Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis

Name of Candidate: Alexey Tsapenko

PhD Program: Physics

Title of Thesis: Enhancing Optoelectronic Performance of Randomly Oriented Single-Walled Carbon Nanotube Films

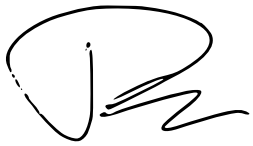
Supervisors: **Prof. Albert Nasibulin, Skoltech, Russia**

Prof. Esko Kauppinen, Aalto, Finland

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

Date of Thesis Defense: October 4, 2019

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:**  **Date: 13-08-2019**

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 the latest on August 13th. 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

The thesis of Alexey Tsapenko describes a thorough study on the effects of chemical doping on the optoelectronic properties of single-walled carbon nanotube films synthesized via aerosol chemical vapor deposition, as well as those of hybrid structures incorporating graphene oxide reduced via various means. The work uses appropriate methods to address important research questions on a high international level.

Apart from the impressive optoelectronic performance metrics that the candidate has been able to achieve that are promising for technological applications, the thesis provides new and improved physical understanding on the effects of doping on the film properties. The presented optical measurements and their analysis are of particular scientific relevance, although here the THz and IR spectroscopies contributed by coauthors do appear to play a crucial role.

The study on the role of solvent in the doping process also adds new physicochemical understanding, while leading to some of the highest performance films ever reported. It appears that the spray method introduced by the candidate offers good possibilities of integration with continuous production methods. The only small shortcoming of this aspect of the thesis is a comparison of the stability of various doping schemes.

The thesis is clearly organized and presented in good English (apart from a few minor idiosyncrasies), and the publication record and the contributions of the candidate are commendable. He has clearly mastered many important characterization techniques during the course of his doctorate, and demonstrated the capability for independent scientific work.

I therefore recommend that the candidate is awarded the doctoral degree upon the successful defense of his thesis.

I have a few minor comments and questions to be considered in an optional revision or during the defense.

- p.19: why is there increased absorption beyond 2500 nm in the doped sample? What is the cause of the small peak at 2700 nm?
- p.21: What does it mean that vanished vHs can be seen in Fig. 2.3.4-2? Is this the fact that the curves show no peaks? Are all the curves for doped nanotubes, and if so, what would the undoped response look like?
- p.24: Is this a real spectrum or just an illustration? The shape of the vHs contribution, especially on the higher energy side of each peak, appears strange. Or is this simply due to the logarithmic x-scale?
- p.28: The phrase "laser exposure time of 50 Hz" sounds strange. Either the unit is incorrect, or this should not be called an exposure time. Also, Raman laser power is not limited only to avoid destroying the sample, but also to avoid heating that causes changes in the response.
- p.36: Fig. 4.1.1-1 caption "(black dots, black lines)" probably should read "(black dots, red lines)". Also, it is not clear what "dashed lines (a) and (d)" refer to; it is hard to distinguish any such lines, should this read (c) and (f) instead? Finally, the 5 K label in (a) is poorly placed, and the presentation of the y axis scale could be unified between (a) and (d).
- p.38: What is the given Fermi velocity based on, is this from the literature? If so, reference should be given.
- p.39: Is the Boltzmann constant missing from the equation? Also, it is not clear from the text how exactly were the tunnel gaps determined. Lower down on the page, it is mentioned that the effective was 0.2 m_e, what is this based on? If literature, reference should be given.
- p.43: Fig. 4.1.2-1 caption mentions "green circles connected by a black line", but none are visible. Should the extra red filled circles in (a) and (b) top be colored green instead (and connected by a line)? What is the magnitude of the FWHM change? In the text, the word "dipper" probably should read "deeper".
- p.44: The trion lifetime mentioned in the text needs a literature citation. Also, the mentioned solid lines in Fig. 4.1.2-2 are probably missing from the figure.
- p.47: It is unclear what the relevance of the heated Al surface experiments are for the hybrid material where the surface would consist of a nanotube network. Surely the two surfaces have very different properties?
- p.48: Reference to supplementary material seems spurious. Also, it is not clear from the text what is meant by contact angle.

- p.49: Panel (c) of Fig. 4.2.1-2 could be taller, it is very hard to see the C1s component peaks.
- p.51: There seems to be a discrepancy between the equivalent resistance values given on p.48, and those show in Fig. 4.2.1-4. Are these different samples?
- p.52: Is the comparison to literature data shown in Fig. 4.2.1-5 fair? Looking at the scatter plot of Fig. 4.2.1-4 (c), there appears to be no hybrid film sample that has a sheet resistance of 73 Ohm at 90% transmittance. How was this value obtained? And on p. 54, an even better value is given..?
- p.53: What is the origin of the small sharp dips at ~1300 and ~2250 nm in the HAuCl4-doped film?
- p.61: Mention of Supporting Information is spurious.
- p.63: Using the disappearance of the vHs peaks as an indirect measure of the work function is a clever idea. However, since UPS could give this information directly, was the method cross-verified? Or why were UPS measurements not performed?

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*