A RIGOROUS COMPARISON OF METHODS FOR MULTI-WALLED CARBON NANOTUBES PURIFICATION USING RAMAN SPECTROSCOPY

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ABSTRACT

Multi-walled carbon nanotubes (MWNT's) were synthesized using chemical vapor deposition (CVD) method in a fluidized bed reactor under the flow of methane and hydrogen gases. A Cobalt-molybdenum/magnesium oxide (Co-Mo/MgO) nanocatalyst was used as the catalyst of the process. The samples were analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. The effects of different combinations of purification methods, including oxidation, HCl treatment, and HNO_3 treatment and the sequence of performing these methods on the quality of the carbon nanotubes are discussed. Raman spectroscopy with a laser excitation of 532 nm was utilized as the measurement tool. The results provide the best purification methods of synthesized carbon nanotubes. The I_G/I_D ratio for the optimum sample is equal to 1.28. Moreover, as another application of Raman analysis results, the apparent Young's modulus of MWNT's was calculated by the use of intensity ratio I_D/I_G. As expected, the optimum sample had the highest apparent Young's modulus of 40459.85 MPa.

Keywords: Multi-walled Carbon Nanotubes, Purification, Chemical Vapor Deposition, Raman Spectroscopy, Young's Modulus

INTRODUCTION

Carbon nanotubes have remarkable electronic, thermal, and mechanical properties which can influence many different branches of science and technology. The multi-walled carbon nanotubes (MWNT's) were first produced by Ijima in 1991 by the use of arc discharge method [1], while the single-walled carbon nanotubes were discovered in 1993. These nanomaterials have found a wide variety of applications such as filters, membranes, gas adsorbents, catalyst supports, microelectronic devices, etc. [2].

Generally, carbon nanotubes can be produced by the use of three different methods which include laser ablation, arc discharge method, and chemical vapor deposition (CVD) [3-7]. The last method (CVD), among these methods, has been known as the best method for the large-scale production of CNT's, since it is simple, cost-effective, and highly efficient and needs lower temperature [8-13]. However, unfortunately, since in the CVD method carbon nanotubes grow in catalyst tips, metal particles could

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usually be observed in the produced CNT bodies. Moreover, some impurities such as amorphous carbon or other nano-structured carbons like fullerenes and carbon nanofibers are observed. In many end-use applications, it is desirable to use high-purity nanotubes containing minimal amounts of residual catalyst metal and support material and extraneous carbon. Hence the purification process is a necessary and crucial step in order to remove residual catalyst particles and amorphous carbons and obtain high-quality desired nano-tubes. Although some such studies have previously been carried out [14-21], to the authors' knowledge, it has not yet been implemented for the system used in this work.

In the present work, multi-walled carbon nano-tubes were synthesized by dissociation of methane and natural gas over a Co-Mo/MgO nano-catalyst in a fluidized bed reactor. The influence of different combinations of purification methods such as oxidation and acid treatments on the quality of carbon nanotubes was investigated to find the optimum method for the purification. Raman spectroscopy was utilized as the measurement tool, since it has proved to be a nondestructive and non-dissipative characterization method for lower dimensional materials like nanomaterials. Recently, it has widely been used for the study of carbon nanostructures such as carbon nanotubes. In addition, the apparent Young's modulus of MWNT's was calculated by the use of intensity ratio I_D/I_G obtained from Raman spectra data.

EXPERIMENTAL

In the current work, a Co-Mo/MgO nanocatalyst was selected as the catalyst of carbon nanotube growth, because MgO support could usually be eliminated easier than other supports such as silica and alumina [22], leading to the reduction of purification costs. This nanocatalyst was prepared by using a special sol-gel method [23].

The catalysts were shaped in spherical beads to prevent their erosion inside the fluidized bed reactor. After catalyst loading stage, they were reduced. After reduction, the treatment of the catalyst was performed by the use of a mixture of hydrogen and nitrogen flow, and then the methane or natural gas flow with a diluter was fed to the reactor. The reaction was taken place and the products came out of the cyclone continuously. The experimental set up for carbon nanotube growth is shown in Figure 1. The reactor with an inner diameter of 20 mm and a height of 1,400 mm is made of quartz. For distributing the gas and holding the nanocatalyst particles, a porous quartz disc has been used. The gas enters the reactor after a preheating section. The reactor is placed in a programmable vertical furnace. As-prepared products were analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) the results of which are shown in Figures 2 and 3 respectively. As it is obvious from these figures, some impurities are present in the as-prepared sample. For instance, in the XRD pattern (Figure 3), the diffraction peaks at 2θ=25-26 are attributed to carbon nanotubes [24], while others are attributed to the catalyst support and metal residues. Hence it is necessary to purify the carbon nanotubes.
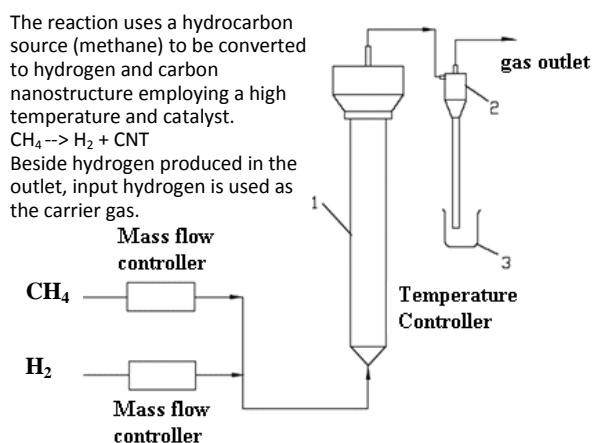
The reaction uses a hydrocarbon source (methane) to be converted to hydrogen and carbon nanostructure employing a high temperature and catalyst.
$CH_4 \rightarrow H_2 + CNT$
Beside hydrogen produced in the outlet, input hydrogen is used as the carrier gas.

Figure 1: Schematic of the experimental setup; (1) fluidized bed reactor, (2) cyclone, and (3) product container
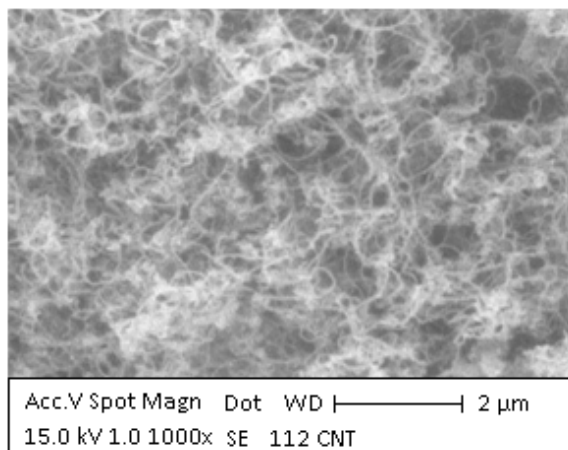
Figure 2: SEM photograph of the as-prepared multi-walled carbon nanotube
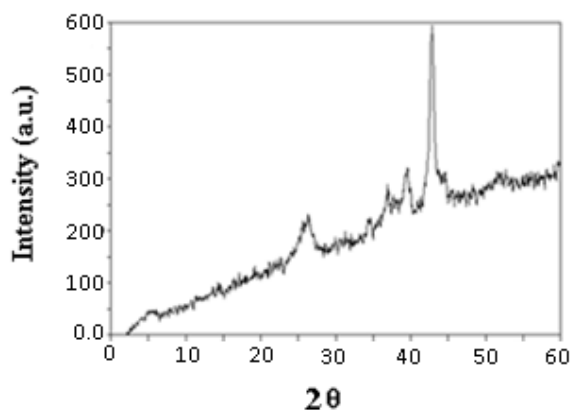

Figure 3: X-ray analysis of the as-prepared multi-walled carbon nanotube

Three different purification methods are applied in this study, namely oxidation, hydrochloric acid treatment, and nitric acid treatment. More-over, based on the previous experience, the effects of the combination of these methods and their sequences are discussed. Oxidation process can remove the amorphous carbons and acid treatment can eliminate catalyst particles.

RESULTS AND DISCUSSION

Table 1 shows the six samples used in this study. Sample 1 is the as-prepared CNT without any purification, while at least one purification method is applied on the other samples. After performing different experiments, it was found that the optimum condition for oxidation pro-cedure was a temperature of 300 °C and time of 30 minutes; for HCl treatment the optimum

condition was 6 molar acid wash at 50 °C for 16 hours while it was 3.5 molar acid wash at 60 °C for 3 hours for HNO_3 treatment.

Table 1: Six different MWNT samples with different purification methods

Sample	Step 1	Step 2	Step 3
1	-	-	-
2	Oxidized	-	-
3	Oxidized	HCl-treated	-
4	Oxidized	HCl-treated	HNO_3-treated
5	HCl-treated	HNO_3-treated	Oxidized
6	Oxidized	HNO_3-treated	HCl-treated

The Raman spectra are used for understanding the quality of carbon nanotubes. It should be noted that the D band at about 1340 cm^{-1} is attributed to symmetry-lowering effects such as defects or deformation vibrations of a hexagonal ring and the presence of the amorphous carbon, while the G band at about 1580 cm^{-1} wave length is assigned to a single crystalline form of graphite. The G′ band appears at about 2690 cm^{-1} and shows the overtone of D-band. The ratio of G band intensity to D band intensity (I_G/I_D) indicates the quality of the products. The higher the ratio is, the higher the quality of the products would be. Figure 4 shows the Raman spectra of six samples.
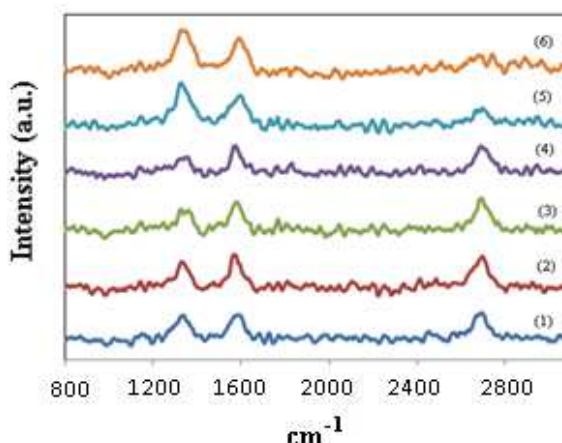

Figure 4: Raman spectra of six MWNT samples

The I_G/I_D ratio is calculated for various samples and the results are shown in Table 2. As seen in

this table, the as-prepared sample has an I_G/I_D ratio of 1.01. This ratio increases for samples 2, 3, and 4, while it decreases for samples 5 and 6. The optimum sample is number 4, with an I_G/I_D ratio of 1.28, purified by oxidation, HCl treatment and HNO_3 treatment respectively. Figure 5 represents the XRD pattern of this sample, which proves the elimination of catalyst support and particles.
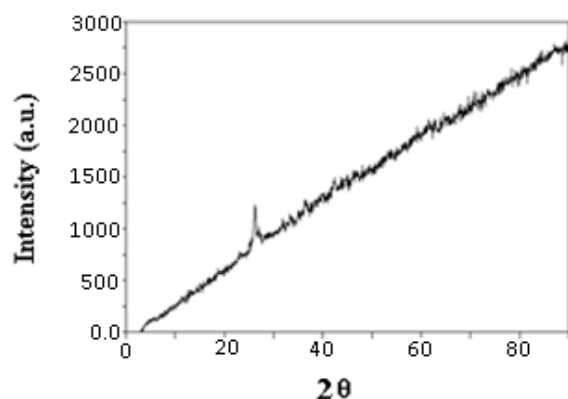

Figure 5: X-ray analysis of optimum multi-walled carbon nanotube

Table 2: Raman spectroscopy results of the MWNT samples

Sample	D	G	G'	I_D	I_G	I_D/I_G
1	1333	1582	2691	82.23	83.10	1.01
2	1329	1564	2693	81.18	94.18	1.16
3	1325	1577	2689	71.26	90.52	1.27
4	1350	1573	2689	74.48	95.91	1.28
5	1325	1595	2695	111.10	88.60	0.79
6	1326	1588	2740	108.54	93.75	0.86

It should be mentioned that the results are consistent with the fact that multi-walled carbon nanotubes have smaller values of I_G/I_D in comparison with single-walled carbon nanotubes.

MWNT's are usually produced at lower temperatures, and because of containing several layers, the impurities between layers are hardly eliminated; however, SWNT's are synthesized at higher temperatures and contain less impurity [25].

Finally, the Young's moduli are calculated by the use of an empirical relation, suggested by Enomoto et al. [26]:

$$E_a = 2.7 \times 10^4 \left(\frac{I_D}{I_G} \right)^{-1.6} \tag{1}$$

where, E_a is Young's modulus in MPa and I_D/I_G is the crystallinity factor obtained from Raman spectra. The calculated Young's moduli are reported in Table 3. The results are in agreement with literature [26]. Furthermore, it is obvious that sample 4 has the highest Young's modulus.

Table 3: Result of Young's modulus of the MWNT samples

Sample	I_D	I_G	I_D/I_G	E_a
1	82.23	83.10	0.99	27458.32
2	81.18	94.18	0.86	34244.88
3	71.26	90.52	0.79	39587.17
4	74.48	95.91	0.78	40459.85
5	111.10	88.60	1.25	18798.78
6	108.54	93.75	1.16	21356.74

CONCLUSIONS

Multi-walled carbon nanotubes were synthesized by the use of catalytic chemical vapor deposition over a Co-Mo/MgO nano-catalyst in a fluidized bed reactor. The influences of different combinations of purification methods and their sequences on the quality of the carbon nanotubes were evaluated and the optimum purification was reported. Purifica-tion methods included oxidation, HCl treatment and HNO_3 treatment. The sample which was purified by oxidation, HCl treatment, and HNO_3 treatment respectively had the largest I_G/I_D value of 1.28 as well as the largest Young's modulus of 40459.85 MPa.

ACKNOWLEDGMENT

NOMENCLATURE

MWCNT   Multi-walled Carbon Nanotubes

SWCNT   Single-walled Carbon Nanotubes

a.u.   Arbitrary unit

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