Journal of Physics and Chemistry of Solids 61 (2000) 1025–1030

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

www.elsevier.nl/locate/jpcs

Measuring physical and mechanical properties of individual carbon nanotubes by in situ TEM

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Abstract

Nanomaterials are a fundamental component of nanoscience and nanotechnology. The small size of nanostructures constrains the applications of well-established testing and measurement techniques, thus new methods and approaches must be developed for synthesis, property characterization and device fabrication. This has been the focus of our research, aiming at exploring state-of-the-art techniques for materials processing and characterization. This paper reviews our progress in using in situ transmission electron microscopy to measure the electric, mechanical and field emission properties of individual carbon nanotubes with well-defined structures. Quantum conductance was observed in defect-free nanotubes, which led to the transport of a superhigh current density at room temperature without heat dissipation. A nanobalance technique is demonstrated that can be applied to measure the mass of a tiny particle as light as 22 fg (1 f $= 10^{-15}$). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon nanotube; Quantum conductance; Bending modulus; A. Nanostructures; Nanobalance

1. Introduction

There are three key steps in the development of nanoscience and nanotechnology: materials preparation, property characterization, and device fabrication. Due to the highly size and structure selectivity of nanomaterials, the physical properties of nanomaterials could be quite diverse. The electric properties of carbon nanotubes, for instance, depends on the helical angle of how the graphitic sheet being rolled in forming a tube shape structure. To maintain and utilize the basic and technological advantages offered by the size specificity and selectivity of nanomaterials, it is imperative to understand the principles and methodologies for characterization the physical properties of individual nanoparticle/nanotube.

It is known that the properties of nanostructures depend strongly on their size and shape. The properties measured from a large quantity of nanomaterials could be an average of the over all properties, so that the unique characteristics of individual nanostructure could be shadowed. The ballistic quantum conductance of a carbon nanotube [1], for example, was observed only from defect-free carbon nanotubes grown by arc-discharge technique, while such an effect vanishes in the catalytically grown carbon nanotubes because of high density of defects. Thus, an essential task in nanoscience is the property characterization of an *individual nanostructure* with well-defined atomic structure.

Characterizing the properties of individual nanoparticle/nanotube/nanofiber (e.g. nanostructure) is a challenge to many existing testing and measuring techniques because of the following constrains. First, the size (diameter and length) is rather small, prohibiting the applications of the well-established testing techniques. Tensile and creep testing of a fiber-like material, for example, require that the size of the sample be sufficiently large to be clamped rigidly by the sample holder without sliding. This is impossible for nanostructured fibers using conventional means. Secondly, the small size of the nanostructures makes their manipulation rather difficult, and specialized techniques are needed for picking up and installing individual nanostructure. Finally, new methods and methodologies must be developed to quantify the properties of individual nanostructures.

In facing these problems, research in nanomaterials opens many new challenges, both in fundamental science and

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PII: S0022-3697(99)00350-9

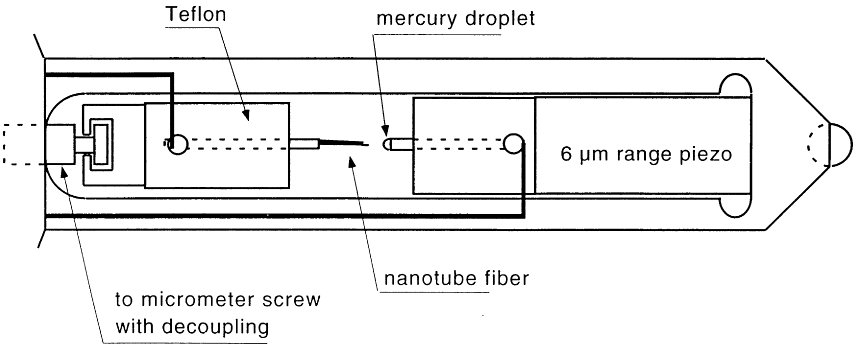

Fig. 1. Schematic diagram of the newly built TEM specimen holder for in situ measurement the mechanical properties of a single nanofiber.

practical technology. This is likely to be the reason that nanomaterials are so exciting and attractive. Scanning probe microscopy (STM, AFM) has been a major tool in detecting the properties of individual nanostructures. We have recently developed in situ transmission electron microscopy (TEM) as an effective tool for measuring the properties of individual carbon nanotubes. This is a new approach that not only can provide the properties of an individual nanotube but also can give the structure of the nanotube through electron imaging and diffraction, providing an ideal technique for understanding the property–structure relationship of a well-defined nanotube. This paper reviews our recent progress in applying in situ TEM for characterizing the electrical, mechanical and field emission properties of carbon nanotubes.

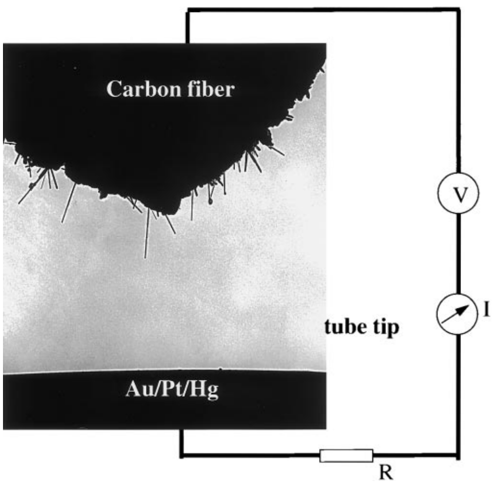

Fig. 2. TEM image showing carbon nanotubes at the end of the electrode and the other count electrode. A constant or alternating voltage can be applied to the two electrodes to induce electrostatic deflection or mechanical resonance.

2. Experimental approach

TEM is a powerful tool that can provide the structure of individual nanotubes. To carry out the property measurement of a nanotube, an TEM specimen holder was specially built for applying a voltage across the nanotube and its count electrode (Fig. 1) [2]. The specimen holder requires the translation of the nanotube via either mechanical movement by a micrometer or axial directional piezo. The nanotubes were produced by an arc-discharge technique, and the tubes were agglomerated into a fiber-like rod. Carbon nanotubes have diameters 5–50 nm and lengths of 1–20 μm. The fiber was glued using silver paste onto a gold wire, through which the electric contact was made. The count electrode can be a drop of mercury for electric contact measurement or Au/Pt balls for field emission characterization. The end of the carbon fiber and the count-electrode can be directly seen under TEM (Fig. 2), where the individual carbon nanotubes sticking out of the surface are clearly imaged. An electric potential was applied across the electrodes to carry out a variety of measurements. Thus, the measurements can be done on a specific nanotube whose microstructure is determined by transmission electron imaging and diffraction.

2.1. Electric transport properties

Electrical properties of carbon nanotubes are rather attractive because of their importance in electronic devices. The conductance of a carbon nanotube has been measured using scanning tunneling microscopy [3] and four-point contact technique [4]. The results indicated the strong dependence of the conductance on the structure of the tube and the defect. We have measured the electric property of a single multiwalled carbon nanotube using the set-up of an atomic force microscope (AFM) [1]. A carbon fiber from the arc-discharge chamber was attached to the tip of the AFM; the carbon tube at the forefront of the fiber was in contact with a liquid mercury bath. The conductance was measured as a function of the depth the tube was inserted into the mercury. Surprisingly, the conductance shows

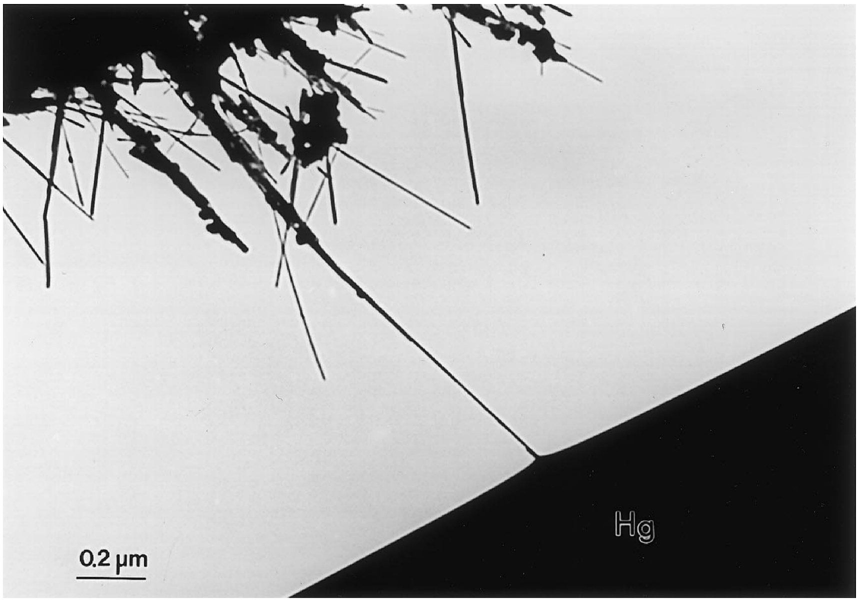

Fig. 3. In situ TEM image showing the contact of a carbon nanotube with a liquid mercury during the electric transport measurement.

quantized stairs (Fig. 4), and the stair height matches well to the quantum conductance $G_0 = 2e^2/h = 1/(12.9\ \mathrm{k}\Omega)$. For a single tube, the conductance is G_0, and the jump to $2G_0$ occurs once the second nanotube touches the mercury. This effect shows up only if the carbon nanotube is defect free, which means the tubes produced by arc-discharge rather than catalytic growth. The conductance is quantized and it is independent of the length of the carbon nanotube. No heat dissipation was observed in the nanotube. This is the result of ballistic conductance, and it is believed to be a result of single graphite layer conductance. A recent observation using a different technique has confirmed our result [5]. The experiments had been repeated over 100 times in AFM and it was repeated in TEM using the in situ specimen holder [6].

Fig. 3 shows the contact of a carbon nanotube with the mercury electrode, and the conductance of G_0 was observed. It is also interesting to note that the contact area between the nanotube and the mercury surface is curved. This is likely due to the difference in surface work function between nanotube and mercury, thus, electrostatic attraction could distort the mercury surface. This effect may also account for the rounding corner observed in the conductance curve when the nanotube first touched the mercury surface (see the step indicated by an arrowhead in Fig. 4) [7].

The observed quantum conductance may have great impact on molecular electronics. Carbon nanotubes could be used as interconnects for molecular devises without heat dissipation, with nicely defined geometry, smoothness and uniformity. The covalent bonding of the carbon atoms is also a plus for molecular device because of the chemical and bonding compatibility.

2.2. Mechanical properties

One of the significant challenges in nanoscience is the measurement of mechanical properties of individual constituents that comprise the nanosystem. The problem arises due to difficulties in gripping and handling fibers that have nano-size diameters. Mechanical characterization of individual nanofiber has been performed in the past on AFM. By deflecting on one-end of the nanofiber with an AFM tip and holding the other end fixed, the mechanical strength has been calculated by correlating the lateral displacement of the fiber as a function of the applied force [8,9]. Another technique that has been previously used involves measurement of the bending modulus of carbon nanotubes by

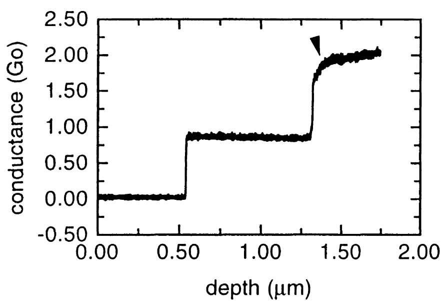

Fig. 4. Conductance of carbon nanotubes observed using the set up in an AFM, showing the independence of the conductance on the depth into the liquid mercury the tip being inserted. The second stair is introduced as another nanotube touches the mercury.

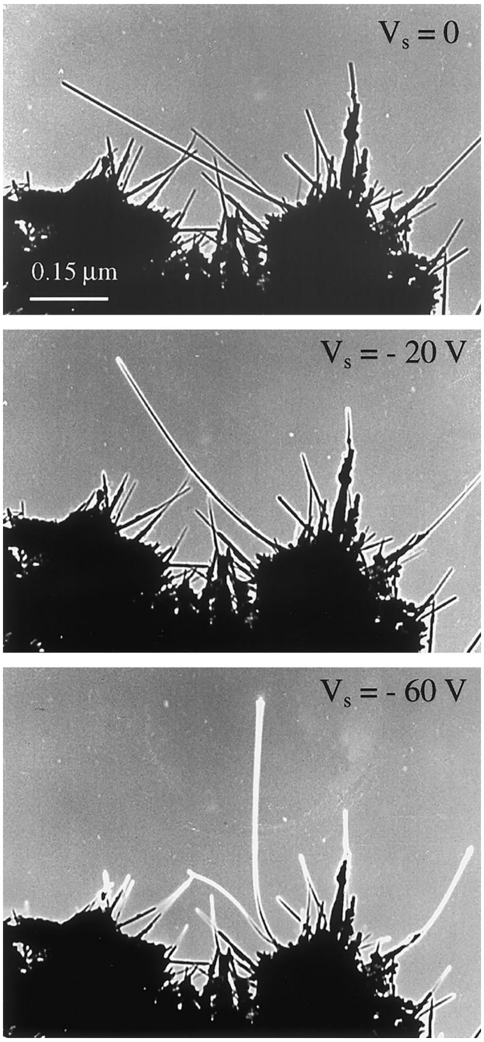

Fig. 5. Electrostatic deflection of a carbon nanotube induced by a constant field across the electrodes. Quantification of the deflection gives the electrical charge on the carbon nanotube and the mechanical strain on the fiber.

measuring the vibration amplitude resulting from thermal vibrations [10].

We have recently demonstrated a new technique for measurement the mechanical strength of single carbon nanotubes using in situ TEM [11]. The carbon nanotube can be charged by an externally applied voltage. The induced charge is distributed mostly at the tip of the carbon nanotube and the electrostatic force results in the deflection of the nanotube (Fig. 5). The nanotube is a very flexible structure and it can be bent to 90° and still recovers its original shape. Subjecting the tube to negative and positive voltages can give rise to cyclic loading of the carbon nanotube. This is the approach for applying a load to an individual nanostructure, allowing a direct measurement on its elastic limit.

Alternatively, if an oscillating voltage is applied on the nanotube with ability to tune the frequency of the applied voltage, resonance can be induced. When the applied voltage frequency equals to the natural frequency of the nanotube (Fig. 6), resonance is obtained and the frequency can be accurately measured. Resonance is nanotube selective because the natural vibration frequency depends on the tube diameter (D), the length (L), the density (ρ), and the bending modulus (E_b) of the nanotube [12]:

$$\nu_i = \frac{\beta_i^2}{8\pi}\frac{D}{L^2}\sqrt{\frac{E_b}{\rho}}$$

where $\beta = 1.875$ and 4.694 for the first and the second harmonics. In the above formation, the tube is assured to be a solid and the inner radius of the tube is ignored. The bending modulus of nanotubes has been measured as a function of its diameter [11]. The bending modulus is as high as 1.2 TPa (as strong as diamond) for nanotubes with diameters smaller than 8 nm, and it drops to as low as 0.2 TPa for those with diameters larger than 30 nm. A decrease in bending modulus as the increase of the tube diameter is a result of the rippling effect of the nanotube.

2.3. Nanobalance based on carbon nanotubes

In analogous to a spring balance, the mass of a particle attached at the end of the spring can be determined if the vibration frequency is measured, provided the spring constant is calibrated. This principle can be adapted to the case outlined in Section 2.2 to determine a very tiny mass attached at the tip of the free end of the nanotube. The resonance frequency drops more than ~40% as a result of adding a small mass at its tip (Fig. 7). The mass of the particle can be thus derived by a simple calculation. This newly discovered "nanobalance" has been shown to be able to measure the mass of a particle as small as 22 ± 6 fg ($1\ \text{f} = 10^{-15}$). *The most sensitive and smallest balance in the world*. We anticipate that this nanobalance would have application in measuring the mass of large biomolecules and biomedical particles, such as virus.

2.4. Carbon nanotubes for field emission display and molecular electronics

The unique structure of carbon nanotubes clearly indicates they are ideal objects that can be used for producing high field emission current density in flat panel display. This was first shown by de Heer et al. [13] who used aligned carbon nanotubes. The measured *I–V* curve showed extraordinarily high current density. With consideration the variation in diameters and lengths of the aligned carbon

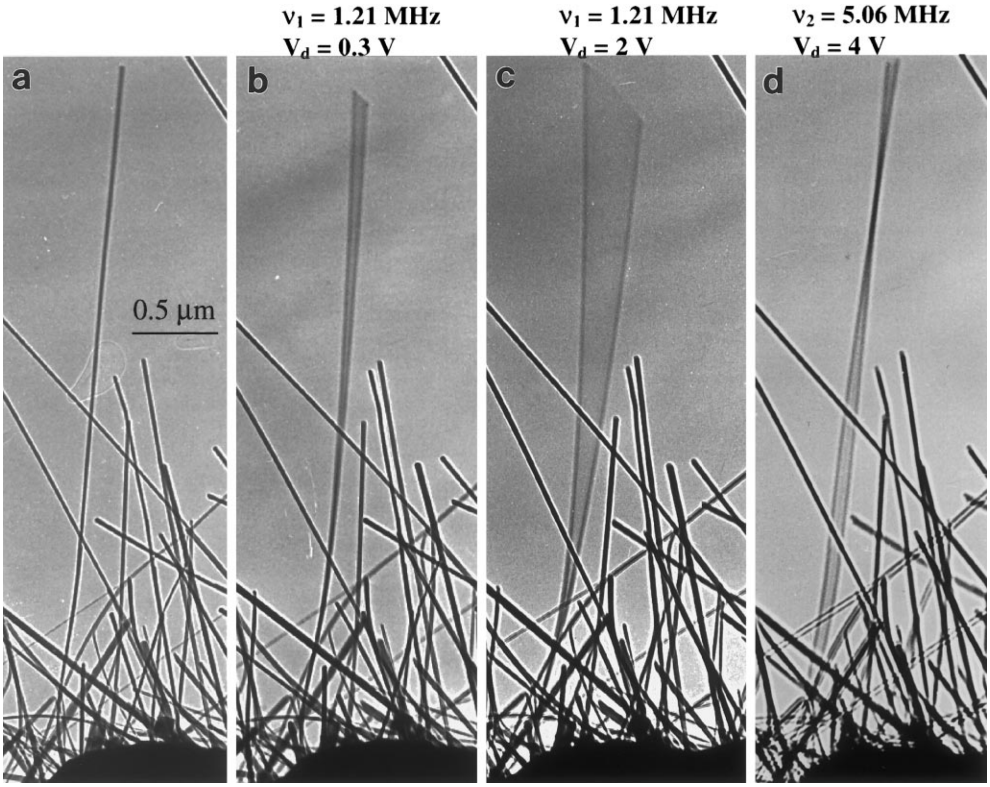

Fig. 6. A selected carbon nanotube at (a) stationary, (b,c) the first harmonic resonance ($\nu_1 = 1.21$ MHz) and (d) the second harmonic resonance ($\nu_2 = 5.06$ MHz). V_d is the magnitude of the applied voltage.

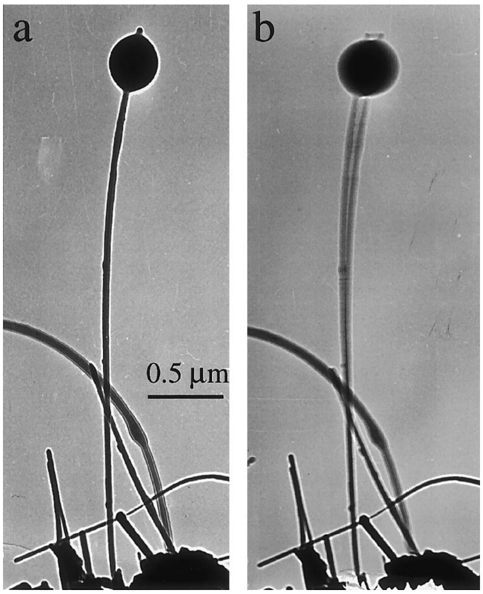

Fig. 7. A small particle attached at the end of a carbon nanotube at (a) stationary and (b) first harmonic resonance ($\nu = 0.968$ MHz). The effective mass of the particle is measured to be ~22 fg (1 f = 10^{-15}).

nanotubes, the measured *I–V* curve is an averaged contribution from all of the carbon nanotubes. Using the in situ TEM setup we built, the electric field induced field emission characteristics of a single carbon nanotube has been studied. Fig. 8 shows an TEM image of the carbon nanotubes that are emitting electrons at an applied voltage. The dark contrast near the tips of the nanotube is due to the field induced by the tip charged electrons as well as the emitting electrons. A detailed analysis of the field distribution near the tip of the carbon nanotube by electron holography is under the way, which is expected to provide the threshold field for field emission and many other properties.

3. Conclusions

Nanomaterials are a fundamental component of nanoscience and nanotechnology in the twenty-first century. Research in nanomaterials faces many challenges in synthesis, property characterization and device fabrication. The small size of nanostructures, however, constrains the applications of the well-established testing and measurement techniques, thus new methods and approaches must be developed. This has been the focus of our research,

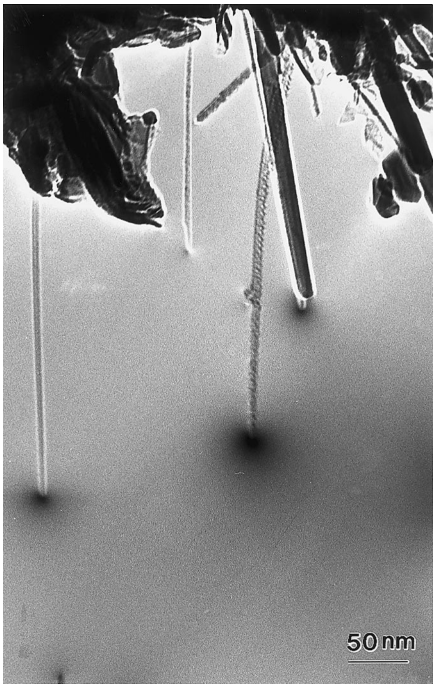

Fig. 8. In situ TEM observation the electric field induced electron emission from carbon nanotubes. The applied voltage is 60 V and the emission current ~20 μA.

aiming at exploring state-of-the-art techniques for materials processing and property characterization. The approaches demonstrated here using in situ transmission electron microscopy for measurements the electrical, mechanical and field emission properties are a new area in nanoscience, which are expected to have a great impact in the field.

Acknowledgements

The financial support of NSF grants DMR-9733160 and DMR-9971412 is greatly acknowledged.

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