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Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Maria Zhilyaeva

PhD Program: Materials Science and Engineering

Title of Thesis: A novel straightforward wet pulling technique to fabricate carbon nanotube fibers

Supervisor: Professor Albert Nasibulin

Name of the Reviewer: Krisztian Kordas

I confirm the absence of any conflict of interest	**Date: 08-11-2021**

Reviewer's Report
In her doctoral dissertation, M.Sc. Mariia Zhiliaeva discusses on a novel carbon nanotube fiber pulling method (referred as *wet pulling*) and related applications that she worked out at the Skolkovo Institute of Science and Technology under the supervision of Prof. Albert Nasibulin. Carbon nanotube fibers are unique assemblies that mimic the structure and hence the mechanical properties of conventional yarns pulled and twisted from cotton and wool. The original process, which is as old as the human civilization, has been since serving mankind with advanced materials to produce e.g. strong ropes for tools and woven textiles for cloths. Practically any fine fibrous material can be arranged into ropes provided the attraction forces between the elongated particles is strong enough to hold the structure together. Capitalizing on the van der Waals forces acting between single-walled carbon nanotubes in close proximity, the first demonstration of their macroscopic ribbons was shown (B. Vigolo et al., Science 2000, 290, 1331) by injecting aqueous carbon nanotube dispersions to a vortex of an antisolvent, in which shear forces align and bring close the nanotubes during their precipitation. Later, several other methods have been shown to produce macroscopic fibers, e.g. by pulling nanotubes from their aligned forests (M. Zhang et al., Science 2004, 306, 1358) or from non-woven sponges (L. Song et al., Carbon 2012, 50, 5521) followed by twisting to result in yarns. The process *wet pulling* published by M.Sc. Mariia Zhiliaeva and her co-workers (M. Zhilyaeva et al., Carbon 2019, 150, 69) applies stripes of thin entangled films of single-walled carbon nanotubes and subsequent capillary force induced folding in solvents that add on to the previously demonstrated techniques by providing a simplified route yet excellent control on the produced fiber structure to tune its electromechanical properties (S.D. Shandakov et al., Mater. Sci. Eng. B 2021, 269, 115178) and making such fibers suitable for a variety of sensor applications (M.A. Zhilyaeva, submitted to Soft Robotics, 2021). These discoveries are not only bringing closer the famous visions of R. Smalley on the potential applications of carbon nanotubes, such as the space-elevator, light-weight metal-free electric cables, and interconnects in microcircuits (*Wires of Wonder*, Technology Review, 2001, March 1) but suggest many more as shown with excellent examples in the thesis of M.Sc. Mariia Zhiliaeva describing new types of

force and vibration sensors to monitor physiological functions (breathing and heart beat) and to record acoustic waves of sound by a so-called *nanophone*.

The described method of producing carbon nanotube fibers by wetting and pulling stripes of thin films of carbon nanotubes is simple, yet it allows for controlling the diameter and mechanical properties of the wire-like structures by adjusting the thickness and width of the original nanotube film stripes. The Young's modulus, strain-to-failure and electrical conductivity of the fibers are similar to other carbon nanotube fibers reported by others. As demonstrated, the *wet pulled* fibers may be twisted, coiled and can be embedded in PDMS showing the robustness of the structure. The large gauge factors of *wet pulled* fibers make them ideal for force and pressure sensing even after encapsulation in PDMS. Training of the sensors was found essential to stabilize the structure thus mitigating sensor drift and random resistance fluctuations superposed on the drift. Detection of mechanical vibrations (caused by impact) and monitoring of radial and carotid pulses (this latter combined with breath detection) was demonstrated. To show the high sensitivity of the fibers encapsulated in PDMS, the devices were implemented as *nanophones* to record music. In addition, proof-of-concept studies of the nanotube fibers to be used as conductive wires in flexible circuits as well as in adjustable force sensors were also presented in the thesis.

The dissertation is structured in a logical manner. After a short **Introduction** to carbon nanotube fibers and force sensing devices, the thesis continues with a brief description of the **Experimental** methods. Specific details of the experiments along with thorough discussion of the corresponding results are elaborated in the subsequent chapter **Results and discussion**, which is split to several sub-chapters dealing with the production, characterization and post-processing the nanofibers before showing the details of their applications. Lastly, the results and their implications are summarized in the chapter **Conclusions**.

The thesis is well written, which makes it easy to follow each part of the highly extensive study. The text is supplemented with 38 figures (schematic drawings and camera photos of setups and devices, SEM images of materials, plots of electrical and mechanical properties as functions of several variables) along with 6 links to different video footages (on fiber production and sensor operation) that help visualizing the experiments and assessing the results throughout the manuscript. Furthermore, the appendix lists numerous music recordings using both commercial microphone and the developed *nanophone* thus enabling the comparison of their sound quality.

Although the text cites the contemporary literature very well, and refers to tens of papers published on carbon based piezoresistive sensors, somehow a good comparative table compiling various carbonaceous materials and device structures/assemblies with their gauge factor and applicable stress/strain window is missing. This is only a minor flaw that may be fixed by showing and discussing some related data of peers (in the light of the results presented in the thesis) during the public examination.

According to the declaration on the **Author's contribution** to the papers upon which the thesis is based on, M.Sc. Mariia Zhiliaeva had the main lead in writing papers I and III, and her share in design and execution of experiments is substantial.

In summary, the research presented in the thesis is timely and highly relevant. The results are sound, merit significant novelty, and the manuscript meets the highest standards of publishing. The contribution of M.Sc. Mariia Zhiliaeva to the science and technology of carbon nanotube based devices is convincing, thus I warmly recommend her dissertation to be accepted for public defense.

Krisztian Kordas
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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*