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Optical microspectroscopy study on enriched (11,10) SWCNTs encapsulating C_{60} fullerene molecules

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ABSTRACT

The interaction between C_{60} fullerene molecules and single-chirality (11,10) single-walled carbon nanotubes (SWCNTs) is demonstrated by probing the optical transitions in (11,10) peapods by optical microspectroscopy. The results of the (11,10) SWCNTs and (11,10) peapods are compared to multi-chirality SWCNTs and peapods. The absence of the fine structure of the absorption bands in the case of (11,10) SWCNTs in comparison to multi-chirality SWCNTs demonstrates that the (11,10) SWCNTs provide a well-defined environment for studying the interaction between the encapsulated C_{60} molecules and the nanotubes. As compared to (11,10) SWCNTs, the absorption bands in (11,10) peapods show a large red shift and a reduction of the spectral weight. These findings suggest that the filling of the (11,10) SWCNTs with C_{60} molecules increases the internal dielectric constant and induces a charge transfer between the SWCNTs and the encapsulated C_{60} molecules. For testing the effect of the internal dielectric constant and charge transfer on the optical properties of the (11,10) SWCNTs, the (11,10) peapods were transformed to double-walled carbon nanotubes (DWCNTs) using the laser irradiation method. The transformation of the encapsulated fullerene molecules into inner wall reduces the environmental dielectric constant as well as the charge transfer from the outer tube.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], carbon nanotubes stimulate the scientists' curiosity to explore their unusual properties. Single-walled carbon nanotubes (SWCNTs) exhibit exceptional optical, electronic, and mechanical properties, which can be modified by strain, pressure or doping. Their robust mechanical properties are due to the strong sp^2 covalent bonds between the carbon atoms network [2].

As far back as more than fifteen years ago, great achievements have been taken in their synthesis, purification, and explanation of their fundamental physical and chemical properties. Important steps have been taken towards realistic and practical applications of SWCNTs, such as nano-electronics, opto-electronics, energy storage devices, flexible electrodes, nano-composites, and sensors [3]. Therefore, several attempts have been made to tailor their electronic properties, such as chemisorption and physisorption of atoms on the SWCNTs outer surface, substitution of carbon atoms, intercalation of the nanotubes bundles with atoms or molecules, and filling of the nanotubes' inner cavity [4,5]. Among others, filling is attracting great interest. Due to the tubular structure of SWCNTs, they can be filled with various species: metals, metal halides, organic, organometallic compounds, and other substances [5–8]. With this large variety of different fillers, it is possible to fine tune the electronic and transport properties of SWCNTs [7,8].

For example, C_{60} fullerene molecules can be encapsulated in SWCNTs to form a linear chain of fullerene molecules, so-called peapods [9,10]. Encapsulating fullerene and metallofullerene molecules changes the transport properties of the SWCNTs: Scanning tunnelling spectroscopy studies show that the SWCNTs' band gap is modified at the sites where the C_{60} fullerene molecules reside [11,12] and the *p*-type SWCNTs field-effect transistor was changed to be ambipolar by encapsulating $Gd@C_{82}$ metallofullerene molecules [13]. Therefore, it is particularly important to understand the reaction mechanism between the encapsulated fullerene molecules and the SWCNTs. The encapsulation of the C_{60} fullerene molecules in SWCNTs can be discussed in terms of stabilization energy. For SWCNTs with diameter $d_t < 1.2$ nm the interaction between

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nanotubes and C_{60} molecules is endothermic and the formed peapods system is unstable; whereas the interaction is exothermic for the large SWCNTs diameters d ≈ 1.2–1.6 nm and the formed peapods system is stable [14].

Theoretical studies [15,16] predicted that at a critical tube diameter of $d_t \geq 1.37\ nm$ the unoccupied t_{1u} orbitals of the C_{60} fullerene molecules hybridize with the nearly free electron state (NFE) of the SWCNTs. The NFE state is located between the nanotube and the C_{60} molecule and works as an electron acceptor state [15]. Therefore, the hybridization decreases the electronic density in the vicinity of the SWCNTs, and hence the effective tube diameter of the SWCNTs decreases [15–17].

Optical spectroscopy measurements [18–21] on C_{60}-peapods revealed red and blue shifts of the absorption bands in C_{60}@SWCNTs peapods ($\approx \pm 15$ meV) compared to empty SWCNTs with average tube diameter of 1.37–1.5 nm. Also photoluminescence (PL) measurements [22,23] on C_{60}-peapods over a wide range of diameters (≈ 1.22–1.5 nm) found a change in the band gap of the SWCNTs with the C_{60} fullerene filling, where the band gap modifies in a "$2n+m$" family type-dependent manner: $\Delta E_{11} < 0$ and $\Delta E_{22} > 0$ for type I $mod[(2n+m,3) = 1]$ and $\Delta E_{11} > 0$ and $\Delta E_{22} < 0$ for type II $mod[(2n+m,3) = 2]$. The absorption bands E_{ii} correspond to the ith optical transition in the SWCNTs. For SWCNTs with average tube diameter of 1.37–1.5 nm, the maximum change of the band gap was around $\approx \pm 20$ meV.

All the previous SWCNTs samples used for the preparation of the C_{60}-peapods were of multi-chirality character, which prevented a detailed understanding of the interaction between the nanotubes and the fullerene molecules. Single chirality SWCNTs have unique electronic properties and diameter. Therefore, they are ideal candidates for the encapsulation of C_{60} molecules, in order to understand the interaction mechanism between the nanotube and the fullerene molecules. This would potentially open the door to control the chemical and physical properties of SWCNTs, in order to implement such nanostructures in electronic devices.

Here, we report on the preparation of high-yield enriched (11,10) SWCNTs encapsulating C_{60} fullerene molecules, so called (11,10)-peapods, and also the preparation of DWCNTs derived from the (11,10)-peapods. Raman spectroscopy is used to prove the formation of inner wall inside the (11,10) SWCNT. Optical microspectroscopy is applied to study the effect of the interaction between the fillers (C_{60} fullerene molecules, inner tube) and the (11,10) SWCNT on the electronic properties.

In general, optical and infrared microspectroscopy is a powerful technique to characterize the electronic band structure in terms of the energy position and spectral weight of the excited interband and intraband transitions. As demonstrated recently, the optical response is capable of monitoring small changes in the electronic band structure of SWCNTs.

2. Experimental

The single chirality (11,10) SWCNTs (1.44 nm diameter) were prepared using two purification approaches with Cesium chloride (CsCl) sorting and metal-semiconducting (MS) sorting by usual density-gradient ultracentrifugation. The detailed preparation method is described in Ref. [24] The fraction containing the (11,10) SWCNTs was extracted carefully from the top of the centrifugation tube. Vacuum filtration method was used to prepare bucky-paper from the (11,10) SWCNTs over cellulose nitrate substrate. A small piece of the (11,10) SWCNTs film was transferred in an acetone bath. The free standing film was fished by using a stainless steel substrate with many holes in the middle (see Fig. 1 a–c for illustration).

Bundled multi-chirality SWCNTs were purchased from Carbon Solutions Inc. (Type P2, average diameter 1.4 nm). The P2 carbon nanotubes were prepared using the arc discharge method. The received P2 carbon nanotubes sample was purified by the supplier to >90% carbon content purity. The sample was used without any further purification process. Vacuum filtration was used to prepare bucky-paper multi-chirality SWCNTs over cellulose nitrate substrate from Triton X-100 suspension. The above described procedure (shown in Fig. 1 a–c) has been applied to prepare free-standing films of P2 SWCNTs for optical spectroscopy measurements.

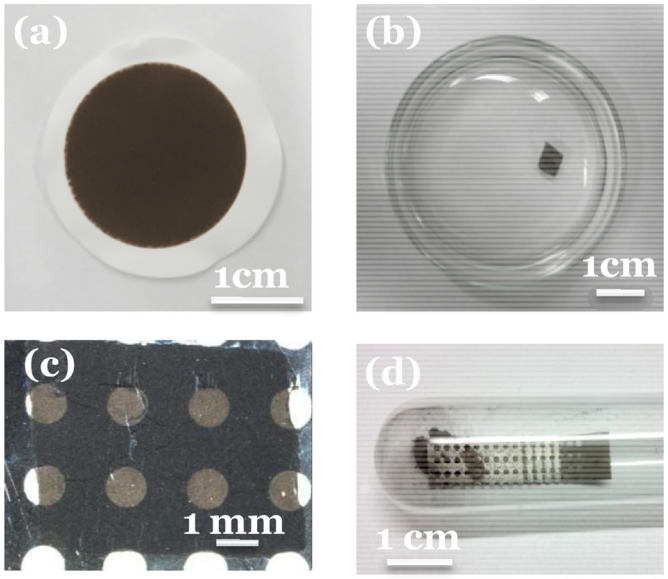

Fig. 1. (a) Photograph of the (11,10) SWCNT bucky paper. (b) Free-standing carbon nanotube film floating in acetone solution after dissolution of the cellulose nitrate membrane in the acetone solution. (c) Optical image of the free-standing film over stainless steel substrate. (d) Optical image of the closed evacuated quartz tube containing the (11,10) SWCNT free-standing film over stainless steel substrate and C_{60} powder. (A colour version of this figure can be viewed online.)

The C_{60} peapods were prepared by the gas phase method using the (11,10) SWCNT film prepared as described above [19,25]. The typical preparation method is as follows: the caps of the SWCNTs were opened by heating the SWCNTs film over the stainless steel substrate in a furnace at 575 °C for 30 min. This process is important to ensure that all the caps are opened and to remove any residuals of amorphous carbon that could be attached to the surface of the SWCNTs. Weighted amount of C_{60} fullerene powder and the (11,10) SWCNT film were degassed under dynamic vacuum at 200 °C for 24 h; after that both samples were sealed in quartz tube under vacuum and heated at 750 °C for 5 days continuously (see Fig. 1 d). To remove the non-reacted fullerene molecules from the surface of the (11,10) SWCNTs, the sample was heated at 700 °C under dynamic vacuum for 2 h [26,27]. The filling of the (11,10) SWCNT film with C_{60} molecules enables to measure the change of the optical properties due to the fullerene filling in a quantitative way. Based on our previous work [19,28] and literature data [29,30] on C_{60} peapods prepared by the gas phase method we can estimate the filling ratio to be higher than 95%.

Transmission data were collected at ambient conditions in the frequency range 2500–23,000 cm^{-1} using a Bruker IFS 66v/S Fourier transform infrared spectrometer in combination with an infrared microscope (Bruker IR Scope II) with a 15× magnification objective. The intensity $I_{sample}(\omega)$ of the radiation transmitted through the free-standing film and the intensity $I_{ref}(\omega)$ of the radiation transmitted through air, as reference, were measured. From $I_{sample}(\omega)$ and $I_{ref}(\omega)$ the transmittance and absorbance spectra were