Purification and Oxidation Studies of Multiwall Carbon Nanotubes using Raman Spectroscopy†

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A process of chemical purification of multiwall carbon nanotubes (MWNTs) is investigated to determine the structural and chemical changes in atomic bond caused by chemical treatment. As-grown multiwall carbon nanotubes were treated in mixture of H_2SO_4, HNO_3 under a refluxing condenser with magnetic stir for different time period 5, 7, 9 and 15 h (samples S1, S2, S3 and S4, respectively) at 70 ºC in order to remove amorphous carbon and catalysts completely. The acid-treated tubes are extensively characterized by means of Raman spectroscopy. Raman spectra were recorded for as-grown as well as post treated multiwall carbon nanotubes samples as prepared for different time duration. The results of Raman spectroscopy suggest that the appropriate mixing ratio between H_2SO_4 and HNO_3 is 3:1 with treatment time from 5-9 h is suitable for purification and create less defect during acid treatment.

Key Words: Carbon nanotubes, Purification, Raman spectroscopy.

INTRODUCTION

Carbon nanotubes (CNTs) have attracted considerable interest due to their properties and potential applications in nanotechnology[1]. The carbon nanotubes as produced by the various synthesis techniques contain impurities such as graphite nanoparticles, amorphous carbon, smaller fullerenes and metal catalyst particles[2]. These impurities have to be separated from the carbon nanotubes before they can be used for applications such as composites, nanoelectronics, chemical sensors, *etc*. Purification techniques have been devised in order to improve the quality and yield of carbon nanotubes and these methods include air oxidation, acid treatment, annealing, micro filtration, sonication, ferromagnetic separation, functionalization and chromatography techniques[3]. The physical methods are non-destructive and do not damage tubes, but are less effective to purification of carbon nanotubes. On the other hand, the chemical methods generally resulting in carbon nanotubes with higher purity but cause remarkable damage to nanotubes morphology[4]. So finding suitable conditions for purification of carbon nanotubes is a crucial step in order to remove the impurities from the as prepared products with lowest damaged carbon nanotubes structure[5-7].

In this work we report the Raman spectra of multi-wall carbon nanotubes and the use of Raman spectroscopy to show the effect of chemical oxidative purification on the multi-wall carbon nanotubes. In the range between 3000 and 1000 cm^{-1}, all spectra exhibiting several prominent resonances including D mode (1370-1330 cm^{-1}), G mode (1580-1569 cm^{-1}) and G' mode (2710-2620 cm^{-1}) were studied[8].

EXPERIMENTAL

As produced multiwall carbon nanotubes (MWCNTs) were purchased from Ahwahnee Technology, Inc. USA. The samples were synthesized by chemical vapour deposition of hydrocarbon gases and were advertised as having 20-60 nm diameters and 95 % purity with 5 % metallic impurities. As-grown multiwall carbon nanotubes were treated in mixture of H_2SO_4, HNO_3 under a refluxing condenser with magnetic stir for different time period 5, 7, 9 and 15 h (samples S1, S2, S3 and S4, respectively) at 70 ºC in order to remove amorphous carbon and catalysts completely. After refluxing, the mixture was cooled to room temperature, diluted with deionized water and filtered through Whatman filter paper. The product on the filter was washed thoroughly with deionized water and dried at 50 °C for overnight. Here in this study the as-grown (raw) and oxidized samples were studied by Raman scattering measurements in a Raman spectrometer (Lab Ram HR 800, JY). The powder samples were put on glass slide and laser beam pass through the samples with laser excitation wavelength 488 nm.

RESULTS AND DISCUSSION

Raman spectroscopy is a valuable tool for the characterization of carbon-based nanostructures. Raman spectra of as-grown and treated multiwall carbon nanotubes were excited with the 488 nm laser line. Fig. 1 shows Raman spectra of the multiwall carbon nanotubes treated at the ratio 3:1 of H_2SO_4/HNO_3 and different oxidation time. Three peaks were observed showing the characteristics of carbon nanotubes, the defects of the structure, named D band at 1356 cm^{-1}, graphite band at 1577 cm^{-1} (G band) and another is the second order overtone mode G' at 2700 cm^{-1}. Usually the I_d/I_g ratio is taken as a measure of defect concentration. It has been argued that the G mode in the Raman spectra of carbon nanotubes originates from a defect induced double resonance scattering process[9]. When the acid treatment of carbon nanotubes was conducted, these observed peaks can still be recognized, indicating that the acid treatment does not destroy the structure of carbon nanotubes[10].
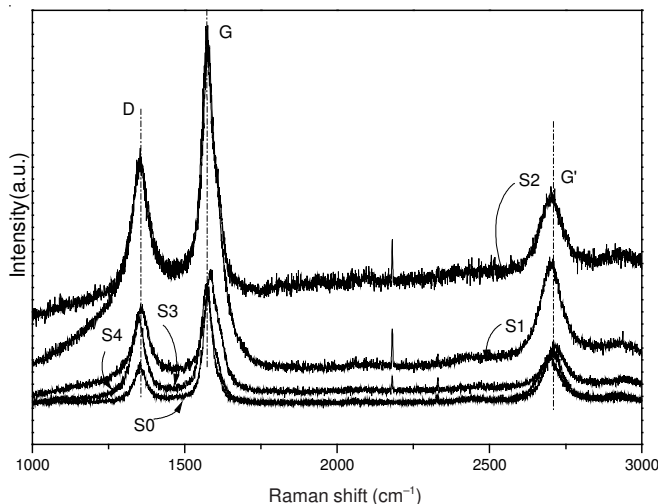

Fig. 1. Raman spectra of multiwall carbon nanotubes treated at the ratio 1:3 of HNO_3/H_2SO_4 for different oxidation time. (S0) for as - grown multiwall carbon nanotubes (S1) for 5 h, (S2) for 7 h, (S3) for 9 h and (S4) for 15 h

In present observation, it is found that when oxidation of nanotubes was performed, the change on the intensity of D band occurred, proving that the acid treatment can damage the structure of carbon nanotubes. Comparing the intensity ratio of D-to G-band (I_d/I_g) and G'-to G band (I_g/I_g) values of chemically treated and as-grown multiwall carbon nanotubes (sample S0), it is observed that after refluxing, the ratio I_d/I_g increase as expected shown in Fig. 2.

These results are generally attributed to the presence of more structural defects[11]. It indicates that the acid treated multiwall carbon nanotubes sample for 15 h contain more amount of defects than the multiwall carbon nanotubes treated by acid for less time period. The intensity ratio (I_d/I_g) increases with increasing the refluxing time which indicates that structural defects on the carbon nanotubes surface increases with increasing processing time in presence of concentrated acid mixture shown in Table-1. In acid treatment process, treating agents can destroy relevant bonds located on the surfaces and chemical groups resulting to the existence of physical defects on the side wall of multiwall carbon nanotubes[10].
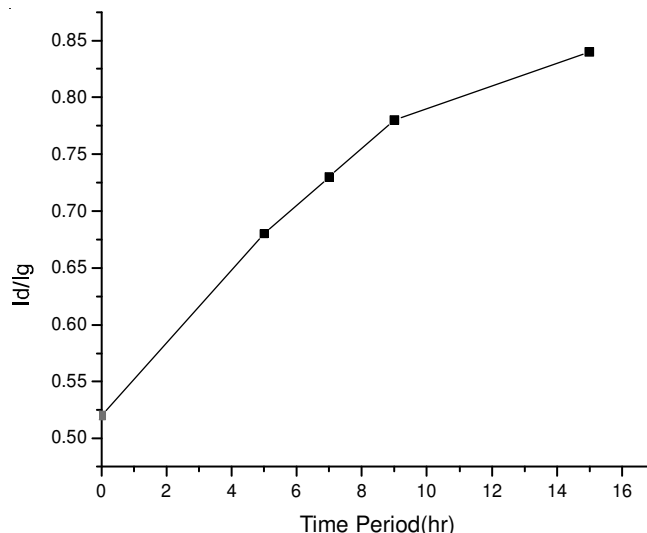

Fig. 2. Ratio between the intensity of the D-and G band by acid-treated method

TABLE-1
INTENSITY RATIOS OF I_d/I_g AND I_g/I_g WITH RESPECT TO PROCESSING TIME IN HOURS

Samples	I_d/I_g	I_g/I_g	Time (h)
S0	0.52	0.63	0
S1	0.68	0.43	5
S2	0.73	0.63	7
S3	0.78	0.57	9
S4	0.84	0.58	15

In Figs. 3 and 4, the I_g/I_g ratio is not increase linearly with increasing the processing time period. These result shows that chemical method for carbon nanotubes purification create defects on the surface of carbon nanotubes, when treated for longer time. The oxidation of carbon nanotubes breaks some of its bonds and inserts chemical groups such as carboxylic group, which can be interpreted as defects on the structure.
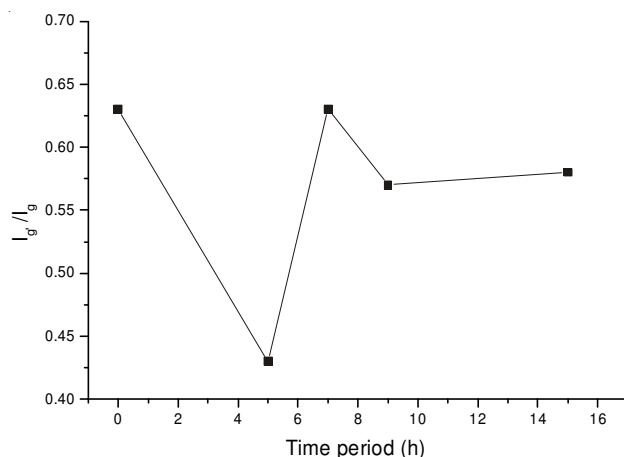

Fig. 3. Ratio between the intensity of the G'-and G band by acid-treated method

The acid treatment leading to the intercalation of acid molecules inside the rope lattice will exert a pressure on the tubes. Such a pressure is likely to upshift the D and G positions. The position of D and G lines is shifted to higher wave numbers (*ca.* 2 and *ca.* 8 cm^{-1}) for S3 while in S4 the position of D and G
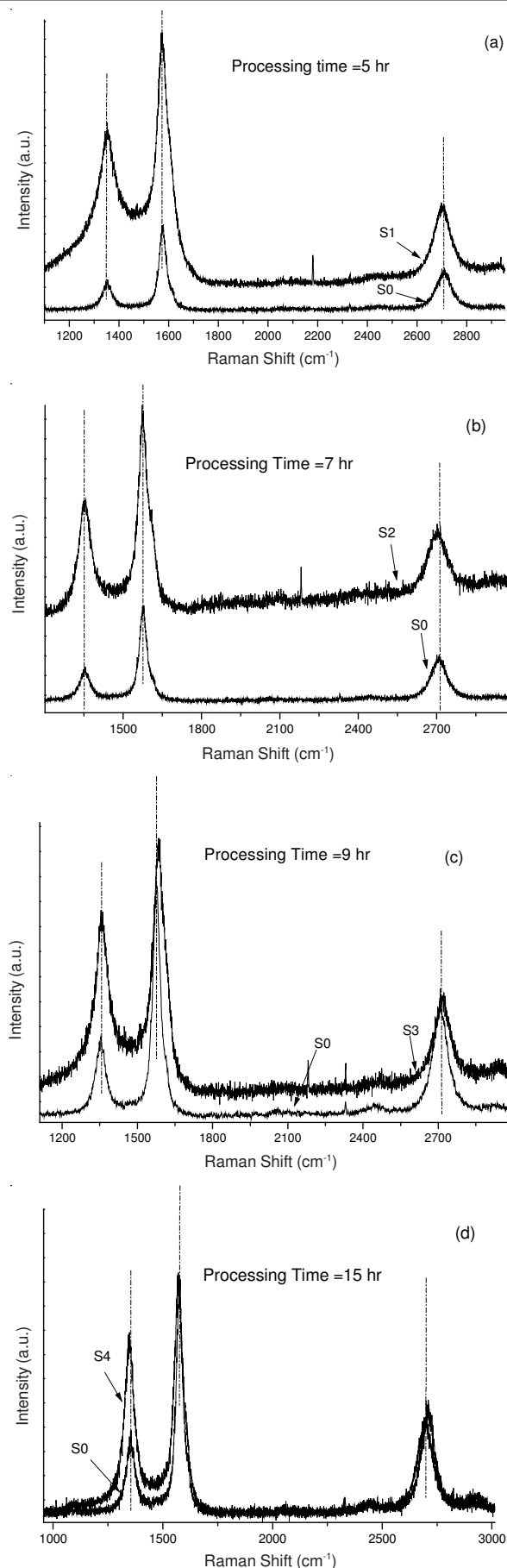
Fig. 4.   Raman spectra of different samples with respect to as grown samples for different processing time

lines is shifted to lower wave numbers. In other samples show different behaviour in S1, D is upshift and G is down shifted and in S2 D is down shifted while G is upshifted shown in Figs. 4 and 5. It has been observed that for carbon nanotubes under hydrostatic pressure the compression strain results in the shortening of C-C bonds and corresponding shift of Raman G peak to higher frequency[12]. The upshift of the tangential modes in acid treated multiwall carbon nanotubes are very likely induced by intercalated acid molecules. However, it is difficult to separate the effects of electron transfer from the carbon skeleton and the effects of strain due to the addition of acid molecules and anions in the interstitial channels between the tubes. While the downshift is interpreted as softening and elongation of the C-C bonds upon electron transfer to the multiwall carbon nanotubes, whereas electron withdrawal from the sp^2 lattice leads to a contraction and hardening the lattice. A plausible explanation for the observed upshift in the G band would be electron transfer from the π states in multiwall carbon nanotubes to the oxygen atoms of nitric acid molecules, forming NO_3^- anions[13].
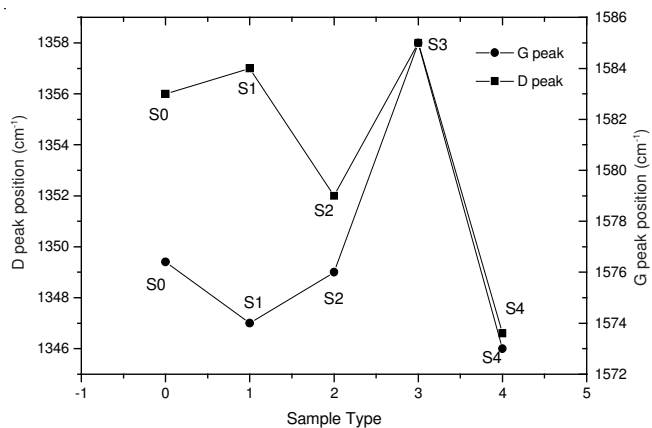

Fig. 5.   Comparison of D and G peak positions for S0, S1, S2, S3 and S4 samples

The purification and functionalization of carbon nanotubes by chemical route show a relevant change on the intensity of D-band. In oxidation by acid treatment, the ends and the surface of nanotube have been found to be covered with oxygen containing group like carboxylic group. This cover range of ends and surface has been attributed to the attack of oxidation acid treatment[14]. The adsorption of functional groups increases the number of defects in the structure of nanotubes, increasing the ratio I_d/I_g and providing the early decomposition of carbon nanotubes. These results indicate certain insertion of defects and/or break on the structure of nanotubes and attach some functional groups which are useful for chemical and gas sensor application as many researchers studied[15].

Conclusion

In conclusion, the result obtained by Raman spectroscopy indicated the modification of structure of carbon nanotubes after chemical treatment. It is observed by Raman spectra that defect will increase with increasing the refluxing time during purification processes and due to the intensity of D-band increases with decreasing the intensity of G-band. Some

functional groups like carboxylic group useful for further modification of carbon nanotubes, attached with the defect sites. It is concluded that the G' band is independent of defect concentration. The optimized condition interpreted from the ratio between the intensity of the D band and the G band was also obtained. It is found that refluxing time between 5-9 h is sufficient for purification by 3:1 of H_2SO_4 and HNO_3 mixture.

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