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Proceeding Paper

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

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Abstract: In this work, I filled single-walled carbon nanotubes (SWCNTs) with nickelocene and cobaltocene molecules. I investigated the inner growth of 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 the catalysts, as well as 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

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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 catalysts inside nanotubes. These are common and amazing examples of filling carbon nanotubes, which is easier to achieve with metals and metal carbides [1–22]. The SWCNTs are filled with metals and metal carbides in the following Refs. [1–22]: there are more than 20 examples, which allows undoubtedly confirming their successful filling with metal and metal carbides. The methods that are applied to confirm the filling are Raman spectroscopy, near-edge X-ray absorption fine-structure spectroscopy (NEXAFS), and photoemission spectroscopy. Photoemission spectroscopy and NEXAFS are long-proven methods for the investigation of metal- and metal-carbide-filled SWCNTs. The magnetic measurements confirm the successful filling. In Refs. [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 the 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 using the gas phase method. Metallocene powder 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 a 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 growth temperature was defined by the tube diameter and chiral angle.

The filling of SWCNTs with cobaltocene was performed using 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 a temperature between 450 °C and 1200 °C to grow the inner nanotubes. The growth of inner nanotubes started at a temperature of 500 °C, and the tubes were completely formed at a temperature of 900 °C.

3. Results

The filled SWCNTs and formed filled DWCNTs were investigated using 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, and (iii) metallic SWCNTs. These samples were compared.

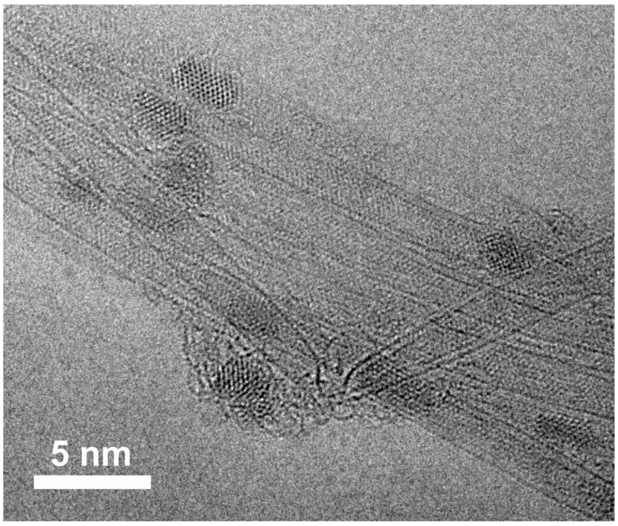

Figure 1. The high-resolution transmission electron microscopy image of nickel/nickel-carbide-filled SWCNTs [28]. Reproduced with permission of the Royal Society of Chemistry. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

For pristine SWCNTs, no growth of the inner tubes was observed. Metallicity-mixed SWCNTs filled with nickelocene grew inner tubes at temperatures between 400 °C and 800 °C, and after that, DWCNTs were formed. Semiconducting SWCNTs grew inner tubes at temperatures higher than 400 °C, and the samples annealed at 1200 °C for 2 h contained pure DWCNTs; however, they still could contain a bit of metal or metal carbide. Metallic SWCNTs grew inner tubes at temperatures higher than 400 °C, and the samples annealed at 1200 °C do 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 still need to be investigated. Raman spectroscopy and XPS show 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 catalysts. Raman spectroscopy, XPS, and UPS proved the metallic/metal carbide state of the catalysts, as well as the formation of inner SWCNTs. This is needed for applications of SWCNTs in buildings.

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