Catalytic growth of single-walled nanotubes by laser vaporization

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Abstract

Direct laser vaporization of transition-metal/graphite composite rods produced single-walled carbon nanotubes (SWT) in the condensing vapor in a heated flow tube. A much higher yield of nanotubes was found, with little of the amorphous overcoating on those produced by the metal-catalyzed arc-discharge method. A mixture of Co with Ni catalyzed about 50% of all the carbon vaporized to SWT. A model for SWT growth is presented for both the present case and the arc in which the metal particle size is limited due to the concurrent carbon condensation.

1. Introduction

The discovery that single-walled nanotubes (SWT) with diameters on the order of 1 nm [1,2] could be exclusively made in the same dc carbon arc apparatus used to make their multiwalled counterparts added impetus to already burgeoning nanotube research. Since multiwalled nanotubes are expected to have unique material properties, it appears reasonable that SWT, which are much more likely to be free of defects, should represent the ultimate form of fullerene fibers. Defective SWT are discriminated against more strongly than defective multiwalled tubes since the latter can survive occasional defects, while the former have no neighboring walls to compensate for defects by forming bridges between unsaturated valences. Thus, SWT should represent the consummate nanotube material.

Until now, the only known method of making SWT was in the same dc arc-discharge apparatus used to prepare fullerenes and multiwalled nanotubes. In this technique, SWT are produced by evaporating from the anode, simultaneously with carbon, a small percentage of transition metal. While advances have been made in optimizing conditions for SWT yield [1–7], including the discovery of Lambert et al. that binary metal *mixtures* can significantly enhance SWT yields [8], there has been little discussion in the literature on the mechanism of their formation. This may result from a tacit assumption that SWT growth proceeds by a mechanism similar to the metal-catalyzed growth of multiwalled nanotubes, some elements of which have been worked out [9,10]. Even so, there remains the further issue to be resolved, central to SWT growth: what limits the size of the catalytic metal particle so that larger, multiwalled tubes cannot form? To our knowledge, this question has not yet been addressed.

We present here a new method for synthesizing SWT in which a mixture of carbon and transition metals are vaporized by a laser impinging on a metal–graphite composite target. In contrast to the arc method, direct vaporization allows far greater control over growth conditions, permits continuous

operation, and produces nanotubes in higher yield and of better quality. Despite these differences, we shall argue that the fundamental aspects of SWT formation are the same as in the arc. Such a situation places constraints on possible growth mechanisms, and so we advance a detailed growth model at whose center is a limitation, placed by the condensing carbon itself, on the catalytic metal particle size.

2. Experimental

The oven laser-vaporization apparatus (Fig. 1) used in the present work is the same as that used to produce fullerenes and metallofullerenes [11], and multiwalled nanotubes [12]. A scanning laser beam (Continuum DCR-16S, 300 mJ/pulse at 0.532 μm), controlled by a motor-driven total reflector (Newport 850-1B, 45° at 0.532 μm) was focused (200 cm focal length, 75 cm focal distance) to a 6–7 mm diameter spot onto a metal–graphite composite target. The laser beam scans across the target surface under computer control to maintain a smooth, uniform face for vaporization. The target was supported by graphite poles in a 1 inch quartz tube evacuated to 10 mTorr and then filled with 500 Torr argon flowing at 50 sccm (mass flow controller MKS 1159). The flow tube was mounted in a high-temperature furnace (Lindberg, 12 inches long), with a maximum temperature of 1200°C. The soot produced by the laser vaporization was swept by the flowing

Ar gas from the high-temperature zone, and deposited onto a water-cooled copper collector positioned downstream, just outside the furnace.

Targets were uniformly mixed composite rods made by the following three-step procedure: (i) the paste produced from mixing high-purity metal or metal-oxide with graphite powder (Carbone of America) and carbon cement (Dylon) at room temperature was placed in a 0.5 inch diameter mold; (ii) the mold was placed in a hydraulic press equipped with heating plates (Carvey) and baked at 130°C for 4–5 h under constant pressure; (iii) the baked rod was then cured at 810°C for 8 h under an atmosphere of flowing Ar. Fresh targets were heated at 1200°C under flowing Ar for 12 h, and subsequent runs with the same target proceeded after two additional hours heating at 1200°C. The following metal concentrations were used: Co(1.0 at%), Cu(0.6), Nb(0.6), Ni(0.6), Pt(0.2), Co/Ni(0.6/0.6), Co/Pt(0.6/0.2), Co/Cu(0.6/0.5), Ni/Pt(0.6/0.2). The soots of the condensed vapor were prepared by sonicating 1 h in methanol, and examined using a JEOL 2010 transmission electron microscope (TEM), with beam energy 100 keV.

3. Results

A series of mono- and bi-metal catalysts were evaluated for yield and quality of SWT, showing yield trends in qualitative agreement, where there is
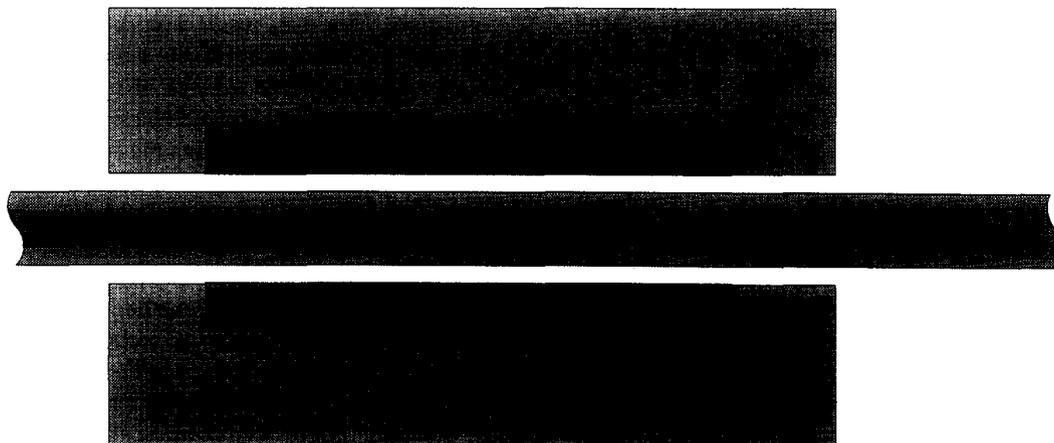

Fig. 1. Oven laser-vaporization apparatus.

overlap, with those of Seraphin for arc-grown SWT [3]. No multiwalled nanotubes were seen. Yields were always seen to increase with temperature up to the oven limit of 1200°C. At that temperature, of the single-metals studied, Ni produced the greatest yield, followed by Co. Pt yielded a very small number of tubes, while no tubes were observed with Cu or Nb alone. For bi-metal catalysts, Co/Ni and Co/Pt mixtures yielded SWT in similarly high abundance, with SWT yields 10–100 times that for the single metals alone. These were closely followed by Ni/Pt, and a Co/Cu mixture produced a small quantity of SWT.

The best catalysts (i.e. Co/Ni and Co/Pt) produced deposits on the copper collector that were removed intact as a sheet of rubbery material. We estimate that in these cases nanotubes comprised at least 15% of all the carbon vaporized. One Co/Ni run, however, produced rubbery deposit of which a small piece did not fully disperse even upon two hours sonication in methanol, in contrast to other cases that produced a homogeneous suspension after 30–60 min sonication. The images shown in Fig. 2 derive from this sample, which was simply torn apart and imaged at the freshly exposed edges. These images reveal that the vast majority of the deposit consists in SWT; we estimate the yield of SWT here to be about 50%. No attempt was made to optimize the yield for this run, i.e. no control parameters were varied from prior Co/Ni runs. The higher yield may have resulted from the fact that the target had been outgassed at 1200°C for a much longer period than in previous runs, or from inhomogeneities in the metal concentration. The main point, however, is that it is possible with this method to obtain exceptionally high SWT yield. Further work will explore optimization conditions such as temperature, metal concentration, inert gas pressure and flow rate, and laser energy density.

Fig. 2 shows TEM images of this high-yield Co/Ni-catalyzed nanotube material deposited on the cold copper collector. SWT typically were found grouped in 'highway' structures in which many tubes run together in van der Waals contact over most of their length. This morphology required a very high density of SWT in the gas phase 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 this alignment. Indeed, the deposit morphology of lower-yield runs favor individual tubes, rather than bundles. Evidence that SWT growth occurs in the gas phase, as opposed to, for instance, on the walls of the quartz tube, was provided by our previous work on multiwalled nanotubes using the same method [12], and by the work of Saito et al. [13], who collected SWT very near the evaporation source in the arc apparatus. The high yields are especially remarkable considering that the soluble fullerene yield was found to be about 10%, and much of the remaining carbon consists in giant fullerenes and onions.

A notable aspect of SWT produced this way is their cleanliness. Typical arc-produced SWT are covered with a thick layer of amorphous carbon, limiting their usefulness. Much less such coating is seen with tubes produced here. This is at least partly related to the high yield, since less carbon is freely available to coat the sides, and also because the bundling results in much less surface area to coat. However, even the SWT formed in lower yield are quite clean, indicating there may be something intrinsic in the method that prevents extensive coating.

4. Growth model

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 [2]). 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.

Condensation of *pure* carbon vapor in the laser vaporization apparatus under the same conditions used here to produce SWT, is known to produce C_{60}
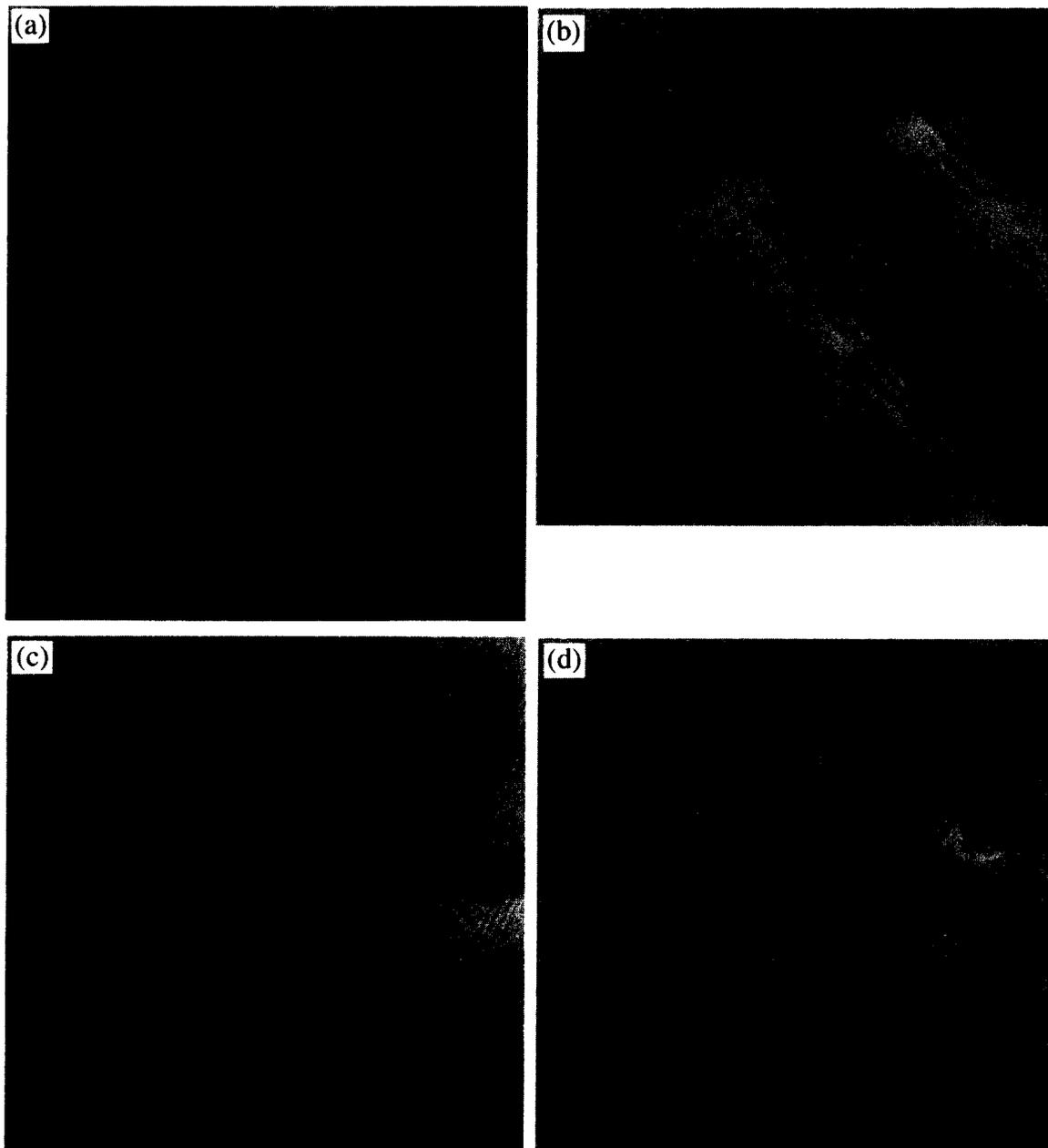
Fig. 2. Transmission electron micrographs of single-walled nanotubes catalyzed by a Co/Ni mixture (0.6/0.6 at%), with oven temperature 1200°C. (a) Medium-magnification view (scale bar is 100 nm) showing that almost everywhere, tubes are bundled in "multilane highways." Metal particles ranging in diameter from 30 nm down to the resolution limit of the TEM ($\approx$ 0.2 nm) are seen as dark spots. (b) High-magnification image of a highway consisting of many adjacent SWT. The SWT diameters are all about 1 nm, with similar spacing between adjacent nanotubes, which adhere to one another by van der Waals forces. (c) Several overlapping highway bundles, two of which are bent. (d) Several bent bundles, one of which is quite sharp, illustrating the strength and flexibility of such nanotube 'rope' (e) A remarkable cross-sectional view of a seven-tube bundle, imaged as it bends up parallel to the electron beam. Other nearby bundles can also be seen in the image. Images (b)–(e) clearly illustrate the lack of amorphous overcoating, typically seen in arc-grown SWT.
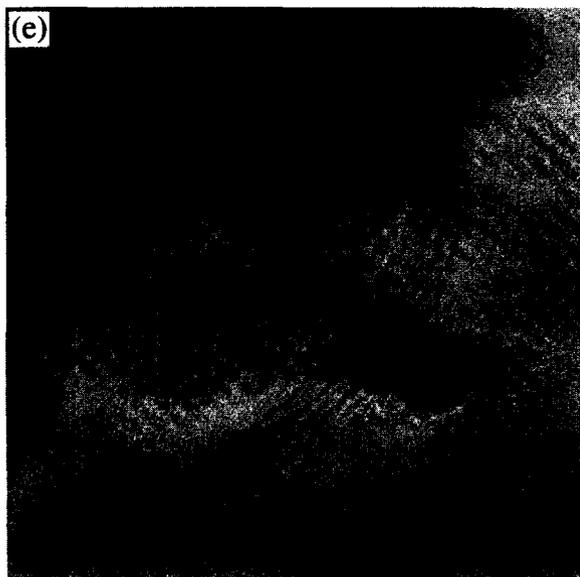
Fig. 2 (continued).

and other small spheroidal fullerenes in extremely high yield [11] (up to 40% of all carbon vaporized). Under the prevailing annealing conditions, precursers including mono- and poly-cyclic rings, and shells incorporate pentagons to reduce their dangling bonds, ultimately closing to form fullerenes [14]. 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 precurser 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.

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

[15]. In the first, during which single metal atoms dominate the vapor, the principal mechanism of M_n-cluster growth (M_n denotes an n atom metal cluster) is by M-atom addition. The nucleation rate ($n \leq 5$) 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_n 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_n–$M_{n'}$ 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 precursers 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_n–$M_{n'}$ 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 observed enhancement in yield from the bimetal catalysts compared with either metal alone

strongly suggests that formation of SWT in *all* cases (i.e. mono- or bi-metallic catalyst) involves more than just a few metal atoms decorating the nanotube edge. A new property must emerge from the binary metal cluster that greatly affects SWT nucleation and/or growth rate. One possibility is that the particle size distribution is different for bimetals versus monometals, the metal cluster size being well known to correlate strongly with reaction rates [16]. However, in the kinetic model presented above it is difficult to see how particle size would be affected by a metal mixture, particularly since the condensation rates of all the metals studied are much slower than that of carbon. We suggest that the principal effect of a mixture is to increase the mobility of carbon on and/or within the metal particle, resulting in a greater rate of SWT precipitation from the particle.

While the cost of the laser photons used in this work to vaporize the graphite target prohibit large scaleup directly, other means of vaporization such as inductive heating, inductively coupled plasmas, plasma jets, or solar furnaces, as envisaged for large scale fullerene production [17], may make the present method viable for bulk production of SWT. Arc generation is necessarily a batch process, whereas the present method requires only a continuous feedstock (buckyballs may be an ideal source!). Moreover, this technique holds much promise for nanotube production due to the far greater control over growth conditions compared with the arc, together with the greater yield and cleanliness of the nanotubes. Finally, the growth model discussed provides another illustration of the remarkable tendency of both multiwalled [12,18] and single-walled nanotubes to change their environment in order to effect their own growth.

Acknowledgement

References

[1] S. Iijima and T. Ichihashi, Nature 363 (1993) 603.
[2] D.S. Bethune, C.H. Klang, M.S. De Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, Nature 63 (1993) 605.
[3] P.M. Ajayan, J.M. Lambert, P. Bernier, L. Barbedette, C. Colliex and J.M. Planeix, Chem. Phys. Letters 215 (1993) 509.
[4] Zhou, S. Seraphin and S. Wang, Appl. Phys. Letters 65 (1994) 1593.
[5] S. Seraphin, J. Electrochem. Soc. 142 (1995) 290.
[6] Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K. Suzuki, A. Kasuya and Y. Nishina, J. Phys. Chem. Solids 54 (1993) 1849.
[7] Y. Saito, M. Okuda, M. Tomita and T. Hayashi, Chem. Phys. Letters 236 (1995) 419.
[8] J.M. Lambert, P.M. Ajayan, P. Bernier, J.M. Planeix, V. Brontons, B. Coq and J. Castaing, Chem. Phys. Letters 226 (1994) 364.
[9] T.W. Ebbesen, Ann. Rev. Mater. Sci. 24 (1994) 235, and references therein.
[10] G.G. Tibbetts, Carbon 30 (1992) 399.
[11] 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 (1991) 627.
[12] T. Guo, P. Nicolaev, A.G. Rinzler, D. Tomanek, D.T. Colbert and R.E. Smalley, J. Phys. Chem. (1995), in press.
[13] Y. Saito, M. Okuda, M. Tomita and T. Hayashi, Chem. Phys. Letters 236 (1995) 419.
[14] R.E. Smalley, Accounts. Chem. Res. 25 (1992) 98.
[15] 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.
[16] M.D. Morse, M.E. Geusic, J.R. Heath and R.E. Smalley, J. Chem. Phys. 83 (1985) 2293.
[17] F.L.P. Chibante, A. Thess, J.M. Alford, M.A. Diener and R.E. Smalley, J. Phys. Chem. 97 (1993) 8696.
[18] D.T. Colbert, J. Zhang, S.M. McClure, P. Nikolaev, Z. Chen, J.H. Hafner, D.W. Owens, P.G. Kotula, C.B. Carter, J.H. Weaver, A.G. Rinzler and R.E. Smalley, Science 266 (1994) 1218.