

Uniform Field Emission from Carbon Nanotubes Fabricated by CO Disproportionation

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Field emission of carbon nanotubes (CNTs) fabricated by disproportionation of CO has been studied. CNTs fabricated on well-ordered Co nanowire arrays formed on the porous anodic aluminum oxide templates were well graphitized, uniform in diameter and aligned vertically with respect to the plane of the template, and showed a good field emission property. Very uniform emissions were observed from the CNTs fabricated at relatively low temperature, 500-600 °C. Low fabrication temperature such as 500 °C could make it possible to fabricate CNTs on soda lime glass, a low-cost substrate, for display panel.

Key Words : Carbon nanotube, Anodic aluminum oxide, Carbon monoxide, Field emission

Introduction

Carbon nanotubes (CNTs) have recently attracted considerable interest because of their unique properties and potential applications.¹⁻³ CNTs are promising for field emission applications since they have excellent field emission properties such as high aspect ratio, high chemical stability, high thermal conductivity, and high mechanical strength.¹

There have been many reports on field emission of CNTs but only a few reports have showed field emission patterns and they are not homogeneous.³⁻⁹

CO has been used as a carbon source in synthesis of CNTs.¹⁰⁻¹² When the disproportionation of CO, *i.e.* the Boudouard reaction occurs on metal surface, only C and CO₂ are produced.¹³ CO₂ is a very stable gas and desorbs from the surface without further reaction. Therefore, the Boudouard reaction can provide pure carbon as a carbon source in synthesizing CNTs.

The CNTs fabricated by disproportionation of CO in previous were not aligned¹⁰⁻¹² or contaminated the surface of the aligned CNTs¹⁴ and no field emission property of them has been reported. Recently we have succeeded to fabricate, without contamination, aligned CNTs by disproportionation of CO, using Co nanowire arrays formed in an AAO template and reported the field emission property.¹⁵ The field emission has been very uniform. The CNTs has been fabricated at 600 °C. This temperature is higher than the melting point of soda lime glass (550 °C) that is a low-cost substrate for display panel. Therefore, it may be necessary to study the field emission properties of the CNTs fabricated at a lower temperature, by CO disproportionation.

Here, we report the field emission properties of aligned CNTs fabricated at 500-600 °C by disproportionation of CO, using Co nanowire arrays formed in an AAO template.

Experimental Section

The method to prepare ordered AAO templates using a two-step anodization technique¹⁵ has been published.^{14,17,18} A second anodization was performed in a 0.3 M oxalic acid solution at 17 °C by applying 40 V DC for 5 min and then a voltage drop from 40 V to 18 V was done. The pore depth was about 660 nm. Co was deposited near to the mouth of the pores of the templates at 13.5 V. After the deposition of Co, the template was dipped into 0.01 M sulfuric acid for 30 s and then 0.1 M NaOH solution for 90 s.

After placing the template in a tube furnace, CNTs were fabricated by flowing carbon monoxide (100 mL/min) at 500, 550 and 600 °C for 12 hour. Fabricated templates and CNTs were analyzed by using a scanning electron microscopy (SEM: Philips FEG XL, 30 kV). A phosphor coated indium tin oxide (ITO) glass electrode was used to monitor the electron emission pattern of the CNTs fabricated on AAO templates and to measure the emission current versus the applied voltage. The distance between the tip of the CNTs and the anode was about 200 nm and the pressure of the vacuum chamber was 1.6×10^{-6} Torr.

Results and Discussion

Figure 1a represents a SEM image of an AAO template surface before being treated with H₂SO₄ and NaOH solution after Co electrodeposition. It is seen that Co metal is filled within all pores. The white dots are Co. Some of the white dots are much bigger than the pore diameter due to overdeposition. Filling Co metal near to the mouth of the pores was controlled by monitoring the electric current during the electrodeposition. When Co metal grows from the pore bottom, the current decreases monotonically except a sharp increasing at the initial stage. As soon as the pore filling has completed and overdeposition takes place, the current increases again, abruptly. The electrodeposition was stopped when the current started to increase. Figure 1b shows a SEM image of the AAO template surface deposited

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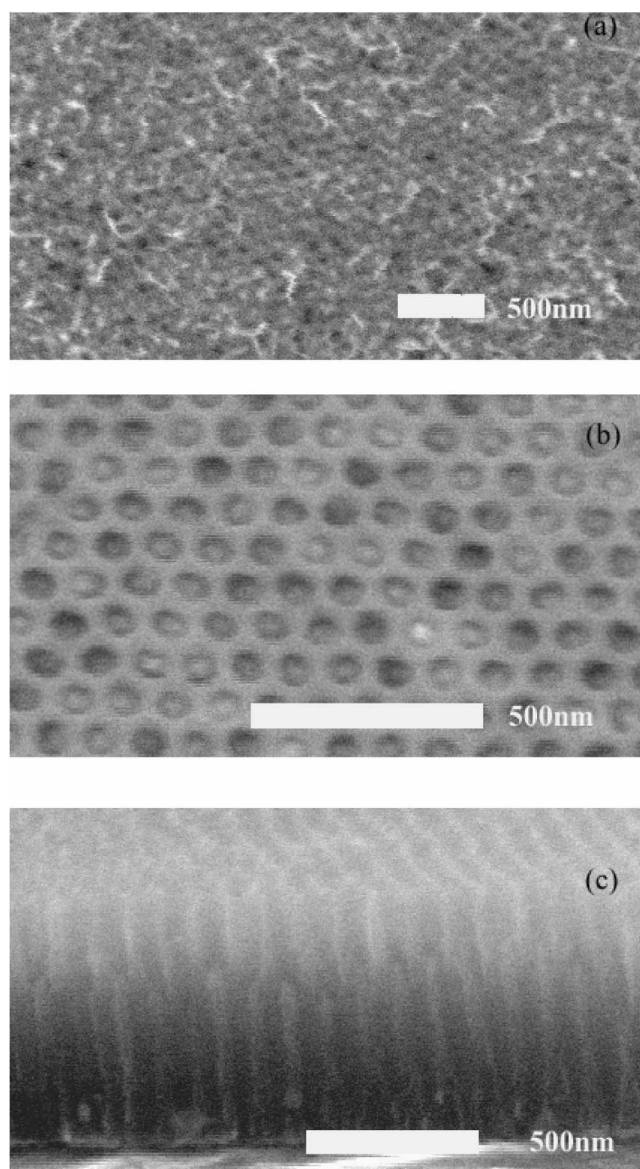


Figure 1. SEM images of an AAO template deposited Co: (a) the surface view after deposition of Co, and (b) the surface and (c) a cross-sectional views after being treated with H_2SO_4 and then NaOH solutions. Co is about 160 nm below the surface in the pores after etching in acid and base solutions.

Co after etching in H_2SO_4 and then NaOH solutions. The overdeposited Co was removed by dissolving in H_2SO_4 solution. Although the nanopores are slightly deformed by etching they exhibit almost a perfect 2-D array with a hexagonal pattern. Before being treated, the average diameter and interpore distance were 28.6 ± 1.0 nm and 104.2 ± 2.3 nm, respectively. The pore density is about 1.1×10^{10} pores/ cm^2 . By using of overdeposition and etching techniques, we could prepare well-ordered Co nanowire arrays without contaminating the surface, by eliminating the mechanical polishing process. The SEM image of a cross-sectional view after being treated with H_2SO_4 and then NaOH solutions is shown in Figure 1c. Co is about 160 nm below the surface in the pores. This is due to the fact that the dissolving rate of

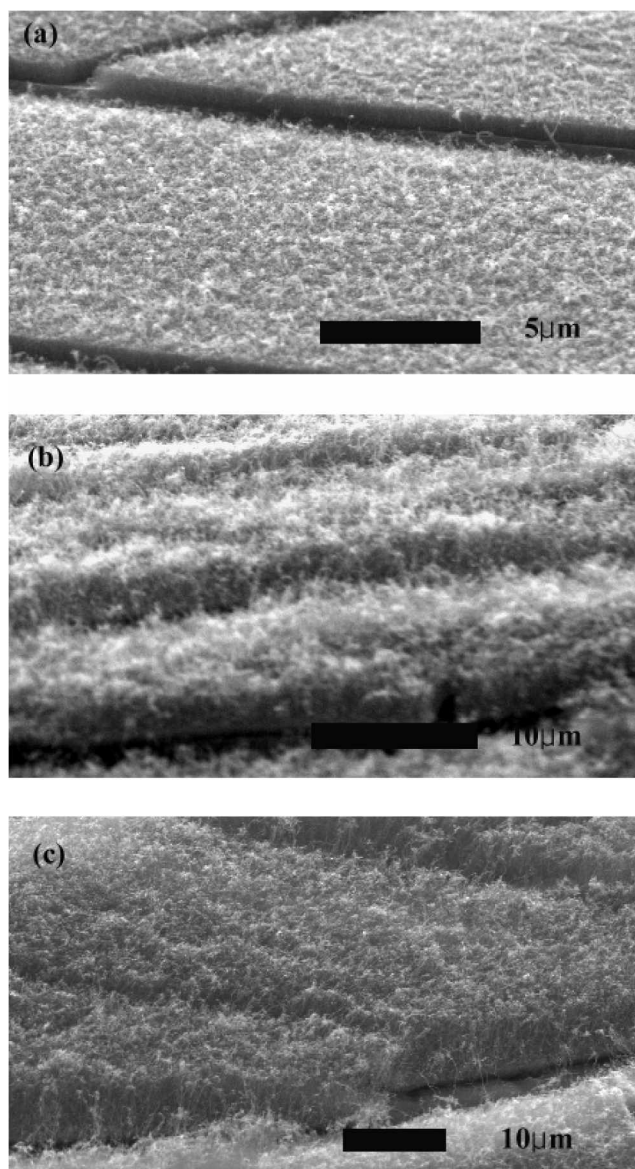


Figure 2. SEM images of the CNTs fabricated by CO disproportionation at (a) 500, (b) 550, and (c) 600 °C. Cracks were made intentionally to observe the side views.

the Co nanowires in sulfuric acid solution is much faster than that of alumina of the template. By etching with NaOH after dipping in H_2SO_4 solution, the part of each pore where no Co was filled has been widened.

Figure 2 shows SEM images of CNTs fabricated on the AAO template etched in H_2SO_4 and then NaOH solutions after Co deposition, by disproportionation of CO at three different temperatures: 500, 550 and 600 °C. Nanotubes cover the whole surface of each template. Tubes fabricated at relatively high temperature are vertically well aligned although a few appear to be tangled or curved. For the case of 500 °C, most CNTs are bundled together. By close examination, tubes are grown from all the pores. The diameters of these tubes are very uniform as 32 nm but the length of them increase with increasing temperature: about 0.5, 2.5 and 7 μm , respectively. The fabrication time was the

same in all cases. This means that the fabrication temperature in this temperature range critically affects the growing rates of the CNTs. At 650 °C, the template was deformed during fabrication although the temperature is lower than the melting point of aluminum, 660 °C. By the high resolution TEM image, the CNTs were well graphitized and consisted of about 32 concentric shells of carbon sheets and their inner and outer diameters were about 10 and 32 nm, respectively.

The CNTs in Figure 2 are grown out from the pores but they are not as ordered as the CNTs made in the pores of AAO templates.¹⁷ The CNTs formed in the pores as the shape of the pores are made by catalysis of alumina of AAO templates when hydrocarbons like acetylene are used as a precursor.¹⁹ CO is not catalyzed by alumina of AAO templates. Therefore, the CNTs fabricated by CO disproportionation are made by catalysis of Co deposited in the pores. It is known that the CNTs are growing out from the pores of the AAO templates deposited Co by the tip growth mechanism.¹⁹

A well graphitization of the CNTs is supported by the Raman data (see Figure 3). The Raman bands are well developed even in the region of higher-order Raman process. The relative intensity of the D band at 1353 cm^{-1} to the G band at 1585 cm^{-1} is low and it decreases with increasing the fabrication temperature. The D band is known due to the disordered and small crystalline size sp^2 carbons.²⁰ It is known that the weak relative intensity of D band to G band indicates that the carbon nanotubes have a good graphitized structure.^{14, 21} For most tubes fabricated by chemical vapor

deposition (CVD), D band is more broad and stronger than G band.²⁰ It is concluded that CNTs fabricated by disproportionation of CO are well graphitized and the graphitization is improved by increasing fabrication temperature.

The measured emission current as function of applied voltage for samples fabricated at 500, 550 and 600 °C is shown in Figure 4. We could not measure the field emission from the CNTs fabricated at 650 °C because the template was deformed during fabrication. Current-voltage (I - V) curves are relatively smooth and reproducible. The size of the sample plates were 1.0×1.7 - 2.6 cm^2 . The field-emission data was analyzed using the Fowler-Nordheim model²² ($\ln(I/V^2) \sim 1/V$). Replotting of the data as $\ln(I/V^2)$ vs $1/V$ is inserted in Figure 4 and indicates the Fowler-Nordheim type field emission behavior. The enhancement factor β is derived from the slope by assuming a work function of CNTs as 5 eV. The β values for CNTs fabricated at 500, 550 and 600 °C are 1690, 3000, and 3520, respectively. The β value of CNTs fabricated at 500 °C is relatively low. This may be mainly due to the bundling of the tips of CNTs fabricated at 500 °C. These values are higher than some reported ones.^{8, 23} The CNTs fabricated here are so dense that the field emission could be greatly decreased by the field screen effect^{24, 25} provoked by the proximity of the neighboring tubes. Also, it is known⁹ that the bottom barrier layer of AAO templates affects greatly to the field emission but for the samples used here the bottom barrier layer has not been removed. If one considers the field screen and bottom barrier effects, there is no doubt that the CNTs fabricated by CO disproportionation

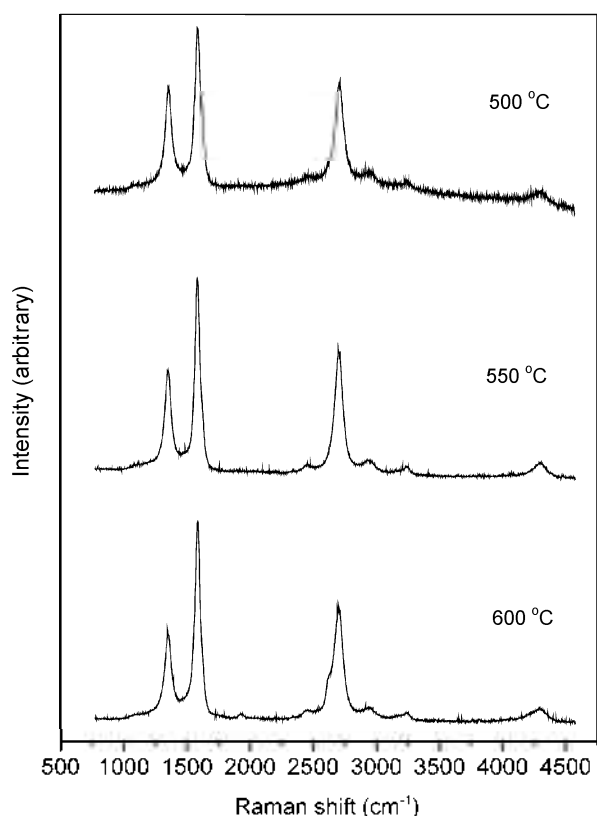


Figure 3. Raman spectra of CNTs fabricated by CO disproportionation at 500, 550 and 600 °C.

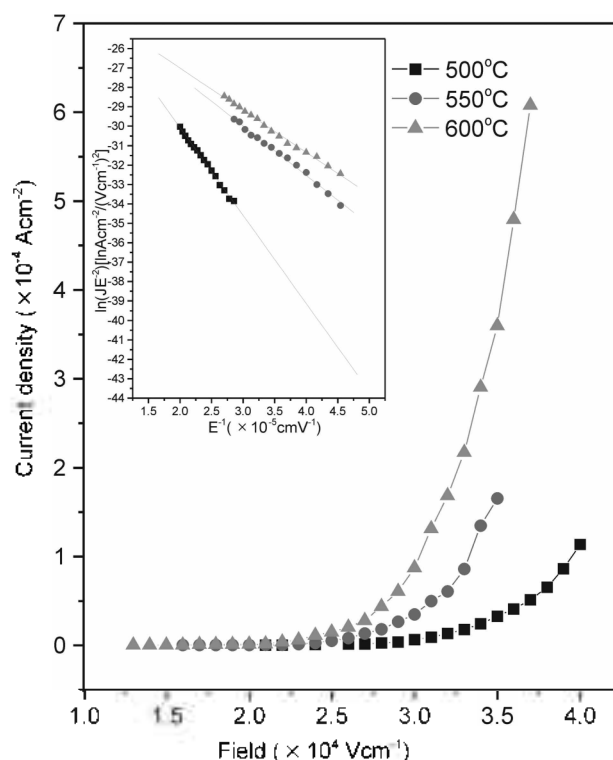


Figure 4. Field emission current density vs electric field for the CNTs fabricated by CO disproportionation at 500, 550, and 600 °C. Inset is the corresponding Fowler-Nordheim plots.

are a good field emitter.

During current density measurements, emission patterns were monitored with a phosphor screen. The CNTs fabricated at 500, 550, and 600 °C started to emit electrons at the fields of 1.9, 1.6 and 1.1 V/μm, respectively, but the emissions were not homogenous. As the applied field was increased, more uniform emission occurred on a phosphor screen in all cases. The phosphor screens became quite homogenous over the all area when the applied fields were 4.0, 3.4 and 3.1 V/μm, respectively (see Figure 5). Very homogeneous emissions may be due to the uniformity in height and diameter, high quality and well alignment of the tubes.

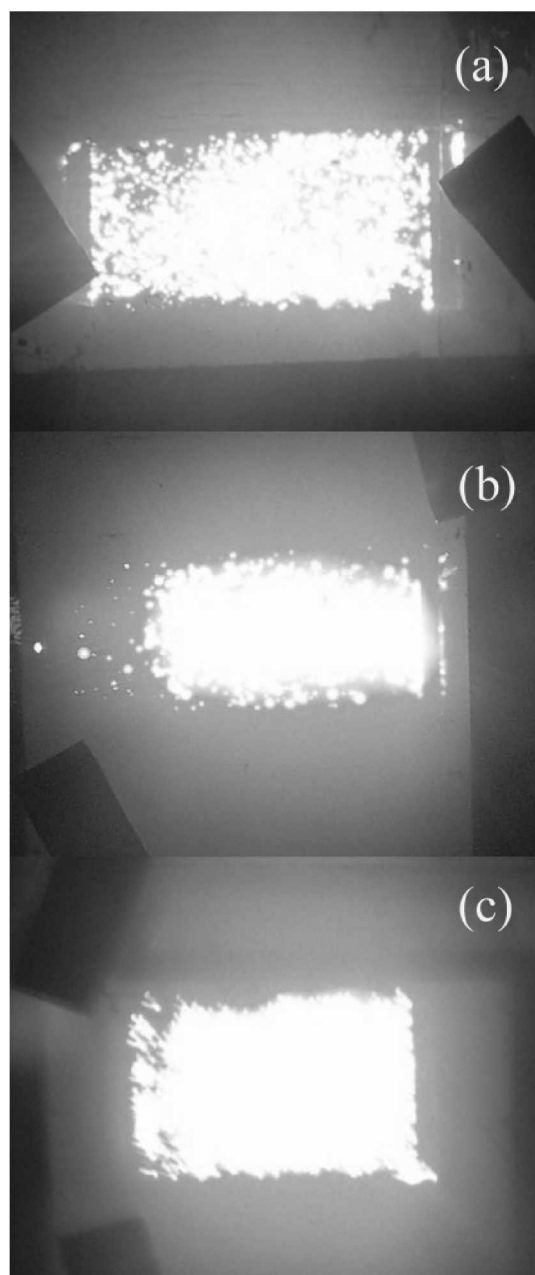


Figure 5. Emission patterns of the CNTs fabricated by CO disproportionation at (a) 500, (b) 550, (c) 600 °C by applying 4.0, 3.4 and 3.1 V/μm, respectively.

The CNTs studied here are fabricated relatively at low temperature but they show good field emission properties. These could be due to CO used as the precursor. When CO is disproportionated on the catalyst surface, only C and CO₂ are produced. The byproduct, CO₂ is a very stable gas and will desorb from the surface without further reaction. Therefore, pure carbon will be provided in the process of growing carbon nanotubes. Anyway, many hydrocarbons have been used as precursors. For using hydrocarbons as a precursor, there is no guarantee to provide pure carbon in the fabrication of CNTs. For example, the decomposition process of C₂H₂ is much complicated and some intermediate species like CH or C₂H can be involved in the process of growing carbon nanotubes. In this case, dangling bonds due to hydrogen atoms could be made in carbon nanotubes. These hydrogen atoms will be removed by further decomposition during fabrication or annealing but the defects due to these hydrogen atoms in the crystalline structure of carbon nanotubes will not be recovered completely.

As discussed earlier, the AAO templates were not deformed or cracked when CNTs were fabricated at 600 °C or at lower temperature. In a practical aspect, low fabrication temperature such as 500 °C is very important since it is lower than the melting point of soda lime glass (550 °C), which is commonly used as a low-cost substrate for display panel.²⁶ By using hydrocarbons as the precursor, it is difficult to fabricate CNTs directly on the soda lime glass at lower temperature than its melting point because CNTs could grow at least 600 °C or higher temperature.

Conclusions

In conclusion, the CNTs fabricated on AAO templates by disproportionation of CO have excellent field emission properties like uniform emission, high enhancement factor, and relatively low turn-on voltage. This may be due to high quality and vertical alignment of the CNTs fabricated on AAO templates by disproportionation of CO. Low fabrication temperature such as 500 °C could make it possible to use soda lime as the substrate for display panels.

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