Synthesis of single-walled carbon nanotubes with selective diameter distributions using DC arc discharge under CO mixed atmosphere

Yanjie Su, Zhi Yang, Hao Wei, Eric Siu-Wai Kong, Yafei Zhang

Key Laboratory for Thin Film and Microfabrication Technology of the Ministry of Education, National Key Laboratory of Nano/Micro Fabrication Technology, Research Institute of Micro/Nanometer Science and Technology, Shanghai Jiao Tong University, Shanghai 200240, China

1. Introduction

Because of their outstanding electronic, physical and mechanical properties, single-walled carbon nanotubes (SWCNTs) are generally considered to have great potential for future high-performance nanodevices such as field-effect transistors [1,2], and chemical/biological sensors [3,4]. It is well known that the electronic and optical properties of SWCNTs depend sensitively on their diameters and chiralities. However, most as-synthesized SWCNTs have wide distribution of diameters and chiralities, which presents a drawback in their potential application in nanoelectronics. Therefore, it is critical to be able to synthesize high-quality, diameter-controlled SWCNTs if high-performance nanodevices are to be developed and fabricated.

Among the methods to narrow the diameter distribution of SWCNTs, the diameter selective growth is generally recognized as the best approach. Chemical vapor deposition (CVD) methods [5–18] have mainly been used to synthesize SWCNTs due to the convenient control of growth parameters. For example, many groups have achieved diameter selective growth of SWCNTs through the control on the size of catalyst nanoparticles [5–11], varying carbon sources [12,13] and the growth conditions [14–18]. However, there is generally a higher level of structural defects in SWCNTs synthesized by the CVD method, which will influence the electronic properties of SWCNTs to some extent.

As another main synthesis method, DC arc discharge has been used to grow high quality SWCNTs. Indeed, there have been other efforts reported in the literature on towards the control of SWCNT diameter distribution. For example, Takizawa et al. [19] reported that the tube diameter distribution could be controlled by changing the ratio of Ni:Y catalyst. The mean diameter of SWCNTs was found to increase as the Y concentration increased. However, the mean diameter of SWCNTs was not sensitive to the Ni concentration. Saito et al. [20] demonstrated that helium pressure could affect the diameter of SWCNTs produced by arc discharge. The tube diameter distribution shifted to large diameter with the increase of helium pressure. Bae et al. [21] investigated the effect of plasma rotating anode process on the formation condition of SWCNTs. The results indicated that centrifugal force by the rotation of anode could influence the diameter distribution of SWCNTs. However, it is still a challenge to perform large scale synthesis of SWCNTs with selective diameters. Here, we report the synthesis of SWCNTs with selective diameters using DC arc discharge method, in which the catalyst is a mixture of Ni and Y, and carbon monoxide (CO) is mixed with helium as buffer gases.

2. Experimental

The synthesis of SWCNTs was performed in a DC arc discharge furnace. In a typical experiment, the anode was a sintered graphite rod (6 mm diameter, 100 mm length) with the catalyst Ni/Y, in which the mole ratio among C/Ni/Y was 94.8:4.2:1.0. The powders were mixed by ball milling at a speed of 300 rpm for 12 h. Then the
mixture was extrusion molded to form graphite rods with coal tar as a binder. Finally, the graphite rods were annealed at 1000 °C for 6 h under nitrogen atmosphere at a flow rate of 200 sccm. The cathode was a pure graphite rod with 8 mm diameter and 300 mm length.

The discharge current was 100 A with a voltage of about 50 V during electric arc discharge process, and the total pressure of buffer gases was maintained at 30 kPa, in which the ratios of helium and carbon monoxide are 30:0, 29.6:0.4, 28:2, 26:4, 22:8, 18:12, and 0:30 for sample CO-0, CO-0.4, CO-2, CO-4, CO-8, CO-12, and CO-30, respectively. The arc gap between anode and cathode was kept at a constant value of 2–3 mm.

Field emission scanning electron microscopy (FE-SEM) was performed using Zeiss Ultra55 instrument. Transmission electron microscopy (TEM) was carried out in a JEOL JEM-2100 instrument operating at 200 kV. Raman spectroscopy was characterized using Jobin Yvon LabRAM HR 800UV micro-Raman system with laser wavelengths at 514 nm, 632.8 and 785 nm. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1. TGA samples were analyzed at a heating rate of 10 °C/min up to 850 °C in air atmosphere.

3. Results and discussion

Fig. 1 illustrates cross-sectional SEM images of as-synthesized SWCNTs under different CO concentration. It can be seen that samples synthesized under buffer gases with low CO concentration (Fig. 1a and b) consists of abundant SWCNTs with several micrometers in length. The amount of impurities will increase when CO concentration in buffer gases further increases (Fig. 1c–f). It is worth noting that an amount of carbon nanoparticles can be observed when the buffer gases consist of CO.

To investigate the effect of CO on the growth of SWCNTs, TEM was employed to compare the sample CO-12 and CO-30 shown in Fig. 2. Some catalyst particles and bundles of SWCNTs in sample CO-12 were observed in Fig. 2a. From the high magnification TEM image in Fig. 2b, SWCNTs with clean surfaces can be easily observed. We noted that in the electron micrograph (Fig. 2c), a large amount of poor-crystalline carbon coexisted with SWCNTs in sample CO-30. The surfaces of SWCNTs in CO-30 were coated with some impurities. The mean diameter of SWCNTs in samples has been evaluated to be about 1.66 nm.

Thermal Gravimetric Analysis (TGA) was performed to investigate the effect of different CO pressure on SWCNT products. The TGA results are shown in Fig. 3, indicating that there are two peaks at about 420 °C, 480 °C for all samples except for CO-30. The first peak can be attributed to the burning of amorphous carbon. The second peak has been diagnosed to be due to the combustion of SWCNTs. Sample CO-30 shows a main peak at 500 °C, which can be attributed to the burning of carbon nanoparticles due to its more stability to thermal oxidative destruction. From samples CO-0 to CO-12, the second peak shifts to higher temperature with the increase of CO concentration, indicating that abundant CO can
accelerate the growth of carbon nanoparticles. From the relative intensity of the derivative thermogravimetry (DTG) peaks (Fig. 3b) at 420 and 480 °C, it can be concluded that the pressure of CO with between 8 kPa and 12 kPa is an optimum condition that minimizes the presence of amorphous carbon.

The frequencies of radial breathing mode (RBM, $\omega_{\text{RBM}}$) of SWCNTs can provide the information on the diameter ($d$) of SWCNTs: $\omega_{\text{RBM}} = \frac{224}{d} + 14$ [22]. Therefore, the change of diameters of SWCNTs can be estimated from the RBM regions. Fig. 4 shows RBM peaks of SWCNTs samples synthesize under different CO pressure with different excitation wavelength (514 nm, 633 nm and 785 nm, respectively). Fig. 4a shows that the RBM peaks shift from 178 cm$^{-1}$ (1.36 nm) to 164 cm$^{-1}$ (1.49 nm) due to adding CO pressure. It can also be observed clearly in Fig. 4c that the intensity of RBM peaks at 180 cm$^{-1}$ (1.35 nm), 188 cm$^{-1}$ (1.28 nm) SWCNTs decrease and disappear from sample CO-0 to sample CO-30, while the relative intensity of RBM peaks at 145 cm$^{-1}$ (1.71 nm) increases. Two strong RBM peaks at 145 cm$^{-1}$ (1.71 nm) and 164 cm$^{-1}$ (1.49 nm) are left when CO pressure is larger than 8 kPa. RBM peaks (Fig. 4e) with excitation wavelength 785 nm are used to verify the change of diameter of SWCNTs synthesized under different CO concentration. There are four peaks at 150, 163, 178, and 199 cm$^{-1}$, which corresponds to the diameters of 1.65, 1.50, 1.36, and 1.21 nm, respectively. In synthesis condition under higher CO concentration, there are two main peaks at 150 cm$^{-1}$ and 163 cm$^{-1}$ in RBM regions. Hence, the diameters of SWCNTs can be controlled in 1.50 nm and 1.65–1.71 nm, which is consistent with the result of our TEM observations. The disorder induced band (D band) in Raman spectra of SWCNTs shows that there are defects containing impurities or other symmetry-breaking defects [23]. Fig. 4b, d and f shows that there is a slight increase in the intensity of the D band as the concentration of CO increases. However, the enhancement of intensity of D band in sample CO-30 indicates that the defect and impurities increase, which is in agreement with the aforementioned SEM and TEM observations.

To understand the potential mechanism about the diameter selective growth of SWCNTs, we have to focus on the chemical reaction and CO pressure applied [24] during the growth process. Carbon sources in our system consist of two parts: carbon clusters vaporized by the anode and those from the CO disproportionation [25]. The experimental results show that CO plays an indispensable role in diameter selective growth of SWCNTs. The reactions between catalysts and carbon clusters from two carbon resources in our system are quite complex. Firstly, the strong affin-

![Fig. 2.](image)

Fig. 2. (a) Low and (b) high magnification TEM images of sample CO-12. (c) Low and (d) high magnification TEM images of CO-30.

![Fig. 3.](image)

Fig. 3. (a) TGA and (b) DTG of the samples synthesized under different CO pressure.
ity of Ni for CO may result in CO dissociation on the surface of Ni clusters during exposure to CO. Abundant carbon atoms from two carbon sources precipitate on the Ni clusters formation, which reduces the growth rate of catalysts clusters [13,26]. Secondly, CO decomposition could produce oxygen atoms at high temperature. SWCNTs with small diameters are easily etched by oxygen atoms because of their large curvatures and high energy. Furthermore, CO molecules preferentially absorb the outer edge of tube and increase the diameter of SWCNTs under high temperature [27]. Additionally, Chen et al. [28] found that reaction at high CO pressure lead to SWNTs of uniform diameters in Co-MCM-41, which is attributed to SWNTs growth quickly once the catalyst cluster reaches the required size/conformation. Any individual effect of CO on catalysts and carbon sources cannot give diameter selective growth of SWCNTs [29]. In addition, in the presence of pure CO atmosphere, large catalysts clusters will be covered with carbon nanoparticles as they are exposed to CO [28], which will cause lower the rate of SWNT growth. Accordingly, large amount of carbon nanoparticles can be observed in sample CO-30.

4. Conclusions

We have demonstrated that SWCNTs with selective diameters can be synthesized by DC arc-discharge method under the mixed gases of CO and helium. It is found that the growth of SWCNTs with small diameters can be suppressed when the pressure of CO gas is larger than 4 kPa. However, pure CO as buffer gas can result in the formation of much more carbon nanoparticles. Certain CO pressure (>8 kPa) can suppress the formation of amorphous carbon, and results in the diameter selective growth of SWCNTs, in which the diameter of as-synthesized SWCNTs can be controlled in the range of 1.5–1.7 nm. This simple and effective method opens up the possibility of technological advancement for SWCNT-based nanodevices with high performance.

Acknowledgments

This work is supported by National Natural Science Foundation of China No. 50730008, No.50902092 and No. 61006002, Shanghai-Applied Materials Collaborative Research Program No: 09520714400, and Shanghai Science & Technology foundation (No: 09JC1407400 and No: 1052nm02000).

References


