Journal of
Nanoscience and Nanotechnology
Vol. 6, 1346–1349, 2006

Fabrication of Small Diameter Few-Walled Carbon Nanotubes with Enhanced Field Emission Property

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A unique type of carbon nanotubes with 2 to 5 layers of sidewalls and diameters less than 10 nm was synthesized by the thermal chemical vapor deposition (CVD) method with MgO supported Fe/Mo catalyst. Unlike the typical CVD grown multi-walled carbon nanotubes, these few-walled carbon nanotubes (FWNTs) have a high degree of structural perfection. They have enhanced electron field emission characteristics compared to the current commercial nanotubes, with a low threshold field for emission and improved emission stability.

Keywords: Nanotube, FWNTs, CVD, Field Emission, Display.

Since the discovery in 1991, carbon nanotube.[1] (CNT) has attracted extensive attention due to its unique properties and potential applications. Up to now, most of the research works have focused on two distinct kinds of CNT, single-walled carbon nanotube[2,3] (SWNT) that consists only single graphite layer and multi-walled carbon nanotube (MWNT) that consists multiple layers of sidewalls. Both the SWNTs and the MWNTs can be synthesized by several techniques, including laser ablation, arc discharge, and chemical vapor deposition (CVD) methods.[4] In general, the SWNTs have less structural defects than the MWNTs, especially the CVD grown MWNTs. However, the synthesis and purification of the SWNTs are much more challenging than the MWNTs, limiting their use in applications that need a large amount of nanotubes. Here we report the synthesis of a unique type of nanotubes with comparable degree of structural perfection and morphology to the SWNTs but can be readily produced in relatively large quantities. These nanotubes which we refer to as "Few-Walled Carbon Nanotube" (FWNTs) are composed of nanotubes with 2–5 layer of graphene shells on their sidewalls and generally with diameter smaller than 10 nm. They can be considered as a new type of nanotubes that bridge the gap between the SWNTs and the normal MWNTs. Strictly speaking, they are MWNTs with small diameters and high structural perfection. Interestingly, these FWNTs possess some unique properties that make them ideal for certain bulk applications, including field emission and composite materials.

Carbon nanotubes (CNTs) based "cold-cathode" vacuum electronic devices are among the most studied potential applications of nanomaterials today.[5] Prototype devices with the CNT emitters such as flat-panel field emission displays (FED),[6,7] and field emission X-ray sources[8–10] have already been demonstrated. The CNTs are found to have a lower threshold field for emission and improved emission stability compared to the conventional Spindt tips.

Extensive research in the last few years shows that the emission properties of the CNTs depend sensitively on their structure and morphology. On the individual tube level, the emission characteristics can be correlated with the diameter, the aspect ratio and the degree of structural perfection. For a macroscopic cathode comprising a layer of CNT film, the morphology also plays a key role. The SWNTs made by the laser ablation process typically show better emission characteristics than the MWNTs because of parameters including their small diameters and low defect density. They are however expensive to fabricate and not practical for applications that require a large quantity of nanotubes. It is therefore important for applications of CNT based devices to search for materials that have better or comparable emission properties compared to the laser-grown SWNTs and can be produced in relatively large quantities at low cost.

In this paper, we report the synthesis of FWNTs by the thermal CVD method using MgO supported Fe/Mo

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 1533-4880/2006/6/1346/004 doi:10.1166/jnn.2006.140

catalyst. The electron field emission properties of macroscopic cathodes comprising FWNTs are evaluated and compared to cathodes comprising SWNTs and MWNTs fabricated under otherwise identical conditions. The results show that the emission characteristics of the FWNTs are better than the commercially available CNTs, the CVD grown SWNTs, and are comparable to the SWNTs fabricated by the laser ablation process at UNC.

The Fe/Mo catalyst supported by MgO was prepared by modified glycine combustion method. Typically, desired amount of $Fe(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, (NH_4) $6Mo_7O_{24} \cdot 4H_2O$, glycine, and citric acid dissolved into deionized water to make a clear solution, then the solution was slowly heated at 120 °C for 12 h to obtain a viscous precursor. When increasing the temperature to over 300 °C quickly, the precursor combusted suddenly to produce large amount of porous powder. The catalyst for CNT growth was finally obtained after annealing the porous powder at 550 °C to remove any organic residues.

FWNTs were synthesized in a simple CVD setup made of a horizontal tube furnace and gas flow control units.[11,12] Methane was employed as carbon source and hydrogen was also added with certain ratio to control methane decomposition rate. In a typical growth experiment, Fe/Mo supported MgO catalyst was put into a quartz tube and was flushed with hydrogen, while the catalyst was heated to growth temperature. Methane was then introduced. After the reaction lasted for desired time (10–30 min), methane flow was turned off and hydrogen flow was still turned on while the system being cooled down. The raw materials were then characterized using TEM. The current productivity of the material is about 50 g per day. After an oral presentation at the 2004 American Chemical Society March meeting and the filing of a U.S. patent application on the synthesis of the FWNT materials (U.S. 11/012,341),[13] we also noticed a publication of a similar method on the production of small diameter multiwalled carbon nanotubes.[14]

Figure 1a shows a low magnification TEM image of the FWNTs. High quality isolated or small bundles of FWNTs were revealed. It was shown that the bundle diameters were in the 15–30 nm ranges while the individual nanotubes were usually smaller than 10 nm. Figure 1b showed a typical HRTEM images of FWNTs, which confirmed that the isolated nanotubes were around 5 nm and composed of three to five walls. Most FWNTs were long and straight in morphology, indicating that these nanotubes have relatively perfect graphitic structure and less defects as SWNTs. Both raw and purified FWNTs were used for field emission studies and showed similar performance in our studies.

To evaluate the electron field emission properties, macroscopic CNT films (typically 1 cm in diameter) were deposited on ITO (indium tin oxide) coated glass substrates using the electrophoretic deposition (EPD) method developed at UNC and Xintek (EPD).[15,16] EPD is a

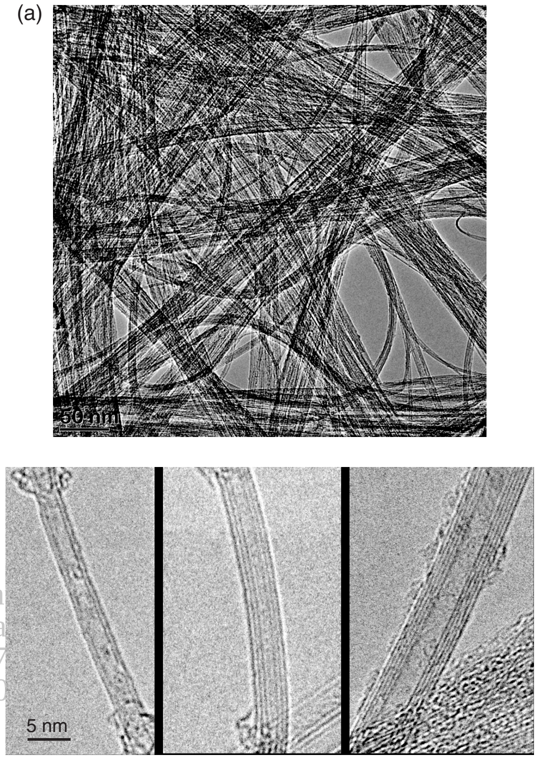

Fig. 1. (a) Low resolution TEM image of FWNTs and (b) high resolution TEM images of individual FWNTs with 2, 3, and 5 layers, respectively.

room-temperature liquid-phase process that has been applied to fabricate patterned field emission cathodes for displays.[17] It has several advantages over other post-processing methods such as screen printing which is often used for making CNT cathodes for FEDs. In this process, the pre-formed CNTs were processed and dispersed in a suitable solvent. They were deposited onto the selected areas of the substrate surface when subjected to an electrical field. The cathode made by electrophoretic deposition is a thin film composed of randomly oriented CNTs which are partially embedded in an inorganic matrix. The surface morphology of the FWNT film is comparable to that of the SWNT film. The same deposition conditions were used in both cases. SEM examinations show that after activation there is a low density of CNTs protruding from the matrix surface, which are presumable the active emitters. There is a strong adhesion between the film deposited and the substrate surface. Arcing, which is a good indication whether there is evaporation of CNTs during field emission, is usually not observed at low anode voltage (<30 KV).

The field emission properties of the CNT films/cathodes were studied under the diode mode inside a vacuum chamber at 10^{-7} base pressure. The experimental setup is illustrated in Figure 2. During measurement, the CNT cathode was grounded and a positive DC or pulsed voltage was applied to the anode. The electrons emitted from CNTs were all collected by the anode. For measuring the emission uniformity, the metal anode was replaced by a

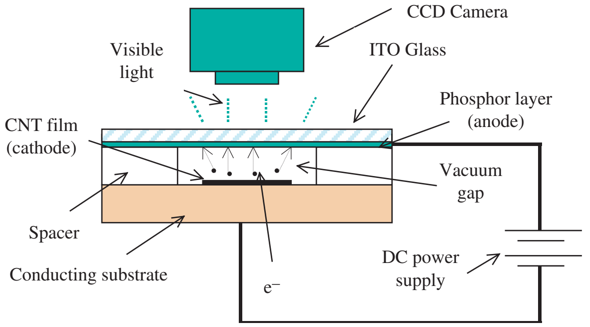

Fig. 2. The schematic drawing of the experimental setup used in our lab for measuring the electron field emission properties of the CNT cathodes.

phosphor coated ITO glass. The images formed on the anode were captured by a CCD camera placed outside the vacuum chamber.

The FWNT cathodes show an excellent emission current density (J) versus electric field (E) characteristics with a low turn-on field is less than 1.5 V/μm at current density of 10 μA/cm^2 for the cathode and stability at the high emission current density. Figure 3a shows the J–E curves measured consecutively from a FWNT cathode with 0.049 cm^2 emission area in DC mode. A current density over 50 mA/cm^2 was achieved at <3 V/μm electric field. Figure 3b plots four consecutive J–E curves of a cathode of 0.6 mm in diameter measured in the pulse mode. An emission current density as high as 4.39 A/cm^2 is achieved on the cathode at 16.2 V/μm. The data also show very good stability and reproducibility during the whole measurement process.

Comparison was made with the cathodes fabricated using other types of CNTs. CNTs studied include SWNTs

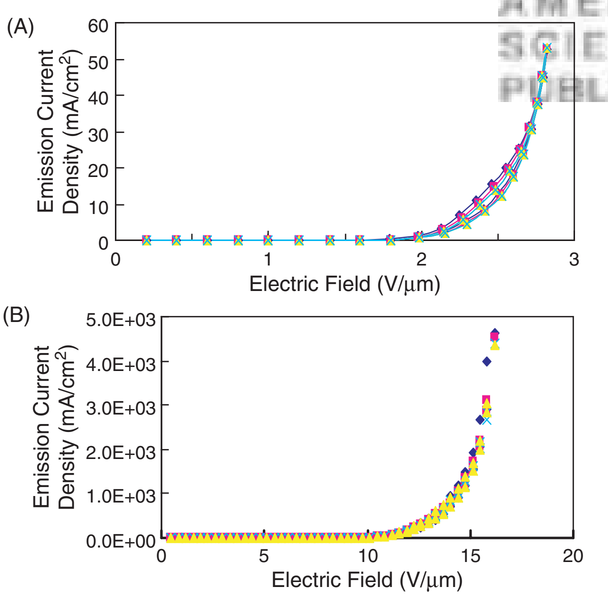

Fig. 3. (a) Four consecutive J–E curves of a FWNT cathode of 2.5 mm in diameter measured in DC mode. (b) Four consecutive J–E curves of a nanotube cathode of 0.6 mm in diameter measured in pulsed mode.

by the arc-discharge method (commercial), the CVD (fabricated at Duke)[11, 12] and the laser ablation method (produced at UNC);[18] MWNTs by CVD (grown at Duke and from commercial sources) and arc-discharge (from commercial sources) methods. The cathodes were prepared the same EPD process under the same conditions. The threshold fields for emission of the FWNT cathodes were found to be substantially lower than the values obtained from all the MWNTs and the arc-discharge and CVD grown SWNTs. The turn-on fields for 10 μA/cm^2 current density obtained from these materials are in the range of 3–5 V/μm, to be compared with less than 1.5 V/μm for the FWNTs. The values are comparable or lower than those from the SWNTs by the laser ablation method.

The FWNT cathodes also have excellent long-term emission stability. Figure 4 shows the voltage and emission current versus time curves of a cathode with 0.049 cm^2 emission area measured continuously under the constant current mode. During the experiments, the emission current from the cathode was maintained at 100 μA by varying the applied voltage. After the first 20 hours initial "burn-in," the emission current underwent no decay for the next 100 hours.

The emission uniformity of the FWNT cathodes by the EPD process was evaluated by taking images formed on the phosphor screen used as the anode. The emission image from one representative 1 cm diameter cathode is shown in Figure 5. The data was taken at 1300 V peak anode voltage, 10% duty cycle and 1 mm cathode–anode gap. The peak emission current measured is 7 mA.

In summary, we have developed a CVD method that can produce a large amount of small diameter few-walled carbon nanotubes (FWNTs) that possess excellent field emission properties. Structural characterization showed that these FWNTs have much less structural defects than the CVD MWNTs. The field emission properties of the materials are as good as the laser grown SWNTs. Low emission threshold field, high emission current and long term emission stability were observed in cathodes prepared from these nanotubes using electrophoretic deposition at

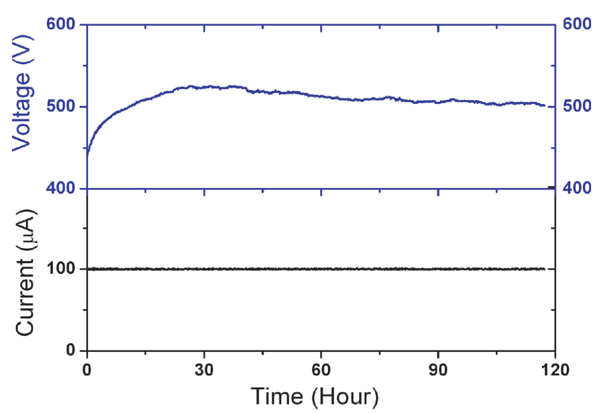

Fig. 4. Voltage and emission current versus time curves of a FWNT cathode with 0.049 cm^2 emission area measured in continuous DC mode.

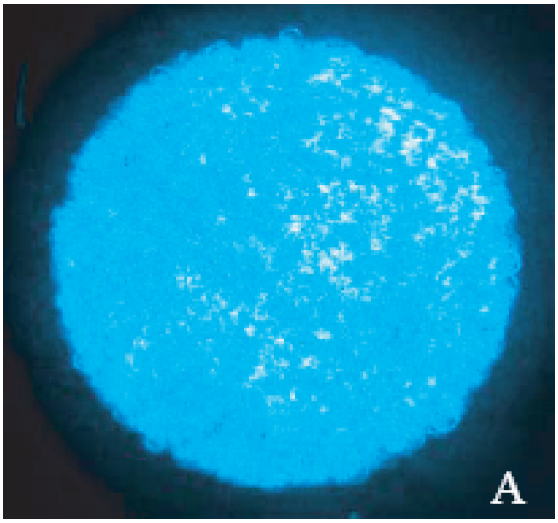

Fig. 5. The emission image from one representative 1 cm diameter cathode.

room temperature. Comparing with other types of nanotubes, these materials combined the easiness in preparation of MWNTs and the outstanding emission properties of SWNTs. They represent a realistic and scalable choice for the development of nanotube based field emission applications such as flat panel FED, portable X-ray sources, etc.

Acknowledgment: The work at Duke is funded by a grant from NASA Langley (Grant #: NNL04AA09A).

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Received: 25 May 2005. Revised/Accepted: 29 November 2005.