Skoltech
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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Artem Grebenko

PhD Program: Physics

Title of Thesis: Carbon nanomaterials: synthesis and charge transport

Supervisor: Professor Albert Nasibulin

Co-supervisor: Dr. Dmitry Krasnikov

Name of the Reviewer: Prof V Antonov

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 06-06-2022**

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 thesis concerns the experimental study of carbon nanomaterials, carbon nanotubes, and CVD graphene. The author has elaborated a few experimental techniques and designed the apparatus for the fabrication of the carbon material. Extensive metrological methods have been applied for the characterization of the material and optimization of the fabrication process. Finally, the experiments have been done on the transport properties of the SWNT films and graphene, and a new AFM lithography of the SWNT films has been experimented with.

A large part of the thesis is devoted to the technology of the production of carbon materials. The author has focused on the techniques, which potentially can be used for a scalable industrial fabrication. The apparatus and technology are filed in patents and explained in scientific publications. The SWCNT and graphene are synthesized through carbon monoxide disproportionation, so-called the Boudouard reaction. One of the main advantages of the method is that the growth rate can be controlled with a small amount of CO_2. The copper and ferrocene metallic particles catalyzed the reaction. SWCNTs were generated with a standard floating catalyst spark-discharge reactor, while the graphene was grown in a newly designed CVD reactor. New technology for encapsulating graphene with Parylene-N was developed.

When growing the SWCNT a dopant $AuCl_3$ was used to vary work function. It was experimentally found that doping allows to vary the optical absorption of the material, particularly at the THz end of the spectrum.

Several metrological techniques are used for the analysis of the material: SEM, FIB, XRD, LEED, EBSD, AFM, STM, KPFM, THz-MIR-TDS, Raman spectroscopy, XPS, ARPES, NEXAFS. The metrology shows that CVD graphene is aligned with the Cu crystal, a Moire pattern may be developed when graphene is grown on (111) lattice of cooper.

The synthesized materials were used to demonstrate quantum phenomena: Coulomb blockade of transport through the SWCNT, the shot noise in SWCNT, quantum Hall effect in macroscopic CVD graphene films. The latter indicates the high quality of the graphene films.

Finally, the densification of the film consisting of SWCNT is demonstrated. The “lithography” is done with AFM. Quite a few patterns have been produced with the method for the application in optics. The method is time-consuming. But it may be used for some applications.

The work was done systematically with high experimental accuracy. The thesis is based on a respectful amount of experimental data. I appreciate a wide range of experimental hardware designed and constructed to perform this work. Analysis of experimental data is clear, and self-consistency checks are made where needed. The important parameters are described.

The thesis is coherently written with good English grammar. The pictures are clear and of good quality. All borrowed materials are properly referenced. A good introduction and background are given at the beginning of the thesis. All findings and conclusions are summarized, and directions for future research are discussed. The material of the thesis is published in 6 refereed journals with a high impact factor and disseminated at several conferences. I believe the thesis is a standard for Doctor of Philosophy work.

Particular questions and corrections:

P36 Last line in figure caption. " (I) Moire pattern…" What kind of this image, KPFM Image?

P.37 Line 8 from the top. " Most probably … The statement needs detailed explanation.

P 42 Line 5 from the bottom. Would it possible to add arrows in the Fig 14d pointing at the SWCNT with changing potential

P43 Line 3 from the top. What kind of charge peculiarities author think of?

P47 Line 7 from the bottom. Statement "sequential tunnelling is forbidden….." should be extended with details.

P47 What is the motivation of the experiment of Section 4.1.4? Do you want to get some characteristics of material?

P48 Please decrypt colour coding of lines in Fig. 19.

P48 The caption of Fig. 19. "…voltage ranges…." -> "…current ranges"

P48 Line 2 from the bottom. What kind of resonance?

P49 Line 1 at the top. "…independent tunnelling processes". Explanation details are needed.

P49 Line 3 at the top "… these conditions..". He conditions should be clearly stated

P49 Last line "… different quantum states. .." . The states should be explained: are they dimensional quantization, Coulomb blockade,…?

P50 Caption of Fig. 20 ".. (E-G)" to "…(F-H). Colour scale? Fig 20H: any details in the caption?

P52 Line 7 from the top. Add commas :"…, like interference,.." . "..often occur.."

P59 Line 9 from the top. " …of a 134 nm thick parafilm,.. "

P55 line 2 from the bottom "…lateral…" ->"…longitudinal…"?

P60 At which particular wavelength one would expect a benefit to have modulated reflection of SWCNT film?

P62 Line 7 from the top. Would it be better to have somewhere a table of materials to compare?

P63 Line 3 from the top. "Microscopical analysis further helped to understand the contribution of the defects and tunnel junctions into the FIR-THz ranges". In which section these were discussed?

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*