Research Article

An Investigation on the Formation of Carbon Nanotubes by Two-Stage Chemical Vapor Deposition

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Received 21 August 2011; Accepted 12 January 2012

Academic Editor: Teng Li

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High density of carbon nanotubes (CNTs) has been synthesized from agricultural hydrocarbon: camphor oil using a one-hour synthesis time and a titanium dioxide sol gel catalyst. The pyrolysis temperature is studied in the range of 700–900°C at increments of 50°C. The synthesis process is done using a custom-made two-stage catalytic chemical vapor deposition apparatus. The CNT characteristics are investigated by field emission scanning electron microscopy and micro-Raman spectroscopy. The experimental results showed that structural properties of CNT are highly dependent on pyrolysis temperature changes.

1. Introduction

In 1993, Iijima's group reported the synthesis of carbon nanotubes (CNTs) by a simple technique [1]. They had been selected as excellent candidates, which were largely derived from their unique structural, mechanical, and chemical properties [2]. The CNT can be divided into three types: single-walled, double-walled, and multiwalled nanotubes [3]. From the application and industrial point of view it is highly desirable to synthesize well-ordered and dense arrays of purified CNT at low processing temperature and cost and high mass production approach, and mostly it should follow a safe and high-quality specification. Several pyrolysis techniques have been introduced, including the most prevailing method: thermal [4] or plasma [5] chemical vapor deposition (CVD). In our approach, our group appraise the potential custom-made two-stage catalytic CVD [6] natural hydrocarbon camphor oil as a carbon source and titanium dioxide (TiO₂) solution as a catalyst to synthesize CNT.

TiO₂ is extensively used for wide-range applications such as energy storage and conversion, starting photocatalyst material, corrosive and bacterial protection and is also to remove of organic contaminants from wastewater [7–10]. TiO₂ powder and solution are commercially available in the market but it is more recommended to use self-prepared TiO₂ solution for desired properties and to ease compositional modification. This is due to its lower vaporization temperature and molarity compared to the commercialize samples.

2. Experimental

A standard ethanol (EtOH) solution with $M = 46.07$ g/mol, purity $\approx 99.8\%$ from Fluka chemical was used as a solvent, and titanium (IV) isopropoxide (TTiP) ($M = 340.33$ g/mol, purity $\approx 99.995\%$) from Sigma Aldrich was used as a precursor. Glacial acetic acid (GAA) ($M = 60.05$ g/mol, purity $\approx 99.98\%$) and triton-x ($M = 646.8$ g/mol, purity

FIGURE 1: Schematic diagram of custom-made two-stage catalytic CVD.

$\approx 98.0\%$) were purchased from Baker. For this work, TiO_2 solution was synthesized using the sol gel method [11, 12]. In present work, the simple synthesis procedure for TiO_2 solution is as follows: the hydrolyzation process of 18.91 mL of TTiP using 2.50 mL of GAA under room temperature, 0.20 mL of distilled water together with 0.02 mL of triton-x as the stabilizer and 78.40 mL of EtOH as the solvent are mixed under continuously mechanical stirring at 4 rpm and 60°C for 1 hour. After the period, the solution was stirred continuously at 3 rpm. The solution was left for 24 hours of ageing time. The custom-made two-stage catalytic CVD is a part of lab-scale equipment and compatible for feasibility studies. The desired quantity of 10 mL purified 0.5 M TiO_2 solution and 10 mL of camphor oil were placed in a separate alumina boat without further treatment. Those alumina boats were located side by side inside quartz tube at the centre of the first furnace in the custom-made two-stage catalytic CVD as in Figure 1. A slower 15-bubble-per-minute nitrogen gas flow was used to remove atmospheric air from the reaction tube for 5 minutes. The flow rate of nitrogen gas was reduced to 10 bubbles per minutes simultaneously activating the set vaporization temperature switch at the first furnace. When the first furnace achieved this set vaporization temperature, the set pyrolysis temperature at reaction zone was activated to pyrolyze the carbon and catalyst content for 1 hour. The operation was then followed by thermal annealing at the same pyrolysis temperature for 30 minutes, and then both furnaces were let to cool down naturally to the ambient temperature under a flowing nitrogen gas condition. Black powder was observed on the inner wall of quartz tube at the second furnace zone [13]. The dimension, arrangement, and surface morphology of the production CNT were characterized using field emission scanning electron microscopy (FESEM) (ZEISS 77 Supra 40VP) and micro-Raman spectroscopy with a laser of 514 nm (Horiba Jobin Yvon 79DU420A-OE-325).

3. Results and Discussion

In this work, our group successfully synthesized at various pyrolysis temperatures from 700 to 900°C at increments of 50°C . The hydrocarbon source derived from camphor oil was selected due to its low vaporization temperature, lower dependence on crude oil, and safer handling material. To the best of our knowledge, due to depletion of fossil-based carbon precursor that leads to high prices, we were taking proactive steps in strategizing to utilize camphor-oil-based natural hydrocarbon to produce CNT. Based on our humble knowledge, there was no documented experimental study on the initial stage of the formation of CNT by custom-made two-stage catalytic CVD. A hydrocarbon feedstock camphor oil contains 10 carbon atoms, 16 hydrogen atoms, and 1 oxygen atom flowed to the reaction chamber. The pyrolysis temperature range in the second furnace was sufficient enough to break the chemical bonding between carbon atoms, hydrogen atoms, and oxygen atom in the camphor oil molecules. There were no attachments between carbon, hydrogen, and oxygen atoms resulting in those free carbon atoms to attach to the catalyst clusters due to perfect catalytic effect and bind together with other carbon atoms to form CNT. The Ti clusters were trapped inside the CNT structure during deposition process. The major parameter used in this process was pyrolysis temperature. The pyrolysis of CNT was increased with the increasing of pyrolysis temperature. This was supported by FESEM micrograph analysis that shows the top view micrograph of CNT at various pyrolysis temperatures as in Figure 2 where the numbers of CNT were increasing directly with the pyrolysis temperature. In Figures 2(a), 2(b), and 2(c), the samples still contain traces of the carbonaceous byproduct which in this case is the amorphous carbon that caused the irregular structure. In Figures 2(d) and 2(e), regular structure of CNT was formed. These results show fairly good agreement with previous studies where the shape of carbon-based materials gradually changes from spherical-like structure to a perfect tubular structure with the increase in pyrolysis temperature [14].

Figure 3 illustrates the micro-Raman measurements on the samples synthesized at various pyrolysis temperatures confirming the disappearance of the single-walled CNT synthesized at 700 until up to 900°C . The peaks in the micro-Raman spectra, which laid in the Raman shift from 100 to 400 cm^{-1} , can be attributed to the appearance of single-walled type of CNT [15]. This pattern was known as radial breath mode. Generally the carbon content has two major peaks: a D band peak at $1325\text{--}1372\text{ cm}^{-1}$ and G band peak at $1609\text{--}1630\text{ cm}^{-1}$ for samples synthesized at 700 to 900°C . The D band peak represents a finite crystal size and lattice defect inside the graphene atomic layer known as disordered structure, on the other hand, the G band peak represents a perfect hexagonal of graphite structure. The intensity of micro-Raman patterns increases slightly with the increasing of pyrolysis temperatures. This result confirms that the graphite structure of the CNT is highly dependent on the pyrolysis temperatures at the second furnace. The main reason is that the catalytic activity of TiO_2 solution is becoming more excellent at higher temperature. This is

FIGURE 2: FESEM top view of micrographs of the CNT at different pyrolysis temperatures: (a) 700, (b) 750, (c) 800, (d) 850, and (e) 900°C.

due to the TiO_2 solution total decomposition, which results in the production of small Ti clusters with higher catalytic effect that induces the pyrolysis of CNT at high reaction temperature. It was slightly different when we measured the intensity of micro-Raman spectra at lower temperature. The Ti/C clusters produced cannot be fully decomposed in the second furnace due to TiO_2 and carbon feedstock solution cannot be fully pyrolyzed. Subsequently, it has low catalytic effect for the formation of CNT. The ratio of D and G band (I_D/I_G) features intensity provides information on

the quality of production of CNT. The information on the quality of the CNT is shown in Figure 4. The I_D/I_G ratio decreases with an increase in pyrolysis temperature. The lowest magnitude ratio gives the best well-ordered structure of CNT. The smallest value of I_D/I_G ratio was registered at 900°C and was about 0.76, the temperature that was highly selective for synthesis of CNT. As discussed before, at higher pyrolysis temperature Ti cluster is fully decomposed for the formations of CNT and has higher catalytic activity effect. Moreover, these observations show that the CNT synthesized

FIGURE 3: Micro-Raman patterns of CNT at different pyrolysis temperatures.

FIGURE 4: I_D/I_G ratio patterns of CNT at different pyrolysis temperatures.

at 700°C has higher disorder compared to CNT synthesized at higher temperature: 900°C. This was due to the poor catalytic activity of the Ti cluster over the CNT pyrolysis at this lower temperature. The peak position and I_D/I_G ratio for those samples are summarized in Table 1. It was noted that micro-Raman results were consistent with FESEM analysis.

4. Conclusions

The analysis of pyrolysis temperatures to synthesis camphor-oil-based CNT using TiO_2 solution as a catalyst was studied. The results show that the higher pyrolysis temperatures favor the pyrolysis of CNT. The form of CNT was found to grow at higher temperature ($\sim 900^\circ\text{C}$), with good dimension which showed unique lateral alignment, uniform nanotubes diameter within 10 to 40 nm, and distribution within the bundle when compared to other samples at lower pyrolysis temperature. In the same context, the production of TiO_2

TABLE 1: The D and G peak position and ratio of I_D/I_G growth of CNT at different pyrolysis temperatures.

Pyrolysis temperature ($^\circ\text{C}$)	D peak (cm^{-1})	G peak (cm^{-1})	Ratio I_D/I_G
700	1352	1610	1.20
750	1350	1605	0.98
800	1351	1611	0.88
850	1353	1604	0.86
900	1352	1609	0.76

solution plays an important role as a catalyst to be used in a custom-made two-stage catalytic CVD. Hence, it is a good idea to grow CNT for laboratory commercialization.

Acknowledgments

This work was supported by Sime Darby Research Sdn Bhd, Malaysian Ministry of Higher Education (MOHE), Malaysian Ministry of Science, Technology and Innovation (MOSTI), and Universiti Teknologi MARA through Excellence Fund under Contact no. 600-RMI/ST/DANA 5/3/Dst 435/2011).

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