Carbon Nanotubes as Ideal AFM Probes

An Update

Carbon nanotubes (CNT) have been demonstrated since 1996 as ideal probes for scanning probe methods because of their nano-size, their cylinder geometry and their mechanical properties. Their use hasn’t spread out as expected, due to lack of control of their fabrication and of their interaction with surfaces. Sixteen years later, this knowledge is now acquired. Carbon nanotube probes can provide more than high resolution thanks to their high mechanical and chemical stability and surface sensitivity.

CNT as Ideal AFM Probes

Carbon nanotubes are nanosized cylinders made of carbon in a hexagonal array. A unique cylinder (fig. 1a) is named Single Walled Carbon Nanotube (SWCNT) whereas multiple tubes sharing the same axis (fig. 1c) are named Multi Walled Carbon Nanotubes (MWCNT).

Because CNT probes offer both a known tubular geometry able to reproduce more satisfactorily holes in the samples and a size comparable to molecular size, they were predicted since the beginning as ideal probes. Multiple publications demonstrated their use for demanding AFM samples such as biological or highly structured samples. The limitation of their use originated in difficulty to control the CNT probe and its complex mechanical behavior. Recently, those difficulties have been overcome. This review includes two opposite fabrication strategies to fulfill the CNT probes constraints, a simple mechanical description of their interaction with the samples, and illustrations of their intakes as AFM probes. We will see that their most valuable intake is their life time as compared to commercial Si or tips which are AFM consumables.

CNT Probes Synthesis

Early methods such as arc discharge, laser vaporization [1; 2] won’t be described here as they are not used for AFM probe synthesis. This paper will concentrate on the most convenient CVD (for Chemical Vapor Deposition) method. Typical carbon nanotube synthesis requires a carbon source usually in gaz form, a catalyst in which to dissolve carbon and a source of energy, often temperature. Because most
CVD CNT fabrication techniques lead to numerous entangled CNTs with catalysts particles, the probe constraints are challenging.

One single CNT should protrude from the AFM tip with the right orientation, a firm attachment to the tip and a controlled length. Figure 2 describes two opposite successful strategies to obtain CNT probes for AFM: one direct with Hot Filament CVD for SWCNT direct growth on AFM tip from A.M. Bonnot [3] and one requiring two steps: CVD growth on a filament followed by manual attachment to AFM tip according C.V Nguyen's procedure [4]. Other approaches can be found in [5].

**CNT Mechanical Properties**

The mechanical properties of CNT were early calculated as exceptional with a resistance to deformation similar to diamond and the ability to sustain large deformations without modification of their structure and properties [6]. Those properties were very encouraging for AFM probes fabrication. But following mechanical studies of CNT probes demonstrated reduction of their Young modulus due to defects, their complicated mechanical behavior due to loose fixation on the AFM tip or mechanical instabilities when interacting with a rough sample [7]. The control of the CNT fixation on the tip and of its length (not too long) are therefore prerequisite for easy interpretation of AFM experiments conducted with CNT probes.

Despite their nanosize, CNT mechanical properties can finally be described with two components: a bulk contribution with elasticity and a surface contribution due to adhesion on the sample [8]. Figure 3 compares experimental data with an analytical model described in [8], enabling to evaluate adhesive and elastic properties of the CNT probe with the sample.

**CNT Intakes as Compared to AFM Commercial Tips**

CNTs have a high surface ratio which induces a high sensitivity to their surface conditions when interacting with a sample that may affect their mechanical properties. Figure 4 illustrates the CNT mechanical sensitivity that enables to characterize different surfaces.

To demonstrate the CNT probe's intake, many scientists ask for direct comparison between commercial tips and CNT probes AFM results. It is usually not easy to find a fair comparison as one image never proves that better results might not be obtained in other modes or with particular probes. One solution is to compare results done in the exact same conditions, such as represented in figure 5. In this
case, the reduced CNT interaction force with the sample enables a better resolution for the CNT probe as compared to the Si tip. CNT probes indeed enable to reach high resolution but it might also be obtained with improved commercial probes with sharpened Si tips.

Finally, the major intake of CNT probes is better demonstrated by a collection of results. As an illustration, it has been possible to probe 7 different samples (SAMs, graphen, two different phospholipids, DNA origamis and deposits of antibody or protein coated gold nanoparticles) with one single SWCNT probe [9], recording 320 approach-retract curves and 140 images. The carbon surfaces smaller reactivity (as compared to Si commercial tips) and the CNT small size limit its interaction with the sample, they reduce CNT apex coverage with sample contaminants. More particularly, the CNT hydrophobic properties limit probe contamination in liquid environments, a very convenient property to study biological samples. Conjugated with the CNTs exceptional ability to sustain large deformations, their relative chemical inertness results in long life time.

**Conclusion**

With the control of the CNT probes fabrication and comprehensive understanding of CNT probe interaction with the samples, time has come to enlarge the use of CNT probes. CNT probes enable to reach high resolution or to penetrate into holes, but their contribution to AFM can be richer. Their limited contact area reduces tip adhesion that often induces uncontrolled soft sample modifications, and hides smaller forces. CNT small size and high aspect ratio is linked with stable mechanical properties. CNT probes therefore are less fragile than sharper Si tips (such as FIB carved) necessary to reach high resolution. The CNT chemical small reactivity and their hydrophobic behavior limit probe contamination. Together with their mechanical stability, those properties confer them unprecedented long life time. Using long lasting probes saves experimental time but also enables comparison of many different samples with a stable probe, a common AFM experiment, where the tip stability cannot usually be assured. The CNT high surface composition induces a high surface sensitivity that may enable characterization of different surfaces materials or chemical groups at the nanoscale. Finally, long flexible CNT may be a mean to reduce the force applied on soft and loose samples thanks to the elastic force component taken by the CNT.

**Outlook**

For the next years, four development directions emerge:

industrial fabrication of CNT probes at a lower cost (actual CNT probes values are between € 150 to € 600 depending on the quality) with large distribution
development of industrial process for application in electrical, electrostatic or
magnetic measurements insertion of the CNT probe fabrication protocol into new high technology systems for oscillation in liquids, or for forcing at high frequency for fast AFM controlled chemical or biological functionalization of the CNT apex only to ensure real local interaction study.

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