Improvement of the field emission properties of carbon nanotubes by CNT/Fe_3O_4 composite electrophoretic deposition*

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Abstract: A simple CNT/Fe_3O_4 composite electrophoretic deposition method to improve the field emission cathode properties of carbon nanotubes (CNTs) is proposed. It is found that CNT/Fe_3O_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_3O_4 composite electrophoretic deposition is an easy and effective cathode preparation for field emission display applications.

Key words: carbon nanotubes; Fe_3O_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_3O_4 composite inorganic materials were reported by Liu, Wei *et al.*[13]. Many fundamental researches on CNT/Fe_3O_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_3O_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_3O_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_3O_4 suspensions. 5 g CNTs (diameters: 8–16 nm, length $\approx$ 30 μm and purity $\geqslant$ 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_3O_4 (diameter $\approx$ 16 nm and purity $\geqslant$ 99.9%) were dispersed in 1 L isopropyl alcohol using the same ultrasonic cell crusher at power 5% for 10 min, to form the nano-Fe_3O_4 suspension.

For the CNT electrophoretic process, 10 mL of the CNT suspension and 0.2 g $Mg(NO_3)_2\cdot 6H_2O$ 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_3O_4 electrophoretic process was carried out in a 1 L nano-Fe_3O_4 suspension at DC 11 V for 3 min as depicted in Fig. 1(b).

For the CNT/Fe_3O_4 composite electrophoretic deposition process, 10 mL of the CNT electrophoretic suspension was added to 1 L nano-Fe_3O_4 suspension (as mentioned above) for 30 min ultrasonic treatment at 5% power to form the CNT/Fe_3O_4 composite electrophoretic suspension. Then the CNT/Fe_3O_4 composite electrophoretic deposition process was carried out as depicted in Fig. 1(c). The voltage in the process was DC 11 V for 3 min.

Finally, all the cathodes were dried in an oven at 200 ℃ for

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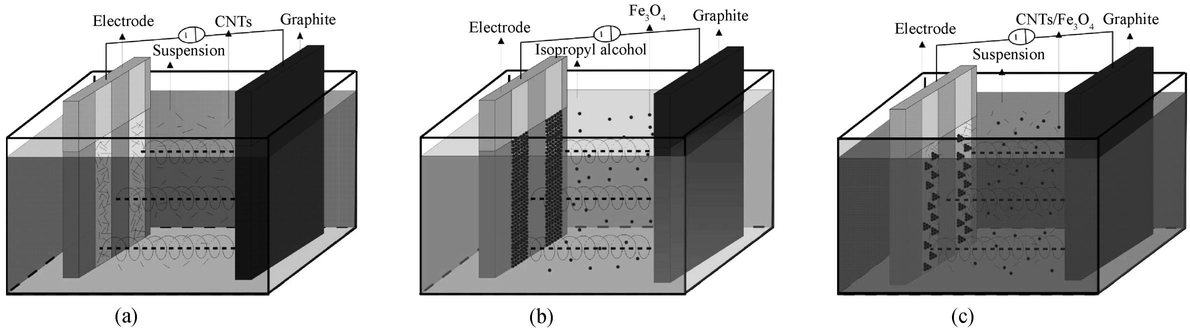

Fig. 1. Eletrophoresis process of (a) CNTs, (b) Fe_3O_4, and (c) CNT/Fe_3O_4.

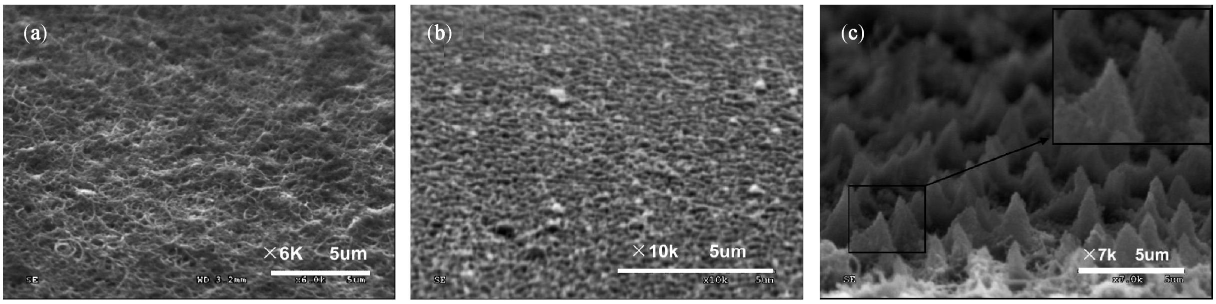

Fig. 2. SEM images of morphologies of (a) CNTs, (b) Fe_3O_4, and (c) CNT/Fe_3O_4 on the cathode after electrophoresis (inset: enlarged image of the spindts).

20 min and sintered in an oven filled with 99.99% nitrogen at 500 ℃ 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 cm^2. Indium tin oxide (ITO) glasses coated with greenphosphor were used as the anode. The gap between the cathode and anode was 1100 μm.

3. Results and discussion

Figure 1 shows the eletrophoresis processes of the CNTs, Fe_3O_4, and CNT/Fe_3O_4 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 (Mg^{2+}, H^+, etc.) and magnetic field produced by the electric current. Through control of the electric and magnetic fields, the Fe_3O_4 particles travelled through the Fe_3O_4 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 Fe_3O_4 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 Fe_3O_4 particles as well as the CNT layer on the cathode surface.

Figure 2 shows SEM images of the morphologies of CNTs, Fe_3O_4, and CNT/Fe_3O_4 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 Fe_3O_4 particles well distributed on the cathode surface at a magnitude of 10^4, while in Fig. 2(c), there were spindts composed of Fe_3O_4 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-Fe_3O_4 composites exhibit good ferromagnetic properties at room temperature. With a DC voltage supply of 11 V for 3 min, there was an electric current produced by the moving ions (Mg^{2+}, H^+, etc.) and a magnetic field produced by the electric current. From the effect of electric current and magnetic field, the Fe_3O_4 particles together with the CNTs travelled though the composite suspension and formed Fe_3O_4 spindts as well as a CNT layer on the cathode surface.

Figure 3 shows the FE characteristics of the CNTs, Fe_3O_4, and CNT/Fe_3O_4. In Fig. 3(a), the turn-on electric field (at a current density of 0.1 mA/cm^2) for the CNTs, Fe_3O_4, and CNT/Fe_3O_4 is respectively 0.882, 1.560, and 0.500 V/μm, and the emission current density (at an electric field 0.64 V/μm) is respectively 0.003, 0.001, and 1.137 mA/cm^2. It is observed from Fig. 3(b) that the field emission properties of the CNTs, Fe_3O_4, and CNT/Fe_3O_4 qualitatively follow the conventional Fowler–Nordhein (F–N) theory. According to the F–N equation, the emission current density is $J = A(\beta E)^2 \times \exp(-B\phi^{3/2}/\beta E)$, where A and B are constants, E is the applied electric field, ϕ is the work function and β is the field enhancement factor. From the assumption that the work function ϕ of the CNTs is equal to that of graphite (5.0 eV) and the

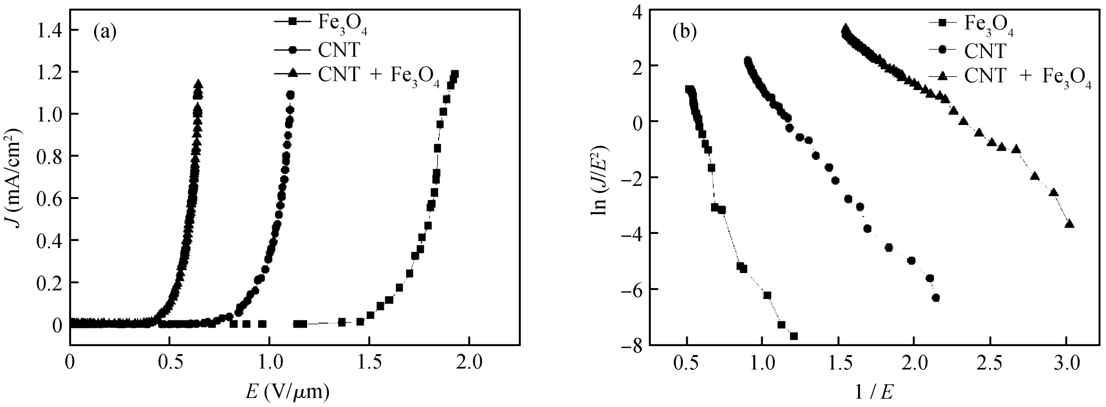

Fig. 3. Field emission characteristics of CNT emitters. (a) I–V curve. (b) F–N plot.

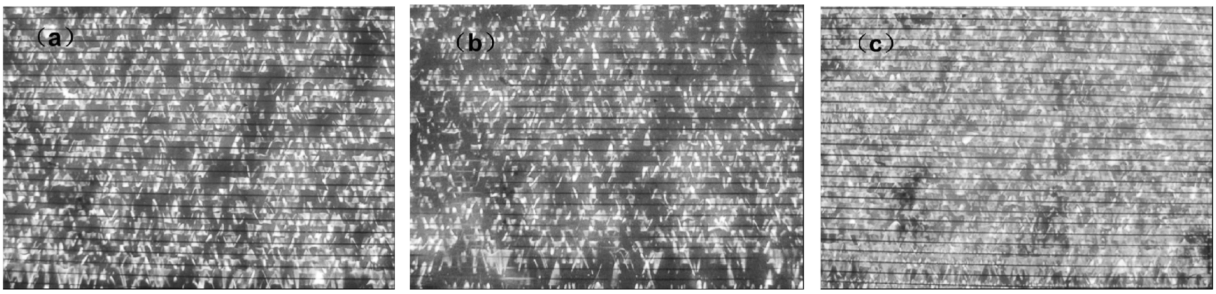

Fig. 4. Field emission images of (a) CNTs, (b) Fe_3O_4, and (c) CNT/Fe_3O_4.

work function ϕ of CNT/Fe_3O_4 is 5.5 eV higher than that of the CNTs, the field enhancement factor β of CNT/Fe_3O_4 composite electrophoretic deposition is 2690 higher than that of the CNT electrophoresis 1430.

The field-emission images of CNTs, Fe_3O_4, and CNT/Fe_3O_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 ϕ 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_3O_4, which means that (a) it is more difficult for an electron to emit from the Fe_3O_4 surface to the vacuum, (b) the work function ϕ of Fe_3O_4 is much higher than that of Fe and the CNTs, and (c) the field emission properties of Fe_3O_4 are lowest.

It is clear that the CNT/Fe_3O_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_3O_4 has good electrical conductivity which contributes to reducing barrier. The inverse spinel structure type (Fe_3O_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 $Fe^{3+}(Fe^{2+}Fe^{3+})O_4^{2-}$. 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_3O_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_3O_4 spindt, as shown in Fig. 2(c), has a higher field enhancement factor β than that of the Fe_3O_4 that is well distributed on the surface as shown in Fig. 2(b), which contributes to the improvement of the FE prop-

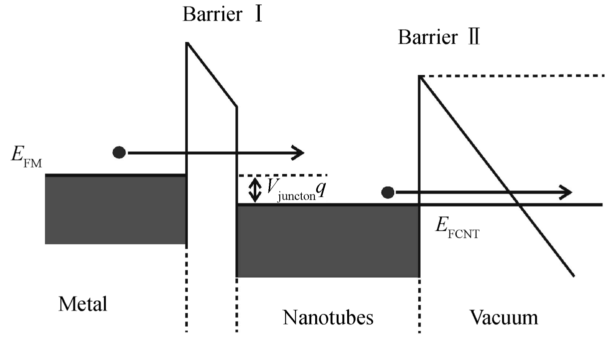

Fig. 5. Band structure of the double-barrier model for field emission of CNT film. E_{FM} and E_{FCNT} is the Fermi level of the substrate metal and CNTs, respectively. $V_{junction}$ is the voltage dropped on the substrate–CNT junction.

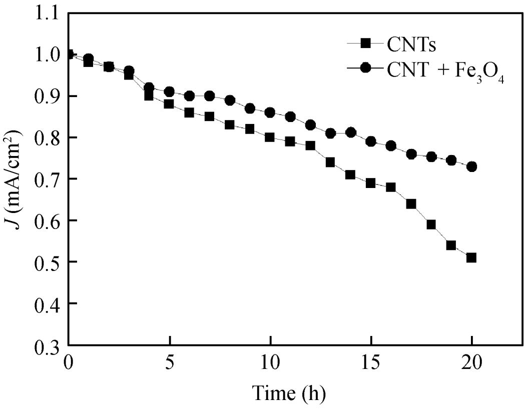

Fig. 6. Field emission stability test of the two cases: CNT/Fe_3O_4 and CNTs.

erties. Third, in the CNT/Fe_3O_4 composite electrophoretic deposition, after attachment to the substrate, under the influence of the Fe_3O_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_3O_4 and the CNTs. As presented in Fig. 6, after 20 h, the current density of the CNT/Fe_3O_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_3O_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_3O_4. Therefore, it is confirmed that CNT/Fe_3O_4 composite electrophoretic deposition has advantages over single CNT electrophoresis.

4. Conclusion

The work demonstrated that CNT/Fe_3O_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_3O_4 composite electrophoretic deposition is a simple and effective method to improve the field emission properties of CNTs.

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