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Chemical, and Physical State of Catalyst in the Growth of Single-Walled Carbon Nanotubes inside Metallocene-Filled Single-Walled Carbon Nanotubes †

Marianna V. Kharlamova

Centre for Advanced Materials Application (CEMEA), Slovak Academy of Sciences, Dúbravská cesta 5807/9, 845 11 Bratislava, Slovakia; mv.kharlamova@gmail.com

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Abstract: In this work, I reveal the state of catalyst during the growth of single-walled carbon nanotubes (SWCNTs) inside metallocene-filled SWCNTs. I use high resolution transmission electron microscopy, Raman spectroscopy to study the kinetics of nanotube growth. I use Raman spectroscopy, and X-ray photoelectron spectroscopy to study the chemical state of catalyst inside carbon nanotubes. I showed that catalyst present in carbidic form in the beginning of nanotube growth, and it is present in metallic state in the continuation of the growth process. The growth process is characterized by two growth rates α, β, two activation energies E_α, E_β.

Keywords: carbon nanotube; growth kinetics; metal; metal carbide; chemical state; physical state; Raman spectroscopy; X-ray photoelectron spectroscopy

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1. Introduction

Chemical, physical state of catalyst defines the growth process of material. The catalyst can be in the form of metal, or metal carbide during the growth of carbon nanotubes. The physical state of catalyst is liquid, or solid. The chemical, and physical state of catalyst can change in the process of growth. This is defined by the synthesis parameters. In literature, it is known that single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs) can grow at metallic, or metal carbide catalytic nanoparticles [1,2], which present in molten, or solid state [3,4]. In Ref. [5], the chemical transformation of catalytic particles during the nanotube growth was studied by in situ X-ray photoelectron spectroscopy (XPS), and it was shown that surface carbide layer is formed on the metallic particles. There are other works dedicated to chemical transformation of catalysts [6–9]. The aim of my work is to reveal the state of catalyst during the growth of SWCNTs inside metallocene-filled SWCNTs. I use high resolution transmission electron microscopy, Raman spectroscopy to study the kinetics of nanotube growth. I use Raman spectroscopy, and XPS to study the chemical state of catalyst inside carbon nanotubes. I showed that catalyst present in carbidic form in the beginning of nanotube growth, and it is present in metallic state in the continuation of the growth process. The growth process is characterized by two growth rates α, β, two activation energies E_α, E_β.

2. Experimental

The SWCNTs were filled with nickelocene, and cobaltocene molecules by the gas phase method. The SWCNTs were placed inside a glass ampoule where metallocene powder was located. The ampoule was sealed under vacuum. A half ampoule was heated at the low temperatures, and then it was flipped, so that other half of ampoule was heated. The process of synthesis was performed for about one week. The kinetics of growth of inner nanotubes was studied by Raman spectroscopy during annealings at different temperatures for 2–4094 min. The annealing temperatures were 480, 500, 520, 540, 560, 580, 600 °C for nickelocene-filled SWCNTs, and temperatures equaled 540, 560, 580, 600, 620, 640 °C for cobaltocene inside carbon nanotubes [10–12]. The Raman spectroscopy was performed at different laser wavelengths. Different lasers excite different chirality nanotubes. The XPS was used to study the chemical transformation of catalyst. The SWCNTs were annealed at different temperatures for 2 h, and studied by XPS. Nickelocene-filled SWCNTs were annealed at 250–1200 °C for 2 h. SWCNTs included nanotubes of three samples: semiconducting, metallic, and mixed SWCNTs. Metallicity-sorted SWCNTs were annealed at temperatures between 340–1200 °C for 2 h for XPS analysis.

3. Results

The annealing of metallocene-filled SWCNTs leads to the decomposition of metallocene with the formation of metal, and metal carbide inside nanotubes (Figure 1). Using Raman spectroscopy, and XPS, it was shown that metal carbide catalyzes the growth of carbon nanotubes in the beginning, and metallic catalyst particle catalyzes continuation of growth of carbon nanotubes. The first stage is characterized by the growth rate α, and activation energy E_α. The second stage is characterized by the growth rate β, and E_β. Thus, four stages of chemical transformation of catalyst inside SWCNTs can be defined. At the first stage, metallocene molecules decompose inside SWCNTs. At the second stage, carburized metal nanoparticles surrounded by excess carbon are formed. At the third stage, they act as a catalyst for the inner tube growth. At the fourth stage, the growth of the inner tube continues on the metallic catalyst nanoparticle.

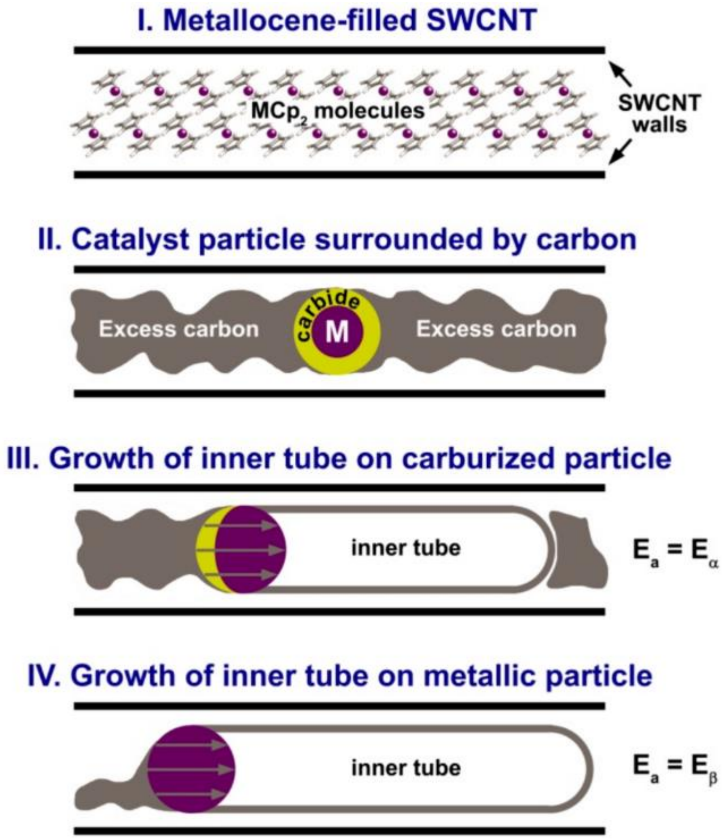

Figure 1. Illustration of the growth model of the inner tubes inside the metallocene-filled SWCNTs. MCp2 (M = Ni, Co) molecules encapsulated into the channel of SWCNT. Copyright 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license [12].

4. Conclusions

I studied the chemical transformation of catalyst inside SWCNTs during the growth of carbon nanotubes. It was shows that catalyst has carbidic nature in the beginning of growth process, and the catalyst has metallic nature in the continuation of growth of carbon nanotubes. These differences in chemical state reveal different stages of growth kinetics of carbon nanotubes.

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