

Synthesis and Raman characterization of single-walled carbon nanotubes growth by injection chemical vapour deposition

Zs. SZEKRÉNYES*, P. NEMES-INCZE, AI. DARABONT, N. S. DAROCZI^c, A. A. KOOS^a, Z. E. HORVATH^a, S. AȘTILEAN, D. R. T. ZAHN^b, L. P. BIRÓ^a

Faculty of Physics, Babeș-Bolyai University, 400084 M. Kogălniceanu str., no. 1, Cluj-Napoca, Romania

^aNanostructures Laboratory, Research Institute for Technical Physics and Materials Science of the Hungarian Academy of Sciences, Budapest H-1525, P.O. Box 49, Hungary

^bSemiconductor Physics Dept., Chemnitz University of Technology, D-09107 Chemnitz,, Germany

^cFaculty of Chemistry, Babeș-Bolyai University, Arany János str., no. 11, Cluj-Napoca, Romania

In this paper, single-wall carbon nanotubes growth with the injection chemical vapour deposition method is presented. Ferrocene was dissolved in ethanol and such a solution was sprayed into a heated quartz tube reactor under Ar atmosphere. Raman spectroscopic studies using the intensity ratios between the D and G line reveal a very good crystallinity. The spectra display several lines in the low frequency region associated with the radial breathing mode. Based on our results the method presented appears to be more efficient than other more expensive methods like arc-discharge or laser ablation.

(Received November 15, 2006; accepted December 21, 2006)

Keywords: Single-wall carbon nanotubes, Spray pyrolysis, Raman spectroscopy

1. Introduction

Carbon nanotubes (single- and multi-wall) have generated a great deal of interest due to their exceptional physical properties [1]. In particular, single-wall carbon nanotubes (SWCNTs) are more attractive from the nanoscience point of view because they provide a remarkable one-dimensional (1D) system. SWCNTs have proven to be unique in the study of Raman spectra of 1D systems, and at the same time Raman spectroscopy has proven to be a powerful tool for the characterization of SWCNTs [2]. The production of SWCNTs appears to be more complex and expensive, when compared to that of multi-walled carbon nanotubes (MWCNTs).

In our earlier work we proposed an inexpensive and upscalable method to synthesize MWCNTs [3], using the injection chemical vapour deposition (CVD) or spray pyrolysis method. In that work we have shown that using our experimental setup for the pyrolysis of liquid hydrocarbons we can obtain high purity MWCNTs [3-4]. In this paper we show that single walled carbon nanotubes can be also obtained by using the same experimental setup. Only a slight modification of experimental parameters is needed to produce SWCNTs by the pyrolysis of ethanol. The use of ethanol as a carbon source is not new. Other groups have obtained single and multi-wall carbon nanotubes by the thermal decomposition of alcohols [5, 6]. An important advantage to using ethanol for SWCNT synthesis is that, it makes possible the low temperature deposition of SWCNTs and avoids the use of hazardous

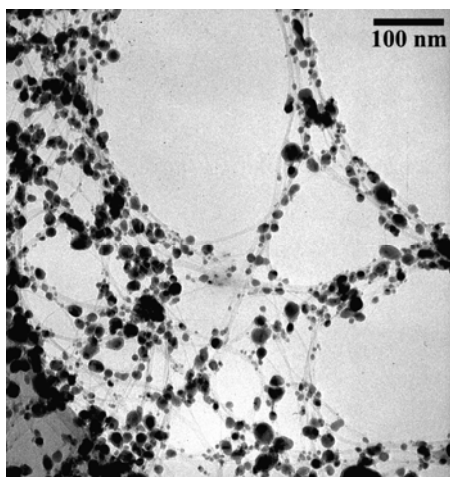
substances in the production process, such as H₂ and toxic carbon sources like CO, or aromatic hydrocarbons [5, 6].

2. Experimental

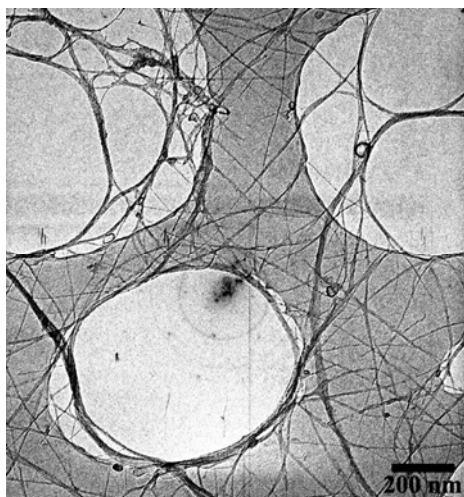
SWCNTs were synthesized in our experimental setup which were initially designed for the production of MWCNTs. A detailed description of the experimental setup and procedure can be found in the literature [1, 3, 16]. Solutions of ethanol (C₂H₅OH) and ferrocene (Fe(C₅H₅)₂) were sprayed into a quartz tube reactor, heated by an electrical furnace to the reaction temperature of 970 °C. The effective heating length of the furnace is 20 cm and the inner diameter of the quartz tube is 1.8 cm. The ferrocene ethanol solution, 0.5 g ferrocene in 50 ml of ethanol, was introduced into the reactor through a sprayer, using Ar gas. Ar flow rate was maintained at 300 l/h, providing a fine spray of the solution. The solution flow rate was 1 ml/min. Before the synthesis experiments, the quartz tube interior was cleaned of impurities with a mixture of nitric acid and hydrofluoric acid. Before each run, the reactor is flushed of air, using a flow of Ar gas (~50 l/h), while heating it to the desired temperature. Single wall carbon nanotubes deposit outside the hot-zone of the reactor, at the outlet of the furnace. The thickest deposit is reached at a length of about 7 cm from the furnace, where the temperature on the outer wall of the quartz tube is 170°C. This low temperature region is vital to the formation of SWCNTs, since we found no trace of single wall tubes in the material removed from the reactor hot-zone. In addition the SWCNT material, which

deposited outside the hot zone does not contain MWCNTs (Fig. 1a). The deposit of single wall nanotubes is a web-like soot, easily removable from the surface of the quartz reactor.

Two synthesis runs were carried out, in one case 50 ml of solution was sprayed into the reactor, in the other 200 ml of solution was introduced. Experimental data, regarding both synthesis runs can be seen in Table 1. Using this technique ~0.1 g of SWCNT material can be produced every 3 hours, though the process needs further optimization of reaction parameters.



a



b

Fig. 1. TEM images of raw SWCNT sample (a) and the sample purified by nitric acid refluxing (b).

The sample outside the furnace (S1o) was purified using nitric acid (40 vol%) by following a procedure described elsewhere [3], which basically consists of refluxing the sample for 6 hours in nitric acid (40%). This treatment is followed by further boiling of the treated sample in distilled water. This procedure removes most of the iron encapsulated in graphite from the samples, sometimes leaving empty graphitic shells (see Fig. 1.b).

TEM investigations were conducted with a Philips CM20 microscope operating at 200 kV. After dispersion in

ethanol in an ultrasonic bath, the samples were drop dried on holey amorphous carbon film suspended on a copper grid. Raman spectra on these products were obtained using a Dilor XY 800 spectrograph in backscattering configuration. Five different laser excitation energies were used to collect Raman scattering from our sample: 457.9 nm (2.71 eV), 488.0 nm (2.54 eV), 514.5 nm (2.41 eV), 647.1 nm (1.92 eV) and 676.4 nm (1.83 eV), respectively.

Table 1.

Sample	Volume of solution	Quantity of the obtained soot	
		inside the hot-zone (S1i)	outside the hot-zone (S1o)
S1	50 ml	0.1642 g	0.0126 g
S2	200 ml	0.8947 g	0.1287 g

3. Results and discussion

The powder formed inside the furnace ($T=970\text{ }^{\circ}\text{C}$) and the web-like soot from the cold zone were investigated by TEM and Raman spectroscopy. Further work on AFM and STM measurements are in progress. Firstly, several spectra from different places were recorded in order to obtain a general characterization of our sample using the green line (514.5 nm) of Ar^+ laser. Secondly, different laser energies were used for a better characterization of the sample. The $1\text{ }\mu\text{m}^2$ excitation laser spot allow us to obtain information from a small amount of carbon nanotubes. Based on a number of peaks from radial breathing mode (RBM), 5-6 different types of CNTs contribute to one Raman spectra. Raman results on powder formed inside the hot zone (results not shown) reveal no trace of SWCNTs. The absence of the RBM, the very strong disorder-induced D mode and the single peak structure for G mode prove that inside the hot zone only amorphous carbon and MWCNTs were synthesized.

The Raman spectra of raw SWCNT collected from the cold zone is shown in figure 2 (a). In SWCNTs, the G band and the lower frequency RBM are usually the strongest features in SWCNT Raman spectra [4]. The RBM is a bond-stretching out-of-plane phonon mode for which all the carbon atoms move coherently in the radial direction and its presence in the Raman spectrum indicate that a sample contains SWCNTs. The RBM frequency is inversely proportional to the tube diameter and this dependence comes from the fact that the mass of all carbon along the circumferential direction is proportional to the diameter [4, 7]. These RBM frequencies occur between 140 and 260 cm^{-1} for nanotube diameters in the range $0.9 < d_{\text{SWCNT}} < 1.7\text{ nm}$ (see inset figure 2 (a)). Here, the following correlation between diameter and RBM shift: $\omega_{\text{RBM}} = A/d + B$ is used to determine the tube diameter (where $A=234\text{ cm}^{-1}\text{nm}$ and $B=10\text{ cm}^{-1}$ has been used, B is an upshift in ω_{RBM} due to tube-tube interactions in SWCNTs bundles) [8]. The RBM spectra for SWCNT bundles (inset figure 2 (a)) contain contribution from different SWCNTs in resonance with the excitation laser line. Using the 514.5 nm wavelength there are two

dominant components in the RBM region at 148 and 178 cm^{-1} . Using the above mentioned relation between SWCNT diameter and ω_{RBM} , the tube diameter for these two values are $d \approx 1.7$ and 1.4 nm. Other RBM signals located at 203, 244 and 258 cm^{-1} correspond to $d \approx 1.2$, 1.0 and 0.9 nm respectively.

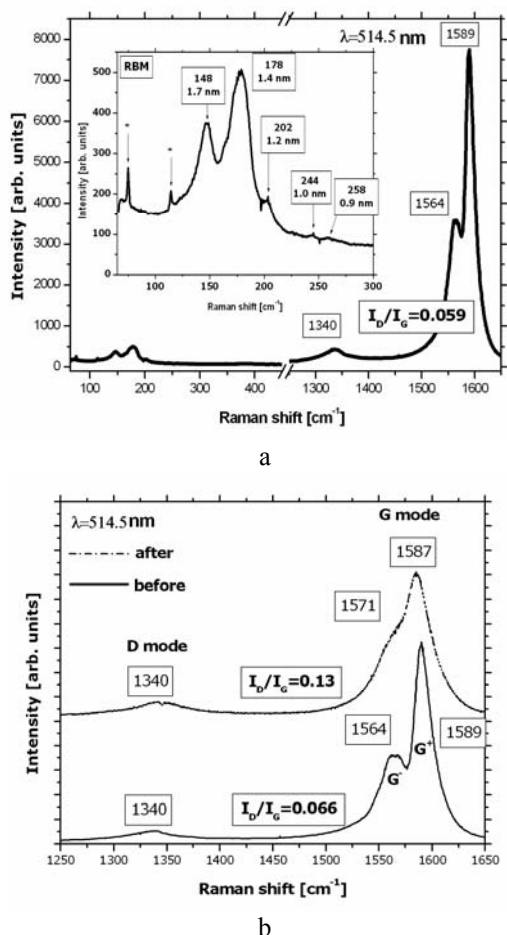


Fig. 2. (a) Raman spectra of the raw SWCNTs sample using a 514.5 nm laser line. (b) Comparison of the D and G modes before (lower spectra) and after (upper spectra) nitric acid treatment. All peaks marked with '*' are laser plasma lines.

The D band located at 1340 cm^{-1} has been known in graphite from 1970 [9]. This mode is induced by disorder and the intensity of this mode increases linearly with decreasing crystallite size. In our sample (Fig. 2 (a)) this disorder induced band is of low intensity compared to the G mode located at ~ 1580 cm^{-1} ($I_{\text{D}}/I_{\text{G}} = 0.06$). This is an indicative of non-defect SWCNTs presence in high yields but also low contents of defect carbon structures.

In the high energy region of the Raman spectrum the G band is an in-plane out-of-phase phonon mode which involves the two dissimilar carbon atoms in the unit cell of graphite. In contrast to the graphite G band (single Lorentzian peak at 1582 cm^{-1}), the SWCNT G band exhibits a multi-peak structure due to the phonon wave

vector confinement along the SWCNT circumferential direction [4, 11]. Fig. 2 (a) indicates that there are two main components for the G band of SWCNT, one peaked at 1589 cm^{-1} (G^+) and one peaked at 1564 cm^{-1} (G^-). The G^+ feature is associated with vibrations of carbon atoms along the nanotube axis and the G^- feature is associated with carbon atom vibrations along the circumferential direction of the SWCNT [2, 4]. The line shape of the G^- is sensitive to whether the SWCNT is semiconducting (Lorentzian line shape) or metallic (asymmetric non-Lorentzian line shape) [10]. In Fig. 2 (a) the G^- mode exhibit a Lorentzian line shape which lead us to consider that using $\lambda=514.5$ nm laser excitation line the main contribution originate from semiconducting SWCNTs.

Fig. 2 (b) shows a comparison of the high energy modes before (lower spectra) and after nitric acid treatment (upper spectra). After nitric acid treatment several changes can be noted. Firstly, a decrease of the relative intensity for both the G and D line can be noted. Also the intensity ratio between D and G lines is higher after acid treatment. These changes are related to the oxidation of the samples by the HNO_3 treatment [12]. SWCNTs have suffered a high degree of degradation by the partial destruction of the nanotube wall. A possible intercalation of HNO_3 molecules into the SWCNT bundle could be the reason for the upshift of the G^- mode [13].

In order to gain a better characterization of the sample several measurements were performed using different excitation laser lines (Fig. 3). The sample was fixed during these measurements in order to get Raman signals from the same place for different wavelengths. Fig. 3 (a) and (b) present the entire Raman spectra for the raw SWCNTs sample and figure (c) and (d) show the Raman spectra after nitric acid treatment. There are two dominant features for 488.0 nm located at 156 and 201 cm^{-1} . For 514.5 nm laser line there are two new peaks at 148- and ~ 180 cm^{-1} and the peak at 156 cm^{-1} is imperceptible. For 647.1 nm and 676.4 nm new peaks appear (at 175- and 194 cm^{-1}) and the peak at 202 cm^{-1} is absent. The peak at 175 cm^{-1} is very weak for 647.1 nm laser line and is the dominant feature for 676.4 nm. The RBM signal located at 194 cm^{-1} is the dominant signal when 647.1 nm laser line was used. From all these observations results that for different excitation laser lines SWCNTs with different diameters and chiralities are in resonance (figure (a) and (c)). Fig. 3 (b) and (d) shows clearly that the G^- mode is highly sensitive to whether the SWCNT is metallic or semiconducting. Based on the line shape of the G^- mode [10], for $\lambda \leq 514.5$ nm, semiconducting SWCNTs are more in resonance than metallic ones and the main contribution to the G mode comes from semiconducting nanotubes. For $\lambda \leq 647.1$ nm the line shape of the G^- mode is asymmetric and in this case contributions from metallic SWCNTs are expected. The frequency of the D mode is shifted with the energy of the exciting laser line (Fig. 3 (b) and (d)) [14, 15]. These shifts were first found in graphite [14], but a similar shift is found also in multi-wall and single-wall nanotubes. The frequency of the D mode changes by 53 cm^{-1} as a result of changing the laser energy by 1 eV [4].

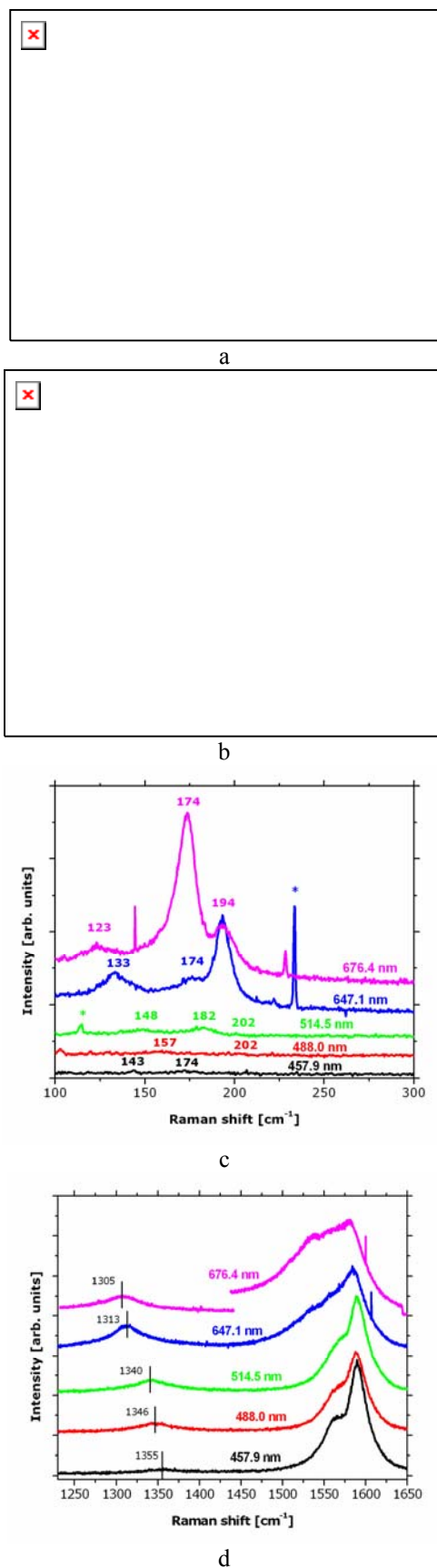


Fig. 3. Raman spectra of raw SWCNTs (a, b) and nitric acid-treated sample (c, d) for several laser excitation lines. See text for details.

4. Conclusions

We have demonstrated that SWCNTs could be produced by pyrolyzing ferrocene-ethanol solution at 970°C . Only a slight modification of experimental parameters is needed to produce SWCNTs by the pyrolysis of ethanol. SWCNTs are deposited as a web-like soot outside the hot zone. TEM and Raman spectroscopy were used for the characterization of the as grown samples. Based on TEM and Raman spectroscopy results we can conclude that there are no traces of MWCNTs outside the hot zone. In this region only SWCNT bundles have been synthesized. The nitric acid purification process applied, leads to an efficient elimination of the metal impurities, but at the same time induces defects in the nanotube crystalline structure, as evidenced by Raman spectroscopy measurements. Due to the simplicity of this technique, it is a very promising and inexpensive method to produce SWCNTs on a large scale. Ethanol is much less toxic than other precursors, used for SWCNT growth, such as aromatic hydrocarbons, or carbon monoxide, used in the HIPCO process. Finally we need to stress the importance of the low temperature involved in the synthesis. Although the reactor is heated to 970°C , single-wall carbon nanotube deposition takes place in the low temperature region of the quartz reactor. This can allow SWCNT deposition, or possibly growth on substrates sensitive to high temperatures, making this technique ever more convenient for industry.

References

- [1] R. Saito, G. Dresselhaus, M. S. Dresselhaus: Physical Properties of Carbon Nanotubes (Imperial College, London 1998).
- [2] M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman Spectroscopy of carbon nanotubes, Physics Reports, **409**, 47 (2005).
- [3] Z. E. Horváth, K. Kertész, L. Pethő, A. A. Koós, L. Tapasztó, Z. Vértesy, Z. Osváth, Al. Darabont, P. Nemes-Incze, Zs. Sárközi, L. P. Biró, Current Applied Physics **6**(2), 135 (2006).
- [4] L. P. Biró, Z. E. Horváth, A. A. Koós, Z. Osváth, Z. Vértesy, Al. Darabont, K. Kertész, C. Neamtu, Zs. Sárközi, L. Tapasztó, Direct synthesis of multi-walled and single-walled carbon nanotubes by spray pyrolysis, J. Optoelectron. Adv. Mater. **5**, 661 (2003).
- [5] F. Lupo, J. A. Rodriguez-Manzo, A. Zamudio, A. L. Elias, Y. A. Kim, T. Hayashi, M. Muramatsu, R. Kamalakaran, H. Terrones, M. Endo, M. Rühle, M. Terrones, Pyrolytic synthesis of long strands of large diameter SWCNTs at atmospheric pressure in the absence of sulphur and hydrogen, Chem. Phys. Lett. **410**, 384 (2005).
- [6] L. F. Su, J. N. Wang, F. Yu, Z. M. Sheng, Hyuk Chang, Chanho Pak, Continuous production of SWCNTs by spray pyrolysis of alcohol with dissolved ferrocene, Chem. Phys. Lett. **420**, 421 (2006).

- [7] R. A. Jishi, L. Venkataraman, G. Dresselhaus, Phonon modes in carbon nanotubes, *Chem. Phys. Lett.* **209**, 77 (1993).
- [8] M. Milnera, J. Kürti, M. Hulman, H. Kuzmany, Periodic resonance excitation and intertube interaction from quasi-continuous distributed helicities in single-wall carbon nanotubes, *Phys. Rev. Lett.* **84**, 1324 (2000).
- [9] F. Tuinstra, J. L. Koenig, Raman spectrum of graphite, *J. Chem. Phys.* **53**, 1126 (1970).
- [10] M. A. Pimenta, A. Marucci, S. Empedocles, M. Bawendi, E. B. Hanlon, A. M. Rao, P. C. Eklund, R. E. Smalley, G. Dresselhaus, M. S. Dresselhaus, Raman modes of metallic carbon nanotubes, *Phys. Rev. B* **58**, R16016-R16019 (1998).
- [11] S. Reich, Carbon Nanotubes: Vibrational and electronic properties (PhD dissertation), Berlin (2002).
- [12] M. T. Martinez, M. A. Callejas, A. M. Benito, M. Cochet, T. Seeger, A. Ansón, J. Schreiber, C. Gordon, C. Marhic, O. Chauvet, W. K. Maser, Modifications of SWCNTs upon oxidative purification treatments, *Nanotechnology* **14**, 691-695 (2003).
- [13] C. Bower, A. Kleinhammes, Y. Wu, O. Zhou, *Chem. Phys. Lett.* **288**, 481 (1998).
- [14] R. P. Vidano, D. B. Fischbach, L. J. Willis, T. M. Loehr, Observation of Raman band shifting with excitation wavelength for carbons and graphites, *Solid State Commun.* **39**, 341 (1981).
- [15] C. Thomsen, Second-order Raman spectra of SWCNTs, *Phys. Rev. B* **61**, 4542 (2000).
- [16] L. Tapasztó, K. Kertész, Z. Vértesy, Z. E. Horváth, A. A. Koós, Z. Osváth, Zs. Sárközi, Al. Darabont and L. P. Biró, Diameter and morphology dependence on experimental conditions of carbon nanotube arrays grown by spray pyrolysis, *Carbon* **43**, 970 (2005).

*Corresponding author: szezsol@gmail.com