Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis

Name of Candidate: Vsevolod Iakovlev

PhD Program: Physics

Title of Thesis: Advanced Synthesis of Single-Walled Carbon Nanotubes Films by Aerosol Method for Electro-Optical Application

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

Prof. Esko Kauppinen, Aalto, Finland

Chair of PhD defense Jury: Prof. Keith Stevenson, Skoltech ***Email:*** *K.Stevenson@skoltech.ru*

Date of Thesis Defense: October 4, 2019

Name of the Reviewer: Toma Susi

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** **Date: 15-08-2019**

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 Vsevolod Iakovlev describes a comprehensive study on the aerosol chemical vapor deposition synthesis of single-walled carbon nanotube films, comparing a novel reactor design that separates the catalyst particle creation from the growth to current state-of-the-art techniques. Further results using artificial neural networks to predict the properties of the films from experimental parameters as well as laser-treatment of the films and their application to electro-optical elements give the thesis additional technological relevance. The work applies well-justified methods to address important research questions at a good international level.

The spark generator reactor appears to be a promising and versatile method for generating high-quality SWCNT films, and the candidate has convincingly demonstrated that the yield can be tuned without adversely affecting the film properties. While it would had been useful to have extra breakdown voltage

measurement points to more robustly establish the parabolic dependence, the results are nonetheless very interesting especially considering the independent control over multiple film properties.

While I find the claims of novelty of the spark reactor design a bit oversold considering its similarity to the design developed in Aalto several years ago, I do appreciate that no catalyst is diverted to the exhaust here. It would however have been helpful to further highlight the differences to more clearly demonstrate the original contributions to the design made by the candidate. Nonetheless, the synthesis parameter space has been studied in great detail and significant useful new information including on the role of CO2 addition has been generated.

The thesis is written in rather good English and well organized, although some sections of the introduction are a little sparse. The publication record and the contributions of the candidate are commendable, and during the course of his doctorate he has applied numerous techniques related to sample synthesis, characterization and even simple machine learning. This demonstrates a capability for independent scientific work.

I therefore recommend that the candidate is awarded the doctoral degree upon a successful defense.

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

- p.12: Placement of Fig. 2.5 is one line off (breaking a text paragraph)
- p.15: Typo "non-linier"
- p.18: Using a software screenshot to illustrate UV-Vis-NIR is a questionable choice: it's hard for the reader to understand what it tries to communicate. Also, Fig. 3.2 appears to be based on a preview image of the Kataura plot: if one looks at the original (http://www.photon.t.u-tokyo.ac.jp/~maruyama/kataura/katauran.pdf), there are no spurious red circles along the x-axis.
- p.19: Breaking captions to a different page as the figure should be avoided. Same on p.21.
- p.20: Section 3.1.4 title is missing a preceding break.
- p.22: Raman laser power is not limited only to avoid destroying the sample, but also to avoid heating that causes changes in the response.
- p.23: Within the phrase "accuracy of the measurement" I presume precision is meant instead.
- p.23: Descriptions of SEM, TEM and AFM could include actual introductions to the techniques instead of just listing what instrument was used with which parameters. Same applies to TGA on p.26.
- p.24: There is probably a typo in Equation 3.3: I believe the denominator should read "log(10/9)" and the separate (10/9) factor is spurious.
- p.28: What is meant by "contact time of 6 s"? Should this rather read "residence time"? Same term is used on p. 36 and p. 38.
- p.32: Were the Raman I(G)/I(D) ratios calculated from the maximum peak values or the areas beneath each peak? The latter would be more reliable by minimizing the influence of any possible peak broadening.
- p.34: Why are panels (a) and (b) not comparing the same set of breakdown voltages, or is there a typo in the legends? Why was a sample synthesized at 3.1 kV not measured?
- p.35: Why does panel (a) not include a curve for 5 LPM N2 flow? Also, the caption of panel (b) is not consistent with the legend: the caption states that the total CO + N2 flow was 6 LPM in each case, while the legend does not reflect this.
- p.36: While it is true that the TEM statistics of Fig. 4.7 show little effect, and this is consistent with the Raman RBMs at those flow rates, the 3 LPM spectrum in Fig. 4.6 appears to have a significantly different diameter distribution (but also a higher D band and a much greater 2D/G ratio).

- p.42: What are the Raman I(G)/I(D) ratios corresponding to the data of Fig. 4.2?
- p.47: How were the mean diameters determined exactly? Presumably from the optical absorption spectrum, but was a background subtracted and were multiple peaks fitted?
- p.50: It is not clear whether the artificial neural network has been applied to nanotubes synthesized with the ferrocene or the spark generator reactor. If the former, why is that considering most of the thesis concentrates on the spark generator? If the latter, why are the spark parameters not included as input for the model?
- p.51: Typo "nods" should read "nodes". Same on p.53.
- p.52: What did the data augmentation exactly do?
- p.53: How were the network hyperparameters "manually varied"? What were the criteria for ending up with the paremeters in Table 5.1?
- p.54: The phrase "experimental error" is misleading when describing the variance in the experimental data.
- p.55: Why did some networks perform better than others, e.g. diameter was accurately predicted but Raman G/D ratio rather more poorly. Was it verified that the same network structure (number of layers and nodes) was optimal for each case? Why were there fewer training epochs for the poorer performing networks?
- p.58: Mention of "laser-assisted" nanowelding could use a literature reference.
- p.61: What changes were there to the C1s XPS response by the laser treatment? While iron particle oxidation may play a role, removal of carbonaceous contamination seems likely to contribute to the greater transparency. Also, the sheet resistance changes reported in Table 6.2, although inconsistent, appear much larger than the measurement precision, what would the error values be?
- p.64: The caption of Fig. 7.2 could use definitions of the variables.
- p.65: The phrase "the temperature drops significantly with lowering the sample sensitivity" seems inverted (ie., sensitivity drops with temperature, not the other way around).
- p.67: Figure 7.3 could use definitions of the used acronyms. Same applies to Fig. 7.5 on p.69.
- p.72: How was the thickness of the coating determined?
- p.76: How is the spark generator reactor more scalable than the ferrocene reactor, considering the latter has much higher yield?

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*