proceedings

Extended Abstract

Tuning the Electronic Properties of Single-Walled Carbon Nanotubes by Filling with Electron Donor and Acceptor Compounds †

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

1 Moscow Institute of Physics and Technology (State University), Institutskii pereulok 9, 141700 Dolgoprudny, Russia
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 Online-Conference on Nanomaterials, 15–30 November 2020; Available online: https://iocn2020.sciforum.net/.

Published: 15 November 2020

Abstract: The endohedral chemical functionalization of single-walled carbon nanotubes (SWCNTs) allows tuning their electronic properties toward applications. It was demonstrated that the SWCNTs can be filled with elementary substances, chemical compounds and molecules. It this work, we performed the filling of SWCNTs with metal halogenide (cobalt iodide, CoI_2) and metal carbide (nickel carbide, Ni_3C). The filling of SWCNTs with CoI_2 was conducted by the melt method. The filling of SWCNTs with Ni_3C was performed by the thermal treatment of nickelocene-filled nanotubes. The filled SWCNTs were investigated by the high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The HRTEM data prove the encapsulation of compounds inside the SWCNTs. By combining the Raman spectroscopy and XPS data, it was shown that the encapsulated CoI_2 causes *p*-doping of nanotubes accompanied by the downshift of the Fermi level of nanotubes. The embedded Ni_3C leads to *n*-doping of SWCNTs with upshifting of the Fermi level of nanotubes. The obtained results allow applying the filled SWCNTs in the range of fields such as nanoelectronics, energy storage, sensors, catalysis and biomedicine.

Keywords: single-walled carbon nanotubes; filling; doping; electronic properties; metal carbide; metal halogenide

1. Introduction

The filled single-walled carbon nanotubes (SWCNTs) attract ever increasing attention of the research community due to their extraordinary physical and chemical properties. Tuning the electronic properties of SWCNTs by filling with electron donor and acceptor compounds opens the way for application of the filled nanotubes in various fields, such as nanoelectronics, energy storage, sensors and nanomedicine [1–3]. The filled SWCNTs have homogenous properties, including defined metallic or semiconducting conductivity type and electronic properties [4]. It was demonstrated that the SWCNTs can be filled with elementary substances, chemical compounds and molecules [4].

In our work, we chose electron acceptor - cobalt iodide (CoI_2) and electron donor - nickel carbide (Ni_3C) for the encapsulation inside SWCNTs and investigated the modification of the electronic properties of SWCNTs. The properties of filled SWCNTs were analyzed by the high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Materials and Methods

The filling of SWCNTs with CoI_2 was performed by the melt method. The 1.4 nm-diameter metallicity-mixed SWCNTs and CoI_2 were sealed inside a quartz ampoule under high vacuum, and it was heated in a tube furnace up to the temperature that exceeded the melting point of the salt by 100 °C (615 °C) and kept at this temperature for 10 h. Then, the ampoule was slowly cooled down to room temperature to obtain the homogeneous crystallization of the salt. The filling of SWCNTs with Ni_3C was performed by the two-step method. The 1.7 nm-diameter metallicity-mixed SWCNTs and nickelocene powder were sealed inside a quartz ampoule under high vacuum, and it was heated up to 50 °C and kept at this temperature for 5 days. Then, the ampoule was heated up to 250 °C and kept at this temperature for 2 h to convert nickelocene to nickel carbide.

3. Results

The HRTEM prove the filling of internal channels of SWCNTs with both compounds. In the case of CoI_2, one-dimensional nanocrystals of the salt were formed. For nickel carbide, the formation of ~1–2 nm-size nanoclusters was observed. The Raman spectroscopy data of the CoI_2-filled SWCNTs show the modifications of the radial breathing mode (RBM) and G-bands of SWCNTs. The RBM and G-bands of Raman spectra of the pristine and filled SWCNTs were fitted with individual components. The data show the shifts and changes in peak intensities in the RBM-band of the filled SWCNTs as compared to the pristine SWCNTs. This testified to changes in the electronic properties of SWCNTs due to doping accompanied by the charge transfer between the nanotubes and salt [5]. The Raman spectroscopy data of nickel carbide-filled SWCNTs do not show noticeable differences as compared to the pristine nanotubes. The XPS data of the CoI_2- and nickel carbide-filled SWCNTs show the down- and upshift of the C 1s XPS peak, respectively, as well as its broadening as compared to the pristine nanotubes. This was attributed to the down- and upshift of the Fermi level of SWCNTs, respectively [6]. By combining the Raman spectroscopy and XPS data, it was shown that the encapsulated CoI_2 and nickel carbide lead to *p*- and *n*-doping of SWCNTs, respectively.

4. Conclusions

The metallicity-mixed SWCNTs were filled with CoI_2 and nickel carbide (Ni_3C). The electronic properties of the filled SWCNTs were investigated in detail by Raman spectroscopy and XPS. It was shown that the embedded CoI_2 causes *p*-doping of SWCNTs with downshifting of the Fermi level of nanotubes. Ni_3C results in *n*-doping of SWCNTs with upshifting of the Fermi level of nanotubes. These results allow for implementation of the filled SWCNTs in devices for various applications, such as nanoelectronics, energy storage, sensors, catalysis and biomedicine.

Author Contributions: M.K. performed the synthesis, characterization of the filled SWCNTs and data analysis. C.K. assisted in the Raman spectroscopy investigations. D.E. supervised the research work. All authors have read and agreed to the published version of the manuscript.

Funding: M.V.K. acknowledges funding for Postdocs with experience of international work in leading research centers for conducting research in leading laboratories of the Moscow Institute of Physics and Technology.

Acknowledgments: We thank T. Saito (Nanotube Research Center, AIST, Tokyo, Japan) for providing SWCNTs; M. Sauer, T. Pichler (University of Vienna, Vienna, Austria) and L. Yashina (Lomonosov Moscow State University, Moscow, Russia) for assisting in the XPS spectroscopy investigations; H. Shiozawa (University of Vienna, Austria) for assisting in the Raman spectroscopy measurements; Y. Sato, K. Suenaga (Nanotube Research Center, AIST, Japan) and N. Kiselev (Institute of Crystallography of the RAS, Russia) for the HRTEM measurements.

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. Fukumaru, T.; Fujigaya, T.; Nakashima, N. Development of n-type cobaltocene-encapsulated carbon nanotubes with remarkable thermoelectric property. *Sci. Rep.* **2015**, *5*, 7951
2. Shiozawa, H.; Briones-Leon, A.; Domanov, O.; Zechner, G.; Sato, Y.; Suenaga, K.; Saito, T.; Eisterer, M.; Weschke, E.; Lang, W.; et al. Nickel clusters embedded in carbon nanotubes as high performance magnets. *Sci. Rep.* **2015**, *5*, 15033
3. Jordan, J.; Lowe, G.A.; McSweeney, R.L.; Stoppiello, C.T.; Lodge, R.; Skowron, S.T.; Biskupek, J.; Rance, G.A.; Kaiser, U.; Walsh, D.A.; et al. Host–guest hybrid redox materials self-assembled from polyoxometalates and single-walled carbon nanotubes. *Adv. Mater.* **2019**, *31*, 1904182
4. Kharlamova, M.V. Advances in tailoring the electronic properties of single-walled carbon nanotubes. *Prog. Mater. Sci.* **2016**, *77*, 125–211.
5. 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
6. Kharlamova, M.V.; Kramberger, C.; Rudatis, P.; Pichler, T.; Eder, D. Revealing the doping effect of encapsulated lead halogenides on single-walled carbon nanotubes. *Appl. Phys. A* **2019**, *125*, 320