

Determination of the metallic/semiconducting character of Single-Wall Carbon Nanotubes by Electric Force Microscopy

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Single Wall Carbon Nanotubes (SWNTs) can either be metallic or semiconducting depending on their chirality and diameter [1-3]; but controlling this property and, therefore, optimizing their electrical response is a difficult task. For these reasons, it would be highly desirable to investigate the electric character of individual nanotubes.

Most of the studies regarding their electronic properties have addressed their conductivity and used transport measurements to distinguish metallic from semiconducting nanotubes. Less attention has been paid to their electrical response to polarization [4-5]. The present work brings a new perspective to the process of SWNTs polarization, where Electric Force Microscopy (EFM) data are analyzed through a model yielding distinct behaviors depending on the metallic/semiconducting character. Specifically, we find that metallic nanotubes present a uniform charge/polarization distribution during the EFM polarization, while semiconducting nanotubes present a non-uniform signal. Such “metal” or “semiconductor” labeling of SWNTs was further confirmed via Raman spectroscopy.

EFM is a dual-pass technique as shown in figure 1. During the first pass, the AFM topography image is recorded in intermittent-contact mode. Then, the probe is retracted from the surface to a fixed distance, a variable bias is applied between tip and sample, and scanning is repeated. During this process, an opposite image charge is induced in the nanotube. Therefore, changes on the cantilever oscillation frequency, due to changes on the tip-sample capacitance and/or sample charging/polarization, are collected to form the EFM image.

Figure 2 shows some typical EFM images, acquired from metallic (a) and semiconducting (c) SWNT, and their respective line profiles ((b) and (d)). A metallic SWNT shows a steady increase of the EFM signal (frequency shifts to more negative values) as the probe approaches the exact nanotube position (figs. 2a and 2b), creating a characteristic “V”- shaped line profile (fig 2 b). Semiconducting SWNTs, on the other hand, show a different EFM line profile: as the probe approaches the nanotube, the frequency also shifts to more negative values. However, when the probe is exactly on top of the nanotube, the EFM signal decreases (smaller frequency shifts), creating a “W”- shaped line profile (fig. 2 d).

The qualitative features in figure 2 can be explained by a phenomenological model: the polarization response of SWNTs depends on tip-sample distance, which depends on their longitudinal polarizability [4-5]. When the tip scans the surface, due to the long range of the electrical interaction, it polarizes the nanotube before being exactly above it. This happens for both metallic and semiconducting tubes and their longitudinal dielectric properties differentiate them. For a metallic tube, the high longitudinal dielectric constant screens the external field effectively and forms equal potential surfaces parallel to the axis (see insert of fig. 2b). For the semiconducting tube, screening of the external field is less effective and, when the tip is directly above the tube, localized bound charges accumulate below it (see insert of fig. 2d) [4]. Consequently, the voltage difference between the tip and the nanotube is larger in metallic tubes, which results in stronger attraction (larger frequency shifts).

The developed experimental procedure (EFM imaging of SWNTs to distinguish their electrical character) is quite simple, fast and precise, allowing accurate monitoring of the identification process. It does not require electrical contact to the nanotubes and, thus, is an attractive method for the characterization of any given SWNT on heterogeneous samples. In other words, the EFM response is a fingerprint univocally discriminating metallic from semiconducting SWNTs.

References:

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Acknowledgements: (optional)

The authors are thankful to A. S. Ferlauto for the sample growth and A. Jorio and J. S. Soares for the Raman measurements.

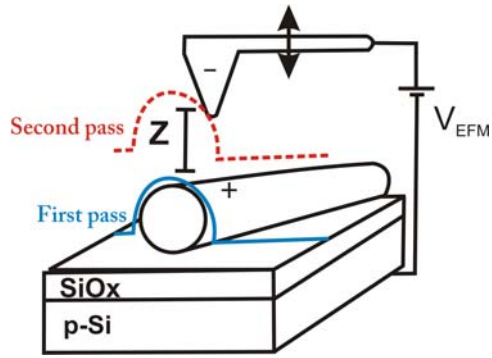


Figure 1 – The EFM experimental setup.

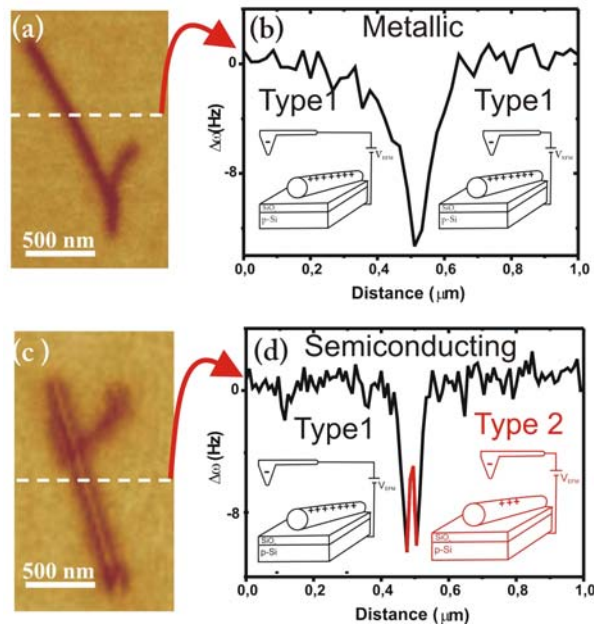


Figure 2 – EFM-based discrimination between metallic and semiconducting SWNTs. **a**, EFM image of a metallic nanotube and **b**, its respective profile showing the attractive signal of SWNT (“V”- shaped line profile). **c**, EFM image of the semiconducting nanotube and **d**, its respective line profile showing two regimes of attractive signal, forming a “W”- shaped profile.