Unraveling Nanotubes: Field Emission from an Atomic Wire


Field emission of electrons from individually mounted carbon nanotubes has been found to be dramatically enhanced when the nanotube tips are opened by laser evaporation or oxidative etching. Emission currents of 0.1 to 1 microampere were readily obtained at room temperature with bias voltages of less than 80 volts. The emitting structures are concluded to be linear chains of carbon atoms, C₆₀ (n = 10 to 100), pulled out from the open edges of the graphene wall layers of the nanotube by the force of the electric field, in a process that resembles unraveling the sleeve of a sweater.

Because carbon nanotubes (1) are intrinsically nanoscopic in two dimensions and both mechanically stiff and electrically conductive for macroscopic distances, we have been working to develop them as individually mounted probes for scanning microscopy. In the course of this work, we have discovered bizarre aspects in the field emission behavior of nanotubes when their tips are opened. Most surprisingly, the field emission is far more intense when the open tip is at room temperature than when it is laser-heated to 1500°C. After considering alternative explanations, we conclude below that the emitting structure at room temperature is an "atomic wire" of 10 to 100 sp²-bonded carbon atoms pulled out from the open graphene sheet of the nanotube by the electric field. Such structures may provide the ultimate atomic-scale field emitters (2).

Carbon nanotubes used in this study were prepared in an optimized DC carbon arc apparatus (3) to produce a boule which was then baked in air at 650°C for 30 min to oxidatively etch away all but the best nanotube material (1). Individual nanotubes extending out of the surface of a piece of this boule were then attached to graphite fiber electrodes and mounted in the vacuum apparatus (Fig. 1). Figure 1B shows images at magnification for a typical mounted nanotube prepared in this fashion. The mounted nanotube was positioned with a micrometer so that the tip was 1 mm above a Faraday cup connected to an external circuit for measurement of the field emission current. A continuous wave (cw) laser (514 nm) focused to a 5-μm spot was used to adjust the temperature of the nanotube tip. An optical microscope connected to a charge-coupled device (CCD) camera (4) allowed us to image the nanotube either by scattered light or, with appropriate filters, by incandescence. Nanotube tip temperatures were estimated by comparing the brightness of the incandescence image relative to that typically seen from tubes heated to sublimation (∼3000°C), assuming black body wavelength and power dependence of the incandescence on temperature.

The tips of these multiwalled nanotubes were found to be readily opened (5) by laser heating in high vacuum to near sublimation temperature for a few seconds while the nanotube was held at −75 V. Alternatively, some of the nanotubes were opened by exposure to several miliatmospheres of O₂ while laser-heating the tip to 1000°C to 1500°C, monitoring the field emission at −75 V bias as a sensitive indicator of precisely when the tip had opened. Reclosure of open-tipped nanotubes to form a smooth hemi­fullerene surface on the end ("dome closure") was found to occur within a few seconds whenever the tip was heated in high vacuum at zero bias voltage to the point that it began to shorten by sublimation (6).

Figure 2 displays the measured field emission from a typical nanotube in this apparatus when biased to −75 V, and alternatively laser-heated to −1500°C and then cooled to room temperature with the laser blocked. Laser heating was used to ensure that the tip of the nanotube was free of any

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A. G. Rinzler, J. H. Hafner, P. Nikolaev, P. Nordlander, D. T. Colbert, R. E. Smalley, Center for Nanoscale Science and Technology. Rice Quantum Institute, and Department of Chemistry and Physics, Mail Stop 100, Rice University, P.O. Box 1900, Houston, TX 77251, USA.
L. Lou, WaveFunction Corp., 18401 von Karman, Suite 370, Irvine, CA 92715, USA.
S. G. Kim and D. Tománek, Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824-1195, USA.

1550

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chemisorbed O or H atoms arising from reactions with residual H2O and other molecules in the 10^-7 torr background gas of the vacuum chamber. As is evident in the comparison of Fig. 2. A and B, a dramatic difference was found between the closed (Fig. 2A) and open (Fig. 2B) state of the nanotube.

For the dome-closed nanotube, field emission at room temperature became measurable (>0.1 pA) only for negative biases greater than -83 V. Accordingly, in Fig. 2A where the bias voltage was only ~75 V no field emission was measured when the laser was off. With the laser on, however, the nanotube tip was heated to ~1500°C and thermal enhancement of the field emission process was sufficient to give a steady, reproducible emission current of 35 pA.

Figure 2B, in contrast, shows the field emission results from this same nanotube after it had been opened. Note that the emission current with the laser on was 8 nA—more than 100 times greater than seen from this tube when the tip was closed (Fig. 2A). Because there can be no chemisorbed H or O atoms surviving on the nanotube surface at this high temperature, the 100-fold enhancement of the laser-on field emission upon tube opening must be due to the atomic-scale roughness of the exposed graphene sheet edges of the open tip as compared to the smooth hemi-fullerene surface of the dome-closed tip.

The most striking aspect of Fig. 2B, however, is that when the laser was blocked and the nanotube rapidly cooled from 1500°C to room temperature, the field emission did not go down as one would expect. Instead, it rapidly went up by a factor of 100 to a level of 0.4 to 0.6 nA, more than 1 million times greater emission than observed in Fig. 2A for the dome-closed tube at room temperature. Figure 2C shows an expanded time scale of a 2-s period of the data, reveals that the emission current in this mode switched rapidly between fixed levels. With our present measurement electronics, these excursions were found to be faster than 2.5 x 10^-4 s, our smallest time resolution, and we expect they were due to individual atomic-scale events (7). Note that none of these excursions changed the net emission current by a factor of 5 to 10, indicating that at times nearly the entire current was being emitted from a single structure.

Lowering the magnitude of the bias voltage while the open nanotube was in this high field emission state revealed that the emission onset was not achieved at only -41 V, less than half the -83-V emission onset voltage measured for this same nanotube when the tip was closed. This low onset, and the dramatic increase in emission current seen in Fig. 2B, must be due to the formation of either an especially sharp and exposed structure extending far off the tip of the opened nanotube or arise from some site with an especially low work function. In either case, the special site must be one that is readily destroyed by laser heating.

One conceivable explanation is that the dangling bonds on the exposed edges of the open tip are susceptible to reactions with the residual gases in the vacuum system, resulting in chemisorbed species that are dramatically better field emitters than the exposed Ca atoms. Exposing to the laser then heats the nanotube to 1500°C and describe these species, resulting in a lower field emission even though the temperature is much higher. However, we found that intentionally increasing the level of any of the known background gases (H2O, H2, O2, CO, and small hydrocarbons) actually quenched the field emission (8). Furthermore, the rate of rise of the emission current when the laser was blocked never correlated with the background gas pressure, although experiments equivalent to Fig. 2B have now been completed on more than 50 different nanotubes at pressures ranging from 1 x 10^-7 to 5 x 10^-6 torr. For these reasons, among others (9), we are confident that whatever the special emitting structure is, it is not produced by chemisorption. Instead, it must be some sort of sharp structure pulled out from the nanotube tip under the influence of the electric field. It must be made entirely of carbon, and its emission is deactivated by chemisorption reactions with the background gas.

Increasing the magnitude of the bias voltage on the open nanotube while in the high field emission state saturated the field emission. For a typical open nanotube at -100 to -110 V bias, the field emission ranged from 0.5 to 1.5 nA. Under these conditions, we detected a very faint incandescence at the tip of the nanotube (10) with the CCD camera. At slightly higher bias voltages, the nanotubes were typically found to shrink back by a process that was highly episodic. One particularly striking event is shown in Fig. 3, where successive panels are the integrated signal for successive 30-s intervals while the nanotube was held at -107 V. In Fig. 3, B and C, the nanotube incandesced dimly at the tip. However, during the 30-s exposure in Fig. 3D, an extremely bright event occurred that lit up the side of the nanotube for 8 μm along its length. Figure 3, E and F, reveals that this event must have been restricted to the outermost few layers. The tip is still in its original position, incandescing at the same dim level as in Fig. 3, B and C. This selective burn-back of the outer layer of a nanotube was an unusual but highly revealing event. As detailed below, we believe that it can only be explained by the unconstrained unraveling of a carbon chain from the outer "sleeve" of the nanotube.

More typically, open nanotubes biased substantially above -110 V and field emitting more than 2 μA suffer catastrophic burn-back events that are not restricted to their sides. These produce a single bright streak in the CCD camera as they evaporate back to the point of attachment.

We have become convinced that there is only one viable explanation for the field emission behavior described above. The structures responsible for the data of Figs. 2B and 3 are individual linear carbon chains...
unraveling the carbon chain from the open edge of the graphene sheet. Remarkable as this atomic wire hypothesis may at first seem, it is actually the most straightforward explanation given that the emitting structure must be some arrangement of carbon evolved from the open edges of graphene sheets. Many other alternatives have been considered in detail. The best of these is a section of one of the layers of the nanotube which has rearranged under the influence of the electric field into a roughly triangular section extending above the rest of the open tip. However, because the surface of the open tip is already covered with atomically sharp edges of the various layers, this special field emitting structure would have to extend far out to explain the enhanced field emission. Detailed modeling of the emission from the top of such a structure shows that it would have to extend out from the end of the open multiwalled nanotube by more than 2 to 3 nm (~20% of the tip diameter) to begin to explain the observed enhancement. This process

\[ (\text{11-13})_\text{C}_n \text{ atomic wires—} \text{that have pulled out from the open edges of the graphene sheets of the nanotube as shown in Fig. 4 and are held taut under the influence of the electric field. Inasmuch as the first atom in the chain at the point of attachment is bonded to the delocalized } \pi \text{-orbitals of the graphene sheet, this all-carbon atomic wire is both physically and electrically well coupled to the macroscopic world in a distinct, reliable, and easily modeled way. The conduction band of these wires is derived from the overlap of the cylindrically symmetric } 2p\pi \text{-atomic orbitals on each successive sp-hybridized carbon atom. Although such one-dimensional atomic wires are susceptible to Peierls-like distortions (14) opening up a small band gap, the bond length alternation for the pure } \text{C}_n \text{ chain is calculated to be very small (<2%) (13), showing that the dominant electronic structure is closer to the cumulenic form } (\ldots \text{C} = \text{C} = \text{C} \ldots), \text{than to the bond-alternate polyyne } (\ldots \text{C} \equiv \text{C} = \text{C} \equiv \text{C} \ldots). \text{Transport of electrons injected from the negatively charged nanotube down to the tip of the chain is therefore expected to be quite facile. The delocalized, cylindrically symmetrical } \pi \text{-bonding along the chain produces a nearly metallic screening, concentrating the electric field to extremely high values at the end of the last atom on the tip of the chain (15). The result is that high-current field emission is obtained at low voltage in a room-temperature environment from what is effectively an atomic wire.}

\[ \text{Fig. 3. (A) A schematic showing the simple geometry in (B) through (F), which are optical microscope images of the incandescence from an individually mounted nanotube held at ~107 V, integrated by a near-infrared-sensitive CCD camera over successive 30-s intervals. The faint glow seen at the tip in (D), (E), and (F) is caused, we propose, by the incandescent glow of a few } \text{C}_n \text{ chains extending off the open tip of the nanotube as they are heated by their own thermal emission. In (C), an extremely bright incandescent event (30 to 100 times brighter per pixel) occurred during this 30-s interval, lighting up the side of the nanotube for an 8-μm length back from the tip. It is believed to have been caused by an uncontrolled, complete unraveling of the outermost layer of the nanotube. Diffraction effects cause the nanotube to appear to be 1 μm thick in this image. It was actually 15 nm in diameter.}

\[ \text{Fig. 4. Model of the tip of a multiwalled nanotube showing a single } \text{C}_n \text{ "atomic wire" extending out from the inner layer, held taut and straight by the electric field. The nanotubes used in this study were larger in diameter than the one shown here, having typically a diameter of 10 to 15 nm and composed of 10 to 20 concentric tubular layers. Note the single-atom "spot welds" that interconnect the adjacent layers at the open end. Such atom-bridge structures are critical in helping the electric field to keep the nanotube tip open at high temperatures (17). These spot welds and more extensive bridging structures serve to hang up the unraveling process, stabilizing the atomic wire and emitting structures at lengths less than the 5- to 50-nm circumference of a nanotube layer.}

\[ \text{Fig. 5. Schematic of the unraveling process. For simplicity, only a double-walled nanotube is shown. When the electric field has become high enough to begin to pull at the most exposed C atom (1) with sufficient force to break C-C bonds, there are three possible bonds to break: The direction of the applied field favors breaking the [2]-[3] bond. Note that only when the chain is extended by breaking this bond is the total dangling bond count kept constant. This occurs because atom [2] can compensate the loss of its bond to [3] by concurrently increasing the bond order of its attachment to [4]. The net effect is to increase the carbon chain length by two atoms without any decrease in the total bond order of the entire structure. Any other choice increases the dangling bond count by at least one. Further pulling by the electric field on the chain re-establishes the process, effectively unraveling the carbon chain from the open edge of the graphene sheet. Note, however, that when the unraveling reaches a site that is "spot-welded," such as [7] in this schematic, there is no way to continue the unraveling process without increasing the overall dangling bond count.} \]
would require successive, independent re-arrangements of hundreds of atoms as the structure is built under the influence of the applied field, at a cost of many additional dangling bonds. We can find no plausible mechanism for the sudden assembly of such a structure at room temperature such as is required by the data of Fig. 2B, nor for its sudden disappearance when the laser heating is turned off. Neither is there a mechanism apparent whereby all of the atomically sharp emission sites near the top of such a graphene structure can be deactivated by a single chemisorption event as is required by the data in Fig. 3C.

Figure 3 addresses the question of how and why C5 chains would be pulled out by the electric field in these experiments, showing that the entire process can occur with no net decrease in the effective bond order (16). This expected ease of unraveling a linear carbon chain then brings up the question of why it does not continue indefinitely, destroying the nanotube completely when it is in a high electric field. In fact, we believe that this is exactly what happens to produce the catastrophic burn-back events discussed above for biases greater than -110 V in magnitude. In the special case of Fig. 3D, we believe that the incandescent flash that illuminated the side of the nanotube was caused by the outermost layer unraveling down the side of the tube to the point of attachment to the tip, 8 μm back. The bright incandescence was caused by resistive heating of the unraveling carbon chain as the emission current from the tip was 1 to 2 μA. The dim incandescence seen at the tip of the nanotube in the earlier and succeeding panels is, we assume, due to a few carbon chains also heated to incandescence by the emission current, but somehow held up in their unraveling process. As shown schematically in Figs. 4 and 5, we believe it is the presence of C5 atoms bridging between the layers of the multi-walled nanotubes that ordinarily keeps this unraveling process in check. The simplest possible bridge is a single C5 atom like that labeled atom 8 in Fig. 5, acting as a one-atom "spot weld" between the two adjacent layers. Such a structure will serve as a barrier to further unraveling because it forces an increase in the dangling bond count. These layer-to-layer spot welds have been implicated in other research on multi-walled nanotubes from this group (17) and in recent calculations (18). If this is the correct mechanism (19), the unraveling of the outermost layer will be unique. Once this layer has etched back through the inner layers, bridging spot welds are no longer possible, and there is nothing to stop the unraveling. We know of no other way of explaining Fig. 3D.

The sudden destruction of these field-emitting C5 atomic wires when the laser is unblocked in the experiments of Fig. 2B is readily understood as thermally induced evaporation of C5 and other small carbon radicals from the tip of the chain until this chain is so short that the electric field at the tip is no longer sufficient to produce efficient emission. We expect that there is a very steep temperature dependence of the effective resistance of the carbon chain, with nearly ballistic transport when the chain is cool, but frequent scattering and consequent chain heating and further increase in resistance once the vibrations of the chain become excited.

The fundamental and practical aspects of these one-dimensional atomic wires seem likely to emerge as fascinating topics for further study and application. They may turn out to be excellent coherent point sources of monochromatic electron beams and to have wide applications as probes, emitters, and connectors on the nanometer scale.

REFERENCES AND NOTES

7. For instance, a thermally driven laser diode has etched back 5 μm from the tip of a perfect nanotube.
8. In the calculation, the laser field excites the nanotube linearly.
9. In the calculation, the laser field excites the nanotube linearly.
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