Short communication

Preparation of carbon nanotubes by DC arc discharge process under reduced pressure in an air atmosphere

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Abstract

Carbon nanotubes (CNTs) were grown using a DC arc discharge process in an air atmosphere and relevant process parameters were investigated. Without using an inert gas, multi walled carbon nanotubes could be synthesized in the deposit area of the cathode even in an air atmosphere, but single walled carbon nanotubes were not detected in the soot area despite using the same process conditions as in the inert gas. The air pressure for the highest yield of multi walled CNTs was 300 Torr. In addition, the quantity of amorphous carbon and other nanoparticles in the process chamber was remarkably reduced by this technique, showing that an efficient, feasible method of large scale CNT fabrication could be achieved by the arc discharge process.

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1. Introduction

Carbon nanotubes (CNTs) were first reported by Iijima in the carbonaceous deposits on the cathode obtained during the DC arc discharge process of a graphite electrode in helium gas [1]. The application of CNTs in various fields is expected due to their unique electrical, mechanical, and chemical properties [2]. Among several methods for preparing CNTs, arc discharge is the most practical for scientific purposes because the method yields highly graphitized tubes due to the high process temperature [3]. However, besides CNTs, arc discharge methods produce many by-products. As a result, the process requires complicated and well controlled purification steps [4]. To overcome this disadvantage and to get a large quantity of high-quality CNTs, various researchers have proposed optimizing the catalyst and process conditions, including various kinds of ambient gases. The atmosphere, under which the arc discharge is made, is one of the important key factors affecting the yield and morphology of the CNTs. Although an inert gas is used, like helium or argon, other ambient gas discharge has been extensively used to produce CNTs. Some researchers reported that the multi walled carbon nanotubes (MWNTs) produced by hydrogen arc discharge contain very few coexisting nanoparticles [5,6]. They deduced that the reason might be the high thermal conductivity and activity of the hydrogen arc. For MWNT production, the hydrogen arc is more effective than an inert gas but hydrogen is difficult to control and dangerous to use in large quantities.

We expected that CNTs could be produced in an air atmosphere, since Cui et al. prepared MWNTs under a nitrogen atmosphere [7]. In addition, oxygen is a reactive gas so that it reacts with carbon easily to form strong covalent C–O bonds. Thus, it is rationally deduced that a properly adjusted ratio of nitrogen and oxygen in the arc discharge can be used to form CNTs and reduce the amorphous carbon by selectively etching it around the CNTs to form C–O gas at the same time. Because of the ultimate safety and convenience for tooling, dry air can be the most profitable process gas, but there have been few reports yet about the preparation of CNTs in an air atmosphere.

2. Experiment

The arc system used in this study is basically the same chamber we employed earlier for the production of CNTs [8]. The chamber was connected to a vacuum line with a rotary pump
and to a dry air supply. The anode and cathode were made of pure graphite (that is, with a purity of 99.999%). A rod-shaped carbon anode with dimensions of 6 mm (Ø) × 80 mm (length) and a cube-shaped carbon cathode of 40 mm (length) × 40 mm (height) × 10 mm (thickness) were used for the experiment. The 0.5–2 mm gap between the graphite electrodes was controlled manually by advancing the consumed anode. Arc plasma was generated at currents from 40 to 80 A under voltages from 18 to 30 V. The pressure of the chamber was also varied approximately from 100 to 760 Torr in 100 Torr steps using a continuous flow of dry air. The apparatus and carbon cathode were cooled by a cold water line. The products were collected at different sites inside the apparatus, such as the central area of the carbon cathode, the flakes of soot around the cathode, and the upper cold water line.

3. Results and discussion

After the arc plasma process without using the catalyst, we found that the quantity of soot on the chamber wall was remarkably reduced. In the case using helium as the ambient gas, the chamber wall and cooling water line were all covered by the black soot. But there was little soot when using air as the ambient gas even if the quantity of soot was varied according to the process conditions such as pressure and current. At high current and low pressure, the quantity of soot increased but it was relatively much lower than that of the helium gas. This might be attributed to the efficient etching reaction of oxygen in the dry air. Considering that one of the problems of arc discharge for the mass production of CNTs is the soot which covers the chamber wall during arc discharge, this result will be more adaptable if the process conditions are optimized.

Fig. 1 shows SEM images of the samples which were synthesized (a) in an air atmosphere at 300 Torr, and (b) in the helium atmosphere at 500 Torr. The unpurified raw materials have three main components: CNTs, carbonaceous particles, and carbon pellets. Two samples showed a similar yield but the diameters of the CNTs were slightly different. Various researchers have proposed optimizing the helium pressure to get a high yield of CNTs. Initially, Ebbesen et al. reported that the total yield of nanotubes as a proportion of graphitic starting material was optimal around 500 Torr [9]. In the more recent study by Waldorff et al., they pointed out that highest SWNT relative concentration could be obtained at background pressure of about 200–300 Torr [10]. It is interesting that the air pressure for the highest yield of CNTs was 300 Torr. It has been believed that the inert gas acts as a “quench” for the carbon vapor, which attains supersaturation followed by nucleation and growth of carbon nanotubes [11]. Helium has a higher thermal conductivity (0.152 W/m K at 300 K) than air (0.0256 W/m K at 300 K), so it might be a more efficient quench for carbon vapor to condense and form nanotubes at the same condition. From this view point, the air pressure for the optimized process condition was expected to be higher than that of helium. But in the higher pressure of air, the oxidation etching rate also increased so that both the quantity of deposit and CNTs decreased. Around 500 Torr, the quantity of deposit was 30% of the quantity of the anode consumed, but it was reduced less than 10% at 760 Torr. In fact, we only gained 10% of the quantity of the anode loss at 760 Torr; the other 90% of the anode loss was not detected in the form of soot. The chamber wall was clean and we gained few residual carbon particles. The quantity of gain per anode consumed increased with lowering the pressure at the same current, but in lower pressure, the yield of CNTs decreased due to poor quenching in air. In our experiment, the optimized process pressure was around 300–400 Torr, which is similar to the nitrogen atmosphere [7]. At this range of pressure, although the quantity of deposit after the arc discharge reduced slightly, by about 20%, the yield of CNTs was nearly similar to the sample synthesized in the He atmosphere. The evaporation velocity of the anode in air was higher than in the inert gas. If the process condition was equally maintained, the difference of velocity reached five times. At the same pressure in the air atmosphere, the evaporation velocity increased with increasing process current.

Fig. 2 shows that the diameters of the synthesized CNTs in the air atmosphere were smaller than those in the helium atmosphere. The diameter of CNTs was determined through TEM
Fig. 2. Boxplot for the diameters of samples which were synthesized in the air and He atmosphere.

We deduced that the outer shell of the CNT was more easily etched away by oxygen and it decreased the diameter of the CNTs.

Fig. 3(a) shows TEM images of deposit samples treated with ultrasonication and acid treatment. To purify for the CNTs, the raw materials were subjected to ultrasonication in acetone to crush them and a 2 M HNO₃ acid treatment to etch away carbon nanoparticles. Finally, the sample was washed in deionized water and heated at 873 K in air for 1 h to remove the final carbonaceous particles. The TEM samples were prepared in an identical way and typical MWNTs are shown in the TEM image. Unlike in the hydrogen atmosphere [6], open-ended nanotubes were not observed.

For synthesizing single walled carbon nanotubes (SWNTs), catalyst metal (Fe, Ni, Co) was also introduced by evaporating metal powder which was embedded with carbon powder in the hall of the anode. It has been reported that SWNTs are only detected in the soot area of the chamber [12], but we could not obtain the black soot in the chamber. Gray and web-like soot were detected on the chamber wall, collector, and cooling water line. Fig. 3(b) shows a TEM image of the gray soot which was collected in the collector of the chamber. Metal particles about 10–30 μm and amorphous carbon are observed but there were no nanotubes in the collected gray soot. To explain this result, we considered two types of oxidation reactions: metal oxidation and carbon oxidation. First, according to the VLS mechanism for synthesizing CNTs [13], the catalyst should be evaporated in air and the carbon species should be supersaturated in the melted catalyst. In this process, the melted catalyst will more easily react with oxygen and form a metal oxide. Because this metal oxide does not act as a catalyst, SWNTs would not be detected. Second, in the soot area for synthesizing SWNTs, the carbon density is relatively lower and the temperature gradient is higher than that of the deposit area [14]. In the deposit area, although some outer shells of MWNTs were etched away, MWNTs could form due to a higher carbon density. But in the lower carbon density soot area, it would be difficult to form SWNTs with surmounting carbon oxidation.

To quantify the quality of the CNTs, thermogravimetry (TG) analysis was used to characterize MWNT samples which were synthesized in air at 300 Torr and He atmosphere at 500 Torr.

Fig. 4 shows the result of the TG analysis. In the raw sample before purification, the weight starts diminishing near 650 °C. From Fig. 4, there is no difference in the diminishing temperature for nanotubes which were synthesized in the inert gas and in an air atmosphere. This temperature is high compared with that of MWNTs fabricated in a CVD process. These results indicate that our sample has a higher thermal stability than
4. Summary

In this study, we have demonstrated that MWNTs can be prepared by a DC arc discharge under an air atmosphere. In fact, without using dry air, MWNTs could be synthesized only by optimizing the pressure of the chamber. From our experimental results, the cost and safety of preparing MWNTs can be reduced and improved remarkably, compared to helium and hydrogen atmospheres, respectively.

References