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Single Measurement Determination of Mechanical, Electrical, and Surface Properties of a Single Carbon Nanotube *via* Force Microscopy

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ABSTRACT

Carbon nanotubes (CNTs) have attracted significant attention due to their remarkable mechanical and electrical properties. Although it is assumed that the most important questions about CNTs have been addressed, the opposite is true. CNTs have high mechanical stiffness and electrical conductivity and, due to their small diameter and size, the measurement of those properties at nanoscale level is challenging. Here, we present a unique method to determine their mechanical and electrical properties by using interactions between vertically aligned multiwall CNTs and a metal-coated tipless atomic force microscope cantilever. We used a force–distance measurement (FDM) method with concurrent monitoring of electrical current. We could identify the number of CNTs in contact with the cantilever, stiffness of each individual CNT, the adhesion force between the cantilever and individual CNTs, and the electrical conductivity of each CNT. The method is also suitable for characterizing other vertically aligned nanostructured materials, such as nanowires. This method addresses the long-standing problem of property determination of materials such as CNTs and nanowires and is an important addition to the toolbox of nanoscale characterization methods.

1. Introduction

Carbon nanotubes (CNTs) were first reported in 1970 [1] and since then their remarkable properties have been discussed many times [2,3]. The widespread interest in this material was triggered by the publication of preparation methods for multiwall CNTs (MWCNTs) and single-wall CNTs (SWCNTs) in 1991 [4] and 1993 [5], respectively. The CNTs were predicted to be a material with an extremely high Young's modulus (E) in the range from hundreds of GPa (MWCNTs) to 3 TPa (SWCNTs) [6]. The experimental verification of CNTs' mechanical properties is challenging due to their diameter in the nanometer range and difficulties in manipulation [7]. The first experimental determination of CNTs' E was achieved in 1997 by measuring the amplitude of their intrinsic thermal vibration in the transmission electron microscope [8] or vibrations induced by an electrostatic field [9]. Subsequently, researchers tried to bend individual CNTs by using an atomic force microscope (AFM) tip [10,11] and they derived the nanotube stiffness from the tip–tube interaction force curve [12]. The method was reliable but, unfortunately, it required isolated individual CNT and it is rather difficult to separate CNTs from each other. In 2009, a fluorescence-based technique was used to determine the MWCNT spring constant [13]. The nano-indentation technique was also reported to determine the mechanical properties of CNTs [14,15]. So far, this is the only method that allows the determination of mechanical properties of CNTs without time-consuming sample preparation. However, the drawback was the uncertainty of the tip–CNT contact angle, which induces measurement error [16].

The electrical properties have also been studied by using a four-probe method [17] or AFM-based techniques [18–20]. This again required labor intensive sample preparation as the CNTs were randomly placed on the planar surface structure of the electrode. The contact resistance between an individual nanotube and a deposited metal film was controlled by laser ablation technique to tailor the CNT length [21]. The CNT electrical resistance was also studied as a function of CNT length [22]. All the above-mentioned methods require labor intensive sample preparation such as the careful separation of an individual CNT as well as firmly anchoring it to the substrate.

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CNTs are currently produced by several methods [6,23,24], which results in CNTs with different properties and shapes. The chemical vapor deposition (CVD) technique allows producing vertically aligned nanotubes (VACNTs) in the form of a nanometer-sized bamboo-like forest. These VACNTs are closely packed and have almost identical height. An earlier method, called "force–distance measurement" (FDM) [25] was presented to determine the interaction between an individual gecko lizard spatula and the tipless AFM cantilever to investigate the gecko's adhesion force [26]. The cantilever came into contact with individual spatulas even though they were in close proximity to each other. Here, we present a unique FDM as a method to determine mechanical, electrical, and surface properties of a single CNT from a VACNTs "forest" by analyzing the CNT–cantilever interaction. This method addresses the long-standing problem of property determination of materials such as CNTs and nanowires and is an important addition to the toolbox of nanoscale characterization methods.

2. Experimental Details

2.1. CNT Growth

The vertically aligned forest of MWCNTs was fabricated using different CVD methods. A thermally grown silicon dioxide layer with thickness of ≈500 nm on a silicon wafer with [100] crystallographic orientation was used as a starting substrate. Subsequently, a catalytic layer of Co with a thickness of ≈5 nm was deposited by e-beam evaporation. The thickness was determined by monitoring the change of natural frequency of quartz crystal microbalance. The CNTs growth was conducted by decomposition of ethylene diamine $C_2H_4(NH_2)_2$ at temperature of ≈900 °C for ≈600 s as described elsewhere [27]. The CNTs for electrical properties measurements were prepared by decomposition of CH_4 using the plasma-enhanced chemical deposition technique (PECVD) with Fe as catalyst at pressure of ≈1133 Pa (≈8.5 torr) for ≈120 s at temperature of ≈800 °C on an electrically conductive substrate [28].

2.2. Measurement of Mechanical Properties

The interaction between two objects, such as the AFM cantilever and the sample, can be monitored by FDM, where the interacting force (*F*) is a function of the cantilever displacement in the *Z*-direction (ΔZ). The AFM cantilever is brought down (or sample is raised) until it comes into close proximity with the sample. All surfaces are at ambient environment covered with a layer of water with thickness of a few nanometers [29]. At close proximity between the AFM cantilever and the sample, a spontaneous water condensation occurs, forming a water bridge between them and causing the cantilever to snap to the substrate, which is shown as a little dip on the FDM curve. The dip amplitude depends on the surface properties, relative humidity, and applied electric field, if there is any [30]. With the cantilever further pushed against the sample, the cantilever bends up and the sample deforms with the force exerted by the cantilever. The cantilever–sample interaction provides the sample stiffness as well as the sample surface properties.

A scanning electron microscope image of a typical VACNTs sample is shown in Fig. 1A and an AFM image with a line profile analysis to determine a CNT diameter in Fig. 1B and C. The diameter, length and spring constant will be used to determine the modulus *E* of the CNTs.

The *Z*-direction resolution of the AFM is significantly better than the height difference among adjacent CNTs; thus, we are able to determine the individual events of interaction between CNTs and the cantilever similar to the earlier reported measurement of the gecko lizard adhesion force [26]. We assumed that the interaction between a sample consisting of VACNTs and an AFM tipless cantilever will be similar to the previously measured interaction with gecko feet covered with seta [31]. While the cantilever comes into contact with the CNT at a typical angle of ≈12° (Fig. 2A) during FDM, it first snaps and then starts to bend itself as well as the CNT (Fig. 2B). Further pushing cantilever against the VACNT results in the cantilever interaction with more CNTs (Fig. 2C and D). We derived (Supplementary Section 1) the composite spring constant (k_T) of both the cantilever and the CNT as:

$$k_T = \frac{k_C k_{CNT} \cos\theta}{k_C \sin^2\theta + k_{CNT}}, \quad (1)$$

where k_C and k_{CNT} are the spring constants of cantilever and CNT, respectively, and θ is the angle between the cantilever and horizontal plane.

2.3. Measurement of Electrical Properties

We also propose to measure the CNT electrical conductivity from the interaction between a tipless cantilever coated at its bot-

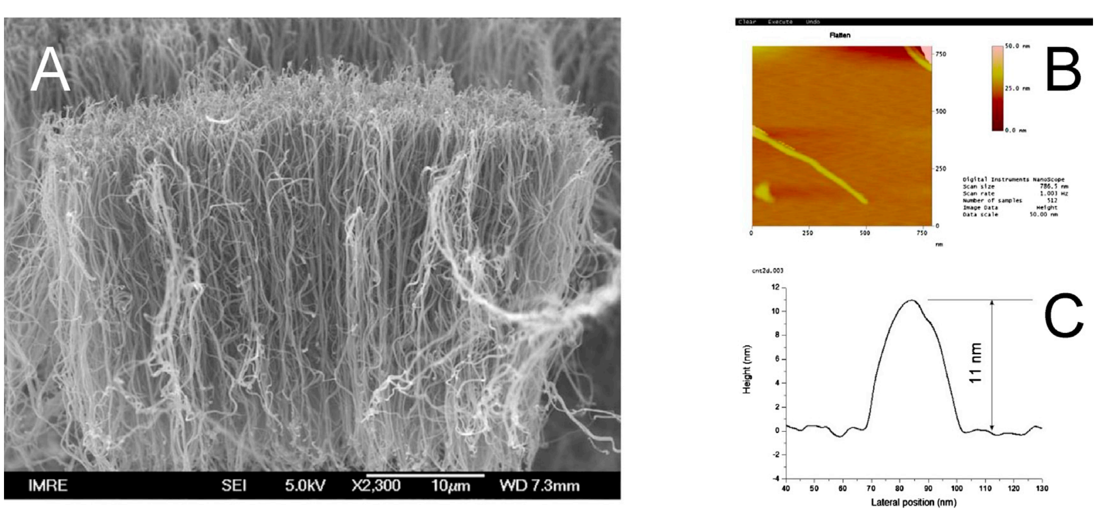

Fig. 1. (A) Scanning electron microscope image of a typical sample of VACNTs. The sample with CNTs was scratched with a needle and some CNTs were transferred onto a freshly cleaved mica substrate. (B) Sample topography was determined by an AFM in a tapping mode. (C) CNT diameter was extracted from a single scan across the CNT and found to be ≈11 nm.