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Proceeding Paper

Raman Spectroscopy, and Angle-Resolved Photoemission Spectroscopy of Metallicity Sorted Nickelocene-Filled Single-Walled Carbon Nanotubes †

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Abstract: In this work, we measured Raman spectra, and angle-resolved photoemission spectra of metallicity sorted nickelocene-filled single-walled carbon nanotubes (SWCNTs). Raman spectroscopy proves the filling of SWCNTs, and the formation of inner nanotubes in the annealed samples. For semiconducting, and metallic SWCNTs, the varieties of chemical state differences for elements were found under takeoff different angles in XPS.

Keywords: angle-resolved photoemission spectroscopy; carbon nanotube; nickelocene; filling; electronic properties; doping; Raman spectroscopy

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) have unique chemical, and physical properties, and they can be applied in different fields, such as nanoelectronics, catalysis, sensors, spintronics, thermoelectric power generation, light emission, solar cells, biomedicine [1–4]. The atomic structure of SWCNTs defines their electronic properties. Depending on chiral vector, SWCNTs can have metallic, or semiconducting conductivity type. The metallicity sorting, and synthesis of nanotubes with defined conductivity type are needed for applications [5–9]. This improves work parameters of devices, and increases the efficiency of devices.

The filling of SWCNTs is other way of controllable modification of their properties. The SWCNTs are filled with electron donor (n-dopant), and electron acceptor (p-dopant) to achieve the doping [10–12]. The charge transfer can also be controlled by thermal treatment of molecule-filled SWCNTs. It was shown that annealing of filled SWCNTs leads to p- or n-doping depending on temperature of annealing. The values of charge transfer, their dependence on the tube diameter, and molecule type were calculated, and charge transfer in ferrocene, and nickelocene-filled SWCNTs were compared [13]. The dependence of charge transfer on the tube diameter, and metallicity type is discussed in Refs. [14–18].

In this work, we performed the angle-resolved photoemission spectroscopy (ARPES) studies of metallicity sorted nickelocene-filled SWCNTs. The filled SWCNTs were sorted by the density gradient ultacentrifugation (DGU). We revealed the dependence of photoemission response on the electron takeoff angle. While metallicity-mixed and metallic DWCNTs show an increase of C-O groups at the surface, such a behavior could not be found for semiconducting DWCNTs.

2. Experimental

The 1.6 nm-diameter SWCNTs were filled with nickelocene by the gas phase method. The filled SWCNTs were sorted by the density gradient ultracentrifugation method (DGU) to metallic, and semiconducting SWCNTs. The samples were annealed in vacuum at temperatures of 900 °C which creates DWCNT with Ni still present, and 1200 °C where Ni is removed. The filled SWCNTs were investigated by Raman spectroscopy, and ARPES. The ARPES experiments were conducted under different angles.

3. Results

The Raman spectra of sorted nickelocene-filled SWCNTs prove the filling of SWCNTs, and the formation of inner nanotubes in the annealed samples.

The spectra of ARPES measured at different angles result in different surface sensitivity, where large angles (from sample surface normal) are more surface sensitive. The most obvious differences are in relative content of oxygen, i.e., differences in C/O ratio. Table 1 shows the results of quantification from overview spectra. Oxygen is mostly found close to the CNT surface, e.g., C/O decreases with increasing surface sensitivity. However, this behavior can only be detected for metallicity mixed and metallic CNTs, whereas semiconducting CNTs do not show any significant oxygen signal. C 1s spectra can be deconvoluted into four components, which correspond to carbon nanotubes (sp^2 carbon, C NT), C-H, C-O, and carbon shake-up (C pi-pi*). A comparison of C 1s data taken at high and low surface sensitivity (Figure 1) shows that C-O is significantly increase at the samples surface for metallicty-mixed and metallic CNTs, while the increase is very small for semiconducting CNTs.

Table 1. The results of quantification from overview spectra.

Sample *	Element (at. %)		C/O
	C	O	
$NiCp_2$@SWCNT 27°	96.3	3.7	26
$NiCp_2$@SWCNT 75°	93.7	6.3	15
$sNiCp_2$@SWCNT 27°	>98	<2	>44
$sNiCp_2$@SWCNT 75°	>98	<2	>44
$mNiCp_2$@SWCNT 27°	96.0	4.0	24
$mNiCp_2$@SWCNT 75°	83.9	16.1	5

* $NiCp_2$@SWCNT = nickelocene-filled mixed-metallicity SWCNTs, $sNiCp_2$@SWCNT = semiconducting $NiCp_2$-filled SWCNTs, $mNiCp_2$@SWCNT = metallic $NiCp_2$-filled SWCNTs.

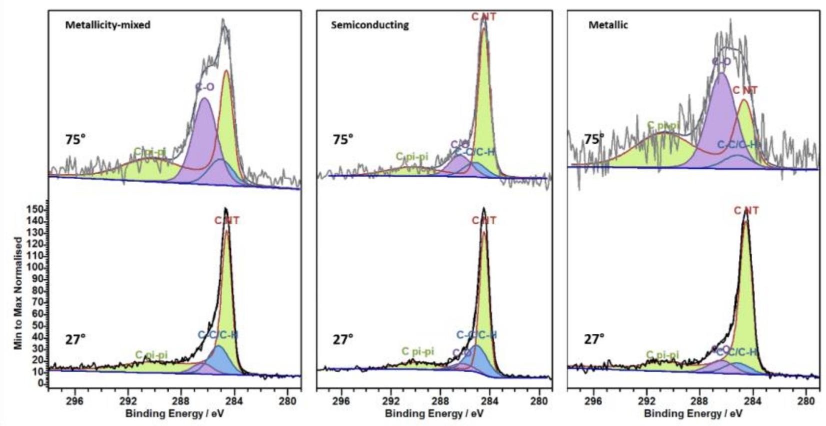

Figure 1. The ARPES spectra of metallicity mixed, sorted semiconducting, and sorted metallic nickelocene-filled SWCNTs obtained at 27° and 75°. The spectra are fitted with individual components. The assignments are denoted, as described in the text.

4. Conclusions

We measured ARPES spectra of metallicity- sorted filled SWCNTs. It was shown that there are different chemical states of elements, which are revealed at different angles. The annealing of sorted filled SWCNTs leads to evaporation of nickel, and growth of inner SWCNTs, with the formation of DWCNTs. Thus, the thermal treatment cares the chemical states of filler inside SWCNTs, and DWCNTs, and this can be revealed by ARPES. Metallicity-mixed and metallic DWCNTs show an improved C-O groups at the surface, whereas such a trend is not found in semiconducting DWCNTs. Please see further details in our paper.

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