Unraveling Nanotubes: Field Emission from an Atomic Wire

A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tománek, P. Nordlander, D. T. Colbert, R. E. Smalley

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, C_n (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 *sp*-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 increasing 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 bias. Alternatively, some of the nanotubes were opened by exposure to several millitorr of O_2 while laser-heating the tip to 1000° 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 alternately 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

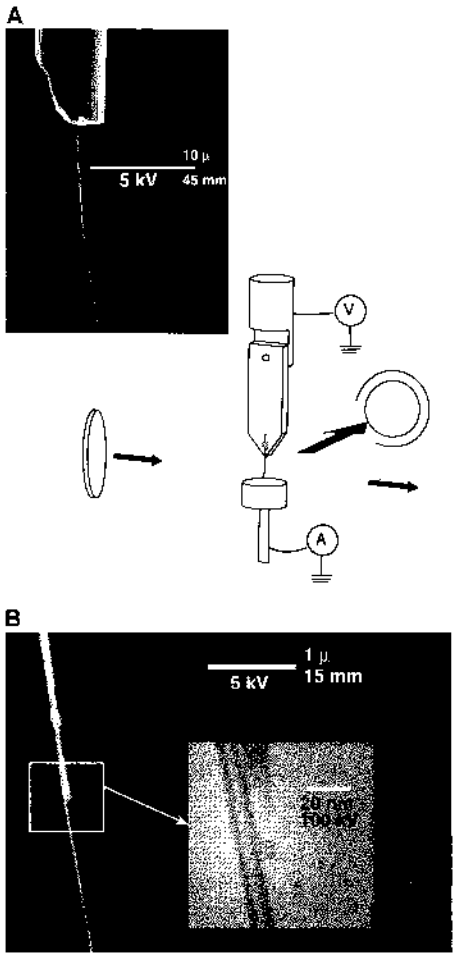

Fig. 1. (**A**) Schematic of the apparatus for measuring the field emission of individually mounted nanotubes. Field-emitted electrons were collected in the Faraday cup mounted 1 mm from the tip of the negatively biased nanotube; the entire assembly resides in a vacuum chamber at 10^{-7} torr. A cw laser beam (514 nm) was focused to a 5-μm spot on the tip of the nanotube to control its temperature, and a 0.45 numerical aperture optical microscope was mounted at 90° to the laser axis so that the nanotube could be imaged either by scattered light or incandescence with a CCD camera sensitive to 1.1 μm. The inset shows a scanning electron microscope (SEM) image of a single multiwalled nanotube attached by van der Waals (vdW) forces to the side of a "stalk" of 5 to 10 other nanotubes which in turn adhered by similar vdW forces to the side of an 8-μm graphite fiber, which in turn was attached with silver paint to the stainless steel electrode. In (**B**), higher resolution images by SEM and transmission electron microscopy (inset) are shown at the end of the stalk and the single nanotube. This vdW adhesion technique works well because the nanotubes are atomically smooth and the graphite fiber's surface is also made of sections of similarly smooth graphene sheets. The expected 10 meV per atom vdW cohesive interaction (*20*) adds up to many electron volts of bonding energy given that tens of thousands of atoms are in vdW contact. If we assume that the electrical resistance of this contact is no worse than the corresponding area of a graphite lattice along the *c* direction, the contact resistance involved in this method of attachment is $<10^{-2}$ ohm, which is negligible compared with the 10^4 to 10^6 ohm resistance expected for a 10-μm length of these multiwalled nanotubes (*21*). We find that this vdW attachment remains strong so long as the mounted nanotube is kept in a dry environment.

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 Departments of Chemistry and Physics, Mail Stop 100, Rice University, P.O. Box 1892, 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 48824–1116, USA.

chemisorbed O or H atoms arising from reactions with residual H_2O 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.

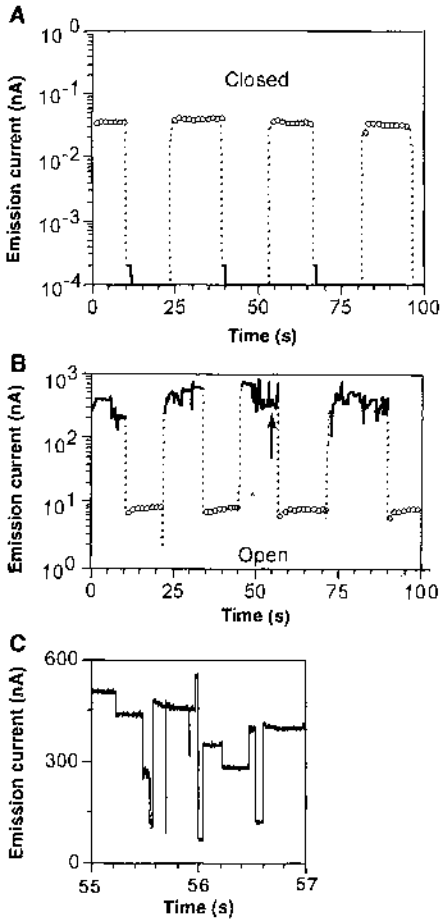

Fig. 2. Field emission at −75 V bias from a nanotube in (**A**) the fully dome-closed state as compared to the same nanotube in (**B**) the open tip state when the nanotube was alternately laser irradiated to heat the tube to ~1500°C (open circles) and then left at room temperature while the laser was blocked (heavy solid lines). (**C**) A section of the high field-emission behavior of the room-temperature open nanotube at expanded time resolution. The instantaneous jumps are thought to be caused by chemisorption and desorption events at the tip of the field-emitting C_n chains and from unpinning events at their base that allow these "atomic wires" to unravel further.

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 hemifullerene 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 0.8 μA, 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 2.5×10^{-4} s, our smallest time resolution, and we expect they were due to individual atomic-scale events (*7*). Note that many 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 now 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 C atoms. Exposing to the laser then heats the nanotube to 1500°C and desorbs 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 (H_2O, H_2, O_2, 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 1×10^{-7} to 5×10^{-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 μA. Under these conditions, we detected a very faint incandescence at the tip of the nanotube (*10*) with the CCD camera. At slightly higher bias voltage, 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

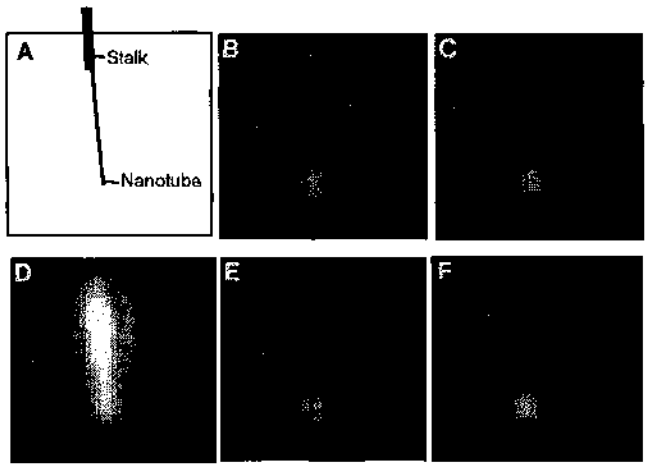

Fig. 3. (**A**) A schematic showing the sample geometry in (**B**) through (**F**), which are optical microscope images of the incandescence from an individually mounted nanotube held at −107 V, integrated by a near-infrared–sensitive CCD camera over successive 30-s intervals. The faint glow seen at the tip in (B), (C), (E), and (F) is caused, we propose, by the incandescent glow of a few C_n chains extending off the open tip of the nanotube as they are heated by their 0.5 to 1 μA emission current. In (D), 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.

(*11*–*13*)—C_n atomic wires—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 π-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 $2p\pi$-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 C_n chain is calculated to be very small (<2%) (*13*), showing that the dominant electronic structure is closer to the cumulenic form (. . .=C=C=C=C:), than to the bond-alternate polyyne (. . .–C≡C–C≡C·). 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 π-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.

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

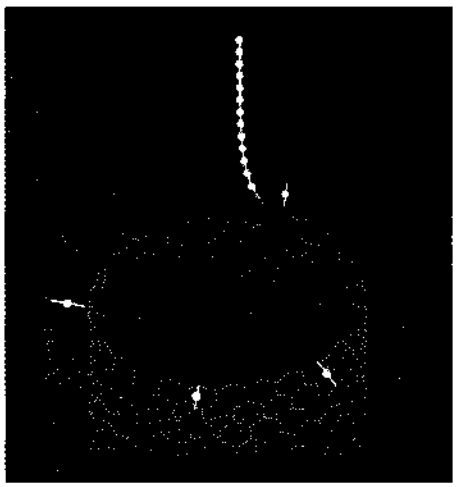

Fig. 4. Model of the tip of a multiwalled nanotube showing a single C_n "atomic wire" extending out from the inner layer, held taut and straight by the electric field. The nanotubes used in this study were larger in diameter than the one shown here, having typically a diameter of 10 to 15 nm and composed of 10 to 20 concentric tubular layers. Note the single-atom "spot welds" that interconnect the adjacent layers at the open end. Such adatom bridging 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 field emitting structures at lengths less than the 5- to 50-nm circumference of a nanotube layer.

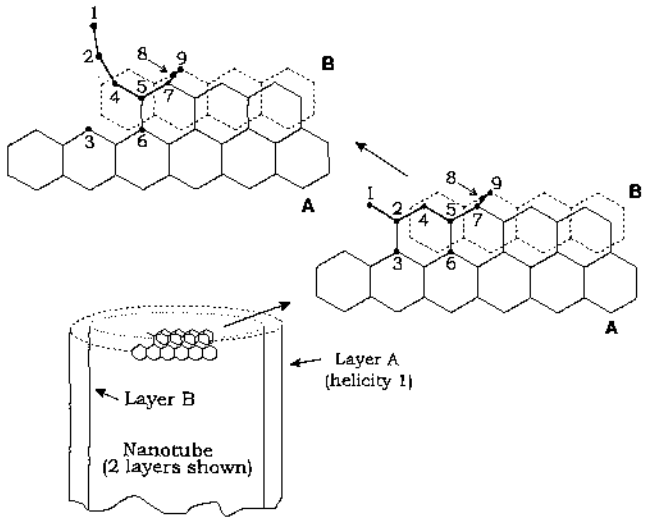

Fig. 5. Schematic of the unraveling process. For simplicity, only a double-walled nanotube is shown. When the electric field has become high enough to begin to pull at the most exposed C atom [1] with sufficient force to break C–C bonds, there are three possible bonds to break. The direction of the applied 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 concertedly 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 repeats 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 rearrangements 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 resumed. 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. 2C.

Figure 5 addresses the question of how and why C_n 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 stalk, 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 C atoms bridging between the layers of the multiwalled nanotubes that ordinarily keeps this unraveling process in check. The simplest possible bridge is a single C 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 multiwalled 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 behind 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 C_n atomic wires when the laser is unblocked in the experiments of Fig. 2B is readily understood as thermally induced evaporation of C_3 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.

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4. Princeton Instruments TEK 512B charge coupled device array sensitive to 1.1 μm in the infrared.
5. Because of the thermally induced vibrations of these individual nanotubes extending unsupported for 5 to 10 μm out from the carbon-fiber electrode mount, we have not yet obtained high-resolution TEM images to show the precise shape of the opened or closed tips. We have inferred the state of the tube tip from the field emission behavior, its dependence on laser heating, and its response to added reactant molecules such as H_2, H_2O, O_2, and C_2H_4.
6. These results strongly support the notion that the most important aspect of a dc carbon arc in producing nanotubes is the high electric field that exists in the plasma layer immediately above the surface of the cathode, and that the most critical role this field plays is in keeping the tips of the growing nanotubes open in spite of the >3000°C conditions on the surface of the cathode that would otherwise rapidly anneal the nanotube tips to full dome closure.
7. The frequency of these excursions was found to be roughly proportional to the background pressure in the 1×10^{-7} to 10×10^{-7} torr range, indicating that they are due to modification of the emitting feature or, in some cases, its complete destruction by ion bombardment or chemisorption events with the background gas or both processes.
8. Hydrogen (H_2) at 10^{-4} torr quenched the field emission of the room-temperature nanotube in less than a few seconds, indicating that the emitting carbon structure has a highly reactive dangling bond at its tip. This result is quite consistent with the cumulenic . . .C=C=C=C structure proposed here for the C_n wire. Chemisorption of a single H atom at the end of the C_n chain is expected to flip the cumulenic electronic structure to the bond-alternate polyyne structure . . .–C≡C–C≡C–H with no dangling bonds on the tip and a much poorer conductivity.
9. The multiwalled nanotubes used in this study typically have 10^3 to 10^4 surface C atoms in the structure of the open tip. Because the tip already has many places of atomic sharpness to act as efficient field emission sites, the special emitting structure formed when the laser is blocked must be very special indeed. Chemisorbed O, H, or OH groups will not be substantially sharper or more exposed so as to concentrate the electric field than the carbon sites already present and would more likely increase rather than decrease the local work function.
10. This constitutes what must be the smallest Edisonian light bulb ever made.
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15. Local density functional calculations of a C_{10} chain in an applied uniform electric field have shown these C_n chains to screen the applied field nearly as efficiently as a metal rod of the same dimension. The C–C bonds are found to be exceedingly strong, undergoing very little change in length until the applied field exceeds 2 V/Å, at which point the peak electric field off the tip of the end atom has risen to more than 10 V/Å. The applied uniform electric field is found to increase the extent of bond-length alternation from <1% at zero field to ±3% at 1 V/Å; L. Lou, P. Nordlander, R. E. Smalley, in preparation.
16. The cohesive energy of carbon in a C_n chain is estimated at 6.1 eV per atom [see (*11*, *12*)], whereas that of an infinite graphene sheet (or larger diameter nanotube) is 7.3 eV per atom (*12*). Therefore, although there is no net change in the formal bound count, there is a cost of ~1.2 eV per atom to pull out a C_n chain from the open tip of a perfect nanotube. However, any other structure will cost more. Estimates of the cohesive energy of graphite flakes (*12*) show that the cost to the overall cohesive energy due to the dangling bonds on the periphery is 1.5 eV per atom. All alternatives to the C_n chain require an increase by more than 2*n* in the number of these energetically costly edge atoms in order to produce a field-emitting structure of the same height.
17. T. Guo *et al.*, *J. Phys. Chem.* **99**, 10694 (1995).
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19. This mechanism predicts that the more extensively the open multiwalled nanotube tip is annealed, the more extensively spot-welded it becomes, and the more difficult it will be to pull out C_n chains of sufficient length to achieve high field emission. Indeed, we find this to be the case. After heating the nanotube to a tip temperature of 2000°C, the field emission with the laser blocked was typically found to be <1 nA. Still, the field emission was found to jump instantaneously between stable levels much as seen in Fig. 2C, inset, for the longer chains. In both cases, we believe the jumps are caused by individual chemisorption, desorption, and ion-bombardment events. Occasionally, we have observed the field emission of a nanotube jump to >100 nA in a few discrete steps after a prolonged period below 10 pA as an unusually long length C_n chain was allowed to pull out.
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