Carbon Nanotube – Polymer Nanocomposites for Field Emission Cathodes

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Keywords: Nanocomposite, carbon nanotubes, electron field emission, displays

Abstract We report the electron field emission characteristics of functionalised single walled carbon nanotube – polymer composites produced by solution processing. We show that excellent electron emission can be obtained by using as little as 0.7% volume fraction of nanotubes in the composite. Furthermore by tailoring the nanotube concentration and type of polymer, improvements in the charge transfer through the composite can be obtained. The synthesis of well dispersed randomly oriented nanotube - polymer composites by solution processing allows the development of carbon nanotube based large area cathodes produced using a scaleable technology. The relative insensitivity of the cathode's field emission characteristics to the electrical conductivity of the composite is also discussed.

1. Introduction

Electron field emission (FE) has emerged as one of the most promising areas for the exploitation of carbon nanotubes (CNTs) due to their excellent electrical properties, mechanical robustness and controllable aspect ratio.^[1] At low current densities, typically less than 10 mA/cm², potential applications include field emission displays (FEDs), where prototype 30-inch full colour CNT based displays have already been demonstrated.^[2] Related applications include back lighting sources for high quality liquid crystal display television, which utilises the ability of FE to provide low cost and high quality local dimming and also for energy efficient solid state lighting.^[3] For small size applications, typically below 5-inch in size, growing CNTs *in situ* via chemical vapour deposition (CVD) on a substrate is a commonly employed route. However, larger area applications, such as widescreen diagonal displays, can be fabricated from nanocomposites with nanotubes dispersed in liquid media using methods such as spraying, screen printing or inkjet printing.^[4,5] Latex technology methods have also been employed in which single walled nanotubes are mixed with latex nanoparticles which after drying produce a nanotube - polymer composite.^[6] The use of such a hybrid nanostructure allows additional multifunctionality not present in the individual components of the composite.

In principle, the greater the density of nanotubes, the larger the current available, however in CVD grown non-aligned random mats of nanotubes only a tiny fraction, perhaps as low as 1 in 10⁵ nanotubes, is actively participating in emission. This is due to a combination of different nanotube heights and radii (resulting in different aspect ratios) and through electrostatic screening; both these effects lead in turn to reduced and non-uniform emission. According to Nilsson *et al.*, screening occurs when the separation between the nanotubes is less than twice the length of the nanotubes.^[7] Hence for CVD nanotubes grown on a substrate with a typical length of 5 µm, proximity screening effects will occur for concentrations in excess of only 10⁶ cm⁻². While CVD has the advantage of being a mature

technology and the ability to control the position of the nanotubes by correct positioning and design of the catalyst is readily possible, most of the nanotubes will not be emitting. This represents a significant drawback in the use of CVD grown CNTs as electron sources. As an alternative to the CVD route in producing cathodes, solution processing leading to composite formation allows for accurate control and determination of the nanotube concentration leading to larger area cathodes. As a result optimization of emission from as few CNTs as possible will maximize emission and at the same time will avoid unnecessary material wastage. Embedding a nanotube in a polymer also offers some protection to the emitter material. These are some of the advantages of using a composite cathode technology over CVD grown forests of nanotubes.

Carbon nanotube composites can form electrical percolation networks at very low loadings, typically less than 0.1 vol.%, due to their high aspect ratio. As a result composites can display significant electrical conductivity at relatively low nanotube content.^[8] In addition, the correct choice of polymer allows alternative architectures, such as flexible and transparent sensors and emitters using, for example, aligned CNTs in a poly(dimethylsiloxane) matrix to be realised.^[9] However, the technological development of CNT - composites has been hampered by issues such as poor nanotube solubility and subsequent aggregation.^[10] Such issues have been addressed through covalent functionalisation of nanotubes ^[11] where functionalisation allows the tubes to remain well dispersed even at concentrations required for composite formation.^[12] Furthermore careful choice of the functional group potentially allows the nanotubes to be dispersed in any solvent and made compatible with any matrix polymer. One possible disadvantage of chemical functionalisation is the possibility of affecting the π electron system of the nanotube walls while sonication may also result in damage to the nanotubes. Both of these treatments may in turn affect the intrinsic electrical conductivity of the nanotube and lower the overall conductivity of the composite. However, for many applications efficient dispersal of the

CNTs remains an important prerequisite so the effects of a particular treatment also need to be considered. Here we report the electron field emission characteristics of single walled CNT (SWNT) – polymer composites produced by solution processing of water - soluble, functionalised nanotubes in solutions of polyvinyl alcohol (PVA). We show that excellent emission characteristics at low nanotube content can be realised despite relatively low electrical conductivity. We further compare the results obtained here with other composite systems, in particular, the cases of using the conjugated polymer poly *m*-phenylenevinylene-co-2,5-dioctoxy-*p*-phenylene vinylene (PmPV) and polystyrene (PS). Finally, we examine the rate limiting step for emission and generalise our discussion for the design and application to other composite cathode systems.

2. Results and Discussion

A representative scanning electron microscope image of one sample with 3 vol.% fraction is shown in **Figure 1a**, demonstrating excellent nanotube dispersion. **Figure 1b** shows the measured two terminal conductivity of the composite as a function of nanotube loading. It can be seen that the conductivity increases from less than 10^{-9} S/m at low nanotube content to about 2.9×10^{-7} S/m at a loading of 6.6 vol.% and then up to 10^{-3} S/m at the highest concentration of 15 vol.%. In the case of electrical transport controlled by percolation, the conductivity, σ , at a volume fraction p , is given by the power law $\sigma = \sigma_0(p - p_c)^t$, where p_c is the critical volume fraction. The inset in Fig. 1b shows the variation of the conductivity with volume fraction with the data fitted with $p_c = 0.0036$ or 0.36 vol.%. To put some of these numbers in context, both higher and lower critical volume fractions have been previously reported with Bryning *et al.* reporting some of the lowest values of p_c of $(5 - 10) \times 10^{-3}$ vol.% for composites of SWNTs produced by the laser-oven method and $(8 - 23) \times 10^{-3}$ vol.% for nanotubes produced by the HiPCO method^[13], with the conductivity of these composites ranging from 10^{-6} to 10^{-2} S/m. For composites produced

with PmPV, the dc conductivity ^[14] ranged from 9×10^{-7} to 10^{-5} S/m for loadings up to 4.3 wt%. There are a number of possible explanations for the low conductivity in polymer based composites, including the effects of chemical treatment, sonication or poor dispersion. However, we believe that the most important factor limiting the conductivity is the presence of a thin polymer coating surrounding the nanotubes. The presence of such a thin polymer coating has been observed for nanotubes dispersed in aqueous solutions of PVA and the polymer coating which may well be retained during the drying of the composite. Evidence for this nanotube - polymer coating comes from differential scanning calorimetry (DSC) and electron microscopy ^[15]. The net effect is the presence of a resistive nanotube-polymer-nanotube tunnel junction which acts to inhibit efficient charge transfer. While values of conductivities of 1 S/m are regularly reported for composites made with commercial grade nanotubes, a value of conductivity of 1000 S/m has recently been reported in a composite made from 2 wt% nanotubes grown in vertically aligned films.^[16] As shall be discussed in detail below, having high values of electrical conductivity is not a strict requirement for field emission applications. This is because the rate limiting step for emission will not be the transport of carriers through the composite film but the electron tunnelling into the vacuum through a potential barrier of typically 5 eV. Indeed, a characteristic of a poor cathode would be one for which the field emission current is predominantly determined by electron transport through the film. It is therefore one of the aims of this paper to highlight this important fact as it opens up the way of using low mass fraction composites whose electrical characteristics may be insufficient for, say, transparent electronics on plastic, but could still be sufficient as a cold cathode material.

Figure 2 shows a representative set of CNT - PVA composites field emission current – field (I - E) characteristics for different nanotube loadings. Detailed analysis of the emission characteristics can be quantitatively seen more clearly in **Figure 3a** where the average threshold applied electric field for different reference current levels in the range of

0.1 to 1000 nA is plotted as a function of volume fraction. For volume fractions in the range 0.72 – 6.6%, the average value of the applied electric field, E_{th} , for each of the reference current levels is largely independent of nanotube loading. This is a significant result as it shows that excellent and uniform emission at low nanotube content is possible and that there is little benefit in using a 7 vol.% nanotube loading when compared with a 0.7 vol.% containing film. The lowest threshold fields are found, not surprisingly, in the samples with the highest loading (≥ 10 vol.%) and analysis of the I - E data for these samples within the Fowler-Nordheim formulation (see later) shows that only at the highest current levels is their evidence of current saturation. It is also interesting to note that the value of E_{th} decreases with increasing CNT content. In other studies such as Poa *et al.* using undoped and B doped multiwalled CNTs, the value of the threshold field actually increased with loading.^[17] Emission site density measurements from this previous study showed uneven emission and the increase in E_{th} with loading was attributed to screening effects associated with high local concentrations of nanotubes possibly due to poor dispersion. It should be noted that obtaining successively lower and lower threshold electric fields is not considered a key technology driver since in FEDs since the on/off behavior of emission in a composite pixel will be controlled by a nearby (low) voltage gate electrode. Switching low voltages to obtain an applied field of, say, 10 V/ μm is not difficult. The key results being reported in this paper refer to good emission from cathodes with low volume fractions of nanotubes.

The different shapes of the I - E curves in Figure 2 as the nanotube loading is changed can also provide valuable information. For loadings above 0.72 vol.%, the I - E curves turn on sharply at low applied field and deliver high currents with some evidence of leveling off of the emission only at higher values of current. The I - E curves for the composites with less than 0.72 vol.% loading are qualitatively different with only a gradual rise in current with applied field. This behaviour is inextricably linked to the transport of carriers in the composite. The data in Figures 2 and 3a represents how the emission characteristics depend

on the applied or macroscopic electric field, E_A . This field differs significantly from the much larger local electric field, E_L , experienced at the tip of the emitter which arises from a geometric amplification of the applied field as a result of the nanotube's high aspect ratio.^[18] It is this local electric field that is ultimately responsible for emission and the amplification is described by the field enhancement factor, β . A crude approximation that is often employed for the enhancement factor for a single nanotube is half the aspect ratio. The largest values of β will then naturally arise when the CNT is oriented parallel to the electric field lines coming from the anode with the electric field lines concentrating on the tip of the nanotube. In composites, the orientation of the nanotube will not, in general, be aligned in the direction parallel to the field lines and lower values of β than those predicted by simply taking the aspect ratio will be present. Achieving alignment to maximize the enhancement factor from a solution processed composite remains a significant challenge, however, the inherent advantages of a wide area production method with controllable nanotube content remains attractive. For efficient electron emission, values of E_L should be a few V/nm and this can be achieved at macroscopic electric fields of a few V/ μm for sufficiently large values of β (typically several hundred to a few thousand). Evidently the values of β found in the samples of this study are sufficient for emission to be observed. Electrons tunnel through an approximately triangular potential barrier at the nanotube - vacuum barrier (taken as the work function, Φ , of the nanotube) as a result of the high local electric fields. This is the basis of the Fowler-Nordheim (F - N) description of electron emission; a key feature of which assumes that the emission current is not limited by the replenishment of the emitted electrons and analysis of the I - E characteristics using the F - N theory allows estimates of the field enhancement factor and hence local electric field to be made (see later).

Further confirmation of the different behaviour between the lower (< 0.5 vol.%) and higher volume fraction composites can be seen using the F - N representations of the emission

characteristics. **Figure 3b** shows four of the emission characteristics for samples with volume fractions of 0, 0.36, 0.72 and 15 vol.% in the usual F - N representation. All of the emission curves from samples in the 0.7 – 15 vol.% range exhibit a similar two slope behaviour with the larger of the two slopes found at lower currents. This behaviour is characteristic of a F - N type emission mechanism and the reduction in the slope at higher current levels has been reported previously for other nanotube based emitters and variously attributed to the presence of a non-metallic density of states at the tip of the nanotube or the onset of current limitation.³ For samples below 0.7 vol% the larger slope in the F - N plot is found at higher current levels - a behaviour not previously reported for CNT based emitters - suggesting that the emission mechanism is not solely based or controlled by F - N tunnelling. As a result estimates of the local electric field, E_L , can then only be made with confidence (**Figure 4a**) up to about 100 nA of emission current from the Fowler - Nordheim analysis of the emission characteristics for samples with loadings greater than 0.7 vol.% assuming a value of $\Phi = 5$ eV.^[20]

The most important conclusion that can be drawn from Figure 4a is the appearance of two regimes. For composites with greater than 0.7 vol.%, the local electric fields are largely constant, between 4.5 – 7.5 V/nm for the different current levels; it is only for films with less than 0.7 vol.% that this description breaks down. To understand this behaviour of the local electric fields with loading it is important to consider the rate limiting step for emission. This can be ascribed to one or more of the following three processes of (i) injection: what is the source of the electrons, (ii) transport: how they are transported through the film and (iii) emission: how they are extracted into the vacuum. For a metal, the high conductivity and high density of states at the Fermi level results in emission being controlled by the properties of the front surface with little or no field penetration. In metals, emission is controlled by Fowler-Nordheim tunneling at the surface with replacement of the electrons being readily achieved due to the high electron supply function. For flat metal films, with little field enhancement (equivalent to $\beta = 1$), large applied fields (> 500 V/ μm) are required for

emission and this requirement has resulted in the development of Spindt tip based metal emitters.^[21] At the other end of the conductivity scale are wide gap semiconductors and insulators such as diamond and GaN. These materials have relatively low barriers to emission as inferred by their electron affinities. However, in these wide gap materials the large energy gap results in a low concentration of electrons in the conduction band and *injection* from the back contact into the conduction band of the emitter and *transport* through the semiconductor film to the front surface are the important controlling factors^[22, 23] for emission. It should further be noted that recent studies by Chiu and Roth have also noted the importance of the different transport and tunneling behaviour in carbon nanotube intramolecular junctions where by there is a change from direct tunneling to field emission at high fields.^[24]

So what about the case of CNT - polymer composites in which the high conductivity and tip based carbon nanotube is embedded in an insulating matrix? Previously we have shown that in the case of CNT - PmPV composites the FE characteristics could be explained by a percolation controlled Fluctuation Induced Tunnelling (FIT) conduction mechanism of transport limited behaviour of electrons through the disordered network of the composite film.^[25] A plot of the local electric field (for a 10 nA reference emission current) reflected the transport through the film and exhibited a strong linear (mass fraction)^{-1/3} dependence (closed squares) as shown in **Figure 4b**. As mentioned earlier, on the basis of the DSC and electron microscopy measurements, surrounding the nanotubes is a thin polymer coating and the variations of the polymer coating, coupled with different nanotube - nanotube separations results in a variation of effective tunnel barriers for conduction. Having previously suggested that FIT is a significant contributing factor for the emission from the CNT - PmPV samples, it is instructive to see if this is the case in the CNT - PVA composites. Analysis of the local electric field for the CNT - PVA composites between 0.72 and 6.6 vol.% within the FIT formulism is presented in Figure 4b for reference currents of 1 nA and 10 nA. It is apparent that there is a much weaker dependence of the local fields with loading at either of these

reference currents; suggesting that FIT and hence transport in the composite network is not a significant factor. This does not imply that in these films no polymer coating is present; only that the effects of the tunnel barrier on the conduction in the film are masked by the high front surface barrier to emission.

3. Conclusions

Summarizing the data of Figures 2 to 4, it is possible to explain the field emission from the CNT - PVA samples as follows: for films with above 0.72 vol.% content the emission does not appear to be significantly limited by the transport through the film. Emission is via tunnelling from the tip of the nanotubes due to the presence of high (4.5 – 7.5 V/nm) local electric fields. This differs significantly from the case of the CNT – PmPV composites where emission was limited by the bulk charge transfer (via FIT) through the film. The key difference between the CNT - PVA composites in this study and the CNT - PmPV composites of our previous study is the improved dispersion. By contrast studies using polystyrene with mass fractions ranging from 11 wt% to 33 wt% showed that the threshold field actually increased with loading; an effect attributed to nanotube proximity screening.^[17] While emission was observed of single wall CNTs in poly(3-octylthiophene), (P3OT) the sample contained a high mass fraction (33%) of nanotubes.^[26]

On the basis of these results some important conclusions can be drawn for the general design of composite cathodes. First of all high nanotube loadings are not required for good cathode performance. While the lowest values of E_{th} were found at the highest loading it is the virtually constant values of the threshold fields in the 0.7 to 6.6 vol.% range that shows significant promise. No evidence of electrostatic screening is seen in these cathodes; a significant advancement when compared with other studies. The key to good cathode performance is the dispersion of the nanotubes which is a direct result of the processing. Even if the two terminal conductivity is low this does not appear to significantly inhibit the

emission characteristics and it is worth pointing out that in highly conductive films (e.g. films which may find applications in electromagnetic shielding) the externally applied field would be screened which would result in poor transport and replenishment of the emitted electrons. Our study shows electron field emission from water soluble CNT - polyvinyl alcohol composites has been demonstrated at low nanotube loadings, much lower than those reported previously, and despite the relatively low electrical conductivity opens up the possibility of large area nanotube solution based field emission displays or back lighting units.

4. Experimental Details

Single walled carbon nanotubes functionalised with poly(*m*-aminobenzene sulfonic acid) (SWNT - PABS) were purchased from Carbon Solutions and used as supplied. Due to the presence of these functional groups, SWNT - PABS can be dispersed in water as very small bundles (<5 nm diameter) at concentrations of up to ~ 4 - 6 mg/ml (see ref. 11). Polyvinyl alcohol ($M_w = 30 - 70$ kg/mol) was purchased from Aldrich and used as supplied. The PVA was dissolved in deionised water at 30 mg/ml by ultrasonication for four hours in a sonic bath (Ney Ultrasonic). To this solution was added SWNT - PABS such that the nanotube concentration was 6 mg/ml. This dispersion was then sonicated for ten minutes with an ultrasonic tip (Model GEX600; 240 W, 60 kHz) followed by two hours in a sonic bath followed by a further ten minutes sonication using the sonic tip. This dispersion was left to stand undisturbed overnight, after which time there was no visible sign of aggregation. Absorbance measurements showed that no sedimentation had occurred overnight. This stock dispersion was used to prepare a range of dispersions with different volume fractions by blending with a pure PVA solution (30 mg/ml). Each new dispersion was then sonicated with the sonic tip for two minutes after blending. Films were prepared by spin coating (1500 rpm, 60 s) onto substrates which had been coated with evaporated gold electrodes (thickness 80 nm). Composite film thicknesses were measured to be ~130 nm by interferometry (Zygo New

View 100 White Light Interferometer). Two films were prepared for each volume fraction. For each volume fraction, one film was partially coated with an evaporated gold electrode and current voltage measurements were made through the film using a Keithley Source meter. In this sandwich structure the current will be determined by the percolating pathway through the sample. The second set of films were used for FE characterisation in an evacuated two terminal arrangement employing a 5 mm diameter stainless steel ball bearing anode connected to an adjustable high precision manipulator.^[19] Threshold applied electric fields for various reference currents are found by the variable relative anode – cathode separation method in which the I - V curves were taken at various separations and the separation between the anode and sample adjusted using the high precision manipulator. This method is superior to the probe contact method since no damage on contacting to the sample occurs. Absolute values of separation were confirmed *after* I - V testing by bringing the probe into contact with the sample. Typical anode – sample separations were in the 40 to 80 μm range. Each sample was tested at least five different locations to gauge reproducibility.

Acknowledgements

Research at Surrey was supported by the Engineering and Physical Sciences Research Council. Research in Dublin was supported by Science Foundation Ireland.

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Figure 1. (a) Scanning electron microscope image of a composite sample with 3 vol.% SWNT loading showing the excellent dispersion. (b) Variation of two terminal electrical conductivity with nanotube mass fraction. Inset Variation of the conductivity showing the power law with a critical volume fraction p_c of 0.0036 or 0.36%.

Figure 2. Representative current - field emission characteristics for different volume fractions as indicated. For clarity not all data points have been shown. The volume fractions are indicated next to each curve.

Figure 3. (a) Variation of average threshold electric field with volume fraction for different reference currents: 0.1 nA (●), 1 nA (○), 10 nA (■), 100 nA (□) and 1000 nA (◆). (b) Emission characteristics of four samples with 0% (●), 0.36% (○), 0.72% (■) and 15.3 vol.% (□) nanotube loading plotted in the usual Fowler - Nordheim representation.

Figure 4 (a) Variation of local threshold field with loading for different reference current levels 0.1 nA (●), 1 nA (○), 10 nA (■) and 100 nA (□). The dashed line indicates the lower limit of the validity of emission controlled by the Fowler – Nordheim theory. (b) Variation of local field with loading within the FIT formulism at different reference currents: (●) 1 nA and (□) 10 nA. Data in (b) is presented in mass fraction to be consistent with the data for CNT - PmPV composites which is also shown (■) at 10 nA reference current (from ref. 25).

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Well dispersed carbon nanotubes composites can be produced by solution processing from which electron emission can be observed at low nanotube content. The synthesis of randomly oriented nanotube - polymer composites by solution processing allows the development of carbon nanotube based large area cathodes produced using a scalable technology.