engineering proceedings

Proceeding Paper

Gallium Selenide, and Rubidium Iodide Filling of Single-Walled Carbon Nanotubes as p, and n-Dopant Chemical Compounds †

Marianna V. Kharlamova [1,2]

[1] Centre for Advanced Materials Application (CEMEA), Slovak Academy of Sciences, Dúbravská Cesta 5807/9, 845 11 Bratislava, Slovakia; mv.kharlamova@gmail.com or dr.marianna.kharlamova@gmail.com
[2] Moscow Institute of Physics and Technology, 9 Institutskiy per., 141700 Dolgoprudny, Russia

† Presented at the 2nd International Electronic Conference on Processes: Process Engineering—Current State and Future Trends (ECP 2023), 17–31 May 2023; Available online: https://ecp2023.sciforum.net/.

Abstract: I filled the single-walled carbon nanotubes (SWCNTs) with gallium selenide (GaSe), and rubidium iodide (RbI) as p, and n-dopant chemical compounds. The filling was confirmed by high-resolution transmission electron microscopy. I investigated the electronic properties by Raman spectroscopy, optical absorption spectroscopy, near edge X-ray absorption fine structure spectroscopy, and X-ray photoelectron spectroscopy. I proved the p-doping of SWCNTs by the introduced GaSe. The data featured the n-doping of carbon nanotubes in RbI-filled SWCNTs.

Keywords: gallium selenide; rubidium iodide; carbon nanotubes; electronic properties; doping; Raman spectroscopy; optical absorption spectroscopy; near edge X-ray absorption fine structure spectroscopy; and X-ray photoelectron spectroscopy

Citation: Kharlamova, M.V. Gallium Selenide, and Rubidium Iodide Filling of Single-Walled Carbon Nanotubes as p, and n-Dopant Chemical Compounds. *Eng. Proc.* **2023**, *37*, x. https://doi.org/10.3390/xxxxx

Published: 17 May 2023

1. Introduction

The interest to single-walled carbon nanotubes led to many interesting applications, such as nanoelectronics, thermoelectric power generation devices, optoelectronics, biomedicine, sensors, catalysis, electrochemical energy storage devices. The filled SWCNTs are promising components of these devices. An approach to tailor the properties of SWCNTs by filling was started in our works [1–8]. After that the SWCNTs were filled with chalcogenides, halogenides of metals, and the modified properties were studied by Raman spectroscopy, optical absorption spectroscopy, X-ray absorption spectroscopy, and photoemission spectroscopy. It was shown that electron donors, and electron acceptors modify the properties of SWCNTs [9–21]. Modifications of spectra are changes in peak positions, and profiles of bands, appearance of new peaks [22]. The methods of filling of SWCNTs were developed to fill SWCNTs with large ratios. Among them are liquid phase methods of filling with metals, melt method of filling with metal halogenides, gas method of filling with molecules. It is difficult to fill metal chalcogenides inside SWCNTs in a single step process, because they have large melting points. In this work, I fill the SWCNTs with gallium selenide by the single-step process. The melting point of GaSe is 960 °C, and this is a unique case of filling of high melting compound in SWCNTs by the melt method. I investigate the electronic properties of filled SWCNTs by spectroscopic techniques to study the influence of encapsulated compound on SWCNTs.

The filler inside SWCNTs leads to electron donor, or electron acceptor doping effect. There are many compounds that were encapsulated inside SWCNTs. Among them are metal halogenides, metal chalcogenides, metals. The influence of substances on the electronic properties of SWCNTs is determined by its work function (WF). There are three cases. If the work function of substance is larger than the WF of SWCNTs, the p-doping of carbon nanotubes is observed. If the work function of substance is smaller than the WF of SWCNTs, the n-doping of SWCNTs occurs. If the work function of substance equals the WF of SWCNTs, no modification of the electronic properties is observed [22]. Typical donors of electrons are metals with the WF that is significantly smaller than the WF of SWCNTs. Molecules can also lead to donor doping of SWCNTs. Among metal halogenides, rubidium iodide has smaller WF than the value of SWCNTs. It is expected to have n-doping effect on SWCNTs. The filling of SWCNTs with rubidium iodide is convenient way of n-doping of SWCNTs. This is caused by several reasons. Firstly, the filling of SWCNTs with RbI is made by single-step melt method, which is simple, and it leads to clean samples. Secondly, RbI has low melting point, which simplifies the combinations of synthesis, and integration processes at lab, and industrial scale. Thirdly, RbI has very low WF (about 1 eV lower than the value of SWCNTs). This can result in very large modifications of Fermi level of SWCNTs. The downshift of several hundreds of meV is expected [22].

2. Experimental

I put the SWCNTs and GaSe in a quartz ampoule, seal it under vacuum, and heat to temperature of 1060 °C, which is higher by 100 °C than melting point of GaSe. The SWCNTs were pre-opened by annealing in air at 500 °C for 30 min. The diameter of SWCNTs is 1.4 nm. The quartz ampoule was cooled down to room temperature to crystallize the compound inside SWCNTs. RbI was placed inside quartz ampoule where SWCNTs were located. The system was maintained at temperature that is 100 °C higher than the melting point of RbI ($T_{melting}$(RbI) = 656 °C). The samples were cooled slowly to room temperature. The electronic properties of SWCNTs filled with GaSe, and RbI were investigated by Raman spectroscopy, optical absorption spectroscopy, near edge X-ray absorption fine structure spectroscopy (NEXAFS), and photoemission spectroscopy (X-ray photoelectron spectroscopy, XPS).

3. Results

It was found that GaSe is filled inside SWCNTs. Figure 1 shows the high resolution transmission electron microscopy (HRTEM) image of GaSe-filled SWCNT bundle. It is visible that the channels of carbon nanotubes are filled. The homogenous filling of carbon nanotubes is confirmed. The filling materials is recognized inside the inner cavities of carbon nanotubes.

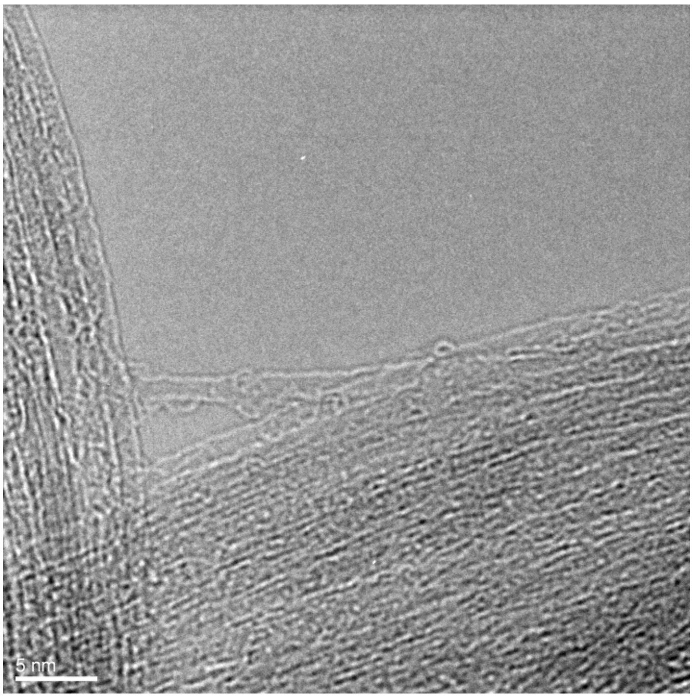

Figure 1. The HRTEM image of bundle of GaSe-filled SWCNTs.

Figure 2 presents the HRTEM image of individual filled SWCNTs. In this image, one can see the two filled SWCNTs in the bottom. It is visible that there is the filler within the walls of carbon nanotubes. For comparison, the two unfilled SWCNTs are visible in the middle of the image. It is visible that the space inside the channels is not filled. Thus, it is obvious that GaSe is filled inside SWCNTs.

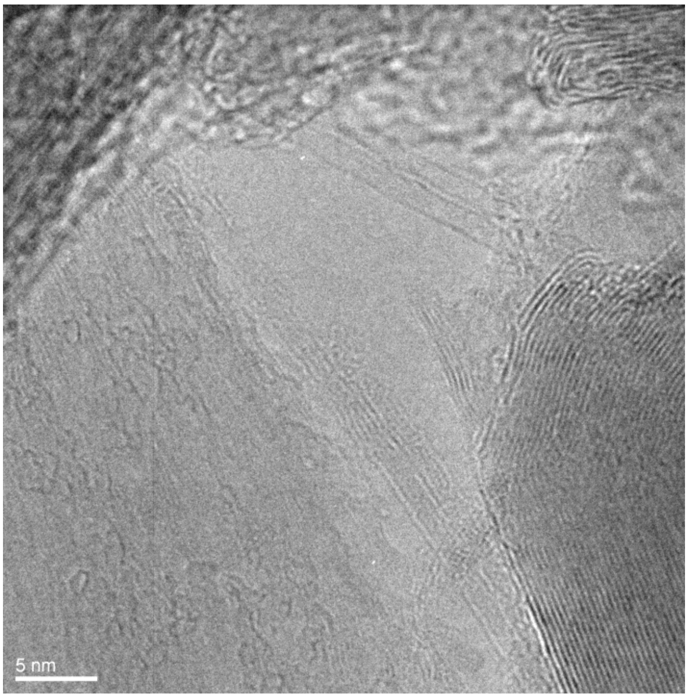

Figure 2. The HRTEM image of individual GaSe-filled SWCNTs.

Here, I show the HRTEM data of RbI-filled SWCNTs. Figure 3 shows the low-magnification image of the filled SWCNTs. It is visible that there are encapsulated materials in channels of carbon nanotubes. They are filled throughout the sample. White contrast lines correspond to filler within SWCNTs.

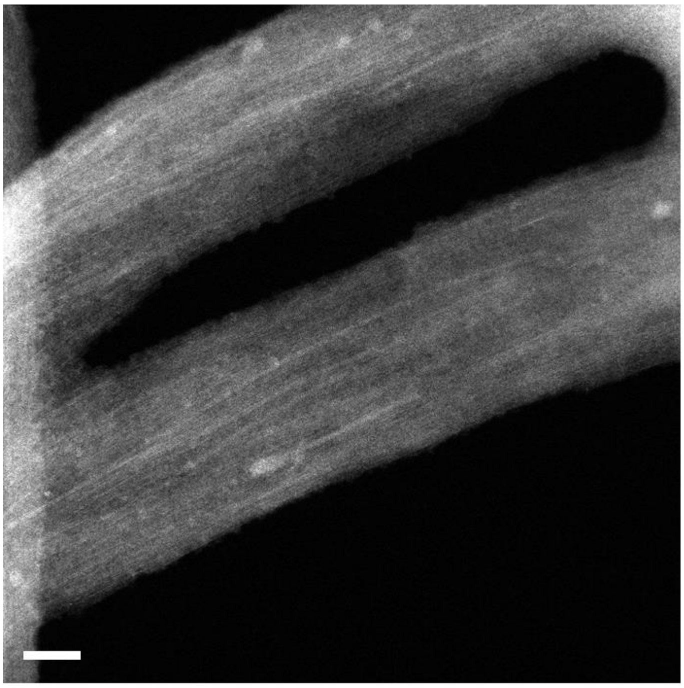

Figure 3. The HRTEM image of bundles of RbI-filled SWCNTs.

Figure 4 presents the high-magnification image of filled SWCNTs. The atoms of introduced salt are visible inside carbon nanotubes. The atoms are white dots. They are located in two columns, and atoms in columns are periodically positioned. There are pairs of atoms that are symmetrically located within the SWCNTs. The walls of SWCNTs are also visible, and it is obvious that the diameter of atomically-thick crystals is smaller than the diameter of SWCNTs. The crystals inside SWCNTs have cubic structure, as in the case of bulk compound [23].

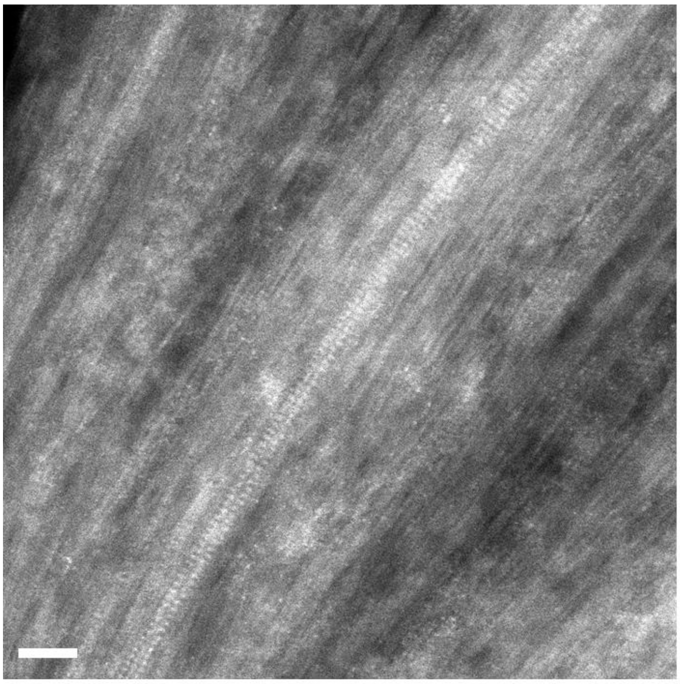

Figure 4. The HRTEM image of individual RbI-filled SWCNTs.

The data of Raman spectroscopy shows that GaSe has an electron acceptor effect on SWCNTs (Figure 5a). The NEXAFS shows no formation of chemical bonds between SWCNTs and GaSe. The data of XPS shows the shift by 0.28 eV to lower binding energies. This testifies about the p-doping of SWCNTs by the introduced compound. The electronic properties of SWCNTs filled with RbI were investigated by Raman spectroscopy, and X-ray photoelectron spectroscopy. It was shown that RbI has n-doping effect on SWCNTs (Figure 5b). This is a unique case of n-doping of SWCNTs by metal halogenide, and the success of this experiment opens new ways to applications of filled SWCNTs in nanoelectronics, including p-n transitions with similar morphology, and atomic structure compounds, and simple preparation methods, integration routes, cleaning procedures, manipulation in devices. This filling is very important achievement, which opens new chapter in applications of filled SWCNTs, because it gives lots of information on chemical, and physical properties.

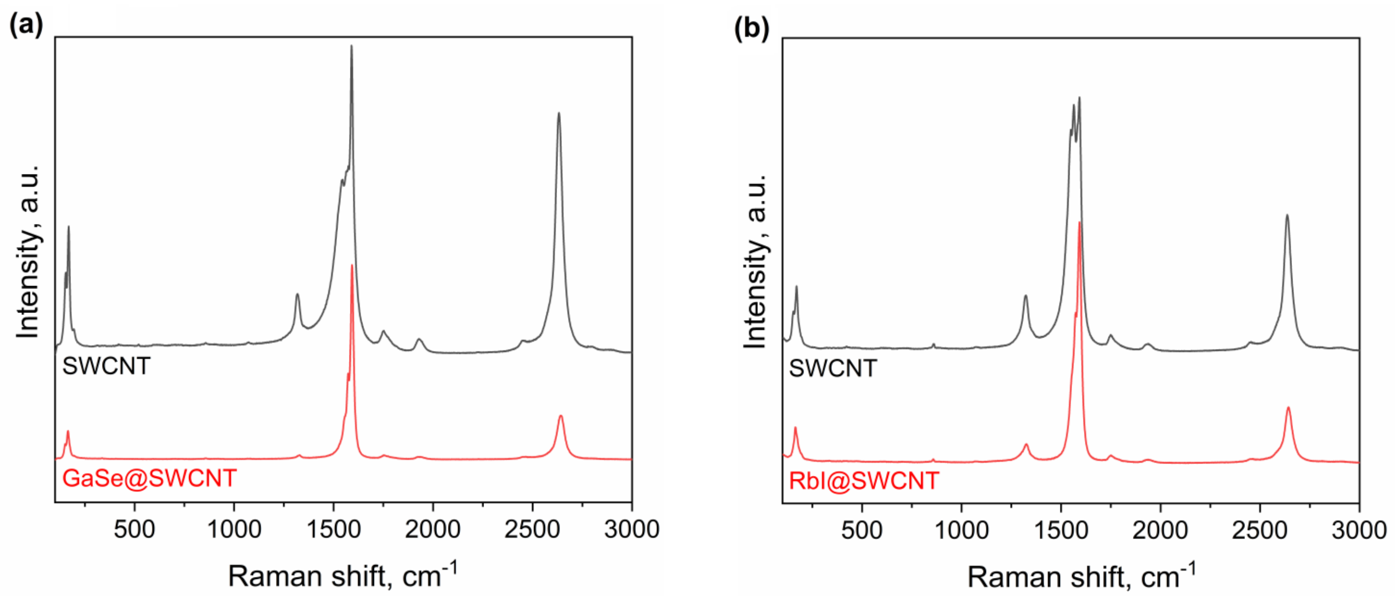

Figure 5. The Raman spectra of GaSe-filled SWCNTs (**a**), and RbI-filled SWCNTs (**b**).

4. Conclusions

In this work, I filled SWCNTs with GaSe, and investigated the electronic properties by spectroscopic techniques. The HRTEM data proved the filling of SWCNTs, and the data of four spectroscopic methods confirmed the p-doping of SWCNTs by encapsulated GaSe. I filled SWCNTs with RbI by the melt method. I investigated the atomic structure of filled SWCNTs by HRTEM. It was shown that the channels of SWCNTs are filled. The electronic properties of filled SWCNTs were investigated by Raman spectroscopy, and X-ray photoelectron spectroscopy. The introduced compound leads to n-doping of SWCNTs. This leads to easy preparation, integration, and applications of RbI-filled devices.

Author Contributions: The manuscript is written solely by M.V.K.

Funding: These studies were partly performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by Research & Innovation Operational Programme funded by the ERDF.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kharlamova, M.V.; Kramberger, C.; Saito, T.; Sato, Y.; Suenaga, K.; Pichler, T.; Shiozawa, H. Chirality-dependent growth of single-wall carbon nanotubes as revealed inside nano-test tubes. *Nanoscale* **2017**, *9*, 7998–8006. https://doi.org/10.1039/c7nr01846k.
2. Kharlamova, M.V.; Kramberger, C.; Sato, Y.; Saito, T.; Suenaga, K.; Pichler, T.; Shiozawa, H. Chiral vector and metal cata-lyst-dependent growth kinetics of single-wall carbon nanotubes. *Carbon* **2018**, *133*, 283–292.
3. Burdanova, M.G.; Kharlamova, M.V.; Kramberger, C.; Nikitin, M.P. Applications of Pristine and Functionalized Carbon Nanotubes, Graphene, and Graphene Nanoribbons in Biomedicine. *Nanomaterials* **2021**, *11*, 3020. https://doi.org/10.3390/nano11113020.
4. Kharlamova, M.V.; Brzhezinskay, M.M.; Vinogradov, A.S.; Suzdalev, I.P.; Maksimov, Y.V.; Imshennik, V.K.; Novichikhin, S.V.; Krestinin, A.V.; Yashina, L.V.; Lukashin, A.V.; et al. The formation and properties of one-dimensional FeHal2 (Hal = Cl, Br, I) nanocrystals in channels of single-walled carbon nanotubes. *Nanotechnol. Russ.* **2009**, *4*, 634–646. https://doi.org/10.1134/s1995078009090080.
5. Kharlamova, M.V.; Mochalin, V.N.; Lukatskaya, M.R.; Niu, J.; Presser, V.; Mikhalovsky, S.; Gogotsi, Y. Adsorption of proteins in channels of carbon nanotubes: Effect of surface chemistry. *Mater. Express* **2013**, *3*, 1–10. https://doi.org/10.1166/mex.2013.1102.
6. Kharlamova, M.V.; Kramberger, C.; Domanov, O.; Mittelberger, A.; Yanagi, K.; Pichler, T.; Eder, D. Fermi level engineering of metallicity-sorted metallic single-walled carbon nanotubes by encapsulation of few-atom-thick crystals of silver chloride. *J. Mater. Sci.* **2018**, *53*, 13018–13029. https://doi.org/10.1007/s10853-018-2575-y.
7. Kharlamova, M.V.; Kramberger, C. Applications of Filled Single-Walled Carbon Nanotubes: Progress, Challenges, and Perspectives. *Nanomaterials* **2021**, *11*, 2863. https://doi.org/10.3390/nano11112863.
8. Kharlamova, M.V. Comparative analysis of electronic properties of tin, gallium, and bismuth chalcogenide-filled single-walled carbon nanotubes. *J. Mater. Sci.* **2014**, *49*, 8402–8411. https://doi.org/10.1007/s10853-014-8550-3.
9. Kharlamova, M.V. Novel approach to tailoring the electronic properties of single-walled carbon nanotubes by the encapsulation of high-melting gallium selenide using a single-step process. *JETP Lett.* **2013**, *98*, 272–277. https://doi.org/10.1134/s0021364013180069.
10. Kharlamova, M.V.; Eliseev, A.A.; Yashina, L.V.; Petukhov, D.I.; Liu, C.-P.; Wang, C.-Y.; Semenenko, D.A.; Belogorokhov, A.I. Study of the electronic structure of single-walled carbon nanotubes filled with cobalt bromide. *JETP Lett.* **2010**, *91*, 196–200. https://doi.org/10.1134/s0021364010040089.
11. Kharlamova, M.V.; Yashina, L.V.; Eliseev, A.A.; Volykhov, A.A.; Neudachina, V.S.; Brzhezinskaya, M.M.; Zyubina, T.S.; Lukashin, A.V.; Tretyakov, Y.D. Single-walled carbon nanotubes filled with nickel halogenides: Atomic structure and doping effect. *Phys. Status Solidi B* **2012**, *249*, 2328–2332. https://doi.org/10.1002/pssb.201200060.
12. Kharlamova, M.V. Raman Spectroscopy Study of the Doping Effect of the Encapsulated Iron, Cobalt, and Nickel Bromides on Single-Walled Carbon Nanotubes. *J. Spectrosc.* **2015**, *2015*, 1–8. https://doi.org/10.1155/2015/653848.

13. Kharlamova, M.V. Electronic properties of single-walled carbon nanotubes filled with manganese halogenides. *Appl. Phys. A* **2016**, *122*, 791. https://doi.org/10.1007/s00339-016-0335-x.
14. Kharlamova, M.V.; Yashina, L.V.; Volykhov, A.A.; Niu, J.J.; Neudachina, V.S.; Brzhezinskaya, M.M.; Zyubina, T.S.; Belogorokhov, A.I.; Eliseev, A.A. Acceptor doping of single-walled carbon nanotubes by encapsulation of zinc halogenides. *Eur. Phys. J. B* **2012**, *85*, 34. https://doi.org/10.1140/epjb/e2011-20457-6.
15. Kharlamova, M. Comparison of influence of incorporated 3d-, 4d- and 4f-metal chlorides on electronic properties of sin-gle-walled carbon nanotubes. *Appl. Phys. A* **2013**, *111*, 725–731.
16. Kharlamova, M.V.; Yashina, L.V.; Lukashin, A.V. Charge transfer in single-walled carbon nanotubes filled with cadmium halogenides. *J. Mater. Sci.* **2013**, *48*, 8412–8419. https://doi.org/10.1007/s10853-013-7653-6.
17. Kharlamova, M.V.; Kramberger, C.; Pichler, T. Semiconducting response in single-walled carbon nanotubes filled with cadmium chloride. *Phys. Status Solidi B* **2016**, *253*, 2433–2439. https://doi.org/10.1002/pssb.201600300.
18. Kharlamova, M.V.; Kramberger, C.; Mittelberger, A.; Yanagi, K.; Pichler, T.; Eder, D. Silver Chloride Encapsulation-Induced Modifications of Raman Modes of Metallicity-Sorted Semiconducting Single-Walled Carbon Nanotubes. *J. Spectrosc.* **2018**, *2018*, 5987428. https://doi.org/10.1155/2018/5987428.
19. Kharlamova, M.V.; Kramberger, C.; Domanov, O.; Mittelberger, A.; Saito, T.; Yanagi, K.; Pichler, T.; Eder, D. Comparison of Doping Levels of Single-Walled Carbon Nanotubes Synthesized by Arc-Discharge and Chemical Vapor Deposition Methods by Encapsulated Silver Chloride. *Phys. Status Solidi B* **2018**, *255*, 1800178. https://doi.org/10.1002/pssb.201800178.
20. Kharlamova, M.; Kramberger, C. Phemenology of Filling, Investigation of Growth Kinetics and Electronic Properties for Applications of Filled Single-Walled Carbon Nanotubes. *Nanomaterials* **2023**, *13*, 314.
21. Kharlamova, M.V.; Volykhov, A.A.; Yashina, L.V.; Egorov, A.V.; Lukashin, A.V. Experimental and theoretical studies on the electronic properties of praseodymium chloride-filled single-walled carbon nanotubes. *J. Mater. Sci.* **2015**, *50*, 5419–5430. https://doi.org/10.1007/s10853-015-9086-x.
22. Kharlamova, M.V.; Kramberger, C. Spectroscopy of Filled Single-Walled Carbon Nanotubes. *Nanomaterials* **2022**, *12*, 42. https://doi.org/10.3390/nano12010042.