

# A Field-Ion Microscope and 3-D Atom-Probe Microscopy Study of Tungsten Disulfide and Carbon Nanotubes

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## Abstract

Fullerene and inorganic fullerene-like nanotubes are molecules with the unique geometry of a single layer or multiple layers of a bulk material oriented in a tube. These molecules have novel mechanical properties and great potential in experimental systems for nanotechnology and nanodevices. The three-dimensional atom-probe (3DAP) microscope is an atomic resolution microscope that can chemically identify specimens evaporated at high voltages. Specimens for the 3DAP are typically metals and must be prepared in a finely tapered tip for use in the 3DAP.

This study applies the method of 3DAP microscopy to tungsten-disulfide and carbon nanotubes to investigate the chemical properties of the nanotubes and expand the functionality of the 3DAP microscope. Specimens of both tungsten-disulfide and carbon nanotubes, attached to metal filaments via conductive epoxy, were prepared for use in the 3DAP microscope.

Atomic resolution micrographs of the tips of both nanotube specimens were collected using field-ion microscopy in the 3DAP microscope. These micrographs exhibited circular patterns indicative of the circular cross-section of the nanotube specimens. Also, multiple specimens of tungsten-disulfide nanotubes were evaporated and chemically identified using time-of-flight mass spectroscopy. Data were collected in the form of a mass spectrum of the detected ions. The tungsten-disulfide nanotubes evaporated as tungsten-sulfur complex ions. These experimental findings

establish the technique of 3DAP microscopy for nanotubes and nonmetal materials.

## Introduction

The discovery of carbon fullerenes has led to much interest and research in such novel molecules, driven by both science and nanotechnology. The fullerenes are single molecules with very organized geometries, including spherical and tubular. Soon after the discovery of pure carbon fullerenes, inorganic fullerene-like (IF) molecules were also discovered.<sup>1</sup> In their native state these inorganic compounds resemble the crystal structure of graphite. Reshef Tenne was the first to achieve bulk synthesis of IF nanotubes, which enabled further study of these novel molecules.<sup>2</sup> The molecules have many applications, including their current use as solid-state lubricants and their potential use for molecular devices.

This study deals with the understanding of the chemical structure of carbon and IF nanotubes, specifically multiwalled carbon nanotubes grown with an iron catalyst particle and tungsten disulfide (WS<sub>2</sub>). Field-ion microscopy (FIM) and 3DAP microscopy were used to image and chemically identify the nanotube specimens.

## Background

Fullerenes are molecules consisting mainly — and often exclusively — of carbon in a conjugated state. One of the most celebrated fullerene molecules is C<sub>60</sub>, also known as Buckminsterfullerene. C<sub>60</sub> is a spherical molecule consisting of neighboring pentagon and hexagon carbon rings. Fullerene nanotubes are long rods of graphite folded upon themselves, with a cap of carbon pentagons and hexagons. Pentagon rings within the

fullerenes cause the curvature and allow these geometries. Carbon fullerenes are usually generated through evaporation of graphite but can also be grown in reactors.

IFs and fullerene molecules behave in a similar fashion because of the sheeted nature of their native states. Irregularities in the crystal surface can lead to folding similar to that of the pentagons of carbon fullerenes. The existence of IF nanotubes was extensively documented through electron microscopy by Tenne et al.,<sup>1,3</sup> while the availability of IF nanotubes increased greatly with the development of a reaction of respective trioxides (WO<sub>3</sub>).<sup>2</sup>

In FIM, a widely used technique for achieving atomic resolution,<sup>4</sup> a high-electric field is created at a sharply pointed tip. That tip then serves as the specimen. Next, an imaging gas is leaked into an evacuated chamber containing a specimen at a high-electric field. The imaging gas molecules on the tip are field-ionized at the apex (where the electric field is highest) via a quantum mechanical tunneling process. The positively charged gas ions are repelled from the tip along the electric field lines and are detected on a phosphor screen with the aid of a channel electron multiplier array that has a gain of 10<sup>3</sup> to 10<sup>4</sup>.

Because the ionization of gas molecules is preferential at atomic sites on the tip, a localized bright spot in an FIM image is a direct consequence of the ionization of imaging gas atoms above a single atom. Thus is atomic resolution achieved. FIM is typically performed with a gas pressure of 10<sup>-4</sup> to 10<sup>-6</sup> torr with the tip at cryogenic temperatures, 20 to 80K.

3DAP microscopy builds upon the principles of FIM.<sup>4</sup> In the case of the atom probe, excitation of a specimen tip (normally through an additional electric

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pulse) causes the tip to field evaporate. The positively charged ions that are field evaporated from the tip then move along the electric field lines. Those lines are orthogonal to the equipotential lines above each atom on the surface of a tip. The ion trajectories and their time-of-flight are used to evaluate their mass-to-charge state ( $m/n$ ) ratio and their relative position on the tip. The  $m/n$  values constitute direct evidence of the chemical species that are field evaporated. Combining this with the two-dimensional spatial location information obtained with the primary detector of the 3DAP microscope leads to a reconstruction of the actual atoms from atom-probe data.

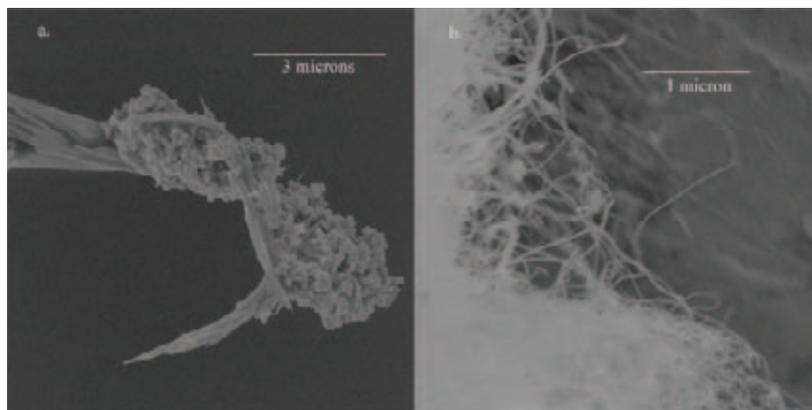
### Approach

In this study, bulk samples of nanotubes were obtained from suppliers. The tungsten disulfide nanotubes, supplied by Reshef Tenne (Weizmann Institute of Science), came in the form of long, twisted bundles and contained bulk tungsten disulfide. The bulk carbon nanotube

samples were much different in structure, with almost no clumping of nanotubes lengthwise. Instead, they came in the form of large bundles consisting of long, drastically tangled nanotubes with curvatures along the length of a nanotube (Figure 1). The objective of the mounting procedure was to place a single nanotube, or small nanotube bundle, onto a metal filament for analysis in the 3DAP microscope. First, the bundles were suspended in ethanol through the use of ultrasonic frequency sound waves. This treatment, known as sonication, helps separate the nanotube bundles and shorten the individual nanotubes. The nanotubes were next sonicated at high power for five minutes. The nanotube suspension was then placed on a glass slide shard, roughly 3 mm by 3 mm square, a few droplets at a time. As the solvent evaporated, clumps began to form on the slide surface. The degree to which the clumps reformed was controlled by the concentration of nanotubes in the solution and the number of drops that were added to the substrate.

The tungsten disulfide nanotubes were not bundled, because isolation of a single nanotube is preferable. The isolated nanotubes were lying flat along the glass substrate, making them difficult to mount onto the metal filament. While past research used bundled tungsten disulfide nanotube specimens, in this study a piece of carbon tape was brought into contact with the nanotube clumps under a low-magnification light microscope (20x) and then pulled away. This procedure oriented the nanotubes and made them accessible for mounting on copper or tungsten filaments with tip radii of approximately 10 to 100 nm.

It is important to note that carbon nanotubes do not bundle in the same fashion as  $WS_2$  nanotubes (Figure 1). Rather than interconnecting lengthwise, carbon nanotubes are tangled in drastic curvatures along the length of a nanotube. If a single nanotube can be individually contacted, it can be pulled out of the collection of nanotubes and isolated for mounting. In order to align these nanotubes for mount-



**Figure 1: Electron microscope images of (a) bulk tungsten disulfide nanotubes and (b) bulk multiwalled carbon nanotubes.**

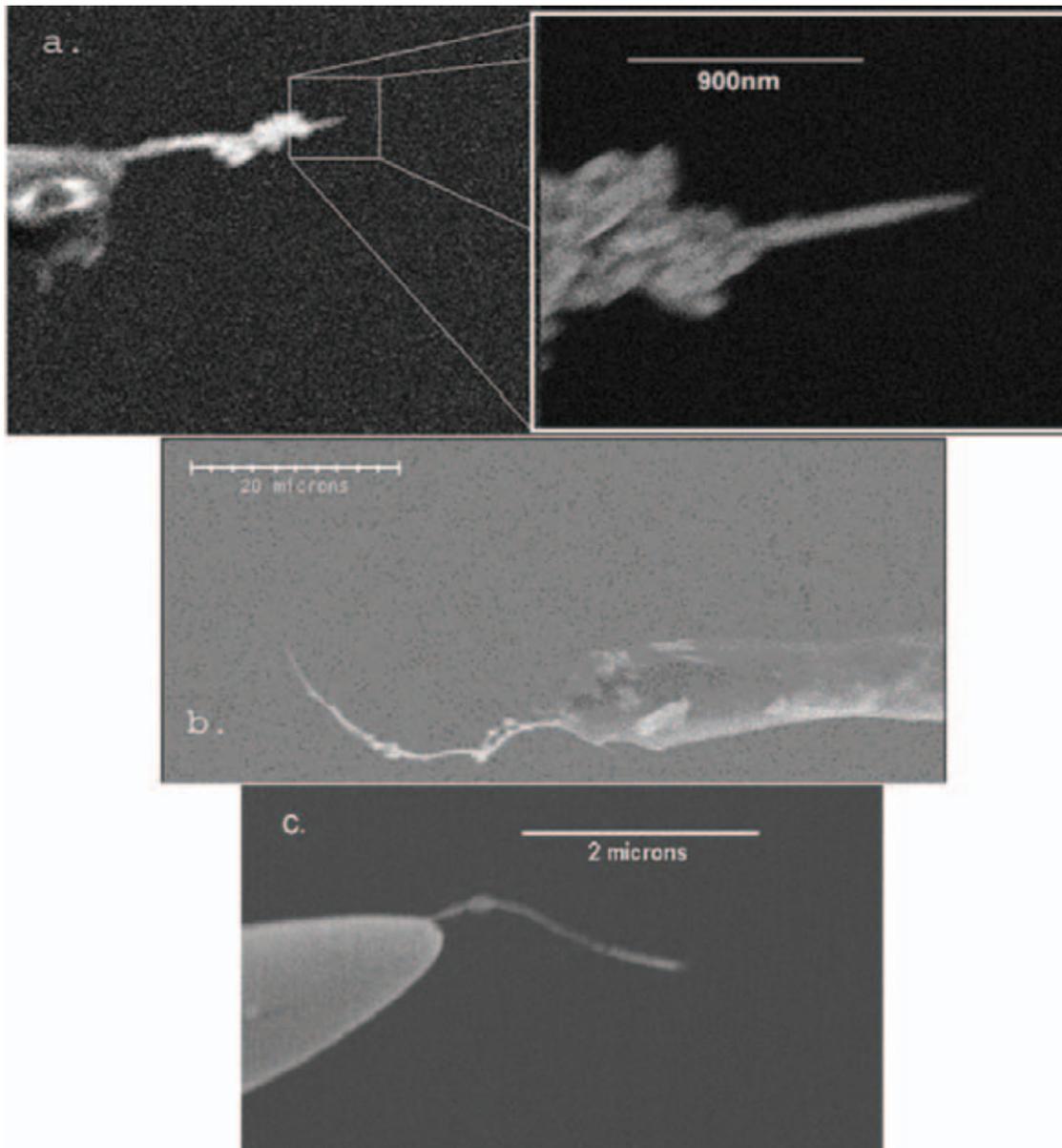
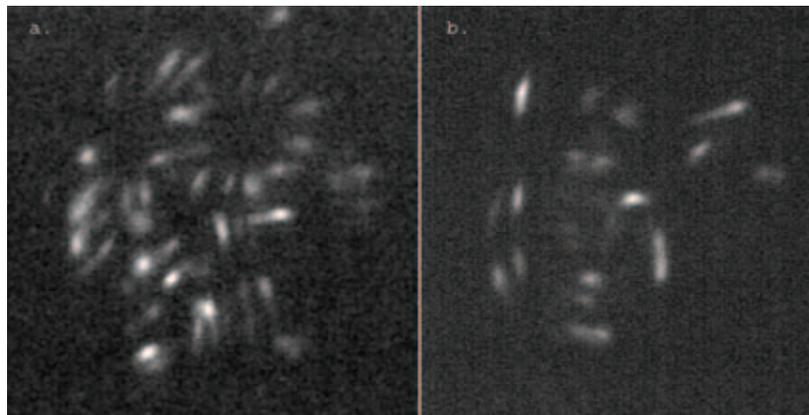


Figure 2: Two successful nanotube mounts: (a) tungsten is the substrate; (b) copper is the substrate; and (c) carbon nanotube on tungsten is the substrate.

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**Figure 3:** Two FIM micrographs of the same specimen, at slightly different voltages, before and after a tip rearrangement: (a) Ne gas at  $2 \times 10^{-5}$  torr, 2.2 kV, and 70 K, and (b) Ne gas at  $2 \times 10^{-5}$  torr, 2.4 kV, and 70 K.

ing, an additional metal filament is used to probe the bundles deposited on the glass or metal substrate. The deposited clumps do not have visible extensions of nanotubes and appear to be exclusively soot. When a metal filament is brought into contact with the clump, a small portion of the clump statically adheres to the metal filament, and when pulled away, single nanotubes protrude radially from the metal tip. These nanotubes can then be contacted for mounting.

In this study, an epoxy polymer filled with silver particles was used to attach the nanotubes to a metal filament. (The silver particles helped make the specimen electrically conductive.) The metal filaments were then prepared through electropolishing. A thin wire of tungsten or copper was suspended in an electrolytic solution surrounded by a metal electrode. An AC current was passed through the wire and electrolytic solution, and the tip was tapered as the metal surface was removed. Sodium hydroxide (NaOH) was used to polish the tungsten wire, and a commercial solution containing phosphoric acid was used to polish the copper wire. Using a high-magnification light microscope

and micromanipulators, an etched filament was maneuvered during the mounting procedure. The dark-field mode on the microscope was used to make the nanotube bundles easily observable. The filament was first dipped into the silver-filled epoxy and then retracted. This was repeated until a small amount of epoxy was fixed on the tip of the filament. The epoxy formed a bead at the tip, with the drop diameter on the order of 0.2–1  $\mu\text{m}$ . Next, the epoxy-coated tip was brought into contact with a protruding nanotube bundle. When a nanotube bundle was selected for mounting, its size and curvature were considered. Specifically, a long, straight, narrow nanotube bundle was the ideal candidate for the 3DAP microscopy experiments.

Caution is essential in such experiments even after the nanotubes are mounted. Because the epoxy cures at room temperature over a 24-hour period, the mounted nanotubes can be reoriented once the epoxy is uncured. In this study, the mount was first manipulated so that the nanotube bundle was protruding straight from the metal filament tip. Larger bundles were oriented pointing downward, so that the

effect of gravity did not misalign the nanotube bundle.

The mounting procedure was refined throughout the course of the research. For example, the size of tungsten disulfide nanotube bundles consistently became smaller. This was a result of finer metal filament electropolishing and using less epoxy to mount the nanotubes. The metal filament used to mount the tip was tapered as much as possible to allow easy contact with the nanotubes. The tapered metal filaments for picking up the silver-filled epoxy were not wetted where the mounting would occur; instead, the cohesive properties of the epoxy caused the tip to dewet and allowed the formation of a bead of epoxy that would then move upward along the metal filament. To avoid this problem, the filaments were polished with as drastic of a tapering angle as possible, approximately  $15^\circ$ . That made beading of the epoxy slightly less favorable. Also, the tip was dipped only slightly into the epoxy so that a minimum amount of epoxy was picked up — just enough to coat the tip of the metal filament but not enough to form a bead conformation of the epoxy. In some instances no

visible amount of epoxy was added to the tip, but mounting still occurred with a small film on the tip.

Further refinement of the mounting technique was required for the carbon nanotube specimens. The ability to isolate a single carbon nanotube, as well as the chemistry of the bonding along the nanotube, made more intense conditions necessary for the FIM and 3DAP microscopy experiments. In all instances the contact between epoxy and nanotubes was too weak, and the carbon nanotubes were stripped off the metal tip. Initially, a thicker layer of epoxy on the mounting metal tip was used. The thinking was that this would increase the strength of the contact between nanotube and metal filament, as more of the nanotube can become wetted by the epoxy. But in this case it was still inadequate for the experiments.

A metal-polishing technique, using a tapering distance of 10 to 20 microns, was subsequently developed using the meniscus formed by electrolyte solution on the metal tip that was being polished. The geometry of the specially designed tip allowed a bead of epoxy to form and remain at the tip of the filament. In turn, this could allow for more contact area between metal tip and nanotube. Finally, one last technique that was proposed but not completed involves forming an epoxy bead on a finely tapered tip, allowing the bead to cure, and then adding epoxy until the bead occurs at the apex of the metal specimen and can be used for mounting. The initially cured epoxy will behave as a block for the subsequent epoxy beads and allow them to move away from the tip apex.

The FIM images collected during this research were obtained using either neon

or helium as the imaging gas at  $2 \times 10^{-5}$  torr. The voltages placed on the nanotube mounting for ionization of the imaging gas ranged from 1500 to 5000  $V_{dc}$ , depending on the size of the nanotube mount. The best images were collected when the specimen temperature ranged between 50 and 70K.

To collect 3DAP data, electrical pulses were used to field evaporate ions from the specimens. A pulse fraction ( $f$ ) of 0.2 was used ( $f$  is the dimensionless ratio of the field evaporation pulse-to-the steady-state DC voltage). Initial field evaporation was performed at standing voltages of 4,000 to 5,000  $V_{dc}$ . As the experiment progressed, higher voltages were needed to maintain a constant field evaporation rate, and so the voltage was increased to

10,000  $V_{dc}$  and higher. 3DAP analyses were performed in ultrahigh vacuum (UHV) at a pressure of  $5 \times 10^{-10}$  torr, while 3DAP data was collected at 100K and at 50K.

## Results

The successful nanotube-mounting procedures performed during this research created several specimens observable by electron microscopy (Figure 2). The electron microscope images reveal that the tungsten disulfide nanotubes are in bundles ranging from 60 to 500 nm in diameter. The tips of these nanotube bundles have either a single narrow protruding nanotube or multiple protruding nanotube ends. The former is preferred because a single nanotube yields a simpler FIM



**Figure 4:** FIM micrographs of different specimens of multiwalled carbon nanotubes. Images are taken in Ne gas at  $2 \times 10^{-5}$  torr and 50 K. (a) The first spot to appear on the micrograph occurs at very low voltages (2030  $V_{dc}$ ). Three images of the same region are taken approximately 10 seconds apart to illustrate the rearrangement of the emitter sites. (b) FIM micrograph at 2056  $V_{dc}$ .

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image. The nanotube bundles range from 10 to 50  $\mu\text{m}$  in length, some with small side branches of bundles or single nanotubes and unidentified clumps of tungsten disulfide. The bundles were rarely straight or rigid, as they had been during mounting. A bundle could be bent drastically and pulled back and forth, sometimes resulting in the bundle breaking. But more often than not, the bundle returned to its original conformation. The same characteristic was noticed in individual carbon nanotubes.

The prepared specimens were imaged using FIM under different operating conditions. For example, the nanotubes imaged well with He gas at  $2 \times 10^{-5}$  torr, at a specimen temperature of 50K, and with imaging commencing as low as 1500  $V_{dc}$ . FIM micrographs from a tungsten disul-

also be seen. It is possible that the stacks of elongated spots are a crystal layer of the nanotube material and the circular arrangements are due to the arrangement of atoms on the tip of a nanotube.

As the specimens were imaged, the standing voltage across the specimen was increased, occasionally causing drastic rearrangements of the FIM. This is associated with a rearrangement of the tip of a specimen and is most likely due to significant numbers of atoms of the nanotube bundle being field evaporated from a tip. It was also noticed that voltage variations result in the rearrangement of spots (atoms) in the image. This can be explained by the increasing electric field across the nanotube bundle mechanically stressing the bundle (the hydrostatic stress is proportional to the electric field squared).

other portions of the image, suggesting that a mechanically moving branch in the ramping electric field could separate the two emitting regions. It is likely that multiple-emitting regions result when they cannot be detected, yet the image is still a superposition of multiple-emission regions.

Field-evaporating the specimens, using the 3DAP microscope and superimposing high-voltage pulses ( $V_{pulse}$ ), helped to determine the chemical identity of what was being imaged. A mass spectrum of the field-evaporated ions was collected, and it exhibits mass peaks due to tungsten ions and tungsten sulfur complex ions (Figure 5). The complex ions are tungsten sulfide and tungsten disulfide. This represents direct experimental evidence that the specimens imaged are composed of tungsten disulfide. A mass spectrum from carbon nanotube evaporation was not collected. A mass spectrum records the frequency of different times-of-flight (TOFs) of the pulse field-evaporated ions. These TOFs are directly related to the mass-to-charge state ( $m/n$ ) ratio of the field-evaporated ions. Identifying the field-evaporated ions using this method is called TOF mass spectrometry.

TOF mass spectrometry is based on conservation of energy of a field-evaporated ion, before and after the field-evaporation event. The energy before the evaporation event is purely potential, and after the evaporation the energy is kinetic. The governing equation, from conservation of energy, is

$$1/2 mv^2 = ne(V_{dc} + \alpha V_{pulse});$$

where  $e$  is the charge of an electron;  $m$  is the mass of the ion;  $n$  is the charge state of the ion;  $v$  is the ion's velocity;  $V_{dc}$  is the standing voltage;  $V_{pulse}$  is the pulse voltage; and  $\alpha$  is the fraction of the voltage

**Potentially, the 3DAP microscopy data can be used to reconstruct ions of the nanotubes; however, the technique must be further optimized, and more needs to be learned about the exact nature of the nanotube bundles.**

fide nanotube are displayed in Figure 3, and FIM micrographs from carbon nanotubes are displayed in Figure 4. Several common features were noticed when imaging a number of nanotube mounts, including both tungsten disulfide nanotubes and carbon nanotubes. For example, the micrograph illustrates numerous predominantly elongated spots, many of which appear to be neighboring emitter sites. These elongated spots are arranged in an organized manner, almost always with other elongated spots in close proximity. Arrangements of stacked elongated spots and circular elongated spots (elongation of spots in the radial direction) can

The nanotubes or bundles of nanotubes were rarely very straight along their whole length, and straightening of the bundles may have occurred during field evaporation of the specimens.

The experiments produced several multiple-emission regions from the nanotube bundle. This resulted in a superposition of two or more field-ion images on the imaging screen. These multiple sites were noticed when ramping the standing voltage ( $V_{dc}$ ) and occurred more frequently with the bundles of tungsten disulfide nanotubes. Specifically, a large portion of the FIM image readjusted relative to

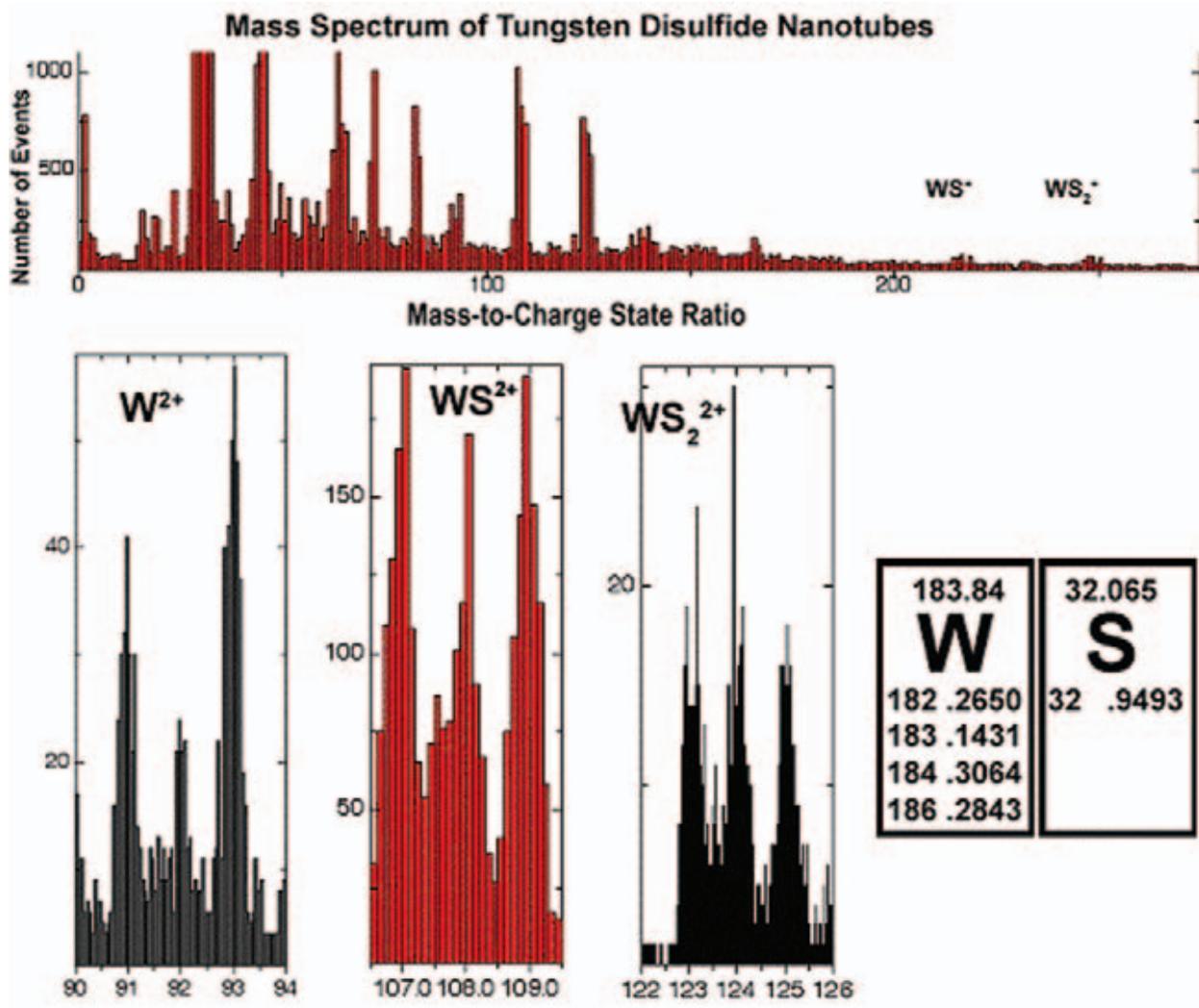


Figure 5: This mass spectrum was obtained using 3-D atom-probe (3DAP) microscope data. The regions involving tungsten and the tungsten sulfur compounds are shown to exhibit the characteristic isotope signature of tungsten. Experimental conditions are 100K,  $2 \times 10^{-10}$  torr, 3000–13000 V<sub>dc</sub> (standing voltage), and a pulse fraction of 0.2.

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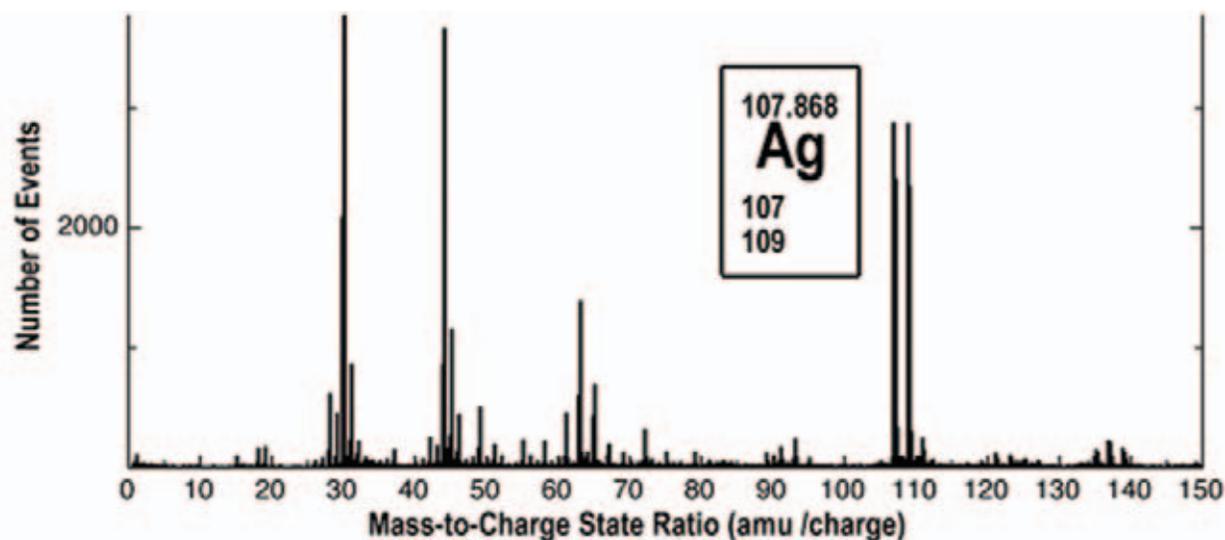


Figure 6a: The mass spectrum of an exposed silver-filled epoxy-coated tip shows the characteristic signature of silver. Experimental conditions are 100K,  $2 \times 10^{-10}$  torr, 4000–1000  $V_{dc}$  (standing voltage) and a pulse fraction of 0.2.

pulse at the tip. The velocity is taken to be a constant because the ion reaches its terminal velocity within a few tip radii (approximately 150 to 200 nm) and then travels to the primary detector (over 60 cm) at constant velocity. Using this fact, Equation 1 becomes

$$m/n = 2\epsilon(t/d)^2 (V_{dc} + \_V_{pulse});$$

where  $t$  is the total time for an ion to reach the primary detector (including the transit time in the electronics), and  $d$  is the flight distance to the detector, which is obtained from a calibration of the 3DAP microscope using known isotopes.

When analyzing a mass spectrum for tungsten, the isotopic abundances of the four most stable and abundant isotopes of tungsten (182.265, 183.143, 184.306, and 186.284 amu) must be noted. These

isotopes lead to a group of closely positioned peaks in the mass spectrum, as opposed to a single peak, which would be characteristic of an element with a single stable isotope. Since sulfur has essentially a single isotope, the four-peak signature of tungsten is used to identify the tungsten sulfur compounds in the mass spectrum, as well as elemental tungsten.

Although the 3DAP microscope experiment was performed under UHV conditions, there is typically some existing contaminant gas in the chamber, usually hydrogen at an ambient pressure of less than  $10^{-10}$  torr. A contaminant gas may also be released from a specimen as it is field evaporated. The contamination gas in the UHV chamber is field ionized during experiments and these gas molecules are detected in the mass spectrum along with the field-evaporated molecules.

This causes some of the spectrum, including much of the low mass-to-charge state ratio range, to be dominated by the contaminant gas.

During the analysis of nanotube specimens, tip conditions are volatile, and the nanotubes can break or be pulled out of their epoxy mount. Under these circumstances, the metal tip can be exposed to a layer of the epoxy. The epoxy is filled with microscopic particles of silver, meaning it is electrically conductive. Trials for evaporation of nanotubes resulting in an exposed epoxy surface produced a mass spectrum containing silver ions (Figure 6). This means the silver particles that are exposed to the surface are evaporating and being detected. In light of this result, a technique is proposed in which small particles of an analyzed material are

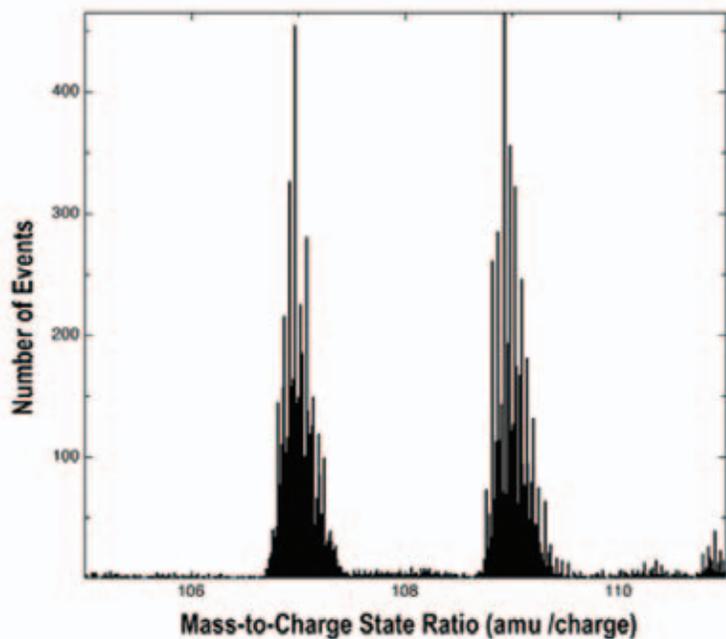


Figure 6b.

mixed into an epoxy paste and applied to a metal tip for experiment.

#### Future Direction

These experiments imaged tungsten disulfide and carbon nanotubes using field-ion microscopy (FIM). Furthermore, they established the technique of 3DAP microscopy for chemically analyzing tungsten disulfide, which belongs to a class of molecules not typically analyzed in this fashion. Much about the atomic scale chemistry of the tungsten disulfide and carbon nanotubes is still unknown. Potentially, the 3DAP microscopy data can be used to reconstruct ions of the nanotubes; however, the technique must be further optimized, and more needs to be learned about the exact nature of the nanotube bundles.

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