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Experimental and thermochemical evaluation of induction thermal plasma grown single-walled carbon nanotube synthesized by commercial carbon blacks with different sulfur contents

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ABSTRACT

The structural quality of induction thermal plasma grown-SWCNTs synthesized through the injection of five different powder mixtures containing $87.2_{\text{commercial carbon black}}/2.6_{\text{Ni}}/2.6_{\text{Co}}/7.6_{\text{Y}_2\text{O}_3}$ (wt%) with variable sulfur content of 0.02, 0.6, 1.1, 2 and 2.5 (wt%) in carbon black was investigated using Raman spectroscopy. The results showed an increase in G/D intensity ratio with sulfur content up to 2.0% implying higher structural quality of SWCNTs followed by reduction of intensity with 2.5%. The equilibrium composition of the mixtures as a function of temperature calculated using FactSage thermo-chemical software revealed a lower end temperature of total gas phase as a result of the sulfur addition and the heat related to the formation of Y_2S_3 solid phase which eventually increases the structural quality of SWCNTs. However, the higher amount of dissolved sulfur in the liquid solution of metallic catalysts for the mixture with 2.5% sulfur can results in the poisoning effect.

1. Introduction

Since their initial discovery by Iijima [1,2], carbon nanotubes and particularly single-walled carbon nanotubes (SWCNTs) have increasingly attracted the interest of the most areas of science and engineering due to their extraordinary electronic, chemical and structural properties as well as their unique mechanical behavior leading to many potential applications [3–5]. Scientists are now looking for an economical way to produce large quantities of SWCNTs while maintaining the quality for the advanced technological applications [6]. To date, induction thermal plasma [7–13], laser ablation [14,15] and arc-discharge [16,17] are the most common high temperature techniques to synthesize high quality SWCNTs based on vaporization–condensation of solid carbon from carbon containing precursors. High temperature methods produce SWCNT with higher quality as a result of better graphitization process compared to low temperature methods such as chemical vapor deposition (CVD) [18,19]. However, high temperature SWCNTs synthesis techniques like laser ablation and arc-discharge have their own disadvantages. Contrary to the laser ablation method with a production rate about a few grams per day, a high rate of yield is achieved through the arc-discharge process but with significant amount of carbonaceous impurities. In the present study, radio frequency (RF) inductively coupled thermal plasma was utilized to synthesize SWCNT with high structural quality comparable to that of laser grown. The arc-discharge process uses ionized gas to reach the high temperature necessary to vaporize carbon containing substances and the metal catalysts necessary for the ensuring SWCNT growth. The thermal plasma is induced by high frequency oscillating currents in a coil, and is maintained in flowing inert gas. Typically, a feedstock composed of a powder mixture of commercial carbon blacks (CB) and transition metal catalysts containing Ni, and Co as well as Y_2O_3 is fed into the plasma plume via inert carrying gas (Ar) with the temperature up to about 10,000 °C to ensure complete vaporization of the mixture and is then cooled down to form SWCNTs. Its production rate is higher than the arc-discharge or the laser ablation methods. The detail of plasma reactor, synthesis process and probable carbon nanotube growth mechanism on the surface of metallic catalysts [20,21] can be found in previous publications of the authors [11,12].

Although the process parameters as well as the catalysts ratio in the injected powder mixture were kept constant for each plasma synthesis test, the results differed in terms of structural quality of SWCNT in consequence of applying different commercial CBs with various sulfur contents. The presence of sulfur was found to encapsulate cobalt or cobalt carbide particles by graphitic polyhedral in arc-discharge process [22]. Sulfur is also known to assist the graphitization of vapor-grown carbon fiber, but the mechanism detail is

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Table 1
Different commercial CBs used for the synthesis process.

Commercial carbon black	Sulfur content (wt%)	Supplier
Super P	0.02	Timcal Co.
Raven 860 Ultra	0.6	Columbian Co.
M880	1.1	Cabot
M280	2.0	Cabot
M120	2.5	Cabot

not yet fully understood. Moreover, it was observed that the addition of sulfur to liquid metal catalysts decreases the solidification temperature and lowers the surface tension which are favorable for the formation of carbon nanotube [23]. The effect of sulfur was considered to be even more significant for the synthesis processes at low temperature. Ren et al. [24] investigated the effect of sulfur on structure of carbon nanotube produced through CVD method by floating catalyst. They reported that the addition of sulfur is essential to enhance the growth of single-walled (SW) and double-walled (DW) carbon nanotubes. Wei et al. also claimed that CNT nucleates and grows on the active surface area of iron catalyst in a typical CVD process where sulfur accumulates in the form of a FeS–Fe eutectic phase [25].

The authors of the present paper have already observed the difference in structural quality of SWCNT synthesized using induction thermal plasma and concluded that sulfur content in CBs can be considered as one of the factors affecting the quality of SWCNT [13]. In this study, thermodynamic effect of different sulfur contents in commercial CBs is studied on equilibrium compositions of a mixture containing CB and metal catalysts of Co, Ni, Y_2O_3 as a feedstock for the synthesis of SWCNTS. In this regard, FactSage thermochemical computation software [26] was used to calculate the equilibrium composition of such systems at a temperature range from 500 °C to 6000 °C. The calculated diagrams were then investigated to validate the results of the synthesis experiments carried out by induction thermal plasma reactor in term of quality of SWCNT containing products.

2. Experimental procedures

A powder mixture of $CB_{commercial}/Ni/Co/Y_2O_3$ with mass ratio of 87.2/2.6/2.6/7.6 (all mixture compositions are given in wt% unless otherwise stated) was selected to be injected into the induction thermal plasma reactor. Table 1 represents the sulfur content in the commercial CBs used in this study. Ternary mixture of catalysts containing nickel (Ni, 99.5%, <1 μm), cobalt (Co, 99.8%, <2 μm) and yttrium oxide (Y_2O_3, 99.9%, −325 mesh) were added to the CBs in the aforementioned proportion. The synthesis process was performed on powder mixtures with different CBs using operating conditions such as plate power of 40 kW, feeding rate of 1.5–2.0 g/min, operating pressure of 66.7 kPa, flow rate of the sheath gas (He: 120 slpm), of the central gas (Ar: 25 slpm) and of the powder carrier gas (Ar: 5 slpm).

SWCNT-containing product sheets (soot) were collected from the filter unit and were analyzed by high resolution scanning electron microscopy (HR-SEM, Hitachi, S4700) coupled with EDS analysis, XRD analysis as well as Raman spectroscopy at $\lambda_{ext} = 633$ nm.

3. Theoretical calculations

Thermodynamic equilibrium composition of the mixture composed from different CBs and metallic catalysts were calculated as a function of temperature using FactSage 6.2 software based on a minimization of the Gibbs free reaction energy for a range of temperature between 500 °C and 6000 °C. Two databases, Fact53 and FSstel, were selected to cover the entire solutions and compounds available in the databases in gas, liquid and solid state for a given mixture system. The main objective of these calculations is to predict the effect of sulfur content on chemical composition of the mixture used for the synthesis of SWCNT. All calculations were carried out at a pressure of 66.7 kPa and the formation of gaseous ions (plasma) was also considered at high temperature. Table 2 shows the compositions of the eight mixtures selected for theoretical calculations. The sulfur content changes variably between 0 and 2.5 wt% in order to approximately take into account the sulfur contents in the five commercial CBs.

Table 2
Composition of the mixtures selected for theoretical calculations.

No.	Ni (wt%)	Co (wt%)	Y_2O_3 (wt%)	S (wt%)	C (wt%)
1	2.6	2.6	7.6	0	87.2
2	2.6	2.6	7.6	0.02	87.1
3	2.6	2.6	7.6	0.5	86.7
4	2.6	2.6	7.6	0.8	86.4
5	2.6	2.6	7.6	1.5	85.7
6	2.6	2.6	7.6	2.0	85.2
7	2.6	2.6	7.6	2.2	85.0
8	2.6	2.6	7.6	2.5	84.7

4. Results and discussion

4.1. Characterization of SWCNT products

Fig. 1 shows HR-SEM images of the as-produced samples (soot) synthesized through induction thermal plasma using the feedstock mixture with different commercial CBs. The sheet-like products collected at the filter section of plasma reactor is called soot. The presence of abundant SWCNT bundles entangled with impurities like amorphous carbon particles are clearly observed in each image. The diameter of the SWCNT bundles was measured to be approximately 10–20 nm.

To identify the elements present in the products, EDS analysis was performed on SWCNT containing product soot synthesized by Raven 860 ultra (0.6% S) and M120 (2.5% S) carbon black. Fig. 2 indicates the EDS analysis of these samples. The presence of carbon, oxygen, nickel, cobalt, yttrium and sulfur in the synthesized soot is clearly observed. During EDS analysis spherical shaped particles which seemed to be metal catalyst was observed in the samples. Elemental mapping, shown in Fig. 3, detected cobalt as such round particle while other catalysts, namely nickel and yttrium were also observed in the sample. The size of these catalysts can vary from hundreds of nanometer to several microns. The gray-black region of the image corresponds mostly to the carbonaceous materials including SWCNTs. It must be noted that another shapeless Co particle was also identified with particle size about 3 μm implying the presence of non plasma treated Co particle in the sample.

The normalized Raman spectra of the SWCNT produced with different grades of CBs are depicted in Fig. 4. Since Raman spectroscopy is capable to determine a relative quality of SWNT, it is commonly used to compare different samples produced under the same operating condition. Radial breathing mode (RBM) at low frequencies is the most dominant Raman feature confirming the presence of nanotube in the product and highly depends on the nanotube diameter [27]. Fig. 4 indicates that the variable amount of sulfur in CBs has no significant effect on RBM implying the production of nanotubes with the same size. The tangential mode, so-called G-band, is the most intensive high-energy modes of SWCNTs [28] which is typically observed at around 1600 cm^{-1}. Disorder-induced, D-band, is generally observed at 1300–1400 cm^{-1}. A large G-band peak compared with the D-band peak (G/D intensity ratio) usually means a good resonance