



Progress in Carbon Nanostructures: From Synthesis to Applications

Marianna V. Kharlamova ^{1,2,*}, Christian Kramberger ¹ and Alexander I. Chernov ^{3,4}

- ¹ Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria; christian.kramberger-kaplan@univie.ac.at
- ² Phystech School of Biological, and Medical Physics, Moscow Institute of Physics and Technology, National Research University, 9 Institutskiy per., 141701 Dolgoprudny, Russia
- ³ Russian Quantum Center, Skolkovo Innovation City, 30 Bolshoy Bulvar, 121205 Moscow, Russia; ach@rqc.ru
- ⁴ Center for Photonics and 2D Materials, Moscow Institute of Physics and Technology, National Research University, 9 Institutskiy per., 141701 Dolgoprudny, Russia
- * Correspondence: mv.kharlamova@gmail.com

Significant progress in carbon nanostructures has been achieved in the past 20 years; however, there is plenty of room for further study. Researchers must bring developments from the laboratory to an industrial scale. The interest in carbon nanostructures is ever growing. Carbon nanotubes, graphene, graphene nanoribbons, 2D heterostructures, fullerenes, nanodiamonds, filled carbon nanotubes (CNTs), and related carbon nanostructures should be realized in applications. On the fundamental side, topics such as synthesis and growth methods, as well as modification of properties, have been considered. Theoretical studies for modeling properties have also been reported. In experimental materials science, the chemical and physical properties of new carbon nanostructures are considered to be promising. The kinetics of the growth of carbon nanostructures is attractive for fundamental and applied research. Activation energy and growth rates inside metallocene-filled carbon nanotubes have been measured for applications. On the applied side, four spectroscopic methods have been implemented on carbon nanostructures to study the kinetics and electronic properties of materials in depth. Among them are Raman spectroscopy, near-edge X-ray absorption fine structure spectroscopy, photoemission spectroscopy, and optical absorption spectroscopy. Applications of new carbon nanostructures include molecular electronics, thermoelectric power generation, light emission, construction materials, and medicine.

In this Special Issue, entitled "Progress in Carbon Nanostructures: From Synthesis to Applications", we have published four papers, including two review papers [1–4].

In Ref. [1], M. Kharlamova considered issues of the kinetics of growth of filled singlewalled carbon nanotubes (SWCNTs) and their electronic properties. Spectroscopic data on carbon nanotubes were discussed. The kinetics included the calculations of growth rates and activation energies of SWCNTs inside SWCNTs encapsulating metallocene molecules. The highlighted spectroscopic methods are Raman spectroscopy, near-edge X-ray absorption fine-structure spectroscopy (NEXAFS), photoemission spectroscopy (PES), and optical absorption spectroscopy (OAS) (Figure 1). Metal halogenides and metal chalcogenides result in n- or p-doping of SWCNTs [5–18]. In this review, the correlations between the chemical nature of the compound and its electronic properties are summarized. They are related to the work function differences between the pristine carbon nanotubes and the compounds.

In Ref. [2], the issues of the cytotoxicity of carbon nanotubes, graphene, fullerene, and dots were considered. The materials characterizations and theoretical considerations are covered. The data of scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, OAS, fluorescence spectroscopy, and Fourier transform infrared spectroscopy are discussed. Cell viability and drug release issues are highlighted



Citation: Kharlamova, M.V.; Kramberger, C.; Chernov, A.I. Progress in Carbon Nanostructures: From Synthesis to Applications. *Nanomaterials* **2023**, *13*, 2181. https:// doi.org/10.3390/nano13152181

Received: 21 July 2023 Accepted: 24 July 2023 Published: 26 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). (Figure 2), and bioimaging issues of carbon nanomaterials are described. As a perspective, the single-cell viability of carbon nanotubes is discussed. Cancer prevention in single cells is needed. This stimulates the development of single-cell methods of analysis, such as microscopy and spectroscopy. Further advancements in drug loading and bioimaging are needed to lower the cytotoxicity.



Figure 1. OAS spectra of cobalt iodide-filled SWCNTs [1]. Copyright 2023 by the authors. Licensee: MDPI, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.



Figure 2. Lemna minor after treatment of raw graphene and graphene oxide (GO). Control group: (**a1–a6,a13,a14,a16,a17**) after treatment of pristine graphene; (**a7–a12,a15,a18,a19**) after GO treatment. Copyright 2021 by the authors. Licensee: MDPI, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license [19].

In Ref. [3], the authors developed a new method for directly growing patterned vertical graphene on a SiO_2/Si substrate by plasma-enhanced chemical vapor deposition (PECVD) with patterned Cr film. The quality of the grown vertical graphene was investigated by Raman spectroscopy (Figure 3). The Raman spectrum of graphene includes the characteristic D, G, and 2D modes. Mapping results for D, G, 2D, and ratios D/G and 2D/G are presented. In Figure 4, the schematic of the patterned vertical graphene growth mechanism is presented. The steps are before growth (Figure 4a), heating (Figure 4b), reaching a maximum ($\sigma_{max} = -660$ MPa) compressive stress σ_{max} in the Cr film (Figure 4c), growth (Figure 4d), cooling (Figure 4e), and decreasing temperature to T_y, where vertical graphene/Cr cracks and warps (Figure 4f). This method is very promising, and it proves the possibility of growing graphene on Cr films.



Figure 3. (a) Raman spectra of random points on and outside the patterned vertical graphene area. Mapping results for D (b), G (c), 2D (d), and ratios D/G (e) and 2D/G (f). The mapping area is 150 μ m × 150 μ m, and 2601 data points were used. Copyright 2023 by the authors. Licensee: MDPI, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license [3].



Figure 4. Schematic of the patterned vertical graphene growth mechanism. The steps are before growth (**a**), heating (**b**), reaching a maximum (σ max = -660 MPa) compressive stress in the Cr film (**c**), growth (**d**), cooling (**e**), and decreasing temperature to Ty, where vertical graphene/Cr cracks and warps (**f**). Copyright 2023 by the authors. Licensee: MDPI, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license [3].

We acknowledge all authors for their contributions. Please submit your original articles and review papers to the Special Issue "Advanced Carbon Nanostructures: Synthesis, Properties, and Applications II."

Author Contributions: M.V.K.—writing, C.K. and A.I.C.—review, and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: Marianna V. Kharlamova acknowledges the coauthors of all reviewed papers.

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

References

- 1. Kharlamova, M.V. Kinetics, Electronic Properties of Filled Carbon Nanotubes Investigated with Spectroscopy for Applications. *Nanomaterials* **2023**, *13*, 176. [CrossRef] [PubMed]
- Kharlamova, M.V.; Kramberger, C. Cytotoxicity of Carbon Nanotubes, Graphene, Fullerenes, and Dots. Nanomaterials 2023, 13, 1458. [CrossRef] [PubMed]
- 3. Qian, F.; Deng, J.; Ma, X.; Fu, G.; Xu, C. Direct Growth of Patterned Vertical Graphene Using Thermal Stress Mismatch between Barrier Layer and Substrate. *Nanomaterials* **2023**, *13*, 1242. [CrossRef]
- 4. Komlenok, M.; Pivovarov, P.; Popovich, A.; Cheverikin, V.; Romshin, A.; Rybin, M.; Obraztsova, E. Crystallization of Copper Films on Sapphire Substrate for Large-Area Single-Crystal Graphene Growth. *Nanomaterials* **2023**, *13*, 1694. [CrossRef] [PubMed]
- 5. 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. [CrossRef] [PubMed]
- 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. [CrossRef]
- 7. Kharlamova, M.V.; Kramberger, C.; Domanov, O.; Mittelberger, A.; Yanagi, K.; Pichler, T.; Eder, D. Endohedral Functionalization of Metallicity-Sorted Single-Walled Carbon Nanotubes. *Proceedings* **2020**, *56*, 33. [CrossRef]
- 8. 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. [CrossRef]
- Kharlamova, M.V.; Kramberger, C.; Rudatis, P.; Yanagi, K.; Eder, D. Characterization of the electronic properties of single-walled carbon nanotubes filled with an electron donor—Rubidium iodide: Multifrequency Raman and X-ray photoelectron spectroscopy studies. *Phys. Status Solidi B* 2019, 256, 1900209. [CrossRef]
- 10. 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. [CrossRef]
- 11. 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. [CrossRef]
- 12. Kharlamova, M.V.; Kramberger, C. Phemenology of filling, investigation of growth kinetics and electronic properties for applications of filled single-walled carbon nanotubes. *Nanomaterials* **2023**, *13*, 314. [CrossRef]
- Kharlamova, M.V.; Kramberger, C. Metal and Metal Halogenide-Filled Single-Walled Carbon Nanotubes: Kinetics, Electronic Properties, Engineering the Fermi Level. *Nanomaterials* 2023, 13, 180. [CrossRef] [PubMed]
- 14. Kharlamova, M.V. Rare-earth metal halogenide encapsulation-induced modifications in Raman spectra of single-walled carbon nanotubes. *Appl. Phys. A* 2015, *118*, 27–35. [CrossRef]
- 15. 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. [CrossRef]
- 16. 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. [CrossRef] [PubMed]
- 17. Kharlamova, M.V.; Kramberger, C. Applications of Filled Single-Walled Carbon Nanotubes: Progress, Challenges, and Perspectives. *Nanomaterials* **2021**, *11*, 2863. [CrossRef] [PubMed]
- 18. Kharlamova, M.V.; Kramberger, C. Metal cluster size-dependent activation energies of growth of single-chirality single-walled carbon nanotubes inside metallocene-filled single-walled carbon nanotubes. *Nanomaterials* **2021**, *11*, 2649. [CrossRef] [PubMed]
- Jaworski, S.; Strojny-Cieślak, B.; Wierzbicki, M.; Kutwin, M.; Sawosz, E.; Kamaszewski, M.; Matuszewski, A.; Sosnowska, M.; Szczepaniak, J.; Daniluk, K.; et al. Comparison of the Toxicity of Pristine Graphene and Graphene Oxide, Using Four Biological Models. *Materials* 2021, 14, 4250. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.