Synthesis and purification of Multiwall Carbon Nanotubes (CNTs) synthesized in a floating catalyst reactor

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Abstract
Xylene was used as carbon source for synthesis of carbon nanotubes (CNTs) in a floating catalyst reactor. Nitrogen and ferrocene were used as carrier gas and catalyst, respectively. CNTs purification was performed by oxidation and acid treatment. Characterization of CNTs before and after purification was carried out using SEM, TEM and Raman spectroscopy. The results demonstrated that CNTs with high density, length and purity were obtained after HNO treatment.

Keywords: Carbon nanotubes (CNTs), Chemical vapor deposition (CVD), Floating catalyst reactor, Amorphous carbon.

1. Introduction

Carbon nanotubes (CNTs) are novel materials well known for their extraordinary aspect ratio and exotic properties. They are mostly synthesized by various chemical vapor deposition (CVD) methods. One of the recent branches of CVD is the floating catalyst method. In this method an organometallic substance, usually metallocenes, enters continuously along with a hydrocarbon and a carrier gas to instantly produce metal nanoparticles, which then catalyze the CNT synthesis. This method has been used to produce both SWNTs and MWNTs using a range of solvents, which also serves as carbon sources, catalysts and synthesis conditions [1].
All the raw materials produced by CVD method contain impurities of amorphous carbon particles, graphite, nanoparticles and metal catalysts. The presence of these impurities may significantly affect characteristic of CNTs and behavior of any device that are based on them. Therefore purification of CNTs is very important for applications that exploit their intrinsic properties. Another important point is that, tips of raw CNTs are often close. CNTs tips opening, which are very beneficial to Membrane process, can be obtained by oxidation [2]. Porro et al. investigated the influence of purification treatment on structural properties of CNTs, which could increase available surface area and decrease concentration of the residual catalyst inside the grown material [3]. Purification of CNTs with physical and chemical oxidation has been extensively investigated. Physical oxidation is based on the fact that

oxidation temperature of carbonaceous particles is different from that of CNTs in air or oxygen. However, the persistent problem, associated with physical oxidation is that materials such as transition metallic catalyst particles remain encapsulated in wall structure can affecting its performance in many practical applications. Chemical oxidation can remove the metal catalyst particles remained in as-prepared CNTs. In chemical oxidation metal catalysts can be dissolved by the purification solutions such as acids. Su et al. investigated effects of acid treatment on structural properties of CNTs. They involved sulphuric/nitric acid solutions of various concentrations for various purification times. They observed that a 1/3 concentrated sulphuric/nitric acid solution for 24 h yieldes highly pure CNTs [4]. Bandow et al. developed a method of purification by microfiltration, which separates impurities from SWNTs [5]. Also, Shelimov et al. suggested a purification method of SWNTs by ultrasonically assisted filtration [6]. According to literatures some parameters such as acid type, acid concentration, time and temperature of purification process can affect morphology and structure of CNTs.
The objective of this paper is to report synthesis of dense and entangled CNTs using xylene and ferrocene as carbon source and catalyst, respectively, via a simple CVD system. Advantages of the proposed CVD method are: absence of a prepatterned catalytic substrate, absence of hydrogen as carrier gas and hazardous gases such as acetylene as carbon source, use of one-stage tube furnace, use of a simple set up and formation of hollow CNTs. Also, in this work, the as-grown CNTs was purified by oxidation and different acid treatments and characterized using SEM, TEM and Raman spectroscopy.

2. Experimental

2.1. Synthesis of CNTs

A schematic diagram of the experimental CVD set-up is shown in Figure 1. The CVD system consisted of a horizontal stainless steel reactor (70 cm long, 3.2 cm in diameter) housed in a one stage cylindrical furnace. A flask (steel container) containing reagents was connected to the reactor [7]. The reagents were prepared by dissolving ferrocene (purity≥98%, B.D.H) in xylene (purity≥98%, Merck) with mass ratio of 1:20. Ferrocene was used as catalyst compound, as a good precursor for production of iron nanoparticles, which play the role of catalyst in formation of CNTs [8]. Evaporating the reagents was performed using an oil bath. Nitrogen was used as carrier gas connected to the reactor nearby the reagent inlet to carry the gas mixture of precursors towards the center of furnace, where pyrolysis of the gases takes place.
At first, the reactor was purged with nitrogen at room temperature, in order to eliminate oxygen from the reaction chamber. The reactor was preheated to preset temperature (at 850 ˚C); subsequently the flask containing the reagents was placed in the oil bath (at 300 ˚C) for immediate vaporization process. The obtained vapor was carried by nitrogen with flow rate of 400 cm^3min^{-1} towards the high temperature zone of the reactor. The reactor pressure was kept constant at about 2 bar during the CVD reaction. Pyrolysis of the vapors took place and CNTs was deposited on the high temperature zone of the reactor. After the CVD reaction, the furnace was switched off and the reactor was cooled down to room temperature under nitrogen atmosphere. Finally, the as-grown CNTs were removed from the reactor for purification and characterization.

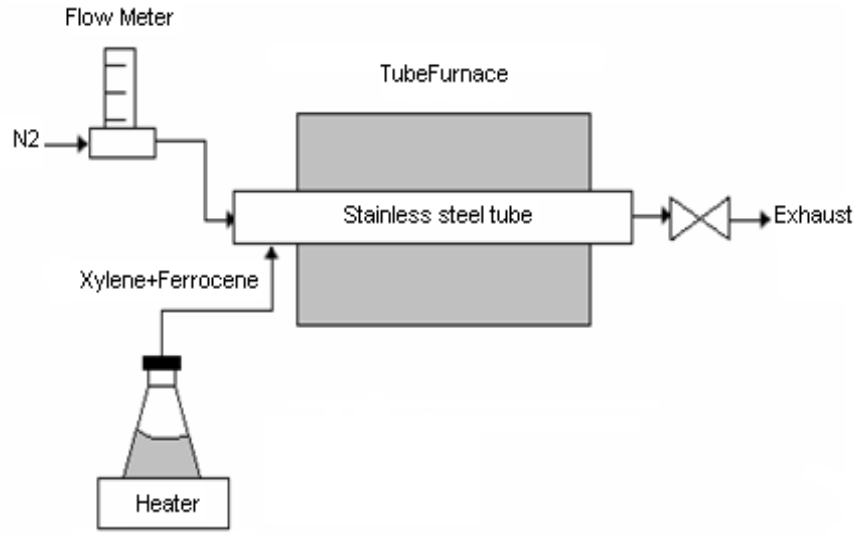

Figure 1. Schematic diagram of the experimental CVD set-up.

2.2. Purification of CNTs

At first, the as-grown CNTs were placed in the reactor. Air with flow rate of 250 cc/min was injected inside the reactor. The reactor was heated to 485 ˚C and maintained at that temperature for 30 min. Afterwards the reactor was switched off and cooled to room temperature then CNTs was removed from the reactor for characterization and further processing. Oxidation was eventuated for removing of amorphous carbon, but could not omit metal catalysts. CNTs was soaked in acid solution and refluxed at 120 ˚C for 3 h and then CNTs was centrifuged and washed with distilled water for many times until pH of about 7 was obtained. Refluxing with acid solution resulted the metal catalysts to be dissolved and consequently removed from CNTs.

2.3. Characterization of CNTs

The structure of as-grown CNTs was characterized by scanning electron microscope (SEM), transmission electron microscope (TEM) and Raman scattering.

Scanning electron microscope (SEM, Philips: XL30) was used for analysis of the CNTs morphology. Nanostructure of the CNTs was determined by transmission electron microscope (TEM, Philips: CM200). Also Raman scattering was used for characterization of the CNTs. The micro-Raman apparatus was operated with a 488 nm laser of 1.2 μm spot size with an acquisition time of 30.0 s, and a laser power of 3.0 mW. Also, SEM and Raman scattering were used to show the structural properties of CNTs purified with oxidation and acid treatment.

3. Results and Discussion

Purification of CNTs is every important in its structural modification. Oxidation and acid treatment are the most common methods for purification of CNTs.

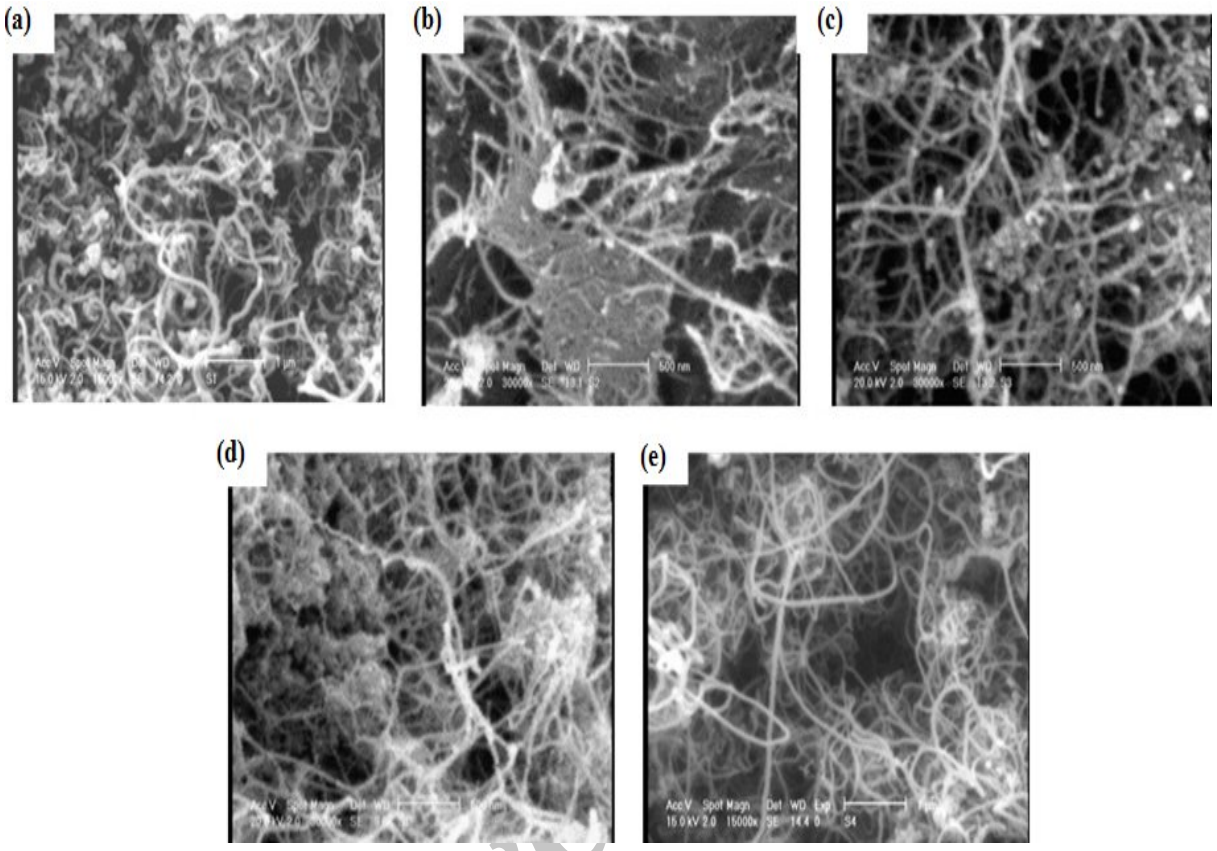

Figure 2. SEM images of (a) raw CNTs, (b) CNTs treated with HNO /H SO (1/3), (c) HNO /H SO (1/1), (d) HCl 8 M and (e) HNO 8 M .

Figure 2(a) presents the SEM image of as-grown CNTs synthesized in the CVD reactor. Based on the SEM image, it is plainly visible that the CNTs are entangled in a skein manner and compactly grown. The length of CNTs is more than 7 µm. Amorphous carbons and deactivated catalyst particles can be also observed in Figure 2(a).

Oxidation can just remove amorphous carbons and is not effective for omitting deactivated catalyst particles. Acid treatment is an effective method for purification and tips opening of the CNTs. HNO , H SO and HCl are the most common acids that are used for acid treatment. At the same conditions, the CNTs were purified by HNO 8 M, HCl 8 M and HNO /H SO (1/1, 1/3). Figure 2(b-e). presents the SEM images of each acid treatment.

It must be mentioned that acid treatment can destroy the structure of CNT's array. It means that the long array of CNTs is being shorter after acid treatment. Sulphuric acid as a strong acid makes the CNTs more brittle. As can be observed in Figure 2(b), HNO /H SO (1/3) treatment causes the CNTs to be broken into smaller portions and as a result become shorter. Although, HNO /H SO (1/3) treatment reduces the density of CNTs. As see in Figure 2(c), acid treatment with HNO /H SO (1/1) have less destroying effect on the CNTs than HNO /H SO (1/3). Figure 2(d) presents the SEM image of CNTs treated with hydrochloric acid 8 M treatment of CNTs. It can be observed that density and compaction of CNT's bundles treated with hydrochloric acid are better than those treated with HNO /H SO (1/3) and HNO /H SO (1/1). The best result of acid treatment is for HNO 8 M, as can be

observed in Figure 2(e). By using this treatment method, high pure CNTs with dense aggregation and high length can be obtained.

Raman spectra of the CNTs before and after acid treatment are illustrated in Figure 3. The Raman spectra show D and G bands at ~ 1355 and 1575 cm^{-1}, respectively. D and G bands originate from defect and graphite, respectively. Parameter of I /I presents ratio of defect band to the graphite bond. For the raw CNTs (before purification), value of I /I is 0.64. The Raman spectra also show that after purification of the CNTs with HNO 8 M the value of I /I decreases to 0.34, this presents that purification have significant effect on structural properties of CNTs and results removing amorphous carbon and deactivate catalyst particles.

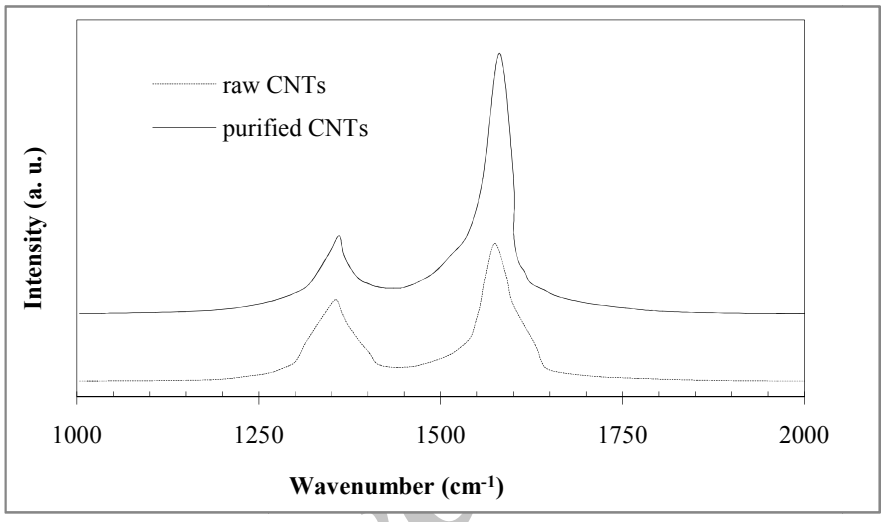

Figure 3. Raman spectra of raw and purified CNTs.

TEM image of the purified CNTs is presented in Figure 4. The internal and external diameters of CNTs are about 15 and 75 nm, respectively. According to the TEM image, it can be concluded that the mentioned purification method can remove the catalyst particles completely. As observed, a very thin layer of amorphous carbons with a thickness of about 2 nm covers the external surface of CNTs.

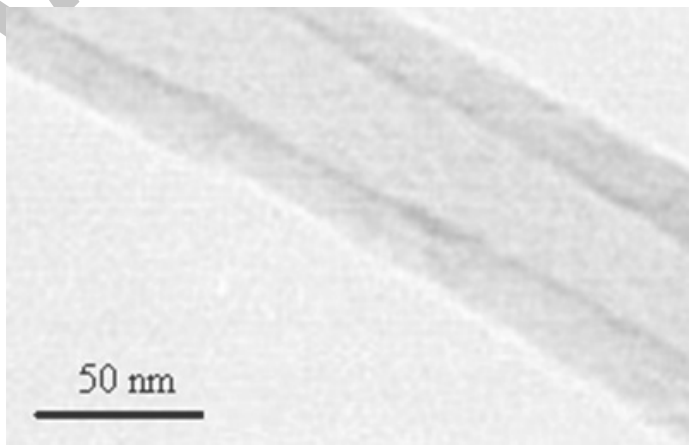

Figure 4. TEM image of purified CNTs.

4. Conclusions

Entangled structure of MWCNTs was synthesized via a simple CVD method using xylene as carbon source. CNTs purification was performed by oxidation and acid treatment. Characterization of CNTs before and after of purification was carried out using SEM, TEM and Raman spectroscopy. According to the SEM and TEM results, oxidation and acid treatment with HNO 8 M can remove impurities such as amorphous carbons and deactivated catalyst particles from the CNTs with less destroying effect. As confirmed by Raman spectroscopy, after purification, the value of I /I decreases from 0.64 to 0.34. The results demonstrated that the mentioned purification method can effectively remove all impurities from the yielded products (CNTs) of the floating catalyst reactor.

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سنتز و خالص سازی نانو لوله های کربن چند دیواره (MWNTs) در راکتور کاتالیست شناور

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چکیده

زایلن به عنوان منبع تامین کننده کربن به منظور سنتز نانولوله های کربنی در راکتور کاتالیست شناور به کار گرفته شد. همچنین گاز نیتروژن به عنوان گاز حامل و فروسن به عنوان کاتالیست استفاده شدند. خالص سازی نانولوله های کربن با روش اکسیداسیون و اسید شویی انجام شد. آنالیزهای SEM، TEM، Raman بر روی نانو لوله های کربنی قبل و بعد از اسید شویی انجام شد. نتایج آنالیز ها نشان می دهد که نانو لوله هایی که توسط اسید نیتریک تصفیه شدند دارای طول مناسب و دانسیته بالایی می باشند و درصد خلوص در این شرایط بسیار بهتر است.

واژه‌های کلیدی: نانو لوله های کربن، نشاندن بخار شیمیایی، راکتور کاتالیست شناور، کربن آمورف