materials proceedings

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Proceeding Paper

Metal/Metal Carbide Catalyst of Growth of Single-Walled Carbon Nanotubes: New Examples of Filling of Single-Walled Carbon Nanotubes †

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† Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: https://iocn2023.sciforum.net.

Abstract: In this work, I filled the single-walled carbon nanotubes (SWCNTs) with nickelocene, and cobaltocene molecules. I investigated the growth of inner carbon nanotubes on metallic, and metal carbide catalysts. Raman spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy proved the metallic/metal carbide state of catalysts, and the formation of inner SWCNTs. This is needed for applications of SWCNTs in buildings.

Keywords: metal; metal carbide; carbon nanotube; growth; electronic properties; Raman spectroscopy; near edge X-ray absorption fine structure spectroscopy; photoemission spectroscopy

Citation: Kharlamova, M.V. Metal/Metal Carbide Catalyst of Growth of Single-Walled Carbon Nanotubes: New Examples of Filling of Single-Walled Carbon Nanotubes. *Mater. Proc.* **2023**, *14*, x. https://doi.org/10.3390/xxxxx

Published: 5 May 2023

1. Introduction

The synthesis of carbon nanotubes, such as single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and multi-walled carbon nanotubes (MWCNTs) on metallic, and metal carbide catalysts leads to the filling of catalyst inside nanotubes. These are common, and amazing examples of filling of carbon nanotubes, which is easier to achieve with metals, and metal carbides [1–22]. The SWCNTs are controllably, and aimly filled with metals, and metal carbides in the following Refs. [1–22]: there are more than 20 examples, which allows undoubtly confirm successful filling with metal, and metal carbides. The number of methods that are applied to confirm the filling are Raman spectroscopy, near edge X-ray absorption fine structure spectroscopy (NEXAFS), photoemission spectroscopy. Photoemission spectroscopy, and NEXAFS are long proven methods of investigation of metal, and metal carbide filled SWCNTs. The magnetic measurements confirm the susscesssful filling, too. In Ref. [3–6], iron was filled inside SWCNTs, and magnetic properties were investigated. In this work, I filled SWCNTs with nickelocene, and cobaltocene, which are usually used for synthesis of carbon nanotubes [23–27], and I grew the inner nanotubes inside SWCNTs on metallic, and metal carbide catalysts.

2. Experiments

The filling of SWCNTs with nickelocene was performed by the gas phase method. The powder of metallocene was mixed with SWCNTs in a glass ampoule, and sealed under vacuum. The ampoule was heated for 5 days at 39 °C. The ampoule was then slowly cooled to room temperature. The nickelocene-filled SWCNTs were annealed at temperature of 375 °C to 1200 °C for 2 h to grow the inner tubes. The formation of inner tubes started at 400 °C after 2 h of annealing. The tubes were formed completely after annealing at 800 °C for 2 h. The temperature of growth was defined by the tube diameter, and chiral angle.

The filling of SWCNTs with cobaltocene was performed by the gas phase method. The SWCNTs and cobaltocene powder were mixed in a glass ampoule, and it was sealed under vacuum. I heated the ampoule at 59 °C for 5 days to achieve the filling. The ampoule was then cooled to room temperature. The filled SWCNTs were annealed at temperature between 450 °C and 1200 °C to grow the inner nanotubes. The growth of inner nanotubes started at temperature of 500 °C, and the tubes were completely formed at temperature of 900 °C.

3. Results

The filled SWCNTs, and formed filled DWCNTs were investigated by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS). Several types of samples were used: (i) metallicity-mixed SWCNTs (Figure 1), (ii) semiconducting SWCNTs, (iii) metallic SWCNTs. These samples were compared.

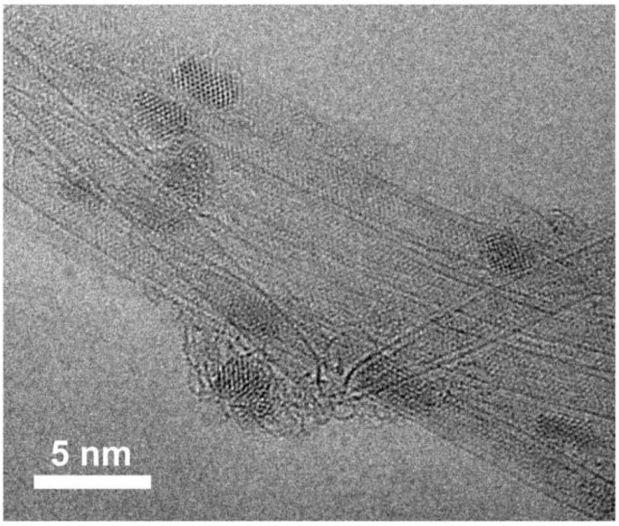

Figure 1. The high resolution transmission electron microscopy image of nickel/nickel carbide—filled SWCNTs [28]. Reproduced with permission of the Royal Society of Chemistry. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

For pristine SWCNTs, no growth of inner tubes was observed. Metallicity-mixed SWCNTs filled with nickelocene grew inner tubes at temperatures between 400 °C, and 800 °C, after that DWCNTs were formed. Semiconducting SWCNTs grew inner tubes at temperatures higher 400 °C, and the samples annealed at 1200 °C for 2 h contained pure DWCNTs, however, they still could contain a bit metal, or metal carbide. Metallic SWCNTs grew inner tubes at temperatures higher 400 °C, and the samples annealed at 1200 °C does not contain metal, or metal carbide. Metallicity-mixed SWCNTs filled with cobaltocene grew inner tubes at temperatures between 500 °C, and 900 °C. At higher temperatures the DWCNTs were formed. Semiconducting, and metallic filled SWCNTs are still need to be investigated. Raman spectroscopy, and XPS shows the formation of DWCNTs at high temperatures, which means the growth of inner nanotubes.

4. Conclusions

In this work, I grew the inner carbon nanotubes inside nickelocene, and cobaltocene-filled SWCNTs. I investigated the growth of inner carbon nanotubes on metallic, and metal carbide catalyst. Raman spectroscopy, XPS, and UPS proved the metallic/metal carbide state of catalysts, and the formation of inner SWCNTs. This is needed for applications of SWCNTs in buildings.

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: The data are available on request of Marianna V. Kharlamova.

Acknowledgments: Marianna V. Kharlamova thanks Christian Kramberger-Kaplan (University of Vienna, Vienna, Austria).

Conflicts 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.

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