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

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Abstract: In this study, the state of catalysts is revealed during the growth of single-walled carbon nanotubes (SWCNTs) inside metallocene-filled SWCNTs. High-resolution transmission electron microscopy and Raman spectroscopy were used to study the kinetics of nanotube growth. Raman spectroscopy and X-ray photoelectron spectroscopy were employed to study the chemical state of catalysts inside carbon nanotubes. The catalyst was present in carbidic form at the beginning of nanotube growth, and was present in a metallic state over the continuation of the growth process. The growth process was characterized by two growth rates, α and β, and two activation energies, E_α and 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

The chemical and physical state of a catalyst defines the growth process of a material. The catalyst can be in the form of metal, or metal carbide, during the growth of carbon nanotubes. The physical state of a catalyst can be liquid or solid. The chemical and physical state of a catalyst can change in the growth process. This is defined by the synthesis parameters. 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 states [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 the surface carbide layer was formed on the metallic particles. Other studies have been dedicated to the chemical transformation of catalysts [6–9]. The aim of this study is to reveal the state of catalysts during the growth of SWCNTs inside metallocene-filled SWCNTs. High-resolution transmission electron microscopy and Raman spectroscopy were used to study the kinetics of nanotube growth. Raman spectroscopy and XPS were utilized to study the chemical state of a catalyst inside carbon nanotubes. The catalyst was present in carbidic form at the beginning of nanotube growth, and was present in metallic state throughout the growth process. The growth process is characterized by two growth rates, α and β, and two activation energies, E_α and E_β.

2. Experimental Section

The SWCNTs were filled with nickelocene and cobaltocene molecules using the gas phase method. The SWCNTs were placed inside a glass ampoule where metallocene powder was located. The ampoule was sealed under vacuum. Half an ampoule was heated at low temperature, and then it was flipped, so that other half of the ampoule was heated. The synthesis process was performed for about one week. The growth kinetics of inner nanotubes were studied by Raman spectroscopy during annealing at different temperatures for 2–4094 min. The annealing temperatures were 480, 500, 520, 540, 560, 580, and 600 °C for nickelocene-filled SWCNTs, and temperatures equaled 540, 560, 580, 600, 620, and 640 °C for cobaltocene inside carbon nanotubes [10–12]. Raman spectroscopy was performed at different laser wavelengths. Different lasers excite nanotubes of different chirality values. XPS was used to study the chemical transformation of the 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 and 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 initially catalyzes the growth of carbon nanotubes, and metallic catalyst particles catalyze throughout the growth of carbon nanotubes. The first stage is characterized by the growth rate, α, and the 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. In the first stage, metallocene molecules decompose inside SWCNTs. In the second stage, carburized metal nanoparticles surrounded by excess carbon are formed. In the third stage, these act as a catalyst for the inner tube growth. In the fourth stage, the growth of the inner tube continues on the metallic catalyst nanoparticles.

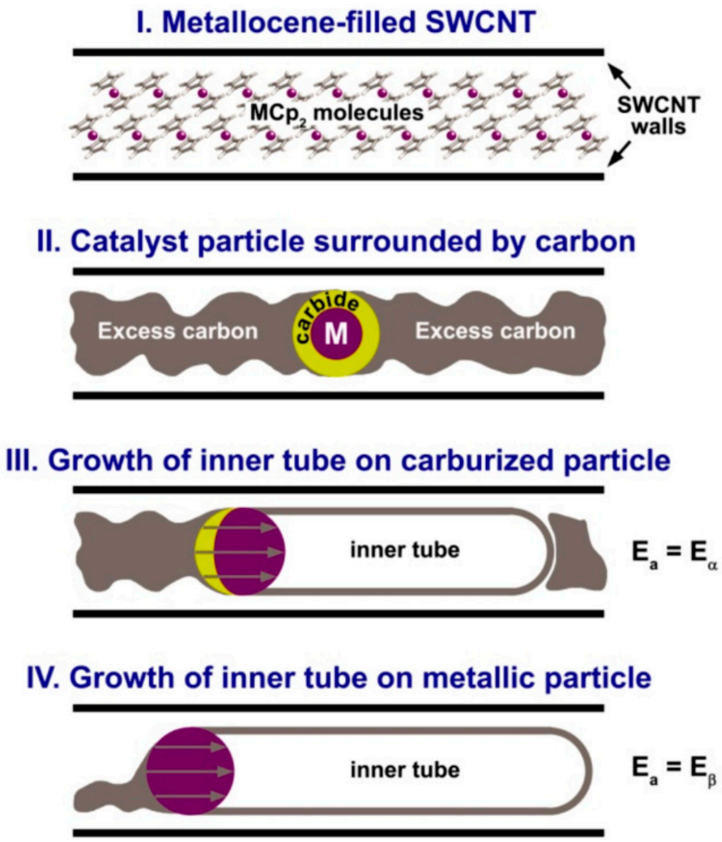

Figure 1. Illustration of the growth model of inner tubes inside the metallocene-filled SWCNTs. MCp2 (M = Ni, Co) molecules encapsulated into the channel of SWCNT. Copyright 2021 by the authors. Licensee: MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and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

4. Conclusions

The chemical transformation of a catalyst inside SWCNTs was studied during the growth of carbon nanotubes. The catalyst exhibited carbidic nature at the start of the growth process, and the catalyst had a metallic nature in the continuation of carbon nanotube growth. These differences in chemical state reveal different stages of growth kinetics of carbon nanotubes.

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