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Electric-field-induced diameter control of carbon nanofibers

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ABSTRACT

A novel process is introduced for controlling diameter of carbon nanofibers by changing electric field in a chemical vapor deposition system. It was found that an increase in electric field produced a smaller diameter and narrower diameter distribution of carbon nanofibers, that is, the carbon nanofiber diameter varied in series of 19.2 ± 8.6, 13.8 ± 4.7, and 8.0 ± 2.4 nm corresponding to the electric field of 0, 25,000, and 50,000 V/m, respectively. The theoretical calculation reveals that the mechanism for this change is because Ni catalyst particles become liquid at the reaction temperature and the diameter of the Ni catalyst becomes smaller under the electric field.

1. Introduction

One-dimensional carbon nanomaterials (ODCNMs) including carbon nanotubes (CNTs) and carbon nanofibers (CNFs) which is a kind of solid-cored fiber are new forms of carbon materials with many outstanding properties and potential applications. It has been recognized that the metallic, semiconducting and mechanical properties of ODCNMs depend strongly on their diameters [1,2]. Recently, there are several methods have been developed to control diameter of ODCNMs. For example, in an arc-discharge, the single walled carbon nanotube (SWCNT) diameter can be controlled by rotating the electrode and changing rotate speed [3]. As a most widely used process for synthesizing ODCNMs, the diameter control in a chemical vapor deposition (CVD) system is of crucial importance [4]. Generally, the value of the ODCNM diameter depends upon the size of catalyst particles [5–10]. According to the treating to catalyst particles, the diameter control methods can be divided into two types:

(1) Original catalyst particle treatments, such as: changing the particle size by using variant catalyst calcination temperature [5] or thermal annealing time [6]; or filling the pores of porous anodic aluminum oxide templates with different concentration catalytic metal ion solutions [7]; and other special approaches [8–10]. These kinds of methods always make the synthesis more complicated.
(2) On-line catalyst particle treatment during synthesizing, that is, changing the particle size by changing reaction temperature [11], and pressure in a reactor [12]. However, the exact size control is very difficult.

In our previous work [13,14], we proposed an effective method for controlling the diameter of CNTs and CNFs through controlling of the plated grain size by adjusting the plating parameters including output pulse frequency (f) and the duty cycle (r). That is, firstly electrodeposited a metal (Fe or Ni) nanocrystalline layer upon a substrate using periodic reverse (PR) pulse plating, then the homogenous sizes of CNTs or CNFs were synthesized on the plated substrates in flames. However, sometimes the process was also difficult to be exactly controlled. Adding an electric field in a CVD or flame systems is a simple and effective approach for growing well-aligned CNTs and CNFs [15–17]. Our recent work also revealed that an additional electrostatic field could not only align the CNTs, but also improved the diameter uniformity and the crystallinity of graphite sheets [15–17]. In this work, the CNF diameter has been controlled by changing electric field in a chemical vapor deposition system.

2. Experimental

The detailed process of the experiment is described as follows:

Electrodepositing a Ni nanocrystalline layer: The substrate was a cooper sheet sized in 10 mm × 20 mm and the surface was mechanically polished to a mirror finish. The sampling surface was modified by a Ni nanocrystalline layer using a pulse electrodeposition technique for 1 min (two pulse numerical controlled electrodepo-

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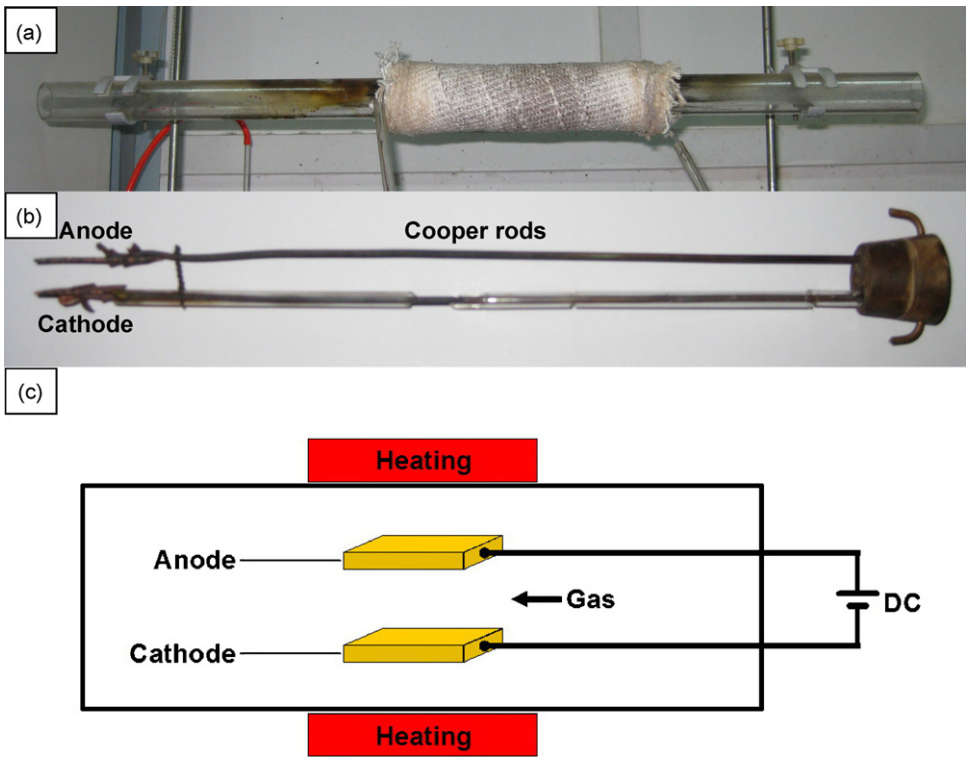

Fig. 1. The image of the (a) CVD reactor, (b) cathode, anode and two cooper rods, and (c) schematic diagram of the experimental apparatus.

sition power supply, GKDM 30-15, Xin Du, China). The electrolyte and parameters have been described elsewhere [13].

Applying an electric field: The electric field was supplied by a direct current power supply of which change scope was 0–700 V. As Fig. 1a shows, the reactor is a quartz tube with heating system. The substrate as the cathode and another electrode as the anode were linked with the power supply by two cooper rods and the distance between the electrodes was 6 mm, as shown in Fig. 1b. In the process of synthesis, the cathode and anode lay inside the CVD reactor as shown in Fig. 1c. The CNFs grew without or with electric field of 25,000 and 50,000 V/m (corresponding voltage was 150 and 300 V). When the voltage exceeded 350 V, a typical arcing was observed between the electrodes due to electric discharge.

Synthesis of the CNFs: The synthesis of CNFs was carried out at atmospheric pressure. After the substrate and another electrode were put into the reactor, air in the reactor was eliminated in Ar flow with rate of 200 sccm for 40 min. Then the reactor was heated and heating sustained about 40 min. Subsequently, high purity acetylene with flow rate of 30 sccm was introduced in the reactor with an electric field (substrate was linked to the cathode of the power supply) for 3 min when the reactor was heated at 600 °C. Finally, the substrate cooled to room temperature with Ar flow.

Theoretical calculation: The electric force acting upon Ni nanocrystal in the electric field was simulated and calculated by using a Maxwell 2D simulation program (Maxwell SV, Ansoft Corp.).

Characterization: The morphology of the CNFs was characterized by using a transmission electron microscope (TEM) (JEM 2010 TEM, JEOL, Japan). The TEM specimens were prepared by scraping the CNFs off the substrate, dispersing them in an ethanol ultrasonic bath for 30 min, and dropping the suspension onto 3 mm diameter copper microgrids. To obtain the diameter distribution, 150 CNFs were measured for each sample.

3. Results and discussion

In the present work, the effect of an electric field upon the diameter variation of the CNFs in a CVD system was studied experimentally and theoretically. It is expected to find an effective method for controlling the diameter of ODCNMs simply and exactly.

Fig. 2 shows the TEM micrographs of solid-cored CNFs and corresponding diameter distributions in variant electric field. Fig. 3 illustrates the average diameter and standard deviation of the CNFs with respect to the applying electric field. Obviously, an increase in electric field produced a smaller CNF diameter and narrower diameter distribution. That is to say, the CNF diameter varied in series of 19.2 ± 8.6, 13.8 ± 4.7, and 8.0 ± 2.4 nm corresponding to the electric field of 0, 25,000, and 50,000 V/m, respectively, which indicates that the CNF diameter has been controlled continuously and exactly by using an electric field. In addition, in case of without electric field, the CNF diameters distributed in a wide range from 6 to 45 nm, while it becomes narrower when the electric field was induced, such as from 4 to 11 nm at 50,000 V/m.

Obviously, the electric field plays a key role during the CNF growth. In order to understand the CNF diameter-controlling mechanism in an electric field, the electric force acting upon a Ni catalyst particle was calculated. This calculation was based on a finite element method by using Maxwell SV. Fig. 4 illustrates the simulation of the macroscopic electric field between two electrodes. It can be seen that the electric field between the electrodes was uniform. In the present model, the catalyst particle was assumed to be as a 'hemisphere' model with diameter 20 nm, as illustrated in Fig. 5. The electric force acting upon the catalyst particle under an electric field of 12,500, 25,000, 37,500, and 50,000 V/m were calculated. The calculation showed that the force upon the particle upward the substrate and increased when electric field enhancing, as illustrated in Fig. 6.

The average diameter of pristine Ni catalyst particles is less than 20 nm, which could be concluded from the CNFs average diameter of 20 nm when no electric field was used. The melting point of Ni catalyst will reduce a lot because of the surface energy influence in nano-size [18,19]. On the other hand, the presence of a little sulfur in the reaction gas can also reduce the melting point of Ni catalyst [19]. So Ni catalyst particles become liquid at the reaction temperature of 600 °C [19]. The Ni catalyst liquid is stretched along the direction of electric field under an electrostatic field which makes the diameter of the Ni catalyst becomes smaller. The stretch of Ni catalyst liquid is hindered by the gravity against the electric force and the surface tense force which will increase when the stretch

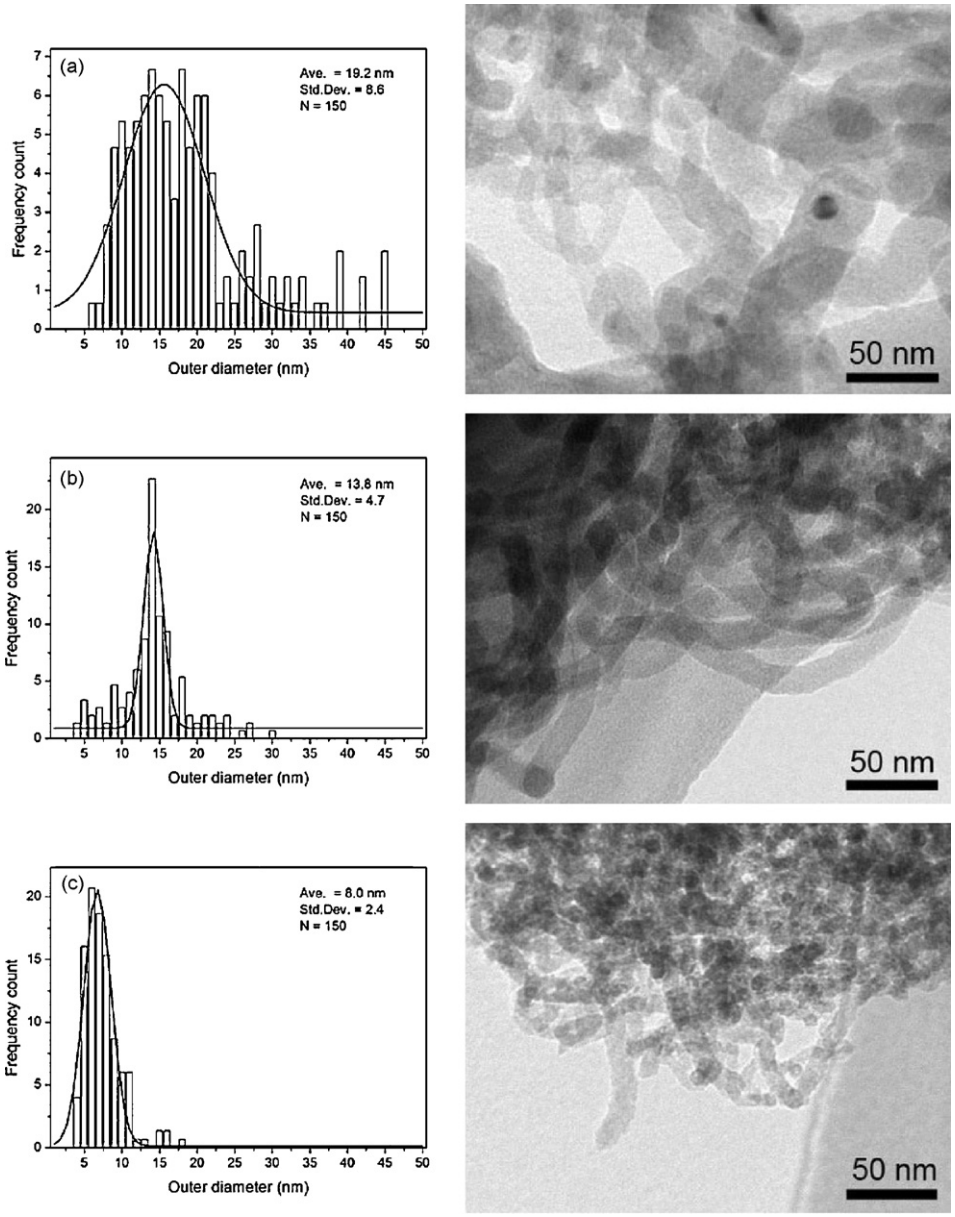

Fig. 2. (Left) Histogram of CNF diameter distributions; (right) TEM images of CNF grown (a) 0 V/mm, (b) 25,000 V/m, and (c) 50,000 V/m.

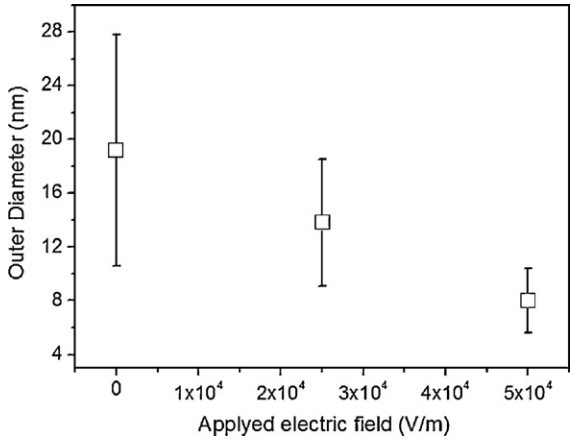

Fig. 3. Plot of the average diameters ± standard deviation of CNFs as a function of electric field.

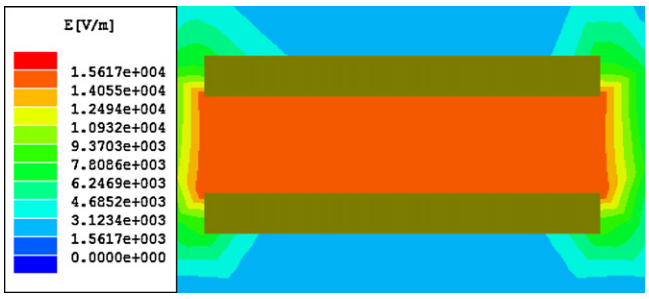

Fig. 4. Macroscopic electric field between two electrodes.

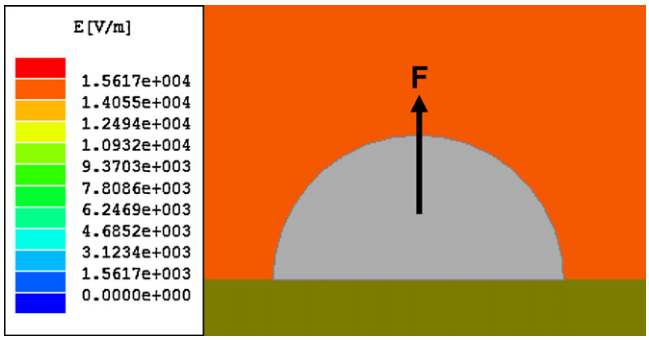

Fig. 5. Local electric field around a Ni catalyst particle and electric force upon it.

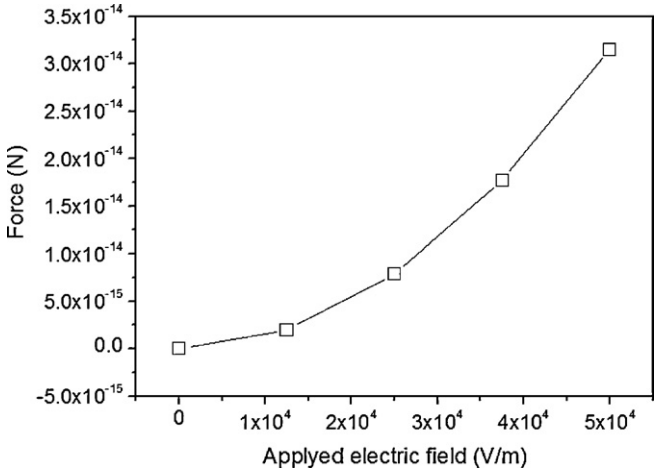

Fig. 6. The electric force acting upon a catalyst particle as a function of electric field.

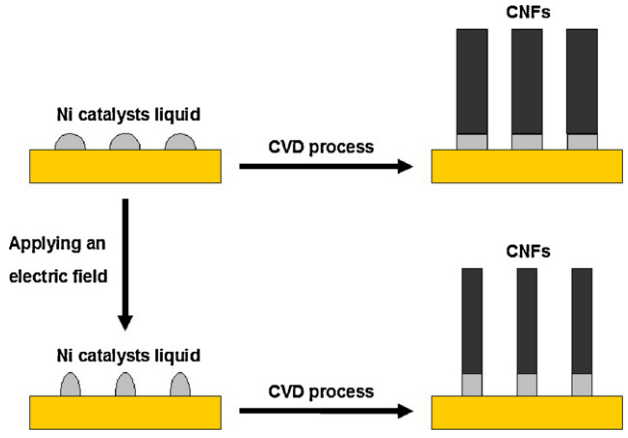

Fig. 7. Schematic diagram of electric-field-induced diameter control of CNFs.

enhancing. Finally, the stretch of Ni catalyst liquid maintains stable when the three kinds of force achieve equilibrium. When electric field enhancing, the stretch of Ni catalyst liquid will increase and the diameter of the Ni catalyst becomes smaller, so that smaller CNFs are obtained, as illustrated in Fig. 7. Therefore, controlling the CNF diameter can be put into practice through changing the electric field to adjust the stretch force upon catalyst liquid and control the size of Ni catalyst.

4. Conclusions

When producing CNFs in a CVD system, applying an electric field can control the CNF diameter and narrower the diameter distribution. The theoretical calculation revealed that the Ni catalyst particles become liquid at the reaction temperature and are stretched under the electric field to become smaller so that CNFs grew from the Ni nanocrystal had smaller diameter. The present method has advantages of controlling the CNF diameter continuously and exactly.

Acknowledgments

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