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Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Evgenia Gilshteyn

PhD Program: Materials Science and Engineering

Title of Thesis: Components for Stretchable Electronic based on Single-walled Carbon Nanotubes

Supervisor: Prof. Albert Nasibulin

Chair of PhD defense Jury: Prof. Nikolay Gippius, ***Email****: N.Gippius@skoltech.ru*

Date of Thesis Defense: 05 October 2018

Name of the Reviewer: Prof. Sergey Shandakov

I confirm the absence of any conflict of interest	**Signature:** **Date: 03-09-2018**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The dissertation consists of 3 chapters, conclusion and list of literature. The first chapter presents the field of research, substantiates the relevance of the research topic and provides a review of scientific publications on the topic under consideration. In the second chapter, methods for obtaining and studying materials are considered. The third chapter presents the results obtained and their discussion. The Conclusion presents the main results obtained. The bibliography includes 95 papers. The structure of the work presentation corresponds to the requirements for the thesis.
The author has made a very valuable and qualitative research carried out in the actual field of materials science. However, the following remarks are available:
1. In the work there are mistakes and misprints, which, however, do not interfere with understanding the meaning of the text:

- in the title the word "Electronics" is written as "Electronic", i.e. without the letter "s";
- on p. 8 in abbreviation list the TEM is indicated as tunneling electron microscopy instead transmission electron microscopy as used in the text;
- on p. 9 the CG used in the caption of fig. 9 is absent in abbreviation list;
- on p. 15 in sentence "… the CNT films were deposited on a PET substrate, which was bent around 30 000 times with the curvature angle of 1 mm" it is unclear why angle dimension is in mm;
- at the bottom of p. 28 the reference to Fig. 11 goes after reference to Fig. 13;
- on p. 39 in the sentence "The capacitance of the device, Csp, calculated according to Equation 1 achieves the value of 7.4 F g^{-1}" the appropriate equation is absent;
- on p. 53 the symbol "m" used in the Eq. 2 is not described;
- on p. 53 the numbering of the formulas is not ordered (in 3.2.4 the last formula number is 4, in 3.5.3 the first formula number is 2);
- on p. 56 in the sentence "… can be explained by the effect of better electrolyte diffusion and electron transport through the layers due to stretching of the electrodes with the deposited gel electrolyte, which was also discussed in our previous work" the reference to this work is absent.

2. The drop in transparency in the visible region with the removal of tension (after stretching) of CNT / hydrogel is explained by a drop in the transparency of the hydrogel (see p. 28). In this case, it would be worth to analyze the subtracting spectra (with subtraction of hydrogel spectra). In addition, a discussion of the reason of the hydrogel transparency drop after stretching is absent.
The comments made are secondary and do not diminish the significance of the results obtained by the author.

The thesis is devoted to the actual direction of nanomaterials and nanotechnologies. The problem of obtaining and studying the properties of carbon conducting and transparent nanomaterials is of considerable interest, especially for the recently developed flexible (stretchable) electronics in the light of the possibility of developing transparent and highly stretchable electrodes and sensors on their basis. The relevance of the topic of the thesis in question is beyond doubt.

The work is characterized by the use of modern scientific equipment sufficient to obtain reliable results on the study of the structural, mechanical, electrical and optical properties of the studied materials based on single-walled carbon nanotubes: For the characterization of optical properties absorbance of the samples was measured by Lambda 1050 UV-vis-NIR spectrophotometer. Morphology of the SWCNT/elastic structures were investigated using FEI Versa Dual Beam scanning electron microscope (environmental mode) with a special tensile stage Gatan 200N and homemade stretching device with the structures fixed under the clips for an in situ visualization of stretching/releasing processes. TEM images were obtained with a Tecnai G2 F20 transmission electron microscope. The electrochemical measurements and stability of transparent stretchable supercapacitors was studied with an Autolab PGSTAT100 potentiostat at various scanning regimes. Cyclic voltammograms at different ranges and scan speeds were recorded with an Elins Potentiostat-galvanostat P-40X.

The results obtained have a scientific significance and compliance with the international level and

current state of the art. In the work the new transparent, stretchable, conductive and biocompatible structures of elastic polymers, such as polydimethylsiloxane (PDMS) and hydrogels, modified by SWCNT films are used to create passive electrodes and active sensors for wearable and skin-like electronics.
The stretching mechanism of SWCNT/PDMS structures (i.e., SWCNT thin films deposited on PDMS substrate) is investigated by means of in situ scanning electron microscopy (SEM) and compared with the computational studies. In the work a one-step universal method based on aerosol CVD synthesis of SWCNT is applied for SWCNT/hydrogel and SWCNT/PDMS structures fabrication, withstanding intrinsic stretching up to 100% strain. This method holds advantages, compared to those reported previously, as it is a direct transfer from the filter onto a hydrogel surface without the need for a sacrificial layer or any other intermediate steps. In order to create energy storage devices, which could be further integrated with such active sensors it is successfully developed highly stretchable supercapacitors, based on SWCNT films as current collectors and electrode material. All-solid stretchable supercapacitors based on PVA–H2SO4 gel electrolyte showed specific cell capacitance of 7.4 F g^{-1}. In order to increase durability to stretching of stretchable supercapacitors it was performed technique based on pre-stretching of the electrodes with the deposited gel electrolyte. This approach allowed using the effect of better electrolyte diffusion and electron transport through the electrode layers and obtain the capacitance value of 17.5 F g^{-1}, significantly higher than previously reported. High-performance, stable, low equivalent series resistance all-nanotube stretchable supercapacitor based on SWCNTs film electrodes and a boron nitride nanotube separator demonstrates electrochemical double layer capacitance mechanism in a two-electrode test cell configuration and retains 96% of its initial capacitance after more than 20 000 electrochemical charging/discharging cycles and withstands at least 1000 cycles of stretching with low resistance of 250 Ω. The piezo-supercapacitor system provides a new promising direction in the supercapacitor research for the development of next generation self-powered sustainable power sources for wearable and flexible electronic devices.

The developed approach was applied to create a new set of soft and robust components, such as electrodes for electrocardiography monitoring and active sensors for a human motion detection. An open circuit voltage of the flexible and transparent supercapacitor reached 500 mV within 20 s during the mechanical action, which allow to further extend it for providing sustainable power source of various types of sensors integrated into wearable units. Integration of such supercapacitors into a flexible piezo-supercapacitor system with poly(vinylidene-trifluoroethylene) film to harvest and store the energy was demonstrated. The simple piezo-supercapacitor fabrication procedure could be easily scaled-up to large-scale production. The stretchable, transparent SWCNT based components and devices were prepared without dispersion in an elastic matrix, without time consuming and expensive lithographic techniques and patterned simply using dry transfer method. In the future, it could be possible to use these principles, materials and devices to design electronics that “echo and imitate the natural world by bending, stretching and flexing” and make sense as technology integrated more and more into our lives, our environments, and even our bodies.

The results are presented in 5 publications including 4 papers published in journals with high impact factor (JCR IF is in the range from 3 to 8). Approbation of the results took place at an international conference on nanotechnology.

Provisional Recommendation

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*
☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*