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DC Biasing Effects on Carbon Nanotube Formation in Microgravity Diffusion Flame

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Abstract

The effects of a direct-current electric field on carbon nanotube(CNT) synthesis in a flame method utilizing a planar diffusion flame were investigated under microgravity and atmospheric pressure.

Ethylene and oxidizer(75vol%O_2-25vol%Ar) are supplied to the parallel rectangular burner to form the planar diffusion flame above it. 100%Ar is ventilated around the flame. Ferrocene was used as a metal catalyst for CNT formation. Carbonaceous compounds generated in the flame were collected on biased TEM grids and analyzed by TEM. The results showed that electric bias strongly affects the CNT formation. One new finding of the study is the existence of a specific condition to generate large amounts of CNT with aid of DC bias, where no CNT was formed without the DC bias.

1. Introduction

Since CNT were discovered in 1991, numerous techniques have been developed for the synthesis of CNT, including arc discharge[1], laser ablation[2], chemical vapor deposition(CVD)[3]-[5], and flame synthesis method. The flame synthesis method offers a number of advantages over the other methods, because it has no need for complicated equipment such as an electric furnace, vacuum chamber, arc discharger, or laser but is simply arranged and put into effect. As a result the flame synthesis method developed here would be easier to scale-up than the other methods. Moreover, the supplied fuel in the method acts as a carbon source, so the fuel system can also be simplified.

There are a number of reports of CNT formation by the flame method[6]-[10], but the conditions and mechanisms of flame synthesis have not been fully established. One reason why flame synthesis is not understood well is that flames formed under normal gravity are complicated by natural convection. To remove the influence of natural convection on flame synthesis, a microgravity environment was utilized in the investigation here.

The flame zone for the CNT formation field in the present work includes a variety of ions, chemical species, and electrons. Therefore, the flame would be affected by the electric field[11]. It has been reported that an electric field promotes the CNT growth rate and forms vertically aligned CNTs on catalytic substrate[12,13]. However, the effects of an electric field on the initiation of CNT synthesis in the flame method have not been reported. This study investigates the effects of direct-current(DC) electric bias on CNT synthesis in microgravity diffusion flames to establish the initiation process of CNT formation.

2. Experimental

A pyrex-glass parallel slot burner was employed to establish the planar flame, as shown in **Fig.1**. Fuel (ethylene) is supplied from a 5mm x 50mm slot (30mm/sec.) and oxidizer gas (75vol%O_2-25vol%Ar) is supplied from another 8mm x 50mm slot (30mm/sec.). The exits of fuel and oxidizer gas are stuffed with glass-wool to obtain uniform gas flows of both fuel and oxidizer. Argon (30mm/sec.) is ventilated around the flame parallel to the burner, so that the flame is formed only at the boundary between fuel and oxidizer, not at the outside of the burner.

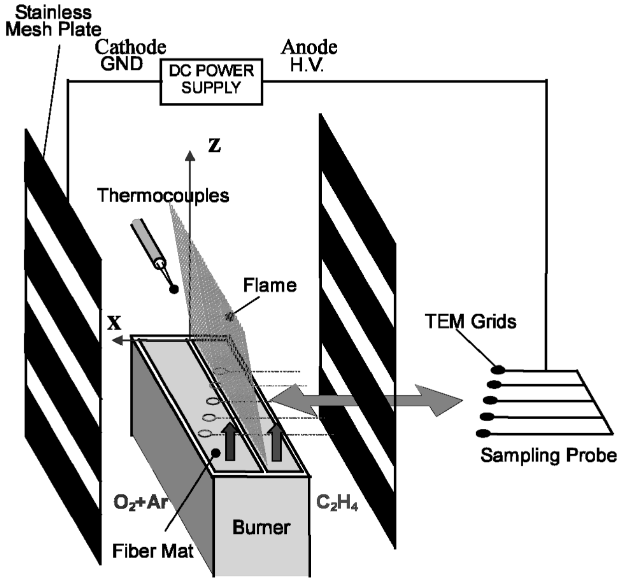


Fig.1 Burner set up

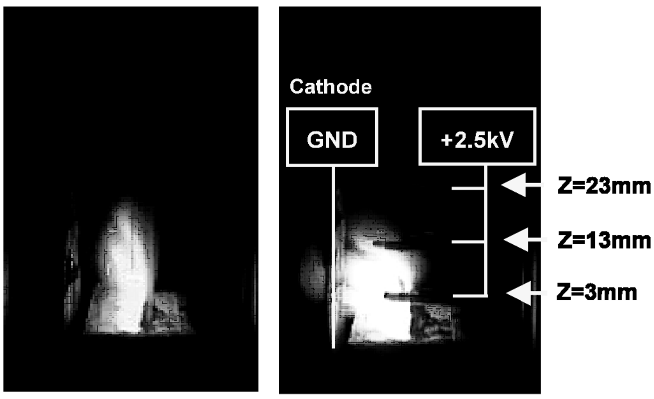
Thermophoretic sampling was employed to capture the products formed around the flame on TEM (Transmission Electron Microscopy) grids which are made of thin copper plate. Since there are limitations in the number of opportunities to conduct microgravity experiments, sampling was carried out simultaneously at several positions. The insertion period into the flame was about 0.7s. A TEM(Japan Electron Optics Laboratory Co., Ltd. JEM2000FX) was used to analyze the deposit on the grid without processing or purification. The relative abundance of CNT was determined on the basis of TEM images of the sampled material.

Ferrocene($(C_5H_5)_2Fe$), which is used as a metal catalyst for CNT synthesis, is sublimated by an electric heater located upstream of the fuel slot and is carried into the flame with the fuel flow. The flow rate of ferrocene is about 0.21mg/min.

This study investigated the effects of a DC electric field on the formation of CNT. Stainless steel mesh plates are installed near the oxidizer and fuel slot, as shown in Fig.1. A 2.5kV DC voltage was applied between the stainless mesh plate at the oxidizer side and the sampling probes. After the flame is ignited and a stable flame has been established, the electric field is added and the biased sampling probes are inserted into the flame. Therefore, a strong electric field is employed only during the sampling, and especially near the sampling grids. Five grids at the same height are inserted into the flame simultaneously to observe the effect of the sampling position relative to the flame position as shown in Fig.1. Though the difference of sampling position may cause some differences of electric field strength, the authors assume that the primary effect of electric field on the CNT formation could be investigated with the system because the strongest electric field attained only at very close position to the electrode[14]. The experiments were carried out in microgravity attained by parabolic flights of an air plane managed by Diamond Air Service Inc.(DAS). The flight provides around 20-seconds of microgravity and a gravity of less than 3×10^{-2} G.

3. Results and Discussion

It is known[11] that a major effect of electric fields on flames is governed by the body force caused by positive ions in the flame, also known as an ionic wind. **Fig.2** shows images of flames without and with DC bias. It is observed that the luminous flames are attracted to the cathode in Fig.2(b). In the method proposed here, the flame is exposed to the electric field when sampling grids are inserted into



(a) without DC bias (b) with DC bias

Fig.2 Ethylene diffusion flames

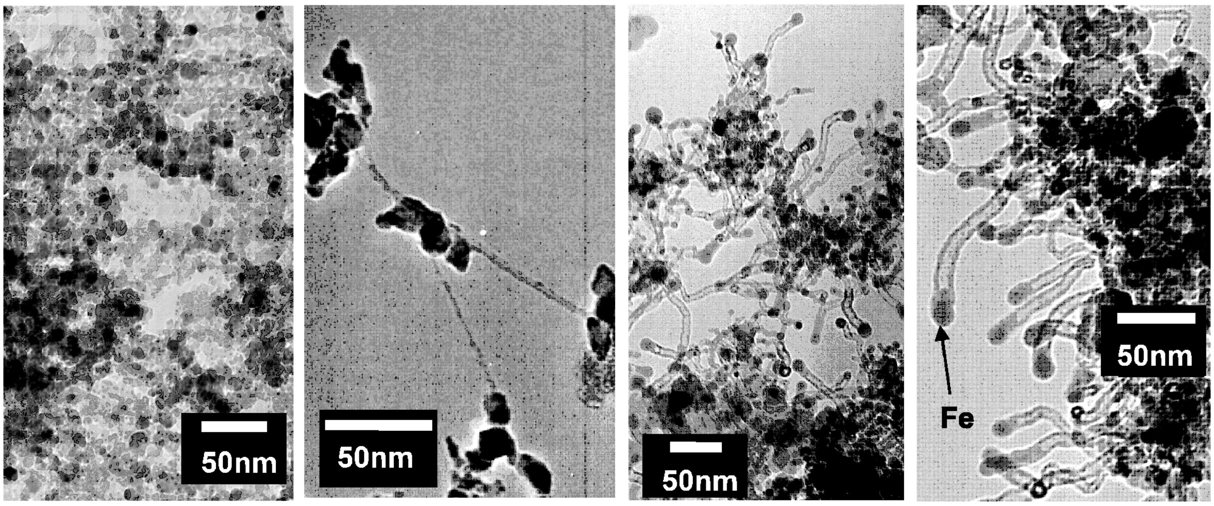
the flame because a high voltage bias is applied to the sampling grids. In general, the gradient of an electric field near the electrode plate is much steeper than at positions away from the electrode, so the strong electric field is formed in a limited area near and around the sampling grids. Ions and electrons are strongly accelerated by the electric field in the area close to the electrodes.

When the sampling grids are inserted into the flame, carbonaceous compounds formed in the flame drift to the sampling grid and deposit on the grid by thermophoretic and electrostatic induction forces. This allowed carbonaceous compounds in the flame to be sampled by the grids both with and without DC bias application.

In the sampling without bias, there were no CNT in the sampled compounds. The sampled compounds in the flame without DC bias look like clusters which contain catalyst particles covered with amorphous carbon(See **Fig.3(a)**). When DC bias is applied to the sampling grids, much CNT is generated. Two types of CNT were observed with the DC bias, a relatively thin and straight [Type-1] CNT (**Fig.3(b)**), and a thick and wavy [Type-2] CNT (**Fig.3(c)**). Both Type-1 and Type-2 are accompanied by agglomerated clusters, and it appears that the CNT has grown out of these clusters. **Fig.3(d)** shows an enlarged image of Type-2 CNT. The EDX analysis showed that Type-2 CNT includes a Fe catalyst particle at the tip of the CNT. This suggests that a tip growth mechanism[15] may be involved in the Type-2 CNT formation in this condition. As described here, CNTs are formed with DC bias application, while no CNT is formed with the condition without DC bias. This implies that the DC bias application could be a cause of the initiation of CNT formation, which is a newly established result of the present study.

The TEM grid has many polygonal holes, and the number of CNTs on a unit length of a hole edge (typical length of a side of hole is about 210 μm) were counted with TEM images. The averaged number of CNTs on three-holes in the vicinity of the center of the grid were used. This evaluation includes uncertainties because an exact count is not possible due to the overlap of CNTs, covering with soot-like media and the limitations of the focal depth, however the amount of CNT could be estimated qualitatively. The number of CNTs was classified into five grades, and **Fig.4(a)** shows the CNT formation by the five grade classification for Type-1 and Type-2 CNT.

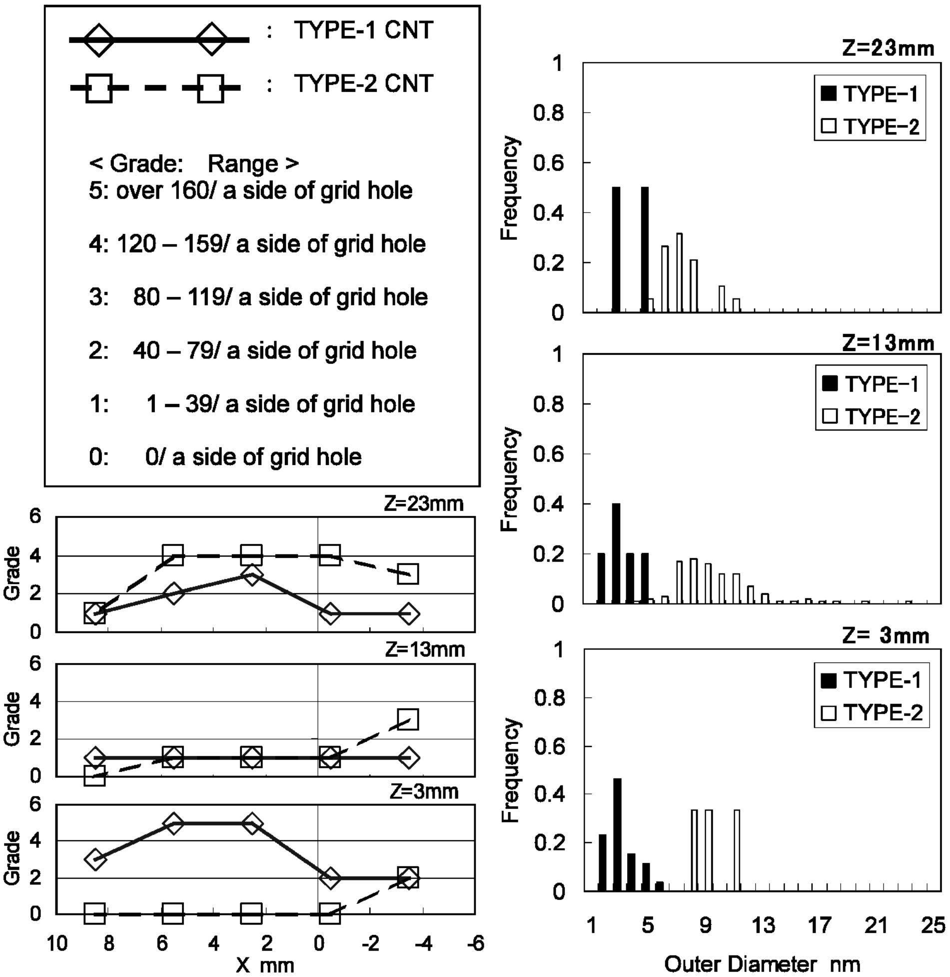
In the upstream area(Z=3mm), the Type-1 CNT generated at the oxidizer side (X=2.5～8.5mm) is more numerous than that generated at the fuel side (X= -3.5 ～ 0.5mm). At Z=13 and 23mm, the dependence of the amount of Type-1 CNT on the X position is not clear. The Type-2 CNT generation is limited to the fuel side (X=-3.5mm) upstream area (Z=3mm), and the area broadens as the height above



(a) without DC bias (b) Type-1 CNT (c) Type-2 CNT (d) Enlarged Type-2 CNT

with DC bias

Fig.3 Sampled formed carbonaceous product



(a) CNT generating area (b) CNT diameter distribution

Fig.4 CNT generating area and diameter distribution the burner increases; the amount of generated Type-2 CNT increases with increasing Z.

The outer diameter of the CNTs were measured and classified from the TEM micrographs. Over 70 CNTs were measured at each sampling position, and the distributions of CNT diameters for Type-1 and Type-2 CNTs are shown separately. Some Type-2 CNTs have larger outer diameters at the tip of the CNT than at the root, and the average of three positions (tip, center and root) of these CNT was calculated as the CNT diameter of Type-2 CNTs. **Fig.4(b)** shows the distribution of CNT outer diameters with the DC 2.5kV bias.

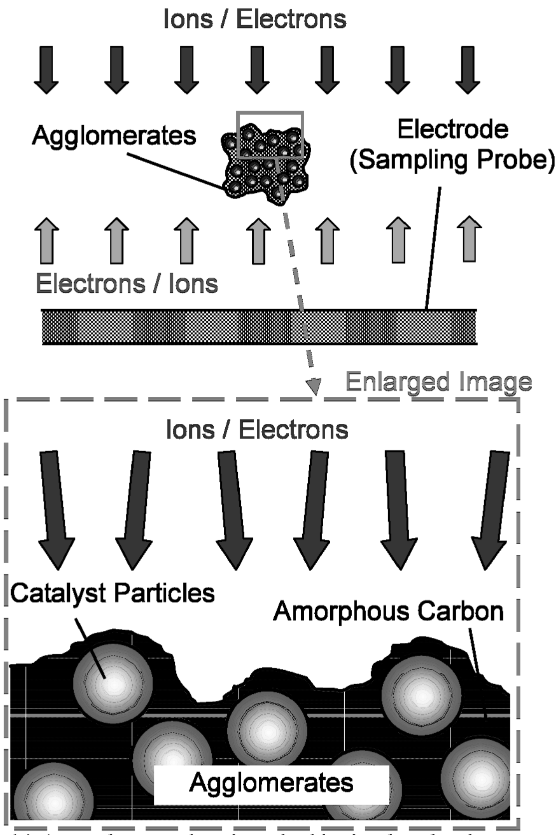
It was observed that the Type-1 CNT has a narrow distribution in a small diameter range(less than 6nm), while the Type-2 CNT has a broader distribution in a larger diameter range(4-23nm). In the upstream area (Z=3mm), Type-2 CNTs are limited to within a given outer diameter of less than 11nm. It is known[16] that the CNT diameter depends on the size of the catalyst particles. Therefore, this result suggests that the catalyst particles do not reach large sizes, or that the amounts of dissolved carbon in the catalyst particles is not sufficient to form the large diameter CNT at Z=3mm. In the downstream area(Z=13 and 23mm), there are larger diameter CNTs than in the upstream region. In spite of the short exposure time to the flame, CNTs were observed in all the sampling positions with DC bias, even at Z=23mm where no visible flame appears.

Two biasing effects that may occur in CNT generation have been reported[13]: (1) to help well-aligned CNT formation and (2) to increasing the CNT growth rate. Although the mechanism of the second effect is not fully established, it is suggested that the CNT growth rate is increased by the ion supply[17], that is, ionic compounds transported by electric bias enhances the ion supply to the catalyst particles.

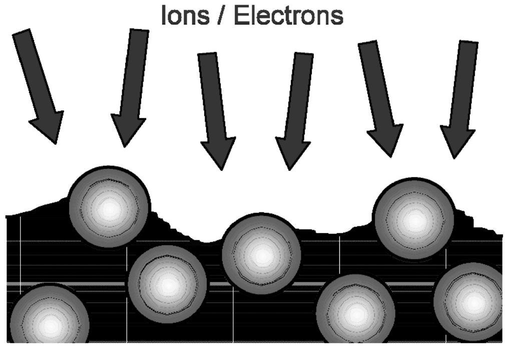
According to this explanation, ionic compounds (and/or electrons) may hit the catalyst surface especially when there is a strong electric field to accelerate ions or electrons near the catalyst, and this ion bombardment etches the amorphous carbon. It is suggested[12] that the relatively weak amorphous carbon would be removed by electron strike while the CNTs are being grown.

In the flame conditions of this study, a large amount of soot is formed, and the formed soot suppresses the CNT synthesis because catalyst(Fe) particles are covered with amorphous carbon without the DC bias[See Fig.3(a)].

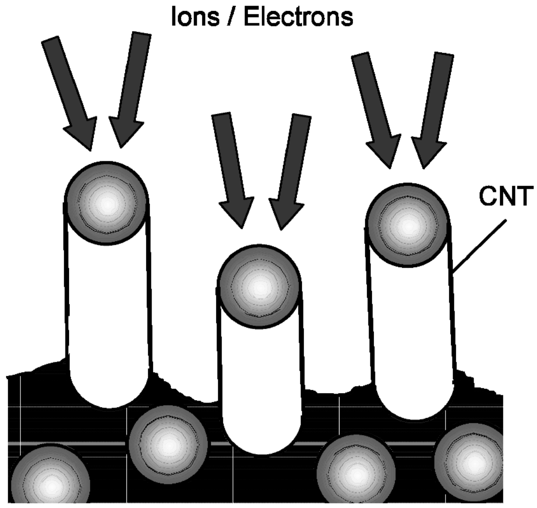
In the case with DC bias, we propose a model of the initiation of CNT synthesis as shown in **Fig.5**. When the biased sampling grids were inserted, positive ions and electrons, generated in the flame, are accelerated by the electric field, and move toward cathode and anode, respectively. Near the



(a) Amorphous carbon is etched by ion bombardment



(b) Fe particles recovered the catalytic activity



(c) CNT synthesis is initiated

Fig.5 Proposed model of the initiation of CNTsynthesis with DC bias condition electrode positive ions or electrons bombard floating agglomerates which include catalyst(Fe) particles and the relatively weak amorphous carbon which covers the catalyst surface is etched. Consequently, the CNT synthesis is initiated because Fe particles recovered the catalytic activity as the amorphous carbon is removed from the catalyst surface.

4. Conclusion

CNTs formation in flame method with DC bias is examined by using the ethylene diffusion flame under microgravity. It was found that there were no CNT in the sampled compounds without DC bias at the sampling condition adopted in the present work, while there were much CNT with DC biased sampling grid. It is considered that the CNT synthesis is initiated with DC bias because Fe particles recovered the catalytic activity as the amorphous carbon is removed from the catalyst surface by ion bombardment induced by DC electric field.

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