

## Fullerene nanowires

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**Abstract:** A method has been found which produces nanowires in high yield. These wires are cylindrical single-walled fullerenes: hollow carbon tubes 1.2–1.4 nm in diameter,  $>20\ \mu\text{m}$  in length, constructed of a single hexagonally-bonded graphene sheet wrapped into a cylinder, with hemispherical endcaps involving 6 pentagons. They are produced by laser vaporization of a composite rod of graphite with 1–2 atom percent of a catalyst such as 1/1 Ni/Co, inside a quartz tube at  $1200^\circ\text{C}$ , in a  $1\ \text{cm sec}^{-1}$  flow of argon at 500 Torr. The yield is greater than 50% of all the carbon vaporized. The wires are found to be aligned to form ropes of 10–100 parallel tubes held together in a closed-packed hexagonal array by van der Waals forces. The ropes are often found with overall length greater than 0.1 mm. Due to their expected high electrical conductivity, especially when doped with metals either down the hollow inside region or on the outside, intercalated in the triangular gaps between the adjacent tubes, these new materials may provide the first source of wires on the nanometer scale whose electrical conduction is truly metallic. It may also be possible to make them much longer.

Buckminsterfullerene (1),  $\text{C}_{60}$ , has become not only the prototypical member of a vast class of new carbon cage molecules collectively known as the fullerenes (2,3) but a major stimulus for fanciful dreams of architecture in general on the nanometer scale. One of the most extreme of these dreams is to extend the  $\text{C}_{60}$  cage in one direction, inserting one extra belt of 10 carbon atoms to make  $\text{C}_{70}$ ; opening it again and inserting a second belt to make a now capsule-shaped  $\text{C}_{80}$ , repeating this process over and over, making a hollow tube of increasing length. When extended to infinity, this process results in the most perfect possible carbon fiber: effectively a single crystal of carbon in one linear dimension, but only 0.7 nm in width.

Made of a single sheet of graphene (i.e., an individual hexagonally bound layer of carbon in ordinary crystalline graphite) and wrapped into an infinite tube, this dream fiber would have fantastic properties. Its tensile strength, for example, is expected to be roughly 100 times higher than that of steel, while having less than one fifth the weight. In the form of a multistrand rope ( $10^{14}$  strands/cm<sup>2</sup>) this fiber would provide the ultimate structural cable. Its thermal conductivity along the fiber axis should be extremely high -- similar to that of diamond. But most intriguing would be the electrical properties. It would be metallic (4). Particularly when doped with metal atoms arrayed like peas in a pod down the central axis, or "intercalated" in the spaces between adjacent tubes in a multistranded composite, the electrical conductivity of these nanoscale wires at room temperature may be dramatically higher than gold. One can imagine these fullerene wires replacing all the power cables in the world, or used individually to interconnect electronic devices on a molecular scale.

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This is the dream of nanowires (5), and the association with fullerenes and Buckminster Fuller could hardly be more appropriate. Richard Buckminster Fuller (6) was certainly the sort of man who would have dreamed such dreams, talked about them endlessly, and invented whole new worlds based on their wonderful properties.

But how about reality? Is it possible to trick carbon into assembling in such a way? There is no question that these hollow cylinders are not the most stable possible form of carbon. Graphite is still the thermodynamic optimum for carbon under standard conditions. Even on the nanometer scale, nanotubes are known to have less cohesive energy than a single-shell spheroidal fullerenes with the same number of atoms (7), and these in turn are known to be less stable than "bucky onions" composed of concentric shells starting with  $C_{60}$  surrounded by  $C_{240}$ , then  $C_{540}$ , then  $C_{960}$ , etc. (8); the general formula for the  $n$ -th shell being  $60 \cdot n^2$ . If fullerene nanowires (single-walled nanotubes, or SWT) are to be made, there will have to be something tricky in the physics and chemistry that drives the kinetics along this path.

In a recent publication (9) our group has reported what appears to be just such a trick using a simple extension of the laser vaporization/heated oven technique developed earlier in this group to produce  $C_{60}$  and other small fullerenes in 30-40% yield (10). Stimulated by the success of Iijima *et al.* (11) and Bethune *et al.* (12) in producing small amounts of single-walled nanotubes by incorporating a transition metal such as iron or cobalt in the anode of a carbon arc, and the results of Lambert *et al.* (13) in enhancing the yield by using a mixture of such metals, we prepared a composite graphite rod with 1-2% (atom) of a 50:50 mixture of Ni/Co powder. Laser vaporization of this material (2nd harmonic of a Q-switched Nd:YAG laser, 514 nm, 300 mJ/pulse focused to a 6-7 mm spot on the front of the target, and scanned under computer control over the surface of the target so as to maintain a uniform flat surface as the material was progressively vaporized) in a quartz tube heated to 1200°C produced a material which was transported as an aerosol in a 50 sccm flow of Argon at 500 Torr, forming a black deposit on a downstream collector cooled to 10°C.

Figures 1 and 2 show transmission electron micrographs (TEM) of high-yield Co/Ni-catalyzed nanotube material deposited on the cold collector. Single-walled nanotubes (SWT) typically were found grouped in structures in which many tubes run together aligned in van der Waals contact over most of their length. This morphology requires a very high density of SWT in the aerosol for so many tubes to have collided and aligned prior to landing on the cold collector, with very little other carbon available to coat the SWT prior to their alignment. The high nanotube yield (we estimate that 50-60% of all the carbon vaporized becomes nanotubes) is especially remarkable considering that the soluble fullerene yield from the same run was found to be about 10%, with much of the remaining carbon consisting of giant fullerenes and onions.



Fig. 1 Single-walled nanotube ropes. Fringes are spaced by about 1.2 nm in both figures.



Fig. 2 A cross-sectional view of a rope.

Single-walled nanotubes produced in this way are particularly clean, as one might expect given such high yields. Typical arc-produced SWT are covered with a thick layer of amorphous carbon, limiting their usefulness. Much less coating is seen with the present tubes, the bundling leaving much less surface area exposed.

The formation of SWT by laser-vaporization provides clues for revealing the growth mechanism. In both the present experiments and in the arc, essentially *all* catalytically produced nanotubes have a single wall with a very narrow distribution of diameter (although in the arc, adding sulfur to the mix broadens this distribution (12)). Formation of multiwalled nanotubes by metal-catalyzed chemical vapor deposition is widely thought to proceed via solvation of carbon vapor in the metal particle, followed by nanotube precipitation. The particle size is assumed in these models to control the outer diameter of the associated nanotube. We similarly assume here that single-walled nanotubes must originate from particles whose diameters were too small to nucleate and grow the second wall. As addressed below, the kernel of any mechanism for SWT formation is therefore explaining how metal particles are prevented from getting too big.

It is instructive first to review briefly the condensation of *pure* carbon vapor to produce fullerenes, since the roughly 1 at% of metal constitutes only a small, but crucial, departure from the pure case. Under the same conditions in the laser-vaporization apparatus used here to produce SWT, condensation of pure carbon vapor is known to produce C<sub>60</sub> and other small spheroidal fullerenes in extremely high yield (14) (30–40% of all carbon vaporized). Under the prevailing annealing conditions, precursors including mono- and polycyclic rings, and shells incorporate pentagons to reduce their numbers of dangling bonds, ultimately closing to form fullerenes (15). However, in these new experiments, when on the order of 1% of the atoms in the vapor are metal, a dramatic change occurs. Before the fullerene precursor closes, a few metal atoms (perhaps only one) chemisorb on the carbon cluster and migrate to the dangling bonds at the carbon cluster edge, inhibiting closure of the fullerene by partially satisfying the previously dangling bonds. Carbon that now collides with this segregated metal/carbon cluster will readily diffuse at the 1200°C oven temperature to its most energetically stable site, inserting between the carbon edges and the metal particle, lengthening the fullerene. Metal atoms that collide will also diffuse and add to the growing metal particle. However, as we now discuss, the attached carbon cluster itself limits the size of the metal particle, thus accomplishing the trick asked about above.

In condensing *pure* metal vapor, a very broad distribution of cluster size is seen, extending out to particles containing thousands of atoms. The kinetics of pure metal cluster growth evolves in two epochs (16). In the first, during which single metal atoms dominate the vapor, the principal mechanism of M<sub>n</sub>-cluster growth (M<sub>n</sub> denotes an n-atom metal cluster) is by M-atom addition. The nucleation rate ( $n \lesssim 5$ ) is very slow since such small clusters require a third body, provided by a buffer gas, to dissipate excess energy. The rate of M-atom addition rapidly increases as condensation continues due to increasing reaction cross section of the growing M<sub>n</sub> clusters, so nucleation of new particles quickly gives way to growth of existing ones. The second epoch begins when few single atoms and small clusters remain; the main mechanism for particle growth is then M<sub>n</sub>-M<sub>n</sub> coalescence, whose rate similarly increases as condensation progresses (until particles exit the collision region). This process rapidly produces very large clusters.

Metal condensation in a *carbon-rich* environment, however, can lead to quite different metal particle growth kinetics. The fullerene precursors discussed above act as third-body nucleation sites for metal condensation, vastly increasing the number of nucleated metal clusters and foreshortening the first epoch. During the second epoch of metal particle growth, M<sub>n</sub>-M<sub>n</sub> collisions are inhibited by the presence of a growing nanotube “tail” attached to the metal cluster. Rather, collisions between the long nanotube tails are much more likely. Depending on the rate of nanotube formation, this mechanism may very suddenly quench the metal particle size at 100–300 atoms to form the required 1–2 nm diameter catalytic particles.

We note, however, that continued growth of the single wall nanotube will still be favored even when the metal particle at its tip grows beyond the initial 1-2 nm diameter. While the lower strain energy of a second layer precipitated from a larger metal particle would be energetically favorable compared with adding to the inner layer, the unavoidable open edges introduced as this second layer nucleates would present a high energetic barrier. This view therefore places emphasis on the constrained metal particle size only during initial lengthening of the nanotube. This may explain why there has been no observed correlation between nanotube diameter and catalytic particle size.

The most intriguing aspect of these results is that the yield is so high. This must mean that the "live" end of the growing nanotube is capable of efficiently using large carbon clusters as a feedstock. In particular, it is quite possible that C<sub>60</sub> itself is consumed by the catalytic Ni/Co cluster at the end of the growing nanotube, adding 60 atoms to extend the tube length. This then suggests the possibility of vastly protracting the growth stage of the SWT. For example, suppose we insert a network of tungsten wires into the downstream gas flow after the carbon/Ni/Co target but well before the end of the heated zone of the oven. Suppose further that this wire network is arranged so that many of the still-growing nanotubes are caught with their live ends trailing out in the blowing wind of the inert carrier gas flow. It may then be possible to feed the growing "live" ends with C<sub>60</sub> vapor. Since further laser vaporization of the graphite/Ni/Co target is unnecessary it should be possible to continue growth indefinitely without overcoating the sides of the nanotube with amorphous carbon, or growing the catalytic particle too big by further addition of Ni and Co vapor. Variations on this theme may ultimately permit very clean single wall nanotube "ropes" to be grown of many cm length, all aligned in the flowing wind.

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## REFERENCES

- <sup>1</sup>H W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* 318, 165 (1985).
- <sup>2</sup>P. W. Fowler and D. E. Manolopoulos, *An Atlas of the Fullerenes*, Clarendon Press, Oxford (1995).
- <sup>3</sup>A. Hirsch, *The Chemistry of the Fullerenes*, Georg Thieme Verlag, Stuttgart (1994).
- <sup>4</sup>Y. Miyamoto, A. Rubio, X. Blase, M.L. Cohen, and S. Louie, *Phys. Rev. Lett.* 74, 2993 (1995).
- <sup>5</sup>C. Jin, T. Guo, Y. Chai, A. Lee, and R. E. Smalley, *Proc. of 1st Italian Fullerene Workshop on Fullerenes: Status and Perspectives*, C. Taliani, G. Ruani, and R. Zamboni, editors, pp 21-30, World Scientific, Singapore (1992).
- <sup>6</sup>R. Buckminster Fuller, *Synergetics*, Macmillan, N.Y. (1975-79).
- <sup>7</sup>D. Tomanek and M. A. Schluter, *Phys. Rev. Lett.* 67, 2331 (1991).
- <sup>8</sup>D. Ugarte, *Nature* 359, 707 (1992); J.P. Lu and W. Yang, *Phys. Rev. B* 49, 11421 (1994).
- <sup>9</sup>T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley, *Chem. Phys. Lett.* in press (1995).
- <sup>10</sup>R. E. Haufler, Y. Chai, L. P. F. Chibante, J. Conceicao, C. Jin, L.-S. Wang, S. Maruyama, and R. E. Smalley, *Mat. Res. Soc. Symp. Proc.* 206, 627(1991).
- <sup>11</sup>S. Iijima and T. Ichihashi, *Nature* 363, 603 (1993).
- <sup>12</sup>D. S. Bethune, C. H. Klang, M. S. DeVries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature* 363, 605 (1993).
- <sup>13</sup>J.M. Lambert, P.M. Ajayan, P. Bernier, J.M. Planeix, V. Brontons, B. Coq, and J. Castaing, *Chem. Phys. Lett.* 226, 364 (1994).
- <sup>14</sup>R.E. Haufler, Y. Chai, L.P.F. Chibante, J. Conceicao, C. Jin, L.-S. Wang, S. Maruyama, and R.E. Smalley, *Mat. Res. Soc. Symp. Proc.* 206, 627 (1991).
- <sup>15</sup>R.E. Smalley, *Accts. Chem. Res.* 25, 98 (1992).
- <sup>16</sup>D. J. Frurip and S. H. Bauer, *J. Phys. Chem.* 81 (1977) 1007; S. H. Bauer and D. J. Frurip, *J. Phys. Chem.* 81 (1977) 1015.