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A solution method for the large scale production of multiwall carbon nanotubes

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Large scale production of multiwall carbon nanotubes (MWCNTs) has been achieved by a solution method. A heated bubble chamber is used as a hydrocarbon source from liquid n-hexane, and a Fe catalyst precursor is prepared by $Fe(CO)_5$ which is dissolved into the n-hexane. The temperature and dissolved Fe concentration in the n-hexane have influences on the synthesis of MWCNTs. The synthesized MWNTs are collected by an electromagnet. SEM shows the diameters of MWNTs are in the range of 20-60 nm and are several micrometres in length.

Key words: Carbon nanotubes, Solution method, Carbon nanotubes mass production.

Introduction

Carbon nanotubes have became an important material for industrial uses, such as in electronic devices [1, 2], plastic composites [3, 4] and for gas storage [5, 6]. For the industrial usage of MWNTS, large scale synthesizing of MWCNTs has become an important research area. Although many synthesizing technologies for CNTs have been reported, such as chemical vapor deposition, arc and plasma methods, most of these methods give trouble as a continuous process due to the need to supply catalyst continuously into the reaction furnace. As a continuous CNTs synthesizing process, the aerosol method has been introduced which used gas-phase synthesis and a floating catalyst method during the CNTs synthesizing process [7-9].

In the aerosol method, the pyrolysis method uses a liquid carbon source, and catalyst precursors which are dissolved into the liquid carbon sources, for synthesizing CNTs, Mayne *et al*. reported pyrolytic synthesizing of MWNTs using dispersed benzene/ferrocene-based aerosols which are collected on the quartz tube in a furnace [10]. Andrews *et al*. reported pyrolytic synthesizing of MWNTs using dispersed xylene/ferrocene-based aerosols [11]. Although they reported a gas-phase synthesis and a floating catalyst method during the synthesizing process for CNTs, there is an ambiguous point for the growth of MWNTs also where the synthesis process takes place in the gas-phase which is on particles suspended in the gas, or supporting materials (or substrates). Because most of the MWNTs are collected on the quartz walls in the reaction furnace, two formations of MWNTs should be expected from the gas phase and the substrates on the quartz tube walls.

Nasibulin et al. reported the synthesis of CNTs from alcohols using a floating catalyst method which a CO hydrocarbon source and a floating metal catalyst were put separately into a furnace [12]. They used a metal wire and a hot wire generator to make the floating metal catalyst. This process controls the CO hydrocarbon source and catalyst separately during the synthesis process. Although they reported a gas-phase synthesis and a floating catalyst method during the synthesizing process of CNTs, they used two different heating processes to synthesize CNTs.

Because the synthesizing process for CNTs in the aerosol method has to be done in the gas phase, synthesized CNTs should be collected on the outside of a collector and not on the surface of quartz tube walls. Therefore, this paper reports research on the growth of MWCNTs by a pyrolysis method. Technically, our method used a heated bubble chamber as the vaporized liquid hydrocarbon source, and an electromagnet was used to collect the MWNTs which were synthesized in the gas phase. In a pyrolysis method, because catalyst particles are suspended in the gas-phase throughout the entire MWNTs synthesizing process, the electromagnetic collection method of synthesized MWNTs in the gas-phase became necessary [13, 14]. Thus there is no chance that MWNTs are formed on the quartz tube walls.

Experimental

The reactor consists of a bubble chamber, an electromagnet, and a heated horizontal tubular furnace

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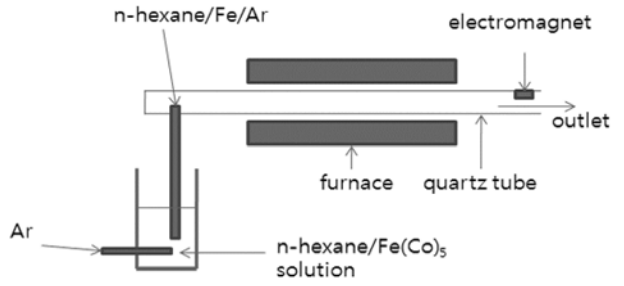


Fig. 1. A schematic of the pyrolysis apparatures.

(Fig. 1). A quartz tube, with an internal diameter of 45 mm, 50-cm length furnace has been used as the reactor. The bubble chamber consists of a resistively-heated thin iron wire (0.25 mm in diameter) located outside the quartz tube. The end of the bubble chamber was placed where the reactor wall temperature was about 400 ºC. This temperature was found to be optimum, since it allowed us to reduce the particle growth due to coagulation at a reasonable nucleation rate of the Fe catalyst vapor. The metal catalysts, which were $Fe(CO)_5$ dissolved into the liquid carbon source, were driven into the reactor with argon gas with the vaporized hydrocarbon source. In the heated furnace, the dissolved hydrocarbon source became supersaturated on the surface of the metallic catalyst particles. Synthesized MWNTs were collected by an electromagnet. Fig. 2 shows the collection capture of MWNTs in the quartz tube which is located outside the reaction heating zone. Because gas-phased synthesized MWNTs are collected inside the quartz tube but located outside the reaction zone, there is no chance for the formation of MWNTs on the quartz tube walls.

The synthesis of MWNTs was carried out by the catalytic reaction of n-hexane and the Fe catalyst in a fixed quartz furnace. $Fe(CO)_5$ (99.99%, Aldrich) was dissolved in n-hexane for 1 h. In our experiment, the molar ratio of Fe catalyst and n-hexane was Fe : n-hexane 1 : 1. For the synthesis, catalysts were dissolved in the liquid carbon source and inserted into the bubble chamber at 80 ºC. The quartz tube was heated to 950 ºC with an argon atmosphere. Subsequently, the argon gas was injected into the bubble chamber. Argon gas passed through the bubble chamber at 80 ºC, and the argon gas contained both the carbon source and the Fe catalyst. The mixed gas containing the catalyst

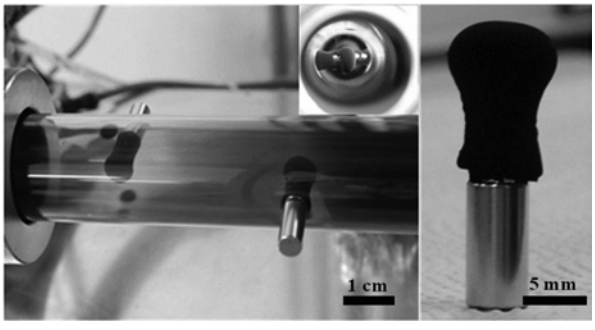


Fig. 2. MWNTs collection using an electromagnet.

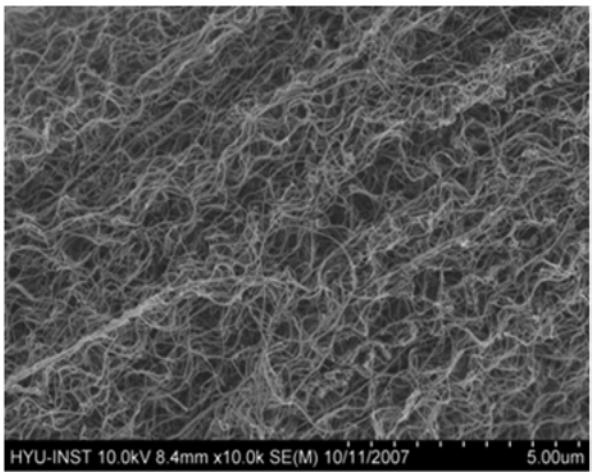


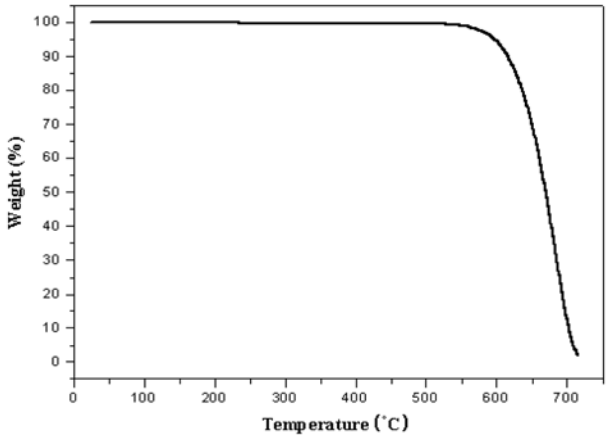
Fig. 3. SEM image of the as-synthesized carbon material produced by catalytic reaction of n-hexane over Fe catalyst at 950 ºC.

and hydrocarbon source was introduced into the quartz tube for the synthesis of MWNTs. The synthesis of MWNTs was conducted at 950 ºC for 30 minutes at atmospheric pressure. The flow rate of Ar was 100 sccm. The morphology and microscopic structure of CNTs were characterized by scanning electron microscopy (SEM) (Hitachi, S-4700), transmission electron microscopy (TEM) (JEOL, JEM-3011, 300 kV), and a Raman spectrometer (Bruker, RFS- 100/S).

Results and Discussion

Fig. 3 shows SEM images of the as-synthesized carbon material produced by the catalytic reaction of n-hexane over the Fe catalyst at 950 ºC. This shows a large amount of un-entangled MWCNTs with lengths greater than several tens of micrometres. In the SEM images, our solution synthesis method is preferable to obtain large scale production without the recrystalization that occurs in the catalytic chemical method. In the solution method, the reaction temperature is very important for the synthesis of MWNTs using the catalytic reaction of n-hexane and the Fe catalyst. At a reaction temperature of 950 ºC, the morphology of the as-synthesized MWNTs is smooth and clean, when the reaction temperature is less than 950 ºC, the yield of MWNTs rapidly decreases and amorphous carbon material also appear on the MWCNTs. High magnification SEM image showed the MWCNTs have diameters in the 20-60 nm range.

Fig. 4 is the TGA output of MWNTs after the mechanical purification. Fe catalyst particles have been almost completely removed (over 95%) after mechanical purification using a high vacuum (1.3×10^{-10} MPa) and a high temperature (~ 1500 ºC). The output exhibits that the yield of MWCNTs is about 98%. Oxidation and high vacuum purification processes of MWCNTs are used to remove the metal and unwanted carbon without affecting the structure of the MWNTs, because the impurities existing in the as-grown carbon MWNTs are the metals which were used as catalysts for the growth of the amorphous carbon. Metals



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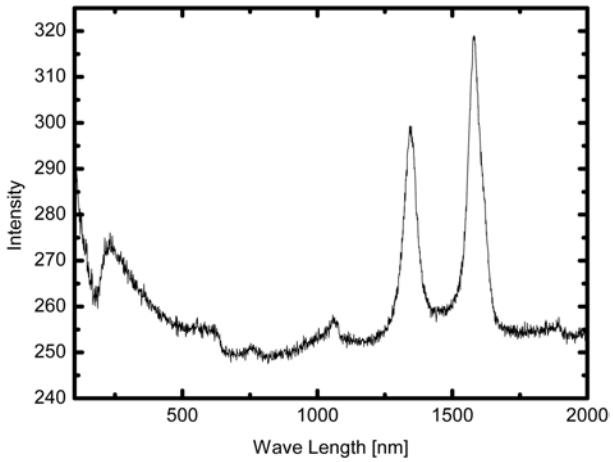

Fig. 5. Raman spectrum of the MWCNTs synthesized at 950 °C.

exist as nanoparticles and are typically encased in the carbon outer layers that make them impervious to dissolution in an acid. The oxidation process and vacuum process produced high purity MWCNTs samples. In the oxidation purification process, as-grown soot on the MWCNTs first undergoes a nitric acid refluxing process. Oxidation of the acid-treated MWCNTs is then carried out in air at 500 °C for 30 minutes, leaving behind MWNTs having a weight of 20% of the initial as-grown material. After the oxidation purification process is finished, the encapsulated metal catalysts are removed by a vacuum extraction process using an ultra high vacuum chamber. In the high vacuum process, encapsulated catalysts in MWCNTs melted out due to the high temperature of 1500 °C and the pressure of 1.3×10^{-10} MPa in the vacuum chamber. These purification methods gave over 98 wt.% pure MWCNTs in the sample. The purified sample was documented by TGA.

Fig. 5 is a Raman spectrum of the as-synthesized MWCNTs. The spectrum exhibits the characteristic frequencies of MWCNTs. The peak centered at 1571 cm^{-1} (G-band) is narrow and strong in the spectrum, indicating that structural defects along the tube wall are low. The peak at 1334 cm^{-1} (D-band) is related to the level of disordered carbon. The weak D-band demonstrates that the as-synthesized samples contain very small amounts of amorphous carbon material. A Raman technique was used to optimize the synthesizing temperature of MWCNTs. Raman spectra showed that a low growth temperature gives a higher D-band than high temperature grown MWCNTs. This is because a low temperature did not give sufficient energy for pyrolysis of the liquid carbon source. Therefore, defects in the MWCNTs increase with a decrease in the growth temperature.

Conclusions

High-quality MWCNTs have been synthesized by a solution method. As-synthesized MWCNTs have a diameter of 20-60 nm. With a reaction temperature of 950 °C, the morphology of the as-synthesized MWCNTs is smooth, clean and they are entangled. The temperature dependence of the Raman spectra has been studied. At a low growth temperature, the defect density increases due to insufficient energy for the pyrolysis of the liquid carbon source. Our results indicate that a Fe catalyst dissolved into n-hexane is useful for the large-scale synthesis of high-quality MWCNTs. This method can offer mass production of high-quality MWCNTs for many technological applications.

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