Fabrication of Carbon Nanotubes Field Emission Cathode by Composite Plating

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Carbon nanotubes (CNTs) have high aspect ratio and have great potential to be applied as the field emission cathode because of its large field enhancement factor. In this work, a high performance carbon nanotube field emission cathode (CNTFC) was fabricated by using a composite plating method. The CNTs were purified by acid solutions and then dispersed in electrobath with nickel ions at temperatures of 60, 70, or 80 °C for the electroless plating process on glass substrate. The resulting CNT-Ni composite film has strong adhesion on the glass substrate. The degree of graphitization and the microstructure of the CNTFCs were studied by Raman spectroscopy and scanning electron microscopy. The field emission properties of the CNTFCs show a low turn-on electric field E_{on} of about 1.2 V/μm, and a low threshold electric field E_{th} of about 1.9 V/μm. Such a composite plating method could be applied to the fabrication of large area CNT field-emission displays.

Keywords: Carbon Nanotube, Field Emission Cathode, Composite Plating.

RESEARCH ARTICLE

1. INTRODUCTION

Carbon nanotubes (CNTs) can be used on novel chemical and physical devices because of its small diameter, unprecedented mechanical properties, unique chemical properties, interesting electrical properties, and excellent environmental stability.[1–4] It can also be applied to cold cathode field emitter because of its high aspect ratio, large field enhancement factor, and high emission current density with low turn-on electric field.[5] CNT field emission cathodes (CNTFCs) can be made by various methods, such as direct growth,[6] electrophoresis,[7] screen-printing,[8] and spray method.[9]

The synthesis of CNTs has been extensively investigated. Many growth methods of CNTs, such as chemical vapor deposition (CVD),[10] arc deposition,[11] and laser ablation[12] requires high temperature or high vacuum processes. This would limit the choice of substrate materials. Post-deposition of grown CNTs on substrates could be processed at low temperature.[7–9] However, such kind of process usually has the problems of weak adhesion between CNTs and substrates. Moreover, large area deposition of CNTs can be realized by using a paste screen-printing method, which has advantages of low cost and simple process. However, it usually has poor electron field emission

due to the surface modification of CNTs, and also has the problem of poor adhesion. Spray is also an easy method to deposit CNTs for field emitter cathodes. However, in order to improve the adhesion, it uses indium, which is costly and sparsely, as a binder. By contrast, the composite plating of CNTs with Ni can achieve large area with well adhesion, and suppress the degradation of CNT emission tips.[13] In this case, the hydrophobic property of CNTs, which causes poor dispersion of CNTs in the electrobath, needs to be further resolved.

In this work, an acid oxidation method was used to improve the dispersion property of CNTs in a Ni bath.[14] Processed multiwall carbon nanotubes (MWCNTs) and Ni were co-deposited by an electroless plating method, forming a conducting CNT-Ni composite film on a slide glass substrate. Adhesion, film uniformity, field emission characteristics, microstructure and graphite properties of the CNTFC film deposited at different temperatures were investigated. The luminescence generated by the CNTFC backlight unit was also demonstrated.

2. EXPERIMENTAL PROCEDURE

Ordinary glass slides were used as the substrates for the deposition of the CNT-Ni composite films. To clean the surface, the glass substrate was cleaned with sonication

by deionized (DI) water, ethanol, and acetone for about 10 min, respectively. Then, an air plasma system (PDC-001, Harrick Plasma) was used to clean the substrates. The cleaned glass substrates were sensitized in a solution consisting of stannous chloride (SnCl$_2 \cdot$H$_2$O) and hydrochloric acid (HCl) for an hour, and then activated in a solution consisting of palladium chloride (PdCl$_2$) and HCl for another hour. In this "two-step" method, the sensitization process leads to the adsorption of Sn^{2+} on the substrate, while the activation process forms fine Pd particles on the substrate through the displacement reaction of Sn^{2+} with Pd^{2+}.

In this work, the CNTs were synthesized by the DC arc discharge method. The anode was a graphite rod of 150 mm in length, and the cathode was a graphite disc mounted on a water-cooled copper block. To purify, the resulting CNT powders were immersed in a mixed solution of 75% nitric acid and 25% hydrochloric acid for 24 hrs. After filtering, they were further acid-oxidized in a mixed solution of 75% nitric acid and 25% sulfuric acid for also 24 hrs. Then the CNTs were washed by DI water for several times and filtered through a 1.6 μm polycarbonate filter. Finally, the resulting CNT powders were dried by heating at 120 °C in air ambient. Such acid treatment could modify the surface of the MWCNTs and enhance the interfacial adhesion between the MWCNTs and metals.[15]

An amount of 2 mg of the prior purified CNT powder was dispersed in 5 ml DI water with 1 mg surfactant (PVP K30, Aldrich), resulting in a CNT black suspension solution. To form CNT-Ni composite, the black solution were mixed with 5 ml nickel sulfate solution, resulting in a 10 ml solution that composed of 87 g/L NiSO$_4 \cdot$6H$_2$O, 14 g/L NaH$_2$PO$_2 \cdot$H$_2$O, 4.1 g/L C$_2$H$_2$(COONa)$_2 \cdot$6H$_2$O, 2 g/L C$_3$H$_4$(OH)(COOH)$_3 \cdot$H$_2$O, 1.5 mg/L Pb(CH$_3$COO)$_2 \cdot$3H$_2$O, 30 g/L CH$_3$COONa$\cdot$3H$_2$O, 1 mg PVP K30, and 2 mg CNT. All prior chemicals were analytical reagent grade. The pH value of the mixed solution is about 5.4. By using a heater, the mixed solution was heated from room temperature to deposition temperatures (T_D) in 3 min. Then, the glass substrate with Pd particles on its surface were dipped into the mixed solution with T_D controlled at 60 °C, 70 °C, or 80 °C to deposit the CNT-Ni composite film. After deposition, the sample was washed by DI water and then processed by air plasma for 15 min to remove residual organics on the surface of CNTFC.

The surface morphology of both pristine MWCNTs and the deposited CNTFC was observed by field-emission scanning electron microscope (FESEM). Raman spectroscopy (excitation wavelength 514.5 nm) was used to measure the graphite property of the CNT-Ni composite film. The field emission characteristic of the CNTFC was measured via a diode structure with an indium tin oxide (ITO) glass coated with phosphor powders as the anode. The gap between the CNTFC and the anode was about 150 μm. Vacuum pressure was about 6×10^{-6} Torr while measuring the field emission.

3. RESULTS AND DISCUSSION

The pristine CNT powders after synthesized by the DC arc discharge method contain lots of carbon nanotubes as well as amorphous carbons and impurities, as shown in Figure 1(a). After purification by acid treatment, considerable amorphous carbons were removed, as shown in Figure 1(b). It also displays that these purified MWCNTs form bundle structures. Because of strong inter-tube van der Waals attraction, the CNTs have a tendency to aggregate into packed ropes or entangled networks, which may hinders a homogenous coating of metal layers on individual nanotubes.[16]

Raman spectroscopy is a powerful and sensitive technique for studying the structure of carbonaceous materials. The spectrum of CNTs typically has two characteristic peaks at about 1350 and 1580 cm^{-1}, respectively.[17–19] The peak at around 1580 cm^{-1} (with density I_G) can be identified as the G band of crystalline graphite arising from zone-center E_{2g} mode. On the other hand, for the graphite-like materials with defects, the peak at around 1350 cm^{-1} (with density I_D) is identified as D band, which is activated due to defects and disorders of carbonaceous material. Thus, a smaller ratio of I_D to I_G implies a better graphite structure and a higher degree of graphitization. Figure 2 shows the Raman spectra of the pristine MWCNTs and the purified MWCNTs. The corresponding intensity ratios (I_D/I_G) are 0.33 and 0.18, respectively. It reveals that the purified MWCNTs have fewer defects and better graphite
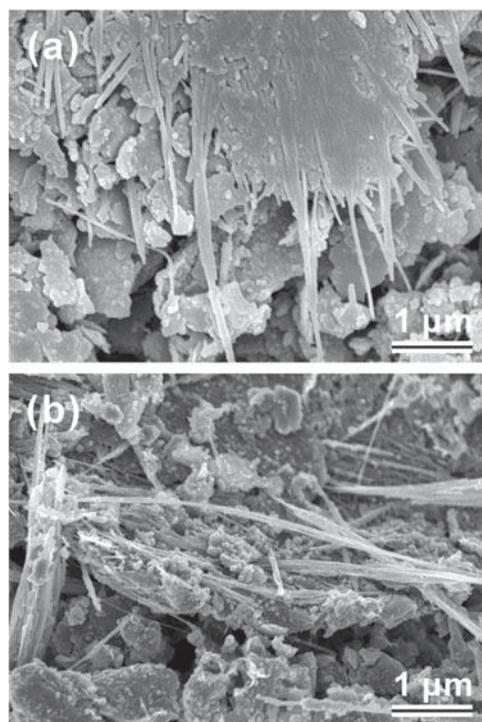
Fig. 1. SEM images of MWCNTs powders. (a) Pristine MWCNTs, and (b) acid processed MWCNTs.
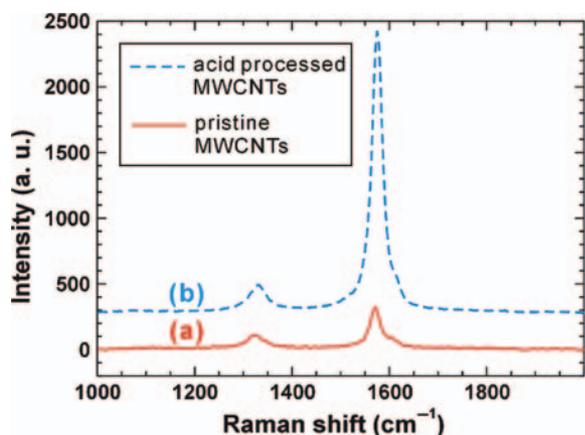
Fig. 2. Raman spectrums of MWCNTs. (a) Pristine MWCNTs and (b) acid processed MWCNTs.

structure. Such purification and graphitizing of CNTs can induce more sp^2 bonding in the sample. Since the delocalized electrons in the π orbital of sp^2 bond have higher mobility, they are easier to emit from CNTs under applied electric field than the localized electrons in σ bonds.[20] Therefore, more sp^2 bonding would be able to improve the field emission properties.[19]

The plating bath of nickel ions was prepared by dissolving analytical grade $NiSO_4 \cdot 6H_2O$ and other reagents in DI water, resulting in a green-colored transparent solution, as shown in Figure 3(a). After adding pristine MWCNTs or purified MWCNTs with surfactant PVP K30 in the plating solutions, the mixed solutions were proceeded with sonication for 1 hr. Then, after left standing for 3 days, they became double-decked in the bath, or still a black-colored solution, as shown in Figures 3(b) for the pristine CNTs and 3(c) for the purified CNTs. Even adding PVP K30 in the solution with the pristine MWCNTs, the CNTs still aggregate and precipitate in 1 hr. It indicates that purified MWCNTs with surfactant modification were more hydrophilic and had a good dispersivity in an aqueous solution.
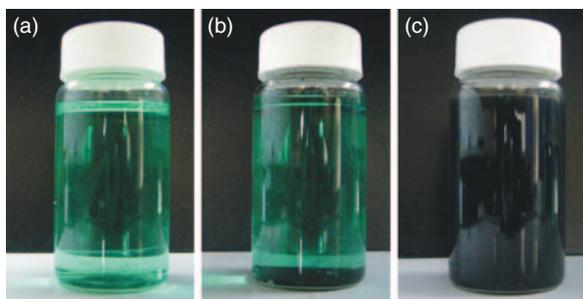
Fig. 3. Photographs of plating solutions. (a) Electroless solution without CNTs, (b) pristine MWCNTs in electroless solution, and (c) purified MWCNTs in electroless solution. These solutions were left standing for 3 days before photographing.

After deposition by composite plating, the morphology of the CNTFC was measured by FESEM. For comparison, a Ni film was also deposited by the electroless plating method with no CNTs in the plating bath. Figure 4(a) shows the SEM images of the fabricated Ni film, which has uniform thickness with good adhesion to the substrate. When CNTs were added in the plating solution, the fabricated CNTFC film contains both Ni and a lot of CNTs. The conductivity and adhesion of the CNT-Ni composite film were quite good for the practice of field emission measurement. Figures 4(b–d) show the FESEM images of the CNTFCs fabricated at different deposition temperatures. For $T_D = 60$ °C, the resulting surface structure of the CNTFC film is porous and complicated. Many individual CNTs stick out, as shown in Figure 4(b). At $T_D = 70$ °C, the film is less porous, as shown in Figure 4(c). Besides, it was observed that almost all CNTs were coated with Ni, resulting in lots of CNT-Ni composite rods, and further jointed with Ni to form a film. The CNT-Ni composite structure deposited at 80 °C shown in Figure 4(d) is much dense with less pores. This should be related to the higher growth rate of the composite film at 80 °C. The thicknesses of the films deposited at $T_D = 60$, 70 and 80 °C are about 105, 170, and 290 nm, respectively. Thus, a higher deposition temperature may not only benefit to the CNT-Ni composite structure, but also increase the growth rate of the film, resulting in a high quality CNTFC with high throughput. However, if T_D is increased up to 90 °C, the composite film has flaking phenomenon on glass substrate. Hence, 80 °C is the preferred deposition temperature for plating the CNT-Ni composite film.

The field emission properties of the fabricated CNTFCs were measured in high vacuum with a base pressure of
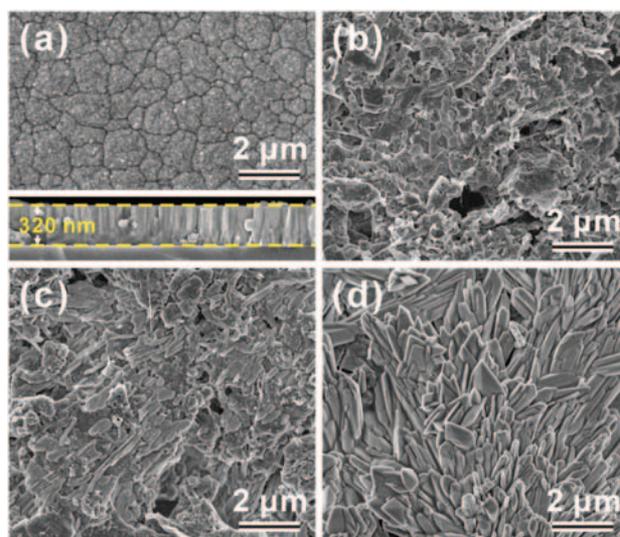
Fig. 4. SEM images of Ni film and CNT field emission cathode. (a) The surface and the cross-section images of Ni film. (b), (c), (d) CNTFCs deposited at 60 °C, 70 °C, and 80 °C, respectively.
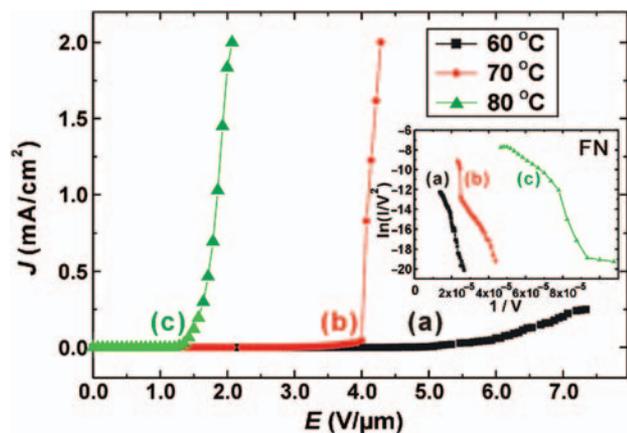
Fig. 5. Field emission current densities as a function of electrical field for CNTFCs fabricated at the deposition temperature of (a) 60 °C, (b) 70 °C, and (c) 80 °C. The inset is their corresponding FN plots.

about 6×10^{-6} Torr. Figure 5 and its inset show the current density-electric field (J–E) plot and the corresponding Fowler-Nordheim (F-N) plot of the CNTFCs deposited at different temperatures, respectively. According to the FN equation, the emission current density is the function of E, β, and ϕ: $J = A\,(\beta E)^2 \exp(-B\phi^{3/2}/\beta E)$, where J is the current density, E the applied electric field, A and B are constants, β the field enhancement factor, and ϕ the work function.[21] With $T_D = 60$, 70, and 80 °C, the field enhancement factors β are about 1220, 1480, and 2860, respectively. Therefore, the CNTFC deposited at a higher temperature has better enhancement factor. Besides, with higher T_D, the CNTFC exhibits lower turn-on electric field
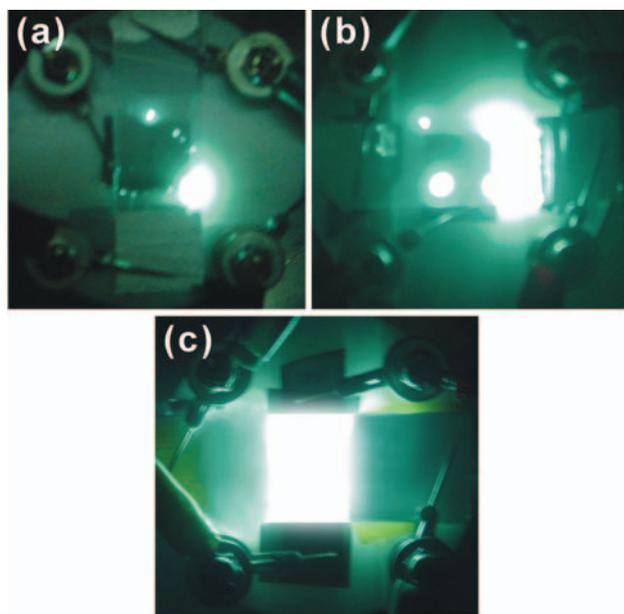
Fig. 6. Photographs of the luminescence of the phosphor screen when measuring field emission properties. The used CNTFCs were fabricated at the deposition temperature of (a) 60 °C, (b) 70 °C, and (c) 80 °C.

(E_{on}) and lower threshold electric field (E_{on}). Where, E_{on} and E_{th} are defined as the required electric fields corresponding to current densities of 1 μA/cm^2 and 1 mA/cm^2 in field emission measurement, respectively. With $T_D = 60$ and 70 °C, the related E_{on} of the CNTFCs are about 4.5 and 2.8 V/μm, respectively. For the CNTFC deposited at 80 °C, its E_{on} and E_{th} are only about 1.2 and 1.9 V/μm, respectively.

The uniformity of the emission current from the CNTFC can be evaluated from the luminescence of the phosphor coated on the anode plate, as shown in Figures 6(a–c). The applied electric field was 4 V/μm for the measurements. For CNTFCs deposited at lower temperatures (60–70 °C), the uniformity of luminescence is poor. However, for the CNTFC deposited at 80 °C, lots of bright sites were uniformly presented on the phosphor screen. As a result, our composite plating method could fabricate uniform and high quality CNTFC with high throughput at $T_D = 80$ °C.

4. SUMMARY

In summary, CNT field emission cathodes have been fabricated on glass substrate with good adhesion by using the composite plating method. As deposition temperature increases from 60 to 80 °C, the resulting CNT-Ni composite structures become less porous, and the corresponding field emission properties become better. For the CNTFC deposited at 80 °C, a low turn-on electric field of about 1.2 V/μm and a low threshold electric field E_{th} of about 1.9 V/μm are acquired. Besides, the uniformity of its emission was also good. Thus, it is possible to fabricate large area, uniform, and flexible CNT-metal composite film by this method. These results should be beneficial for the development of large area CNT field-emission displays, and many other CNT-based devices.

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