ROLE OF SULPHUR IN THE A- CVD GROWTH OF SINGLE WALL CNTs

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Single-walled carbon nanotubes (SWCNTs) have exceptional electrical and unique optical properties, rendering them being applied in various application fields, especially in transparent conducting films (TCFs). The fabrication methods of SWCNTs play a big role in their obtaining and controlling the diameters and structures..

For many years sulphur has been known as a good promoter to growth of carbon fibers in the metal-catalyzed chemical vapor deposition systems. In the present paper the Single Wall carbon nanotubes (SWCNTs) were synthesized by means of Aerosol CVD method. A little amount of pure sulphur powder was mixed with Ferrocene, which is used as a catalyzer and high frequency (800 kHz) transducer transformed the solution (ferrocene/sulphur/x-lene) to the aerosol. The growth processes were carried out at 850-1000^{0}C in the horizontal reactor at the atmospheric pressure.

The morphology of the samples was observed by SEM and Raman spectroscopy with 532 nm laser being used to analyze the diameter distribution of the obtained nanotubes. The presence of 1- 1.4 nm diameters of SWCNTs in the samples has been determined.

Keywords SWCNTs, Raman, Sulphur, A-CVD, SEM
PACs: 85.35.Kt; 81.16.Be

INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) have exceptional electrical and unique optical properties, rendering them being applied in various application fields, especially in transparent conducting films (TCFs). The fabrication methods of SWCNTs play a big role in their obtaining and controlling the diameters and structures.

The synthesis methods as arc – discharge [1], laser ablation [2, 3] are suitable to grow SWCNTs with low diameter, high – quality and purity, but the drawback is the high cost of synthesis. The catalytic CVD method has drawn much attention due to it being different from all above. CCVD has a potential for producing SWCNTs continuously and in large amount, in which SWCNTs are grown on a substrate or as agglomerates in the reactor with the use of pure hydrocarbon gases or carbon monoxide as feedstock [4-6]. Additionally, CNTs are synthesized by CCVD method, in which a carbon containing gas is decomposed at high temperature in the presence of a metal catalyst [7, 8]. The metallic catalyst is often a transition metal, with iron, cobalt and nickel being the notable ones.

Other metals such as chromium, platinum, molybdenum, palladium and copper are used as catalyst promoters [9,10]. Such promoters change the electronic structure of the catalyst, which lowers the activation energy for dissociation. Kim et.all. used Pd film as a gas activator to decrease the growth temperature of carbon nanotubes [11].

Among the metallic promoters, nonmetallic promoter materials are used in the growth process to decrease the diameter of CNTs. Sulphur and sulphur containing materials are effective in controlling the diameter as well as the number of walls of grown carbon nanotubes [12]. Sulphur can influence SWCNT growth by blocking active sites on the catalyst particle, lowering the melting point of the catalyst, or interacting with the growing nanotube [13].

In the present paper the Single Wall carbon nanotubes (SWCNTs) were synthesized by means of Aerosol CVD method using pure sulphur as promoter together with iron catalyst.

EXPERIMENT

The synthesis process was carried out by conventional aerosol-assisted chemical vapor deposition (A-CVD) technique from SCIDRE, Germany, which uses liquid hydrocarbon as carbon source. MWCNTs with diameters of 10-85 nm and a small percent of SWCNTs with diameters of 0.85 and 1.14 nm has been grown by the aerosol chemical deposition method in our previous report [14] .

A small amount of pure Sulphur powder was mixed with Ferrocene (Fe:S)=10:1 (atomic weight) and x-lene in a special flask, which then inside of high frequency (800 kHz) transducer transformed into the aerosol during the synthesis process. The growth processes were carried out at 850- 1000^{0}C in the horizontal reactor at the atmospheric pressure. Ar/H_2 mixture was used as a transport gas which the total flow in the ratio of 10:1. H_2 gas was flowed to the system during the synthesis process. The system is cooled under the Ar flow.

The morphology of the samples was analyzed by scanning electron microscopy (Auriga cross beam SEM rom Carl Zeiss, installed in IMEM, CNR) and RBM mode of crystalline phases of the CNT samples were analyzed by Raman spectroscopy using Tokio Instruments Nanofinder 30 Confocal Laser Spectroscope setup with green excitation laser beam at 532 nm. All the measurements were performed at room temperature. The Raman signal was collected by a back-thinned CCD.

RESULT AND DISCUSSION

In order to gain a better understanding of the role of sulphur in the growth of SWNTs by the aerosol CVD system, we produced different types of nanotube materials by varying the reaction furnace temperature from 850 to 1000^0C, using a fixed Ferrocene/Sulphur concentration of 22mg/ml in x-lene. By analyzing the works of other authors [15, 16], we decided on 10:1 relation between Fe and S.

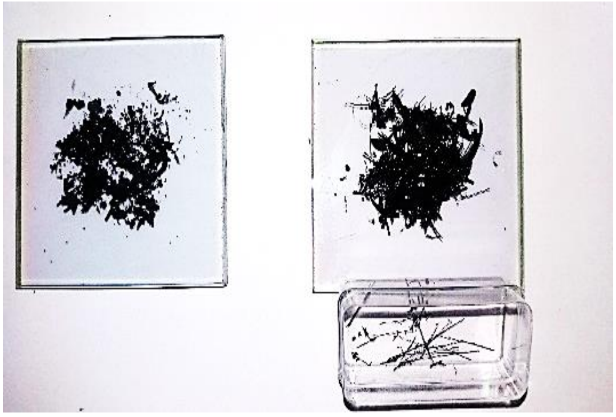

Fig. 1. Photography of the sample grown without (left) and with (right) pure Sulphur

Fig.1. shows produced CNTs without (left) and with (right) sulphur in the starting solution. Visually it is seen that the presence of the Sulphur leads to the formation of long (1,5-2.0 cm) whiskers (see right picture) and increase of yield.

We have analyzed one of such whiskers by SEM and show this in fig 2. On the picture it is seen as a twisted thin film.

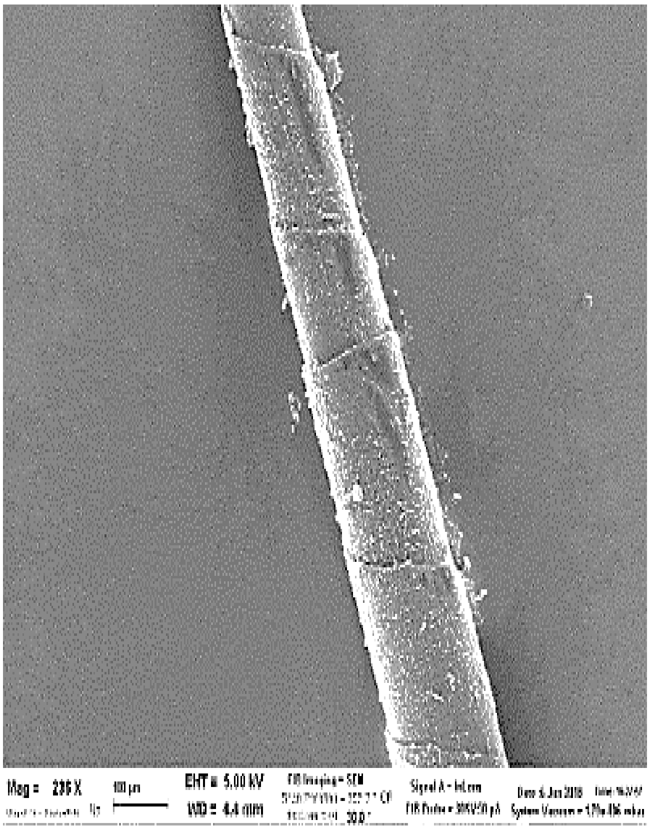

Fig.2. SEM image of one of the whisker

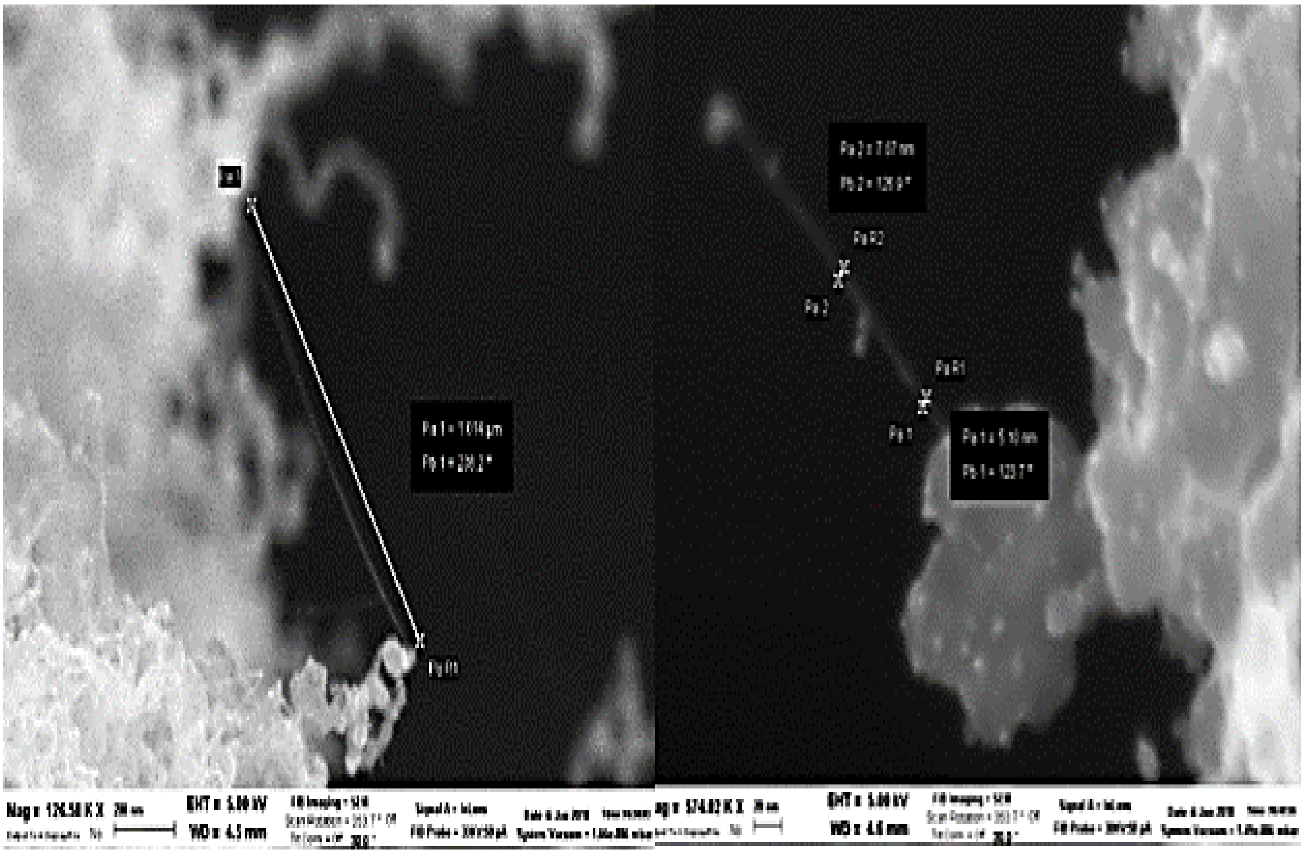

Fig.3. SEM image of the CNTs observed on twisted thin film

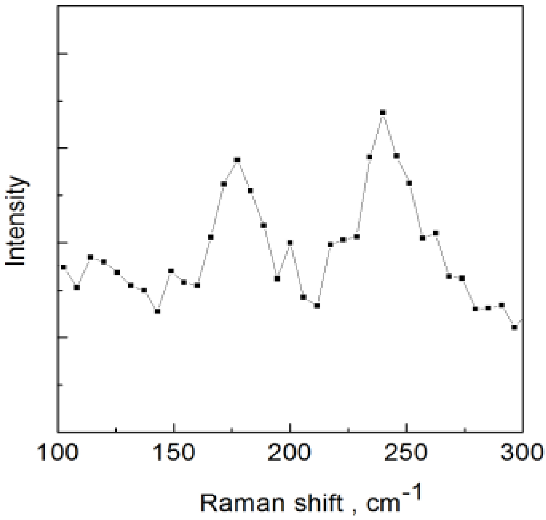

Fig.4. RBM bands of the Raman spectrum of the CNTs observed on twisted thin film

To confirm the obtained results the Raman spectroscopy analysis was carried out. The Raman experiment condition was the same as our previous works [14]. Radial breading mode (RBM), which is characteristic of SWCNTs (due to easy vibration of single wall by low frequency signals), with peaks located at X_{RBM} =178 and 240 cm^{-1}, which confirms the presence of nanotubes of 1.4 and 1nm, respectively (Fig.4).

Regarding the crystallinity of the grown material, we could also use the intensity ratios between the D (defectiveness) and G (graphite) bands (Fig.5). As the D band becomes weaker, the material tends to be more crystalline. We calculated D/G = 0.39. Such value can explain the presence of amorphous carbon among with SWCNTs, and possibly the signal is also detected from a twisted film, which contains amorphous carbon. It is important to have amorphous carbon free single-wall carbon nanotubes.

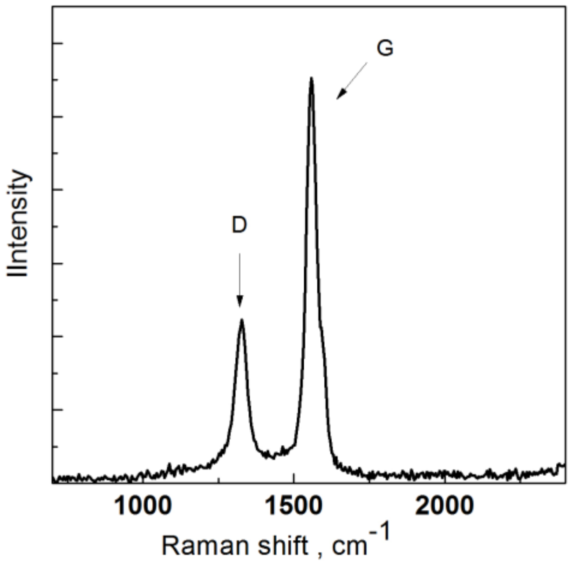

Fig.5. Raman spectrum of the CNTs grown on the twisted thin films

CONCLUSIONS

We concluded that using sulphur makes it easy to decrease the diameters of grown CNTs. By SEM the CNTs with 5 -7 nm diameters are observed, and from RBM peaks of the Raman spectra it is calculated that there are SWCNTs with 1-1,4 nm diameter.

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