CARBON 80 (2014) 50–58

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Low energy electrons focused by the image charge interaction in carbon nanotubes

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ARTICLE INFO

Article history:
Received 6 March 2014
Accepted 12 August 2014
Available online 23 August 2014

ABSTRACT

Electrons with energy in the range of a few eV are strongly affected by the interaction with the polarization charges they induce on a surface. This report shows how this effect is relevant for the data analysis of inverse photoemission spectroscopy (IPS) from carbon nanotube (CNT) arrays. IPS from CNTs exhibit two main resonances, located around 2.5 eV and 12.5 eV above the Fermi level. The intensity of the first resonance is dependent on the average tube diameter and the second one has a distinctive spectral shape, which is related to the graphitization level of the CNT external walls. In order to analyze the origin of these resonances, a phenomenological reconstruction of an IPS spectrum from a CNT collection was performed. This reconstruction successfully reproduces the spectral shape of the 12.5 eV resonance. However, the intensity is lower than the actual measurements in the initial energy range of the spectrum. The analysis of these results suggests that the additional intensity required to reproduce the experimental data, has its origin in an electronic focusing mechanism, induced by the CNT image charge potential. This effect is significant for low energy electrons and small diameter tubes.

1. Introduction

Carbon nanotubes (CNTs) have received a widespread attention due to their interesting physical properties [1] and the promising new applications in a variety of systems [2,3]. Precisely, the interaction of probe particles such as electrons or photons with CNTs and other graphene based nanostructures, is of current scientific interest due mainly to their potential applications in sensors and devices [4,5].

Electron spectroscopies have been widely used to examine the electronic structure of CNTs below the Fermi level (E_F) [6–12], however, there are only few experimental reports dealing with states above this energy level [2,11–13]. Some unoccupied electronic states, which are not linked to the band structure, are the image charge states [14]. These type of surface states in CNTs are generated by the interaction between an external electron and the polarization charges it induces on a nanotube [15,16]. Thus, this long range potential allows the formation of extended unoccupied electronic states around a CNT [17–19]. Additionally, as shown in sub-Section 3.1, when unbound electrons approach the vicinity of a nanotube, as they would in inverse photoemission spectroscopy (IPS), this attractive potential bends their trajectories inducing a focusing effect around the tubes.

This report presents results from a study of the unoccupied electronic states of single wall carbon nanotubes (SWCNTs) and multiple wall carbon nanotubes (MWCNTs) using IPS. Samples were prepared as non-oriented CNT

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http://dx.doi.org/10.1016/j.carbon.2014.08.023

collections, with well defined mean diameters and different levels of graphitization. Under electronic irradiation these samples emit photons by the optical decay of electrons between two originally unoccupied electronic states. Two main resonances in the intensity of the outgoing photons were detected in all CNT samples. A correlation between the intensity of the peak and the mean diameter of the tubes, was observed for the resonance at 2.5 eV above E_F. In Section 3, we discuss the evidence linking the focusing effect with an enhanced transition probability into the π^* bands. The enhancement is indeed significant for small CNT diameters and low energy incident electrons. In addition to this low energy peak, a wide resonance located close to 12.5 eV was also found. This feature has a distinctive spectral shape which can be correlated with the graphitization level of the CNTs. The origin of these two resonances has been elucidated by performing a phenomenological reconstruction of an IPS-CNT spectrum, based on measurements obtained from highly oriented pyrolytic graphite (HOPG).

2. Experimental

2.1. *Sample characterization*

For this study eight different CNT samples have been considered. Each one of them has been labeled with an acronym indicating some physical characteristics of the nanotubes they contain, and if it is the case, the treatment to which they have been subjected. In the rest of this section, we describe the microscopic structure of these samples with the purpose of correlating the IPS data with the main physical parameters of each sample.

Fig. 1 displays scanning electron microscopy (SEM) images and Fig. 2 shows transmission electron microscopy (TEM) images from the different samples. Fig. 1(a) is a side view of the "MWS50" sample which is formed by "**MW**CNTs" with a "**S**traight" profile and average diameter close to "50" nm (see Fig. 2(a) and (b)). They were synthesized by pyrolysis of Iron Phthalocyanine at 1000°C over a Si substrate [20]. These MWCNTs grow away from the substrate up to lengths close to 20 μm, however at the top of the sample the nanotubes bend laterally as shown in Fig. 1(b). The sample labeled as "MWS50-IM" was prepared by **I**on **M**illing of sample MWS50, with 1 keV argon ions during one hour. The ion current on the sample was 10 μA per cm^2. Under this dose the CNTs in the samples present extensive damage. Fig. 1(c) and (d) show the corresponding micrographs before and after the irradiation procedure.

Samples labeled as "MWH50" and "MWH10" contain CNTs synthesized by the catalytic decomposition of acetylene at 800 °C and 700 °C over Fe covered SiO_2 substrates [21]. Average diameters close to 50 nm and 10 nm were obtained for these tubes (see Fig. 2(c) and (e)). As shown in Fig. 1(e) and 1(g), the CNTs display the characteristic helical distortion common to many tubes grown from acetylene. Notice that letters "S" and "H", in the sample labels, have been used to describe the: "straight" or "helicoidal" shape of the MWCNTs.

A relevant characteristic of a wide diameter CNT is the degree of graphitization of their walls. TEM was used to

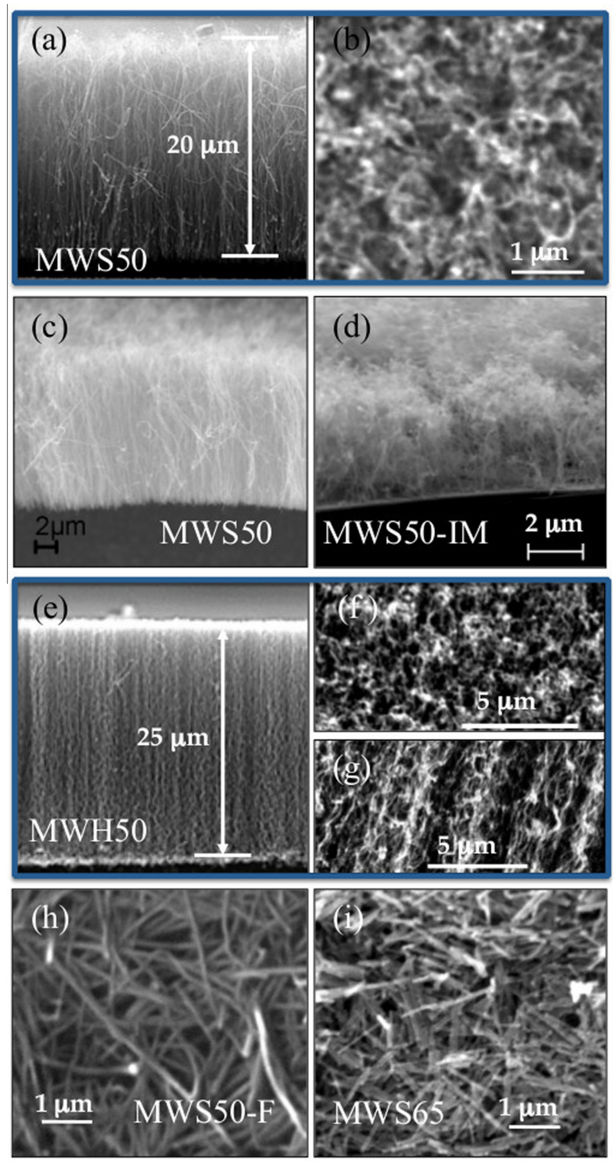

Fig. 1 – Scanning electron microscopy images of different samples used in the course of this study. (a) Is a side view and (b) is a top view image from the sample labeled as MWS50 (see text for sample labels). Images (c) and (d) are respectively 45 degree micrographs of the sample MWS50 before and after an ion milling treatment. Images (e) and (f) are a side and top views of sample MWH50. Image (g) corresponds to a magnified side view of the tubes contained in sample MWH50, where the helical character of the tubes is clearly distinguished. Image (h) is a top view of sample MWS50-F. The tubes were removed from the synthesis substrate and dispersed on a silicon chip. Image (i) corresponds to a top view of sample MWS65, see text for further details. (A color version of this figure can be viewed online.)

identify this feature together with the morphology of the CNTs and the corresponding average diameters of the tubes in each sample. As can be verified in the higher magnification images of Fig. 2, the sample labeled as MWS50 contain CNTs