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Proceedings

Chemical properties of metallocene-filled carbon nanotubes to tailor toxicity on plants†

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Abstract: Metallocenes are toxic chemical that is used for the growth of carbon nanotubes (CNTs). The study of toxicity of metallocenes on plants is very important. It governs the issues of genetics. Toxicity studies should consider (I) the growth kinetics of carbon nanotubes, (II) the chemical reaction of metallocenes inside carbon nanotubes, and (III) investigations into the electronic properties of filled carbon nanotubes. The toxicity studies are influenced with the investigation of growth process of metallocene-filled carbon nanotubes, evaporation of metals, formation of multiple-walled carbon nanotubes. Investigations into the modification of the Fermi level of filled carbon nanotubes also play a role in toxicity studies. Metallocenes are filled into carbon nanotubes through various methods discussed here, including solution methods and gas-phase methods, each differing in methodology and requiring optimization. Many authors published different methodics of filling of carbon nanotubes with metallocenes. They lead to high filling ratios, and allow future modifications of the electronic properties of carbon nanotubes. Kinetics of growth of carbon nanotubes is investigated with different methods. Environmental transmission electron microscopy is applied to study with a time resolution of several nanoseconds. Here, we use Raman spectroscopy to study the growth process, which is revealed with activation energies, growth rates, temperature dependence. The dependence of growth temperature on the tube diameter, and metallocene type is revealed. It is shown that the growth temperature increases with larger diameter of inner CNTs. The growth temperature increases for ferrocene as compared with nickelocene, and cobaltocene. With X-ray photoelectron spectroscopy, we show that the heating of metallocene-filled SWCNTs at 360-600 °C causes n-doping of SWCNTs. The heating at higher temperatures results in p-doping. The obtained data are needed to tailor the toxicity issues of metallocene-filled carbon nanotubes on plants.

Keywords: carbon nanotube; metallocene; filling; electronic properties; spectroscopy

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1. Introduction

Metallocenes are toxic for plants, and they are used for the synthesis of carbon nanotubes (CNTs). It is important to study the physics, and chemistry of metallocenes that influence their toxicity [1-9]. There are several important studies on metallocenes. First, the investigation of growth kinetics of CNTs with metallocenes as catalysts is important [10-18]. Second, the analysis of chemical reactions of metallocenes in CNTs is needed [19]. Third, the investigations of the electronic structure of CNTs is important [20]. Regarding the first issue, activation energies, and growth rates of CNTs depend on the metallocene type [21]. These parameters can be controlled by the tube diameter, and chiral angle. Regarding the second issue, the toxicity of metallocenes inside CNTs can be completely prevented, as the reaction of molecules is dependent on CNTs' characteristics, and synthesis conditions [22]. Regarding the third issue, the investigations of the physics of metallocene-filled CNTs upon annealing is important, as doping effects influence the chemistry of molecules [23].

In this contribution, I consider the growth dynamics, and the electronic properties of metallocene-filled CNTs, as these parameters are important to tailor the toxicity on plants. I filled the single-walled carbon nanotubes (SWCNTs) with nickelocene, cobaltocene, and ferrocene, and I investigated the growth dynamics of inner CNTs by Raman spectroscopy, and I investigated the electronic properties of filled CNTs by X-ray photoelectron spectroscopy (XPS).

2. Experimental

I sealed the pre-opened SWCNTs with dimeter of 1.7 nm, and metallocene powders (nickelocene, cobaltocene, or ferrocene, Aldrich, 99.999%) inside Pyrex-glass tube under ultrahigh vacuum using turbopump. The filling of SWCNTs with nickelocene was conducted at ~50 °C, and the encapsulation of cobaltocene was performed at ~60 °C to prevent the decomposition of molecules. The filling of ferrocene inside SWCNTs was carried out at ~350 °C. Upon heating, the SWCNTs were filled with molecules.

The investigation of morphology of filled CNTs was performed at JEOL JEM2100 microscope. The accelerating voltages were 200 kV. The samples for measurements were prepared in isopropanol. The dispersion of SWCNTs was then dropped on microscope grids. We first measured the overview micrographs with low-resolutions, and then we analyzed in detail the microstructure in high-resolution.

The investigation of growth dynamics of inner CNTs was performed at Horiba Jobin Yvon LabRAM HR800 at laser wavelengths of 458-647 nm. The used lasers are tunable ArKr (with wavelengths of 458-568 nm, and 647 nm), and HeNe (with wavelengths of 633 nm). The measurements were done in low-resolution mode (600 mm^{-1} grid), and high-resolution mode (1800 mm^{-1} grid). The measurements were done on CNT buckypapers.

The investigation of the electronic properties of CNTs was carried out at XPS spectrometer equipped with SPECS R4000 hemispherical analyzer. The measurements were conducted at CNT buckypapers fixed on molybdenum holders. The calibration of spectrometer was made with Au peaks. The annealing of filled CNTs was conducted at 360-1200 °C in ultrahigh vacuum.

3. Results

Figure 1 shows the high-resolution transmission electron microscopy image (HRTEM) of nickelocene-filled CNTs annealed at 900 °C for 2 h. It is visible that the annealing leads to the formation of double-walled carbon nanotubes (DWCNTs). The two walls of DWCNTs are observed in the image. The metal catalyst particles are not visible, as the metal evaporated from the CNTs.

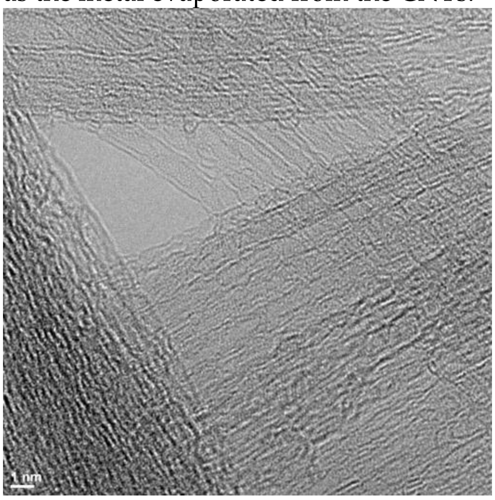

Figure 1. The HRTEM image of nickelocene-filled CNTs annealed at 900°C for 2h.

Figure 2 shows the growth temperature of nickelocene, cobaltocene, ferrocene-filled SWCNTs plotted versus the inner tube diameter. It is visible that the growth temperature is larger for larger diameter inner CNTs. The growth temperature increases in the line with nickelocene-cobaltocene-ferrocene. These data are very important for toxicity evaluations of filled CNTs, as toxicity should be tailored upon the inner tube growth.

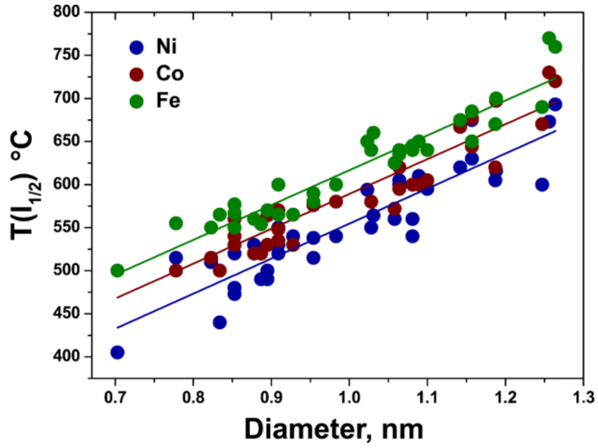

Figure 2. The growth temperature of nickelocene, cobaltocene, ferrocene-filled SWCNTs plotted versus the inner tube diameter. Copyright 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license [16].

Figure 3 shows the dependence of the electronic properties of nickelocene-filled SWCNTs on annealing temperature. It is visible that the heating of filled SWCNTs at 360-600 °C leads to n-doping of SWCNTs. The heating of filled SWCNTs at higher temperatures results in p-doping of SWCNTs. As the chemical reaction of metallocenes influences the electronic properties of SWCNTs, the heating is valuable method to tailor the toxicity.

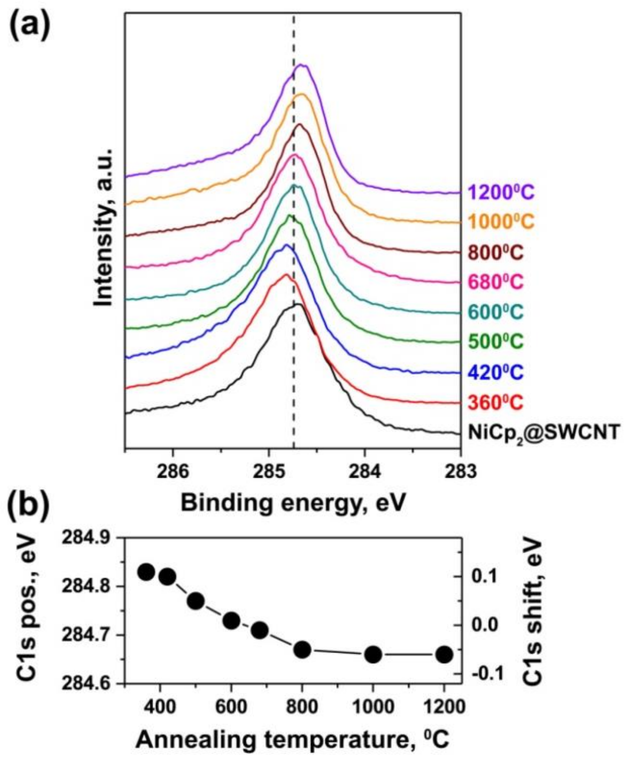

Figure 3. The dependence of the electronic properties of nickelocene-filled SWCNTs on annealing temperature. Copyright 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an

4. Conclusions

In this work, the chemical properties of metallocene-filled SWCNTs, which are important to access the toxicity of metallocenes on plants, were investigated. The morphology of filled SWCNTs using HRTEM was examined, the growth dynamics of inner CNTs was analyzed via Raman spectroscopy, and the electronic properties of filled CNTs were studied with X-ray photoelectron spectroscopy. The significance of this study is in its applicability to access the SWCNT effects on environment. The increase in production of SWCNTs results in pollution risks of environment. However, with detailed studies of SWCNT chemical properties, they can be useful for agriculture. Applications in biotechnology need studies on toxicity of SWCNTs on plants.

Author Contributions: M. V. K. –writing.

Data Availability Statement: The data are available on request from the author.

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Conflicts of Interest: The authors declare no conflict of interest.

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