materials proceedings

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Chiral angle-dependence of growth rates of inner carbon nanotubes inside metallocene-filled single-walled carbon nanotubes †

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
[2] Moscow Institute of Physics and Technology, 9 Institutskiy per., 141700 Dolgoprudny, Moscow region, Russian Federation
* Correspondence: mv.kharlamova@gmail.com
† Presented at 1st International Electronic Conference on Machines and Applications, 15—30 September 2022; Available online: https://iecma2021.sciforum.net.

Abstract: In this work, I calculated the growth rates of inner carbon nanotubes inside nickelocene-filled single-walled carbon nanotubes (SWCNTs). It was shown that the growth rates of inner tubes depend on the diameter of SWCNTs. The growth rates of smaller diameter SWCNTs are larger. The dependence of growth rates of inner nanotubes on chiral angle was also revealed. This is caused by the growth mechanism of carbon nanotubes.

Keywords: growth kinetics; single-walled carbon nanotube; chiral angle; nickelocene; Raman spectroscopy

Citation: Kharlamova, M.V. Chiral angle-dependence of growth rates of inner carbon nanotubes inside metallocene-filled single-walled carbon nanotubes. *Mater. Proc.* **2023**, *3*, x. https://doi.org/10.3390/xxxxx

Published: 5 March

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1. Introduction

Growth kinetics of single-walled carbon nanotubes (SWCNTs) is of special interest, because it opens the way for applications of carbon nanotubes in different fields [1-9]. Growth kinetics of carbon nanotubes was studied by several authors, but these works deal with forests of carbon nanotubes, and growth rates, and activation energies can not be precisely determined. Forests of carbon nanotubes consist of nanotubes with different atomic structures, and physical properties. There are no works on investigations of growth kinetics of carbon nanotube from SWCNTs with certain conductivity type, chiral angle. It would be interesting to investigate the growth kinetics of carbon nanotubes from SWCNTs with certain conductivity type, and chiral angle filled with different precursors, such as metalocenes (ferrocene, cobaltocene, nickelocene) [10]. SWCNTs were filled with molecule-filled SWCNTs, such as metal acetylacetonetes. In these molecules, there are metal atoms, and carbon atoms for catalyzing the growth of SWCNTs, and growth of carbon nanotubes. There are also possibly other molecules suitable for catalysis of carbon nanotube growth, whose growth kinetics is yet to be studied [11].

2. Experiments

In this work, I filled the SWCNTs with nickelocene molecules by the gas phase methods. The SWCNTs were mixed with metallocene powder in quartz ampoule, it was sealed, and then it was heated at low temperatures for filling. These temperatures prevent decomposition of metallocenes. The temperature was as low as 39°C.

The scanning electron microscopy images were obtained at an equipment Supra 50VP (Leo, Germany). The samples for measurements were glued to carbon tape, which was connected to the sample holder.

Raman spectroscopy was performed at an equipment Horiba Jobin Yvon LabRAM HR800. The samples were measured as films. The films of carbon nanotubes were prepared using the procedure of sonication, and filtration in toluene, and methanol, followed by film drying and pealing off the filters. The laser wavelengths of 568 nm (ArKr laser), and 633 nm (HeNe laser) were used. The measurements were performed using the following procedure. In a camera-mode, the laser beam was focused with x50 objective on the film of carbon nanotubes. The SWCNTs were located inbetween two quartz plates inside a narrow quartz tube. The tube was connected to pump. After that in the measurement mode, the spectrum was recorded with laser power of 3.4 mW. The range of measurements was from 50 up to 3000 cm^{-1}. The regime of normal resolution (600 mm^{-1} grating) was used. The measurement was done during 5 s for 12 times to obtain the best data. After that the measurement of radial breathing mode in a high-resolution mode (1800 mm^{-1} grating) was done. The range of measurements was from 100 to 500 cm^{-1}. The measurement was done during 15 s for 72 times to obtain the best data. The measurements were conducted at room temperature. The annealings of samples were made for periods of time between 2 and 4098 min. The annealings were performed one after another. The experiments took about one week at one temperature. The tested temperatures were 480, 500, 520, 540, 560, 580, and 600°C.

The mathematical model was proposed for the calculation of growth rate α in the beginning of growth, and β after longer periods of annealings [1]. A is the amount of carbon that is grown in nanotubes. A part χ is processed at α and the other part $(1 - \chi)$ – at β $(0 \le \chi \le 1)$. The amount of carbon of grown nanotubes is given by C:

$$\frac{dA}{d\tau}=A(\chi\alpha+(1-\chi)\beta) \quad (1)$$

$$\frac{dC}{d\tau} = -\frac{dA}{d\tau} \quad (2)$$

The solution of the system is the following:

$$C(\tau)=A(1-\chi e^{-\alpha\tau}-(1-\chi)e^{-\beta\tau}). \quad (3)$$

Therefore, the growth rates were calculated using the Raman spectra, and peak fitting of the dependences of the normalized peak intensities on annealing time with Eq. (3) with PeakFit v4.12. The growth rates were calculated as the fitting parameters.

3. Results

Figure 1 shows the scanning electron microscopy (SEM) data of the pristine SWCNT material [9]. It is visible that the SWCNTs represent the pure carbon nanotube network. This image confirms the high purity of carbon nanotubes. Such nanotubes can be used for the filling to obtain clean filled material. Applications of filled carbon nanotubes required clean pristine materials.

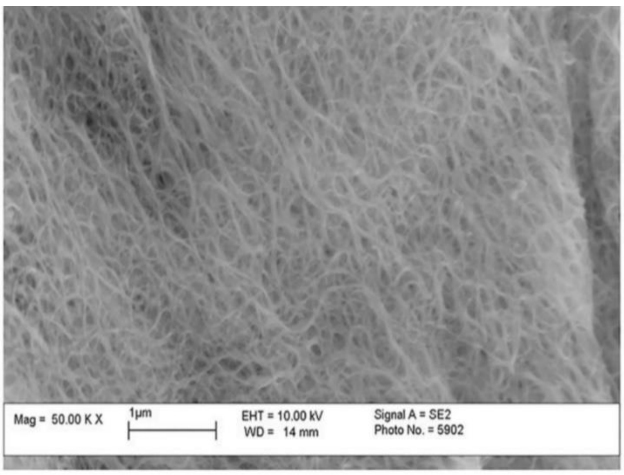

Figure 1. The SEM image of the pristine SWCNT material. Reproduced from Ref. [9] with permission from the Royal Society of Chemistry. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

The growth kinetics of carbon nanotubes was described with two growth rates α, and β. The growth rate α describes the growth of carbon nanotubes in the beginning of the growth process. The growth rate β describes the continuation of growth. The growth rate α is the growth on carburized catalytic particle, and the growth rate β is the growth on metallic particle. Figure 2 presents the growth mechanism of carbon nanotubes, including chemical transformation of metallocene, and growth of carbon nanotubes on metallic catalyst [9].

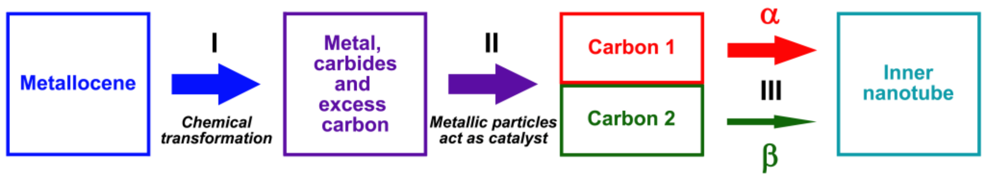

Figure 2. The mechanism of growth of carbon nanotubes [9]. Copyright 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

Figure 3. shows the dependence of growth rates α, and β on diameter of carbon nanotube for nickelocene-filled SWCNTs [9]. The data are shown for different temperatures. It is visible that the growth rates α, and β increase with decreasing of the diameter of SWCNTs. The growth rates are also dependent of the chiral angle of SWCNTs. This causes nonmonotonic diameter dependence for some inner carbon nanotubes.

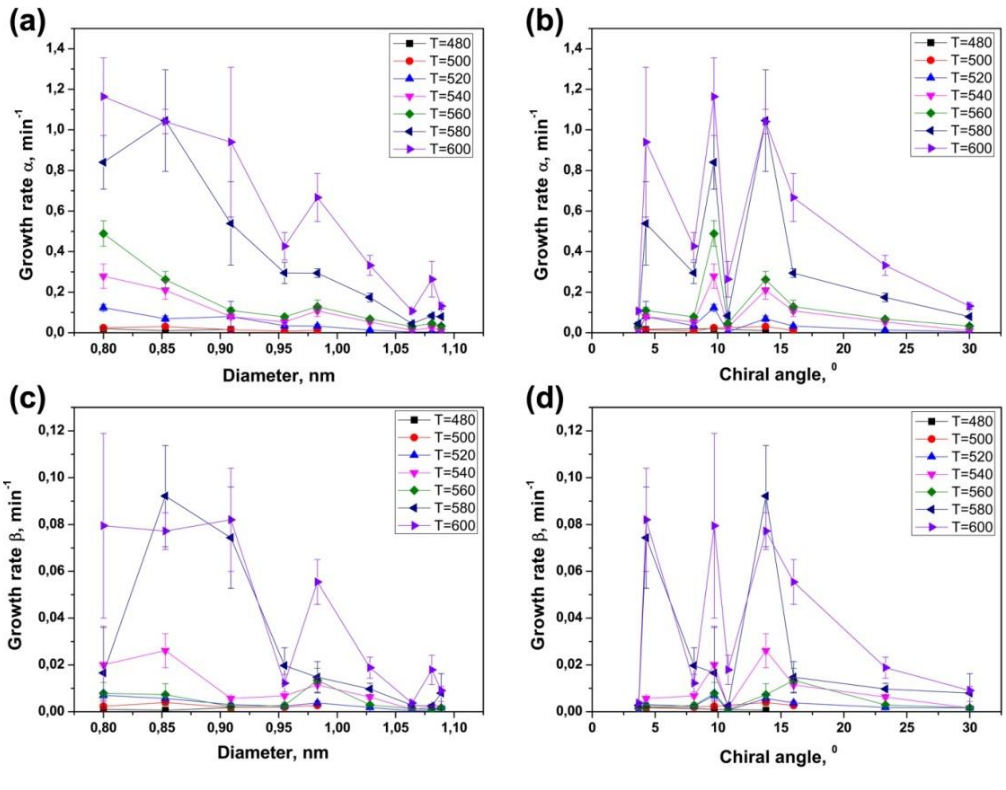

Figure 3. The dependence of growth rates α, and β on the diameter, and chiral angle of SWCNTs inside nickelocene-filled SWCNTs [9]. Copyright 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

4. Conclusions

In this work, I calculated the growth rates of inner carbon nanotubes with chiral vectors of (8,8), (12,3), (13,1), (9,6), (10,4), (11,2), (11,1), (9,3) and (9,2) inside nickelocene-filled SWCNTs. It was shown that the growth rates increase with decreasing the nanotube diameter. The growth rates are dependent on the chiral angle of carbon nanotubes. This can be explained by the growth mechanism of carbon nanotubes.

Author Contributions: The manuscript is written solely by Marianna V. Kharlamova.

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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