Diameter grouping in bulk samples of single-walled carbon nanotubes from optical absorption spectroscopy

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The influence of the synthesis parameters on the mean characteristics of single-wall carbon nanotubes in soot produced by the laser vaporization of graphite has been analyzed using optical absorption spectroscopy. The abundance and mean diameter of the nanotubes were found to be most influenced by the furnace temperature and the cobalt/nickel catalyst mixing ratio. Via an analysis of the fine structure in the optical spectra, the existence of preferred nanotube diameters has been established and their related fractional abundance could be determined. The results are consistent with nanotubes located mainly around the armchair axis. © *1999 American Institute of Physics.* [S0003-6951(99)04241-2]

Currently, single-wall carbon nanotubes (SWNT) are the focus of intense interest worldwide because of their outstanding properties.[1,2] Critical for further understanding of the underlying physical phenomena and the subsequent technological realization of nanotube-based applications are characterization methods which provide information about mean characteristics of bulk samples of nanotube containing material. In this way, x-ray diffraction, Raman spectroscopy, and transmission electron microscopy (TEM) have been used to characterize the diameter distribution in SWNT containing materials.[3–5]

The mean electronic properties of bulk samples of SWNT bundles have been first studied by high-resolution electron energy loss spectroscopy (EELS) in transmission.[6] The existence of several peaks between 0.6 and 3 eV related to interband transitions between the van Hove singularities in the electronic density of states (DOS) of metallic and semiconducting tubes has been observed. Analogous results could be achieved by using optical absorption spectroscopy on SWNT-containing soot.[7] From band structure calculations, a relation between the energy of the interband transition between DOS singularities and the nanotube diameter $E \propto (1/d)$ was predicted[8] and confirmed by scanning tunneling microscopy/spectroscopy measurements[9,10] on individual nanotubes.

In this letter, we study the influence of the synthesis parameters in the laser-vaporization[11] technique on the mean characteristics of SWNT-containing soot by the use of optical absorption spectroscopy. The deposition system consisted of a quartz tube (diameter 17 mm) inside a tube furnace. A Q-switched Nd:YAP laser (wavelength 1.08 μm, pulse duration 20 ns, pulse repetition frequency 15 Hz, pulse energy 300 mJ, run duration 2 min, circular evaporation area 16 mm^2) was used to ablate the targets. These consisted of intimately mixed and pressed $>99.97\%$ purity starting materials (charcoal, metal catalyst composition Ni_xCo_{1-x} with x between 0 and 1, total catalyst content 1.2 at. %). Freshly prepared targets were initially cured (1200 °C, $\approx 10^3$ Pa argon) for 4 h. The tube wall temperatures were varied between 800 and 1260 °C. The vaporization products were transported by the argon gas stream ($p = 0.66 \times 10^5$ Pa, $v = 1.6\, l/h$) and deposited on a water-cooled copper collector. The maximum nanotube yield in the as-synthesized soot was estimated by TEM to be $\sim 40\%$.

For the characterization of the soot with optical absorption spectroscopy, we applied the procedure proposed in Ref. 7. The well-sonicated soot-methanol mixture (1:100 by weight) was sprayed with an airbrush onto a quartz plate which was held at ≈ 70 °C. The optical absorption spectra were obtained using a Shimadzu MPC-3100 scanning spectrophotometer, across a wavelength range of 200-3200 nm with a resolution of 5 nm.

Figure 1 shows a typical optical absorption spectrum after background subtraction. The raw data are shown in the inset. Three broad SWNT-related peaks have been found at energies in agreement with previously reported values.[6,7] The peaks A and B can be related to transitions between DOS

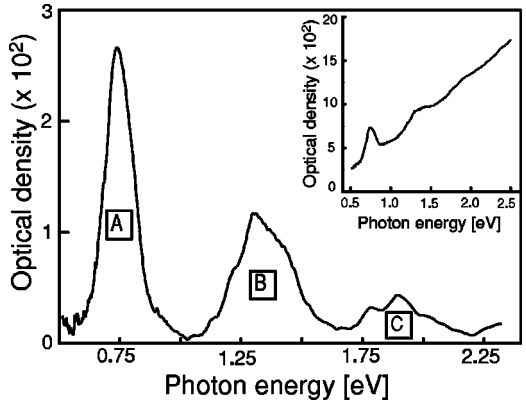

FIG. 1. A typical optical absorption spectrum of SWNT-containing material after background correction. The inset shows the raw data.

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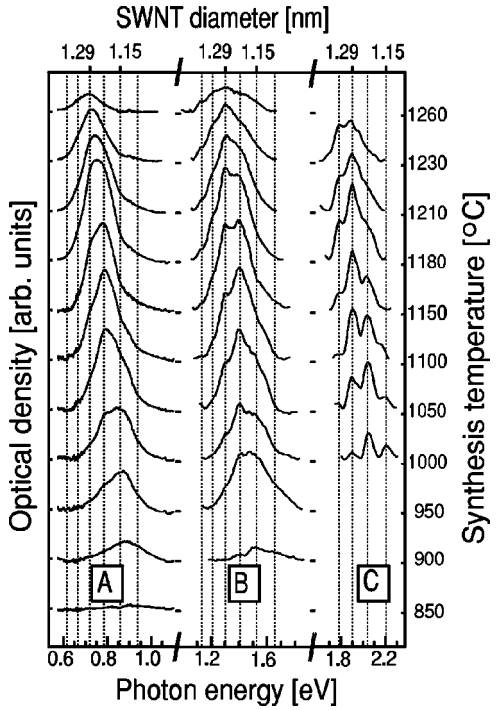

FIG. 2. Optical absorption peaks A (scaled $\times 1$), B (scaled $\times 2.5$), and C (scaled $\times 6$) as a function of the synthesis temperature, T, for a catalyst composition of $Ni_{0.5}Co_{0.5}$, displayed both on an energy and diameter axis. The dotted lines indicate the groups of nanotube diameters separated by $\Delta d \approx 0.07$ nm.

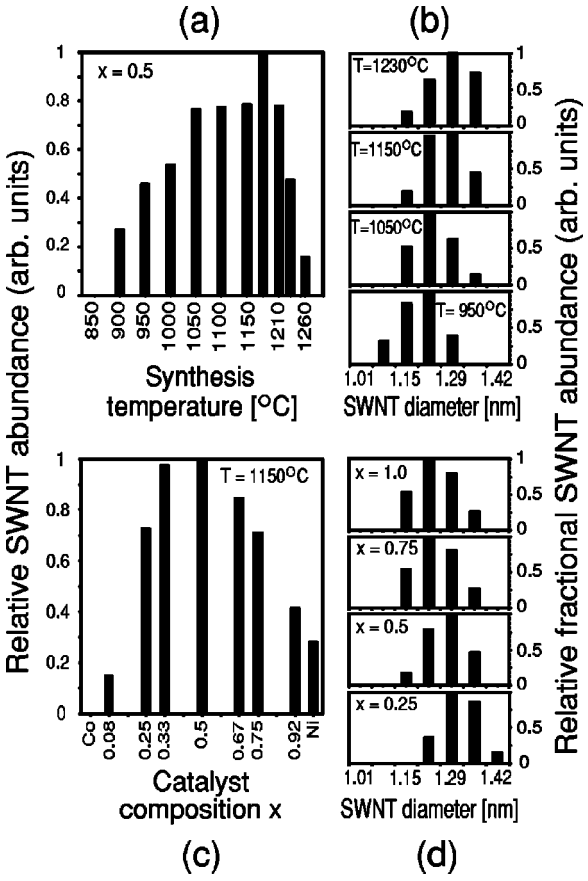

FIG. 3. Relative SWNT abundances obtained from the optical spectra. (a) Overall nanotube abundance as a function of T ($x=0.5$); (b) fractional abundance for the diameter groups, otherwise as (a); (c) overall nanotube abundance for different catalyst compositions Ni_xCo_{1-x} ($T=1150\,°C$); (d) fractional abundance for the diameter groups, otherwise as (c). The largest columns in (a) and (c) correspond to an absolute SWNT abundance determined from TEM measurements of $\approx 40\%$ and $\approx 30\%$, respectively.

singularities in semiconducting tubes, peak C to analogous transitions in metallic tubes.[6,9] The evolution of all peaks as a function of tube wall temperature T is shown in Fig. 2. In general, we observed a shift to higher energies with decreasing synthesis temperature and with decreasing Ni/Co mixing ratio. This shift corresponds to a diminution of the mean SWNT diameter as has been reported previously.[5] In addition to the variation of the synthesis temperatures and the catalyst composition, nearly all of the above-mentioned synthesis parameters have been varied, except the type of carrier gas and the laser settings. Apart from the tube-wall temperature and catalyst composition, none of the other parameters varied resulted in a clear and systematic change of the diameter distribution of the SWNT in the soot.

An important point to note is that the optical data allow a quantification of the nanotube yield and diameter distribution as a function of the varied synthesis parameters. In general, the relative nanotube abundance has been determined by the area below peak A after a normalization at 1.1 eV to account for different film thicknesses and after a linear background subtraction. The temperature dependence of the SWNT abundance shown in Figs. 2 and 3(a) is analogous to that reported using high resolution TEM data[4] in the range below 1050 °C. However, the total maximum yield was observed at higher temperatures of around 1150–1200 °C. Above 1200 °C, a sharp drop of the nanotube yield was observed. The catalyst-dependent data is shown in Fig. 3(c) for $T=1150\,°C$. The optimal yield is achieved for x between 0.33 and 0.5. Interestingly, the optimal yield versus x at 950 °C is shifted to $x \approx 0.25-0.33$.

We now turn to the issue of the diameter distribution. Due to the above-mentioned relation between the transition energies of the van Hove singularities and the nanotube diameter, we can assign the energy position of each of the three peaks to a particular diameter after a calibration. Helpful in this regard are optical measurements we have made of 2 in. furnace SWNT material from the Houston group, which has a well-characterized and relatively narrow diameter distribution[5] centered around 1.36 ± 0.05 nm.

The spectra of Figs. 1 and 2 clearly show a fine structure, which could be analyzed in terms of a number of subpeaks. We found that the positions of the vast majority of the subpeaks (indicated by dotted lines in Fig. 2) remained constant within the resolution limit for all synthesis conditions studied. This points to the fact that the investigated material consists of nanotubes with a discrete number of diameters grouped around preferred values independent of variations of the process parameters. The observed shift of the maximum of the SWNT diameter distribution with variations of the process parameters takes place only through variation of the fractional abundance of the nanotubes with these preferred diameters. Furthermore, we found that the positions of the subpeaks are equidistantly separated on the *diameter* scale with nearly the same values of Δd for both the semiconducting and metallic SWNT. From the nanotube vector map,[8] such an equidistant spacing between groups of preferred nanotube diameters common to both semiconducting and

metallic SWNT is only derivable for multiples of $\Delta d \approx 0.07\,\mathrm{nm}$ (for $m \approx n$ in $d \propto \sqrt{m^2+mn+n^2}$ and wrapping angles close to 30°) and multiples of $\Delta d \approx 0.12\,\mathrm{nm}$ (for $n \approx 0$ and wrapping angles close to 0°). Together with the data obtained from the calibration mentioned above, only the spacing value of $\Delta d \approx 0.07\,\mathrm{nm}$ is consistent with our observations. This strongly indicates the preferred formation of SWNT with wrapping angles close to 30° in the vicinity to the armchair axis. This is supported by the results of Raman investigations.[4]

In order to be able to obtain the fractional abundance of the different diameter groups most accurately, the peak B was fitted[12] after a background correction analogous to that applied to peak A. Figures 3(b) and 3(d) illustrate the influence of the synthesis temperature and the catalyst composition on the fractional abundance of the SWNT diameter groups. All clearly resolvable SWNT diameter groups in our experiments lay within the range of 1.01–1.42 nm which is very similar to TEM data reported by Ref. 4. In Figs. 3(c) and 3(d), the catalyst dependent data show for $x \geqslant 0.75$ that a variation of the catalyst composition leads to a significant change of the SWNT abundance, but not necessarily to a change of the diameter distribution. This indicates the existence of distinct factors responsible for changes of both.

Finally, from the optical data, we did not find evidence for changes of the ratio of semiconducting to metallic SWNT with the applied synthesis parameter variations.

To conclude, we have found that the synthesis temperature and catalyst type are the process parameters that most influence the mean diameter of bulk SWNT-containing material. Furthermore, the optical data prove that the SWNT diameters are grouped around preferred values and are consistent with the formation of nanotubes close to the armchair axis.

The arguments presented here demonstrate the power of optical spectroscopy as an efficient method for the simultaneous analysis of the total SWNT yield and diameter distribution in bulk, macroscopic samples of SWNT. This method should consequently be applied as one of the standard SWNT characterization tools.

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[12] We applied Lorentzian shape analysis on peak B to yield information about the fractional abundance (subpeak area) of the SWNT diameter groups. The full width at the half maximum of all subpeaks was chosen constant on the diameter scale (0.13 nm). Due to the origin of the absorption peaks as a result of DOS singularities, an asymmetric pulse-like shape of the subpeaks has to be expected. Therefore, our fitting procedure should result in a slight overestimation of the abundance of SWNT with small diameters. The usage of the weaker peak B instead of peak A is a compromise between subpeak discrimination ability, subpeak area and fractional abundance determination accuracy.