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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: MIKHAIL O. BULAVSKIY

PhD Program: Materials Science and Engineering

Title of Thesis: Hybrid functional materials based on single-walled carbon nanotubes

Supervisor: Professor Albert Nasibulin

Co-supervisor: Assistant Professor Fedor S. Fedorov

Name of the Reviewer: Prof. Oleg Tolochko

I confirm the absence of any conflict of interest	**Date: 22-11-2023**

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

Even taking in account 30 years history of CNT extensively studied, SWCNTs are still far from the widespread industrial applications. One of its main reasons are the limitations stemming from the nature of the bulk SWCNT material properties. However the possible application areas of SWCNT-based hybrid materials are extremely diverse, hence extensive research has been done to apply them in various fields. That why the aim of the research was to develop the new methods for modification of the SWCNT thin films (to be applied in transparent conducting films and as supercapacitors), establish influence of electrochemical treatment on SWCNT structure and filling efficiency, and study obtained materials properties.

In his PhD thesis Mr. Mikhail Bulavskiy developed a new method of bilateral SWCNT film doping with HAuCl4; the method of controllable SWCNT electrochemical opening; prepared series of SWCNT/polyaniline composites and it was studied its performance of supercapacitors made of flexible SWCNT/polyaniline composites in three- and two-electrode configuration.

Overall structure of the dissertation looks well organized and logical. It consist of 5 Chapters and bibliography. The topic of the dissertation is relevant to its actual content. There are 2 publication of high quality, which were included in thesis, and 1 more papers submitted.

As the main novelty of Dissertation may be marked an possible application of synthesized SWCNT composites as flexible symmetric supercapacitors showing good stability during cycling and bending as well as proposed method to obtain transparent conductive SWCNT films with a record equivalent sheet resistance value .

Some remarks, which can be discussed during the defense, are the following:

There are no XPS data for the heat treated samples. However, It may give an information about quantity and evolution of the functional groups under the heating in air as well as under doping with Au.

To my opinion, it is very important to show sheet resistance of the SWCNT films heat treated at different temperatures, but not only the equivalent one as shown in Fig.2, Fig.4a.

Authors mentioned that typically, blue shifts of the G-mode peak and 2D-mode positions are attributed to the p-doping (Fig.5). Nevertheless, the doping and strain are the most competing factors influencing the the position of G band and it FWHM (full wigth half maximim). Generally the doping has strong effects resulting in the blueshift of the G peak position and the decrease of FWHM for both electron and hole doping [M. Bruna, A.K. Ott, M. Ijas, D. Yoon, U. Sassi, A.C. Ferrari, ACS Nano 8 (7) (2014) 7432–7441]. Please, pay attention that FWHM visually increase in the Fig.5.

As seen from Fig.2 the transmittance of the SWCNT films treated at temperatures over 350 ºC increases in a great extension, but the reason for this phenomenon is not discussed clearly in the text. There are two competitive processes may occur under heating, such as: desorption of the oxygen and moisture and oxidation of the carbon. To clarify the point some additional observations and discussions would be very helpful.

Fig.5, b shows G band change during heat treatment, the shape of the pristine nanotubes G peak looks asymmetrical, which is not corresponded to Fig.5, a, where the whole Raman spectrum is presented. Aslo in the Fig. 5 the change of band D during doping and heat treatment is not shown and does not discussed in the text.

Author says that doping effect (Figure 4b), leads to the appearance of a new peak that corresponds to the nanotubes' intersubband plasmon appearing when the excitonic levels are fully saturated with charge

carriers, those data prove that p-doping caused an efficient downshift of the Fermi level favored by HAuCl4 treatment. This statement may be confirmed by plasmon observation by XPS spectroscopy. For example, on XPS spectra for SWCNT-EH film treated at UVP = 1.3 V plasmon peak is negligible.

At the same time, the noted shortcomings are not of a fundamental nature and therefore do not reduce the value of the work performed. Hybrid material based on SWCNT thin film covered with polymers exhibiting pseudocapacitive behavior is a promising one that may outperform SWCNTs in terms of the energy stored, while preserving its flexibility for application as a wearable electronics power source. Assessing the work as a whole, I believe that in terms of the volume of data obtained, the level of generalization of experimental and theoretical material, and the novelty of the results, publication level it meets all requirements for PhD dissertations.

Provisional Recommendation

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