

FORMATION AND FIELD-EMISSION PROPERTIES OF CARBON NANOFIBERS BY A SIMPLIFIED THERMAL GROWTH

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Abstract. Synthesis and field emission properties of a carbon nanofibers (CNFs) film by a simplified thermal growth were investigated in the present study. Firstly, a Ni-based thin film used as catalyst was deposited on stainless substrate by using a spin-coating method. Using toluene as carbon precursor, a high-density CNF network was grown on Ni-based film at 900 °C. It was found that the grown carbon nanofibers were strongly affected by surface density of Ni film. An increased trend of fiber density and length of carbon nanofibers with Ni amount was observed. Surface and structural analyses indicated that the single CNF with an average size of 100 nm has an imperfect graphitic layered structure. Field emission tests showed that the turn-on voltage of CNFs is at around 7 MV/m, and the thresholds voltage at 10 mA/cm² is at 10 MV/m. Based on Fowler-Nordheim model, the work function of the CNFs was estimated in range of 0.90–3.64 eV.

1. INTRODUCTION

Nearly ten years after their discovery, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) still attract much interest in their potential applications. Due to their unusual structural and electronic properties, the carbon nanostructures can be extensively applied in future fields [1], including field emission display, battery, transistor, nanoscale interconnects, and so on. Numerous studies have devoted to investigating CNFs growth by using various methods [1–7]. Of these methods, chemical vapor deposition (CVD) is widely used for CNFs synthesis due to its high product yield. Generally, CNFs was produced by way of catalytic decomposition of certain hydrocarbons on small metal particles, such as Ni, Fe, and Pt. Up to now, several kinds of CVD methods, such as hot-filament-plasma-assisted CVD [8], microwave plasma CVD [9], etc., have been studied to synthesize CNFs. Although the ways to prepare CNFs have been enhanced, the development of CNFs applications is still hampered. One of mainly problems is how to

develop a large-scale process for synthesizing CNFs.

Accordingly, we sought an alternative method to fabricate the CNFs directly onto substrate. The purpose of this paper is to present a simplified growth process for fabricating CNF electrodes, which is suitable for field-emission (FE) emitters. During catalytic growth reaction, the pressure is only set at 1 atm and the reaction temperature is set at 900 °C. The influence of catalyst density on CNF growth was studied, and the CNFs was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, FE properties from the CNF film were also investigated in this study.

2. EXPERIMENTAL

In order to initiate growth of CNFs, formation of catalyst particles is required. In this experiment, nickelous nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution was prepared as catalyst precursor. The treatment was initiated by spin-coating the nitrate solution onto the stainless foil (2×2 cm²). For easy control of the quantity of metal particle on the substrate, we fixed the

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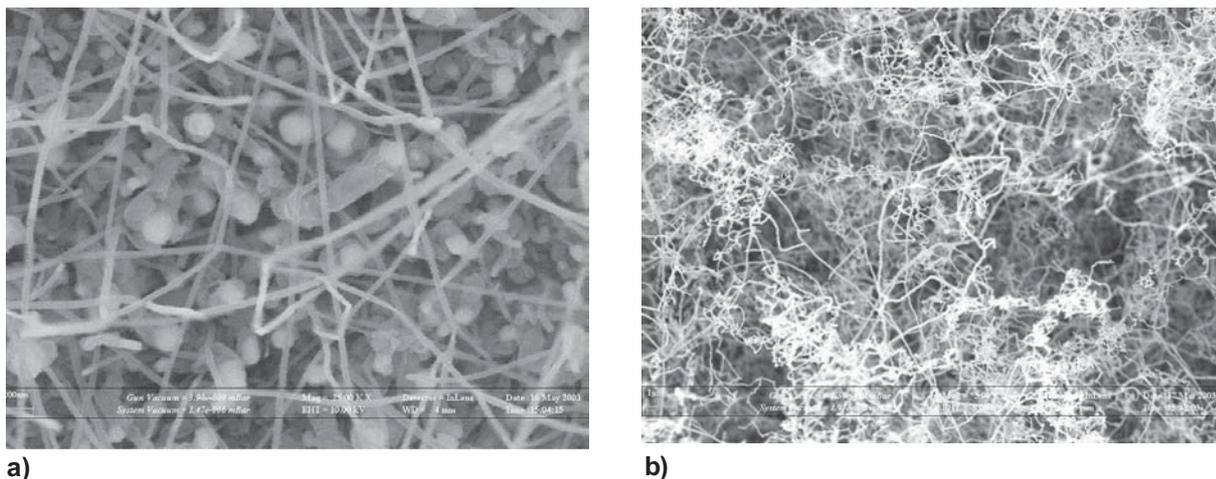


Fig. 1. SEM photographs for the carbon nanofibers grown from (a) high-density and (b) low-density Ni-based catalytic film.

rotational speed of the spin center at 1200 rpm but varied the molar concentration of the colloids by dilution. Then the derived substrate was dried in a vacuum oven at 105 °C for 6 h, followed by 1 h of heating at 350 °C for nitrate decomposition and subsequent cooling, both in Ar, to give the Ni-impregnated catalyst. A commonly solution, toluene (Aldrich) as carbon precursor, was dipped carefully by a plunger-operated pipette, then deposited on the Ni-impregnated substrate.

After that, a simplified thermal growth process was performed in a rectangle reactor installed in an electrical furnace. The prepared substrate was placed in the center of reactor, and a steady argon gas flow was introduced from an inlet. The furnace was heated to the desired temperature of 900 °C at a heating rate of 10 °C/min. The process was kept a pressure of 1 atm, and the growth time was performed for 1 h. Surface morphology of the CNFs formed was observed by SEM (LEO 1530). The crystalline structure of CNFs was characterized by XRD (Philip PW1700).

4. RESULTS AND DISCUSSION

Pervious study [10] has pointed out that the densities of catalyst would be an important factor in affecting the fiber distribution and growth orientation. Generally, the CNF distribution is random and uniform over a wide area of the substrate at low density. At high density, the catalyst particle interacts with neighboring particles and form two-dimensional clusters with local order. In the present work, the amount of Ni film on substrate reasonably increases with the concentration of the colloidal solution, i.e.,

0.04 mg/cm² for 0.2 M, and 0.4 mg/cm² for 1.0 M nickel nitrate solution at the same speed of 1200 rpm. More importantly, the amount of metallic film is reproducibly obtained for a given colloidal concentration. Additionally, chemical composition of catalyst film also affects the CNFs distribution, i.e., activities of catalysts. To confirm this, XRD pattern are employed for this purpose. We observe that these diffraction peaks for the Ni thin films mainly correspond to NiO and Ni metal, implying a heterogeneous catalyst distribution over substrate surface (not shown).

Figs. 1a and 1b show SEM photographs of CNFs grown on different densities of Ni thin films, 0.04 mg/cm² and 0.4 mg/cm², respectively. Obviously, it is found that two types of nanofibers, straight- and coil-type, are obtained from the different density of Ni film, respectively. This indicates that surface density of catalyst significantly affects the growth of nanofibers. In addition, the maximum length of the fiber is estimated to be around 10 μm, and the fiber size is about 100 nm. Even at the heterogeneous catalyst surfaces, i.e., Ni and NiO particles, the CNF arrays can be synthesized to be high-density network. The specific quantity of the nanofibers can be estimated to be 5 mg/cm² at higher Ni density for each batch runs. Compared with other CVD methods, expensive vacuum apparatus and other instruments, e.g. vacuum pump and vacuum chamber, can be negligible. Our simplified method can easily produce the high-density CNFs, demonstrating the possibility of large-scale CNFs production. Thus, the advantages of our method are more efficient, cost-down, and convenient than other methods.

In Fig. 2, we show the XRD pattern for the prepared CNFs. The spectrum exhibits only a few broad peaks with weak intensity, indicating a low crystallinity of the CNFs. The most intense peaks appear close to the position of (002), (100), and (103) peaks of graphitized samples. Based on hexagonal close-packed 'graphite' unit cell, the mean interlayer distance calculated from the maximum of (002) peaks is larger than 3.380 Å. Such broader interlayer space (>3.354 Å for graphite) have been discussed due to some thermal factors, such as heat-treated temperature and graphitization process [11]. The mean crystallite thickness (L_c) deduced from the half-width of the (002) peak is ~ 7.05 Å. Generally, for $L_c \ll 50$ Å, we assume that the CNFs are composed of a short-range order of graphite structure, i.e., a partially graphitized carbon. The broadened (100) and (103) peaks also reflect the disordered character of graphite sheets for the CNFs.

The growth mechanism for CNFs from CVD methods has been reported by past literatures [12, 13]. However, our CVD method for formation of CNFs has not been discussed in detail. Firstly, with the previously spin-coating method, the Ni-based thin-film as catalyst precursor is uniformly dispersed on the substrate surface. After thermal decomposition at 350 °C, the polycrystalline Ni and NiO clusters were embedded in substrate. Then, the liquid-type carbon precursor (toluene here) is covered over the film of Ni catalyst. As the solvent is gradually evaporated with raising temperature, the gas-phase C-atom starts to cover the Ni grain. When the mechanical stress of the carbon grain exceeds the elastic limits, the round grain transforms into a CNF along the one direction. The sizes and distribution of the metal or metal-oxide may play a role in the assorted morphologies. In usual, the stress may be induced during fiber-growth process, and the stress is periodically relieved by the introduction of ring pairs. When the elastic limit is exceeded, the coil-type morphology can be obtained. It is believed that the situation easily happened at higher surface density of catalyst. Then a growth-induced stress may lead to the complicated deformation patterns of the CNFs. Moreover, the change of catalytic activity of the Ni particles varied with the course of time because local poisoning can result in the complicate sharps. Based on the above deductions, we provide a simple process for synthesizing a large-scale CNFs.

FE tests for the high-density CNF film was performed in a vacuum chamber at a pressure of $1 \cdot 10^{-5}$ Torr. A platinum sphere with 1 mm in diameter was

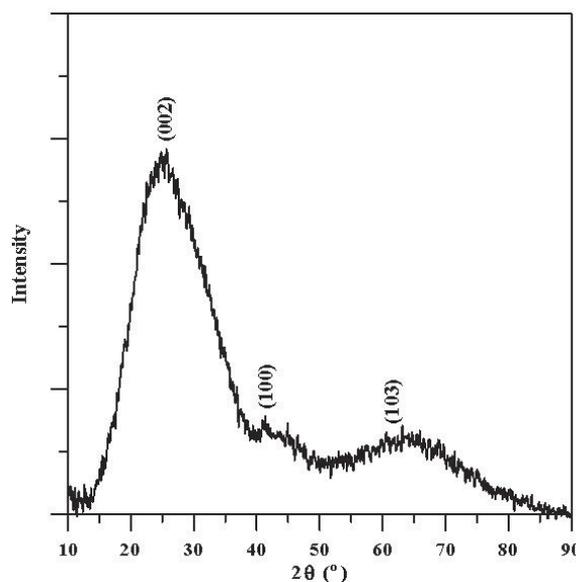


Fig. 2. XRD pattern for the carbon nanofibers grown from Ni-based catalytic film.

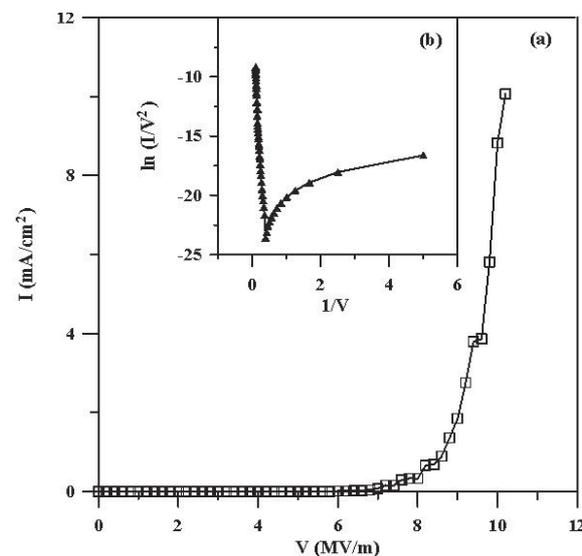


Fig. 3. (a) Typical current density-electric field (J-E) plot of the carbon nanofiber film and (b) its Fowler-Nordheim (F-N) plot.

used as an anode to collect electrons from the CNF samples. The anode was positioned at 100 mm from the samples and the measured emission area was 1 mm². The temperature during the measurement was 25 °C. When a positive voltage was applied to the anode, the FE current was detected at the anode as a function of applied field. Here CNFs have built on substrate, thus, we do not make any treatment in our grown CNF sample.

A typical plot of emission current density vs. applied field (J-E plot) of the high-density CNFs (in Fig. 1b) is given in Fig. 3. In order to verify that the current detected was actually emitted from the nanofibers, no field emission current was observed from a smooth fiber-free substrate when measured in the same apparatus. The turn-on voltage of the nanofibers was at about 7 MV/m. The typical threshold field [14] for obtaining a current density of 10 mA/cm² is 10 MV/m. On commercial viewpoints, a FE current of 1 mA/cm² is required for conventional flat panel displays [15]. Our CNF film can reach at a field of 10 MV/m, which is higher than that of aligned CNTs with diameters of 10 nm (~3 MV/m). However, the FE current usually depends on the work function and geometry of the surface [15]. Smaller tip size of CNFs is probably synthesized in our further procedures if small size of catalyst particles can be well-controlled.

Here, a typical Fowler-Nordheim (F-N) equation is employed to identify the work function of the CNF film. Based on the F-N model, FE current from a metal or semiconductor is attributed to the tunneling of electrons from the material into vacuum under the influence of an electric field. The F-N equation can be described by

$$J = E_{loc}^2 \exp[-6.8 \cdot 10^7 \Phi^{3/2} / E_{loc}], \quad (1)$$

where J is electron current density at the emitting tip, E_{loc} is local electric field, and Φ is work function of the CNFs. For the isolated hemisphere model:

$$E_{loc} = \frac{V}{\alpha R_{tip}}, \quad (2)$$

where V is the applied voltage, R_{tip} is the tip radius of curvature, and α is a modifying factor. Combining with Eq. (1) and (2), we obtain

$$\ln\left(\frac{J}{V^2}\right) = \frac{1}{V}(-6.8 \cdot 10^7 \alpha R_{tip} \Phi^{3/2}) + offset. \quad (3)$$

$\alpha R_{tip} \Phi^{3/2}$ can be estimated from the slope of the F-N plot of $\ln(I/V^2)$ against $(1/V)$ for the emission data. The corresponding F-N plot (inset of Fig. 3) is constructed. The fairly good linearity in F-N plot confirms that the current is attributed to the field emission. In general, the α value between 1 and 10 has been used in past study [14]. Using α of 1–10 with $R_{tip} = 50$ nm for our calculations, the work function (Φ) is in range of 0.90–3.64 eV. Typically, the work function of graphite is about 5 eV. The results indi-

cate that the CNFs can be a promising candidate as FE emitters.

5. CONCLUSION

A simply thermal procedure for CNFs growth was explored at constant pressure of 1 atm, using Ni-impregnated as catalyst and toluene as carbon precursor. SEM observations revealed that the distributions and morphologies of the CNFs were significantly influenced by catalyst densities. With increasing Ni density, the density and length of carbon nanofibers increased. XRD analysis indicated that the nanofibers to be graphitic planes of short ranges, and imperfect graphite structures were confirmed. FE tests showed that the as-received CNF sample exhibited fairly good FE properties. The turn-on voltage at a microampere order of FE current for the CNF sample can occur at 10 MV/m. Based on F-N model, the work function of the CNF film was estimated in range of 0.90–3.64 eV from the one-stage linearity plot. Due to its simply catalytic-growth process, it is convenient to prepare the CNF samples for FE tests. However, studies on growth conditions and well-patterned catalyst particles require a deeper future research for fabricating the well-ordered CNF arrays.

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