

# Raman response from double-wall carbon nanotubes based on metallicity selected host SWCNTs

F. Simon<sup>\*1</sup>, C. Kramberger<sup>1</sup>, H. Peterlik<sup>1</sup>, R. Pfeiffer<sup>1</sup>, K. De Blauwe<sup>1</sup>, T. Pichler<sup>1</sup>, H. Kuzmany<sup>1</sup>, K. Yanagi<sup>2</sup>, Y. Miyata<sup>3</sup>, and H. Kataura<sup>4,5</sup>

<sup>1</sup>Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria

<sup>2</sup>Department of Physics, Tokyo Metropolitan University, Tokyo, Japan

<sup>3</sup>Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

<sup>4</sup>Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8562, Japan

<sup>5</sup>CREST, JST, Japan

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\* Corresponding author: e-mail ferenc.simon@univie.ac.at, Phone: +43 1 42 77 51378; Fax: +43 1 42 77 51375

We studied SWCNTs and derivatives separated according to their metallicity using X-ray diffractometry, optical absorption, and Raman spectroscopy. The X-ray study evidences a complete absence of graphite and metal catalysts. Optical absorption shows that the metallic sample is of high purity, however, a small amount of metallic tubes are present in the

semiconducting sample. We synthesized double-wall carbon nanotubes from the separated SWCNTs by filling-in C<sub>60</sub>'s and heating these samples. The Raman spectra of the inner tubes are markedly distinct in the two types of samples and also allows to characterize the efficiency of the separation.

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**1 Introduction** A general shortcoming for the applications and description of theoretical phenomena in SWCNTs, is the mixed metallicity nature of as-prepared samples. The breakthrough to the separation efforts was provided by the density-gradient ultracentrifugation (DGU) method developed by Arnold et al. [1], which provided a reliable and upscalable method in contrast to previous efforts [2, 3].

The DGU method [1] uses a mixture of reagents which are attaching with a different affinity to the SWCNTs depending on their metallicity. The resulting “dressed” nanotubes are therefore differ in their mass and chemical exterior. Thus they can be then separated by ultracentrifugation in a density-gradient medium. The original procedure was developed for SWCNTs grown with the CoMoCAT [4] and for laser-ablation prepared SWCNTs. The procedure was improved and extended to SWCNTs produced by other methods [5], and to other DGU media [6].

The importance of SWCNTs separated according to their metallicity lies in the possibility to prepare, e.g., transparent conducting electrodes [7]. In addition, these samples have

helped to clarify fundamental phenomena, as e.g., they enabled to study the dimensional cross-over from Tomonaga–Luttinger liquid to Fermi liquid in a fully metallic bundle [8].

Characterization methods for the level of separation include optical absorption spectroscopy [1, 9] and high resolution (HR), aberration corrected transmission electron spectroscopy [6]. Fluorescent spectroscopy [10] can not be used for this purpose as the metallic SWCNTs do not display a luminescence signal. A possibility to study chirality distribution [11, 12] in SWCNTs is resonance Raman spectroscopy. In particular, most reports focused on the study of small diameter SWCNTs (mean diameters around and below 1 nm) where the radial breathing mode (RBM) Raman region contains well resolved peaks due to its inversely diameter-dependent Raman shift. The first resonance Raman study on the separated samples indicated a chirality selective enrichment for a HiPco SWCNT sample [13]. This method, however, does not provide the required spectral resolution for larger diameter tubes (above 1.3 nm) as the Raman modes are strongly overlapping.

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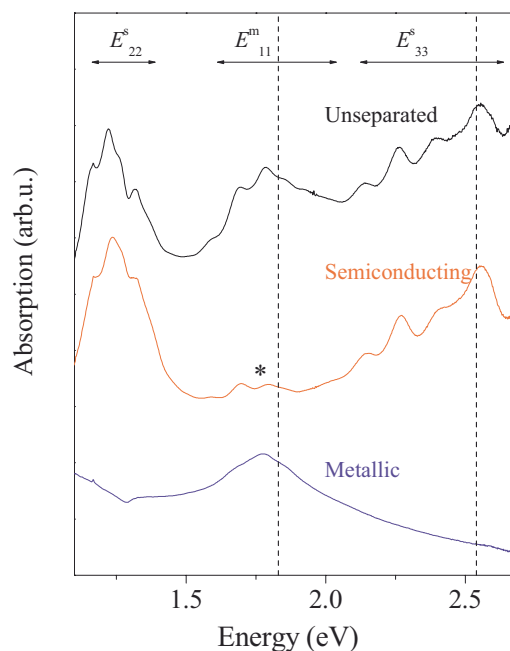
Characterization of such nanotubes is on the other hand of great importance for their application.

A possibility to characterize the diameter and chirality distribution of SWCNT samples with diameters above 1.3 nm with high spectral resolution is provided by the possibility to grow tubes inside from peapod precursors [14]. It was shown previously that the inner tubes in such double-wall carbon nanotubes (DWCNTs) (i) have narrow and well resolved RBM lines [15], (ii) mimic the diameter distribution of the host outer tubes [16], and (iii) even chirality selective assignment of the host outer tubes is possible [17].

Here, we report the synthesis of DWCNTs based on the SWCNT samples which are separated according to their metallicity. We present a characterization of the starting SWCNT sample using X-ray, optical absorption, and Raman spectroscopy. Preliminary resonance Raman results are presented on the inner tubes in these samples which confirm the high level of separation of the starting materials.

**2 Experimental** Arc-discharge prepared SWCNTs based on Ni:Y catalyst with a mean diameter of 1.4 and 0.1 nm variance were prepared and purified by suspending and ultracentrifugation which results in a high purity material [18]. The separation was performed with the DGU method [1, 5]. The unseparated sample was treated equally as the ones containing nominally metallic and semiconducting nanotubes. Self supporting bucky-paper samples were prepared by a subsequent filtration of the suspensions. The SWCNTs were opened by heating in air at 400 °C for 10 min. C<sub>60</sub> peapods were prepared by sealing the SWCNT samples with C<sub>60</sub> in quartz ampoules under vacuum and by heating it at 650 °C for 2 h. A subsequent heating at 650 °C for 1 h under dynamic vacuum removes non-encapsulated fullerenes from the SWCNTs. DWCNTs were prepared from the peapods by a 2 h long annealing in dynamic vacuum at 1250 °C. We refer to the corresponding DWCNTs based on the three samples as *unseparated*, *metallic*, and *semiconducting* DWCNTs in the following.

The Raman spectra were recorded in the backscattering geometry at 90 K using a Dilor XY triple spectrometer equipped with a liquid N<sub>2</sub> cooled charge-coupled device detector. Some spectra were measured in HR which gives 0.5 cm<sup>-1</sup> resolution for red laser excitations. The spectra were obtained with different lasers such as an Ar/Kr, a Ti:sapphire, and a dye laser with Rhodamine 110, 6G and DCM Special, which gives excitation between 1.54 and 2.54 eV. In order to determine Raman cross-sections and to correct for the spectrometer and detector sensitivity, all spectra were normalized to the well-known cross-section for the Si F<sub>1g</sub> mode at 520.2 cm<sup>-1</sup>. Optical absorption spectroscopy was performed by dispersing the sample in sodium deoxycholate (DOC) by ultrasonication and the optical spectra were measured on a Bruker Vertex 80v optical spectrometer in transmission. The bucky-paper samples were studied by small-angle X-ray diffractometry with Cu K $\alpha$  radiation.

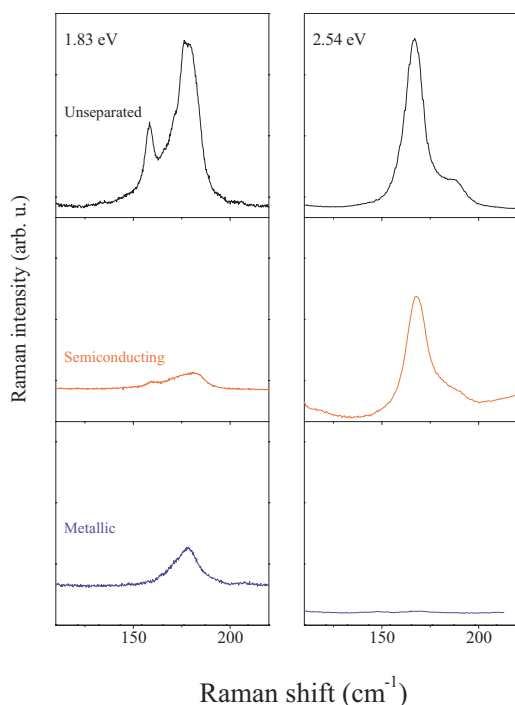


**Figure 1** (online color at: www.pss-b.com) Optical absorption spectra for the three different SWCNT materials. The apparent optical absorption ranges are indexed. Vertical dashed lines indicate the 1.83 and 2.54 eV energies where Raman results are reported. Note the absence of the  $E_{22}^s$  and  $E_{33}^s$  transitions in the metallic sample and the small residual  $E_{11}^m$  transition (marked with an asterisk) in the semiconducting sample.

**3 Results and discussion** The sample purity, and in particular the presence of residual catalyst particles and graphite can be well studied using X-ray diffractometry. It indicates (data not shown) a high level of purity for the three samples in agreement with previous reports [19]. In Fig. 1, we show the optical absorption spectra for the three different samples. For the unseparated sample, we observe the  $E_{22}^s$ ,  $E_{11}^m$ , and  $E_{33}^s$  optical transitions which are in the visible range for the 1.4 nm diameter tubes. For the separated samples, a clear absence of the semiconducting transitions is observed for the metallic sample, which attests the high level of purity (above 99%) of the metallic sample, in agreement with the previous reports [5]. For the semiconducting sample, some residual  $E_{11}^m$  transitions are observed (marked with an asterisk in Fig. 1), which indicates a purity of the semiconducting samples of 95%.

In Fig. 1, we indicate with vertical dashed lines the energy of two laser excitations where Raman spectroscopy was performed. At the lower energy, 1.83 eV (676 nm), metallic SWCNTs are in resonance, whereas for the larger, 2.54 eV (488 nm), the semiconducting SWCNTs are expected to dominate the Raman spectrum.

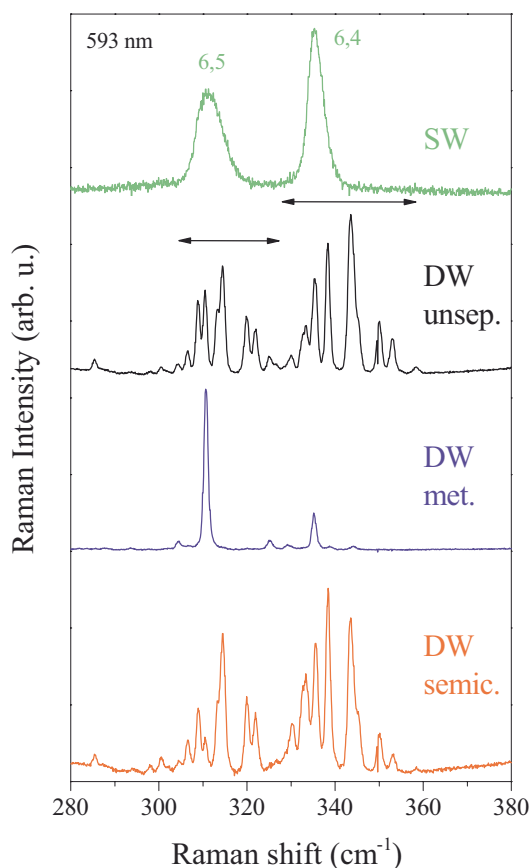
In Fig. 2, we show the RBM spectra for the three samples at these two different laser excitations. At 1.83 eV excitation, we observe a sizeable signal for the metallic sample in agreement with the expected resonance condition. The semiconducting sample shows a signal at this excitation



**Figure 2** (online color at: [www.pss-b.com](http://www.pss-b.com)) RBM spectra for the three different samples (before inner tube growth) at two different laser energies, 1.83 eV (676 nm) and 2.54 eV (488 nm). The Raman intensities are normalized to the laser power. Note the residual signal in the semiconducting sample at 1.83 eV and the absence of a Raman signal in the metallic sample at the 2.54 eV excitation. Different noise levels are due to different acquisition times.

which originates from the residual metallic nanotubes in this sample. For the 2.54 eV excitation, the metallic sample does not display a significant signal, whereas the semiconducting sample has a signal similar to the unseparated sample. These observations confirm the result of the optical absorption spectroscopy, i.e., a higher purity for the metallic sample, whereas the semiconducting sample contains residual metallic SWCNTs.

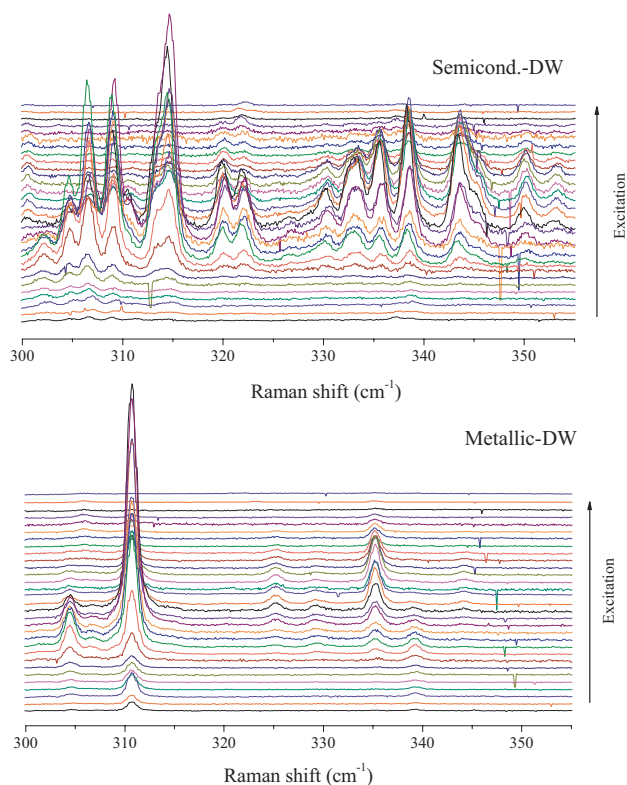
The growth of tubes inside the host SWCNTs in these samples provides additional information on the level of the separation and on their properties. In Fig. 3, we show the inner tube RBM range for the three samples. As reference, we show measurement for an SWCNT CoMoCAT sample. A large number of inner tube modes is observed for the unseparated DWCNT sample. This is due to the fact that an inner tube with a given chirality (e.g., the 6,5 tube) can grow in more than 10 different outer tubes with different diameters. The inner–outer tube interaction causes a splitting of the inner tube RBM spectra and results in the observed structure [17]. Importantly, there are much less visible modes in the metallic DWCNT sample. This is related to the fact that the number of possible outer tube chiralities is limited due to the simple 1:2 ratio of metallic to semiconducting SWCNT abundance.



**Figure 3** (online color at: [www.pss-b.com](http://www.pss-b.com)) High-resolution Raman spectra at 90 K and 593 nm laser excitation for a CoMoCAT SWCNT sample and for three DWCNT samples in the inner tube RBM range. The tube chiralities for the observed modes are given. Note the large number of narrow components for the unseparated DWCNT sample which originate from the same inner tube chirality embedded in outer tubes with different diameters. Also note the much less number of modes for the metallic SWCNT based inner tubes.

In Fig. 4, we show the resonance Raman spectra for the inner tubes inside the semiconducting and metallic outer tubes. The fact that fewer components are observed for the latter sample persists for all excitation energies, it is this not a mere resonance Raman artifact. This observation confirms the high level of separation in these samples, and in particular that the metallic sample is free from the semiconducting chiralities. Yet, we are not able to give a chirality specific identification for the corresponding outer tubes therefore we cannot confirm whether the reported chirality selective enrichment with preference for armchair or near armchair nanotubes [6, 13] is present or not in our samples.

**4 Summary** In summary, we prepared metallicity separated SWCNTs with the DGU method.  $C_{60}$  peapods and DWCNTs were prepared from these samples and studied by X-ray diffractometry, optical absorption, and Raman spectroscopy. These methods allow to characterize the purity



**Figure 4** (online color at: [www.pss-b.com](http://www.pss-b.com)) Resonance Raman spectra for the inner tubes (with high resolution) inside semiconducting and metallic host outer tubes. Note that there are fewer components for the metallic sample for all excitation energies.

and the level of separation in these samples. It is found that the metallic sample is of higher purity than the semiconducting one.

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