

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Mikhail 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 Fedorov

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	Date: 25-11-2023
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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 doctoral thesis “HYBRID FUNCTIONAL MATERIALS BASED ON SINGLE-WALLED CARBON NANOTUBES” by MIKHAIL O. BULAVSKIY is devoted to a relevant and significant issue in modern Materials Science of composites for functional applications – transparent conductive films (touch screens etc.) and supercapacitors as energy storage devices for portable devices and starting elements. It is a systematic, dedicated and comprehensive research report having all necessary components to consider it as a firm scientific work. I am generally positively impressed with the scientific soundness, novelty and practical applicability of the results. Methods are adequate and relevant. The quality of publications is acceptable.

Comments are attached.

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

The doctoral thesis “HYBRID FUNCTIONAL MATERIALS BASED ON SINGLE-WALLED CARBON NANOTUBES” by MIKHAIL O. BULAVSKIY is devoted to a relevant and significant issue in modern Materials Science of composites for functional applications – transparent conductive films (touch screens etc.) and supercapacitors as energy storage devices for portable devices and starting elements. It is a systematic, dedicated and comprehensive research report having all necessary components to consider it as a firm scientific work. Having been generally positively impressed with the scientific soundness, novelty and practical applicability of the main thesis’ outcomes I noticed few aspects which are recommended to be addressed before final submission and formal defense. They are given in the list below as the following:

Page	Comment or question
12	Aims and objectives seem too “technological” for me. Is there any chance to improve phrasing, e.g. “to investigate scientific foundations for the development of modification protocols and techniques ...”
14	«weight of the composite material» - may be density?
15	“The main disadvantage of the method is the low filling efficiency [2].” – this phrase somewhat contradicts to paragraph above. Please, make the sentence more accurate.
26	«For qualitative evaluation of the functional composition of the SWCNT/PANI composites we utilized samples with 70 PANI deposition cycles.» - not clear. Please clear out.
31	“(R90) are quality defining parameters for transparent conductors, we monitored their variations with the” – qualitatively defining?
33	“Such doping effect is manifested in the UV-Vis-NIR transmittance spectra (Figure 4b), leading to the removal of S11, S22, and M11 peaks and the appearance of a new peak” – not obvious for S22. Please, formulate in more accurate manner.
34	Figure 4 b) – I liked Transmittance vs Wavelength chart. Why you used Absorbance vs Wavelength before in Figure 1, since you objective function is Transmittance in the very end? Please, unify these charts through the text. Raw data on Absorbance may stay in Appendix – no problem. “Although at 400 °C higher transmittance should have impacted R90, this effect is negated by a significant sheet resistance jump.” – not clear, difficult to conclude from Figure 4. Please, rephrase.
35	“Gold nanoparticles decorate the outer surface of SWCNTs, forming via spontaneous reduction of [AuCl ₄] ⁻ anions.” -> Gold nanoparticles formed via spontaneous reduction of [AuCl ₄] ⁻ anions decorate the outer surface of SWCNTs.”
40	“However, there is no significant effect on the charge transfer between SWCNTs and Au nanoparticles (Figure 6c) present on the nanotube surface.” May be Figure A6c is correct?
45-46	The attempt to explain (actually to speculate) every little datum is not a robust approach. Taking into account that all these considerations are based on the deconvolution of spectra and confidence intervals are quite broad I would strictly recommend reorganize the discussion of Table 3 to make arguments more robust.
47-48	I appreciate methodologically sound efforts undertaken by authors to quantify the filling of SWCNTs. On the other hand, “at least 0.4 μm ² ” of SWCNT film is not a reliable measure of statistics confidence. The use of ImageJ might be fully welcomed provided the protocol

	of binarization, segmentation, differentiation (nanoparticles from nanowires) had been presented in details. Of course, the discussion of this aspect must be reorganized to make arguments more robust. Molecular dynamics is touched but not described or referred above.
61	The attempt to explain (actually to speculate) every little datum is not a robust approach.
64	Figure 24 reports too different measurements, please, correct. “We conclude that the higher the rate of supercapacitor cell charge, the lower the cell specific capacitance is.” Contradicts to Figure 24 b.

General impression:

* There is a desire to explain all observations and all acquired results. It is quite common for junior researchers, even when synthesis protocol is new and sophisticated what is as usually gives noisy signals or naturally randomized responses. In many cases it is not right practice. Modest but robust conclusions are preferable.

And now few more general issues to be addressed:

- 1) Which protocol of SWCNT modification is ultimately preferable – thermal or electrochemical? Do you expect perspectives in the investigations of different atmospheres for thermal treatments or other chemicals (e.g. hydrogen peroxide) for electrochemical treatment?
- 2) Do you expect better SC performance for your materials if electrolytes based on organic solvents (DNC) will be applied?
- 3) Please, discuss other potentially interesting fillers for SWCNTs after end-openings?