Synthesis of high-quality single-walled carbon nanotubes by high-frequency-induction heating

Zijiong Li\textsuperscript{a,b,*}, Bin Zhao\textsuperscript{a}, Ping Liu\textsuperscript{a}, Bo Zhao\textsuperscript{a}, Da Chen\textsuperscript{a}, Yafei Zhang\textsuperscript{a}

\textsuperscript{a}National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Research Institute of Micro/Nanometer Science and Technology, Shanghai Jiao Tong University, Shanghai 200030, PR China
\textsuperscript{b}Department of Physics, Zhengzhou University of Light Industry, Zhengzhou 450007, PR China

Abstract

High-quality single-walled carbon nanotubes (SWCNTs) have been synthesized by using self-designed high-frequency-induction heating equipment rapidly. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and thermal gravimetric analysis (TGA) were used to characterize the produced SWCNTs. The results indicate that SWCNTs synthesized by this technique have higher purity (about 95%), smaller diameter (0.8–1 nm) and lengths up to 10 \textmu m. The reasons for synthesis of smaller diameters and higher purity SWCNTs by using this technique are also discussed. This novel synthesis technique presents a potential opportunity for cost-effective and commercial production of SWCNTs.

© 2007 Elsevier B.V. All rights reserved.

PACS: 61.46.Fg; 81.10.BK; 72.30. +q

Keywords: Carbon nanotube; High heating rate; Methanol

1. Introduction

Synthesis of high-quality single-walled carbon nanotubes (SWCNTs) is crucial for their applications to nanotechnology since they were reported by Iijima and Ichihashi\cite{1} in 1993. In last few years, techniques to synthesize SWCNTs have been developed by arc-discharge technique, pulsed laser ablation and later chemical vapor deposition (CVD)\cite{2-4}. In these synthesis techniques, CVD is the most promising method to commercialize the carbon nanotubes (CNTs) growth due to the advantages in its low cost, high yield, and easy to be controlled. However, the main disadvantages of traditional synthesis methods are low yield and tube with impurity. It is well known that the purification of CNTs is tedious, time consuming, and usually bring defects to CNT. Various heating methods including direct current, hot filament, microwave, and radio frequency plasma enhanced CVD have been reported for the large-scale production or for the controlled synthesis of CNTs on semiconductor devices\cite{5-7}. Biris et al.\cite{8} used radio frequency technique to improve CNTs yield and quality; Wu et al.\cite{9} used 20% CH\textsubscript{4} in H\textsubscript{2} in the microwave PECVD for the carbon nanowall deposition. Especially, the conventional Hipco synthesis method using the disproportionate reaction of high-pressure and high-temperature CO has produced almost amorphous-free commercial SWCNTs, but the remaining problems of this technique is the risk in the handing of CO, and the higher growth temperature also hinders the direct growth of SWCNTs on semiconductor devices.

In this paper, we report a simple, higher purity and lower temperature synthesis of SWCNTs by using the novel technique of high-frequency-induction heating. In this technique, we used methanol as carbon source, nickel
and yttrium as catalyst. It turns out that the fast heating reactions of forming SWCNTs and etching of amorphous carbon by hydrogen and OH radical play the key role in the high-purify and low-temperature synthesis of SWCNTs. The lower reaction temperature and higher purity features of this method guarantee easy scale-up production at a lower cost. Furthermore, the reaction temperature below 600 °C ensures that this method can be easily applicable for the direct growth of SWCNTs on semiconductor devices.

The using of inductive heating in the synthesis of SWCNTs can significantly reduce the energy consumption and the overall reaction time with direct impact on the final price [8]. Zhou et al. [10] have successfully synthesized high-quality SiC nanowire by using our self-designed high-frequency-heating system. We used the same technique for the first time to synthesis of SWCNTs at lower temperature and pressure. Comparing with traditional method, this approach is more simple and easier to control, and this technique is more economic because the time of the synthesis is short and the high-frequency-induction furnace equipment is inexpensive. Therefore, it provides a potential way to meet the mass production and future broader applications.

2. Experimental detail

2.1. Catalyst preparation

The metal catalyst was prepared by using Ni(NO₃)₂·6H₂O and Y(NO₃)₂·6H₂O. In the catalyst preparation process, the proper amounts of Ni(NO₃)₂·6H₂O (7.56 g, 98.0% purity), Y(NO₃)₂·6H₂O (1.65 g, 98.0% purity) were dissolved in ethanol and the solution was then ultrasonic agitated for 8 min and dried for 10 h at 100 °C. The resulting gray powder was placed on the crucible which installed at the bottom of a quartz tube inside of an electrical furnace.

2.2. SWCNTs growth

The experiment was conducted in a vertical high-frequency-induction furnace equipped with quartz tube (outer diameter 80 mm and length 120 cm) and an inductive heat cylinder which the schematic diagram of it was shown in anywhere [11]. During the heating, an apparatus with a vacuum system and water-cooling system were used. The temperature of the furnace was monitored by a thermometer at the upper surface of the crucible. Gas flow rates were controlled by using mass flow controllers, and reaction pressure is regulated by a capacitance manometer that provides feedback control to the pump inlet valve. After heating up to the desired temperature (600 °C) and evacuation pressure of the system at about 0.01 Torr, an entraining methanol gas flow at a constant rate of 100 sccm (cubic centimeter per minute) was introduced and the growth was initiated and maintained for 3–5 min. After the system was cooled to room temperature, a black web-like product was collected from the inlet of crucible-supported cylinder.

2.3. Characterization of the samples

The collected sample was characterized using Scanning electron microscopy (SEM) (JEOL, JSM-6700), high-resolution transmission electron microscopy (TEM) (JEOL, JSM-2010), Raman spectroscopy and thermal gravimetric analysis (TGA). A small quantity of the sample has been dispersed by ultrasonic agitation in ethanol for 10 min and then placed on copper grids in order to perform detailed observation on CNTs by TEM. SEM was performed in a field emission scanning electron microscopy. The Raman spectra of SWCNTs were collected with a Dilor Labram-1B Raman spectrometer with He–Ne laser at 632.8 nm. The TGA was conducted on a PE TGA-7 instrument with a heating rate of 10 °C/min in air.

3. Results and discussion

Fig. 1 shows the SEM image of as-prepared SWCNTs after a 5 min growth period at 600 °C, it can be found that the purity of the as-prepared SWCNTs is very high. Large amounts of entangled carbon filaments homogeneously distributed over large areas and with diameters ranging from 5 to 10 nm were observed. The average length between two entanglement points was several micrometers. EDX analysis shows the main elements in the collected production are C (94.3 at%), O (2.5 at%), Ni and Y (3.2 at%).

The TEM characterization of the collected production is revealed in Fig. 2. We could rarely observe amorphous carbon, multi-walled carbon nanotubes (MWCNTs), and carbon nanoparticles from the TEM image. Only a few coexisting metal particles were observed. The high-resolution TEM (inset in Fig. 2) studies demonstrate that the
nanotubes are clean SWCNTs free from amorphous carbon and the nanotubes have high crystallinity. Many high-resolution TEM micrographs also show that MWCNTs and double-walled CNTs are rarely found in our samples. From the SEM and TEM microscopy analysis, it can be observed that the SWCNTs have lengths of over 10 μm, so the aspect ratio is in the range of hundreds. Effect of reaction temperature was studied with the Raman measurement by a macro-Raman apparatus with a 50 cm single monochrometer and a CCD detector. Raman spectra of as-prepared sample from methanol for two different of oven temperatures are compared in Fig. 3(A). As a reference, the B spectrum was measured from a sample synthesized by traditional catalyzing CH4 decomposition using the same catalysts. Raman spectra at 632.8 nm excitation shows clear radial breathing mode peaks (RBM, 170–300 cm\(^{-1}\)) which is the typical behavior of SWCNTs [12] and the G-band (about 1590 cm\(^{-1}\)) for both spectra. The D-band signal between 1305 and 1330 cm\(^{-1}\) representing a more disorder structure, which is associated with the vacancies, defects and impurities destroying the symmetry, was quite small for this synthesis technique. The intensity ratio of the G- and the D-bands (G/D value) is widely used as a good index to estimate the relative pure of SWCNTs. The G/D value in our SWCNTs samples were calculated to be higher than 80, which demonstrated the high purity of as-prepared SWCNTs. Moreover, it shows that the D-band in 600 °C case is larger than 900 °C case, probably because of the metal catalyst which also could be observed in the TEM image. The diameter evaluation is made from the well-known relation \(d = \frac{248}{\omega}\), where \(d\) is diameter of the SWCNT in nm and \(\omega\) is the frequency of the breathing mode in cm\(^{-1}\) [13]. The results show that the diameter of SWCNT synthesis at 600 °C is 0.8–1.0 nm. In comparison with synthesized by traditional catalyzing CH4 decomposition using the same catalysts sample, the tube diameter synthesized by using high-frequency-induction heating technique is smaller and more widely distributed, and the diameter distributed is also relied on the temperature.

Furthermore, the TGA profile measured in air atmosphere is shown in Fig. 4. From the TGA curve, we can get the oxidation temperature (a measurement of their stability in air) of the having removed metallic catalyst SWCNTs is about 540 °C. From the higher oxidation temperature, we get the information about the purity of SWCNTs, the crystalline properties and the presence of the wall defects. It is well known that amorphous carbon is oxidized at lower temperature than SWCNTs. Fig. 4 shows the weight...
As shown from Refs. [14,18], a higher localized temperature in this case behaves as a heat transfer ‘bottleneck’ than the temperature of the crucible-supported cylinder, local temperature of the metallic catalysts can be higher due to the generation of high-frequency currents. The localized temperature spikes in the metallic species might be due to the metallic character of the catalyst nanoparticles, the onset of melting and reconstruct smaller metallic systems. Due to the high heating rate and atomic hydrogen, the metallic nanoparticles can remove the amorphous carbon because it may attack amorphous carbon atoms with a dangling band to form CO. Kataura et al. [22] have reported an OH radical efficiently removes the amorphous carbon in the purification process of SWCNTs using H2O2. In the course of nanotube deposition, atomic hydrogen prevents the formation of the additional graphitic layers by etching weakly bonded carbon atoms and small graphitic fragments, and OH radical efficiently removes the amorphous carbon, so we can get high-purity SWNTs during the high-frequency-heating prepared process [23].

4. Conclusion

In summary, using self-made simple and fast inductive heating technique, higher purity and smaller diameter SWCNTs have been synthesized in less than 5 min. SEM and TEM images show SWCNTs diameters of 0.8–1 nm and lengths up to 10 µm. HRTEM picture indicate that the SWCNTs are highly crystalline and with an aspect ratio in the range of hundreds. The Raman spectra as well as the TGA curves further indicate that SWCNTs are of higher purity. The high heating rate and atomic hydrogen prevents the formation of the additional graphitic layers by etching weakly bonded carbon atoms and OH radical removing the amorphous carbon may be the reasons of production smaller diameters and higher purity SWCNTs. The results also suggest a potential opportunity for cost-effective and commercial production of SWCNTs.

Acknowledgments

This work is supported by Shanghai Science and Technology (Grant no. 0552nm033) and National Basic Research Program of China (No. 2006CB300406).

References