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Nanomeasurements in Transmission Electron Microscopy

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Abstract: Nanomaterials have attracted a great deal of research interest recently. The small size of nanostructures constrains the applications of well-established testing and measurement techniques, thus new methods and approaches must be developed for quantitative measurement of the properties of individual nanostructures. This article reports our progress in using in situ transmission electron microscopy to measure the electrical, mechanical, and field-emission properties of individual carbon nanotubes whose microstructure is well-characterized. The bending modulus of a single carbon nanotube has been measured by an electric field-induced resonance effect. A nanobalance technique is demonstrated that can be applied to measure the mass of a tiny particle as light as 22 fg (1 fg = 10^{-15} g), the smallest balance in the world. Quantum conductance was observed in defect-free nanotubes, which led to the transport of a superhigh current density at room temperature without heat dissipation. Finally, the field-emission properties of a single carbon nanotube are observed, and the field-induced structural damage is reported.

Key words: carbon nanotubes, bending modulus, ballistic conductance, nanobalance, electron field emission, in situ transmission electron microscopy

INTRODUCTION

There are three key steps in the development of nanoscience and nanotechnology: materials preparation, property characterization, and device fabrication. Due to the great structural diversity of nanomaterials, the physical properties of nanomaterials strongly depends on their size, size distribution, shape, and chemical composition. The properties measured from a large quantity of nanomaterials could be an average of the overall properties, so that the unique characteristics of individual nanostructure could be lost. The ballistic quantum conductance of a carbon nanotube (Frank et al., 1998), 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.*

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 of the physical properties of an individual nanoparticle/nanotube and correlate the measured properties with the atomic-scale structure of the nanostructure. This is a key challenge to today's research because of the experimental difficulty in measuring the physical properties of a single nanostructure whose size is in the nanometer to micron range. First, the size (diam-

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eter 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 nanostructures. Finally, new methods and methodologies must be developed to quantify the properties of individual nanostructures.

Scanning probe microscopy (SPM) [e.g., scanning tunneling microscopy (STM) and atomic force microscopy (AFM)] has been a major tool in detecting the properties of individual nanostructures. The electrical, electronic, and mechanical properties of a single nanostructure can be quantitatively characterized by SPM, while the intrinsic atomic-scale structure of the nanostructure may not be revealed by the SPM technique. To solve this problem, 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 nanostructure. This article reviews our recent progress in applying In Situ TEM for characterizing the electrical, mechanical, and field-emission properties of carbon nanotubes.

EXPERIMENTAL METHODS

To carry out the property measurement of a nanotube, a TEM specimen holder was specially built for applying a voltage across the nanotube and its count electrode (Fig. 1). 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 used here are multiwalled and have diameters of 5–50 nm and lengths of 1–20 μm. The fiber was glued onto a gold wire using silver paste, through which the electrical contact was made. The counter electrode can be a droplet of mercury for electrical contact measurement of Au/Pt balls for field-emission characterization. The end of the carbon fiber and the counter 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.

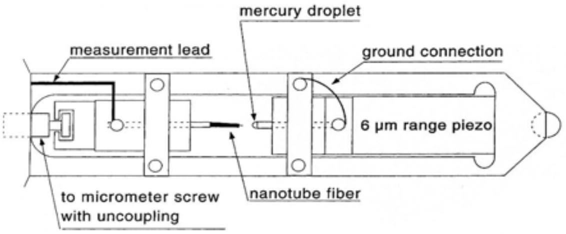

Figure 1. Schematic diagram of the newly built transmission electron microscope (TEM) specimen holder for in situ measurement of the properties of a single fiber-like structure.

Our TEM experiments were carried out in a JEOL 100C, which has the following advantages. First, the relatively poor vacuum at the specimen stage offers the possibility of introducing liquid mercury of higher vapor pressure into the chamber. Secondly, the 100 kV electron beam introduces almost no damage to the carbon structure so that an extensive observation could be carried out on a single nanotube. Finally, the large angular tilting range provides the advantage for precise measurements of the length of a carbon nanotube. This is important in determining the precision of the measurement.

EXPERIMENTAL RESULTS

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-sized 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 (Wong et al., 1997; Salvetat et al., 1999). This type of measurement has

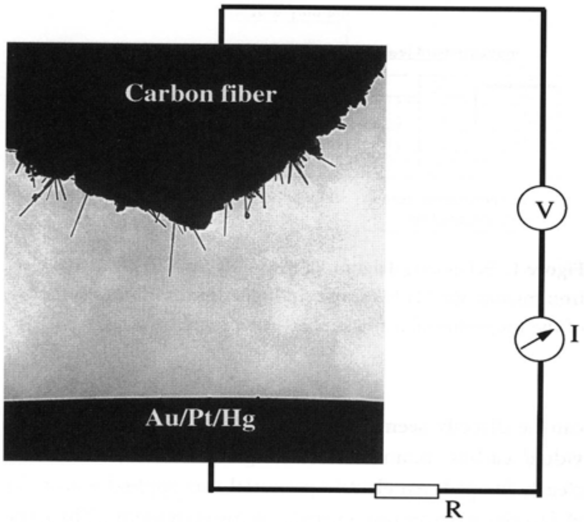

Figure 2. TEM image showing carbon nanotubes at the end of the electrode and the other counter electrode. A constant or alternating voltage can be applied to the two electrodes to induce electrostatic deflection or mechanical resonance.

two major limitations. The calibration of the AFM force can be inaccurate because very small deflection force and the tip-fiber contact and interface sliding can play a very important role in the quality of the data that are obtained. Another technique that has been previously used involves measurement of the bending modulus of carbon nanotubes by measuring the vibration amplitude resulting from thermal vibrations (Treacy et al., 1996). This technique also results in large variations in the measured result which are attributed to experimental errors.

We have recently demonstrated a new technique for measurement of the mechanical strength of single carbon nanotubes using in situ TEM (Poncharal et al., 1999). 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. 3). The nanotube is a very flexible structure; it can be bent to 90° and still recover 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 the ability to tune the frequency of the applied voltage, resonance can be induced. When the applied voltage frequency equals the natural frequency of the nanotube (Fig. 4), resonance is obtained and the frequency can be accurately measured. Resonance is nanotube-selective because the natural vibration frequency depends on the

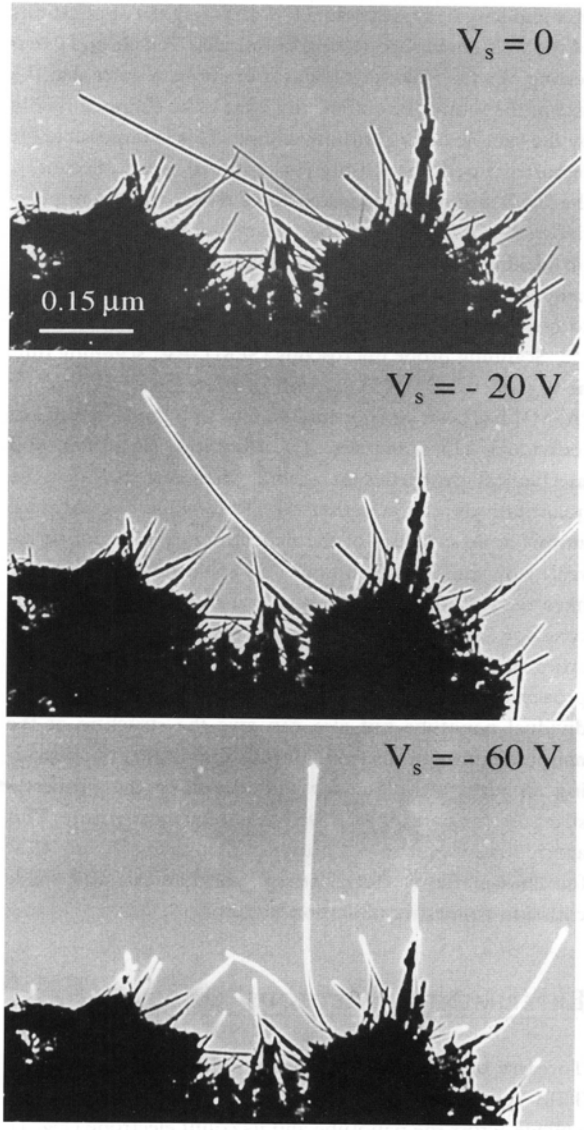

Figure 3. Electrostatic deflection of a carbon nanotube induced by a constant field across the electrodes. Quantification of the deflection gives the electrical charge on the carbon nanotube and the mechanical strain on the fiber.

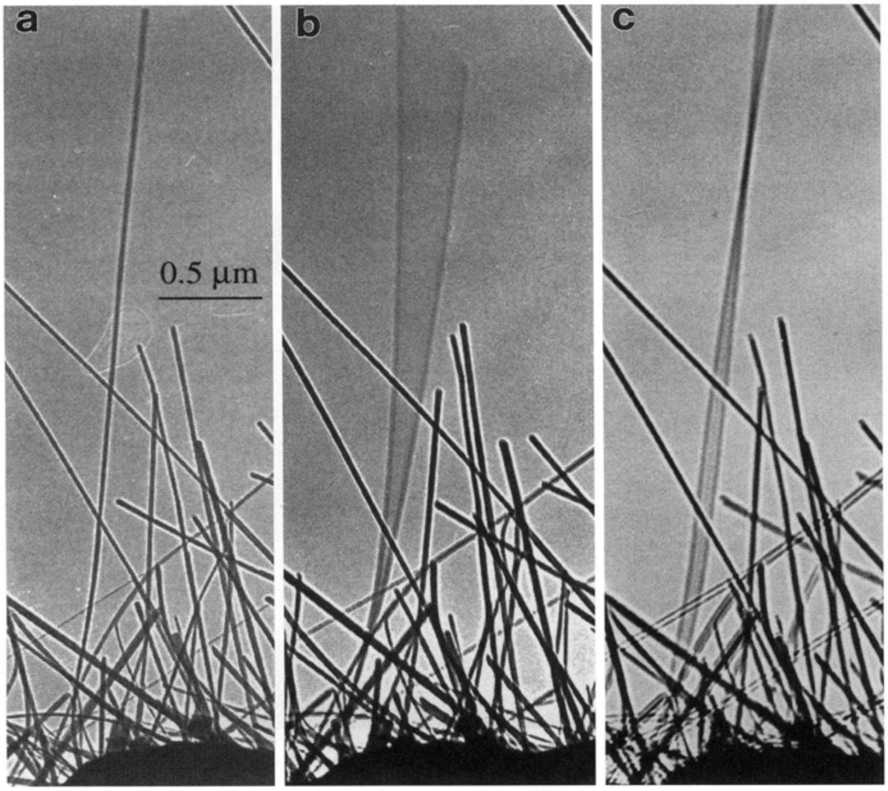

Figure 4. A selected carbon nanotube at **(a)** stationary, **(b)** the first harmonic resonance (ν_1 = 1.21 MHz, V_d = 2V), and **(c)** the second harmonic resonance (ν_2 = 5.06 MHz, V_d = 4V). V_d is the magnitude of the applied voltage.

tube diameter (D), the length (L), the density (ρ), and the bending modulus (E_b) of the nanotube (Meirovich, 1986):

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

where β = 1.875 and 4.694 for the first and the second harmonics, and the inner diameter of the tube is ignored. In the above formation, the tube is assumed 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 (Poncharal et al., 1999). 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 tube diameter increases is a result of the rippling effect of the nanotube.

World's Smallest Nanobalance

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 the previous section 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. 5). The mass of the particle can be thus derived by a simple calculation:

$$\nu = D^2/16\pi L\ (3E_b/Lm_{eff})^{1/2}.$$

For the case shown in Figure 5, D = 42 nm, E_b = 90 GPa, the mass of a particle is 22 ± 6 fg ($1f = 10^{-15}$). This is the newly discovered "nanobalance," *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 viruses.

Electrical Transport Properties

Electrical properties of carbon nanotubes are rather attractive because of their importance in electronic devices. The

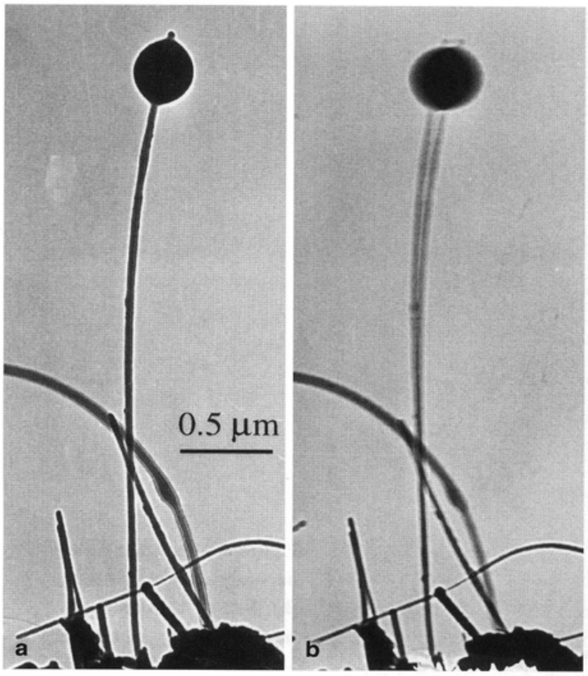

Figure 5. A small particle attached at the end of a carbon nanotube at **(a)** stationary and **(b)** first harmonic resonance ($\nu = 0.968$ MHz). The effective mass of the particle is measured to be ~22 fg ($1\ \mathrm{f} = 10^{-15}$).

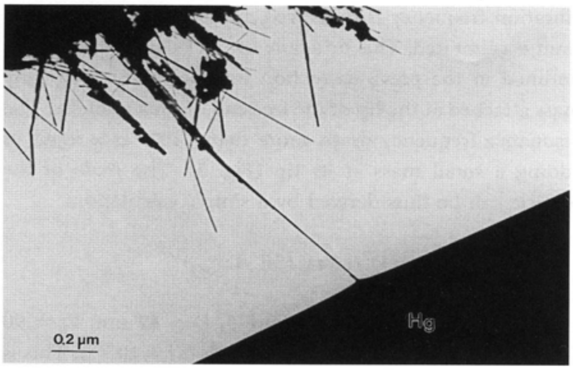

Figure 6. In situ TEM image showing the contact of a carbon nanotube with liquid mercury during the electrical transport measurement.

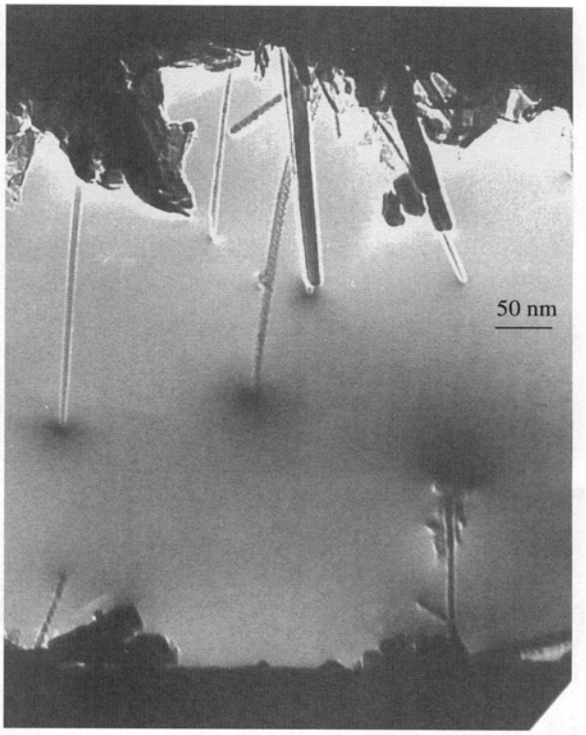

Figure 7. In situ TEM observation of the electrical field-induced electron emission from carbon nanotubes. The applied voltage is 60 V and the emission current is ~20 μA.

conductance of a carbon nanotube has been measured using scanning tunneling microscopy (Dai et al., 1996) and four-point contact technique (Ebbesen et al., 1996). 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 AFM (Frank et al., 1998). 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 that the tube was inserted into the mercury. Surprisingly, the conductance shows quantized stairs, and the stair height matches well to the quantum conductance $G_0 = 2e^2/h = 1/(12.9\ \mathrm{k}\Omega)$. This effect shows up only if the carbon nanotube is defect free, which means that the tubes are 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.

The experiments had been repeated in TEM using the in situ specimen holder illustrated in Figure 1. Figure 6

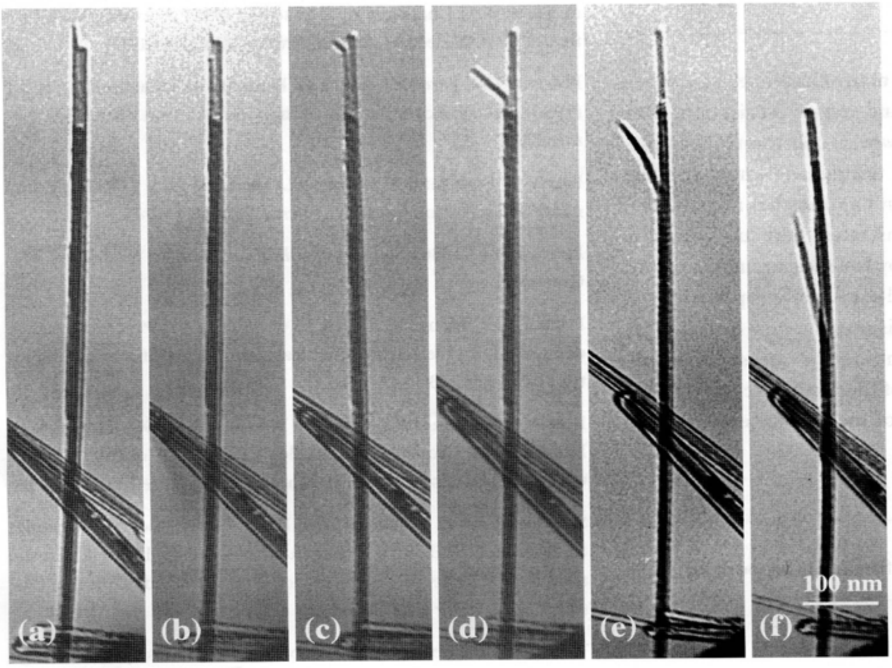

Figure 8. A series of TEM images **(a–f)** showing the electron field emission-induced structural damage at the tip of a carbon nanotube. The applied voltage is 100 V and the emission current is ~200 μA.

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.

Electron Field Emission of a Single Carbon Nanotube

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. (1995) who used aligned carbon nanotubes. The measured I–V curve showed extraordinarily high current density. With consideration of the variation in diameters and lengths of the aligned carbon 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 electrical field-induced field emission characteristics of a single carbon nanotube has been studied. Figure 7 shows a TEM image of the carbon nanotubes which 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 underway, which is expected to provide the threshold field for field emission and many other properties.

Structural damage can be introduced at the tip of a carbon nanotube if the strength of the externally applied field exceeds some limits. Shown in Figure 8 are a series of TEM images recorded from a carbon nanotube during its field emission. The nanotube is experiencing a rapid structural damage starting from the tip. The damage occurs in a form of piling off, so that part of the segments are cut off abruptly and completely. This type of damage is believed to leave a high density of dangling bonds on the surface of the carbon tube as a result of the broken graphitic sheets. This experimental result disagrees with the model proposed by Rinzler et al. (1995), who believed that the damage occurred as an unraveling process in which the carbon atoms were removed string-by-string and layer-by-layer. More importantly, we found that the carbon nanotube vibrates during field emission, resulting in the fluctuation in emission current.

CONCLUSIONS

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. The approach demonstrated here uses in situ transmission electron microscopy for measurements of the mechanical, electrical, and field-emission properties of a single carbon nanostructure. This opens a new direction in TEM, which can uniquely combine the measured result with the atomic-scale structure of the nanomaterial, leading to a quantitative interpretation of the experimental data.

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