

Enhancement of Field Emission of CNTs Array by CO₂-Assisted Chemical Vapor Deposition

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We present a new process to get *in-situ*-growth carbon nanotubes (CNTs) array device with good FE properties by CO₂-assisted thermal chemical vapor deposition (CVD). Field Emission measurement shows that introducing CO₂ into CNTs growth system leads to a significant enhancement in the emission properties, both the turn-on field and threshold field decrease. Raman, SEM and TEM investigation results showed that in this CO₂-assisted thermal CVD, CO₂ can remove amorphous carbon during CNTs growth process, and at the same time, it also creates more defects on the CNTs wall. Both can enhance FE properties of the CNTs at suitable CO₂ concentrations.

Keywords: Carbon Nanotubes, Field Emission, CO₂, CVD.

1. INTRODUCTION

Since the discovery of carbon nanotubes,¹ great attention has been paid to their properties and potential application in nanometer engineering and electronics. A small tip radius and a high aspect ratio combined with chemical interness and mechanical strength make CNTs ideal field emission (FE) electron sources.² CNTs emitters have been applied in devices, such as flat panel displays,³ X-ray source⁴ and vacuum microwave power amplifier devices⁵ etc. Much research work has showed that both the end and wall of the CNTs can act as field emitter source.^{6–11} To enhance the field emission properties of CNTs, some effective methods have been experimented.^{6–19} For example, annealing in oxygen or ozone to open more ends of nanotubes¹² can enhance the field emission (FE) properties of the CNTs, because the open-end nanotubes have circular sharp edges, which may have a smaller radius of curvature than the closed-end nanotubes. Surface treatment of the as-grown CNTs with H₂,¹³ Ar,^{15,16} and CF₄ (Ref. [17]) plasma proved to be another effective method to enhance the field emission properties, for these treatments can cause more defects on the wall of CNTs, and consequently increase the number of the emitter source.

In this paper, we present an *in-situ* treatment by using a CO₂-assisted thermal chemical vapor deposition (CVD) method. Compared to the post-treatment process, this strategy of *in situ* controlled growth is attractive for producing such CNTs with special structure. For instance, introducing H₂O (Refs. [18, 25]) in the CVD growth process could remove amorphous carbon produced with CNTs, and NH₃ (Ref. [19]) could also inhibit the formation of amorphous carbon and create more defects on CNTs properly. In our previous work,²⁰ CO₂ has been used to control the growth of single-walled carbon nanotube (SWNTs) by electrical arc (EA) method, where SWNTs with controlled length and bundle size and much less amorphous carbon were prepared. Here CO₂ was introduced into the system as a weak oxidizer to remove amorphous carbon and create more defects on the wall during the growth of CNTs array, thus enhance their FE properties.

2. EXPERIMENTAL DETAILS

The catalyst was prepared as follows. First a Si₃N₄ layer was plasma CVD coated on a silicon wafer, and then a 10 nm Al layer was formed on this wafer by sequential e-beam evaporation as buffer layer. This Al layer also acted as the conducting layer. Then 3 nm Fe film was evaporated on the Al layer. For investigation on the FE properties, patterned catalyst chips were designed. The Al/Si₃N₄ layer

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were prepared as the above mentioned. Then the substrate was patterned with Fe films (3 nm) by e-beam evaporation through shadow masks, containing squared opening with side length of 200 nm at spacing distance of 50 nm.

CNTs growth was carried out in a tube furnace (First Nano-Easytubes1000) by thermal chemical vapor deposition technique. The reaction temperature was ramped to the set point 775 °C in 12 min under 350 sccm Ar. Then the growth was carried out at 775 °C with ethylene (150 sccm) as the carbon source and hydrogen (200 sccm) and Argon (350 sccm) as carrier gases. After 30 minutes reaction, Ar flow (250 sccm) was kept for 10 min at the reaction temperature before the furnace cooled down. CO₂ was introduced in the reaction system as a mixed gas with Ar (contain 1% CO₂). The total flux of the pure Ar and the mixed Ar with CO₂ was always kept the same at 350 sccm. In the reaction, four types of CO₂ concentration (220/440/735/1470 ppm) was selected. The CO₂ concentration was controlled by the different ratio of pure Ar and the mixed Ar/CO₂ gas.

Used as the cathode, the FE properties of as-grown patterned CNTs array were determined by a home-made instrument in a vacuum chamber with a pressure of about 3×10^{-8} Torr. The anode is a copper probe with a diameter of 1 mm, and the distance between electrodes was kept at 100 m. A Keithley 248 high voltage source measurement and a keithley 6514 E-meter were used to apply a voltage and measure the emission current at the same time. Scanning electron microscopy (SEM, Hitachi S-3500N, at 20 k eV), Transmission electron microscopy (TEM, JEOL TECNAI-20, JEM2010fef, operating at 200 KV) and Raman (RENISHAW inVia) were used to explore the differences in the surface morphologies and microstructures of CNTs films grown at different conditions.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the typical current density of five samples as a function of the macroscopic electric field. These five samples are vertically aligned CNTs (VA-CNTs) patterns grown with different concentration of CO₂ (0/220/440/735/1470 ppm) in the reaction system. Typical overall SEM image of these patterns was showed in Figure 2(a). From Figure 1 it can be found that, the turn-on electric field (E_{to}) of samples grown by CO₂-assisted CVD decreases significantly (E_{to} : 2.24–3.14 V/m) compared to the sample grown without CO₂ (E_{to} = 4.29 V/m). And the threshold electric field (E_{thr}) of those samples grown by CO₂-assisted CVD decreases too, especially the sample grown with 440 ppm CO₂ in the reaction system, of which the E_{thr} decreases to 3.52 V/m and is much lower than the sample without CO₂ (E_{thr} = 10 V/m). It is worthy to note that both of the E_{to} and E_{thr} first decrease, and then increase with CO₂ concentration increasing. The sample produced with 440 ppm CO₂ gave the best FE performance. All the Fowler-Nordheim plots for these measured

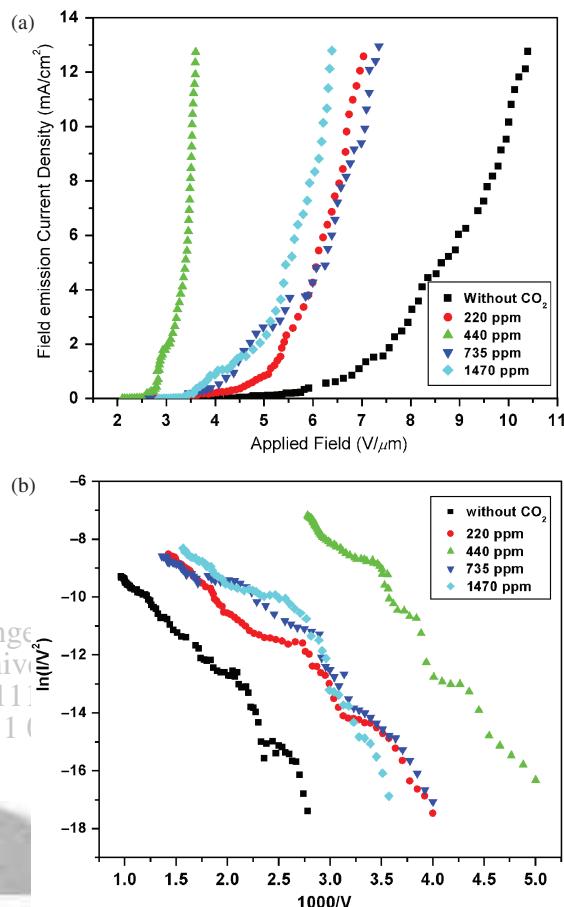


Fig. 1. (a) Typical emission current density versus electric field for CNT film grown with different concentration CO₂ in the reaction system; (b) Fowler-Nordheim plot for CNT film grown with different concentration CO₂ in the reaction system (all the samples grown at 775 °C, the growth time was 30 min).

samples are straight lines (as shown in Fig. 2(b)), indicating that the measured data is in good agreement with the Fowler-Nordheim equation.²¹

Generally speaking, FE properties of CNTs are attributed to open-ended edges^{4,10} and a large number of defects¹⁷ on the wall of the tubes. Reducing the amorphous carbon on the tube of CNTs can also improve the FE properties.²² Several studies have found that weak oxidizer¹⁵ could open the end of CNTs, but the open-ended edges were not the main contributors to the enhancement of FE properties in our study. Scanning electron microscopy (SEM) images in Figure 2 show the side view and top view of our patterned growth CNTs. It can be seen that CNTs at the top of the array (as shown in Fig. 2(d)) are tangled very much, unlike the well aligned side of array. This may result from nanotube growing in random direction and cross each other during the initial growth period²³ in the base-growth mode. This result indicates that most of the electrons emit from the body of the tubes. In another word, the defects on the wall of the tubes acted as the main field emitter source²⁴ in our cases. Thus, the

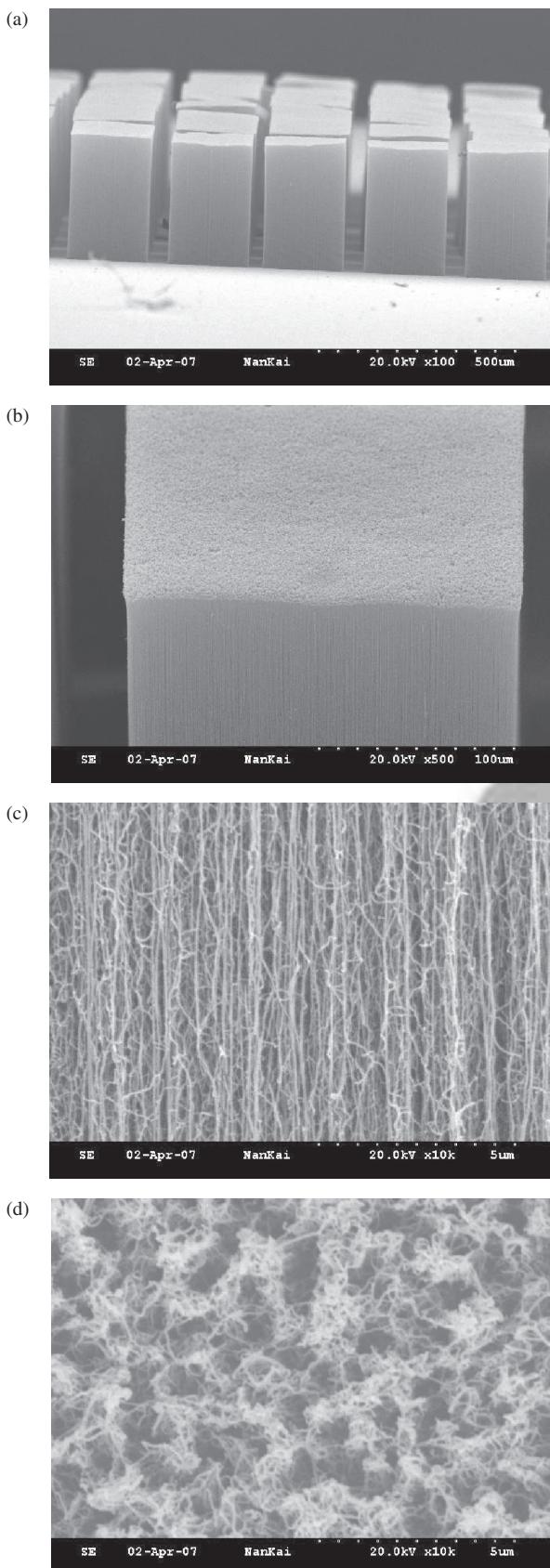


Fig. 2. SEM micrographs of aligned CNTs pattern: (a, c) side view of the patterned CNTs array; (b, d) top view of the CNTs.

enhancement of FE performance of the CNT array produced in our CO₂-assisted CVD growth shall come from microstructure changes on the nanotube wall caused by CO₂ during the growth. Raman spectroscopy and TEM were then used to investigate the changes in the morphologies and microstructure of the CNTs produced with different concentration of CO₂ in our CNT growth system.

Figure 3(a) shows the Raman spectra of the CNTs samples grown with different concentration of CO₂. The ratio of the intensity of G-band at 1590 cm⁻¹ to D-band at 1340 cm⁻¹ (I_G/I_D) calculated from Figure 3(a) is showed in Figure 3(b). It can be seen that I_G/I_D changed with CO₂ content changing. D band in Raman spectra of CNTs is due to disorder-induced features of graphite and the intensity of D band is often associated with the amount of amorphous carbon and/or defects on the tubes. As mentioned previously, weak oxidizer could remove the amorphous carbon produced in the CNTs growth process by CVD.²⁵ In our experiment, introducing CO₂ to assist the

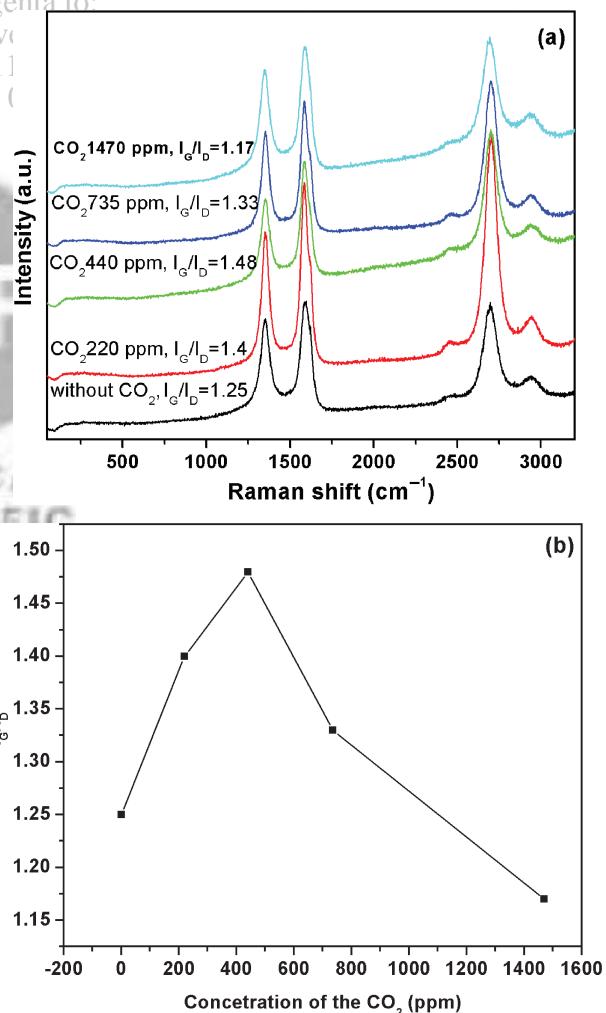


Fig. 3. (a) Raman spectra of CNT film grown with different concentration CO₂ in the reaction system; (b) concentration of the CO₂ dependence of the ratio of G-band to D-band intensity (I_G/I_D) (all the samples grown at 775 °C, the growth time was 30 min).

CNTs growth also influence the microstructure of CNTs. It is clearly shown in Figure 3(b) that, the I_G/I_D first increase then decrease with the concentration of CO₂ increasing, and the turning point appears at 440 ppm CO₂. This turning point may be due to the different reaction activity of the amorphous carbon and CNTs to CO₂. At lower CO₂ concentration, CO₂ mainly reacts with amorphous carbon which is more active, and the intensity of D-band in Raman decrease. With more and more CO₂ appear in the system, those carbon atoms at the edge and defect sites of the CNTs also be oxidized, thus the intensity of D-band in Raman increase.

Figure 4 shows TEM images of two CNTs samples grown with different CO₂ concentration. It can be found that CO₂ gives little influence on the diameter of the CNTs and CNTs grow in both conditions have nearly the same diameter of about 10–20 nm (Figs. 4(c) and (d)). But CO₂ has much more influence on their microstructure. As shown in Figure 4(a), walls of the CNTs grown without

CO₂ are relatively well-graphitized; on the contrast, the sample synthesized under 440 ppm CO₂ have more defects on the wall (Fig. 4(b)).

From the results of the Raman spectroscopy and TEM, it can be inferred that CO₂ could not only remove the amorphous carbon but also damages the CNTs wall structure. The oxidation effect of CO₂ can also be observed by SEM (Fig. 5). When the concentration of CO₂ is less than 440 ppm, CNTs grow nearly the same height as that without CO₂, even a little higher than the latter. But with more CO₂ added to the system, the height of the CNTs array decreased distinctly. CO₂ can react with the active amorphous carbon that wrapping the catalysts like water in Ref. [25], so the CNTs can grow higher. At the same time, it also can react with the active carbon atoms such as at the tip or defeat sites of the CNTs. With CO₂ concentration increased, more and more sections of the CNTs were oxidized by CO₂, thus the CNTs become shorter and as the result, the CNTs grow lower.

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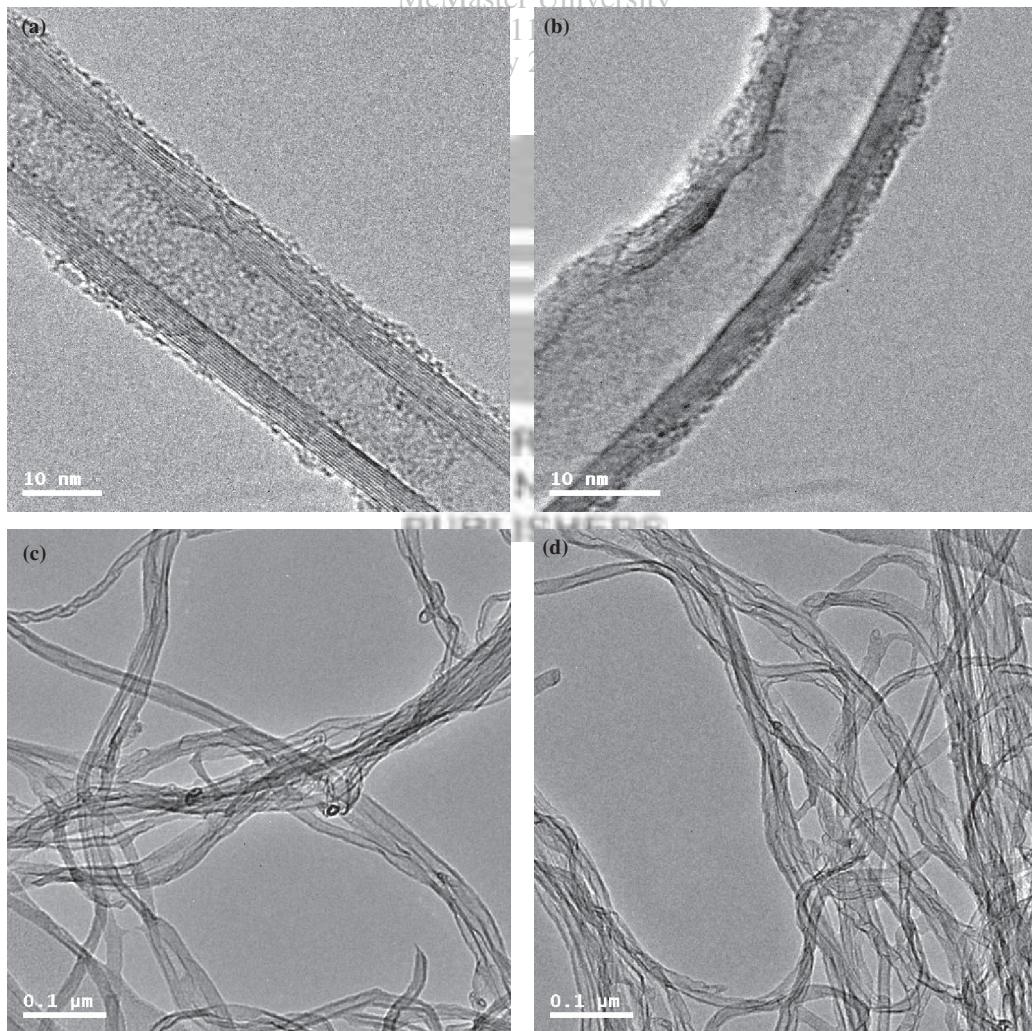


Fig. 4. TEM images of the CNTs: (a, c) grown without CO₂; (b, d) grown with 440 ppm CO₂ (both of the two samples grown at 775 °C, the growth time was 30 min).

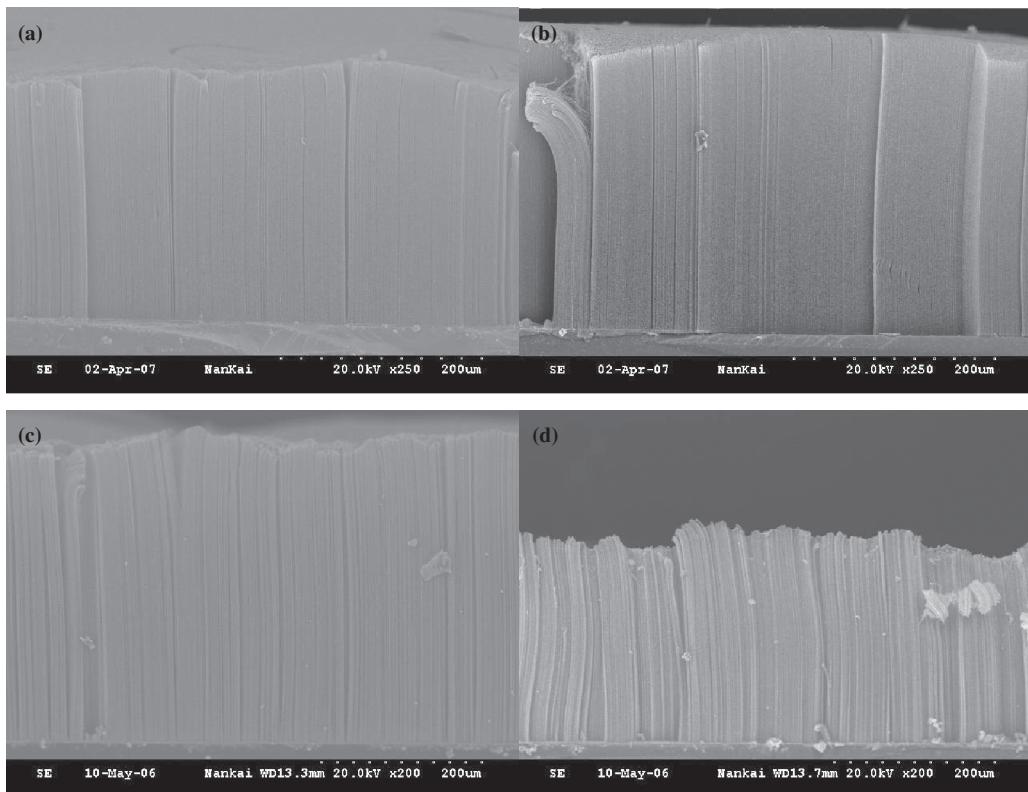


Fig. 5. SEM images of MWNTs arrays synthesized at different CO₂ concentration: (a) No CO₂, (b) 220 ppm CO₂, (c) 440 ppm CO₂, (d) 735 ppm CO₂ (all the samples were prepared at 775 °C for 30 min).

As mentioned previously,¹⁷ more defects on the wall of the tubes will enhance the FE properties because its surface becomes more active to emit electrons. CO₂ can remove the amorphous carbon to expose more CNTs and create more defects on the CNTs wall. Both can enhance the FE properties. So both of the E_{to} and E_{thr} value decrease with the concentration of CO₂ increasing till 440 ppm. But when the concentration of CO₂ more than 440 ppm, the E_{to} and

E_{thr} began increasing. Zhu et al.¹⁸ have indicated that CNTs array grown with water-assisted CVD have a poor adhesion between the CNTs and the substrate, i.e., the interaction between the CNTs and the substrate weakened as the result of the oxidization reaction. Therefore, multilayer CNTs array was produced using an interval-growth process. In this study, we also got multilayer CNTs with the same method under the action of CO₂ (Fig. 6), which indicates that CO₂ can weaken the interactions between the nanotubes and catalyst particles on the substrate. Thus the weakened interaction between the nanotubes and catalyst would hindrance the electrons transport and consequently influence the FE prosperities.²⁶ Therefore, the FE properties of the CNTs decrease when the CO₂ concentration is high. In addition, superfluous CO₂ would damage the structure of the carbon nanotubes much more seriously, which also influence its field emission current density stability.

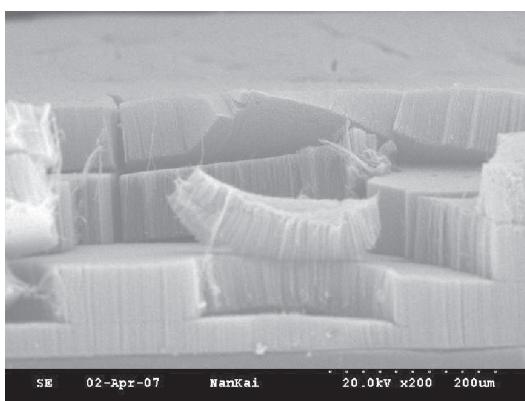


Fig. 6. Multilayer CNTs array was produced with CO₂-assisted CVD through interval-growth process (At 775 °C, ethylene flowed into the CVD system for 4 min, after which the flow was terminated; after 5 min of only water, argon, and hydrogen flow, ethylene was again introduced for 4 times).

4. CONCLUSION

In summary, we have demonstrated an efficient method for improving the FE properties of CNTs array grown using an *in situ* CO₂-assisted CVD growth. SEM image shows that walls of the CNT are the main field emitter source in this study. At low concentrations, CO₂ will clean and expose more tubes out and at the same time promote more defects formed on the wall, and thus increase the number of field

emission points. Such optimized surface and increase in the number defects are believed to make a great contribution to the enhancement of FE properties. However, excessive CO₂ will cause severe damage on the CNT walls and weaken the adhesion between the nanotubes and catalyst particles, which influence the electrons transport seriously. So it is necessary to control the concentration of CO₂. The sample grown with 440 ppm CO₂ in the reaction system possesses the most excellent FE properties.

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