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Original article

Synthesis and field emission properties of carbon nanotube films modified with amorphous carbon nanoparticles by a simple electrodeposition method

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ABSTRACT

Amorphous carbon nanoparticles (a-CNPs) on a multi-walled carbon nanotube (MWCNT) film, deposited on a silicon substrate, were synthesized using an electrodeposition combination from a methanol suspension of polydiallyldimethylammonium chloride-modified MWCNTs. A low-voltage electrophoretic deposition of the MWCNTs and a high-voltage electrochemical deposition of the a-CNPs were carried out to yield homogenously attached a-CNPs on the surfaces of the MWCNTs, and form a composite film with good adhesion to the substrate. This scalable technology can produce a large area of a-CNP/MWCNT film. And the field emission investigations show that the a-CNP/MWCNT film has turn-on electric field of 3.17 V μm^{-1} (at 10 $\mu A\ cm^{-2}$) and threshold field of 4.62 V μm^{-1} (at 1 mA cm^{-2}), which are lower than those of the MWCNT film. The a-CNP/MWCNT film can be deposited simply with large areas and may be a promising cathode material applied in field emission displays.

1. Introduction

Carbon nanotubes (CNTs), a class of one-dimensional carbon nanostructures, have attracted much interest in basic nanoscience and in potential nanoscale applications because of their unique structural identity, high mechanical strength, excellent electronic transport properties, excellent electrical conductivity, and high aspect-ratio [1,2]. Among these novel properties, field emission is one of the properties conveying promising applications in CNT-based materials, with great commercial interest in vacuum microelectronic devices like field emission displays, X-ray sources, and microwave devices [3,4]. Accordingly, there has been much effort to design and synthesize CNT-based cold cathode films with low field emission thresholds and high stable emission currents [5,6]. In practical applications, the large-scale and low-cost fabrication of films from CNT powders has already been highlighted [7,8]. Macroscopic CNT films have been prepared using simple electrophoretic deposition (EPD) [9,10]. The synthesis of well-dispersed, randomly oriented CNT by solution processing allows the development of CNT-based large area cathodes produced using a scalable technology. The EPD also has many advantages [11], such as high deposition rate, good uniformity and controlled thickness of films, the use of a wide range of substrates, low cost, and simplicity. Thus, CNT-based films prepared by EPD have great potential for use in CNT-based field emitters.

In the past several years, we have successfully developed many approaches for preparing amorphous carbon films [12–18]. Among them, similar to EPD, electrochemical deposition (ECD) technique also has many advantages, such as applicability for large area deposition, low deposition temperature, low energy consumption, and simplicity. Amorphous carbon (a-C) films deposited from the liquid phase have shown good field emission properties [12], and by modifying the sp^2/sp^3 ratio, could further improve the emission properties [13–15].

In our previous research, we reported the adding of amorphous carbon nanoparticles (a-CNPs) on a graphene film increased the density of the film and improved the adhesion to the substrate [19]. Thus, it is expected that the a-CNPs on MWCNTs film would also improve the adhesion between the film and substrate, especially the field emission properties. To accomplish this, the simple combination of EPD of MWCNTs at low voltage and ECD of a-CNPs at high voltage is employed using a methanol suspension of polydiallyldimethylammonium chloride (PDDA)-modified MWCNTs. Results have shown that a-CNPs are homogeneously attached to the surfaces of MWCNTs, forming an a-CNP/MWCNT composite film with good adhesion to the Si substrate. Therefore, the a-CNP/MWCNT composite film possessed better field emission properties than the MWCNT film.

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2. Experimental

MWCNTs (10 mg) were dispersed in 50 mL (1%, w/w) PDDA aqueous solution by sonication. The resulting suspension was centrifuged to settle all of the PDDA-modified MWCNTs. After removing the supernate, the precipitate was washed repeatedly with H_2O to remove excess PDDA, and then further washed repeatedly with anhydrous methanol to remove H_2O. A homogeneous methanol suspension of the PDDA-modified MWCNTs (0.05 mg mL^{-1}) was obtained by sonication. A simple electrolytic cell system was used to prepare the a-CNP/MWCNT composite film. Platinum plate was mounted on the graphite anode, and a silicon wafer was mounted on the graphite cathode that was kept 10 mm away from the counter electrode. The above suspension was diluted to 0.001 mg mL^{-1} and was used as the electrolyte. A DC voltage of 300 V was applied for 20 min to deposit MWCNTs on the surface of the Si electrode, the suspension almost colorless. Then, the voltage was adjusted to 1600 V and held for 4 h to deposit the a-CNPs. For comparison, a MWCNT film was prepared by EPD for the PDDA-modified MWCNTs at 300 V for 4 h. And another amorphous carbon film was prepared by the electrolysis of pure methanol at 1600 V. These electrodeposition experiments were carried out under N_2 and at 50 °C. The morphology and microstructure of these electrodeposited films were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6701F), transmission electron microscopy (TEM, JEM-2010) and Raman spectroscopy (JY-HR800, the excitation wavelength at 532 nm). The zeta potentials of different MWCNTs suspensions were measured using a Zetasizer Nano Instrument (Nano-ZS, United Kingdom Malvern Instruments Ltd.), and final data were obtained by averaging three measurements for each sample. The field emission properties of these films were estimated in a vacuum chamber under base pressure of 10^{-6} Pa at room temperature using a computer-controlled power source with an amperometer (Keithley 248). A stainless-steel plate was used as the anode and the silicon substrate coated with MWCNTs film was served as the cathode. The emission area was 0.5 cm^2. The distance between the cathode and the anode was kept at 300 μm, which was adjusted with a spiral micrometer before the measurements. The electron emission turn-on field in the experiment is defined as the electric field (F) for a current density (J) of 10 μA cm^{-2} and the threshold field is 100 μA cm^{-2}. The data were collected automatically by the computer.

3. Results and discussion

In general, the success of EPD requires two key steps. First, charged particles dispersed in the liquid-phase suspension are moved to the oppositely charged electrode under an electric field. Second, these charged particles are deposited onto the surface of the electrode. Herein, we performed the zeta potential measurement to confirm the PDDA-modified MWCNTs and MWCNTs. We can see that the zeta potentials of MWCNTs and PDDA-modified MWCNTs are negative (−5.93 mV) and positive (32.5 mV), respectively. Both of MWCNTs and PDDA-modified MWCNTs are charged particles, but the PDDA-MWCNTs are better dispersed in absolute methanol than MWCNTs (Fig. 1a). Thus, we selected methanol suspension of PDDA-modified MWCNTs as the electrolyte. Under the electric field, PDDA-modified MWCNTs are moved to the cathode. Furthermore, the electrolysis of methanol, by generating CH_3^+ deposits an amorphous carbon film on the cathode by ECD *via* the following mechanism:

PDDA modification can lead to a positive charge distribution on MWCNT surfaces. Under the applied low voltage, positively charged MWCNTs migrated to the negative electrode and were subsequently deposited as a film onto the surface of the negative Si electrode. Moreover, under high voltage, methanol molecules were polarized, and the methyl (–CH_3) group acquired a positive charge due to its low electronegativity. Under a high applied voltage (1600 V in our system), the C–O covalent bonds in the polarized methanol molecules might have decomposed, as the resulting CH_3^+ groups migrated toward the Si electrode. Thus, the CH_3^+ groups were adsorbed on the MWCNT film surfaces on the Si electrode. Subsequently, a-CNPs were generated on these sites, given the reactions of individual CH_3^+ groups with each other. During ECD, some CH_3^+ groups might have attached to the Si surface, as a-CNPs on the surface of the Si substrate were generated. This work was previously reported by our group [12]. A widened interface area between the film and substrate was observed.

In our synthesis, MWCNTs were first modified by the positively charged PDDA polyelectrolyte. After treatment, a uniform methanol suspension of PDDA-modified MWCNTs (0.05 mg mL^{-1}) was obtained, which was stable for more than one week (Fig. 1a). Fig. 1b and c show the typical TEM images of PDDA-modified MWCNTs, demonstrating further that every part of the nanotube surface is coated with a 2 nm-thick PDDA monolayer (see arrows). The figures indicate a strong interaction between the MWCNT and PDDA layer. The PDDA-coating could have created a distribution of positive charges on the surfaces of MWCNTs, thus favoring MWCNT composite film formation.

The a-CNP/MWCNT composite film on the Si substrate was black, as with the MWCNT film. However, SEM images have revealed a difference in morphology between the MWCNT film and a-CNP/MWCNT film. The MWCNTs on the surface of the MWCNT film are interlaced and form a MWCNT network (Fig. 2a). On the other hand, the surface of the composite film exhibits packing of the nanotubes, which have characteristically large diameters

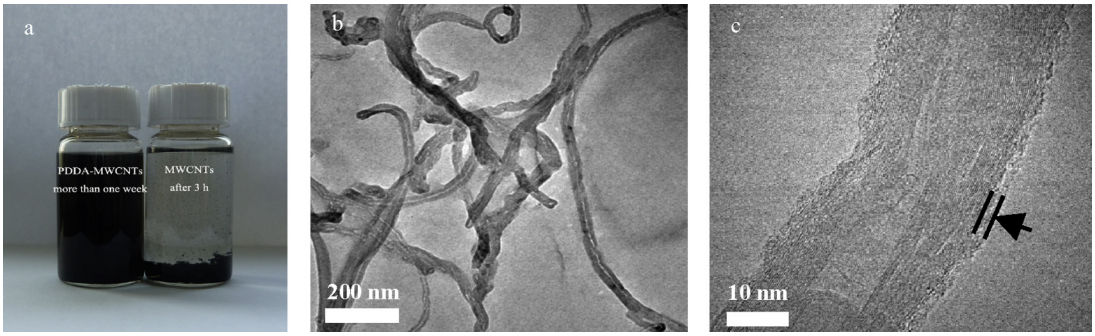

Fig. 1. (a) Optical image (left) of the methanol suspension of PDDA-modified MWCNTs (0.05 mg mL^{-1}) taken after the suspension was undisturbed for one week and (right) the methanol suspension of MWCNTs (0.05 mg mL^{-1}) taken after 3 h; (b) low-resolution TEM images of PDDA-modified MWCNTs; (c) high-resolution TEM images of PDDA-modified MWCNTs.