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Highly efficient low voltage electron emission from directly spinnable carbon nanotube webs

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ABSTRACT

Two methods for increasing the number of free carbon nanotube (CNT) tips in carbon nanotube webs (CNTW) and improving their field emission (FE) performance are proposed. It was observed that by laterally compressing samples by 35 percent it is possible to improve FE performance to some extent, with further compression leading to a loss of FE properties due to folding of webs and adhesion between CNT tips. Multilayered samples were also studied and it was found that samples with successive layers in which the orientation of the nanofibers in successive layers was the same, increased inter-bundle van der Waals forces, leading to more compact webs with no improvement in FE performance. However, it was found that if the fibers in successive layers were perpendicular to each other the inter-bundle attraction was minimized, maximizing the number of active CNT tips and yielding materials that exhibit the best FE performance reported for any material to date.

1. Introduction

Carbon nanomaterials such as carbon nanotubes (CNT) [1–9] and graphene [10–13] are of great interest for their field emission (FE) characteristics but fabricating them into stable, efficient, macro-scale cathodes is proving to be very difficult. A common approach is to incorporate these nanostructures into composite matrix materials, but problems exist such as low conductivity, low thermal stability and low emission stability [5,6,9,10] although bulk metallic glass as the matrix [6] has recently showed improved behavior. A different approach for fabricating functional electrodes with large areas is to use highly aligned, ultrathin directly spinnable carbon nanotube (DSCNT) webs [14–17]. DSCNT webs are made from specially grown arrays or forests of CNTs whereby, if the CNTs in the front face of the forest are drawn away horizontally, the contiguous CNTs, to which they remain attached, are drawn away in turn, leading to the spinning of a continuous ribbon or web of horizontally-oriented CNTs that can be laterally collapsed and twisted into a strong yarn [17]. As formed, the web is of extremely low volumetric density webs of about 50 nm in thickness, of low optical density (transmission ~90%) and produces yarns of significant mechanical strength [17,18]. The spinning process and strong van der Waals interactions cause some bundling of the aligned CNTs although many individual carbon nanotubes tips are free and can align vertically in an external electric field [7,18,19], this phenomenon is further explored in a following paper [20].

Initial results for the FE properties of such CNTWs have been promising [7,8] but a clear understanding of the key parameters affecting performance is desired. This is made difficult because, although there are many synthetic variables, it rarely possible to independently vary the web and CNT characteristics whilst maintaining the spinnability [15,16]. As a consequence, in order to identify the key structural characteristics and improve the FE performance of these

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webs without changing the production parameters, some new approaches need to be found to increase the number or effectiveness of the free carbon nanotube tips on the free fibers (the most efficient emission sites) in such samples.

We report here on studies to improve the FE properties of CNTWs through structural and design modifications of the spun webs, either by laterally compressing these webs or by making multilayered samples with a range of relative fiber orientations of successive layers. We demonstrate that some of these methods are so effective that the turn-on voltages are lower than for any previously-reported system.

2. Experimental section

The general method for the preparation of spinnable carbon nanotube webs is as reported before [15–17,20]. For the synthesis of nanotubes used in this research, He, acetylene and hydrogen gases (1000, 25 and 25 sccm, respectively) and reaction temperature of 680 °C was used. The difference between two samples was in the reaction running time of 15 and 5 min, resulting in nanotube lengths of 325 ± 5 μm and 156 ± 5 μm, respectively. The thickness of webs produced after 15 and 5 min were measured to be 62 ± 9 and 73 ± 6 nm. The optical absorption of webs at 589 nm was used as a measure of density of webs, showing values of 0.082 and 0.088 for these two samples. The effect of these structural parameters (length, web thickness and optical density) of field emission properties of samples is discussed in Ref. [20]. Samples with running time of 5 min were used throughout this research and the other sample was used to confirm the results.

In order to prepare samples for FE measurements, CNT webs were drawn from a CNT forest as a thin sheet (Fig. 1a) and placed on a polished graphite substrate, as reported previously [7,14]. The bonding between sheet and the graphite substrate in this step is relatively weak in a macroscopic sense, and thus it was densified on substrate using a droplet of acetone which subsequently was evaporated away. In order to make multilayer samples, the same procedure was repeated.

SEM images of samples were obtained without any gold coating, by a JEOL 6300F FEG SEM with an operating voltage of 15 kV. Field emission experiments were performed in vacuum ($\sim 10^{-4}$ Pa), using a parallel plate setup. A gold-coated stainless steel sheet was used as anode and a polyimide film was used as the spacer between two electrodes, maintaining a constant distance of 500 μm between two electrodes. In order to measure the thickness of webs a WYKO NT1100, Veeco Optical Profilometer was used, using a method described in supporting information.

3. Results and discussion

Due to the limitations that arise in changing the various production and structural parameters in order to further improve the field emission properties (and not inhibit spinnability), it was necessary to attempt other strategies to increase the number of free carbon nanotube tips and thus improve the field emission performance of these webs. In our research into these materials, several post-processing methods including microwave-plasma, thermal annealing, UV–ozone treatment were tried to modify the surface properties of the webs in order to improve the FE performance, but none of these techniques was successful.

One approach for altering the DSCNT webs is to laterally compress them. Gathering the web together at one point and drawing that creates a narrow triangle with the web width varying from near zero to the width of the drawn forest in proportion to the distance drawn (Fig. 1a).

The compressed web is clearly denser and darker (right side of Fig. 1a) in comparison to the more sparse web (left

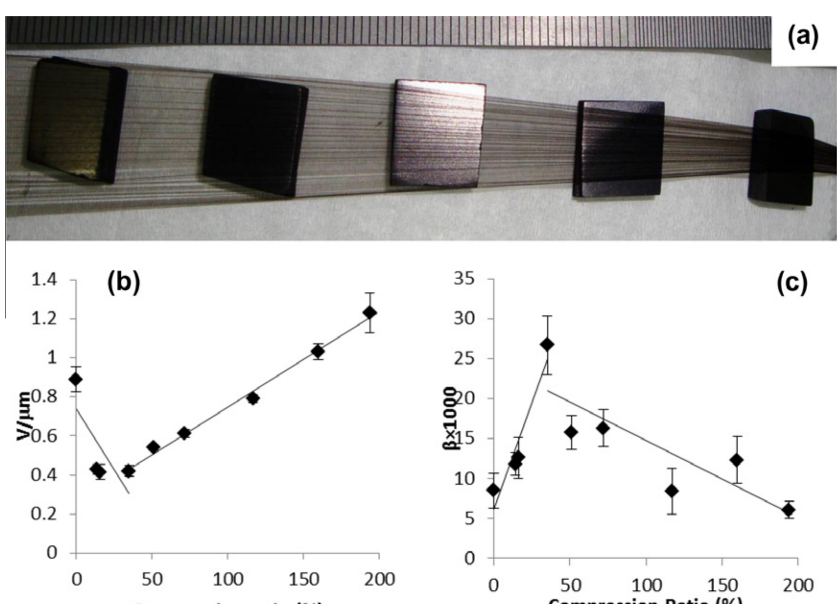

Fig. 1 – (a) Laterally compressing of the carbon nanotube web to produce a denser web, and variations of turn on electric field (b) and field enhancement factor (c) as a function of compression ratio.