Condensed phase growth of single-wall carbon nanotubes from laser annealed nanoparticulates

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Single-wall carbon nanotubes (SWNT) were grown to micron lengths by laser-annealing nanoparticulate soot containing short (~50 nm long) nanotube ''seeds.'' The ''seeded'' nanoparticulate soot was produced by restricting the time spent by an ablation plume inside an 800 °C oven following laser vaporization of a C–Ni–Co target. The soot collected from the laser vaporization apparatus was placed inside graphite crucibles under argon, and heated by a CO_2 laser. *In situ* pyrometry was used to estimate the sample temperature. Length distributions of SWNT bundles in the unannealed and annealed samples were measured by transmission electron microscopy and field emission scanning electron microscopy. Annealing treatments exceeding 1600 °C produced no increase in nanotube length, while lower temperatures in the 1000–1300 °C range were optimal for growth. These experiments indicate that SWNT grow by the conversion of *condensed phase* nanomaterial during annealing, a similar mechanism to that proposed for growth during normal laser–vaporization production. © *2001 American Institute of Physics.*
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The laser vaporization (LV) method is an unexpectedly efficient way to grow high quality single-wall carbon nanotubes (SWNT),[1] however the mechanism and dynamics of growth are still the subject of investigation. High yields of SWNT (microns long) can be grown in the plume of ablated material generated by single laser shots onto composite targets [C(98%), Ni(1%), and Co(1%)], but much of the growth appears to occur during extended annealing times while the plume is suspended in 500 Torr of slowly-flowing Ar at ~1000 °C. Recently, we studied the plume during LV synthesis of SWNT with *in situ* time-resolved laser-induced luminescence imaging and spectroscopy at different times (t) after ablation. By measuring the lengths of SWNT collected after known growth times, we determined that SWNT grow at average rates ~1 μm/s, and that the majority of SWNT growth occurs for times $t>100$ ms from the available feedstock at these times: aggregated clusters and nanoparticles. These aggregates form within a few milliseconds after ablation, and normally anneal for several seconds more as they traverse the oven while suspended in the gas flow.[2,3] Several other recent studies of the plume during long times after ablation appear to confirm this long growth period and dynamics.[4–7] These results imply that SWNT synthesis during LV production occurs by the *condensed phase conversion* (CPC) of carbon clusters or nanoparticles by metal catalyst nanoparticles (diameters <20 nm) during extended annealing periods.[2,3]

In this letter, we report SWNT growth from the annealing of soot condensed outside the LV apparatus, testing the hypothesis that SWNT can grow by CPC of cluster and nanoparticle feedstock. The soot which was annealed was produced by the previously-described LV apparatus[2,3] except that a specially-constructed, windowed oven (also 12 in. long) held the 2 in. quartz tube for *in situ* imaging and spectroscopy of the plume. The C–Ni–Co target of Ref. 2 was positioned 10 cm from the upstream edge of the oven and Rayleigh-scattering imaging was used to track and adjust the propagation of the ablation plume. Images of the plume, oven temperature profiles, and resulting length distributions of the SWNT produced for short growth times at high temperature will be published elsewhere.[8] Briefly, the momentum of the plume carried the ejecta through a region of uniform, high temperatures (for about 15 ms) and then into the temperature gradient near the upstream edge of the oven. The plume was rapidly cooled in this region and exited the oven at $t\sim150$ ms, thermophoretically collecting on the upper surface of the quartz tube. These deposits were collected and stored in air prior to annealing.

Such short growth times in the LV oven at 800 °C produced SWNT, in short (<270 nm long) bundles which were very difficult to find amidst the aggregates of carbon and cobalt/nickel nanoparticles. Figures 1(a)–1(c) are representative field-emission scanning electron microscopy (FESEM),

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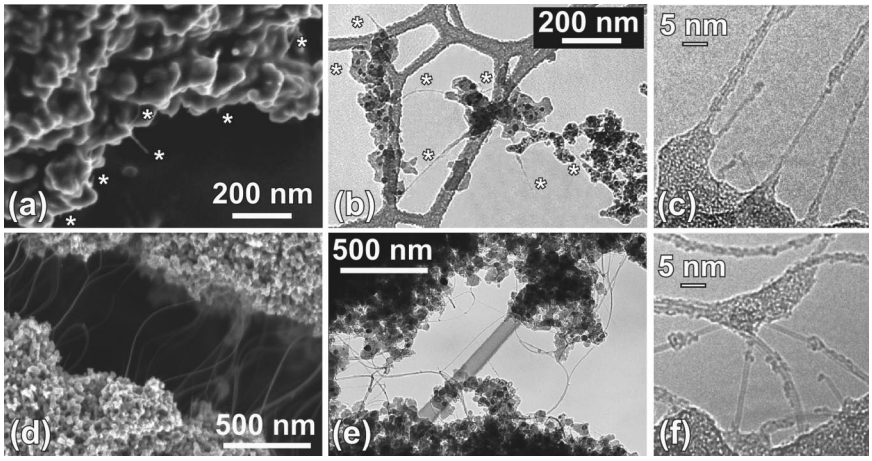

FIG. 1. (a) FESEM, (b) TEM, and (c) HRTEM images of short SWNT seeds amidst aggregated C–Ni–Co nanoparticles produced by time-restricted laser vaporization synthesis. Asterisks mark the location of short SWNT bundles in (a) (soot produced at 800 °C, SWNT lengths <270 nm) and (b) (produced at 1000 °C, lengths <500 nm). (d) FESEM image of long SWNT bundles produced by laser annealing 800 °C soot at $T=1132$ °C for 30 s. (e) TEM image of long SWNT bundles produced by flame annealing 1000 °C soot at ~1000 °C for 30 s. (f) HRTEM image of annealed material shows nearly all the nanotubes are single walled.

transmission electron microscopy (TEM), and high-resolution TEM (HR-TEM) micrographs of the LV-produced soot containing short SWNT ''seeds'' [indicated by asterisks in Figs. 1(a) and 1(b)]. HR-TEM images of this material [such as Fig. 1(c)] reveal that the seeds include single and very thin bundles of SWNT accompanied by numerous (~1 nm diameter) clusters. As shown in Fig. 3(a), the SWNT bundles produced by restricted LV growth at 800 °C had a distribution of lengths which could be roughly fit by a log-normal distribution, with a most-probable length of 47 nm and all measured lengths <270 nm. Restricted LV growth at higher oven temperatures resulted in longer SWNT bundles.[8]

Small pieces of this LV-produced soot were subjected to various annealing treatments. For example, the material was placed in alumina boats or sealed in small quartz tubes under argon, and inserted into 1150–1200 °C ovens for 30 min to 12 h. These treatments produced no observable change in the length or prevalence of the SWNT bundles, although the catalyst nanoparticles were observed to grow in size and decrease in number for long annealing times due to diffusion and coalescence.

By contrast, rapid thermal annealing of the LV-produced soot resulted in the growth of SWNT to much longer lengths. Small pieces of the soot were placed inside small quartz test tubes which were pumped and backfilled with 500 Torr Ar. This material was rapidly heated to glowing (est. T ~1000–1200 °C) with the flame from a H_2/O_2 torch. Heat treatments lasting between 2–30 s with this method produced noticeable SWNT growth in regions of the samples, however, the temperature of the sample was extremely difficult to estimate by this annealing method.

For the experiments reported here, small particles of the soot were placed at the bottom of small, cylindrical graphite crucibles and directly heated with the beam from a CO_2 laser (Synrad G48-2-28, 30 W, $\lambda=10.6$ μm, 1 kHz frequency providing quasi-continuous-wave output) under flowing argon (99.9995%) inside a small vacuum chamber at 760 Torr. The laser beam entered the chamber through a BaF_2 window and 5–10 W of power was typically focused to a 1.5 mm spot ($I=300-600$ W/cm^2) on the bottom of the crucible for 30 s. The laser power was sufficient to rapidly heat the soot sample to very high temperatures, however the crucible and chamber remained relatively cool.

The blackbody emission from the soot particle was used to determine its temperature during the laser-annealing process. Visible light exiting the window was collected by a mirror, fiber optic cable, and 0.3 m spectrometer (Acton VM-503) with a gated, intensified diode array (Princeton Inst. IRY-700RB). After correction for instrumental response [using a National Institute of Standards and Technology traceable calibrated lamp] the spectra were well fit by Planck's law (assuming an emissivity of 1), yielding the particle temperature as shown in Fig. 2(a). With this technique, it was possible to monitor and record the temperature of the sample every 0.2 s during annealing, as shown in Fig. 2(b).

For the experiments reported here, the laser power was switched on and held constant for 30 s, then turned off [although it was possible to rapidly readjust the temperature during the run, as demonstrated in Fig. 2(b)]. The soot could be rapidly heated to temperatures exceeding 2500 °C within 0.6 s with this procedure. A series of runs with different laser powers was performed, achieving different stable temperatures between 1000 and 2000 °C for 30 s. After annealing,

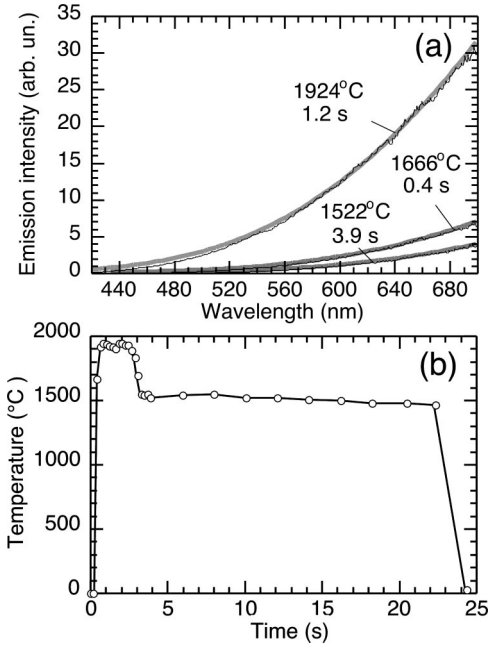

FIG. 2. (a) Emission spectra acquired during CO_2 laser annealing of the soot containing short SWNT. Spectra taken every 0.2 s at the indicated times. Curve fits to Planck's distribution are shown with the derived temperatures. (b) Temporal history of the rapid thermal processing induced by the CO_2 laser irradiation. The laser power was intentionally readjusted during this run at $t=3$ s.

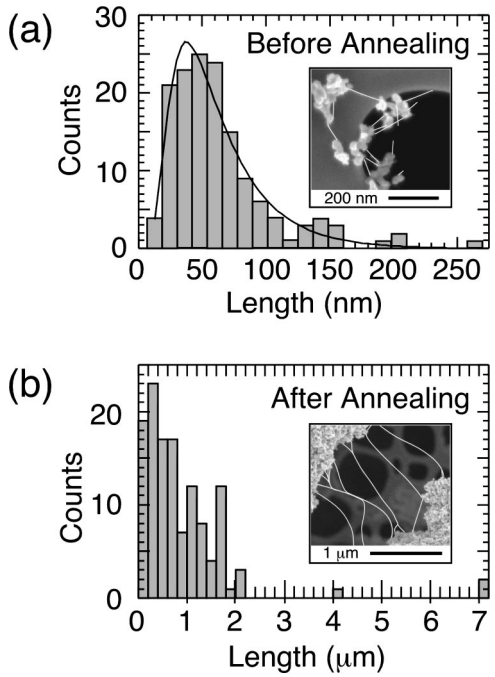

FIG. 3. (a) Length distribution (and lognormal fit) of SWNT generated by laser vaporization of a C–Ni–Co target in an 800 °C oven (plume spent <150 ms inside the oven). (b) Same material as (a) after CO_2 laser annealing for 30 s at 1132 °C (note change of scale). Insets show representative FESEM micrographs (nanotubes have been highlighted).

the material was collected from the crucibles, dispersed in methanol, and samples were collected onto holey-carbon TEM grids for examination by TEM or FESEM (Hitachi S-4700).

As shown in Figs. 1(d), 1(e), and 3(b), regions of the annealed soot samples contained numerous SWNT bundles of much longer length than the starting LV-produced soot. In addition to their length, these long SWNT bundles were much thicker and exhibited numerous splits (similar to those obtained by optical LV production). The SWNT bundles were threaded throughout the remaining carbon and metal nanoparticles to form an interlocking composite, making their length and the overall conversion yield difficult to estimate. HR-TEM of the annealed samples [Fig. 1(f)] confirmed that the nanotubes were predominantly single-walled, and still contained very short SWNT seeds. Occasional multiwall carbon nanotubes and other carbon nanostructures were also found following annealing at higher (>1300 °C) temperatures.

Figure 3(b) shows a rough length distribution of SWNT bundles produced by annealing at 1132 °C for 30 s. FESEM images [as shown in the inset of Fig. 3(b)] were used to estimate the SWNT bundle lengths for this distribution since the bundles were often found on particles which were opaque to TEM imaging. This distribution probably underrepresents the lengths of many of the bundles which disappeared into the carbonaceous matrix.

Despite the difficulties in estimating SWNT lengths and yields, it was evident that samples annealed at >1600 °C showed no noticeable increase in SWNT length or occurrence, while samples annealed at temperatures between 1000 °C and 1300 °C displayed the most numerous SWNT bundles with the longest lengths (optimal annealing temperature estimated between 1100 °C and 1200 °C). In all cases, the overall conversion efficiency (of carbon nanoparticles into SWNT) never approached that produced by normal LV production.

However, the main conclusion of this letter is the comparison of Figs. 3(a) and 3(b) which clearly shows that SWNT grow to much longer lengths at ~1100 °C during the annealing of LV-produced soot containing preformed short SWNT. The relatively low temperatures of 1000–1300 °C determined for growth in these annealing experiments are very similar to the optimal temperatures determined for SWNT growth during normal production by the LV method. Since vaporization of carbon should only occur at much higher annealing temperatures (and we were unable to effect growth at sample temperatures >1600 °C), our measurements indicate that SWNT growth occurs by the CPC of aggregated carbon clusters and nanoparticles, in agreement with the CPC mechanism proposed for growth of SWNT from these gas-suspended aggregates inside the normal LV apparatus.

Annealing experiments using similar soot (produced by LV and other techniques) *without* SWNT seeds resulted in the growth of predominantly multiwall nanotubes and nanofibers, rarely SWNT.[8] Several other approaches for nanotube growth involving heat treatments and apparent growth from *condensed phase* feedstock have been reported recently, however none of these produced SWNT.[9–11] The experiments reported here show that SWNT growth can be reactivated from short SWNT seeds by rapid thermal processing (at ~1100 °C) using condensed phase feedstock. This ability to separate the nucleation and growth steps of SWNT may hold promise for manufacturing of SWNT-based composites and coatings if the efficiency of the separated growth could approach that which occurs naturally during the pulsed LV process.

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