Cooperative Multiwalled Carbon Nanotubes for Enhanced Force Spectroscopy*

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The increased interest to develop novel nanostructured devices, such as those intended for molecular nanoelectronics, requires the development of advanced characterization. We present the properties of carbon nanotube (CNT) atomic force microscopy (AFM) probes for testing multiple properties of nanometer structures, including force spectroscopy. The CNT-AFM probes are made by integrating a high density of MWCNTs in the tip of the probe. In particular, the modulation of the original probe mechanical response due to CNTs in approach-retraction curves is shown, as a consequence of the collective response of the high density of CNTs existing at the tip apex. Illustrative of the potential of the CNT-probe device, the actual determination of physical parameters on HOPG is provided, as a proof of CNT-mediated access to the specific characteristics of the sensed surface. The features observed for the establishment of tip-sample electro-mechanical contact (snap-in and adhesion) reveal the particular interaction forces that are exerted to the CNT tip. The high sensitivity of CNTs to record interaction events comprises both attractive and repulsive mechanisms. Specifically, results suggest the CNT-AFM probe capability to monitor long and short range forces in relation to external electric field and sample charges, capillarity, adhesion and so on. When combined with electrical current monitoring is of extreme precision for conductance determination.

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I. INTRODUCTION

The increased interest to develop novel nanostructured devices, such as those intended for molecular nanoelectronics [1], has motivated and pushed the development of advanced functional probes and probing techniques to test their suitability for the aimed application [2, 3]. The appropriateness of atomic and nanoscale sensing by atomic force microscopy (AFM) [4–6] has profusely been reported since its invention [7], extensively fulfilling the necessities of multidisciplinary research activities in chemistry, biology, physics, engineering, etc [8]. The use of carbon nanotubes (CNT) as a convenient interface between the surface and the mechanical response of the AFM probe is an on-going topic of research. Yet, the challenges are, first, CNT-integrative technology development and, second, novel or unrevealed specific performance of the obtained CNT-probe device [9–11].

In a previous research article, we described the specific valuable properties of our CNT-AFM probes [12] and the fabrication process [13]. The CNT-functionalized AFM probes demonstrated: i) an excellent operation, in different AFM modes of operation, ii) unprecedented tip apex durability (no desorption, no wearing, inertness, etc.), and iii) increased high sensitivity for tip-sample interactions, as a consequence of the intrinsic properties of CNTs [14]. Benefiting from these facts, we address a deeper investigation on the existing interactions for the precise determination of the multiwalled CNTs (MWCNT) role. Within this communication, we present the detailed comprehension of CNT-AFM probes applied to force spectroscopy [15], at room temperature and atmospheric pressure conditions. In particular, the modulation of original probe mechanical response due to the presence of MWCNTs, in approach-retraction curves, is shown. The main parameters involved are discussed and a qualitative model is provided for the observed experimental behavior. Illustrative of the potential of the CNT-probe device, the actual determination of physical parameters on HOPG is provided, as a proof of CNT-mediated access to the specific characteristics of the sensed surface. The features observed for the establishment and release of tip-sample electro-mechanical contact, snap-in and adhesion, reveal the particular interaction forces [16] that are exerted to the CNT tip [17]. The high sensitivity of CNTs to record interaction events comprises both attractive and repulsive mechanisms. Specifically, results suggest the CNT-AFM probe capability to monitor long and short range forces in relation to external electric field and sample charges, capillarity, adhesion, etc. When combined with electrical current monitoring, CNT-mediated force spectroscopy is of extreme precision for optimal conductance determination [18].

II. EXPERIMENTAL

The CNT-AFM probes are fabricated as described elsewhere [19, 20]. Briefly, the fabrication processing consists of integrating a number of MWCNTs in the apex of a silicon probe using local electrodepositing of catalyst (Pd) and microwave plasma enhanced chemical vapor deposition, for the oriented growth of MWCNTs on probe device (Fig. 1). We developed the technology for CNT-functionalized device mounted on commercial Si probes for non-contact, dynamic mode. Recently, we have also started testing other starting devices for definite purposes, as for example, Kelvin probe force microscopy probes. Specifically, Si cantilevers with Al reflection coating are

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FIG. 1: Tilted SEM images of one of the CNT-modified AFM probe that has been tested for force spectroscopy. Synthesized only in the tip apex, packed MWCNTs are vertically prearranged conformal to the Si probe shape. Scale bar is 2.5 µm.

FIG. 2: Force curves on a mica substrate, only retraction is plotted. a) Study of mechanical response as a function of artificial RH in the chamber. No dependence is registered when increasing or decreasing RH as a proof of testing the CNT-AFM probe characteristics (dry-wet-dry cycle is shown). b) Reliability of performance is evident from the invariability of the force curve slope and contact adhesion (Curves labeled, 1-3 for same location, and 4-7 at different positions).

generally used (BudgetSensors Inc. Model: TAP300AL, 300±100 kHz, 40 N/m), as well as, softer cantilevers (SI NanoTechnology Inc. Model: SI-DF3-A, ~27 kHz, ~1.6 N/m, Rh coating) have been employed. The scanning probe microscopy instrument used for the totality of measurements is a Seiko Instruments NanoNaviII E-sweep equipped with an environmental and temperature control system.

III. RESULTS AND DISCUSSIONS

The mechanical response of CNT-AFM probes has been determined on several conditions and various substrates in order to provide a complete description of their intrinsic characteristics and specifications, as follows.

First, the force as a function of piezo vertical position (z) curves for the CNT-probes have been acquired on a freshly cleaved mica substrate, because mica is a non deformable substrate [21]. The procedure is executed in contact mode, where the photodetector signal is typically 3 V (as-purchased probes 7.5-8 V) and laser alignment of the amplitude or detection of bend is set to +0.6 V for the approach for all probes tested. Before the force curves, tip is brought into contact with the sample surface (at a reference value of 10 nm for the engage) and z sweep is executed. The duration of the extension plus retraction displacement is 60 s for a distance of, typically, 100 nm. Figure 2 presents the standard behavior observed (only withdrawal curve is shown) [9]. All these curves correspond to a series of measurements realized with a single CNT-probe, allowing the study of the CNT-cantilever response as a function relative humidity (RH), reproducibility, reliability and tip and probe durability. The robustness of the CNT-lever is demonstrated. The repulsion part of the curve is highly linear, and invariant with the surrounding humidity, which indicates that mechanical contact between surface and MWCNTs is good, without any perceptible slides (Fig. 2 a)). The slope of the curve is identical for the approach part of the curve (data not shown). This is an important fact provided the reported hydrophobicity of vertically aligned CNTs [22], and in order to set the CNT-probes potential for testing, for example, local properties of biomolecular entities. The artificial variation of RH has been tested from dry (below 5%) to wet (84%) conditions and, again to dry (5%) ambience to explore eventual hysteresis phenomena (other parameters of CNT-AFM probes do depend on RH [23]). The results also evidence the robustness of CNT-probe mediated testing, as it is highly reproducible, independently of position or number of approach-retraction events, Fig. 2 b)). More than 20 force curves were acquired for this CNT-probe, as it is shown in Fig. 2. This scenario reinforces the idea of our previous articles [12, 13] claiming for our CNT-probes excellent operation and performance with unprecedented apex durability: no adsorption-desorption of material, no reactivity, etc. Hereby we complement these features with collective MWCNT elastic deformability (reversible bending).

The CNT-modified probes present a different mechanical response as compared to standard AFM probes, in agreement with the results by other authors [24]. In particular, we observe a modulation of intrinsic stiffness of the silicon lever, as depicted in Fig. 3 a)). We define intrinsic stiffness of CNT-probe as the reduced stiffness due to the fact that the MWCNTs bend when applying a force, resulting in a reduction of the slope. This is a fingerprint of the extraordinary flexibility of CNTs, commonly reducing to about one forth the original stiffness value (from 11.3 to 3.6 N/m slope). Additionally, the snap-in force is remarkably reduced, probably related with hydrophobic character of CNTs. These two aspects support the idea of...
FIG. 4: a) Cartoon representing the cooperative performance of the whole MWCNTs that decorate the tip apex of the AFM probe. CNT-AFM probe compound behavior accounts for the elastic cantilever bending and the CNTs deformation during mechanical contact to the surface. b) Force curve/z for the CNT-AFM probe in the inset (scale bar is 1 μm). The low density and disordered structured of the MWCNTs on the tip apex is manifested in the two stages mechanical response for approach-retraction curve.

of the consecution of engage in mild conditions that not only preserve tip apex condition, but also would be advantageous for probing soft materials, such as polymers. In consequence, the overall mechanical response of the probe is altered while keeping response linearity. This fact is of relevance for the field of technological development of probes as it can be used for the consecution of operative resonating structures (such as based in tuning fork devices [25]) tuned with CNTs for profitable sensitivity and resilience, but it is extremely convenient to be used in aimed systems, such as multiprobe microscope [26]. A similar behavior is observed when integrating CNTs into AFM probes lower force constant (Fig. 3 b)). In this case, the reduction is smaller indicating that the intrinsic mechanical response of the lever (without CNTs) and the CNT contribution tend to contribute alike. The direct estimate of the force constant of the cantilever is best determined by other methods [27], or fitting based on force versus tip-sample separation, where the distance is calculated from z piezo position and cantilever deflection.

At this point, we are able to qualitatively build up a consistent model to describe the role of the MWCNTs during the operation of the CNT-probe device. It has been proved [12] that no dangling CNTs structure our devices, which would be challenging for a proper actuation and detection of cantilever oscillation, but they collectively and densely arranged on the tip apex. From present results, we can confirm that proper mechanical response during force spectroscopy is recorded, reinforcing the idea of a good coupling between CNT and cantilever tip. It is important to realize of which are the typical density (packed MWCNTs) and morphology (few tens nm in diameter of 0.5-1 μm length MWCNTs). Noteworthy, the distances that are implied in our approach-retraction curves once engaged do not exceed the difference in length between top CNT and the surrounding ones, so only one to a few CNTs are responsible of contact. Therefore, the concept of cooperative contribution of the tip apex surrounding MWCNTs is introduced. The unique plastic deformability to force loading of the few CNTs in the near apex can be explained as the result of dynamic protection offered by the rest of MWCNTs underneath. This idea is illustrated in Fig. 4 a). While Fig. 4 depicts the reduced force/distance slope due to two contributions: i) the deflection of the cantilever and ii) CNT bending, and highlights the shielding function of bottom located MWCNTs to restore the original shape of top sample-interacting CNTs. The reduction of the slope is rooted in the fact that force value is derived from photodetector signal, which does not discriminate the portion coming uniquely from the cantilever displacement and the deformation of the CNTs underneath. This illustrative model is also supported by the fact that force curves executed with low density (unintentionally) synthesized CNT-AFM probes do present two differentiated ranges of mechanical response for approach-retraction curves (Fig. 4 b)). This behavior might correspond to a first stage where CNTs are bended, and a second stage for higher loading forces, where the deflection of cantilever is the main contribution to the signal.

FIG. 5: Exemplary demonstration of performance CNT-functionalized probes for force spectroscopy. Sensing is executed on freshly cleaved HOPG. Simultaneous acquisition of force/z and electrical current/z provides an ideal method for sample properties analysis (Ambience RH is 56%).

As a clear example of the characteristics for the compound CNT-AFM probe described, we present some force versus distance curves executed on highly oriented pyrolytic graphite (HOPG). The choice of HOPG relies in the fact that is a highly crystalline material, but its layered structure and, hence, compressibility allows us to access to a flat and clean substrate with intrinsic hardness between (hard) closely-packed solid and (soft) polymeric materials, for comparison and complementarily to previous tests on mica. Therefore, Hertz theory [28] would be most appropriate for description of concise (atomic scale) deformation of HOPG. Another interesting property is the electrical conductivity, which implies that the eventual dependence of mechanical properties as a function of, i) tip-sample biasing and, also, ii) actual tip-surface conduction can be investigated. Benefiting from the excellent electrical conduction properties of CNT-probes, as described in [12, 13], we combine approach-retraction curves with simultaneous tip-sample electrical current acquisition.

As it can be observed in Fig. 5, a linear mechanical response is also apparent in any conditions. In this case, both approach and retraction data are plotted for the additional contact mechanisms that can be studied. A constant slope of the force curves is maintained even when bias is applied and, also, if electrical conduction between CNT-tip and sample is established. Moreover, the force/z interaction is strictly mechanical since value does not vary with the applied voltage. A slight variation of the force
force-current spectroscopy with our CNT-AFM probes for force curve data. In consequence, we suggest the use of mechanical contact could be accessed or conjectured from the fact that eventual particular events related to the mechanical response for the so-called force curves measurement. Remarkably, the durability of tip apex is not only of superior robustness, as compared to metal coated commercial probes, but also shows excellent performance for conductivity measurements. Either common used I/V spectroscopy curves or approach-retraction curves with simultaneous monitoring of electrical conduction have been tested. The more complete insight provided by current-force spectroscopy is suggested as an optimal methodology for sample properties electromechanical sensing. Also of increased interest for imaging and testing soft surfaces, such as polymers, the establishment of mechanical and full electrical contact is achieved at forces at least one order of magnitude smaller that the commonly used ones (typically, low spatial resolution extremely hard diamond coated tips, or fragile metal coated tips are used). CNT-AFM probes provide a device for surface testing of excellent properties with the guarantee of minimal sample damage, for both, tip apex or sample degradation due to normal and lateral loading forces. The conservation of the tip integrity is confirmed by the quality of dynamic mode topography images after force spectroscopy and conductivity measurements.

IV. CONCLUSIONS

In summary, present investigation reveals that the integrated CNT-AFM probe operates as a single compound operating device that can be qualitatively described as two coupled strings. In consequence, their actuation at proper resonance frequency results in a proper and controlled probe oscillation. This can be used for correct imaging by dynamic mode. Additionally, the linear mechanical response for the so-called force curves measurements makes possible the use of CNT-AFM probes for force spectroscopy. Remarkably, the durability of tip apex is not only of superior robustness, as compared to metal coated commercial probes, but also shows excellent performance for conductivity measurements. Either common used I/V spectroscopy curves or approach-retraction curves with simultaneous monitoring of electrical conduction have been tested. The more complete insight provided by current-force spectroscopy is suggested as an optimal methodology for sample properties electromechanical sensing. Also of increased interest for imaging and testing soft surfaces, such as polymers, the establishment of mechanical and full electrical contact is achieved at forces at least one order of magnitude smaller that the commonly used ones (typically, low spatial resolution extremely hard diamond coated tips, or fragile metal coated tips are used). CNT-AFM probes provide a device for surface testing of excellent properties with the guarantee of minimal sample damage, for both, tip apex or sample degradation due to normal and lateral loading forces. The conservation of the tip integrity is confirmed by the quality of dynamic mode topography images after force spectroscopy and conductivity measurements.
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