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Characterization of bias-controlled carbon nanotubes

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Abstract

In this study, we focus on the immediately improving quality of growing carbon nanotubes without any pre- or post-treatment. The applied biases during the reaction can directly control the diameter and the quality of carbon nanotubes. This simple step skips additional treatments and is easily used in many deposition systems. The diameter of carbon nanotubes noticeably varies from 45 nm without any amorphous carbon (under +80 V) to 120 nm (under −120 V). Raman spectrums indicate that I_D/I_G ratio decreases with increasing positive bias. This implies applying positive bias could enhance the graphitization of carbon nanotubes. However, positive and negative bias effects slightly vary the field emission enhancement. In addition, carbon nanotubes grown under positive bias possess better field emission characterization. This results from the following reasons: (I) smaller diameter; (II) pure surface; (III) more graphitized structure; and (IV) higher field enhancement β.

Keywords: Bias-effect; Carbon nanotubes; Raman spectrum; Scanning electron microscopy

1. Introduction

Carbon nanotubes (CNTs), since their first discovery in 1991 [1], have been considered for many different applications. Their small dimension, strength and the remarkable physical properties of these materials make them the most promising emitters for field emission devices. Due to the size-effect and structure diversity of nanomaterials, the physical properties strongly depend on their atomic-size structure, size and chemistry [2]. Different diameter, length, chirality of CNTs gives rise to diverse physical and mechanical properties. Before growing CNTs, the pre-treatment of catalyst to synthesize higher density and smaller diameter of CNTs is needed. These methods include varying the morphology; thickness; distribution and size of as-deposited catalyst [3–5] to reduce the grain size of catalyst. Besides, the post-treatment to purify the CNTs is usually used to remove the amorphous carbonaceous impurities on the surface of CNTs [6].

In this study, immediately improving the quality of CNTs during deposition is the main topic. Compared to the aforementioned treatment; applying bias voltages during growth in situ reforms the growing CNTs directly. Furthermore, both positive and negative bias effects on the characterization of growing CNTs have been completely discussed.

2. Experiment

The 150 nm Palladium (Pd) catalysts was deposited on Si by using electron beam evaporation. The reactive gas mixture was CH_4/H_2 with a flow rate of 10/40 sccm. The applied microwave power and pressure during the growth of CNTs were 400 W and 15 Torr, respectively. An optical pyrometer was used to monitor the substrate temperature, that was maintained at approximately 700 °C. Biasing system was conducted with upper and lower electrodes made of Mo with a distance of 1 cm. Samples were placed on the Mo holder, which is attached to the lower grounded electrode. Various biases were applied on the sample, ramped from −160 V to +160 V with the interval of 40 V. The growth time lasted for 10 min. Table 1 clearly lists the growth conditions.

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Table 1
Deposition conditions of CNTs grown under various biases

Sample	[a]Applied bias (V)	[b]Current (mA)
A	−160	16∼20
B	−120	12∼13
C	−80	8∼10
D	−40	3∼5
E	0	0
F	+40	2∼4
G	+80	6∼7
H	+120	11∼13
I	+160	15∼18

Flow rate of reactive gases: $H_2/CH_4=40/10$, Microwave power: 400 W, Substrate temperature: ∼700 °C, Growth time: 10 min, Pressure: 15 Torr.

[a] means the bias applied to the lower electrode as compared with the upper electrode. Thus, conditions A∼D present the samples grown under negative biases.

[b] means the current measured from upper to lower lower electrodes.

3. Results and discussion

3.1. Scanning electron microscope (SEM)

Fig. 1 and Fig. 2 present the scanning electron microscope (SEM) pictures of CNTs grown under various biases. The photograph on the right of each figure is the enlarged image. It clearly displays that the morphology of CNTs changes with various applied biases. According to our SEM results, the relationship between diameter and different bias is plotted in Fig. 3. Each data is the average value of five samples. Obviously, the diameter of CNTs increases with increasing negative bias. Fig. 1 a indicates that CNTs will grow to a sub-micrometer diameter under a higher bias (more negatives than −120 V), revealing that negative biases drastically enhance the growth of CNTs on Pd films.

However, Fig. 2 shows the reverse trend toward increasing positive biases. The diameter of CNTs can

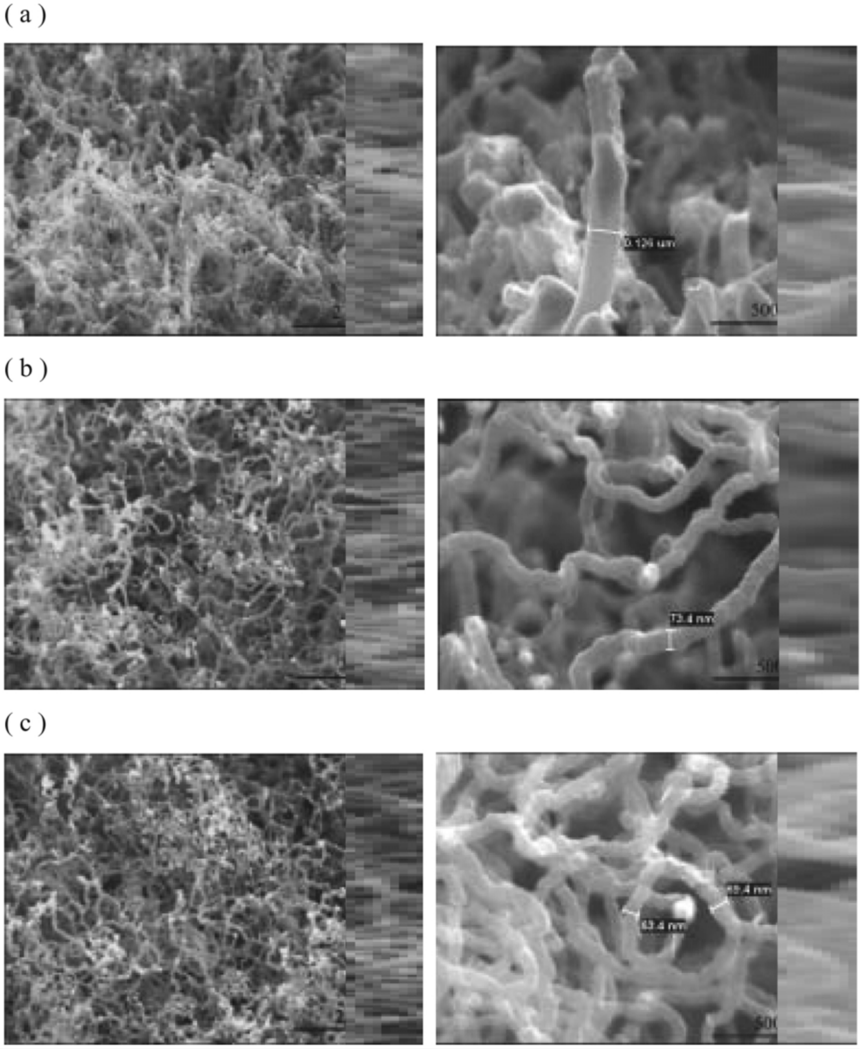

Fig. 1. SEM photographs of CNTs grown under (a) −120 V; (b) −80 V; and (c) 0 V.

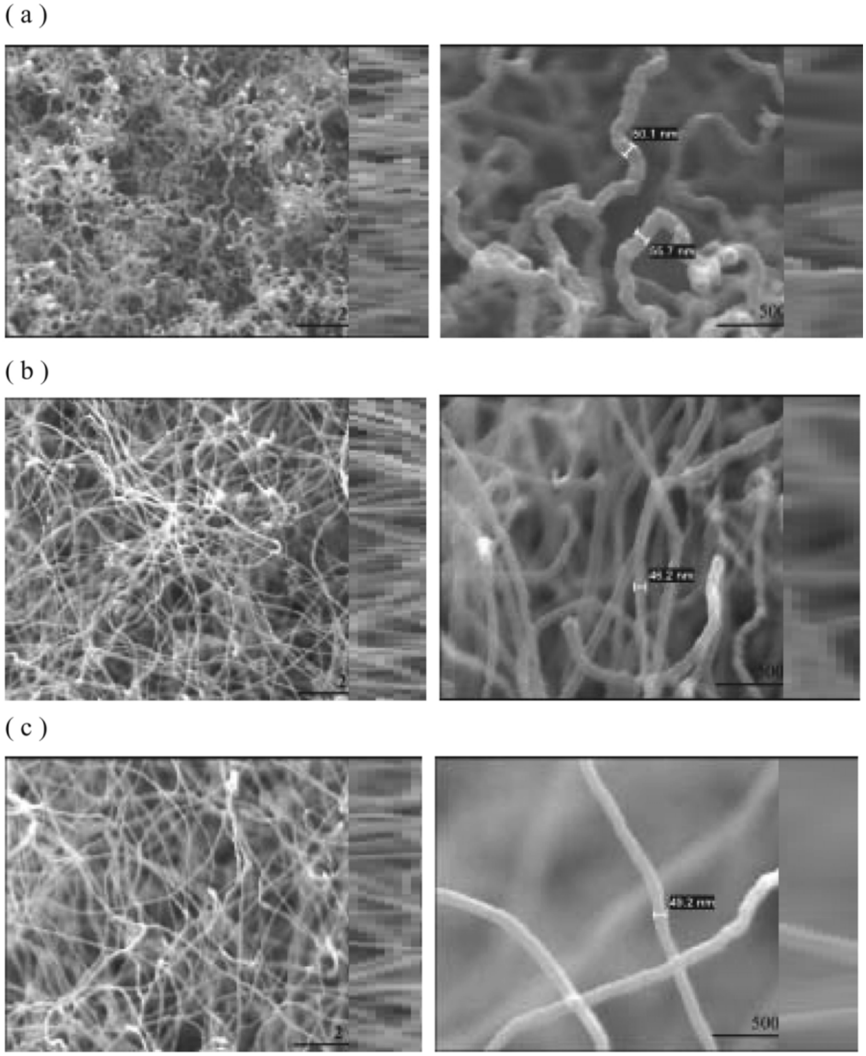

Fig. 2. SEM photographs of CNTs grown under (a) +40 V; (b) +80 V; and (c) +120 V.

be reduced from 65 nm (under 0 V) to approximately 45 nm (under +80 V). Although a positive bias effect decreases the diameter of CNTs, the change of diameter slightly varies under a higher positive bias (more positives than +120 V). Except for the various biases subjected on the samples, it is worth emphasizing that all samples grown under the same conditions, such as thickness of Pd, microwave power and growing time, and so on. Thus, the change of diameter of CNTs result only from different bias during growth.

Unlike the crooked CNTs grown under negative bias, straighter CNTs are easily found in a positive bias condition. Besides, the surface of CNTs grown under positive bias is pure without amorphous carbon (a-C). It is believed that more ions bombard the sample in the plasma under negative bias. Meanwhile, the accelerated carbon species will be accumulated on the sample. This causes the higher growth rate of CNTs with larger diameter in negative bias condition than in positive one. Many reports have presented the method to enhance the nucleation density of diamond by applying negative bias [7–9]. However, under positive bias condition, more electrons strike the sample and remove the a-C gradually.

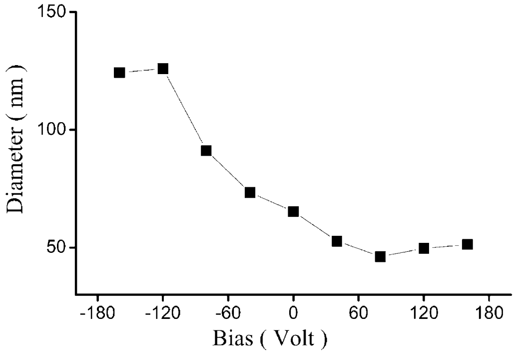

Fig. 3. Diameter of CNTs as a function of applied biases.

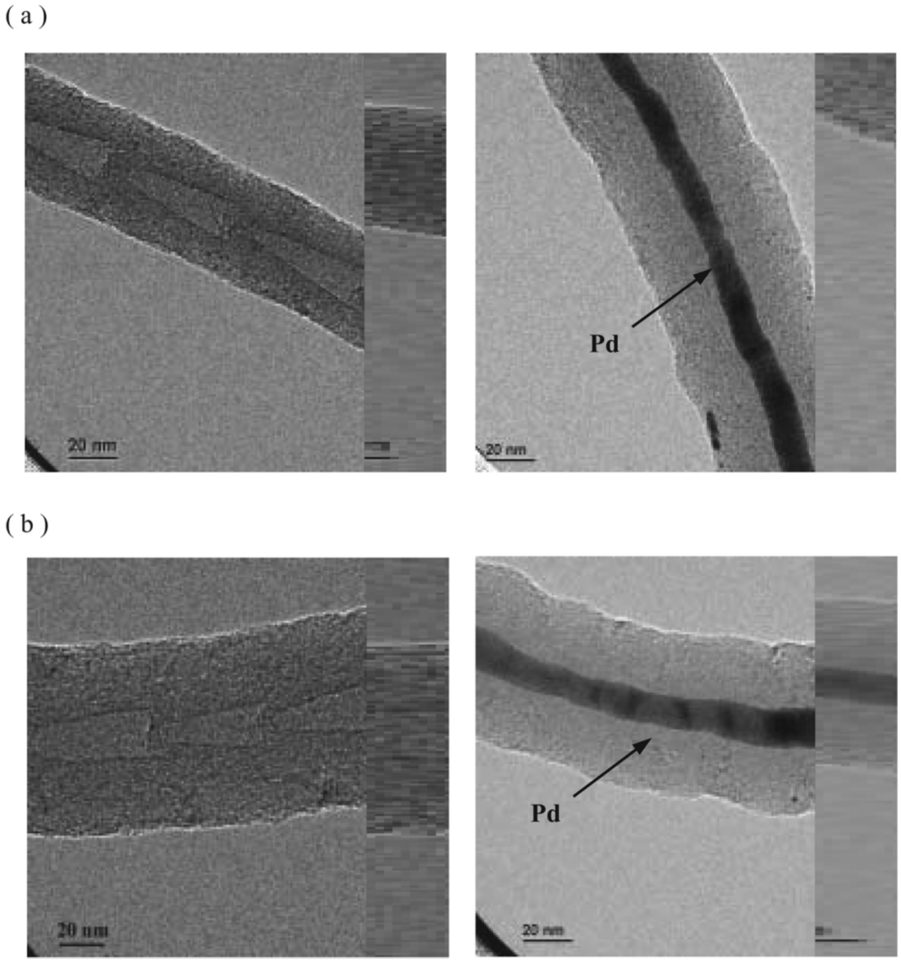

Fig. 4. TEM images of CNTs grown under (a) positive and (b) negative biases.

Thus, it makes the diameter decrease and the surface pure without a-C.

3.2. Transmission electron microscope (TEM)

Fig. 4a and b exhibit the transmission electron microscope (TEM) of CNTs grown under negative and positive biases. TEM images give two same shapes (I) fishbone-like tube and (II) tube filled with catalysts. Although the morphology of CNTs differs from various biases, there is no difference on the nanostructure. Besides, the CNTs grown under 0 V also have two same shapes, indicating that bias effect does not vary the nanostructure of the CNTs. The dark part shown by an arrow is identified as Pd by energy dispersive spectrometers (EDX).

3.3. Raman spectra

Fig. 5a exhibits the Raman spectra of CNTs grown under various biases. All of them have two sharp peaks located at approximately 1345 cm^{-1} and 1580 cm^{-1}, respectively. The peaks imply that CNTs are characteristic of graphite. The first-order Raman spectrum of CNTs shows strong sharp peaks at 1581 cm^{-1} (G line), which is the high-frequency E_2g first-order mode and 1350 cm^{-1} (roughly corresponding to the D-line associated with disorder-allowed zone-edge modes of graphite). The 1350 cm^{-1} band is normally explained by relaxation of the wave vector selection rule, due to the effect of the finite size of the crystal in the material [10,11]. Normally, the intensity of the 1350 cm^{-1} peak increases (i) with an increase in the amount of unorganized carbon in the samples and (ii) with a decrease in the graphite crystal size. In Fig. 5b, it is found that the I_D/I_G ratio decreases with increasing positive biases. Positive bias process makes CNTs possess lower I_D/I_G ratio, implying the more graphitized structures, thereby improving their properties. This phenomenon is corresponding to the previous SEM results.

3.4. I–V characterization

The field emission tests are performed on a diode structure, in which CNTs are separated from the anode, indium-tin-oxide glass, using 500 μm glass as spacers. The emission current (I) is then measured as a function of anode-to-cathode voltage in a vacuum of 1×10^{-6} Torr. The Fowler–Nordheim theory [12] is the most commonly used model for the emission of cold electrons from a metal under a strong applied field. The total current as a function of the local field at the emitter surface F is approximately given by $I\propto(F^2/\phi)$ $\exp(B\phi^{3/2}/F)$, with $B=6.83\times10^7$, and ϕ the work function in electron volt. F is ususlly taken as $F=\beta E=\beta V/d$, where V is the applied voltages, d the distance between cathode and anode, β the field enhancement, and $E=V/d$ the macroscopic field. When Ln (I/V^2) is plotted vs. $1/V$ (F–N plot), one should obtain a straight line with a slope that depend on β, ϕ and d. Fig. 6a and b displays the I–V curve and F–N plot of CNTs grown under −120, 0 and +120 V. We further estimate the field enhancement β from the constant F–N slope in the low current regime with $d=500$ μm and $\phi=5$ eV as for graphite and C^{60} [13]. β is obtained for approximately 2590, 2690 and 2770 corresponding to −120 V, 0 V and +120 V, respectively. It seems that positive and negative bias effects slightly vary the field emission enhancement. The difference may be resulted from the various diameters, geometry and the graphitized structure of CNTs. According to I–V result, it clearly exhibits that CNTs grown under positive bias possess the best field emission property, that is, a turn-on field of 1.38 V/μm and 655 μA/cm^2 under 2.2 V/μm than those grown under zero and negative bias. It is attributed to the following reasons such as: (I) smaller diameter; (II) pure surface, (III) more graphitized structure of CNTs; and (IV) higher field enhancement β.

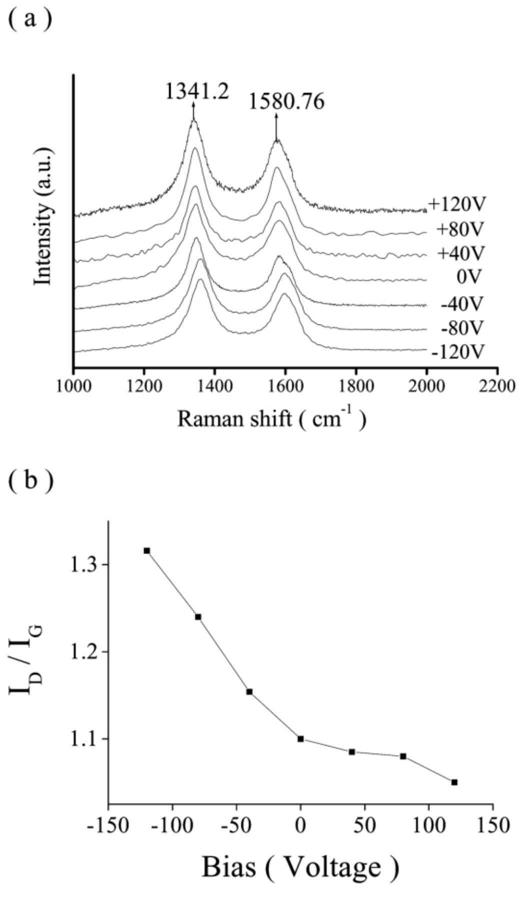

Fig. 5. (a) Raman spectra of CNTs grown under various biases and (b) the I_D/I_G ratio as a function of applied biases.

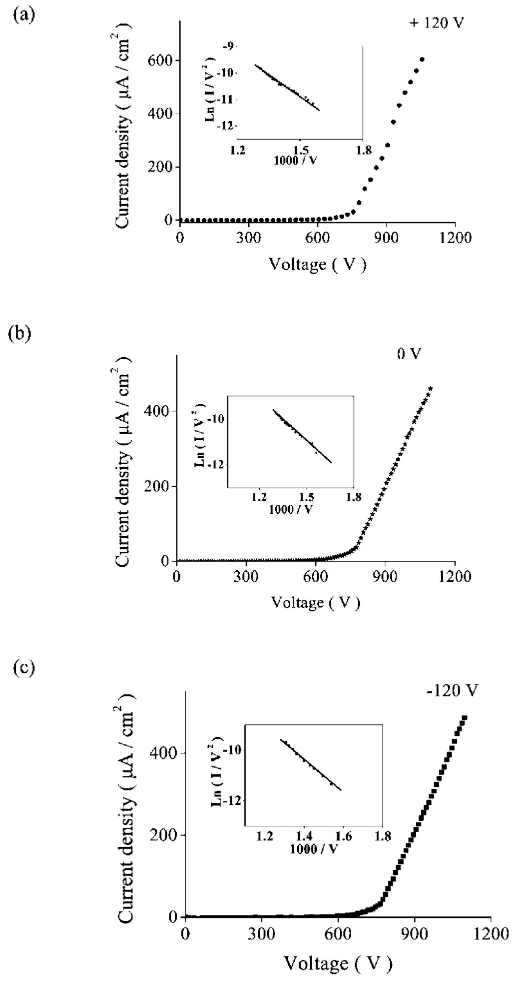

Fig. 6. The I–V curve and an insert of F-N plots of CNTs grown under (a) +120 V, (b) 0 V and (c) −120 V, respectively.

Acknowledgments

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