Improvement of the field emission properties of carbon nanotubes by CNT/Fe$_3$O$_4$ composite electrophoretic deposition

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Abstract: A simple CNT/Fe$_3$O$_4$ composite electrophoretic deposition method to improve the field emission cathode properties of carbon nanotubes (CNTs) is proposed. It is found that CNT/Fe$_3$O$_4$ composite electrophoretic deposition leads to better field emission performance than that of single CNT electrophoretic deposition. The result is investigated using SEM, J-E and FE. After the process, the turn-on electric field decreases from 0.882 to 0.500 V/μm at an emission current density of 0.1 mA/cm$^2$, and the latter increases from 0.003 to 1.137 mA/cm$^2$ at an electric field of 0.64 V/μm. CNT/Fe$_3$O$_4$ composite electrophoretic deposition is an easy and effective cathode preparation for field emission display applications.

Key words: carbon nanotubes; Fe$_3$O$_4$; field emission; electrophoretic deposition

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1. Introduction

Owing to their special geometrical morphology and properties, including high aspect ratio, small tip radius of curvature, high current capacity, large field enhancement factor, and high electrical conductivity, carbon nanotubes (CNTs) exhibit excellent field emission characteristics[1–3]. In general, there are several ways to manufacture CNT field emission cathodes, such as chemical vapor deposition (CVD)[4, 5], screen-printing[6, 7], the spray method[8, 9] and electrophoresis[10–12]. The direct growth of CNT by chemical vapour deposition is difficult to process and control; and the high growth temperature limits the ranges of substrate materials. The screen-printing and spray methods can be carried out at low temperature and have the advantages of low cost and simple processing, among others. However, both the screen-printing and spray methods lead to organic residues and the field emission cathode would be damaged by the high temperature. The electrophoresis method is simple and low-cost, and can be carried out at room temperature, but it has the problem of poor emission performance.

CNT/Fe$_3$O$_4$ composite inorganic materials were reported by Liu, Wei et al.[13]. Many fundamental researches on CNT/Fe$_3$O$_4$ composite inorganic materials have been carried out[14–17]. They have been widely researched in biomedical[18–20], biosensor[21], and electrochemical[22, 23] fields, but have not been reported in the field emission area. Moreover, to the authors’ knowledge, CNT/Fe$_3$O$_4$ composite electrophoretic deposition leads to better field emission performance of CNTs than most other post-treatments.

In this paper, an easy and effective CNT cathode preparation based on CNT/Fe$_3$O$_4$ composite electrophoretic deposition method is presented. Not only does our method use a simple process, it also improves FE performance compared with previous electrophoresis methods[10–12].

2. Experiment

First, we prepared the CNT and nano-Fe$_3$O$_4$ suspensions. 5 g CNTs (diameters: 8–16 nm, length ≈ 30 μm and purity ≥ 95%) and 10 g polyvinylpyrrolidone (K30), were dispersed in 1 L isopropyl alcohol solution, using an ultrasonic cell crusher (model: SCIENT2-II D) at power 2% for 10 min, to form the CNT suspension. 1.3 g nano-Fe$_3$O$_4$ (diameter ≈ 16 nm and purity ≈ 99.9%) were added to 1 L isopropyl alcohol solution, to form the nano-Fe$_3$O$_4$ suspension (as mentioned above). The suspension and 0.2 g Mg(NO$_3$)$_2$·6H$_2$O were added to a 1 L isopropyl alcohol solution for 60 min ultrasonic treatment at 5% power to form the CNT electrophoretic suspension. After this was completed, the electrophoretic process was carried out as depicted in Fig. 1(a): a graphite plate was used as the anode and a glass plate covered by Cr–Cu–Cr electrodes (produced by magnetic control sputter coaters) as the cathode; the voltage in the process was DC 11 V for 3 min.

The nano-Fe$_3$O$_4$ electrophoretic process was carried out in a 1 L nano-Fe$_3$O$_4$ suspension at DC 11 V for 3 min as depicted in Fig. 1(b).

For the CNT electrophoretic process, 10 mL of the CNT suspension and 0.2 g Mg(NO$_3$)$_2$·6H$_2$O were added to a 1 L isopropyl alcohol solution for 60 min ultrasonic treatment at 5% power to form the CNT electrophoretic suspension. After this was completed, the electrophoretic process was carried out as depicted in Fig. 1(c). The voltage in the process was 11 V for 3 min.

Finally, all the cathodes were dried in an oven at 200 °C for...
20 min and sintered in an oven filled with 99.99% nitrogen at 500 °C for 30 min to remove the organic residue, then cooled down to room temperature.

The morphologies of the CNT cathode were characterized by a scanning electron microscope (SEM, S-3000 HITACH). The field emission (FE) images and lifetime measurement of the samples were measured in a conventional diode configuration at a pressure of 7.0 × 10^{-4} Pa. The cathode area was 5 × 8 cm². Indium tin oxide (ITO) glasses coated with green phosphor were used as the anode. The gap between the cathode and anode was 1100 μm.

3. Results and discussion

Figure 1 shows the electrophoresis processes of the CNTs, Fe₃O₄, and CNT/Fe₃O₄ with the graphite plate used as the anode and the glass plate covered by Cr–Cu–Cr electrodes (produced by magnetic control sputter coaters) as the cathode. In Fig. 1(a), with a DC voltage supply of 11 V for 3 min, the CNTs travelled through the CNT electrophoretic suspension and covered the cathode surface. In Fig. 1(b), with a DC voltage supply of 11 V for 3 min, between the cathode and anode there were electric field produced by the voltage, electric current mainly produced by moving ions (Mg²⁺, H⁺, etc.) and magnetic field produced by the electric current. Through control of the electric and magnetic fields, the Fe₃O₄ particles travelled through the Fe₃O₄ suspension and were well distributed on the cathode surface. In Fig. 1(c), with a DC voltage supply of 11 V for 3 min, both the CNTs and Fe₃O₄ particles, under the effect of the electric and magnetic fields, travelled through the composite electrophoresis suspension, reached the cathode surface and formed spindts composed of Fe₃O₄ particles as well as the CNT layer on the cathode surface.

Figure 2 shows SEM images of the morphologies of CNTs, Fe₃O₄, and CNT/Fe₃O₄ on the cathode after electrophoresis, using an SEM (S-3000 HITACH). In Fig. 2(a), the electrophoretic deposition CNTs roughly lay on the surface, with some CNT tips sticking out from the surface at a magnitude of 6000. In Fig. 2(b), there were Fe₃O₄ particles well distributed on the cathode surface at a magnitude of 10⁴, while in Fig. 2(c), there were spindts composed of Fe₃O₄ particles and CNTs on the cathode surface at a magnitude of 7000. The inset in Fig. 2(c) is the enlarged image of the spindts. According to Wang, Zhao and Qu[24], the CNT-Fe₃O₄ composites exhibit good ferromagnetic properties at room temperature. The Fe₃O₄ particles together with the CNTs travelled through the composite suspension and formed Fe₃O₄ spindts as well as a CNT layer on the cathode surface.

Figure 3 shows the FE characteristics of the CNTs, Fe₃O₄, and CNT/Fe₃O₄. In Fig. 3(a), the turn-on electric field (at a current density of 0.1 mA/cm²) for the CNTs, Fe₃O₄, and CNT/Fe₃O₄ is respectively 0.882, 1.560, and 0.500 V/m, and the emission current density (at an electric field 0.64 V/m) is respectively 0.003, 0.001, and 1.137 mA/cm². It is observed from Fig. 3(b) that the field emission properties of the CNTs, Fe₃O₄, and CNT/Fe₃O₄ qualitatively follow the conventional Fowler–Nordheim (F–N) theory. According to the F–N equation, the emission current density is $J = A(\beta E)^2 \exp(-B\phi^{3/2}/\beta E)$, where $A$ and $B$ are constants, $E$ is the applied electric field, $\phi$ is the work function and $\beta$ is the field enhancement factor. From the assumption that the work function $\phi$ of the CNTs is equal to that of graphite (5.0 eV) and the
work function $\phi$ of CNT/Fe$_3$O$_4$ is 5.5 eV higher than that of the CNTs, the field enhancement factor $\beta$ of CNT/Fe$_3$O$_4$ composite electrophoretic deposition is 2690 higher than that of the CNT electrophoresis 1430.

The field-emission images of CNTs, Fe$_3$O$_4$, and CNT/Fe$_3$O$_4$ are shown in Figs. 4(a)–4(c) at a DC voltage of 1300 V. Figure 4(b) shows the lowest brightness and inhomogeneous field emission image. A possible reason could be that the work function $\phi$ of Fe is about 4.5 eV. According to Linus Carl Pauling’s theory, the electronegativity of Fe and O is 1.83 and 3.44 respectively; the 1.61 difference strengthens the ionic bond in Fe$_3$O$_4$, which means that (a) it is more difficult for an electron to emit from the Fe$_3$O$_4$ surface to the vacuum, (b) the work function $\phi$ of Fe$_3$O$_4$ is much higher than that of Fe and the CNTs, and (c) the field emission properties of Fe$_3$O$_4$ are lowest.

It is clear that the CNT/Fe$_3$O$_4$ composite electrophoretic deposition, Fig. 4(c), is brighter and more uniform than the CNT electrophoresis deposition Fig. 4(a). We assume three reasons for the improvement. On one hand, the electrons transporting from the substrate to the vacuum follow the double-barrier model as shown in Fig. 5, the field emission electrons would tunnel through two barriers: first, electrons tunnel through barrier I between the CNTs and the substrate into the CNTs, then they tunnel through barrier II and emit into the vacuum from the CNTs. On the other hand, Fe$_3$O$_4$ has good electrical conductivity which contributes to reducing barrier. The inverse spinel structure type (Fe$_3$O$_4$) is cubic and contains 8 formula units$^{[25]}$. The oxygen atoms in the structure are in a cubic close-packed arrangement with cations occupying one eighth of the tetrahedral interstices and one half of the octahedral interstices. In the structure, the A-site is tetrahedrally coordinated and generally occupied by half of the Fe$^{3+}$ and the B-site is octahedrally coordinated and occupied by the Fe$^{2+}$ and the other half of the Fe$^{3+}$. The configuration is shown as Fe$^{3+}$(Fe$^{2+}$Fe$^{3+}$)O$_2$$^-$$^4$. Because the Fe$^{2+}$ and Fe$^{3+}$ are arranged alternately in the structure, with the supplied electric field, it is easy for the electrons to move from Fe$^{2+}$ to Fe$^{3+}$, which accounts for the good electrical conductivity$^{[26]}$. Therefore, with the nano-Fe$_3$O$_4$ connecting the substrate and the CNTs, barrier would be reduced and it would be easier for the electrons to tunnel through it between the CNTs and substrate, which contributes to the improvement of the FE properties. Second, the field emission material Fe$_3$O$_4$ spindt, as shown in Fig. 2(c), has a higher field enhancement factor $\beta$ than that of the Fe$_3$O$_4$ that is well distributed on the surface as shown in Fig. 2(b), which contributes to the improvement of the FE prop-

![Fig. 3. Field emission characteristics of CNT emitters. (a) I–V curve. (b) F–N plot.](image1)

![Fig. 4. Field emission images of (a) CNTs, (b) Fe$_3$O$_4$, and (c) CNT/Fe$_3$O$_4$.](image2)

![Fig. 5. Band structure of the double-barrier model for field emission of CNT film. $E_{FM}$ and $E_{FCNT}$ is the Fermi level of the substrate metal and CNTs, respectively. $V_{junction}$ is the voltage dropped on the substrate–CNT junction.](image3)
properties. Third, in the CNT/Fe$_3$O$_4$ composite electrophoretic deposition, after attachment to the substrate, under the influence of the Fe$_3$O$_4$, many CNTs are outcropped from the substrate to become emitters.

Lifetime measurements were performed for 20 h with an initial current density of 1 mA/cm$^2$ to compare the degradation rate of CNT/Fe$_3$O$_4$ and the CNTs. As presented in Fig. 6, after 20 h, the current density of the CNT/Fe$_3$O$_4$ decreased to 78% of the initial current, whereas that of the CNTs dramatically decreased to 51% of the initial current, which means that the CNT/Fe$_3$O$_4$ emitters had longer time duration than the untreated ones. The reasons leading to this stable and long-time field emission performance might be as follows: (a) many CNTs outcropped from the substrate became emitters and (b) the combination of CNTs and Fe$_3$O$_4$. Therefore, it is confirmed that CNT/Fe$_3$O$_4$ composite electrophoretic deposition has advantages over single CNT electrophoresis.

4. Conclusion

The work demonstrated that CNT/Fe$_3$O$_4$ composite electrophoretic deposition makes it easier for electrons to tunnel through the barrier $I$, and for many CNTs outcropped from the substrate to become emitters. The field emission properties of CNTs were improved, and the brightness and uniformity of the CNTs’ diode configurations were enhanced. CNT/Fe$_3$O$_4$ composite electrophoretic deposition is a simple and effective method to improve the field emission properties of CNTs.

References