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Abstract

Singlewalled carbon nanotubes (SWNT's) prepared by the electric arc method are characterized by means of spectroscopic techniques, mainly Transmission Electron Microscopy and resonance Raman scattering. TEM observations reveal the existence of nickel particles embedded in an amorphous carbon matrix, but also a large concentration of SWNT's, whose average diameter can be estimated to be near 1.3 nm, arranged in bundles. Raman spectra recorded on the same samples exhibit several features, mainly consisting of two groups. On one hand, in the high frequency region, several bands are observed in the range 1500 - 1600 cm^{-1}, corresponding to a splitting of the E_{2g2} vibrational mode of graphite. On the other hand, several components are recorded between 150 and 240 cm^{-1}, reflecting a distribution in the diameter of the SWNT's. A systematic study of the «collaret», from which samples are extracted, is also presented.

Keywords : Carbon compounds, nanotubes, Raman scattering, High resolution transmission electron microscopy

Introduction

Discovered by S. Iijima in 1991 (1), carbon nanotubes appear nowadays as promising materials to be included in nanostructures due to both their electrical or mechanical properties. The main difficulty which limited such development was their production in rather small quantities. But new methods of synthesis have been presented recently which in addition lead to the formation of singlewalled nanotubes (SWNT's), more attractive in terms of electronic properties. First of all, Thess et al (2) proposed a double laser ablation technique to produce such carbon species. More recently, Journet et al (3), by using the electric arc method, achieved also production of SWNT's in high yield (> 70 %). The latter technique offers in addition the advantage of synthesizing compounds in much larger amounts, allowing an easier characterization.

In this paper, we mainly describe Raman results performed on SWNT's which provide a great deal of information on the nature of the SWNT's studied and put clearly in evidence a diameter size distribution which depends on the location of the extracted sample from the synthesis chamber. We focus our studies on carbon nanotubes prepared by the electric arc method, although comparison is made with samples obtained by different preparation techniques.

Preparation of samples

SWNT's were produced by creating an electric arc discharge between two graphite rods. The anode was drilled and filled with a mixture of nickel and yttrium used as catalysts. The synthesis was performed in a water-cooled chamber first evacuated and then filled with a static pressure of 660 mbar of helium. A current of 100 A was applied and a voltage of about 35 V was maintained constant by continuously translating the anode towards the cathode. Details on the synthesis can be found in Ref. 3. After the synthesis, the extracted product characterized is the "collaret" found around the deposit on the cathode, where the concentration of tubes is given to be near 70 %.

Even if our studies focus on the electric arc method, we have also investigated samples prepared by laser ablation and using solar energy. The first one have been produced in sublimating graphite with a Ni / Co (0,6 / 0,6 at. %) mixture and under a pressure of 500 Torr. The second one was prepared at the Odeillo solar furnace. The flux concentrated in the chamber is near 950 W/m^2. In there conditions, during the evaporation process of the target (graphite / Ni / Co : 96 / 2 / 2 at. %) under an argon atmosphere (400 mbar, flow : 0,2 m^3/h), the temperature increases up to 3000 K, whereas the collected soot should be synthesis between 2000 and 800 K.

Raman experiments

To obtain Raman spectra, two different experimental equipments have been used. In both cases, spectra have been recorded at room temperature and in ambient air. With the first one, a spectrophotometer Jobin Yvon T64000, the use of a microprobe has allowed us to focus the laser spot in a micrometer scale which gives a great sensitivity to its localisation on the sample. Then, spatially resolved features can be obtained providing clear indications on the distribution of tubes at several spots on the samples as it will be shown later. Otherwise, with this set up, argon and krypton lasers have been used with the following wavelengths : 457.9, 514.5 and 676.4 nm. The second set up, a FT Raman Brucker RFS 100 (1064 nm), has allowed the use of Surface Enhancement of Raman Scattering (SERS) method. Contrarely to the first experiments where no preparation is necessary, the SWNT's are in this case firstly ultra-sonicated in solvent (ethanol, $CHCl_3$). In a second step, they are deposited on a rough metallic surface (Au, Ag, Cu). This technique is of great interest since enhancement mechanisms have been put in evidence. These mechanisms can have two different origins. A chemical effect occurs when chemical bonds between the substrate and the molecules are formed increasing the molecule polarisability. The other one is an electromagnetic effect by the creation of a near field due to the roughness of the metallic

surface. One peculiar detail of this second apparatus is the laser spot size. As microprobe is not provided, the laser spot diameter is much larger, near 1 mm, than the one used under the microscope of the Jobin Yvon spectrometer. As a result, the area studied with the FT Raman contains a larger number of nanotubes and studies under these experimental conditions lead to more important macroscopic effects.

Raman results

Each first order spectrum exhibits two main groups of peaks. The first one shows at least four components : 1589, 1562, 1550 and 1530 cm^{-1}. It is associated with the splitting of the E_{2g2} graphite mode (1582 cm^{-1}) due to the introduction of a curvature in a graphene sheet and to the change from 2D to 3D symmetry. So, one A_{1g} mode is upshifted near 1590 cm^{-1} whereas the other one , E_{1g}, is downshifted. With this second mode, the shift will be dependent on the curvature as a lower diameter will lead to a decrease of its frequency. Then the lower the diameter, the broader the splitting.

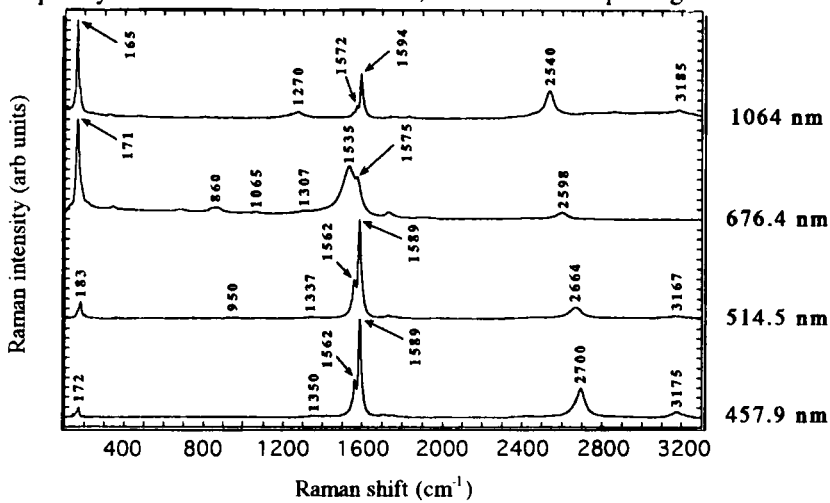

Fig 1 : Raman spectra of singlewalled carbon nanotubes (electric arc sample)

In the low frequency range (100-260 cm^{-1}), we observe the breathing mode of the SWNT's whose frequency depends also on the tube diameter (higher frequency, lower diameter) (3,5) and one peak observed can be associated with one diameter. This is what is shown on Figure 2. Indeed, this figure presents different spectra recorded with different wavelengths, labelled by the letters on the rigth side (B : 457.9, G : 514.5, R : 676.4 and IR : 1064 nm), and different locations on the sample labelled by the numbers. It is clear that for each wavelength, the frequency of the peaks are identical whereas their relative intensities are changing from one location to the other. This means that each peak provides an indication of the concentration of one specific diameter relatively to the others. The entire group gives information

about the diameter distribution. In this way, we can see that the diameter distribution of the G1 spectrum is dominated by large tubes whereas this distribution is shifted to lower diameters in the G3 spectrum. For the three visible wavelengths, we can notice that on each spectrum, several peaks can be observed (B : 9, G : 6, R : 5). This means that whatever the laser line used, we can also see a diameter distribution, even if the overall shape of this lower frequency group of Raman bands is slightly modified even in the apparent peak position. We can reasonably think that all spectra are a superposition of the response of several tube diameters.

This situation is completely different with the near infrared line (1064 nm) where only two bands (165 and 178 cm^{-1}) are present with the predominance of the one peaked at 165 cm^{-1}. In this case, the Raman spectrum is dominated by the response of only one diameter, which is a peculiar effect compared to the studies performed with other wavelengths. This observation can lead to two different assumptions. Firstly, one can suppose that this behaviour comes from the size of the laser spot. Indeed, as described above, the laser spot is $\approx 1\ mm^2$, then much larger than the one available with the microprobe. The fact that few bands are observable suggest that at a macrscopic scale, samples are dominated by one tube diameter. We can then correlate this hypothesis with the X-Ray diffraction studies where only one lattice parameter is seen for the bundles of tubes (2). In a second hypothesis, the wavelength 1064 nm (1.17 eV) is close in energy to an electronic transition of one particular nanotube. So, it is possible to perform a highly selective resonant enhancement which occurs only with one tube diameter.

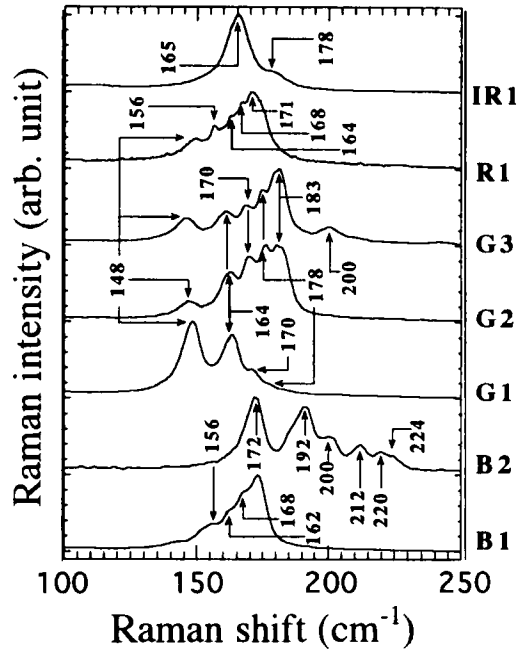

Fig 2 : Low frequency range (electric arc sample)

Other features are also visible in the intermediate frequency range (250-1200 cm^{-1}). In particular, it is possible to identify two asymetric peaks at 750 and 780 cm^{-1} on the G spectra. In fact, only calculations for armchair tubes leads to vibrational modes in the 700-800 cm^{-1} range, which increase in frequency with the diameter. This observation allows us to put in evidence the existence of tubes with this armchair configuration from (6/6) to (12/12). The asymetric profile comes from the superposition of several bands of different intensity since each tube of a specific diameter gives a Raman response

proportional to its concentration at the location studied. As a result, it follows the diameter distribution seen with the low frequency group.

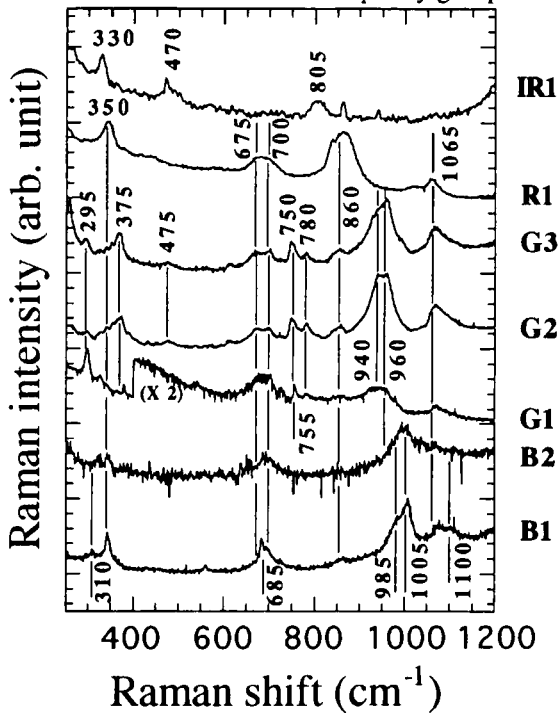

Fig 3 : Frequency range 250 - 1200 cm-1 (electric arc sample)

Since this mode is no longer observed using other wavelengths, we can suggest that armchair tubes are no longer visible and that we observe tubes with other configurations (zigzag or chiral). Apart from the overtones of the low frequency bands near 300 cm^{-1}, it is difficult to assign the other features because no modes are calculated at these frequencies even if it is possible to make some correlations with the diameter distribution. This is the case of the 950 cm^{-1} peak which is shifted to a higher frequency when the diameter decreases.

With all these informations given by the Raman spectroscopy, it is possible to make systematic studies on samples containing SWNT's. For all spectra shown below, the laser excitation wavelength is the argon line at 514.5 nm.

In a first step, we have performed experiments on one collaret. After having splitted it in several parts, we have studied several spots on each as shown in the example of figure 4. We have been able to see a gradual evolution of the diameter distribution on this part with the low frequency group of bands. Then it is clearly observed that along the sample from point 1 to point 6, the diameter distribution changes continuously from low diameter

to higher ones. This is an indication that the conditions in the synthesis chamber are not homogeneous and that the tube production changes from one point to the other and then some specific diameters are favoured compared to others. As a consequence, we can conclude that the location of the extracted sample in the synthesis chamber is of real importance on the production of tubes with a specific diameter.

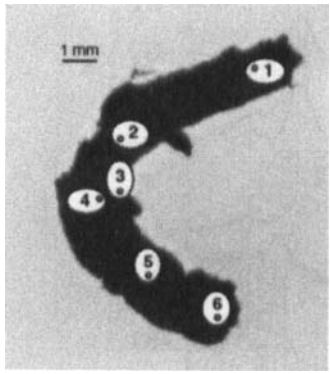

Fig 4 : Part of the collaret with the position of the different spots studied by Raman spectroscopy

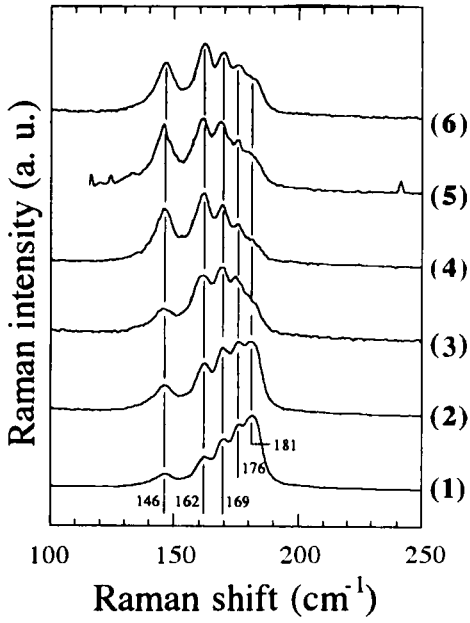

Fig 5 : Collaret study (electric arc sample) excitation : 514.5 nm

In a second step, we have studied samples produced by other methods, namely laser ablation and solar energy. As shown in figures 6 and 7, the two Raman spectra obtained for laser ablation and the upper one of the solar energy look similar to those obtained with the electric arc samples. We can always observe the E_{2g2} splitted mode, the same peaks at the same position at low frequencies or in the intermediate (250-1200 cm^{-1}) range.

The tubes produced by the electric arc or laser ablation seems identical. Or the other hand, some other parts of the solar energy sample lead to the lower spectrum of fig. 6. This spectrum presents a broad peak at 1520 cm^{-1} and more than 10 peaks from 130 to 255 cm^{-1}. This corresponds to a very large diameter distribution shown by the low frequency bands and confirmed by the broader splitting of the E_{2g2} graphite mode. In this case, the diameter is expected to go from a very low value near 8 Å to 20 Å. In this latter case, it seems that the synthesis conditions are not completely comparable to the two previous one, even if a large scale of SWNT's are also produced. From these observations, it can be suggested that the experimental parameters used for the sublimation of graphite do not play a major role in the production of

nanotubes. On the contrary, the plasma conditions after sublimation turn out to be of real importance.

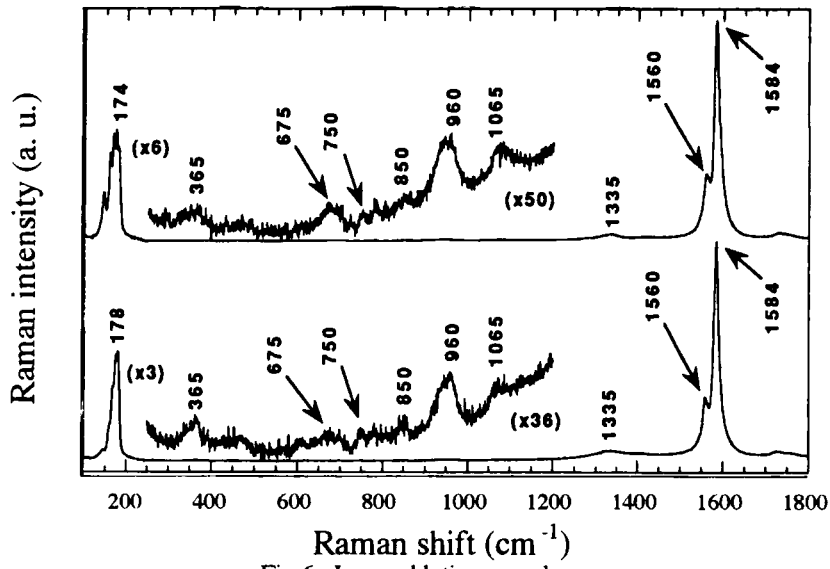

Fig 6 : Laser ablation sample
excitation : 514.5 nm

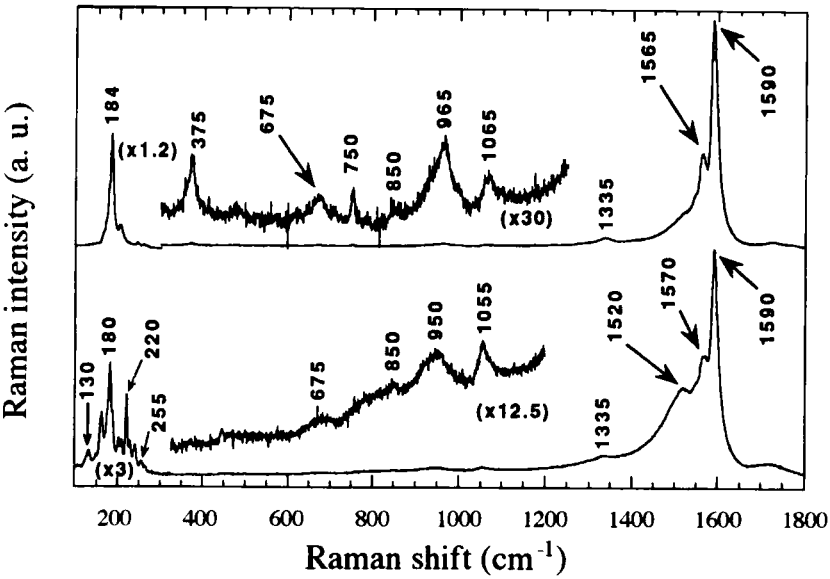

Fig 7 : Solar energy sample
excitation : 514.5 nm

Conclusion

We have presented Raman studies on SWNT's. This non-destructive method is efficient to characterize these materials since we can get a diameter distribution and confirm the existence of "armchair" tubes and induce selective study by resonance effects. Therefore, it is possible to perform systematic studies. As an example, we are able to show that on the collaret, the diameter distribution changes significantly from one spot to another in a gradual way and then, that the location in the synthesis chamber is of a great importance in the tubes production. On the contrary, the sublimation process of graphite seems to have a limited influence, since similar spectra are observed on SWNT's produced by different methods.

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