

Surface Modification of Aligned Carbon Nanotube Arrays for Electron Emitting Applications

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Abstract

We have previously developed a simple pyrolytic method for large-scale production of aligned carbon nanotube arrays perpendicular to the substrate. These aligned carbon nanotube arrays can be transferred onto various substrates of particular interest (e.g. polymer films for organic optoelectronic devices) in either a patterned or non-patterned fashion. The well-aligned structure is important, which not only allows us to prepare aligned coaxial nanowire of carbon nanotubes sheathed with polymers by electrochemical polymerization of conducting polymers on the individual nanotubes but also enables us to develop a facile approach for modification of carbon nanotube surfaces via plasma activation, followed by chemical reactions characteristic of the plasma-induced functionalities. These surface modification methods are particularly attractive, as they allow surface characteristics of the aligned carbon nanotubes to be tuned to meet specific requirements for particular applications while their alignment structure can be largely retained. The aligned carbon nanotubes with tunable surface characteristics thus prepared are of great significance to various practical applications, especially for the use of carbon nanotubes as electron emitters in flat panel displays. Particularly, we found that hexane-plasma coating reduced the turn-on electric field E_{to} , coupled with a concomitant increase in the emission current at a constant V; the turn-on electric field decreased from $E_{to} = 2.5 \text{ V}/\mu\text{m}$, characteristic of the pristine aligned carbon nanotubes, to $E_{to} = 1.5 \text{ V}/\mu\text{m}$ with a significantly increased emission current after the treatment of *n*-hexane plasma at 30 W, 250 KHz and under a monomer pressure of 0.65 Torr for 2 min. In this paper, we will discuss the effects of the surface modification on the electron-emitting properties of the aligned carbon nanotubes by presenting some examples from our recent work.

Keywords: Aligned carbon nanotube, nanotube electron emitter, plasma deposition, flat panel display, surface modification

1. Introduction

Owing to their unique electronic properties and unusual molecular symmetries, carbon nanotubes hold promise for a wide range of potential applications [1]. For instance, carbon nanotubes have been explored for the use as new electron field emitters in panel displays [2]. The carbon nanotube electron emitters work on a similar principle to a conventional cathode ray tube, but their small size could lead to a thinner, more flexible and energy efficient display screen with a higher resolution. Although aligned carbon nanotubes are not necessary for these display applications, the use of aligned/micropatterned carbon nanotubes has been shown to offer additional advantages, including the efficient electron emission and device integration, for the development of low field nanotube-based flat panel displays [2]. However, the high tubular packing density associated with aligned carbon nanotubes often causes

electrical screening effects to weaken the field enhancement at the closely-packed aligned nanotube tips than on the tip of an isolated nanotube. In order to improve the field emission performance of aligned carbon nanotubes, therefore, it is highly desirable to sheath the nanotube wall with a thin layer of polymer coating to minimize the electrical screening effect. In this regard, we have plasma coated the individual aligned carbon nanotubes produced by pyrolyzing FePc under Ar/H₂ at 800–1100°C [3]. The plasma coating was shown to cause no observable change in the alignment structure while the surface characteristics of the aligned carbon nanotubes could be modified in a controllable fashion. The surface-modified aligned carbon nanotubes are particularly attractive for their use as field emitters since their field emission performance was found to be greatly enhanced.

In this paper, we report the effects of surface modification on electron emitting properties of the aligned carbon nanotubes modified by plasma polymerization and water-induced restructuring.

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Table 1. Conditions of hexane plasma treatment carried out on the ACNT array.

Plasma	Monomer Pressure Torr	Power W	Frequency KHz	Discharge Time s
Hexane	0.25	30	250	60
Hexane	0.25	30	250	120

2. Experimental

2.1 Materials

Iron (II) phthalocyanine ($\text{FeC}_{32}\text{N}_8\text{H}_{16}$, designated as FePc) was purchased from Sigma-Aldrich. Analytical grade *n*-hexane was obtained from EM Science and used as monomer for plasma polymerization. All other chemicals were obtained from commercial sources and used without any further purification.

2.2 Syntheses of aligned carbon nanotubes

Aligned carbon nanotube array was prepared on a quartz substrate by pyrolyzing FePc in the temperature range of 800–1100 °C in Ar/H₂ atmosphere [3]. The as-synthesized aligned carbon nanotube (ACNT) array was then transferred from the quartz substrate onto a gold substrate by the HF etching process [3].

2.3 Surface modification of aligned carbon nanotube array by plasma polymerization

n-Hexane was used as the monomer for plasma polymerization over the ACNT array. A custom made plasma reactor powered by a commercially-available high voltage radio-frequency generator operating between 100 – 500 KHz (AG0201HV-ACD) was used to carry out the plasma polymerization. The gold-supported ACNTs were placed on the electrode in the plasma chamber for plasma polymerization of *n*-hexane. Table 1 listed the plasma polymerization conditions.

2.4 Instrumentation

Fig. 1 shows the experimental set-up for measuring the field emission from the ACNTs. In a typical experiment, the whole setup is placed in a vacuum chamber maintained at 10⁻⁶ mbar. The macroscopic electric field (*E*) was obtained by dividing the applied voltage (*V*) by the separation distance between the cathode and anode (*d*). Upon application of a potential *V* between the anode and the nanotube film, the applied electric field $E = V/d$ causes the extraction of electrons from the nanotube tips. The field emission characteristics of ACNTs were tested after each plasma treatment and compared with the emission behavior of pure ACNT. Scanning electron microscopic images were recorded on a HITACHI S-2150 SEM unit while transmission electron microscopic (TEM) images were obtained from JEOL 1200EX II TEM.

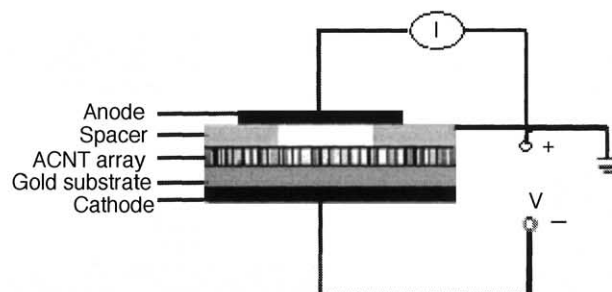


Fig. 1. Schema of experimental setup for measuring the field emission characteristics of ACNT arrays.

3. Results and Discussion

Figs. 2a&b show SEM images the ACNTs before and after the plasma polymerization of *n*-hexane. The insets of Figs. 2a&b give the corresponding TEM images, which clearly show that there is a layer of hexane plasma coating along the nanotube surface (inset of Fig.2b). Comparing the insets of Figs. 2a&b indicates that an average thickness of *ca.*10 nm for the hexane-plasma coating. Closer inspection of Fig. 2b under a higher magnification shows that the individual plasma-coated aligned carbon nanotubes are well separated from each other (Fig. 2c).

Fig. 3 shows the I-E plot to characterize effects of the plasma polymerization time on emission behaviors of the ACNTs. As can be seen, a plasma treatment of 60 s caused a significant change in the emission behavior of the sample. For instance, the plasma treatment led to a shift of the turn-on voltage from about 1.6 V/μm, characteristic of the pure ACNT sample, to a value of *ca.*1.4 V/μm for the same ACNT sample after the plasma polymerization of *n*-hexane for 60 s. Further plasma treatment up to 120 s, the turn-on voltage further decreased to about 1.0 V/μm, coupled with a significant increase in the emission current density at any particular voltage above the turn-on voltage.

The inset of Fig. 3 represents the corresponding Fowler-Nordheim plots. The linear relationship between $\text{Log}(I/E^2)$ and $1/E$ is only observed for the voltages above the turn-on voltage. Fowler and Nordheim explained the phenomenon of field emission on the basis of quantum mechanical tunneling of electrons due to the pending of the potential barrier in the presence of an external electric field [4]. A certain degree of deviation from the Fowler-Nordheim behavior for metal tips has previously been observed and was attributed to the space-charge-limited current mechanism [5].

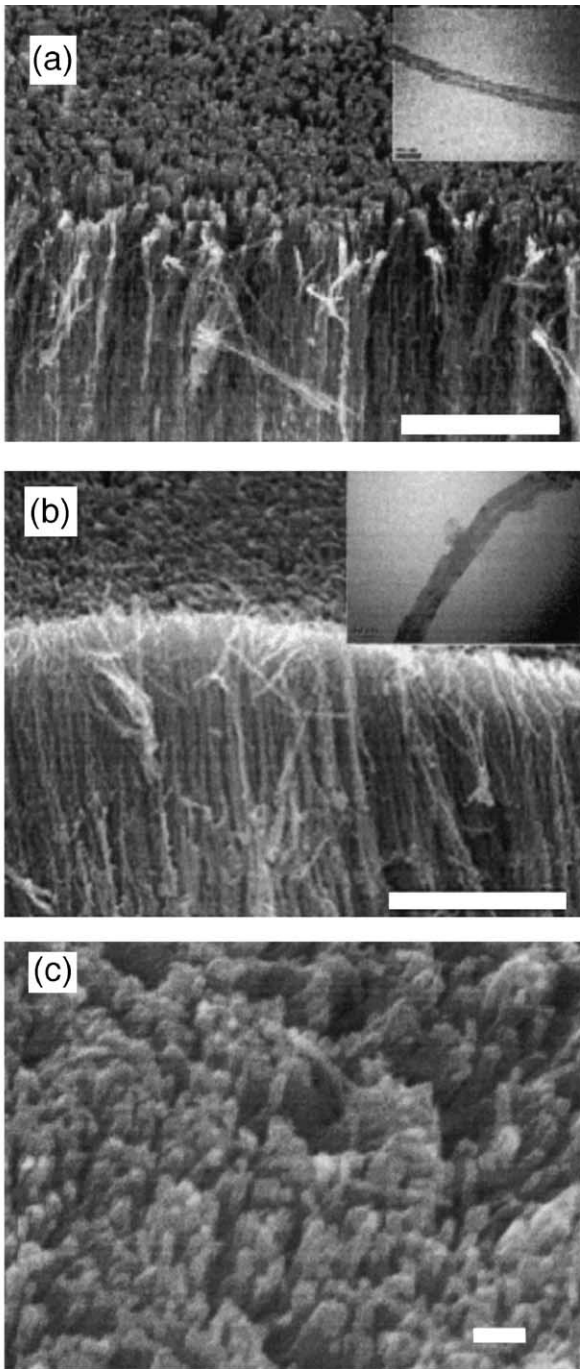


Fig. 2 (a) SEM image of the ACNT array on a gold substrate (Scale bar $10\mu\text{m}$). (inset) TEM image of pure ACNT from the same sample. (b) Hexane plasma treated (discharge time 1.0 min) ACNT (Scale bar $10\mu\text{m}$). (inset) TEM micrograph of the hexane plasma treated ACNT. (c) High magnification SEM image of the same ACNT sample as Fig. 2b (Scale bar $1\mu\text{m}$).

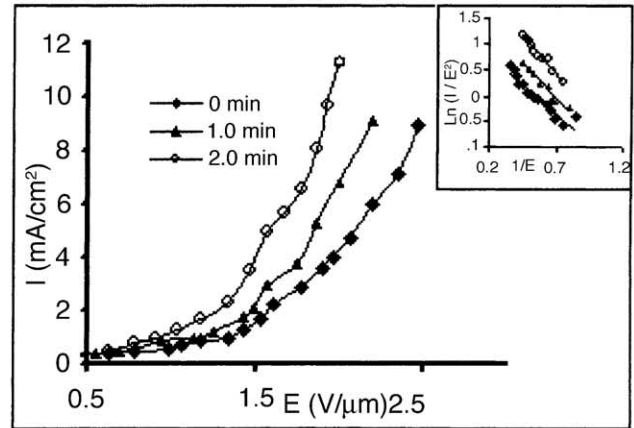


Fig. 3 I/E curves from the pure ACNTs after being treated by hexane plasma consecutively for different periods of time. Inset shows the corresponding Fowler-Nordheim plots.

Along with the plasma surface modification discussed above, we have also followed up the effects of surface topographic structures of the ACNT array on its field emission performance. Fig. 4a shows a top SEM view for a freshly prepared ACNT array after having been transferred from the quartz plate onto a gold substrate by the treatment in a 30–40% aqueous solution of hydrofluoric acid (HF) [3]. By keeping the transferred ACNT array in distilled water for 30 minutes and drying up in air, we found that the ACNT array showed a honeycomb structure (Fig. 4b) in consistent with previous reports [6–8]. The formation of the honeycomb structure can be attributed to the capillary effect caused by water during the drying of the ACNT film in air [8].

We investigated electron emission properties of the newly-formed ACNT honeycomb. It was found that the ACNT honeycomb also exhibited a better emission performance than the pristine bulk ACNT array (Fig. 5); a lower turn-on voltage combined with a higher current density was observed for the ACNT honeycomb. The self-assembly of ACNTs into the honeycomb structure could lead to a surface inhomogeneity-induced enhancement in field emission [9]. However, the possibility for a water-induced decrease in ionization potential of the ACNTs [10, 11], and hence the enhanced field emission with a decreased turn-on voltage, cannot be ruled out as physisorption of H_2O molecules on carbon nanotube surface has been reported to reduce the ionization potential of the nanotube [10, 11].

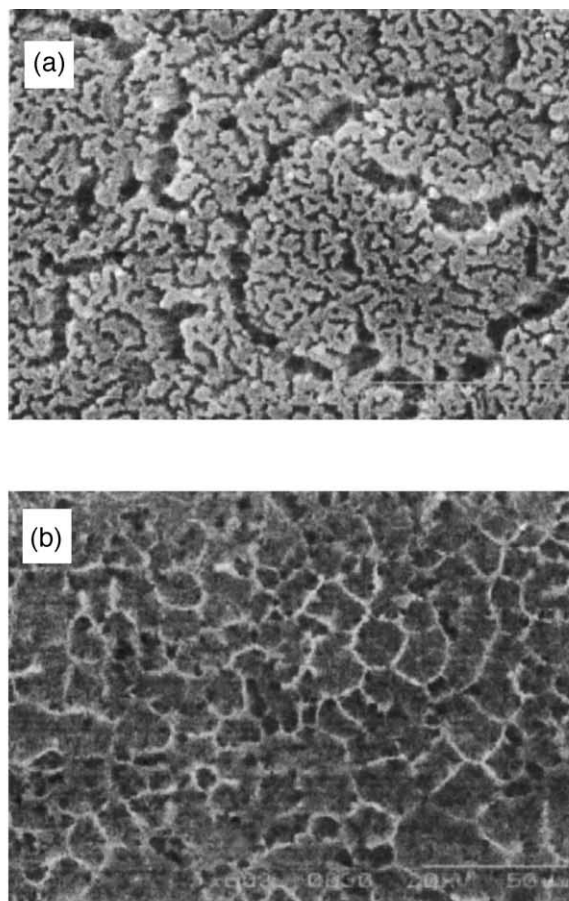


Fig. 4 (a) SEM image of the ACNT array on a gold substrate and (b) the ACNT honeycomb.

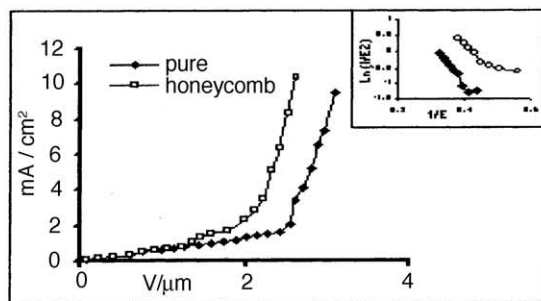


Fig. 5 I/E curves showing the field emission behavior of pure ACNTs before and after the formation of honeycomb. Inset: the corresponding Fowler-Nordheim plots.

4. Conclusion

We have demonstrated that the surface of FePc-generated aligned carbon nanotubes can be modified by the radio-frequency plasma technique whilst their alignment structure is largely retained. The plasma surface coating was found to greatly enhance the electron emission performance of the aligned carbon nanotubes. The formation of the water-induced honeycomb structure was also shown to reduce the turn-on field and increase the field-emission current for the aligned carbon nanotubes. These results clearly indicate that appropriate surface modification could lead to highly efficient electron emitters of practical significance.

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