

Preparation of diameter-controlled multi-wall carbon nanotubes by an improved floating-catalyst chemical vapor deposition method

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Abstract: Multi-wall carbon nanotubes (MWCNTs) with controlled diameters were synthesized by an improved-floating catalyst chemical vapor deposition method, using toluene and ferrocene as a carbon source and catalyst precursor, respectively. Ferrocene was sublimed in a heater and carried as a gas mixed with toluene vapor into a reactor where MWCNTs were formed. The effects of the sublimation temperature, hydrogen content in the gas mixture and gas flow rate on the diameter and diameter distribution of the CNTs formed were investigated. Results indicated that the CNT diameter distributions could be controlled by changing the sublimation temperature. The higher the sublimation temperature, the narrower the distribution of CNT diameters. The average CNT diameter decreased and levelled off with increasing hydrogen content in the gas mixture from 0 to 40 vol%. The CNT diameter decreased with increasing gas flow rate.

Key Words: Improved floating catalytic chemical vapor deposition; Multi-walled carbon nanotubes; Toluene; Ferrocene

1 Introduction

Multi-walled carbon nanotubes (MWCNTs) consist of multiple layers of graphene curled up along axial direction to form a closed tube^[1]. Since the first synthesized in 1996^[2], there has been increasing attention on controlling the growth of CNTs with uniform dimensions and morphologies. CNTs in arrays with a uniform diameter had similar or identical performances to reflect their advantages in material modification, intelligent organs, supercapacitors, li-ion batteries, hydrogen storage and the like^[3-7]. Moreover, CNTs with a smaller diameter had a huger length-to-diameter ratio, extra-larger specific surface area, stronger interface effect, higher thermal and electrical conductivity and so on than those with a larger diameter^[8-12, 34]. Therefore, these CNTs with a small diameter and narrow distribution are required widely in many fields.

Currently, synthesis methods of controlling CNT diameter had been exploited by many researchers. The most attractive means yielding CNTs was chemical vapor deposition (CVD)^[13-18], which included thermal CVD and floating catalytic CVD (FCCVD). Although thermal CVD could prepare small-diameter CNTs, even single-walled CNTs^[19-21], equipment required to prepare the catalyst precursor was quite complex and expensive. Compared with thermal CVD,

FCCVD was an effective approach to realize industrialization of CNTs. It had the advantages of simple production equipment and technology, fast growth rate, high yield, low cost and so on^[1]. So FCCVD sparked numerous researchers' attentions. Most studies utilized injection CVD (ICVD) to control the diameters of CNTs when ferrocene was served as a catalyst precursor and liquid hydrocarbons were used as the carbon sources in FCCVD^[22-28]. Singh et al.^[28] reported the preparation of CNTs with a diameter distribution of 20–70 nm by using the ferrocene–toluene solution with ICVD in 2003. Seyyed Shayan Meysami et al.^[29] obtained MWCNT arrays with a diameter of 10–120 nm by applying a trace pump to inject a ferrocene–toluene solution into a reaction chamber at 1073 K in 2013. ICVD was an effective approach to synthesize CNT arrays, but it was difficult to delicately control CNT diameter distributions when liquid hydrocarbon was selected as a carbon source and ferrocene as a catalyst precursor. The reason was that the liquid-state carbon source could be gasified instantly accompanied by the catalyst particle formation in a reactive chamber at high temperatures. The ICVD method needs improving to synthesize CNTs with a narrow diameter distribution.

In our experiments, toluene and ferrocene were chosen as a carbon source and catalyst precursor, respectively to synthesize CNTs. In an improved FCCVD, ferrocene was

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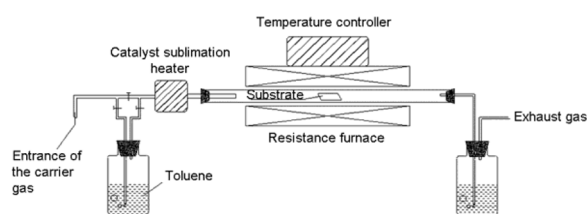


Fig. 1 A schematic illustration of experimental setup.

Table 1 Vapor pressures of ferrocene at different sublimation temperatures.

Temperature (K)	Vapor pressure (Pa)
328	14.6
338	31.8
348	65.8
358	130.7
368	249.3
378	248.3

sublimated in a separate catalyst heater at a low temperature and toluene was brought into reaction chamber in the form of gas by a carrier gas to avoid a liquid hydrocarbon gasification simultaneously in a reactive chamber at a high temperature. This carbon source, catalyst precursor and the carrier gas could be mixed homogeneously before CNT formation in the system in this method. CNTs were prepared with a small diameter and a narrow diameter distribution.

2 Experimental

2.1 Raw materials

Toluene as the carbon source was introduced into a chamber in the form of gas by a carrier gas at room temperature. Solid ferrocene as the catalyst precursor has a high saturation vapor pressure. So it sublimates greatly below its melt point of 446 K. Gaseous ferrocene could be introduced into the chamber by the carrier gas at a low sublimation temperature. The relationship of vapor pressure of ferrocene and sublimation temperature can be expressed as the equation (1)^[20], where P_e is the vapor pressure of ferrocene (Pa), R is the gas constant as 83 145 J/(mol · K), and T is the temperature (K). The vapor pressures of ferrocene corresponding to different sublimation temperatures calculated according to the equation (1) are shown in Table 1. With the increase of sublimation temperature from 328 to 378 K, the vapor pressure of ferrocene was increased by more than ten times rapidly. The low feeding rate of ferrocene was realized through low-temperature sublimation. With less ferrocene introduced into the reactor, the collision among the in situ formed iron atoms decreased, which led to the formation of a smaller diameter catalyst particles and CNTs^[30]. So the CNT diameters can be tuned by the quantities of ferrocene introduced into the reactor.

$$\ln(P_e/P_a) = \frac{273.6}{R} - \frac{81535.7}{R \cdot (T/K)} - \frac{29.6}{R} \ln\left(\frac{T/K}{298.15}\right) \quad (1)$$

2.2 Preparation of CNT arrays

The synthesis of CNTs was realized by the improved FCCVD. Schematic illustration of the experimental setup is shown in Fig. 1. It mainly consisted of a resistance furnace, a quartz tube of 30 mm inner diameter and a catalyst sublimation heater. Quartz substrate was placed in the middle of the reaction chamber. Toluene was introduced into the chamber by the carrier gas in the form of gas. Ferrocene was sublimated at a certain temperature in the catalyst sublimation heater and carried into the reaction chamber in the gas mixture containing the carrier gas and toluene vapor. After CNT growth at 1 073 K under a certain flow rate of the carrier gas for 30 min, the resistance furnace and catalyst sublimation heater were turned off and the carbon source was terminated. Then, the furnace was cooled to room temperature under N_2 flow. CNT array was taken out from the reaction chamber and peeled off from the quartz substrate for further characterization.

2.3 Characterization

The morphology of CNT arrays were observed by using a Hitachi S-4800 scanning electron microscope (SEM). Microstructure of CNTs were observed by a Hitachi H7650 transmission electron microscope (TEM) (Hitachi H7650) and a Jeox JEM-2100 high-resolution transmission electron microscope (HRTEM) (Jeox JEM-2100). The diameters of more than 100 CNTs, in SEM or TEM images, were measured by utilizing the software of Image-Pro Plus 6.0 and their distributions were statistically calculated by using the software of Origin 8.5.

3 Results and discussion

3.1 Modulating the sublimation temperature of the catalyst precursor

Fig. 2 shows the morphologies of CNT arrays. The preparation of CNT arrays were carried out at 1 073 K under a flow rate of 500 sccm nitrogen at different ferrocene sublimation temperatures. When ferrocene was sublimated at 328 and 338 K, no CNT arrays were found (Fig. 2a-b). And CNTs with many impurities could be gathered from the quartz substrate. However, the CNT arrays with few impurities, which would be the iron catalyst encapsulated with carbon or the amorphous carbon^[20], could be found in as-grown products when ferrocene was sublimated at high temperatures (Figs.2c-f). This could be ascribed to the proportion of the feeding quantity of ferrocene to toluene. The quantity of the carbon source introduced into the chamber was constant at room temperature. The feeding quantity of ferrocene increased with the increase of its sublimation temperature^[30]. At a lower

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