

Characterization of Single-Walled Carbon Nanotubes (SWNTs) Produced by CO Disproportionation on Co–Mo Catalysts

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The disproportionation of CO over Co–Mo/SiO₂ catalysts with low Co/Mo ratios results in a high selectivity to single-walled carbon nanotubes (SWNTs) when the reaction is conducted between 700 and 950 °C in a flow of pure CO at a total pressure between 1 and 5 atm. A detailed characterization involving Raman spectroscopy, temperature-programmed oxidation (TPO), and transmission electron microscopy (TEM) shows that the product of this process has a high concentration of SWNTs. Depending on the temperature of operation, the selectivity and nanotube diameter can be varied.

Introduction

Single-wall carbon nanotubes (SWNTs) can be considered as one of the building blocks for nanoscale science and nanotechnology. They exhibit exceptional chemical and physical properties that have opened a vast number of potential applications.¹ The procedures used thus far for SWNT production include arc discharge, laser ablation, and catalytic decomposition of carbon-containing molecules (sometimes referred to as chemical vapor deposition) over a metal catalyst. Although the arc discharge and laser ablation methods are known to produce high-quality SWNTs, the amounts of SWNTs obtained by the two techniques range from milligrams to grams. However, many potential applications of SWNTs will require much larger quantities. The catalytic decomposition of carbon-containing molecules appears as a promising technique for scaling-up the production process at a relatively low cost. A number of researchers have investigated different catalyst formulations and operating conditions.^{2,3} Yet, obtaining high-quality SWNTs has not been always possible with this method. Most attempts have resulted in low selectivities to SWNTs, with significant production of imperfect multiwalled nanotubes and nanofibers.⁴

In this contribution, we describe the characteristics of the carbon nanotubes obtained from a novel catalytic decomposition method based on the disproportionation of CO over Co–Mo/SiO₂ catalysts at moderate pressure and temperature. In a previous study, we fully characterized the structure and chemical state of these catalysts by EXAFS, XANES, UV/vis-DRS, H₂ TPR, XPS,

and DRIFTS of adsorbed NO.⁵ We found that the selectivity of the Co–Mo catalysts toward SWNTs strongly depends on the stabilization of the Co species in a nonmetallic state before exposure to CO, which results from an interaction with Mo. The extent of this interaction is a function of the Co/Mo ratio and has different forms during the different stages of the catalyst life. From the detailed characterization conducted over the catalyst series we concluded that, after calcination, Mo is in the form of well dispersed molybdenum(6+) oxide, while Co is either interacting with Mo in a superficial cobalt molybdate-like structure (at low Co/Mo ratios) or as a noninteracting Co₃O₄ phase (at high Co/Mo ratios). After a subsequent treatment in hydrogen, the noninteracting phase is reduced to metallic Co, whereas Co in the molybdate-like species remains as well-dispersed Co²⁺ ions. During the production of SWNTs under pure CO, the molybdenum oxide species are converted into molybdenum carbide. This conversion disrupts the interaction between Co and Mo and results in the release of metallic Co in the form of extremely small clusters, which are responsible for the production of SWNTs. By contrast, large Co clusters that are formed from the noninteracting Co phase produce the nonselective forms of carbon (MWNTs, nanofibers, filaments, graphite, etc.). This method has resulted in a scalable, cost-effective process.⁶ We show here that this method produces SWNTs of a quality comparable to the products obtained by the arc discharge and laser ablation methods. Moreover, depending on the reaction temperature, this method results in SWNTs of varying diameter.

Experimental Section

Silica-supported Co–Mo bimetallic catalysts were prepared using cobalt nitrate and ammonium heptamolybdate salts as

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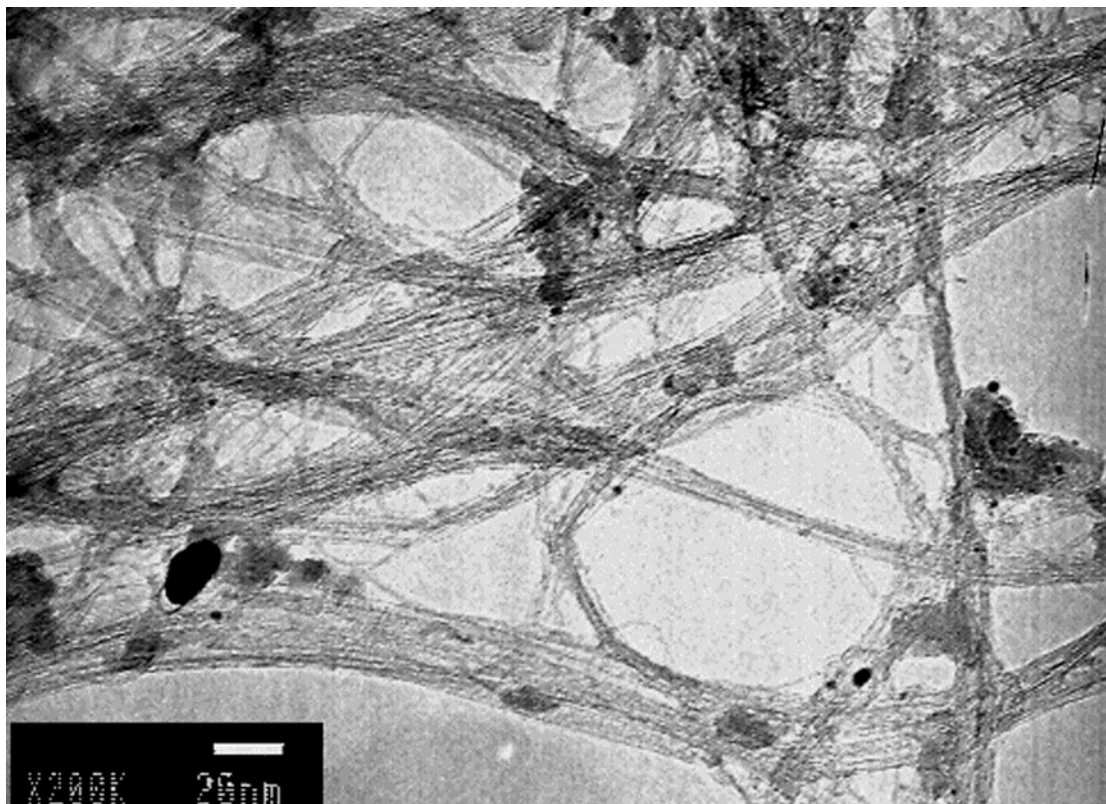


Figure 1. Typical TEM micrograph of SWNTs produced by CO disproportionation at 850 °C on a Co–Mo catalyst with a 1:3 molar ratio for 2 h. The carbon yield on this sample is approximately 15 wt % C.

precursors. The total metallic loading in the catalyst ranged from 2 to 6 wt %, and the Co/Mo molar ratios ranged from 1:3 to 2:1. Prior to the production of SWNTs by CO disproportionation, the catalyst was heated in H₂ flow to 500 °C and then in He flow to the reaction temperature (700–950 °C). This reduction/heating pretreatment was found to be necessary for high selectivity to be achieved.⁷ The CO disproportionation reaction used for the production of SWNTs was conducted in the temperature range 700–950 °C in a flow of pure CO at a total pressure of between 1 and 5 atm. The SWNTs grown by this method remained mixed with the spent catalyst, which is composed of the silica support and the Co and Mo species. Following the reaction, a sequence of treatments was carried out to remove most of these impurities. The first step in this sequence was a low-temperature oxidation for the elimination of the amorphous carbon, which was accomplished by calcination in air at 300 °C for 2 h. The second step was the elimination of the silica support. In this step, 1 g of the material was suspended in a 0.2 M NaOH solution while stirring for 24 h at 65 °C. After being filtered through a 0.2-mm Teflon–PTFE membrane, the remaining solid was washed with deionized water until the pH was neutral, and then the solid was dried overnight at room temperature inside a desiccator. The third step was the elimination of the metals (Co and Mo). This was accomplished by an acid attack in refluxing 2 M nitric acid, until the evolution of NO₂ vapors subsided. Again, the solid part was filtered and washed as before. The total removal of silica and metals after both steps was about 95–99%, as determined by atomic absorption analysis.

The TEM images were obtained with a JEOL JEM-2000FX TEM. For this analysis, a suspension in 2-propanol was achieved by stirring the solid sample with ultrasound for 10 min. A few drops of the resulting suspension were deposited on a TEM grid and subsequently dried and evacuated before the analysis. In the present contribution, the yield is defined

as the total mass of carbon per mass of catalyst, as determined by temperature-programmed oxidation (TPO). Raman spectra were obtained with two different laser excitation sources having wavelengths of 514 and 532 nm.

Results and Discussion

To characterize the SWNTs, we used a combination of transmission electron microscopy (TEM), Raman spectroscopy, and temperature-programmed oxidation (TPO). Figure 1 shows a typical micrograph obtained by transmission electron microscopy (TEM) on a sample obtained at 850 °C on a Co–Mo (1:3)/SiO₂ catalyst. It is interesting to note the small metal clusters that appear intermingled with the nanotubes and that have about the same diameter as the nanotubes. A few larger metal particles are also observed, but they do not seem to be associated with the nanotubes.

Raman spectroscopy is a powerful technique for characterizing the structure of carbon nanotubes. The tangential-mode G band appearing in the 1400–1700 cm⁻¹ region is related to the Raman-allowed phonon mode E_{2g} and involves out-of-phase intralayer displacement in the graphene structure of the nanotubes. It provides information about the electronic properties of the tubes and is a measure of the presence of ordered carbon. The so-called D band at around 1350 cm⁻¹ is related to defects or the presence of nanoparticles and amorphous carbon.⁸ Although pure SWNTs also make some contribution in this region,⁹ the D band provides

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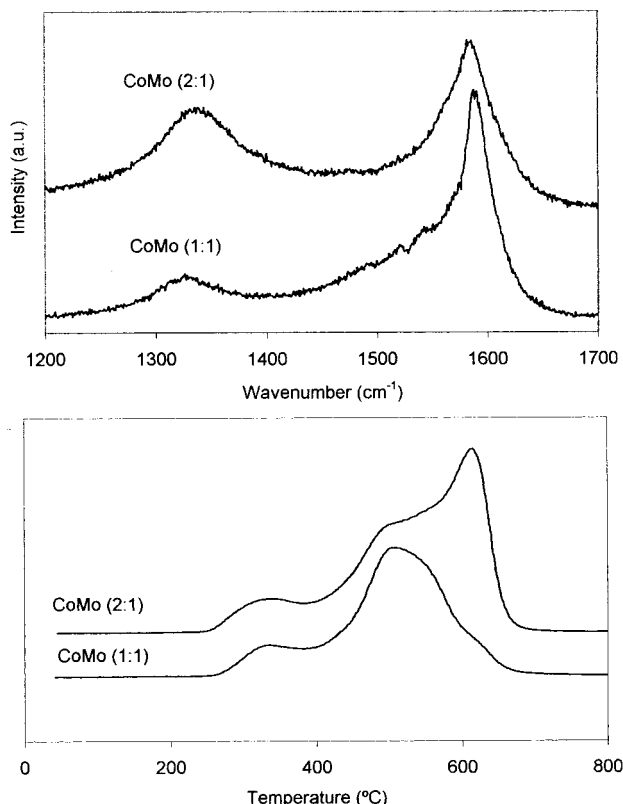


Figure 2. (a) Raman spectra of SWNTs grown by CO disproportionation at 700 °C over two different catalysts with varying Co/Mo ratios. The total metallic loading in both catalysts was 6 wt %. The laser excitation wavelength was 514 nm. (b) Temperature-programmed oxidation profiles conducted on the same samples as in part a.

an indication of the level of disordered carbon. Hence, the size of the D band relative to the G band can be used as a qualitative measurement for the formation of undesired forms of carbon. Finally, information about the distribution of tube diameters can be obtained from an analysis of the radial A_{1g} breathing mode frequency range (RBM), as shown below.¹⁰ Although Raman spectroscopy is very useful for a comparative analysis of the relative amounts of disordered and ordered carbon species, in our case, it cannot provide a quantitative measurement of the amount of SWNTs produced over the whole catalyst sample. On the other hand, TPO can provide a quantitative measure of the carbon yield and selectivity. For instance, we have previously shown that, under TPO conditions, while still immersed in the Co–Mo catalyst, the SWNTs become oxidized in a relatively narrow temperature range that lies below the temperature at which MWNTs, graphite, and carbon fibers are oxidized but above the temperature at which amorphous and chemically impure carbon species are oxidized.⁷ Figure 2 illustrates how Raman spectroscopy and TPO can be used to characterize the SWNTs produced catalytically. As previously shown, the TPO peak with a maximum at about 520 °C is due to SWNTs, whereas that at 620 °C is due to multiwalled nanotubes, nanofibers, and graphitic carbon.⁷ A clear difference is observed when the product from a selective catalyst

(e.g., Co/Mo = 1:1) is compared to that of a nonselective catalyst (e.g., Co/Mo = 2:1). In the TPO of the product obtained on the nonselective catalyst, the high-temperature peak is dominant, revealing the low selectivity of the 2:1 catalyst. These results are very well paralleled by the Raman spectra shown in the same figure. It is clear that the D-band contribution becomes much stronger in the spectrum of the product obtained using the nonselective (Co/Mo = 2:1) catalyst than in the spectrum of that obtained using the selective catalyst (Co/Mo = 1:1). In perfect agreement with these results, the TEM observations indicate the presence of large quantities of MWNTs and fibers on the nonselective catalyst and almost none on the selective catalyst.

A similar characterization routine can be used to investigate the variation of selectivity as a function of reaction time. The rate of growth of an individual SWNT is very fast. Iijima et al., studying the growth of SWNTs by laser ablation, observed the formation of vortexes propagating forward for 200 ms and then flowing downward to the target.^{11,12} They determined that the time available for SWNT growth in the vortexes ranges from a few milliseconds to about 1 s. Similarly, Gorbunov et al., from results obtained at varying Ar flow rates, determined that the growth time is less than 1 s.¹³ By contrast, in the formation of tubes by the catalytic method on a solid catalyst, the carbon deposition is relatively slow and the yield of SWNTs keeps increasing for hours.^{14–16} It is then apparent that the intrinsic growth rate of each individual SWNT is very rapid, and when the growth begins on a given site on the solid surface, it should proceed at a rate comparable to that in the vapor phase. The observed low rate of formation on solid surfaces must then be ascribed to a low rate of nucleation. That is, for nanotube growth to occur, the metal particle and the incipient carbon deposits must acquire a proper configuration, but after nucleation, the growth should be very rapid. It is then interesting to monitor the selectivity of the carbon product as a function of reaction time, because, as the time on stream increases, the metal particles on the catalysts can suffer sintering or other morphological modifications, which might cause losses in their ability to selectively produce SWNTs.

This trend is illustrated in Figure 3, which shows the Raman spectra of the SWNTs obtained as a function of time on stream on the most selective catalyst. As the reaction progresses, there is an increase in the intensity of all of the bands because of the increasing carbon deposition. However, it is interesting to point out that the relative intensity of the D band with respect to the G band clearly increases with reaction time. Figure 4 shows the relative intensity of the D band, together with the carbon yield measured by TPO, as a function of time

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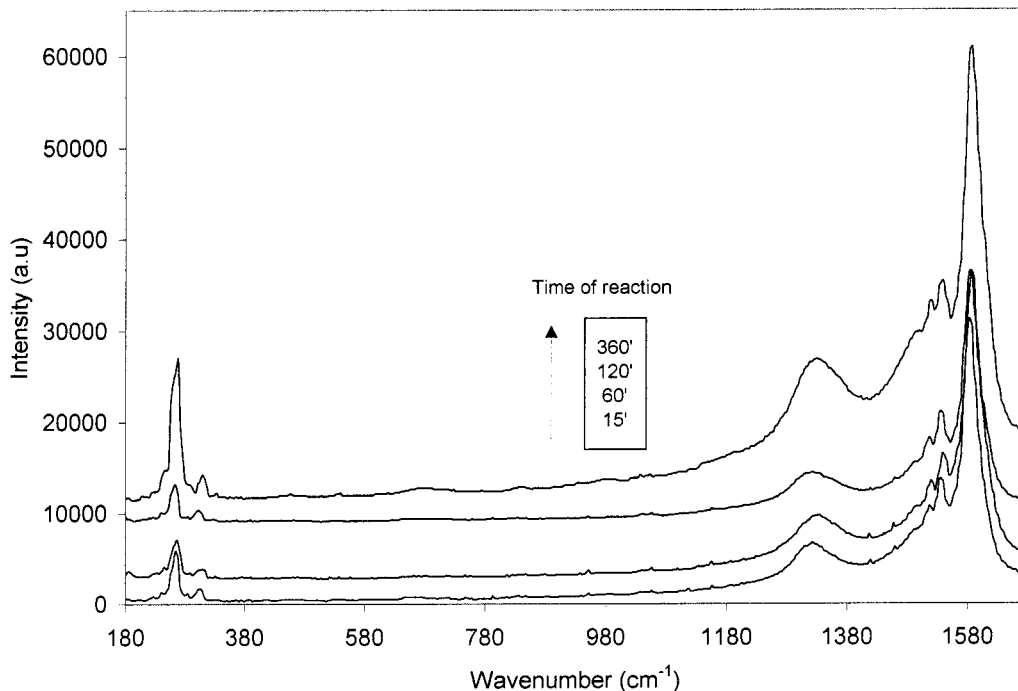


Figure 3. Raman spectra of SWNTs grown at increasing reaction times. The product was obtained at 750 °C in a catalyst with a Co/Mo ratio of 1:3 and a total metal loading of 2 wt %. The excitation wavelength was 514 nm.

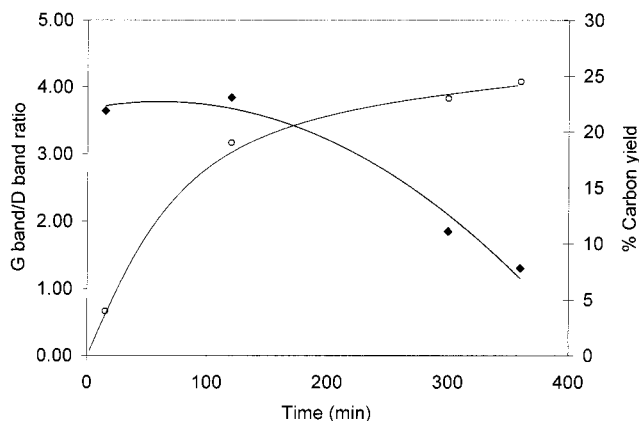


Figure 4. (■) Ratio of D-band to G-band intensity as obtained from the spectra in Figure 3. (○) Total yield of carbon as obtained by TPO

on stream. During the first 2 h, the carbon yield increased rapidly with reaction time, while the SWNT selectivity remained relatively high. However, at longer times, not only did the carbon deposition become slower, but also the selectivity to SWNTs was greatly reduced. The TEM observations were in perfect agreement with these conclusions, showing a higher density of MWNTs and graphite after long times on stream than after the first couple of hours.

To study the effect of the reaction temperature on the structure of the SWNTs obtained by the catalytic method, we conducted the decomposition of CO at temperatures ranging from 750 to 950 °C. In a previous study, we showed that when the temperature is lower than 700 °C, the selectivity to SWNTs is greatly reduced. We have shown that although the amount of carbon deposited on a Co–Mo catalyst with a molar ratio of 1:2 was larger at 600 °C than at higher temperatures (e.g., 700–800 °C), the selectivity greatly decreased at low temperature because of the formation

of larger fractions of MWNTs and fibers.¹⁷ Here, we report more subtle changes observed when the temperature is increased. The Raman spectra (excitation wavelength 532 nm) obtained for runs at different temperatures are shown in Figures 5 and 6 for the high- and low-frequency ranges, respectively. In the first place and in agreement with our previous report, the increase in the G-to-D band intensity ratio with increasing temperature indicates a selectivity improvement as the reaction temperature increases. However, the most interesting result is illustrated in Figure 6 for the radial breathing mode region. The product obtained at 750 °C exhibited a dominant peak centered at around 268 cm^{-1} , which would correspond to a tube diameter of approximately 0.9 ± 0.05 .¹⁸ Much weaker sidebands are also present in the spectrum; they would correspond to small amounts of tubes with diameters of ~ 0.6 and ~ 1.2 nm. By contrast, when the temperature was increased to 850 °C, a new peak appeared at lower wavenumbers (191 cm^{-1}), and when the temperature was increased to 950 °C, the main peaks appeared at 236 and 170 cm^{-1} . The positions of these bands indicate that the SWNTs produced at 850 °C have diameters of 0.9 and 1.25 nm, whereas those obtained at 950 °C have diameters around 1.00 and 1.40 nm. To corroborate these results, we conducted a detailed analysis of several TEM micrographs acquired on the same samples as used in the Raman study. The diameters of 100–150 tubes were measured for each sample, and the results of those measurements are summarized in the histograms shown in Figure 7. The observed distribution matches the Raman results. The results leave no doubt

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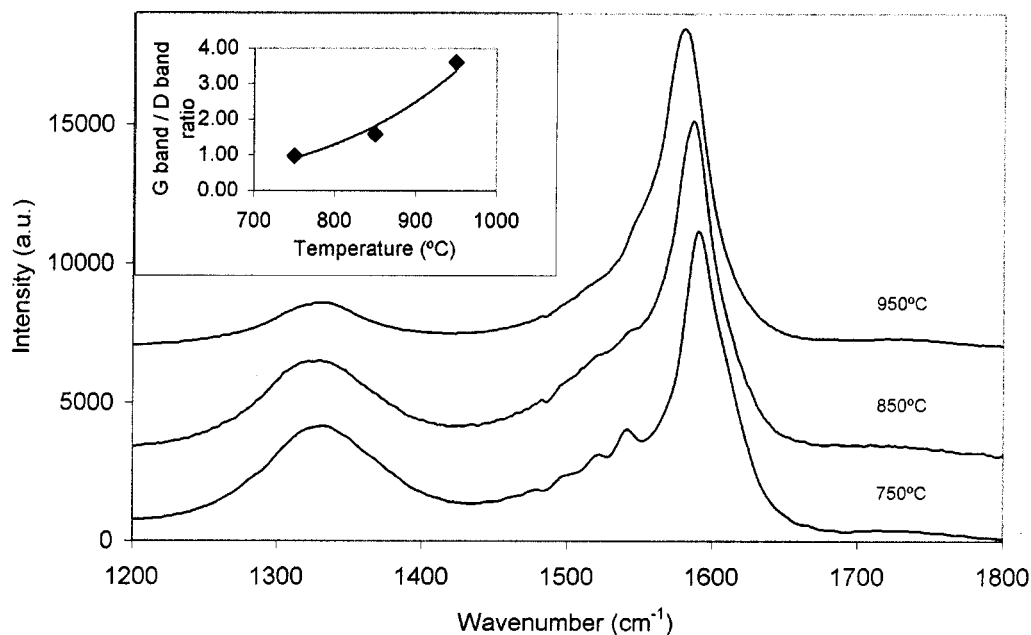


Figure 5. High-frequency Raman spectra of SWNTs grown for 2 h at different temperatures on a catalyst with a Co/Mo ratio of 1:3 and a total metallic loading of 2 wt %. The excitation wavelength was 532 nm. Inset: Ratio of G-band to D-band intensity as a function of reaction temperature.

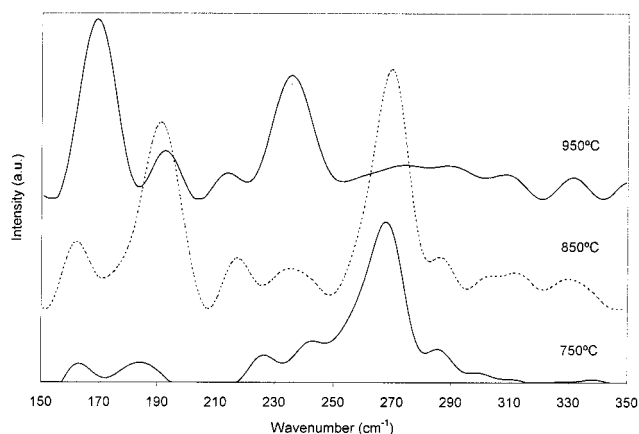


Figure 6. Low-frequency Raman spectra of SWNTs grown for 2 h at different temperatures on a catalyst with a Co/Mo ratio of 1:3 and a total metallic loading of 2 wt %. The excitation wavelength was 532 nm.

that, as the reaction temperature increases, the diameter of the tubes increases. One possible explanation for this increase could be that the sintering of the Co clusters accelerates with temperature. As a result, at higher temperatures, there is a higher density of larger metal clusters on the catalyst surface. These larger clusters are, in turn, responsible for the formation of tubes of larger diameter. Similar increases in tube diameter have been observed when the ambient temperature increases in other vapor-phase techniques.^{19–21}

Although, in this case, the trend observed in the Raman spectra harmonizes with those observed by TEM, we must emphasize that a careful interpretation of the Raman spectra must be done, as the analysis

might not be straightforward. It is well-known that a Raman spectrum of SWNTs is produced by a resonant process associated with optical transitions in the one-dimensional electronic density of states that fall in the visible and near-infrared ranges.^{22,23} That is, when the excitation energy is close to that of an allowed optical transition between singularities in the one-dimensional density of states, the Raman intensity is greatly enhanced. Therefore, because the energy of these transitions depends on both the diameter and the helicity of the tubes, by employing different excitation energies, different tubes can be probed. The energy of the allowed optical transitions depends both on the diameter and on the metallic or semiconductor character of the tubes. This was illustrated in a series of publications that reported the range of the allowed optical transitions for semiconducting and metallic tubes.^{23,24} Accordingly, for the excitation energy of 532 nm used to obtain the spectra of Figures 4 and 5, the resonance conditions for metallic tubes take place in the diameter range 0.9–1.1 nm, whereas that for semiconducting tubes occurs in the range 1.3–1.7 nm.^{25,26} Moreover, the broadening of the tangential-mode band and the appearance of a peak centered around 1540 cm^{-1} are typical features of metallic tubes. Pimenta et al.²³ investigated the variation of the band at 1540 cm^{-1} with respect to that at 1593 cm^{-1} as a function of the laser energy. The 1540 cm^{-1} band can be ascribed to the resonance of the

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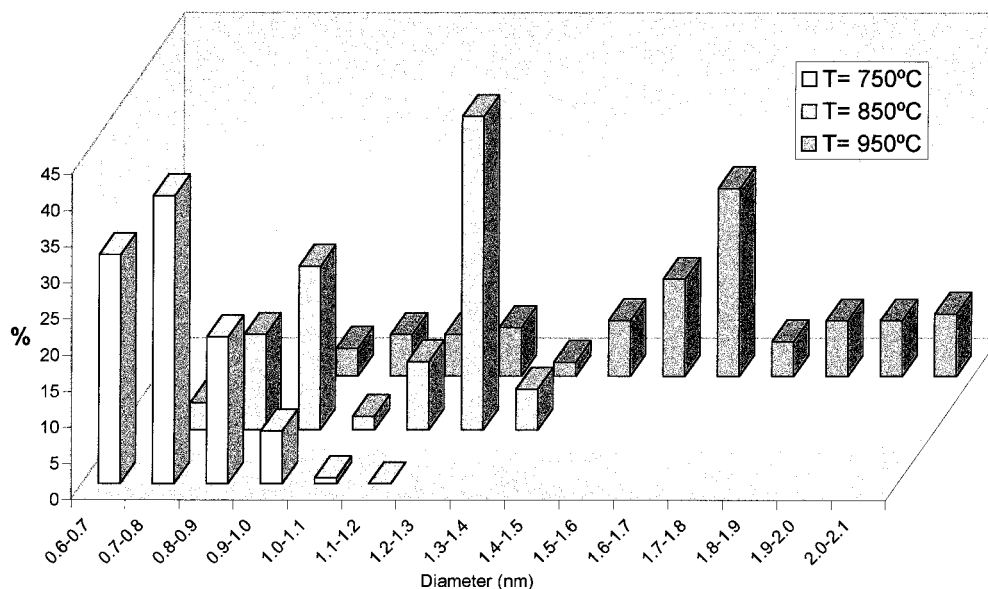


Figure 7. Diameter distribution of SWNTs produced by CO disproportionation at 750 °C on a Co–Mo catalyst with 1:3 molar ratio, as obtained from TEM micrographs.

incident or scattered photon with the lowest optical transition between the singularities in the valence and conduction bands of metallic nanotubes. They observed a large enhancement in the $1540\text{ cm}^{-1}/1593\text{ cm}^{-1}$ intensity ratio, with a maximum in the 1.7–2.2 eV range. The observed enhancement was explained in terms of theoretical calculations that relate the tube diameters to the energy gaps between singularities in the valence and conduction bands of the electronic density of states. The nanotubes used in that particular study had diameters in the 1.1–1.3 nm range. The theoretical calculations²⁶ indicate that, for those diameters, the energy region of resonance falls in the range 1.7–2.2 eV, which agrees very well with the range at which enhancement of the $1540\text{ cm}^{-1}/1593\text{ cm}^{-1}$ intensity ratio is observed. According to the same calculations,²⁶ the metallic nanotubes that we produced at 750 °C, which have an average diameter of 0.89 nm, should have an enhanced $1540\text{ cm}^{-1}/1593\text{ cm}^{-1}$ intensity ratio in the range 2.2–2.8 eV. In agreement with this prediction, we measured this intensity ratio using laser energies of 1.96 and 2.54 eV and observed a 2-fold

increase as the laser energy entered the resonance range.

Therefore, we conclude that the nanotubes produced at 750 °C with an average diameter of 0.89 nm are metallic. Several possible metallic tubes have diameters close to this value. Among them are the “armchair” (6,6) and (7,7) structures with diameters of 0.81 and 0.95 nm, respectively; the “zigzag” (12,0) structure with a diameter of 0.94 nm; and the chiral (9,3) and (8,5) structures with diameters of 0.85 and 0.89 nm, respectively.

In summary, by optimizing catalyst formulation and reactions conditions a SWNT product of good quality can be obtained. Heterogeneous catalysts can be used to gain control of the selectivity and even some control of the nanotube diameter.

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