, L. Barboni, M. Valle, et al., "Towards Tactile Sensing System on Chip for Robotic Applications," *IEEE Sens. J.*, vol. 11, pp. 3216-3226, 2011.
- [25] S. Hannah, A. Davidson, I. Glesk, D. Uttamchandani, R. Dahiya, and H. Gleskova, "Multifunctional sensor based on organic field-effect transistor and ferroelectric poly(vinylidene fluoride trifluoroethylene)," Org. Electron., vol. 56, pp. 170-177, 2018.
- [26] M. Soni, M. Bhattacharjee, L. Manjakkal, and R. Dahiya, "Printed Temperature Sensor based on Graphene Oxide/PEDOT:PSS," in 2019 IEEE International Conference on Flexible and Printable Sensors and Systems (FLEPS), pp. 1-3, 2019.
- [27] C. Bali, A. Brandlmaier, A. Ganster, O. Raab, J. Zapf, and A. Hübler, "Fully Inkjet-Printed Flexible Temperature Sensors Based on Carbon and PEDOT:PSS1," *Materials Today: Proceedings*, vol. 3, pp. 739-745, 2016.
- [28] G. Liu, Q. Tan, H. Kou, L. Zhang, J. Wang, W. Lv, et al., "A Flexible Temperature Sensor Based on Reduced Graphene Oxide for Robot Skin Used in Internet of Things," *Sensors (Basel, Switzerland)*, vol. 18, p. 1400, 2018.
- [29] M. D. Dankoco, G. Y. Tesfay, E. Benevent, and M. Bendahan, "Temperature sensor realized by inkjet printing process on flexible substrate," *Materials Science and Engineering: B*, vol. 205, pp. 1-5, 2016.