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Sengupta, D.; Kottapalli, A. G. Prakash; Chen, S.; Michael, A.; Kwok, C. Y.; Miao, J.; Triantafyllou, M. S.

Published in:

Proceedings of the 13th Annual IEEE International Conference on Nano/Micro Engineered and Molecular Systems April 22-26, 2018, Singapore

DOI:

[10.1109/NEMS.2018.8556930](https://doi.org/10.1109/NEMS.2018.8556930)

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2018

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Sengupta, D., Kottapalli, A. G. P., Chen, S., Michael, A., Kwok, C. Y., Miao, J., & Triantafyllou, M. S. (2018). Flexible Graphitized Polyacrylonitrile Nanofiber Bundles for Strain Sensors. In *Proceedings of the 13th Annual IEEE International Conference on Nano/Micro Engineered and Molecular Systems April 22-26, 2018, Singapore* (pp. 615-618). IEEE. <https://doi.org/10.1109/NEMS.2018.8556930>

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Flexible Graphitized Polyacrylonitrile Nanofiber Bundles for Strain Sensors

Debarun Sengupta, *Member, IEEE*, Ajay Giri Prakash Kottapalli*, Ssu-Han Chen, Aron Michael, *Member, IEEE*, Chee Yee Kwok, *Senior Member, IEEE*, Jianmin Miao, and Michael S. Triantafyllou

Abstract—This work reports the use of graphitized Polyacrylonitrile (PAN) nanofiber bundle for strain sensing applications. Strain sensors employing piezoresistive properties of carbon nanofiber is relatively new compared to conventional piezoelectric electrospun nanofiber based devices. The graphitization of PAN nanofiber bundles annealed at 500°C, 750°C, and 950°C are studied by means of spectroscopic analysis techniques including Raman and X-ray photoelectron spectroscopy (XPS). The nanofiber bundle annealed at 750°C exhibits disordered (D) and ordered (G) peaks similar to the nanofiber bundle annealed at 950°C. This is confirmed by XPS analysis which shows the asymmetric C1s peak at 284.8 eV. Raman analysis has also been performed on the as-spun, stabilized and annealed samples to show the change in D and G peaks. Finally, a strain sensor utilizing the nanofiber bundle annealed at 950°C is fabricated which is sensitive enough to detect overall bending of less than 3° without the use of any external amplifier circuit.

I. INTRODUCTION

In the last decade, a lot of progress has been made in the wearable device industry. Sensors and energy harvesters employing piezoelectric property have been a major area of research and development. In particular, electrospun nanofiber based flexible and wearable devices and energy harvesters leveraging on the piezoelectric property of materials like polyvinylidene fluoride (PVDF) have been extensively researched [1]–[6]. In contrast, sensors utilizing the piezoresistive property of carbon nanofibers are relatively new and have not been explored. In the past, Zussman et al. reported the mechanical and structural characteristics of graphitized electrospun polyacrylonitrile (PAN) nanofibers [7]. In another work, Cai et al. reported the piezoresistive property of individual electrospun carbon nanofiber [8]. However, beyond the fundamental characterization of PAN nanofibers, their utilization in developing sensors has not been explored.

Research supported by National Research Foundation, Singapore.

Debarun Sengupta, Ssu-Han Chen, Aron Michael, and Chee Yee Kwok are with the School of Electrical Engineering and Telecommunications, The University of New South Wales, Sydney, NSW 2052 Australia.

Ajay Giri Prakash Kottapalli* (Contacting Author) was with Singapore-MIT Alliance for Research and Technology, 138602 Singapore. (Phone: 65-93722843; e-mail: ajay@smart.mit.edu). Currently he is with the Faculty of Science and Engineering, University of Groningen, 9712 CP, Netherlands.

Jianmin Miao is with School of Mechanical and Aerospace Engineering, Nanyang Technological University, 639798 Singapore.

Michael S. Triantafyllou is with Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 USA.

In this work, the conductive property of graphitized electrospun carbon nanofiber bundle (combined with the effect of change of conductance path in a carbonized nanofiber web when subjected to external stress) is utilized and demonstrated for strain sensing. This work clearly demonstrates the feasibility of using carbonized PAN nanofiber bundles for wearable and flexible sensor applications.

II. MATERIALS AND METHODS

A. Electrospinning process

The solution for electrospinning is prepared by mixing Polyacrylonitrile powder (MW 150,000 g/mol) with N,N-dimethylformamide (DMF) and stirring for 2 hours using a magnetic stirrer to get a 9% by weight solution. The nanofiber webs are electrospun using Inovenso™ electrospinner with a rotating mandrel collector for aligning the nanofibers. The prepared polymer solution is fed to a needle (18 G) at a constant feed rate of 1 ml/hr using a standard syringe pump. A temperature of 22°C (inside the electrospinning setup) is recorded and kept constant. A constant gap of 15cm is maintained between the needle tip and base of the rotating mandrel collector. PAN nanofibers mats are then prepared by electrospinning at 12 kV for 30 min.

Fig. 1: (a) A schematic showing the electrospinning process. (b) Flow chart showing the steps involved in graphitisation of PAN nanofibers.

B. Stabilization and annealing

The electrospun nanofibers are then stabilized in air. For stabilization, the nanofibers mats are put in a hot air oven and heated up at a constant ramp rate of 5°C/ min up to 245°C and then kept at that temperature for one hour before cooling down to room temperature at the same ramp rate. Three stabilized samples are annealed in a furnace at three different temperatures (500°C, 750°C, 950°C) in N₂ ambient. For

carbonization, the nanofibers mats are put in a hot air oven and heated up at a constant ramp rate of 5°C/ min up to the desired annealing temperature (500°C, 750°C) and then kept at the target temperature for one hour before cooling down to room temperature at the same ramp rate. For the sample annealed at 950°C, there is an additional annealing plateau at 750°C. After stabilization, the whitish as-spun nanofibers turned brown (fig. 2 (b)). Annealing led to change of color of the stabilized samples from brown to black (fig. 2 (c)).

Fig. 2: (a) Photograph of as-spun PAN nanofibers. (b) Photograph of the PAN nanofibers stabilised at 245°C. (c) Photograph of the PAN nanofibers annealed at 950°C. (d) SEM images of carbonised nanofibers showing uniformity after annealing.

The annealed nanofibers are inspected under FESEM. The annealed nanofibers showed overall uniformity after the annealing process (fig. 2 (d)).

III. RESULTS AND DISCUSSION

A. Spectroscopic analyses

The nanofibers are studied by means of Raman and X-ray Photoelectron Spectroscopic analyses to understand the chemical and compositional changes in the electrospun nanofibers after stabilization and annealing. Raman spectroscopy is performed on all the samples to study the formation of D and G peaks (Fig. 3 (a)). For the analyses, InVia Raman spectroscope with 633 nm laser excitation is used. Signal acquisition is performed over the samples with a laser power of 1.45 mw (at sample) accumulated and averaged over ten scans. From the analyses, prominent peaks are observed at 1327 cm^{-1} (D-peak) and 1585 cm^{-1} (G-peak) for the annealed nanofibers signifying the formation of disordered graphite crystals in the nanofibers due to annealing.

X-ray photoelectron spectroscopy is performed to study the change in composition of the nanofibers over different

annealing temperatures (Fig. 3 (b), (c), and (d)). Graphite and graphitic substances are usually known to show strong asymmetric C1s peak at 284.8 eV. In case of the samples annealed at 750°C and 950°C, strong asymmetric peaks are observed at 284.8 eV which signify graphitic C-C bonding. In case of the nanofibers annealed at 500°C, a relatively strong peak is observed at 286.5 eV which signifies C-O-C (carbon oxygen single bond). It is understood that as the annealing temperature is increased, the C-O bonds are replaced with more C-C sp^2 bonds which explains the observed XPS spectra.

Fig. 3: Plots showing (a) Raman analyses of electrospun, stabilized nanofibers and nanofibers annealed at 500°C, 750°C, and 950°C. (b, c, d) XPS analyses of the stabilized nanofibers annealed at 500°C, 750°C, and 950°C respectively.

B. Strain Sensor utilizing graphitized nanofiber bundle

The strain sensor is fabricated by sandwiching the graphitized PAN nanofiber mat annealed at 950°C between PDMS slabs deposited with thermally evaporated gold (Fig. 4). The gold electrodes act as the electrical contacts for the nanofiber mat.

Fig. 4: Schematic diagram showing the fabrication of a flexible strain sensor using the graphitized nanofiber as the sensing element.

Fig. 5: (a) Photograph of the flexible sensor held with hand. (b) Showing the strain sensors made by sandwiching graphitised PAN nanofiber on PDMS slab deposited with thermally evaporated gold. The gold layers act as the electrical contacts to the nanofiber mat.

A real-time experimental calibration of strain sensing during pressing tests is demonstrated. A constant current is injected into the sensor and the voltage across it is monitored. A series of static bending and cyclic pressing tests are performed on the strain sensor to demonstrate the application of such sensors for wearable devices.

The strain sensor is capable of detecting a bending of less than 3° induced in the film without the need of any external amplifier. The sensor is tested with three different bias currents (0.5 mA, 1 mA and 1.5 mA) and the response of the sensor is found to have a linear relationship with the bias current (Fig. 6). The sensor is subjected to periodic fast press and release at regular intervals of one second and the data is recorded by a data acquisition setup and LabView software (Fig. 7).

Fig. 6: Plot showing the calibration of the sensor output for bending test conducted over a range of zero to eight degree bending angle using three different constant bias currents.

Fig. 7: Plot showing the response of the flexible strain sensor to cyclic short duration pressing. The slow response is also attributed to the nature of the PDMS.

IV. CONCLUSION

To summarize, this work demonstrates the feasibility of using polyacrylonitrile precursor based carbon nanofibers for fabricating flexible strain sensors. Effect of annealing temperature on overall chemical and physical properties of the electrospun nanofibers is studied by means of various spectroscopic analysis techniques. Finally a strain sensor made out of graphitized nanofiber bundle is demonstrated.

V. ACKNOWLEDGEMENTS

This research is supported by the National Research Foundation Singapore under its Campus for Research Excellence and Technological Enterprise programme. The Center for Environmental Sensing and Modelling is an interdisciplinary research group of the Singapore MIT Alliance for Research and Technology. The authors would also like to

thank Mark Wainright Analytical Centre UNSW and Australian National Fabrication Facility, NSW node for their assistance in this project.

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