Atomic Force Microscopy Characterization of Carbon Nanotubes

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Abstract. Carbon Nanotubes (CN) form a new class of materials that has attracted large interest in the scientific community because of their extraordinary properties (mechanical, electrical, thermal, etc.), as well as owing to the diversity of the proposed technological applications. The characterization of CN is the result of specific sample preparation procedures and requires the use of selected tools (e.g. SEM, HRTEM, EDX, Micro Raman, AFM, STM). We report some studies we carried out based on the CN characterization with the Atomic Force Microscopy (AFM). The general characteristics of the AFM employed and the sample preparation methods are illustrated. The research activities are focused on the development of specific analysis procedures. In fact, the interaction forces between the AFM cantilever tip and the sample, is the main parameter in the acquisition of a 3D topographic AFM micrograph.

1. Introduction
For several years now at INFN – LNF, we have been addressing various applications using carbon nanotubes and other nanomaterials. A major focus has been the synthesis and characterization of patterned films of aligned carbon nanotubes and comparing results obtained by different deposition methods [1,2]. We have focused on the optimization of the field emission properties of CNTs for the realization of electron sources [3]. Another key effort involves evaluation of the electrical and mechanical properties of CNT based composites for aerospace applications [4-8]. Our work includes composites based on CNTs and silica nanobeads for optical, biosensor and catalytic applications [9-11]. We are also studying the cytotoxicity of CNTs [12]. In addition to carbon nanotubes, nanotubes of aluminum nitride (AlN) have been synthesized through a DC arc plasma process and we characterized them by various techniques (see [13,14] and references therein).

The atomic force microscopy (AFM) is the most widely used instrument among recently introduced scanning probe microscopy (SPM) techniques. The widespread use of the AFM is attributed to the accurate three-dimensional reconstruction of the sample topography with atomic resolution for a relatively low cost and within a short time. Another important reason for using this characterization is that there is almost no restriction on the sample to be analysed. Many researchers use the AFM in different areas [15-18]. Semiconductors, biotechnology, life sciences, materials, and surface characterizations are typical applications. In most of the cases, the morphological study is the main purpose of the AFM, since the latter provides almost real three dimensional topographic information. Furthermore, the AFM data contain important information for structural analysis of the...
surface. For example, the AFM is considered a powerful tool for morphology analysis of nanoscale structures such as quantum dots (QDs).

Carbon Nanotubes (CN) form a new class of materials that has attracted large interest in the scientific community because of their extraordinary properties (mechanical, electrical, thermal, etc.). These nanotubes can be produced by a variety of techniques including carbon arc, laser ablation, chemical vapour deposition and carbon monoxide disproportionation. The as-produced material is known to be inhomogeneous and contain a variety of impurities including carbon-coated metal clusters, amorphous carbon, and other carbon compounds including fullerenes. The type and extent of these impurities change with the production method used. The production process also influences the length, diameter, chirality and surface moiety of the nanotubes (and nanotube bundles).

The characterization of CN requires the development of specific sample preparation procedures and the use of particular instruments (SEM, HRTEM, EDX, Micro Raman, AFM, STM). For each kind of analysis typology, it is possible to obtain specific data relative the morphology of the nanomaterial studied. This paper reports the authors’ studies of the CN characterization with the Atomic Force Microscopy (AFM). The general characteristics of the AFM employed and the sample preparation methods will be illustrated. The research activities will be focalized on the development of specific analysis procedures. In fact, the interaction forces between the AFM cantilever tip and the sample, is the fundamental parameter in the acquisition of a 3D topographic AFM micrograph. With different distance ($d$) between the above tip and sample, in the no contact mode, CN show different behaviors. For example below $d = 0.30 \mu m$ the above interaction forces can modify the CN (sample displacements, cutting, etc.) deposited on the substrate. In this case the AFM 3D topography cannot yield a good characterization of the analysed sample. Instead, increasing the value of $d$, the above interaction force is reduced, and it becomes possible to perform a complete CN characterization without the occurrence of the just mentioned problems. These research activities will be discussed and studied, in order to develop a reliable AFM analysis procedure for CN.

2. Experimental measurements and AFM characterization

The characterization of the AFM employed is illustrated in figs. 1÷3

Figure 1. AFM microscopy employed to the carbon nanotubes characterization.

Figure 2. AFM microscopy characteristics.

Figure 3. AFM microscopy characteristics.

Using the carbon nanotubes (CN), synthesized by the research group of Dr. Stefano Bellucci (INFN – Istituto Nazionale di Fisica Nucleare, LNF – Laboratori Nazionali di Frascati, Laboratory of nanotechnology, NEXT-MINCE Project) [1,2], various AFM analyses have been performed [3].

The following sample preparation procedure has been followed:
- mechanical removal of the CN from the electrode of graphite
- ultrasound treatment in alcohol for 20 minutes
- deposition of the CN on a silicon substrate
- cooling for 3±4 min. at 120 °C.

The AFM cantilever dimensions and characteristics are: length 125 ± 5 μm, width 30 ± 3 μm, thickness 4 μm, resonance frequency 320 KHz, Al coating (thickness 30 nm). The analysis has been performed in the no contact mode.

The distance \( d \) is an important parameter. In fact, during the tests, thanks to the force of interaction, has been observed that the tip can move and damage the carbon nanotubes deposited on the substrate (as shown in fig. 5, for \( d = 0.34 \) μm, displaying both topography and amplitude analysis). Fig. 4 shows a 3D topographic micrograph of the sample. It is possible to observe the presence of irregular shape particles (i.e. no – nanostructured graphite) and of filamentous structures filamentous (presumably CN). The nominal distance (\( d \)) between the cantilever tip and the sample is 0.34 μm, (scan rate 0.5 Hz).

The \( d \) value is calculated with respect to the lowest surface of the region analysed in the no contact mode. Instead, with the imposing of \( d = 1.95 \) μm, the problem of the sample damaging is resolved, as shown in fig. 6. Fig. 6, also, shows two linear topographies (red and green lines) of the above nanostructures. Evaluating the vertical and in plane dimensions, and with the typical CN’s dimensions provided by bibliography, it is possible to affirm that the elements observed are Carbon Nanotubes (with an HRTEM analysis it is possible to obtain a complementary information about the morphology of the nanomaterials studied). Besides, fig. 3 shows the pixel distribution (resolution of the image that is a function of the cantilever tip) and the table with the statistic data analysis of the two linear topographic profiles.

**Figure 4.** 3D AFM topographic micrograph of the sample.

Another aspect is relative the reliability of the information provided by the AFM micrographs. In fig. 6, for example, a 3D topography is shown, with two filamentous nanostructures (a & b).
Figure 5. AFM analysis of the carbon nanotubes damages due to the small distance $d$.

Figure 6. AFM analysis of the carbon nanotubes with the relative 1D topographic profiles of the samples.

They could represent:
1. a splitting of the same structure (one CN doubled in the of the AFM image reconstruction)
2. two CN
3. one CN where $a$ & $b$ are the inner walls, and the dark line is the internal hollow of the nanotube.

The third hypothesis can be immediately abandoned, as in fact the AFM works in topographic scanning mode, and not in transmission mode (as in the case of the TEM).

Note that the black lines indicate the sequence of sample scanning (which could cause the formation of artefacts in the topography).

The first hypothesis is not realistic, thanks to the presence only in $a$, and not in $b$, of a particle (probably a post synthesis residual of graphite as shoved with a black circle in fig. 6).

In this case it is possible to infer the presence of two carbon nanotubes joined by van der Waals forces (second hypothesis).

3. Conclusions
In each step of an advanced nanotechnology system/apparatus the characterization of the nanomaterials and nanostructures employed (synthesised, purified, etc.) is a critical phase. In fact, it is
requested to perform a specific evaluation of the fundamental properties and characteristics of the “nanoelements” integrated in the above advanced system. To observe and to analyse structures with micro and nanometric dimension is not simple and it is necessary to develop a specific standard protocol for all single step, i.e.:

- sample preparation methods
- analysis criteria
- evaluation and interpretation of the results
- analysis reliability and repeatability
- samples storage procedure.

A number of analytical characterization tools have been used successfully in the past years to determine the principal properties of nanostructures and nanomaterials, but lack of standard methodologies make it difficult to compare these measurements. Then, it is requested the development of a protocol in which standardised analysis methods and procedures are defined. The typical characterization analyses, used in the nanotechnology science, are:

1. optical microscopy
2. optical laser microscopy
3. SEM (Scanning Electron Microscopy)
4. TEM (Transmission Electron Microscopy)
5. EDX (Energy Dispersion X-Ray)
6. AFM (Atomic Force Microscopy)
7. STM (Scanning Tunnelling Microscopy)
8. Raman Spectroscopy.

It is clear that the numerous nanomaterials/structures, available thanks to the different nanotechnologies developed and modified by the different processes (synthesis, purification, integration, etc.), demand a close examination while using them for each applications. It is fundamental to have a well characterized material in order to access the variability of the numerous steps requested in the design and in the developments of the above applications.

**AFM (Atomic Force Microscopy):** it allows one to realize a 3D nanotopography and morphologies profiles of the micro and nanomaterials/structures. Besides, with the cantilever tip of this instruments, it is possible to determine the principal mechanical (Young modulus) and electrical (V-I characteristic) nanostructures properties.

With the AFM the following characterizations of the nanomaterials are possible:

- **morphology:** evaluation of the nanometric geometry and characteristics of the nanostructures observed.
- **homogeneity:** that mean to determine the statistical distribution of the various nanomaterials/structures present in a sample
- **dispersability:** to determine the capability of the nanostructures to form stable suspension at specific concentration values in the form of the bundles or single elements
- **purity:** in each phase of the nanomaterials development (synthesis, purification, integration, etc.) the nanomaterials are constituted by nanostructures are amorphous residuals. It is always requested to evaluate the exactly percentage of the each elements typology presents in the sample (powders, massive elements, apparatus, etc.). Clearly, the target consists in the maximum possible reduction of the impurities.

The experimental AFM test showed in this paper allows us to evaluate, and to solve, the principal problems characteristics of this analysis methods. In particular the distance \( d \) between the sample and the AFM cantilever tip represents the parameter that characterises the possibility to perform analysis with, or without, the sample damages.

With respect to the SEM and to the TEM, the AFM microscopy allows one to perform specific studies of the carbon nanotubes, or more in general, of the nanomaterials and structures synthesised, purified, and integrated in advanced nanotechnology systems.
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