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Electronic coupling in fullerene-doped semiconducting carbon nanotubes probed by Raman spectroscopy and electronic transport

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ABSTRACT

We investigate the electronic properties of individual fullerene peapods by combining micro-Raman spectroscopy and (magneto)-transport measurements on the same devices. We bring evidence that the encapsulated C₆₀ molecules strongly modify the electronic band structure of semiconducting nanotubes in the vicinity of the charge neutrality point, including a rigid shift and a partial filling of the energy gap. Using a selective UV excitation of the fullerenes, we demonstrate that the electronic coupling between the contained C₆₀ molecules and the containing carbon nanotube is strongly modified by the partial coalescence of the C₆₀ and their distribution inside the tube. Our experimental results are supported by both numerical simulations of the Density of States and the measured conductance of carbon nanotubes with coalesced fullerenes inside.

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1. Introduction

The encapsulation of various molecules inside carbon nanotubes (CNTs) constitutes promising routes to the engineering of the physical properties of CNTs [1,2]. Among the wide variety of filled CNTs, peapods – i.e., fullerenes encapsulated in single-walled CNTs (SWCNTs) – represent a pioneer hybrid structure discovered in 1998 [3]. Since then, their electronic structures have been subjected to intense and controversial theoretical studies [4–15] together with a limited number of experimental realizations [16–18].

The strength of the hybridization of the C₆₀ states (including the highest occupied and the lowest unoccupied molecu-

lar orbital, HOMO and LUMO) with the CNT band structures depends in a complex manner on the tube radius and helicity [8,13,14], on the fullerene distribution inside the tube [14] and on their orientation with respect to the tube axis [13]. An endothermic encapsulation process is commonly simulated for nanotube diameters smaller than 1.1 nm [4,8,10,13]. Larger diameters go along with an exothermic encapsulation, a decreasing electron charge transfer from the CNT to the C₆₀s, a narrowing of the derived bands from the C₆₀ chain and a reduction of their mixing with that of the containing CNT [8,10,13].

As far as the electronic transport of an individual peapod is concerned, the major parameters driving the current flow

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are the rigid shift of the CNT band structure due to charge transfer and the formation of extra bands in the vicinity of the Fermi energy E_F originating from the molecular orbitals of the C_{60} . Using Density Functional Theory (DFT), pioneer calculations involving the coupling with nearly free electron states of an armchair CNT predict multi-carrier states at the charge neutrality point [4,8,10]. However, more recent simulations state that the LUMO (t_{1u}) remains above E_F [13]. For a semiconducting CNT, the contribution of the t_{1u} orbital depends on the azimuthal symmetry of the tube states and goes decreasing with the tube diameter. In any case, these states form a weakly dispersive band within the energy gap of the CNT or in the conduction band [7,8,13,15]. Last but not least, these theoretical predictions suggest that the strength of the hybridization has to be weak for exothermic encapsulation, preserving the metallic or semiconducting nature of the host CNT.

Experimental characterizations of peapod band structures remain unfortunately puzzling. Early Scanning Tunnel Microscopy experiments demonstrated that the encapsulated C_{60} strongly modify the electronic structure far from the Fermi level [16] while photoemission spectroscopy performed on C_{60} @SWCNTs did not confirm the presence of extra bands crossing the Fermi energy [17]. On the other hand, photoluminescence spectroscopy unveiled shifts in optical transition energies attributed to the local strain and the hybridization between the C_{60} states and that of the nanotube [17]. Complementary electronic transport experiments on individual peapods in the Coulomb blockade regime are also suitable to probe the electronic states close to the Fermi energy: while pioneer experiments gave evidence of highly regular quantum dots, identical to those obtained with defect-free and empty SWCNTs [19,20], more recent results unveiled anomalous resonance states attributed to the encapsulation of short – instead of long range – C_{60} chains inside the tube [21,22]. These disparate results suffer from a lack of structural characterization of the encapsulating tubes and remain hardly comparable to electronic structure simulations.

In this paper, we address the issue of the energy band structure of peapods through electronic transport and micro-Raman spectroscopy performed on the same and individual peapods. Our results suggest that the C_{60} induce a profound modification of the energy spectrum of the semiconducting external tube in the vicinity of the charge neutrality point. The experiments are consistently described by both numerical simulations of the Density of States and the conductance of the peapods. Finally, on the very same devices, we investigate the effects on the electronic properties of a partial coalescence of C_{60} induced by UV irradiation.

2. Experimental section and computational details

SWCNTs are produced by arc discharge and obtained from NANOCARBLAB. Based on transmission electron microscopy (TEM) study, the as-received material contains ~70–80% SWCNTs, a majority of which exhibit diameters in the range 1.4–1.6 nm, and ~20% carbon impurities (mostly multi-walled shells). The material is already ready for filling thanks to the

highly oxidising treatments (which include nitric acid treatment) carried-out by the supplier for purification purpose. Both the as-received SWCNT material powder and fullerite powder are then put into a quartz tube sealed after degassing during 2 h at 200 °C under dynamic primary vacuum. The content in fullerite powder is adjusted so that to be in excess with respect to the amount needed to fill up 100% of the SWCNTs, and to develop a partial vapour pressure between 1 and 2 bars once filling conditions are reached. Peapods are subsequently prepared by the well-known sublimation method, i.e., by heating up the sealed quartz tube at 500 °C for 24 h. After the quartz tube is cooled down ballistically, it is opened and subjected to a 800 °C heat-treatment under dynamic primary vacuum to remove all the excess (not inserted) fullerene molecules. This technique ensures a ~85–90% filling rate of the SWCNTs with C_{60} molecules as assessed by transmission electron microscopy (Fig. 1) and as once quantified by X-ray diffraction studies [23]. Peapods dispersed in water solution with sodium dodecyl sulfate (SDS) surfactant are deposited on a Si/SiO₂ (150 nm) wafer and individually connected with Pt electrodes using the standard electron lithography technique. Prior to the thermal deposition of the metal electrodes, the polymethylmethacrylate (PMMA) resist is developed by a methyl isobutyl ketone (MIBK) + isopropyl alcohol (IPA) solution. The distance between the electrodes is 300 nm. After the metallisation, the wafer surface is rinsed with a mixture of acetone and ethanol so that the SDS is completely removed from the peapod surface. Rapid thermal annealing is performed at 300 °C in a H₂/N₂ gas mixture to improve the contact transparency.

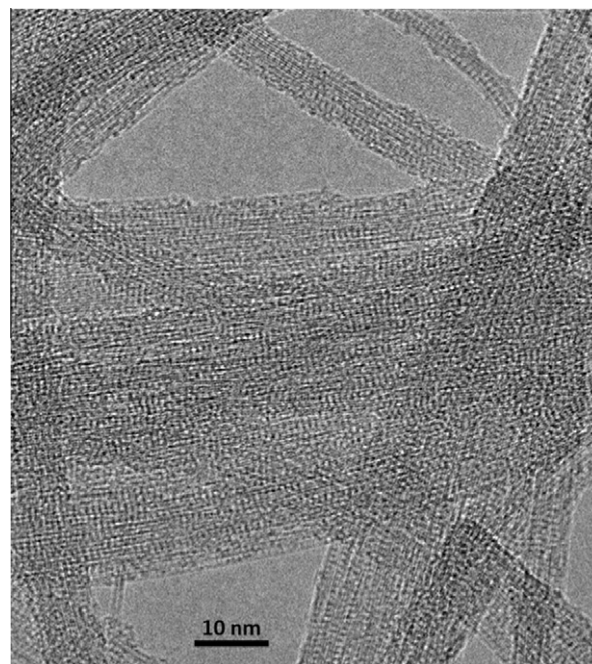


Fig. 1 – Example of the peapod material obtained using the procedure described in the Section 2 (before adjunction of SDS and solubilisation), as seen by medium-range magnification TEM. The dotted aspect is due to the encapsulated fullerene molecules.

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