Li-salt functionalised carbon nanotubes as low work function field emitters

Stephen M. Lyth*, R. A. Hatton and S. R. P. Silva

Advanced Technology Institute

University of Surrey

Guildford, Surrey, UK

*s.lyth@surrey.ac.uk

Telephone: +44 1481 686083, Fax: +44 1483 689404

Introduction

Carbon nanotubes have excellent field emission (FE) properties.¹⁻³ The work function (WF) of materials plays a crucial role in their FE properties. From the well known Fowler-Nordheim equation,⁴ it is evident that reducing the WF should result in an exponential increase in current density at a given electric field. Therefore, for cold cathode applications it is desirable to minimize the emitter WF without compromising the cathode stability towards oxidation. We have recently shown that the WF of acid-oxidized multiwall carbon nanotubes (o-MWNT) can be reduced by exchanging acidic surface groups with alkali metal cations.⁵ We report a method for applying o-MWNT onto carbon fibre (CF) fabric from solution and an improvement in the FE properties after converting carboxylic groups to the carboxylate salt of lithium via cation exchange. It is envisaged that this technique could be applied to a wide range of nanotube emitters to reduce the WF and improve the FE properties.

Experimental

A stable aqueous dispersion was formed by refluxing nanotubes in a concentrated nitric and sulphuric acid mixture, resulting in the formation of carboxylic acid groups attached to the nanotube surface. These interact with water molecules via H-bonding and an o-MWNT ink was formed. The alkali cation exchange (Fig. 1) was achieved by dispersing LiOH in the o-MWNT ink, thoroughly mixing in an ultrasonic bath, filtering and then washing with pure water, ensuring the removal of excess LiOH and resulting in a lithium-functionalized ink (Li⁺MWNT). The CF fabric was hydrophobic, so it was subject to a microwave oxygen plasma treatment. This partially oxidizes the CF surface, creating oxygen containing moieties, which enable H-bonding. Additionally, H-bonding results in strong

adhesion between the CF and the o-MWNT layer. The plasma-treated CF was dipped in o-MWNT and Li⁺MWNT, removed and baked to remove residual water.

Fig. 1: Schematic of the cation exchange process.

Results

Figure 2 shows SEMs of the substrates. Fig. 2(a) shows the pristine CF. Fig. 2(b) shows the CF after oxygen plasma treatment. Fig. 2(c) and 2(d) show the CF after o-MWNT coating (the Li⁺MWNT layer was identical) with a uniform layer across the whole CF surface.

Fig. 2: SEM images of the substrates.

The FE properties were investigated in a diode configuration with a spherical stainless-steel anode. The threshold field (E_{th}) was defined as the macroscopic electric field (E) at which $1nA$ was detected. Figure 3 shows the FE current as a function of E for four different CF fabric samples. The pristine CF fabric had $E_{th} = 0.42 V/\mu m$. After oxygen plasma treatment, $E_{th} = 0.58 V/\mu m$. This increase in E_{th} can be attributed to the increase in the WF of the CF after plasma treatment to $\sim 4.8 eV$.⁶

Fig. 3: Emission current-field curves for the samples.

Coating the plasma treated CF with o-MWNT results in $E_{th} = 0.42 V/\mu m$. This reduction in E_{th} compared with the plasma treated CF is attributed to the modification of the surface geometry of the fibres by the o-MWNT, resulting in an overall increase in geometric field enhancement (β) and therefore a higher local field at the emitting sites. However, since the WF of o-MWNT ($5.0 eV$)⁵ is larger than that of the pristine CF ($4.4 eV$), the beneficial effect of β is offset by the increase in WF.

Coating the CF fabric with Li^+MWNT results in $E_{th} = 0.25 V/\mu m$. This improvement is attributed to the lowering in WF from $5.0 eV$ to $4.6 eV$.⁶ In this case, the extremely low error suggests that there is very little variation in emission properties across the entire surface which is greater than $1 cm^2$. It should also be noted that the hysteresis for the Li^+MWNT coated samples is exceptionally low, indicative of the stability of the emitter during FE. These results are summarised in Table 1.

	E_{th} ($V/\mu m$)	Error ($V/\mu m$)	Hysteresis ($V/\mu m$)	Work function (eV)
Pristine carbon fibre	0.42	± 0.03	0.20	4.4 ^[6]
Plasma treated fibre	0.58	± 0.15	0.23	4.8 ^[6]
o-MWNT coated fibre	0.42	± 0.09	0.08	5.1 ^[6]
Li^+MWNT coated fibre	0.25	± 0.02	0.04	4.6 ^[5]

Table 1: Summary of numerical results.

Conclusion

In summary, CF fabric was surface oxidized, dip coated in o-MWNT and Li^+MWNT , and the FE properties investigated. The threshold field was observed to vary depending on the process applied to the CF fabric, ultimately leading to a substantial reduction in E_{th} from $0.42 V/\mu m$ for o-MWNT to $0.25 V/\mu m$, for Li^+MWNT . This marked reduction in E_{th} is attributed to the reduction in work function from $5.0 eV$ to $4.6 eV$. An associated decrease in hysteresis and an increase in emission uniformity across the sample were also observed. This method provides a simple, cheap and scalable manner in which to create high performance, large area and widely applicable field emitting electrodes.

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References

1. A. G. Rinzler, *et al.* Science **269**, 1550 (1995)
2. W. A. Deheer, *et al.* Science **270**, 1179 (1995)
3. S. M. Lyth *et al.* APL **90**, 013120 (2007)
4. R. H. Fowler *et al.* Proc. Roy. Soc. Ser. A **119**, 173 (1928)
5. N. P. Blanchard *et al.* CPL **434**, 92 (2007)
6. H. Ago *et al.* Phys. Chem. B **103**, 8116 (1999)