

Chapter 6

Bias and reactive gases effects on the growth of carbon nanotubes

6.1. 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 give rise to diverse physical and mechanical properties. Generally, 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 chapter, immediately improving the quality of CNTs during deposition is the main topic. Compared to the aforementioned treatment; applying bias voltages directly reforms the growing CNTs. Furthermore, both positive and negative bias effects on the characterization of growing CNTs have been completely discussed.

Besides, the new reactive gas $\text{CH}_4\text{-CO}_2$, which is patent of our lab's invention is also used to generate CNTs in comparison with the conventional gases (hydrocarbon diluted in hydrogen). Owing to the high carbon concentration in the $\text{CH}_4\text{-CO}_2$, it is predicted to increase the growth rate of CNTs. These reactive gas mixtures may be applied in low growing temperature and high yield requirements.

A: Bias effect on the growth of carbon nanotubes

6.2A. Experiment

The 150 nm Palladium (Pd) catalysts films were deposited on Si by using electron beam evaporation. Then, substrates were put in microwave plasma chemical vapor deposition (MPCVD) to grow CNTs. The reactive gas mixture was CH_4/H_2 with a flow rate of 10/40 sccm. The applied microwave power for generating a plasma and pressure during the growth of CNTs were 400 W and 15 torr, respectively. Various biases were applied on the sample ramped from -160 V to +160 V with the interval of 40 V. The growth time and temperature were lasted for 10 minutes and 700°C , respectively.

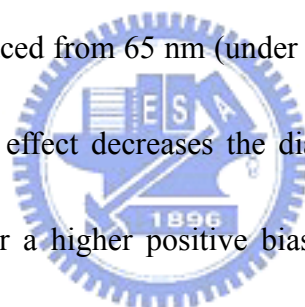
6.3A. Results and Discussion

(I) Scanning electron microscope (SEM)

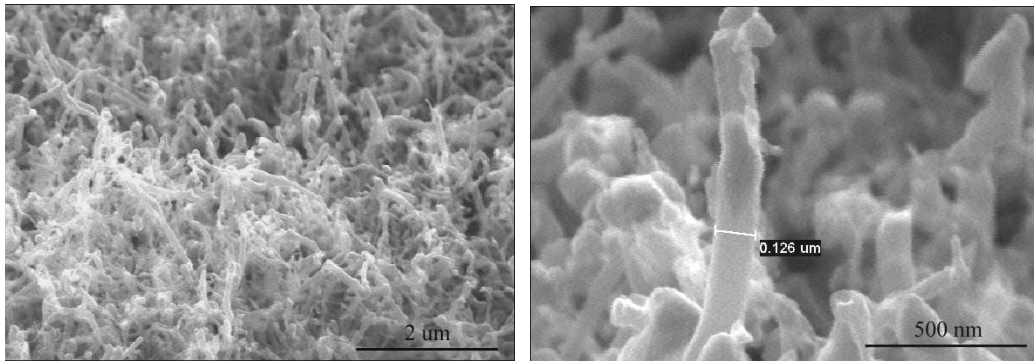
Figures 6.1 and 6.2 present the scanning electron microscope (SEM) pictures of CNTs grown under various biases. The photograph on the right of each figure is the

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. 6.3. Each data is the average value of five samples. Obviously, the diameter of CNTs increases with increasing negative bias. Fig. 6.1 (a) indicates that CNTs will grow to a sub-micrometer diameter under a higher bias (more negatives than -120V), revealing that negative biases drastically enhance the growth of CNTs on Pd films.

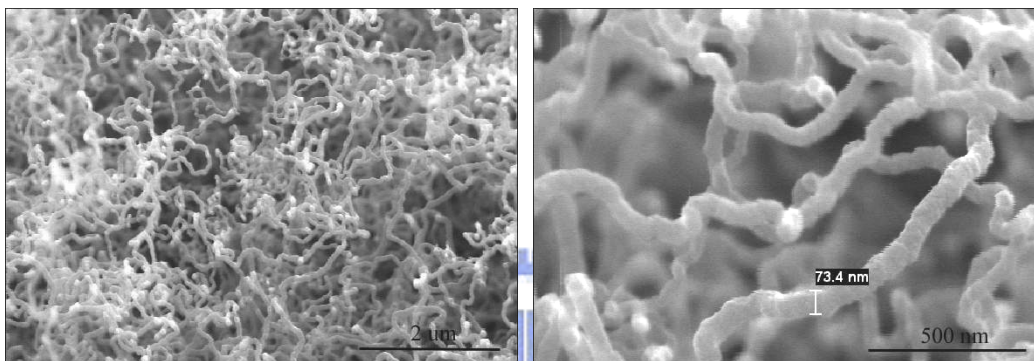
However, figures 6.2 show the reverse trend toward increasing positive biases. The diameter of CNTs can be reduced from 65 nm (under 0 V) to about 45 nm (under +80 V). Although a positive bias effect decreases the diameter of CNTs, the change of diameter slightly varies under a higher positive bias (more positives than +120V). 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 higher positive bias (+120 V) seems smoother than those grown on negative bias condition. This phenomenon indicates that CNTs grown under positive bias show more graphitized structures with less amorphous carbon (a-C).



(a) -120 V



(b) -80 V



(c) 0 V

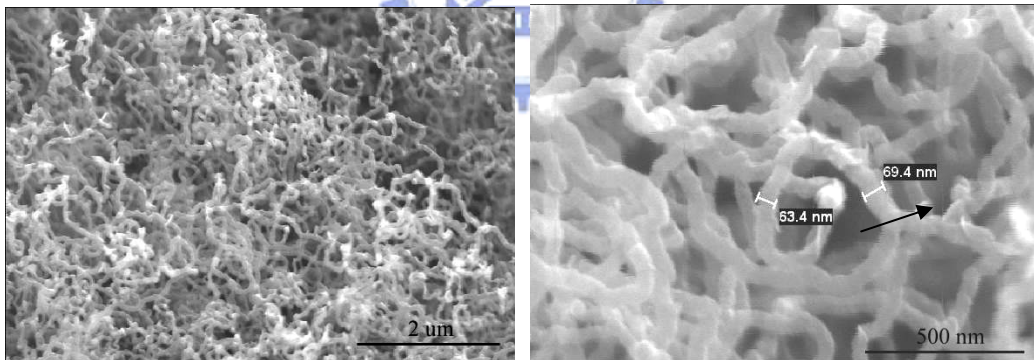
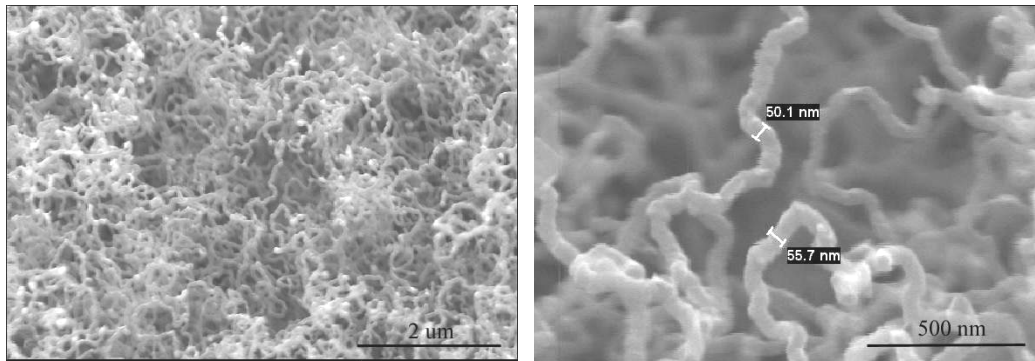


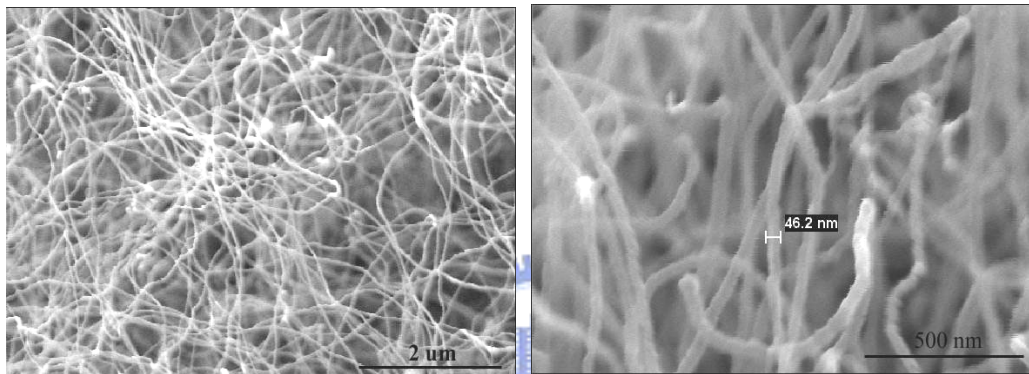
Fig. 6.1 SEM photographs of CNTs grown with CH_4/H_2 under (a) -120V; (b) -80V and

(c) 0V, respectively.

(a) +40 V



(b) +80 V



(c) +120 V

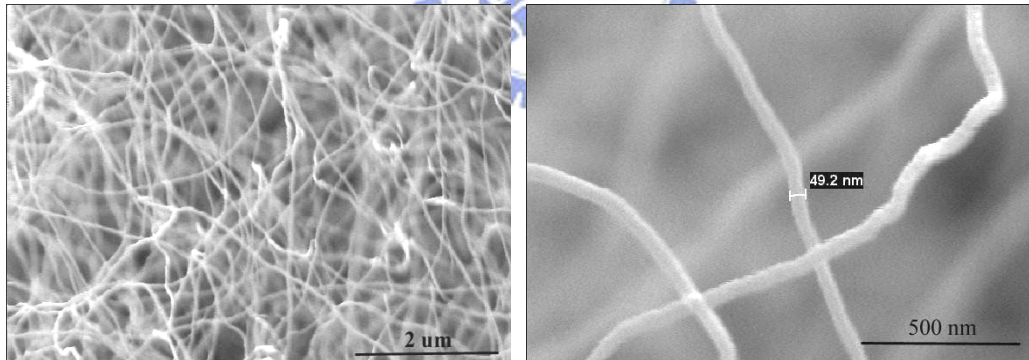


Fig. 6.2 SEM photographs of CNTs grown under (a) +40V; (b) +80V and (c) +120V,

respectively.

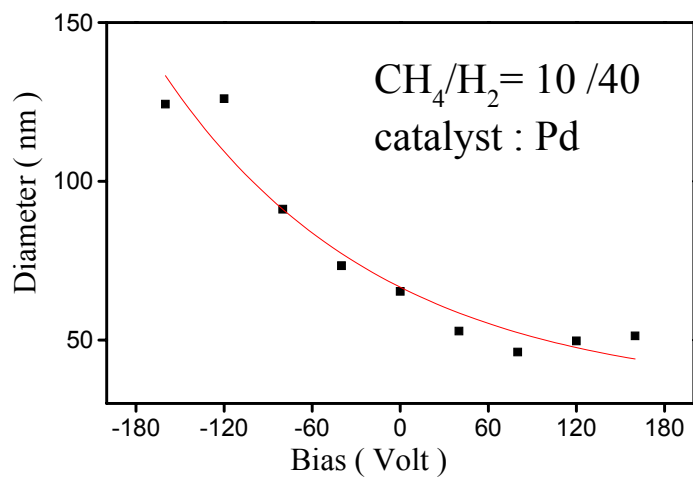
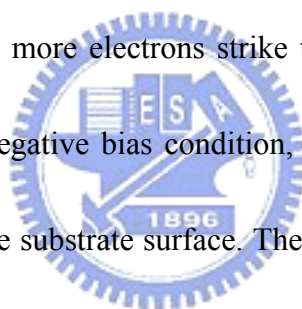


Fig. 6.3 Diameter of CNTs grown with CH₄/H₂ as a function of applied biases.



It is believed that more carbon-containing cations (C^+ , CH^+ , CH_2^+ , CH_3^+ , etc) bombard the sample in the plasma under negative bias. The negative bias accelerates cations in the plasma to the substrate surface. Meanwhile, the accelerated carbon species will be accumulated on the sample. Hence, these bombardments lead to high carbon concentration on the substrate surface, enhancing the growth rate of CNTs.

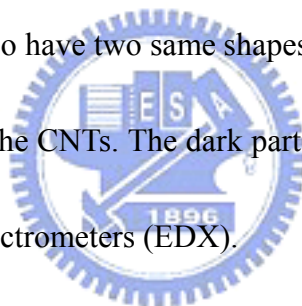
Due to the high increasing growth rate, negative bias effect also generates much amorphous carbon on the surface of CNTs. Many reports have presented the method to enhance the nucleation density of CNTs by applying negative bias [7-9]. However, under positive bias condition, more electrons strike the sample and remove the a-C gradually. Compared to the negative bias condition, it is assumed that the electrons influence the adsorbates on the substrate surface. The decomposition of molecules by the impinged electrons mainly occurred on the substrate surface. The decomposition of H_2 and CH_4 is increased by electron bombardment. These decomposed hydrocarbons effectively contribute to the nucleation of CNTs more than those formed in the gas phase because they are already on the substrate surface. Electron bombardment to the adsorbates on the surface enhances not only growth but also nucleation. The model of bias effect on the CNT growth is shown in Fig. 6.4. Meanwhile, electrons with high kinetic energy impinge the substrate surface and cause the substrate temperature to increase. The increase of nucleation and substrate



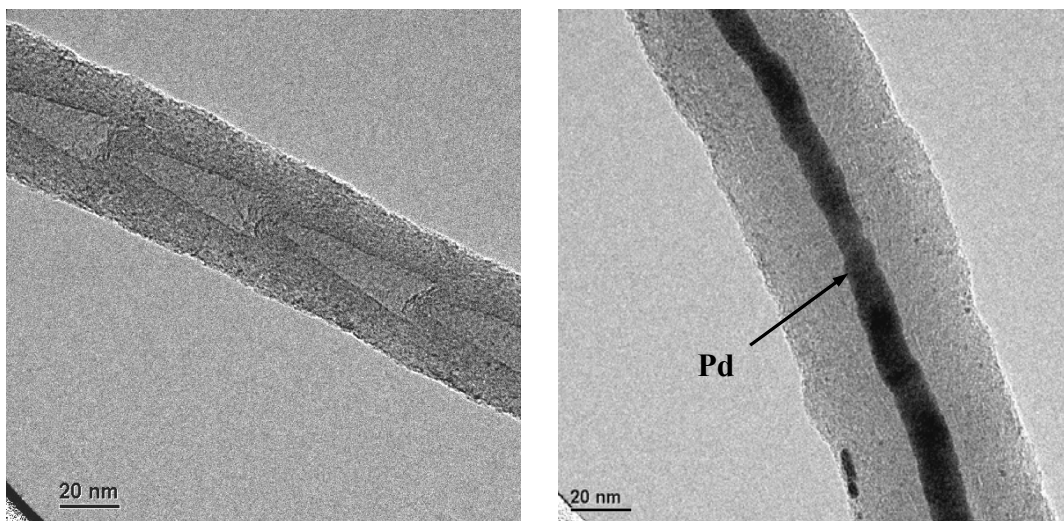
temperature makes the CNTs exhibit more graphitized structure with less a-C on the surface. It is worth emphasizing that both positive and negative bias effects enhance the growth rate of CNTs.

(II) Transmission electron microscope (TEM)

Figure 6.5 (a) and (b) exhibit the transmission electron microscope (TEM) of CNTs grown under negative and positive biases. TEM images give the two same shapes (I) fishbone-like tube and (II) tubes 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).



(a) Positive bias



(b) Negative bias

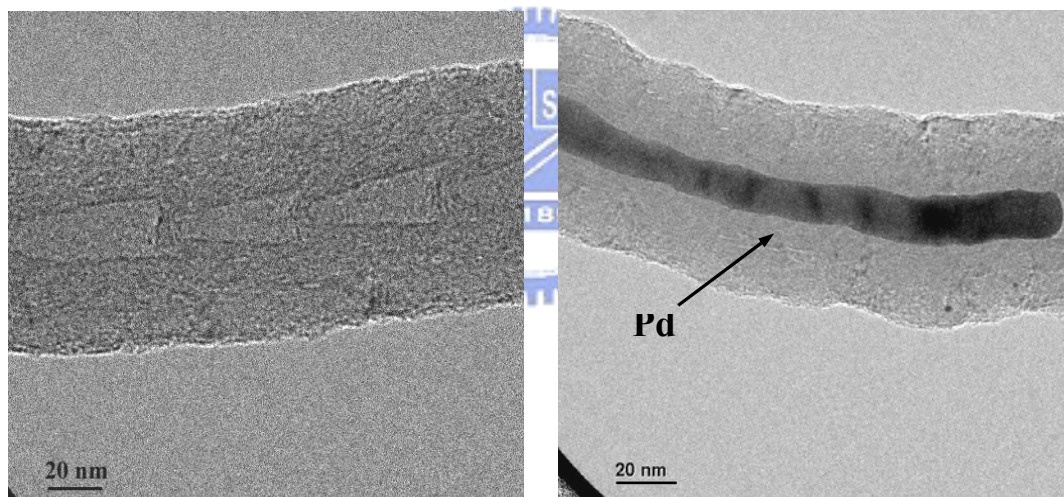
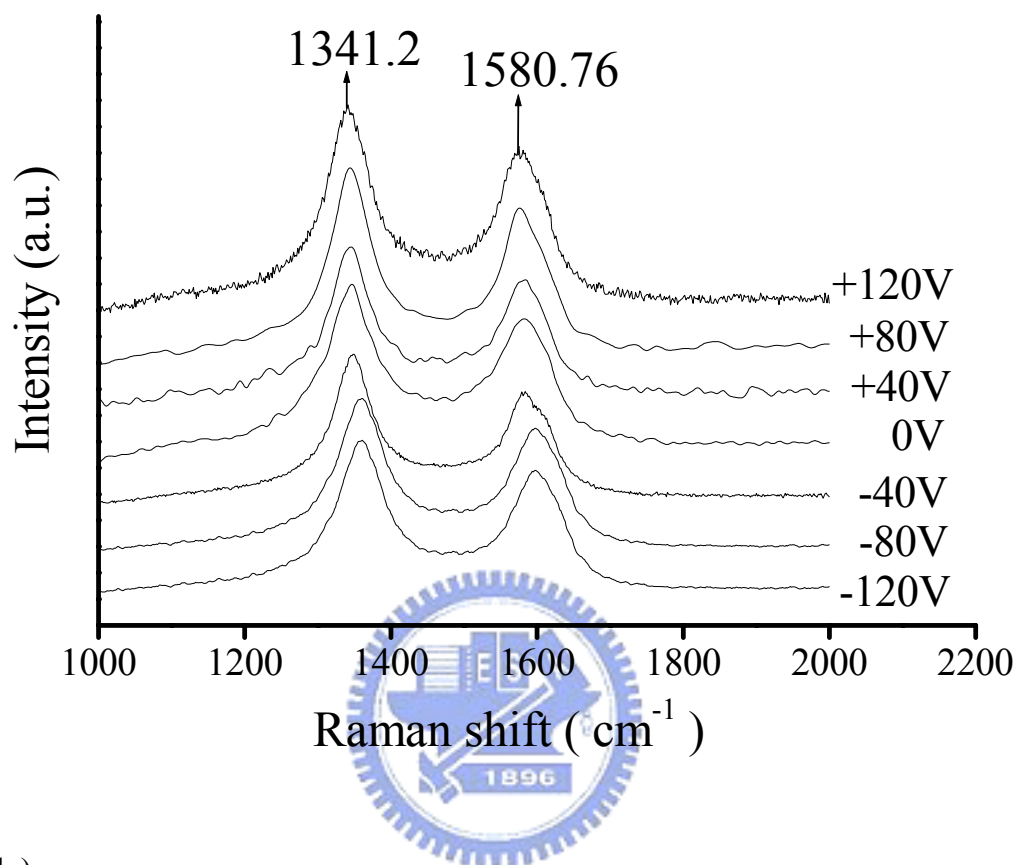


Fig. 6.5 TEM images of CNTs grown with CH_4/H_2 under (a) positive and (b) negative biases.

(III) Raman spectra

Figure 6.6 (a) exhibits the Raman spectra of CNTs grown under various biases. All of them have two sharp peaks located on about 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. It is known that the D-line is related to the defects or carbonaceous particles on the surface of CNTs. Raman spectrum reveals that CNTs have a multiwalled structure with some defective graphite sheets at the wall. According to Raman spectrum, the intensity of D-line peak decreases with increasing positive bias. In Fig. 6.6 (b), 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 with less a-C on the surface, thereby improving their properties. This phenomenon is corresponding to the previous SEM results.

(a)



(b)

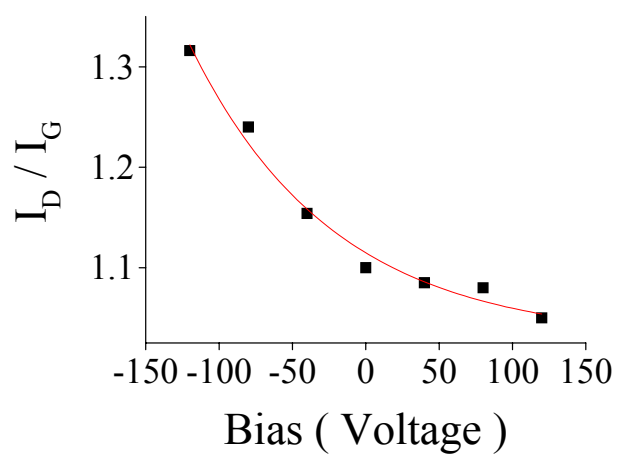


Fig. 6.6 (a) Raman spectra of CNTs grown with CH₄/H₂ under various biases and (b)

the I_D/I_G ratio as a function of applied biases.

(IV) 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 $B=6.83 \times 10^7$, and ϕ the work function in electron volt. F is usually taken as $F = \beta E = \beta V/d$, where V is the applied voltage, d the distance between cathode and anode, β the field enhancement, and $E=V/d$ the macroscopic field. A useful parameter for comparison with other field emitters is E_{to} (turn-on field), i.e., the macroscopic field V/d needed to produce a current of $10 \mu\text{A}/\text{cm}^2$. When $\ln(I/V^2)$ is plotted versus $1/V$ (F-N plot), one should obtain a straight line, implying the emitters show characteristics of field emission. Fig. 6.7 displays the I-V curve and an insert of F-N plot of CNTs grown under -120V, 0V and +120V, respectively. We further estimate the field enhancement β from the constant F-N slope with $d = 500 \mu\text{m}$ and $\phi = 5 \text{ eV}$ as for graphite and C^{60} [13]. β are obtained about 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 $\mu\text{A}/\text{cm}^2$ under 2.2 V/ μm than those grown under zero and negative bias. It is attributed to the following reasons (I) smaller diameter; (II) pure surface, (III) more graphitized structure of CNTs and (IV) higher field enhancement β .



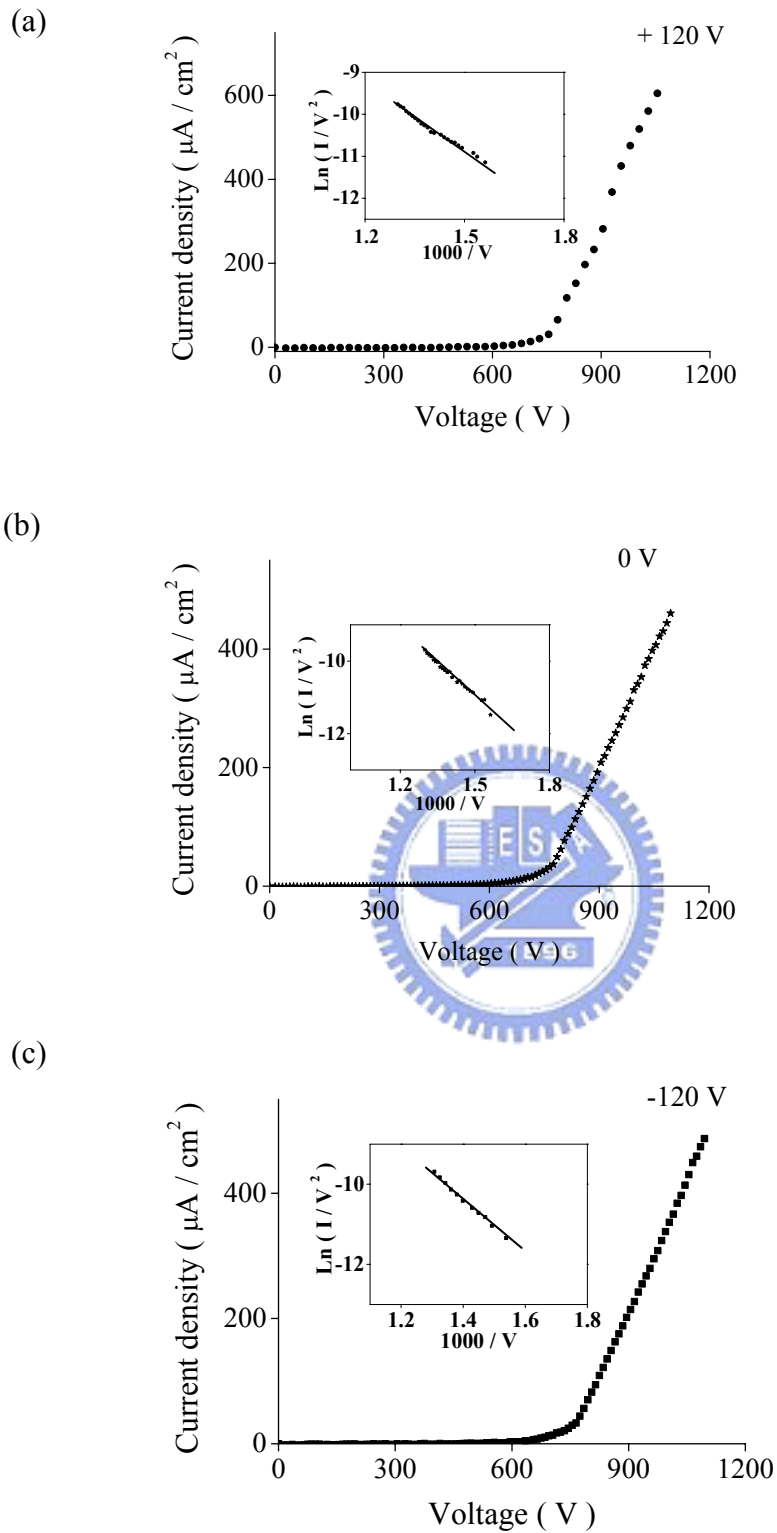


Fig. 6.7 The I-V curve and an insert of F-N plot of CNTs grown with CH_4/H_2 under (a) +120 V, (b) 0 V and (c) -120 V, respectively

B: Reactive gas effect on the growth of carbon nanotubes

6.2B. Experiment

In this section, the reactive mixtures are changed to methane and carbon dioxide. The remaining experimental condition is same to the previous section A.

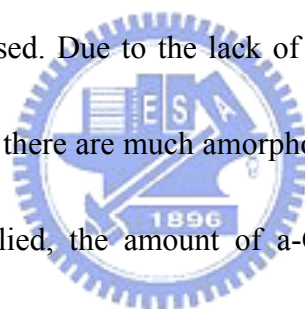
6.3B. Results and Discussion

(I) Scanning electron microscope (SEM)

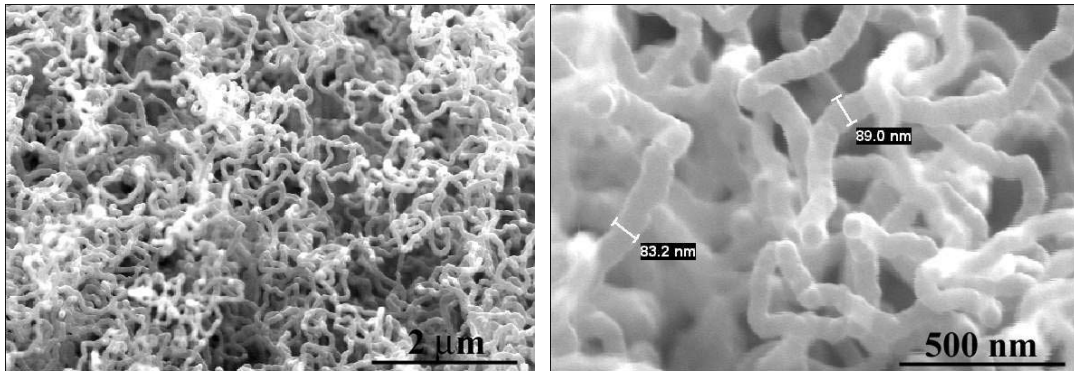
Figure 6.8 and 6.9 illustrate the SEM images of CNT grown with CH₄/CO₂ under various applied biases. The trend of diameter variation of CNTs is also similar to the previous section A. However, the average diameter of CNTs grown under CH₄/CO₂ is larger than those grown under CH₄/H₂. According to the SEM results, it is found the density of CNTs grown under CH₄/CO₂ is about 2.5×10^9 /cm². This yield is approximately one order than CNTs grown under CH₄/H₂. In comparison with the conventional gas mixtures, which is hydrocarbon diluted in hydrogen atmosphere, carbon dioxide provides the extra carbon source into the mixtures. Owing to the high carbon concentration in the reactive gases, the CH₄/CO₂ gas mixtures significantly improve the growth rate of CNTs. This high efficient gas mixture is also valid in the growth of diamond [14-15]. In addition to the mentioned advantage, carbon dioxide is also a kind of safe gases used in lab.

(II) Transmission electron microscope (TEM)

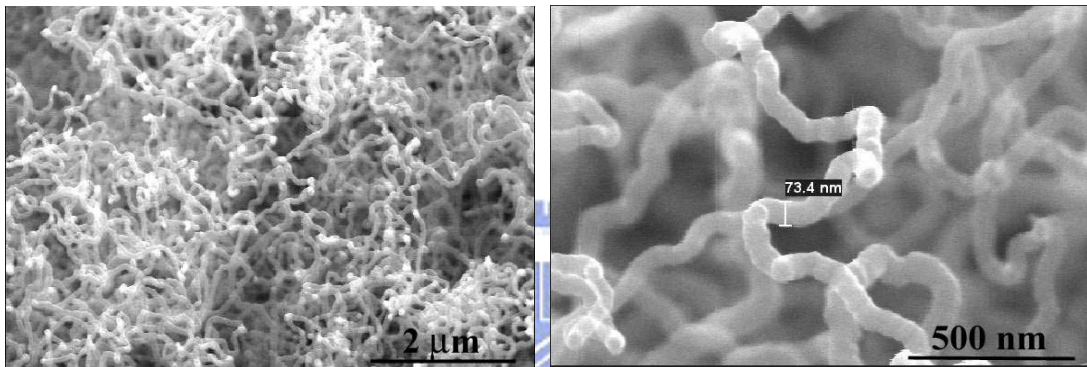
As compared to the section A, TEM images shown in Fig. 6.11 exhibit the same nanostructure of CNTs grown with CH_4/CO_2 , that is (I) fishbone-like and (II) tubes filled with catalysts. Fig. 6.12 depicts the existence of Pd in CNTs. The peak of Cu signal comes from the copper grid, which is used to support the CNTs for TEM preparation. This phenomenon implies that reactive gases only influence the morphology and no nanostructure transformation of CNTs. Nevertheless, in TEM experiment, it is found that the fishbone-like type mostly dominates the CNTs' structure when CH_4/CO_2 is used. Due to the lack of in situ observation system, this result is still unclear. Besides, there are much amorphous carbon (a-C) attached on the CNTs. As negative bias applied, the amount of a-C increases drastically. This is explained by the following two reasons. (I) bias effect (this has been mentioned in section A) and (II) higher growth rate of CNTs in CH_4/CO_2 .



(a) 0 V



(b) -40 V



(c) -150 V

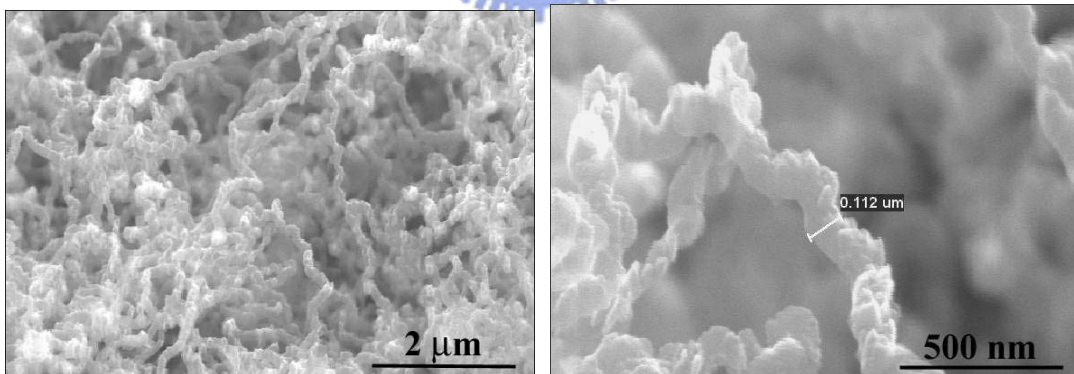
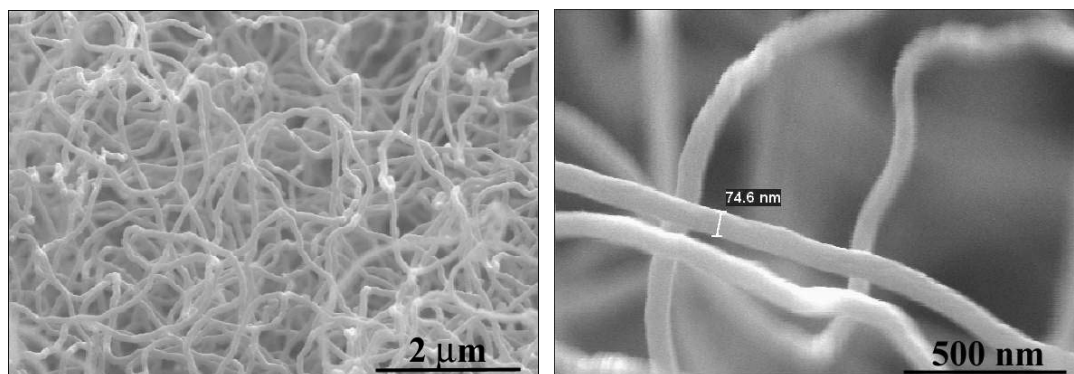
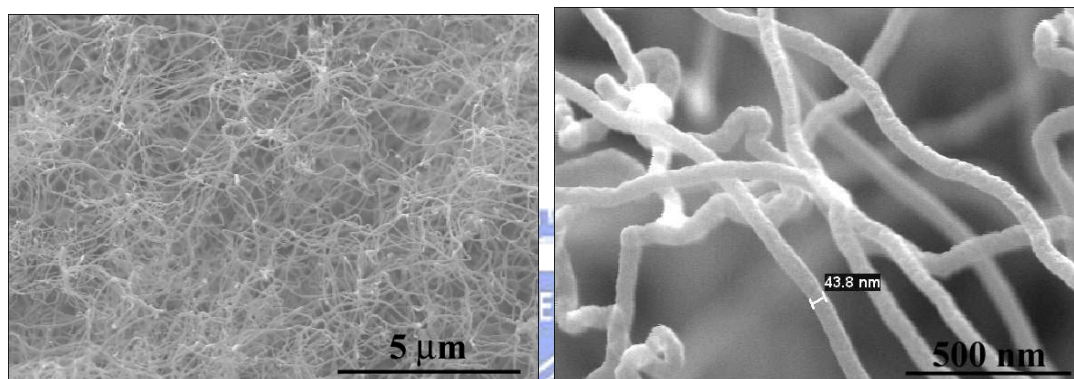


Fig. 6.8 SEM photographs of CNTs grown with CH_4/CO_2 under (a) 0V; (b) -40V and (c) -150V, respectively.

(a) +40 V



(b) +150V



(c) 0 V

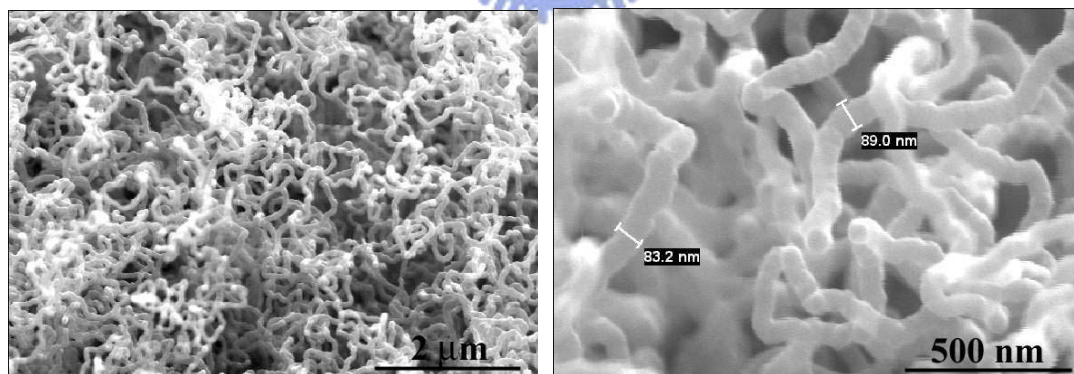


Fig. 6.9 SEM photographs of CNTs grown with CH_4/CO_2 under (a) +40V; (b) +150V and (c) 0V, respectively.

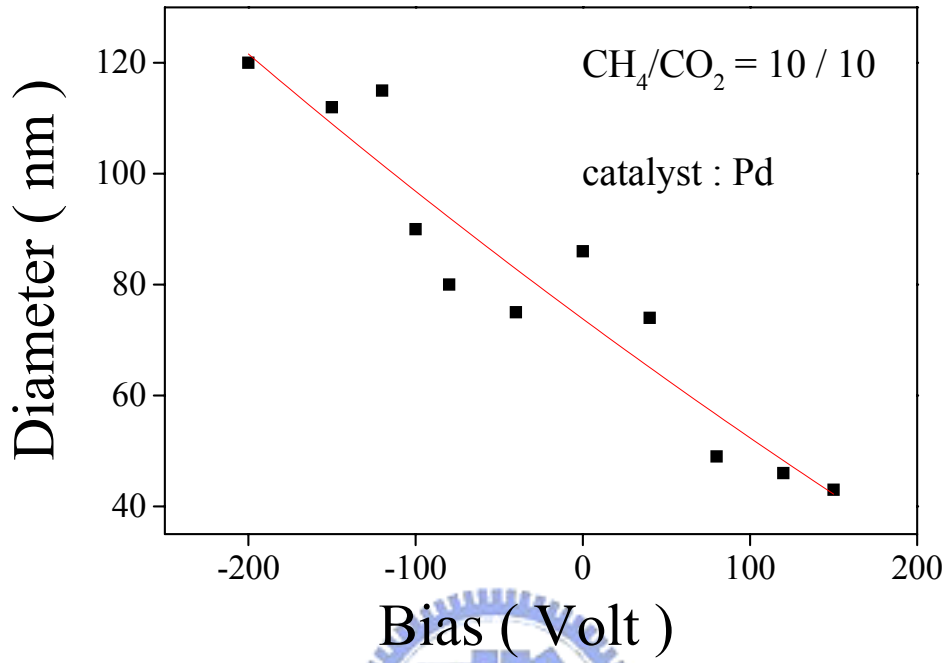
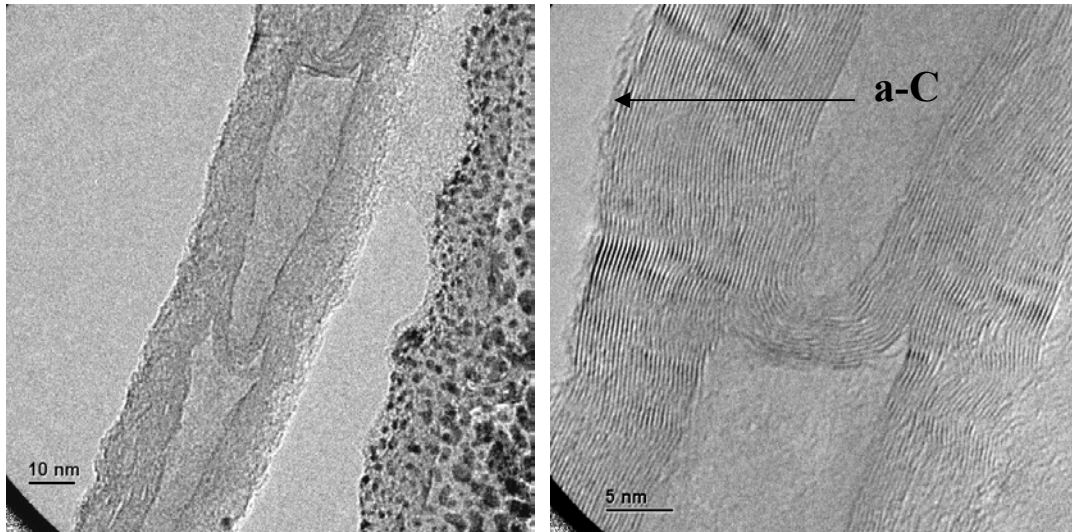


Fig. 6.10 Diameter of CNTs grown with CH₄/CO₂ as a function of applied biases.

(a) Positive bias effect



(b) Negative bias effect

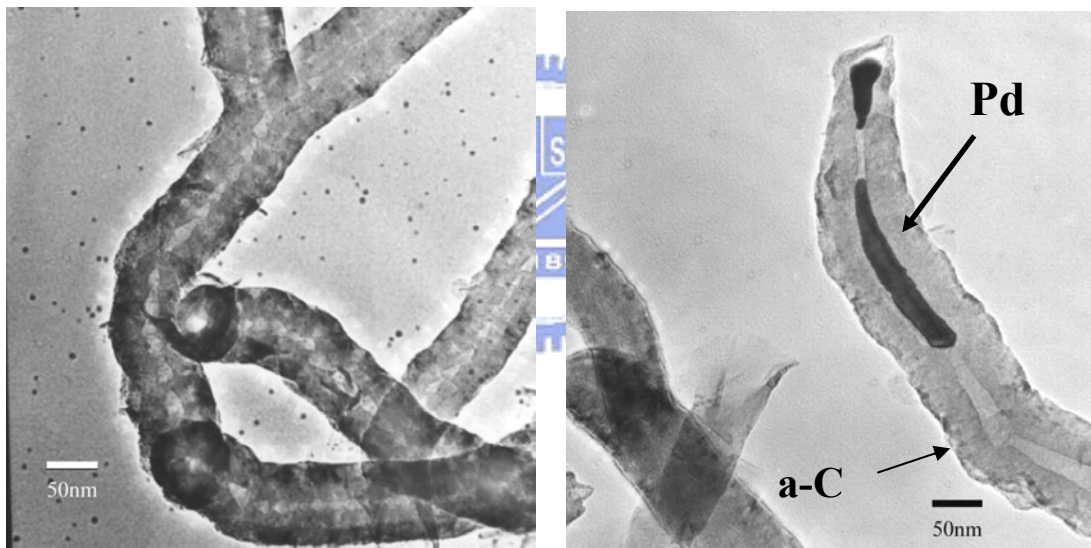


Fig. 6.11 TEM images of CNTs grown with CH_4/CO_2 under (a) positive and (b)

negative biases.

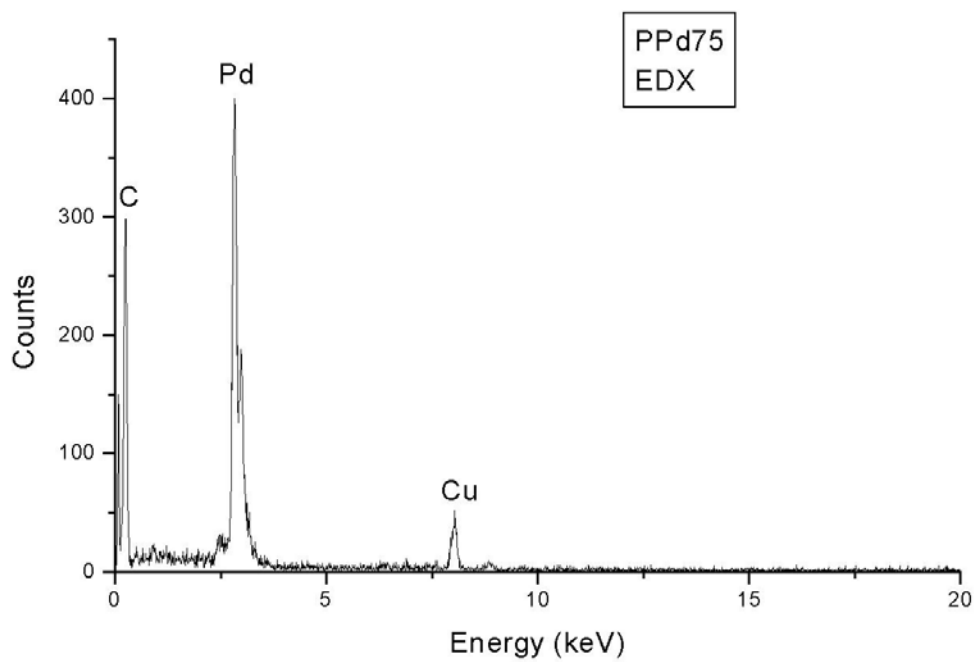


Fig. 6.12 EDX spectrum of CNTs grown with Pd catalyst



(III) I-V characterization

Figure 6.13 depicts the field emission characteristics of CNTs grown under CH₄/H₂ and CH₄/CO₂. By calculating their turn-on field, which is a macroscopic field needed to yield a current density of 10 μA/cm², the turn-on fields of CNTs grown with CH₄/H₂ and CH₄/CO₂ are 1.36 and 1.40 V/μm, respectively. The field emission characteristics between CNTs grown under different reactive mixtures seem very analogous. It is particularly emphasized why CNTs grown CH₄/CO₂ also possess good field emission characteristic under larger diameter and much a-C than those grown under CH₄/H₂. Due to the high carbon concentration in CH₄/CO₂, not only larger diameter and much a-C but also denser yield is produced. Thus, denser CNTs grown on fixed area provide more electrons under high electric field as compared CNTs grown with CH₄/H₂. This result confirms that CH₄/CO₂ gas mixtures have feasible potential on the application of high yield of CNTs with good field emission characteristic. Table 6.1 summaries the comparison of CNTs grown with CH₄/H₂ and CH₄/CO₂ mixtures.

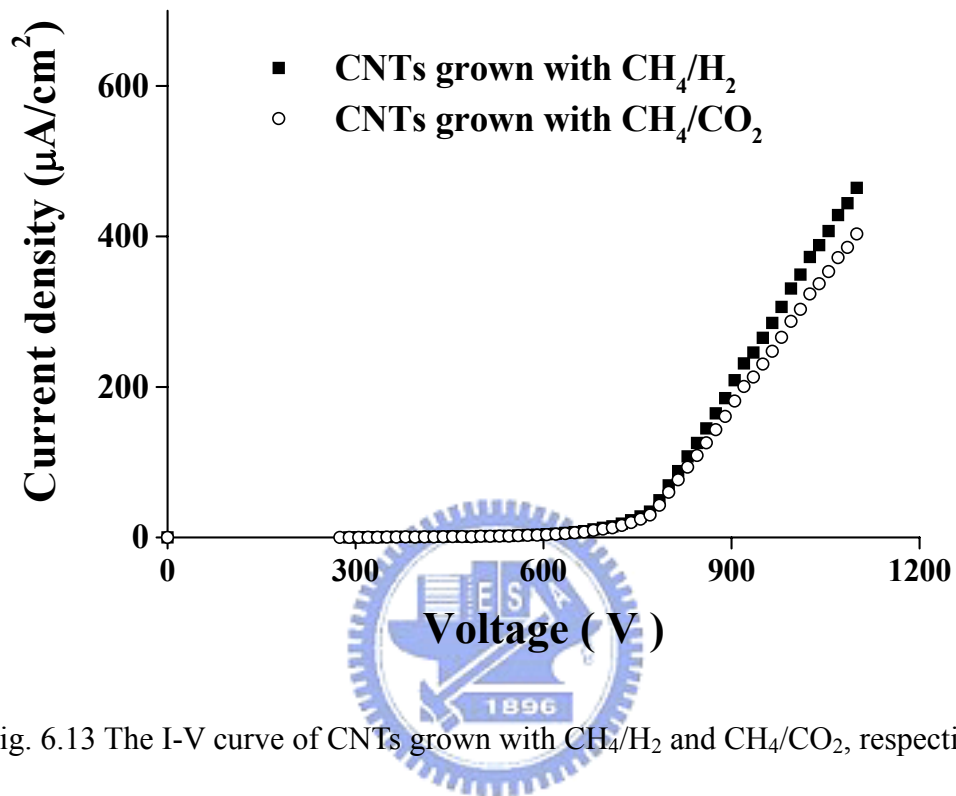


Fig. 6.13 The I-V curve of CNTs grown with CH_4/H_2 and CH_4/CO_2 , respectively.

Reactive gases	Diameter (nm)	Density (cm ⁻²)	Morphology	Nanostructure	Turn-on field (V/ μ m)	Film thickness (μ m/min)	Current density (μ A/cm ²) ^b
CH ₄ /H ₂	65	2.5x10 ⁹	a-C on the surface	<ul style="list-style-type: none"> • fishbone-like • CNTs filled with Pd 	1.36	1.7	464
CH ₄ /CO ₂	83	1.3x10 ⁹	more a-C on the surface	<ul style="list-style-type: none"> •^a fishbone-like • CNTs filled with Pd 	1.4	4.8	405

^a fishbone-like type mostly dominates the CNTs' structure

^b current density were measured at 2.2 V/ μ m

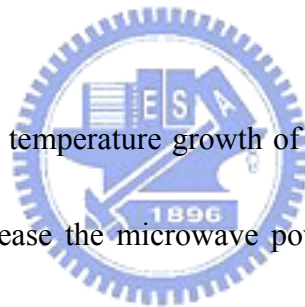
Both CH₄/H₂ and CH₄/CO₂ can be used to grow CNTs on Pd.

Note: without bias effect

Table 6.1 Summaries of the comparison of CNTs grown with CH₄/H₂ and CH₄/CO₂ mixtures.

(IV) Low-temperature growth of carbon nanofibers on soda-lime glass

Soda-lime glass, which has softening at 550°C, is commonly used as substrate of flat panel displays because of its low price and good vacuum sealing. Usually, researchers use the screen-printing method to coat Ag thick films as a cathode on the soda-lime glass. In order to apply the direct growth of CNTs to an electron emitters sealed by a soda-lime glass, the growth temperature must be lower than 550°C. Due to this temperature limitation, most researchers used pre-made CNT as an electron emitter and pasted CNTs into desirable substrate. However, this is not a direct method and wastes time and cost.



For the requirement of low temperature growth of CNTs on MWCVD system, the most efficient way is to decrease the microwave power. Decreasing the microwave power can directly lower the growth temperature and the dissociation of reactive mixtures simultaneously. Under this situation, this would cause CNTs to hardly synthesize. According to the previous mention, bias effect and CH₄/CO₂ gas mixtures may be possible solution for this problem.

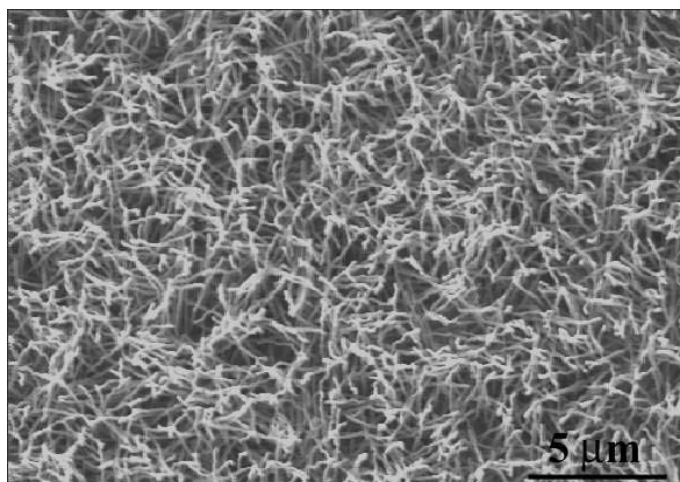
As shown in Fig. 6.14, it is obvious that dense carbon nanofibers (CNFs) grown on catalyst-free substrate with applying -100 V. After deposition, the soda-lime glass without any deformation and fracture implies the growth temperature is below 550°C. Growing conditions are listed as the following table 6.2.

Table 6.2 Deposition conditions of low temperature growth of carbon nanofibers

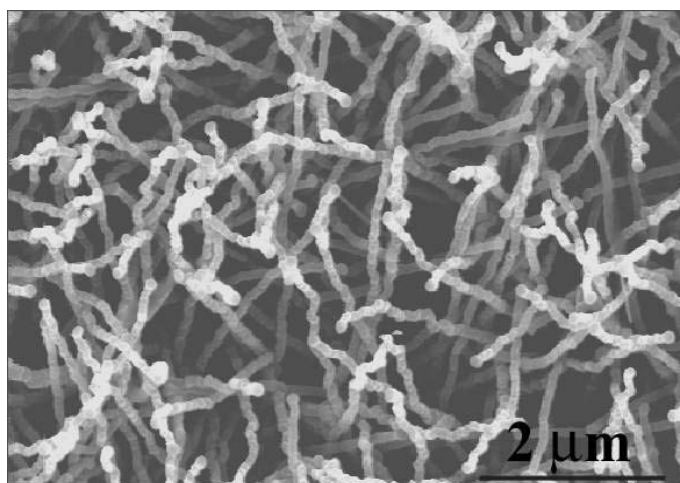
Flow rate of CH ₄ /CO ₂ (sccm)	Deposition time (min)	Negative bias Voltage (V)	Operating Pressure (Torr)	Microwave power (W)	Substrate Temp. (°C)
30/30	30	0~150	6	200	< 550

The diameter of CNFs is approximately up to submicron meter size. Without bias effect, the amount of CNFs seems very sparse. Once increasing the bias to -130 V, high yield of CNFs is generated as well as much a-C on the surface of CNFs illustrated in Fig. 6.15. Nevertheless, high negative bias voltage (more negative than -130 V) would make the soda-lime glass bring about some distortion because of drastic ion bombardment. Hence, the optimum bias should be used on the soda-lime glass in case of the deformation on the substrate. Due to the low-temperature growth; deficiency of dissociated carbon species and catalyst-free, the produced materials are CNFs instead of CNTs. Disregarding the effect of low growth temperature, CNTs are hardly synthesized without catalysts. In addition, it also needs more time to generate carbon materials. It is speculated that CNTs could be obtained on the catalyst coated soda-lime glass because of the activation of catalyst. Besides, many workers have pointed out that CNFs also exhibit good field emission characteristics [16-17]. Our results positively provide the feasible method for direct low temperature growth of carbon nanostructure materials in many applications.

(a)



(b)



(c)

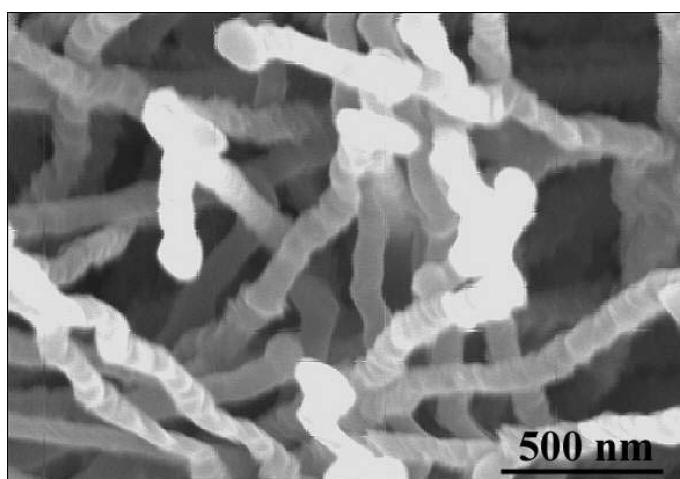
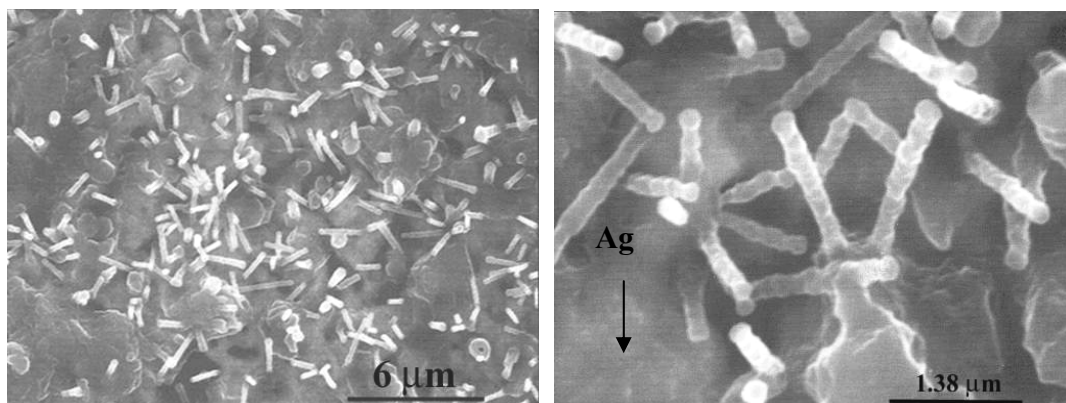
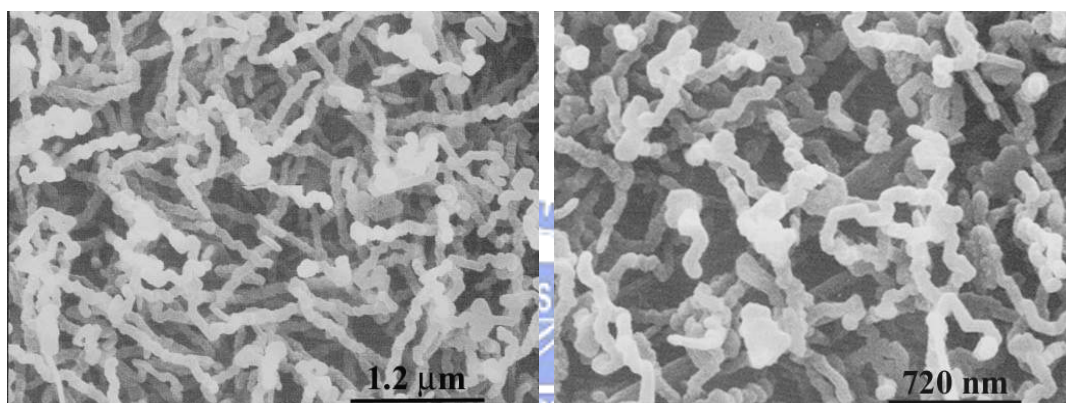


Fig. 6.14 (a) top view, (b) low magnification and (c) high magnification SEM photographs of carbon nanofibers grown with CH_4/CO_2 under applied -100 V on catalyst-free soda-lime glass

(a) 0 V



(b) -50 V



(c) -130 V

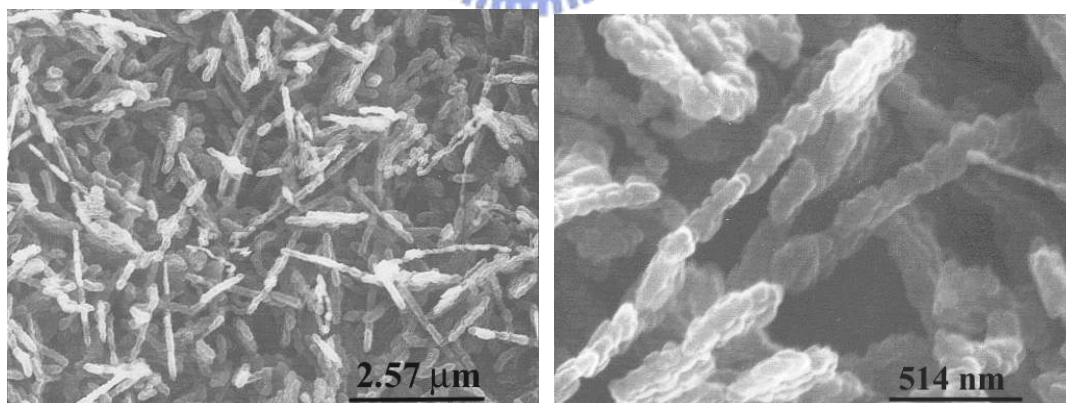
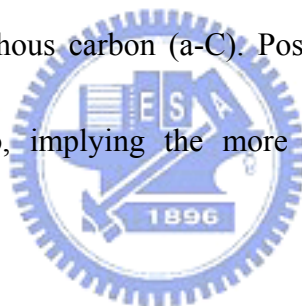


Fig. 6.15 SEM photographs of carbon nanofibers grown with CH_4/CO_2 under various applied biases on catalyst-free soda-lime glass (a) 0 V, (b) -50 V and (c) -130, respectively.

6.4. Conclusion

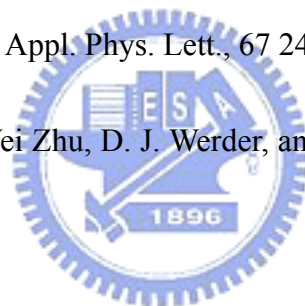
The applied biases during the reaction can directly control the diameter and the quality of carbon nanotubes. Experiment results are summarized as follows.

- (1) The diameter of CNTs increases with increasing negative bias. However, positive bias effect shows the reverse trend toward increasing positive biases.
- (2) The diameter of CNTs can be reduced from 65 nm (under 0 V) to about 45 nm (under +80 V) as compared to the submicron size under (-120V).
- (3) Besides, the surface of CNTs grown under positive bias is more graphitized structure with less amorphous carbon (a-C). Positive bias process makes CNTs possess lower I_D/I_G ratio, implying the more graphitized structures, thereby improving their properties.
- (4) 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 without a-C, (III) more graphitized structure and (IV) higher field enhancement β .
- (5) CH_4/CO_2 gas mixtures could enhance the growing rate of CNTs because of high carbon concentration in the reactive gases.
- (6) CH_4/CO_2 and bias effect can be the feasible solution for the low growth temperature of CNTs in many applications.



6.5 Reference

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