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Proceeding Paper

Chemical Properties of Metallocene-Filled Carbon Nanotubes to Tailor Toxicity in Plants †

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Abstract: Metallocenes are toxic chemicals that are used for the growth of carbon nanotubes (CNTs). The study of the 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. Toxicity studies are influenced by the investigation of the growth processes of metallocene-filled carbon nanotubes, the evaporation of metals, and the 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 the various methods discussed here, including solution methods and gas-phase methods, each differing in methodology and requiring optimization. Many authors have published different methods of filling carbon nanotubes with metallocenes. They lead to high-filling ratios and allow future modifications of the electronic properties of carbon nanotubes. The kinetics of carbon nanotube growth are investigated with different methods. Environmental transmission electron microscopy is applied to studies with a time resolution of several nanoseconds. Here, we use Raman spectroscopy to study the growth process, which is revealed to have activation energies, growth rates, and 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 the larger diameter of inner CNTs. The growth temperature increases for ferrocene compared to nickelocene and cobaltocene. With X-ray photoelectron spectroscopy, we show that the heating of metallocene-filled SWCNTs at 360–600 °C causes the n-doping of SWCNTs. 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 to 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 the growth kinetics of CNTs with metallocenes as catalysts is important [10–16]. Second, the analysis of chemical reactions of metallocenes in CNTs is needed. Third, investigations into the electronic structure of CNTs are important. Regarding the first issue, the activation energies and growth rates of CNTs depend on the metallocene-type. 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 [17]. Regarding the third issue, the investigations of the physics of metallocene-filled CNTs upon annealing are important, as doping effects influence the chemistry of molecules [18].

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

2. Experimental Section

I sealed the pre-opened SWCNTs with a diameter of 1.7 nm and metallocene powders (nickelocene, cobaltocene, or ferrocene, Aldrich, Darmstadt, Germany, 99.999%) inside a glass Pyrex glass tube under an 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 the morphology of filled CNTs was performed using the JEOL JEM2100 microscope. The accelerating voltage was 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 were tunable ArKr (with wavelengths of 458–568 nm and 647 nm) and HeNe (with wavelengths of 633 nm). The measurements were performed in the low-resolution mode (600 mm^{-1} grid) and high-resolution mode (1800 mm^{-1} grid). The measurements were conducted on CNT buckypapers.

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

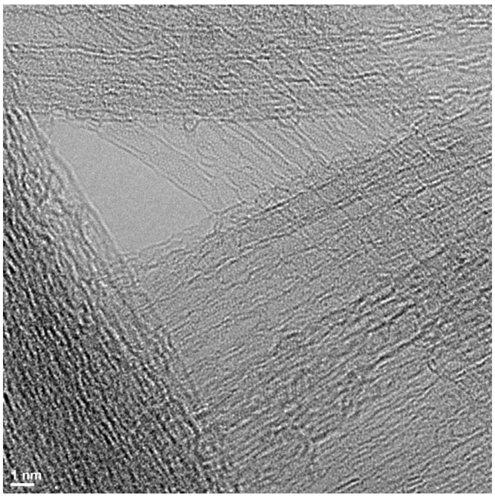

Figure 1. The HRTEM image of nickelocene-filled CNTs annealed at 900 °C for 2 h.

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

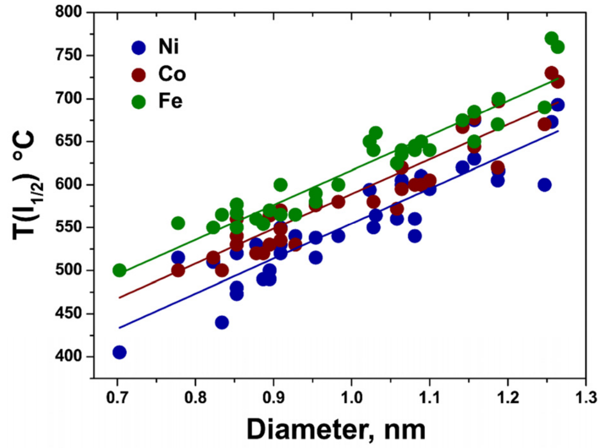

Figure 2. The growth temperature of nickelocene, cobaltocene, and ferrocene-filled SWCNTs was plotted versus the inner tube diameter.

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 the n-doping of SWCNTs. The heating of filled SWCNTs at higher temperatures results in the p-doping of SWCNTs. As the chemical reaction of metallocenes influences the electronic properties of SWCNTs, heating is a valuable method to tailor the toxicity.

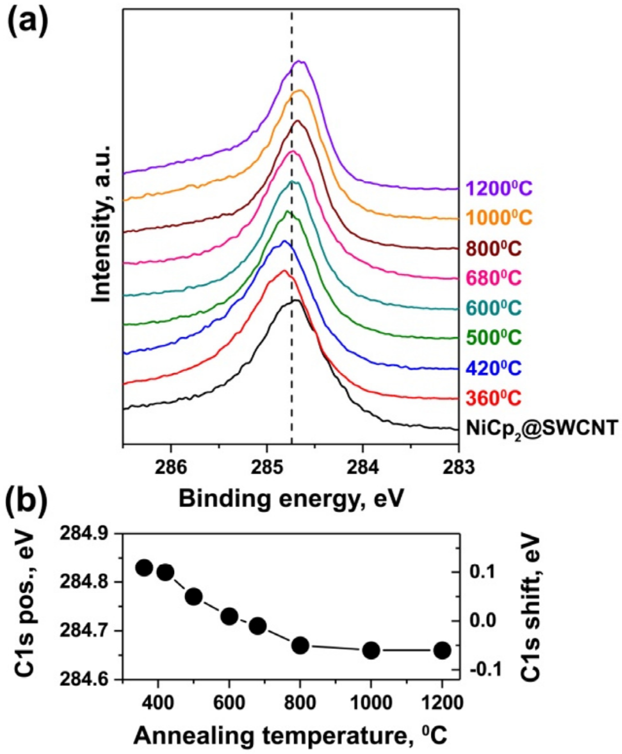

Figure 3. (**a**) The dependence of the electronic properties of nickelocene−filled SWCNTs on annealing temperature. (**b**) The plot of C 1s XPS position against annealing temperature.

4. Conclusions

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

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