Arc synthesis of double-walled carbon nanotubes in low pressure air and their superior field emission properties

Jiang Zhao, Yanjie Su, Zhi Yang, Liangming Wei, Ying Wang, Yafei Zhang *

Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Research Institute of Micro/Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China

ABSTRACT

Double-walled carbon nanotubes (DWCNTs) have been effectively synthesized by direct current (DC) arc discharge in low pressure air using a mixture of Fe catalyst and FeS promoter. Compared with conventional arc methods, this method is easier to implement without using expensive high purity gas sources. A tip structural DWCNT film has been successfully fabricated by a mixing process of electrophoresis, electroplating and electro-corrosion. The field emission properties of tip structural nanotube film are significantly increased compared with DWCNT film fabricated by electrophoresis. The turn-on electric field $E_{to}$ decreases from 1.25 to 0.92 V/μm, the low threshold electric field $E_{th}$ decreases from 1.45 to 1.13 V/μm, and the field enhancement factor $β$ increases from about 2210 to 4450. Meanwhile, this tip structural CNT film shows remarkably stable within 2% fluctuations for several hours. The high-performance emitter material and preparation technologies are both easy to scale up to large areas.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) have been attracted considerable scientific and technological attention for their unique structural, electronic, thermal and mechanical properties [1–4]. Double-walled carbon nanotubes (DWCNTs) which consist of two concentric cylindrical graphene layers have both merits of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). DWCNTs with their outstanding properties are expected to be used in various attractive applications, such as field emission devices [5], solar cells [6], field effect transistors [7], and atomic force microscopy (AFM) tips [8].

Since the pioneering work on CNTs in 1991 [1], great attempts have been made and continue in optimizing CNT preparations. Till today, DWCNTs have been prepared by several methods such as the conventional arc discharge [9–11], the high-temperature pulsed arc discharge [12], the catalytic chemical vapor deposition (CVD) [13], the coalescence of C60 inside SWCNTs at high temperature [14], and separating DWCNTs from SWCNTs by density gradient ultracentrifugation [6]. Among all these methods, arc discharge with its simplicity and reliability is widely used nowadays for preparing high quality DWCNTs because arc-synthesized nanotubes are known to be well graphitized and have less structural defects.

In this work, we demonstrate a promising and low-cost synthetic method for preparing DWCNTs using a mixture of Fe catalyst and FeS promoter by DC arc discharge in low pressure air. Compared with conventional arc methods, this method is easier to implement without using expensive high purity gas sources, such as hydrogen [9–11] and helium [15], which can reduce significantly the cost of preparing DWCNTs and minimize the danger of large-scale application of hydrogen gas. What is more, it also simplifies the preparation process because of the absence of pre-vacuum. Furthermore, a
simple, scalable, and low-cost technique to fabricate a tip structural DWCNT film is developed by a mixing process of electrophoresis, electroplating and electrocorrosion, and emitters made of DWCNT films with and without this tip structure have been studied particularly.

2. Experimental

The procedure of synthesizing DWCNTs was carried out in a home-made stainless steel chamber, where two electrodes were vertically installed, as shown in Fig. 1. The anode with 6 mm in diameter was prepared from a mixture of graphite powders, Fe catalyst and FeS promoter with the molar ratio of 94:4:2. The cathode with 8 mm in diameter was a pure graphite rod which was fixed on the upside. Iron frame was used for collecting cloth-like materials. The air pressure was maintained at 50 Torr when a continuous flow of dry air at about 300–400 mL/min was inputted into the chamber during the whole discharge process. The arc was operated at about 80 A with a gap of 1–2 mm maintained between the two electrodes. After arc evaporation for 20 min, over 400 mg of the cloth-like CNTs was obtained from the iron frame (Fig. 1 (right)).

The as-synthesized DWCNTs were firstly purified using oxidation in air at 450 °C for 1 h in order to remove amorphous carbon. After oxidation, the obtained samples were immersed in HCl for 24 h at room temperature to remove the iron catalyst particles, and then washed with distilled water and dried at 80 °C for 12 h.

The morphologies and microstructures of the obtained products were investigated by field emission scanning electron microscope (FESEM, Ultra 55, Carl Zeiss) and transmission electron microscope (TEM, JEM-2100, JEOL). Raman spectrum was obtained on a BRUKER Senterra Raman microscope (FESEM, Ultra 55, Carl Zeiss) and transmission electron microscope (TEM, JEM-2100, JEOL). TGA measurements were carried out using a Perkin-Elmer Pyris thermal analyzer. The spectrum was obtained on a BRUKER Senterra Raman microscope (FESEM, Ultra 55, Carl Zeiss) and transmission electron microscope (TEM, JEM-2100, JEOL). TGA measurements were carried out using a Perkin-Elmer Pyris thermal analyzer. The air pressure was maintained at 50 Torr when a continuous flow of dry air at about 300–400 mL/min was inputted into the chamber during the whole discharge process. The arc was operated at about 80 A with a gap of 1–2 mm maintained between the two electrodes. After arc evaporation for 20 min, over 400 mg of the cloth-like CNTs was obtained from the iron frame (Fig. 1 (right)).

The as-synthesized DWCNTs were firstly purified using oxidation in air at 450 °C for 1 h in order to remove amorphous carbon. After oxidation, the obtained samples were immersed in HCl for 24 h at room temperature to remove the iron catalyst particles, and then washed with distilled water and dried at 80 °C for 12 h.

The morphologies and microstructures of the obtained products were investigated by field emission scanning electron microscope (FESEM, Ultra 55, Carl Zeiss) and transmission electron microscope (TEM, JEM-2100, JEOL). Raman spectrum was obtained on a BRUKER Senterra Raman microscope (FESEM, Ultra 55, Carl Zeiss) and transmission electron microscope (TEM, JEM-2100, JEOL). TGA measurements were carried out using a Perkin-Elmer Pyris thermal analyzer. The measurements were performed from 50 to 900 °C at 10 °C/min with 20 sccm air flow.

3. Results and discussion

The as-prepared CNT film that was peeled off from the iron frame was torn into small pieces for directly observing with SEM and TEM. Fig. 2a shows typical SEM images of the as-synthesized DWCNT film. Many long filament-like materials are observed in the DWCNTs from SEM image shown in the inset of Fig. 2a. It can be seen that these filaments with some catalyst nanoparticles entangle into nets. The representative TEM images are shown in Fig. 2b and c. Almost all the CNTs that can be distinguished are DWCNTs. These CNTs always form into bundles due to the van der Waals interaction. Most of DWCNTs have inner diameters in the range of 2–4 nm and outer diameters in the range of 3–7 nm, respectively. However, other tubular products such as SWCNTs and triple-walled carbon nanotubes (TWCNTs) are also found as minor product, as observed in Fig. 2c. Moreover, catalytic particles (CPs) surrounded by two to several graphene layers are also observed with interlayer distances of 0.36 ± 0.02 nm. Fig. 2d shows a single DWCNT with clearly straight graphitic layers. The straight nanotube walls with hollow cavities are observed, indicating fewer defects in nanotube. The interlayer spacing between the inner and the outer walls of DWCNTs is about 0.38 nm, which is larger than that usually examined for MWCNTs with about 0.34 nm [16].

The catalysts used for the synthesis of DWCNTs by arc discharge generally contain S and Fe metals in the anode [9,17]. However, we found that hardly any DWCNTs were acquired without S additive when the other parameters being the same. So the appropriate S can improve the carbon deposition on Fe catalyst nanoparticles and promote the growth of CNTs. A possible growth process of DWCNTs is as follows. In arc plasmas, both Fe and FeS are liquefied, and tend to form core/shell particles because of their different melting points (Fe: 1535 °C, FeS: 1193–1199 °C) during their solidification process [18]. Carbon clusters may dissolve in both core and shell portions of the catalyst particles. Graphene layers may dissolve out from both surface of core and shell portions, resulting in the formation of DWCNTs.

Raman spectroscopy has become a powerful structural analytical technique for characterizing the structural integrity and diameter distribution of CNTs [19]. Similar to that of SWCNTs, it is observed that three distinguished features from DWCNT samples, as shown in Fig. 3. A very weak D-band at 1339.5 cm⁻¹ (the disorder-induced phonon mode) and a strong G-band at 1575.8 cm⁻¹ (the E₂g mode) are found in Raman spectrum, respectively. At the low frequency below 300 cm⁻¹, several peaks show radial breathing modes (RBM), resulting from different CNT diameters. We estimate the inner and outer diameters of DWCNTs using the expression \( \omega (\text{cm}^{-1}) = 6.5 + 223.75/d (\text{nm}) \), [5], where \( \omega \) refers to the RBM frequency and \( d \) refers to the DWCNT diameter. The RBM peaks at 77.4, 102.1, 146.5, 168.8, 214.2 and 265.6 cm⁻¹ correspond to the DWCNT bundle diameters of 3.16, 2.34, 1.60, 1.38, 1.07 and 0.86 nm, respectively. Generally, the diameter of CNTs is more than 3 nm, Raman frequencies in the RBM region are hardly detected [5]. So the biggest calculated value of diameter is basically smaller than that observed in HRTEM images. As a result, it is difficult to detect the band of most nanotubes with a large diameter above 3 nm in low-frequency region [20].
Here, we only roughly calculated the diameters of DWCNTs based on Raman peaks. The intensity ratio, $I_D/I_G$, is generally used as diagnostic parameter for estimating the structural perfection of CNTs. The smaller the value of $I_D/I_G$ is, the lower the disorder would be. The ratio of $I_D/I_G$ is about 0.066, which indicates high-quality DWCNTs with a well-graphitized structure are synthesized by arc discharge in low pressure air.

TGA spectra are usually been performed to investigate the weight purity of CNTs. Fig. 4 shows the differentiated TGAs of raw sample and purified DWCNTs. In the raw sample, it can be observed that the weight firstly increases at about 300 °C due to the oxidation of Fe catalyst into Fe$_3$O$_4$ with the reaction of $4\text{Fe} + 3\text{O}_2 = 2\text{Fe}_3\text{O}_4$ [13]. And then, a little weight decreases over 400 °C because of the oxidation of amorphous carbon. The red residue of Fe$_3$O$_4$ left in the crucible at 900 °C reaches to about 39.5 wt.%. It can be deduced that the yield of DWCNTs in the cloth-like soot is more than 60 wt.%. In the purified nanotubes, no weight loss below about 600 °C and gentle degradation slope indicate that various impurities are effectively removed after purification. The total weight loss is 90.7 wt.% at 900 °C. Based on this result, it can be estimated that the DWCNT content of purified sample is about 93.5 wt.% and the remaining Fe catalyst particles (about 6.5 wt.%) exist after purification, which essentially correspond to the obser-
vation from SEM image of purified DWCNTs (inset of Fig. 4). From SEM image of the purified DWCNTs, white spots represented iron catalyst nanoparticles are scattered over the purified nanotubes.

CNTs are considered to be an ideal field emitter due to their low work function, large aspect ratio, good conductivity and high mechanical stability [21,22]. To demonstrate the outstanding electrical characteristic of the DWCNTs prepared by arc discharge in low pressure air, the field emission characteristics were measured. Fig. 5 schematically showed the preparation of DWCNT film with a tip structure for field emission test by a mixing process of electrophoresis, electroplating and electrocorrosion. Cu thin film with a thickness of about 300 nm had been deposited on a piece of glass substrate by a radio frequency (RF) magnetron sputtering (Fig. 5a). A layer of DWCNT film was deposited onto the substrate covered Cu film by electrophoresis of the dark gray suspension. DWCNTs were added to the ethyl alcohol solution with a uniform dispersion by ultrasonic method. (CH$_3$COO)$_2$Cu.H$_2$O with the concentration of about 5 $\times$ 10$^{-4}$ mg/L was used for additive to enhance the electrical conductivity of solution. Steel plate was used as the working and counter electrode, as shown in the above of Fig. 5b. The distance between two electrodes was 1 cm, and a constant potential of 20 V DC was maintained for 30 min. DWCNT film prepared by electrophoresis was shown in the below of Fig. 5b. It was observed that nanotubes were almost spread out flat on the substrate, which did not facilitate the field emission. After electrophoresis process, the CNT film was put into CuSO$_4$ bath to deposit an extraordinary thin Cu coating (Fig. 5c). Electroplating process was performed at 5 mA/cm$^2$ for 2 min, Cu plate was used as the working and counter electrode. In order to form a nanotube tip structure, the nanotube film covered with a thin Cu coating was subjected to an electric field in CuSO$_4$ solution. Unlike electroplating, the substrate and Cu plate were connected to positive and negative electrodes, respectively. As a result, thin Cu coating deposited on the CNT film was gradually corroded. Electrocorrosion process was carried on under an electric field of 10 V for 90 s. Two electrodes were maintained at a distance of 1 cm, as illustrated in the left of Fig. 5d. SEM image of the tip structural DWCNT film after electrocorrosion process is shown in Fig. 5e. This tip structural DWCNT film was dried naturally for about 24 h at room temperature. Further investigation of the electrocorrosion effect was carried out by energy dispersive X-ray spectroscopy (EDS), as shown in the below of Fig. 5e. EDS results reveal that the content of Cu atoms is obviously more than that of carbon atoms in the surface layer of nanotube tips and the carbon content is significantly more than the Cu content with the increase of depth, indicating Cu coating by electroplating has not yet been corroded during the electrocorrosion process. Meanwhile, one end of CNTs arose vertically from the entirely corroded Cu coating under the

Fig. 5 – Schematic of the preparation of tip structural DWCNT film for field emission. (a) Sputtering Cu film on glass substrate. (b) Electrophoresis process (above), SEM image of DWCNT film prepared by electrophoresis (below). (c) Electroplating process. (d) Electrocorrosion process. (e) SEM image of the tip structural DWCNT film (above), EDS spectra of different areas in nanotube tip structure (below). (f) Schematic of the emitter.
electric field. This may be due to Cu(II) ions adsorbed at nanotube tips move to the cathode, leading to the arisen of CNTs. Finally, CNT tip structure was formed after electrocorrosion process. Fig. 5f shows a schematic of the emitter. The tip structural DWCNT film served as the cathode. An indium tin oxide (ITO) glass was used for the anode. The gap between two electrodes separated by mica was about 260 μm. The field emitting area was about 100 mm². The field emission measurements were performed in a vacuum chamber maintained at about 5.0 × 10⁻⁸ Pa at room temperature.

To characterize further the quality of our tip structural DWCNT film and explore its potential applications, the field emission behaviors were studied in detail. In order to contrast, the field emission properties of DWCNT film prepared by electrophoresis were also measured, as shown in Fig. 6. It is obvious that the tip structural DWCNT film requires a much lower driving electric field than DWCNT film. The turn-on field $E_{th}$ defined as producing the current density of 10 μA/cm² occurs at 1.25 and 0.92 V/μm, respectively, which indicates that the tip structural DWCNT film formed from nano-tube film after electrophoretic and electrocorrosion processes can decrease dramatically the turn-on electrical field $E_{th}$. The threshold field $E_{th}$ defined as producing the current density of 1 mA/cm² is found to be 1.45 and 1.13 V/μm, respectively. According to the Fowler–Nordheim (F–N) theory [21,23], the current $I$ (A) is given by the following equation:

$$I = \frac{a \cdot S \cdot E_z^2}{\varphi} \exp \left( \frac{-b \cdot \varphi^{(3/2)}}{E_z} \right)$$

where $S$ is the total effective area of emission sites, $a = 1.54 \times 10^{-6}$ A V⁻² eV, $b = 6.83 \times 10^6$ eV⁻³/² V cm⁻¹, $\varphi$ (eV) is the work function of material, $E_z$ is a local electric field at a given emission site, which is related to the applied voltage $U$ and the inter-electrode distance $d$

$$E_z = \beta \cdot \left( \frac{U}{d} \right)$$

where $\beta$ is the field enhancement factor determined by the geometry and the areal density of emitters. $\beta$ and $S$ are not known and their values may be speculated from F–N plots shown in the inset of Fig. 6(a). The field enhancement factor $\beta$ and the total effective area of emission sites $S$ can be calculated from slope and intercept of linear fitting $F–N$ plots, respectively [24,25]. By assuming that the work function of DWCNTs to be the same as that of graphite (~5 eV) [23], the field enhancement factor $\beta$ of DWCNT film and tip structural DWCNT film are calculated as about 2210 and 4450, respectively. Although there is speculation that random CNTs may stand erected during application of bias, field enhancement for CNT film is almost negligible due to standing-up of randomly oriented CNTs [26,27]. So structural advantage of CNT tips is dominantly responsible for field enhancement. It is noteworthy that the field enhancement factor $\beta$ of tip structural DWCNT film is higher due to the increased aspect ratio as compared with the conventional DWCNT film. While for an individual nanotube tip it may be estimated the field enhancement factor $\beta \sim U/2r$, where $l$ is nanotube length and $r$ is its radius. With an increase in nanotube height for array of nanotubes, the aspect ratio of the tube height to the radius and the field emission will increase simultaneously with relatively low aspect ratio. It has been reported that the screening effect may be the dominant factor when the nanotube height is longer than the intertube distance and the field emission is decreased [28]. The ideal ratio of the distance between the adjacent nanotubes to the nanotube height is about two by theoretical calculations [29]. However, in our samples, the electric field may be concentrated around some longer CNT tips protruded among the other tips due to the non-uniformity of CNT length. Meanwhile, the CNT tips may curl or bundle to form an emitter with a reduced aspect ratio. These non-uniformity of the DWCNT tips may cause the increase of field enhancement $\beta$. In addition, from F–N plots the calculation of total area emission sites for tip structural DWCNT is about $4.29 \times 10^{-2}$ cm². Considering peak emission current can reach up to 8 mA, corresponding peak emission current density is ~186.5 mA/cm².

To evaluate the stability of the field emission current of two types films, we recorded the current density of 10 mA cm⁻² for 300 min (Fig. 5b). For tip structural DWCNT film, a current fluctuation is observed to be less than 2%, exhibiting stable emission. However, the current density shows a declining trend from to about 7 mA cm⁻² for DWCNT film fabricated by electrophoresis. It is considered that the more stable emission properties of tip structural DWCNT film compared to the conventional DWCNT film may result from the erected CNT tips because of electrocorrosion process.

There are some papers devoted to study field emission properties of DWCNTs fabricated by various techniques and
measured by different conditions are summarized in Table 1. Our tip structural CNT film has a relatively lower turn-on electric field $E_{\text{to}}$ threshold electric field $E_{\text{th}}$ and the outstanding field emission properties among the reported results. This high-performance emitter of tip structural DWCNT film is inexpensive, controllable and reproducible. Based on the field emission results, tip structural DWCNT film is superior for field emission, which can be applied as field emission flat panel displays and cold electron sources in display devices.

4. Conclusions

We have successfully synthesized high-quality DWCNTs by DC arc discharge in low pressure air using a mixture of Fe catalyst and FeS promoter. This method is easier to implement without using expensive high purity gas sources than conventional arc methods. Characterizations of TEM and Raman analysis demonstrate that the as-synthesized DWCNTs have well-graphitized structure. DWCNT film with a tip structure can easily generate by a mixing process of electrophoresis, electroplating and electrocorrosion. The field emission results indicate that tip structural DWCNT film exhibits more outstanding field emission properties than DWCNT film prepared by electrophoresis. An extremely lower turn-on electric field $E_{\text{to}}$ of 0.92 V/$\mu$m and a lower threshold electric field $E_{\text{th}}$ of 1.13 V/$\mu$m are obtained. The field enhancement factor $\beta$ of tip structural DWCNT film increases from 2210 to 4450. This high-performance emitter of tip structural DWCNT film is inexpensive, controllable and reproducible, which is promising for development of the CNT-FE technology.

Acknowledgments

The authors gratefully thank National High-Tech R & D Program of China (863, No. 2011AA050504), National Natural Science Foundation of China (No. 61006002), Shanghai Science and Technology Grant (No. 1052 nm05500), Shanghai Pujiang Program (No. 11PJ001), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, the U-M/SJTU Collaborative Research Program and the Analytical and Testing Center of SJTU.

References


Table 1 – Field emission performances of various DWCNTs.

<table>
<thead>
<tr>
<th>Emitter type</th>
<th>Remarks</th>
<th>$E_{\text{to}}$ (V/$\mu$m)</th>
<th>$E_{\text{th}}$ (V/$\mu$m)</th>
<th>$\beta$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD-DWCNTs</td>
<td>Vertically aligned arrays</td>
<td>0.85</td>
<td>1.67</td>
<td>3517</td>
<td>[30]</td>
</tr>
<tr>
<td>Annealed CVD-DWCNTs</td>
<td>Spraying with Ag paste</td>
<td>1.16</td>
<td>2.12</td>
<td>1246</td>
<td>[31]</td>
</tr>
<tr>
<td>Arc-DWCNTs</td>
<td>Spraying film</td>
<td>3.0</td>
<td>~4.5</td>
<td>1625</td>
<td>[5]</td>
</tr>
<tr>
<td>CVD-DWCNTs</td>
<td>Screen-printed CNT film</td>
<td>1.33–1.78</td>
<td>~2.22</td>
<td>3775–5207</td>
<td>[32]</td>
</tr>
<tr>
<td>DWCNTs</td>
<td>Decorated with Ru nanoparticles</td>
<td>1.3</td>
<td>3.9</td>
<td>2231</td>
<td>[33]</td>
</tr>
<tr>
<td>Arc-DWCNTs</td>
<td>Tip structural CNT film</td>
<td>0.92</td>
<td>1.13</td>
<td>4450</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: $E_{\text{to}}$ obtained at 0.1–10 $\mu$A/cm$^2$ and $E_{\text{th}}$ obtained at 1.0 mA/cm$^2$. 


