proceedings

MDPI

Proceedings

Sorting of nickelocene-filled single-walled carbon nanotubes by density gradient centrifugation by conductivity type†

Marianna V. Kharlamova [1,2,*], Christian Kramberger [3] and Dominik Eder [2]

[1] Moscow Institute of Physics and Technology, Institutskii pereulok 9, 141700 Dolgoprudny, Russia; mv.kharlamova@gmail.com
[2] Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/BC/2, 1060 Vienna, Austria; dominik.eder@tuwien.ac.at
[3] Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria; christian.kramberger-kaplan@univie.ac.at
* Correspondence: mv.kharlamova@gmail.com

† Presented at the 2nd International Electronic Conference on Applied Sciences, October, 15-30, 2021.

Abstract: Applications of single-walled carbon nanotubes (SWCNTs) require the nanotube samples with uniform properties. The filling of SWCNTs is a promising method of tailoring their properties. Other way to obtain the samples with homogeneous properties is to perform the separation of filled nanotubes by conductivity type. In this work, we performed the sorting of nickelocene-filled SWCNTs by density gradient centrifugation to metallic and semiconducting fractions. The obtained samples were characterized by optical absorption spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. The investigation showed that the samples have homogenous properties, high quality and high purity. The encapsulated nickelocene has n-doping effect on metallic and semiconducting SWCNTs. The samples were annealed in vacuum at 360-1200°C to grow inner tubes inside SWCNTs, and the electronic properties of these samples were investigated. The annealing of nickelocene-filled SWCNTs leads to decomposition of molecules with the formation of nickel carbides and pure nickel inside double-walled carbon nanotubes (DWCNTs). It was shown that annealing of nickelocene-filled SWCNTs at 360-600°C leads to n-doping of SWCNTs, whereas annealing at 800-1200°C results in p-doping of SWCNTs.

Keywords: single-walled carbon nanotube; double-walled carbon nanotube; filling; sorting; electronic properties; electron acceptor; electron donor

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Proceedings* **2021**, 68, x. https://doi.org/10.3390/xxxxx

Published: date

1. Introduction

Single-walled carbon nanotubes (SWCNTs) attract attention of the research community thanks to their unique electronic, electrical, optical, mechanical and chemical properties. Their physical properties are dependent on their atomic structure, and all synthesized nanotubes contain mixtures of nanotubes with different physical and chemical properties. To resolve this problem, chemical modification methods were established to prepare the samples of nanotubes with homogenous properties. The filling of SWCNTs is a promising method of modification of their electronic properties [1]. The filling of SWCNTs allows obtaining the nanotube samples, which are endohedrally functionalized with appropriate substances with required physical and chemical properties [2-4]. Such samples can be applied in various fields, where the nanotubes with tailored properties are required.

Besides chemical modification methods, the approaches for sorting of SWCNTs were established. For instance, density gradient ultracentrifugation is a technique that allow separation of the nanotubes by conductivity type and even the chirality [5].

In this work, we combine two methods (filling and sorting), and perform two-step procedure to obtain ultra-pure chemically modified SWCNTs. At first step, we perform the filling of SWCNTs with nickelocene powder, and at the second step, we perform the density gradient ultracentrifugation of the filled nanotubes.

2. Experimental

For the filling of SWCNTs, we sealed the 1.67 nm-diameter SWCNTs and nickelocene powder in the ampoule under high vacuum. We heated half of ampoule at 50ºC until all nickelocene was evaporated and then flip the ampoule to let other half of ampoule to be heated. We performed this procedure for 5-10 times during 5 days. The filled SWCNTs underwent the separation procedure, as described in Ref. [6]. As a result, the samples of nickelocene-filled semiconducting and metallic SWCNTs were obtained. The filled and separated SWCNTs were annealed at temperatures of 360-1200°C for 2 h in high vacuum.

The samples were investigated by optical absorption spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Optical absorption spectra were recorded at UV-3600 Shimazu Co. spectrometer. Raman spectra were recorded at Horiba Jobin Yvon LABRAM HR800 spectrometer. The XPS spectra were recorded at VG Scienta XPS spectrometer.

3. Results and Discussion

The optical absorption spectroscopy confirms the purity of the samples of semiconducting and metallic filled SWCNTs. The spectra contain the peaks of corresponding nanotube fractions, and testify to ~99% purity.

The Ni 2p XPS spectra of the separated filled SWCNTs include the peaks of nickel. The annealing of the filled SWCNTs leads to decrease in the intensity of the peaks of nickel. This corresponds to the evaporation of nickel from the sample. The sample annealed at 1200°C does not contain any nickel. The C 1s spectra of the filled semiconducting and metallic SWCNTs is shifted to higher binding energies upon annealing at temperatures of 360-600°C. This testifies that nickel carbides and pure nickel that are formed as a result of decomposition of nickelocene act as electron donors. The annealing of the separated filled SWCNTs at temperatures of 800-1200°C leads to downshift of the C 1s XPS peak. This means that the evaporation of nickel carbides and nickel as well as the formation of double-walled carbon nanotubes (DWCNTs) leads to p-doping of SWCNTs. Thus, there are three overlapping processes that influence the electronic properties of SWCNTs: (i) decomposition of nickelocene to nickel carbides and pure nickel, (ii) evaporation of nickel carbides and pure nickel, (iii) growth of DWCNTs. As a result, the annealing of the separated filled SWCNTs at 360-600°C results in n-doping of SWCNTs, and the annealing of the samples at 800-1200°C leads to p-doping of SWCNTs.

4. Conclusions

The separation of filled SWCNTs by density gradient ultracentrifugation to semiconducting and metallic fractions allowed obtaining ultra-pure nanotube samples, which allowed in-depth investigation of their electronic properties. The processes of decomposition of nickelocene, evaporation of nickel as well as the growth of DWCNTs were disentangled. It was shown that the annealing of highly pure filled SWCNTs at 360-600°C leads to n-doping of SWCNTs, and the annealing of the samples at 800-1200°C results in p-doping of SWCNTs. This process can be performed at an industrial scale and, thus, allow tailoring the properties of SWCNTs for demanded applications.

Author Contributions: M.K. performed the filling of SWCNTs and their investigations. C.K. assisted in optical absorption spectroscopy and Raman spectroscopy measurements of the samples. D.E. supervised the work.

Funding: M.K. acknowledges Moscow Institute of Physics and Technology for a postdoc fellowship.

Acknowledgments: We acknowledge Prof. Kazuhiro Yanagi (Tokyo Metropolitan University, Japan) for assisting in the density gradient ultracentrifugation procedures. We also thank Dr. Markus Sauer (University of Vienna, Austria) for assisting in the XPS measurements. We also acknowledge Prof. Thomas Pichler (University of Vienna, Austria) for providing access to the XPS spectrometer. We also thank Prof. Takeshi Saito (National Institute of Advanced Industrial Science and Technology, Japan) for providing the nanotubes.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Kharlamova, M.V. Advances in tailoring the electronic properties of single-walled carbon nanotubes. *Prog. Mater. Sci.* **2016**, 77, 125-211.
2. 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(1), 34.
3. 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(24), 8412-8419.
4. Kharlamova, M.V., Sauer, M., Saito, T., Sato, Y., Suenaga, K., Pichler, T., Shiozawa H. Doping of single-walled carbon nanotubes controlled via chemical transformation of encapsulated nickelocene. *Nanoscale* **2015**, 7(4), 1383-1391
5. Arnold, M.S., Green, A.A., Hulvat, J.F., Stupp, S.I., Hersam,M.C. Sorting carbon nanotubes by electronic structure using density differentiation. *Nature Nanotechnol.* **2006**, 1, 60-65.
6. Kharlamova, M.V., Kramberger, C., Yanagi, K., Sauer, M., Saito, T. Pichler, T. Separation of Nickelocene-Filled Single-Walled Carbon Nanotubes by Conductivity Type and Diameter. *Phys. Status Sol. B* **2017**, 254(11), 1700178.