Thesis Changes Log

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

The thesis document includes the following changes in answer to the external review process.

I would like to appreciate all Jury Members for their feedback on the doctoral thesis including valuable comments contributed to the quality of the final thesis. Below could be found the responses to the remarks of the reviewers.

Response to the Professor Aleksandr Kvashnin

Comment 1: Some minor issues, in some places along the text there are broken characters like 31±4Ω□-1, which should be fixed.

Answer: Sheet resistance (R_S) is a measure of the electrical resistance of the thin films considered as two-dimensional when current flows along the plane. It is measured using a four-probe testing. Sheet resistance can be considered as a ratio of the bulk resistivity to the thickness of the thin film: $R_S = \frac{\rho}{t}$. Therefore, units of the sheet resistance is the $\frac{\Omega \cdot m}{m}$ that results in pure Ohms. However, to distinguish sheet resistance from bulk resistance units Ω sq^{-1} or Ω □$^{-1}$ are used for the sheet resistance. To clear this out in the text the units Ω □$^{-1}$ were replaced with units Ω sq^{-1}.

Response to the Associate Professor Alexey Yashchenok

Comment 1: Chapter 3, Fig.1: There is a shift of peaks at 500°C to longer wavelength. Is any explanation of this, since at lower temperature values the position of the peaks remain the same?

Answer: Heat treatment at high temperatures in ambient air cause the introduction of structural defects along with chemical functionalization with oxygen containing functional groups. It could be seen from the results of Raman spectroscopy as well as π–plasmon peak reduction in UV-Vis-NIR absorption spectra. Both these processes should cause changes in the density of states of SWCNTs. Heat treatment at temperature 500°C results into S_{11}, S_{22} and M_{11} peaks shift to lower energies. That should be a result of shift and/or shape changes of van Hove singularities in band structure of SWCNTs. Similar changes in peak positions can be observed for defects formation during acid treatment as well [1].

Comment 2: Chapter 3, Fig.3b: The graph showed multiple peaks in RBM region, which can be responsible for different diameter of the tubes and also for the type of the tubes (metallic or semiconductor). Is vanishing a peak here can be attribute to decomposition of nanotubes or its attribute with another reason?

Answer: Radial breathing mode (RBM) of SWCNT Raman spectra is indicating symmetric planar vibrations of carbon atoms in phase in radial direction. Usually vanishing or reduction of intensity of RBM-mode peaks is the indicator of the destruction of the SWCNT structure and attachment of functional groups to the carbon atoms that hinders this type of carbon atom vibrations [2-5].

Comment 3: Is any information of how many nanotubes were filled with gold nanowires with respect to initial amount of gold?

Answer: To evaluate the fraction of filled SWCNTs we should estimate the length of the SWCNTs. For calculation simplicity, let us assume the single SWCNT with the length of all SWCNTs combined. Then we can calculate the surface area of the SWCNT according to the equation (1):

$$S_{SWCNT} = l_{SWCNT} \cdot \pi \cdot D_{SWCNT} \quad (1)$$

where l_{SWCNT} is the total SWCNT length and D_{SWCNT} is its diameter. The area of one hexagon of a lattice (S_{cell}) could be expressed with the equation (2):

$$S_{cell} = \frac{3\sqrt{3} \cdot b^2}{2} \quad (2)$$

where b is the length of the carbon-carbon bond. Thus, number of the carbon atoms in the SWCNT structure could be described as:

$$N_C = \frac{6}{3} \cdot \frac{S_{SWCNT}}{S_{cell}} \quad (3)$$

Therefore, mass of the SWCNT would be:

$$m_{SWCNT} = \frac{N_C}{N_A} \cdot M_C \quad (4)$$

where N_A is an Avogadro number and M_C is a molar weight of carbon. Aerial density of a SWCNT film can be calculated using equation (5):

$$\rho_T = \rho_{0.5} \cdot \frac{\log_{10} T}{\log_{10} 0.5} \quad (5)$$

where T is a transmittance of SWCNTs film at 550 nm, $\rho_{0.5} = 5.5$ µg cm^{-2} is the density of the film with the transmittance of 50 %, and ρ_T is a density of the film with the transmittance T [6]. Aerial density when multiplied by the area would express the mass of the SWCNT:

$$\rho_T \cdot S = m_{SWCNT} \quad (6)$$

where S is the area of the film. Combining together equations (1)-(6) we will get the resulting equation (7) for length of the SWCNT in the film:

$$l_{SWCNT} = \frac{3\sqrt{3}}{4} \cdot \frac{\rho_{0.5} \cdot S \cdot b^2 \cdot N_A}{\pi \cdot D_{SWCNT} \cdot M_C} \cdot \frac{\log_{10} T}{\log_{10} 0.5} \quad (7)$$

Assuming $S = 1$ cm^2, $b = 0.142$ nm, $T = 87$ % and $D_{SWCNT} = 2.1$ nm we will end up with the total length of SWCNT to be 220 km cm^{-2}. Taking into account highest achieved value of Au nanowires length to be 1684 m cm^{-2} we will end up with the filled SWCNT ratio of 0.765 %.

Comment 4: How does gold nanotube filling relate to tube diameter? Can all tubes with different diameter be filled or is there a limit?

Answer: When we consider SWCNT filling with liquids (melts or solutions) we need to take into account the surface tension since capillary induced filling strongly depends on the wetting of SWCNT channel. Threshold for surface tension for successful SWCNT filling was established to be 130-170 mN m^{-1}. However, for filling smaller diameter SWCNTs requires smaller surface tension value. Thus, it was reported that for molten V_2O_5 ($\gamma \sim 80$ mN m^{-1}) the threshold diameter of SWCNT to be filled is 0.7 nm [7].

Comment 5: Fig. 13: Please check for the correct film name (right-hand side) in the schematic illustration.

Answer: I would like to thank Professor Yashchenok for this comment. The illustration was corrected in the thesis file.

Response to the Assistant Professor Alexey Salimon

Comment 1: Page 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 …"

Answer: Aim has been changed in accordance with proposed phrase by Professor Salimon: "*Aim of the thesis research was to investigate scientific foundations for the development of modification protocols of the SWCNT thin films (to be applied in transparent conducting films and as supercapacitors), establish influence of electrochemical treatment on SWCNT structure and filling efficiency, and study obtained materials properties.*"

Comment 2: Page 14 «weight of the composite material» - may be density?
Answer: One of the most important characteristics of the supercapacitors is the gravimetric capacitance (capacitance of the material related to the mass of the material). Therefore, we were mostly addressing weight of the composites, but not density.

Comment 3: Page 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.
Answer: I would like to clarify this ambiguous and challenging point. There are two main approaches for SWCNT filling, namely *in-situ* and *ex-situ*. In its order *ex-situ* approach could be subdivided into different methods, including filling *via* gas phase, filling with melts and filling with solutions. Gas-phase filling and filling with melts have an advantage of the high filling efficiency, however the materials to be inserted using these methods are limited. They should exhibit stability at high temperatures, high vapour pressure (for gas filling method) or moderate melt surface tension not exceeding 130-170 mN m^{-1} (for filling with melts). On the other hand, solution-filling method implies using solvents for promotion of SWCNT channel wetting resulting into the filling with desired initially dissolved agent. The advantage of the solution filling approach is the versatility of the possible filler agents, while the main drawback is the low filling efficiency. To highlight the relation of this disadvantage particularly to the solution filling method but not all the ex-situ methods, the sentence have been changed in the thesis: "*The main disadvantage of the solution filling method is the low filling efficiency [2].*"

Comment 4: Page 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.
Answer: The sentence has been rephrased as follows: "*For the evaluation of the functional composition of the SWCNT/PANI composites we utilized samples obtained through 70 potential sweep cycles of PANI electrodeposition.*"

Comment 5: Page 31 "(R_{90}) are quality defining parameters for transparent conductors, we monitored their variations with the" – qualitatively defining?
Answer: The sentence has been rephrased into: "*Since transmittance in visible spectrum, particularly at 550 nm, and equivalent sheet resistance (R_{90}) are parameters defining quality of transparent conductors, we monitored their variations with the change in the treatment temperature.*"

Comment 6: Page 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.
Answer: The doping effect is strong enough to shift the Fermi level far enough, so that higher energy M_{11} transition vanishes, supporting the idea that S_{22} transition undergoes vanishing coupled with the simultaneous appearance of the intersuubband plasmon peak at the close to S_{22} wavelengths. The sentence has been rephrased to emphasize the difference of origin of S_{22} and intersubband plasmon peak, even though they are located at close wavelengths. "Such doping effect is manifested in the UV-Vis-NIR transmittance spectra (Figure 4b), leading to the removal of S_{11}, S_{22}, and M_{11} peaks and the appearance of a new peak located at the wavelength close to that of the initial S_{22} peak. It corresponds to the nanotubes' intersubband plasmon appearing when the excitonic levels are fully saturated with charge carriers [114,135]."

Comment 7: Page 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.
Answer: Absorbance is a characteristic of the material and it is widely used for the evaluation of the structural destruction. It is exactly what we were addressing in the thermal opening method evaluation. While the transmittance is a parameter of interest for transparent conductive films. Therefore, where we discuss the doping effect on the optical properties we use the transmittance value.

Comment 8: Page 34 "Although at 400 ºC 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.
Answer: The sentence was rephrased into: "*Although at 500 ºC higher transmittance should have improved R_{90}, this effect is negated by a significant sheet resistance jump.*"

Comment 9: Page 35 "Gold nanoparticles decorate the outer surface of SWCNTs, forming via spontaneous reduction of [AuCl4] anions." -> Gold nanoparticles formed via spontaneous reduction of [AuCl4]- anions decorate the outer surface of SWCNTs."

Answer: The sentence has been changed in a way proposed by the Professor Salimon.

Comment 10: Page 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?

Answer: I want to thank Professor Salimon for the feedback on the inaccuracy in the sentence. The reference to the figure was to highlight the presents of the Au nanoparticles on the surface of the material, so that the reference to the TEM image was shifted to the end of the sentence.

Comment 11: Pages 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.

Answer: The analysis of the XPS data has been changed in accordance with the comment.

Comment 12: Pages 47-48 I appreciate methodologically sound efforts undertaken by authors to quantify the filling of SWCNTs. On the other hand, "at least 0.4 μm2" 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.

Answer: I would totally agree with the reasoning that the proper protocol of STEM images processing would contribute into the reliability of the results. However, the low contrast of the STEM images, coupled with significant amount of nanoparticles and ambiguously filled nanotubes significantly hinders the application of standard binarization, segmentation and differentiation process. Therefore, nanowires were counted and measured in manual mode. Molecular dynamics of SWCNTs filling were described briefly in the literature review, highlighting main inference that structural defects and functionalization tend to obstruct efficient flow of liquid into the SWCNT channel. The corresponding references were added into the text.

Comment 13: Page 61 The attempt to explain (actually to speculate) every little datum is not a robust approach.

Answer: The discussion in the described part of the thesis has been changed in accordance with the comment.

Comment 14: Page 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.

Answer: The Figure 24b contained mistake with current rate labels. It has been corrected to match the true experimental conditions. Author strongly believes that even though Figure 24b shows specific capacitance dependence on the current rate, while Figure 24c displays behaviour under bending the device, the Figure 24 should not be split into multiple. This Figure diversely explains charging-discharging features of testing two-electrode supercapacitor devise in a specific geometry: assembled on the PDMS substrate.

Comment 15: 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?

Answer: To compare two opening techniques in terms of filling efficiency, we applied the same filling approach after heating the sample at 350 ℃. The sample showed much more number of nanowires encapsulated inside of SWCNTs, although the mean length was the smallest when compared to the electrochemically treated samples. The length of Au nanowires per a unit f-SWCNT film area for thermally treated film reached value ~920 m cm^{-2}, exceeding values for electrochemically treated samples, except the one treated at UVP = 1.1 V *vs.* RHE. Therefore, we can conclude that electrochemical treatment is more preferable for the filling of SWCNT channels with solution method. Regarding the different atmospheres for opening of the SWCNT, I should note that most of these methods are known in the literature including thermal

treatment in the presence of CO_2, O_3 [8-10]. Addition of oxidative species in the solution for electrochemical treatment might be a promising approach for further investigation.

Comment 16: Do you expect better SC performance for your materials if electrolytes based on organic solvents (DNC) will be applied?
Answer: As shown in the literature SCs based on polyaniline can work in organic solvents (with 1 mol L^{-1} $LiClO_4$) [11]. However the specific capacitance in such solvent is smaller. It could be expected since the mechanism of the polyaniline conductivity is H^+-based. Therefore, the best results are usually observed in the acidic medium.

Comment 17: Please, discuss other potentially interesting fillers for SWCNTs after end-openings?
Answer: Promising fillers might include transition metals such as Fe, which may show electrocatalytic activity even when covered with the single layer of carbon shell as reported for core-shell type nanoparticles in literature [12]. Filling with metals could also find application in gas-sensors or nanoelectronics [13].

Response to the Dr. Dmitry Lyubchenko

Comment 1: I would recommend adding discussion of possible practical applications of final results of the thesis.
Answer: The correction according to the comment have been made.

Comment 2: The language needs to be checked and corrected.
Answer: The language was improved where the author was able to do it.

Comment 3: In the introduction section there are no references. Therefore, the question is: Are all the statements are well known?
Answer: The references have been added to the thesis file according to this comment.

Comment 4: Filling efficiency – more detailed explanation is needed.
Answer: In thesis, the filling efficiency was evaluated as the length of the encapsulated Au nanowires in the SWCNT channels in relation to the area of the film. Calculations of the filled SWCNT ratio is presented above as an answer to the comments.

Comment 5: I would recommend to add more discussion on diffusion mechanisms (p.37), what kind of diffusion, speed, etc. and what is the doping mechanism?
Answer: Diffusion mechanism evaluation would probably strongly contribute to the fundamental value of the thesis, however it was out of the scope of this research. It could be a promising and important topic for further research. The doping mechanism is based on the electron transfer between the SWCNTs and $[AuCl_4]^-$ ions. It results in the extraction of the electrons from the SWCNTs and theis charging with simultaneous $[AuCl_4]^-$ ions reduction into metallic gold. Such charging of SWCNTs cause the significant shift of the Fermi level and therefore results in the *p*-doping effect.

Comment 6: It is not clear for me what is the functionalization of SWCNTs, only doping or any other mechanisms are possible? The discussion is needed.
Answer: In the thesis, we describe different functionalization of the SWCNT films. First, during the heat treatment in the ambient air atmosphere or during electrochemical treatment we expect to observe the formation of covalent functionalization with oxygen containing functional groups. Second, adsorption doping with HAuCl4 can be considered as functionalization of the SWCNT surface. Third, electrodeposition of polyaniline on the surface of free-standing SWCNT film could be considered as the functionalization too, namely functionalization of the surface with the coating material.

Response to the Professor Oleg Tolochko

Comment 1: There are no XPS data for the heat treated samples. However, It may give an information about quantity and evolution of the functional groups under the heating in air as well as under doping with Au.

Answer: I totally agree that XPS data of the heat-treated SWCNT films would contribute to the understanding of the SWCNT structure and functional composition evolution during the treatment. However, we used combination of UV-Vis-NIR and Raman spectroscopies coupled with sheet resistance measurements that allowed us to evaluate structural changes during the treatment with sufficient reliability.

Comment 2: To my opinion, it is very important to show sheet resistance of the SWCNT films heat treated at different temperatures, but not only the equivalent one as shown in Fig.2, Fig.4a.
Answer: The data of sheet resistance of the SWCNT films heat-treated at different temperatures was added to the thesis – Table A4.

Comment 3: Authors mentioned that typically, blue shifts of the G-mode peak and 2D-mode positions are attributed to the p-doping (Fig.5). Nevertheless, the doping and strain are the most competing factors influencing the the position of G band and it FWHM (full wigth half maximim). Generally the doping has strong effects resulting in the blueshift of the G peak position and the decrease of FWHM for both electron and hole doping [M. Bruna, A.K. Ott, M. Ijas, D. Yoon, U. Sassi, A.C. Ferrari, ACS Nano 8 (7) (2014) 7432–7441]. Please, pay attention that FWHM visually increase in the Fig.5.
Answer: I would like to thank Professor Tolochko for the valuable comment regarding G-mode peak shape in the Raman spectra of doped SWCNT films. We have not evaluated the influence of doping on the FWHM of G-mode in Raman spectra. I could assume that the broadening happens in the result of the coverage of SWCNT surface with the doping molecules, although the particular reason requires futher investigation. It might be an promising issue for the further research.

Comment 4: As seen from Fig.2 the transmittance of the SWCNT films treated at temperatures over 350 ⁰C increases in a great extension, but the reason for this phenomenon is not discussed clearly in the text. There are two competitive processes may occur under heating, such as: desorption of the oxygen and moisture and oxidation of the carbon. To clarify the point some additional observations and discussions would be very helpful.
Answer: I totally agree with this comment. At the same time I could say that the desorption of adsorbed species completely happens at the temperature ~350 ⁰C, that stems from the Figure 1b. Therefore, the transmittance increase should be mostly attributed to the carbon oxidation and probably to the oxidation of the residual catalytic nanoparticles. The corresponding changes were introduced into the thesis.

Comment 5: Fig.5, b shows G band change during heat treatment, the shape of the pristine nanotubes G peak looks asymmetrical, which is not corresponded to Fig.5, a, where the whole Raman spectrum is presented. Aslo in the Fig. 5 the change of band D during doping and heat treatment is not shown and does not discussed in the text.
Answer: Raman spectra of pristine SWCNT film at Figures 5a and 5b are identical. They possess some order of asymmetry as typical for SWCNTs. The D-mode of Raman spectra is practically insensitive for adsorption doping, therefore its changes are negligible, and are out of interest for doping efficiency evaluation.

Comment 6: Author says that doping effect (Figure 4b), leads to the appearance of a new peak that corresponds to the nanotubes' intersubband plasmon appearing when the excitonic levels are fully saturated with charge carriers, those data prove that p-doping caused an efficient downshift of the Fermi level favored by HAuCl4 treatment. This statement may be confirmed by plasmon observation by XPS spectroscopy. For example, on XPS spectra for SWCNT-EH film treated at UVP = 1.3 V plasmon peak is negligible.
Answer: I appreciate Professor Tolochko for this comment, I do believe it requires consideration in the future research.

Response to the Dr. Puguang Ji

Comment 1: Nanotubes' opening and filling with gold wires is described with two different methods. Could the filling efficiency of heating and electrochemical opening methods be compared to each other?
Answer: We conducted additional experiment to compare two opening techniques in terms of the filling efficiency. The detailed discussion is presented as an answer to the comment above.

Response to the Dr. Yulia Ioni

Comment 1: There are no references in the literature review part (Introduction).
Answer: The references were added to the text according to the comment.

Comment 2: What is the filling efficiency estimated in the second chapter of the results and discussion? Could the filling efficiency be transferred into a value showing the filled nanotubes amount or fraction? Is it possible to determine the relationship between the number of nanorods and gold nanoparticles obtained with bilateral doping of single-walled carbon nanotubes?
Answer: In thesis, the filling efficiency was evaluated as the length of the encapsulated Au nanowires in the SWCNT channels in relation to the area of the film. Calculations of the filled SWCNT ratio is presented above as an answer to the comments.

Comment 3: What is the reason for the significant increase in transmittance value of single-walled carbon nanotube films upon the heating above 350°C?
Answer: The transmittance increase should be mostly attributed to the carbon oxidation and probably to the oxidation of the residual catalytic nanoparticles. The corresponding changes were introduced into the thesis.

Comment 4: The study shows that SWCNTs are acting as reducing agents in the chloroauric acid filling process. What by-products of this interaction were obtained and how were the resulting composites purified from them? Would not this also led to additional interaction with hydrogen chloride or chlorine, which could be released during the doping?
Answer: The mechanism of the SWCNT doping happens with the charge transfer between Au^{3+} atoms in chloroauric acid anions and SWCNTs. It results into the chlorine anions release and positive charging of SWCNTs. Then the neutralization of the SWCNT happens via interaction with Cl^- and $[AuCl_4]^-$ anions. The H^+ ions are also present in the doping solution formed due to chloroauric acid dissociation. Therefore, we should expect SWCNT surface covered with metallic gold nanoparticles, $[AuCl_4]^-$ anions, H^+ and Cl^- ions that could also form hydrogen chloride. The composites were not purified from the doping process products, but were investigated as after doping.

Comment 5: The thesis contains some inaccuracies that need to be corrected. So, in Fig. 13a, the photo of the sample SWCNT80 has the wrong designation (SWCNT95). Figure A13 (Appendix) is of low resolution and the color symbols and formulas are hard to read. In Fig. A21, there is no point corresponding to the specific power value for the SWCNT80/PANI60 sample, when the point is doubled for the SWCNT80/PANI50 sample. In Fig. A1 (Appendix), all components of the device described in the text should be signed.
Answer: I appreciated Dr. Ioni for this comment, highlighting issues with figures in the thesis. The illustrations described in the comment were corrected accordingly in the thesis file. In Fig. A21 specific power value for the SWCNT80/PANI60 is the same as for SWCNT80/PANI50, so that they overlap and one is not clearly visible under another.

Comment 6: The abbreviation UVP is explained in the Abstract (p. 3), the list of Abbreviations (p. 10) and again in the Introduction on p. 13.
Answer: The UVP abbreviation explanation was removed from page 13. However, it was left on the page 3 as the first mentioning in the text and in the list of abbreviations to follow formal requirements.

References
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