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Electron field emitters based on multi-walled carbon nanotubes coated with conducting polymer/metal/metal-oxide composites

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The present work describes the field emission properties of multi-walled nanotubes (MWNTs)-based conducting polymer/metal-oxide/metal/MWNTs composites (polyaniline (PANI)/SnO_2/Sn/MWNTs). MWNTs were synthesised by chemical vapour deposition technique. SnO_2/Sn/MWNTs were prepared by using chemical reduction followed by calcination. By *in situ* polymerisation method, surface of SnO_2/Sn/MWNTs were coated with PANI. PANI/SnO_2/Sn/MWNTs field emitters were fabricated over flexible graphitised carbon fabric substrate by spin coating technique. High-resolution transmission electron microscopy and scanning electron microscopy were used to characterise the field emitters. Field emission properties have been studied using an indigenously made facility. The fabricated PANI/SnO_2/Sn/MWNTs field emitters exhibited excellent field emission properties with a turn on field of 1.83 V μm^{-1} and a field enhancement factor of 4800.

Keywords: flexible graphitised carbon fabric; PANI/SnO2/Sn/MWNTs; chemical vapour deposition; field emitter; field enhancement factor; turn on field

1. Introduction

Ever since their discovery carbon nanotubes (CNTs) [1] have attracted intensive studies because of their potential as field emitters in vacuum electronic devices such as field emission displays, because of their high aspect ratio, remarkable thermal conductivity, and high mechanical strength. Moreover, significant improvement in turn-on-voltage and emission current can be attained by the electric field enhancement effects owing to the nanometer scale curvature radius of the emitting surfaces [2]. Optimisation of the electron emission from the CNTs is an important technological goal because of the relatively high production cost of the CNTs [3]. Field emission properties of CNTs are greatly influenced by the morphology of the emitting surface. Hence by altering the morphology of an emitter, its field emission properties are expected to vary [4,5].

Carbon nanotubes have a relatively high work function of 5 eV. This undesirably high work function limits the CNTs' ability to emit electrons. One way to overcome this

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shortcoming is to modify the CNT surface by introducing a thin coating of low work function material. The resulting surface structure combines the benefits of the low work function surface coating and the high aspect ratio from the CNTs, presumably enhancing the ability of the CNTs to emit electrons. The surface coating may also provide the additional important benefit of protecting the CNTs from degrading. It is known that CNT emitters require a high vacuum to operate properly and are very sensitive to the residual gases in the environment [4,5].

Metal oxides generally exhibit features such as oxidation resistance and good thermal stability. If we coat the surface of the CNTs with a metal oxide having a low work function, by using the resultant composite material we can fabricate excellent field emitters with lower concentration of CNTs which are having the advantage of improved work function [6]. In a similar way, conducting polymer coated CNT composites can also be used as efficient field emitters due to their improved work function qualities. Polyaniline (PANI) is one of the most extensively studied conducting polymers owing to its high electrical conductivity, environmental stability, relative ease of synthesis, etc [7]. Preparation of PANI-CNT composites with enhanced electronic properties has been reported [7].

It will be interesting to study the field emission properties of a new composite material which is a combination of a conducting polymer, metal, metal oxide and multi-walled nanotubes (MWNTs) in order to find how the emission properties of individual components may vary upon composite formation. Therefore, in the present study we have fabricated a new composite material, namely PANI/SnO_2/Sn/MWNT. For that, we have taken SnO_2/Sn/MWNT and over that conducting polymer PANI was coated using *in situ* polymerisation method.

Apart from the nature of the field emitting material, another important factor which is having influence on the field emission properties is the nature of the substrate. If the substrate and the emitter are of the same material, there will be good adhesion between the two. In addition to that if the substrate is having the advantage of having flexible nature, it can be used for making foldable displays. Hence, it is expected that if a flexible carbon-based substrate is used, it will offer excellent flexibility and good adhesion of the MWNT to the flexible fully carbon-based substrate.

Hence, in this article, a graphitised carbon cloth is used as substrate and the field emission characteristics of PANI/SnO_2/Sn/MWNT field emitters fabricated over graphitised carbon fabric are studied. MWNT have been synthesised by the CCVD of acetylene using novel RE-based C15 type AB_2 ($DyNi_2$) alloy hydride catalysts. PANI/SnO_2/Sn/MWNT field emitters over graphitised carbon cloth have been prepared by spin coating method. The field emission properties have been compared with that of randomly oriented pure MWNT field emitter [8] over the same substrate and the influence of the conducting polymer and metal coating on the field emission properties have been discussed.

2. Experimental

Multi-walled nanotubes were synthesised by the decomposition of acetylene over RE-based AB_2 ($DyNi_2$) alloy hydride powders using a fixed-bed catalytic reactor as discussed in previous work [8]. The as-prepared MWNT were purified by air oxidation

followed by acid treatment [8]. The samples were heated in air at 400°C for 3 h to remove the amorphous carbon, lead to expose the catalytic metal surface. The catalytic impurities were then removed by refluxing with concentrated HNO_3 for 24 h, followed by washing with de-ionised water and then the sample was dried in air for 30 min at 100°C. The crystallinity and purity of the samples were verified by XRD (Cu-Kα radiation) and thermo gravimetric measurements (20°C min^{-1}). The samples were characterised using Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

For the synthesis of SnO_2 coated MWNT, nearly 1 g of tin (II) chloride ($SnCl_2$) was dissolved in 40 mL of distilled H_2O. Subsequently, 0.2 g of the purified MWNT were dispersed in the above solution. This mixture was sonicated for 5–10 min and then magnetically stirred for 24 h at room temperature. After that the product of the reaction was washed three times with deionised water and filtered using cellulose membrane filters having pore size of 0.1 μm. The precipitate was again washed with distilled H_2O for several times, and then dried at 70°C under vacuum for 6 h. Part of the final product was calcined at 350°C for 2 h [9]. The composite was characterised using XRD, TEM, energy dispersive analysis (EDX), and High-resolution TEM (HRTEM).

Deposition of PANI over SnO_2/Sn/MWNT was done by using polycondensation of 0.4 mL aniline by 0.4 g $K_2Cr_2O_7$ in 50 mL of 1 mol L^{-1} HCl. The nanocomposite materials were then filtered and washed with large amount of water and subsequently with ethanol to remove the residual oxidant. Finally, all composites were washed with acetone and dried at 60°C. The content of MWNT in the composites was determined gravimetrically [7] and the wt% of CNTs was kept as 18. The resultant composite was then characterised using TEM and SEM.

The substrate used in the present study, the graphitised carbon fabric, was prepared by deposition of a mixture of micro porous carbon black and poly-tetrafluoroethylene powders onto macro porous layer of carbon fiber fabric (SGL, Germany) in combination with a subsequent rolling process as described in our previous work for which patent has been filed [10].

For the fabrication of field emission arrays of randomly oriented PANI/SnO_2/Sn/MWNT composite over carbon fabric, the composite was first dispersed in 1,2-dichloroethane (DCE). DCE helps the dispersion of MWNT without surface modification, besides being volatile [11,12]. The dispersion process involved the ultrasonication of 50 mg of MWNT in 10 mL of DCE for 1 h, followed by centrifugation at a speed of 5000 rpm for 30 min to precipitate the undissolved PANI/SnO_2/Sn/MWNT. After decanting the supernatants, the PANI/SnO_2/Sn/MWNT-DCE solution was spin coated on the graphitised carbon paper at a speed of 3200 rpm at room temperature to obtain a uniform distribution of randomly oriented PANI/SnO_2/Sn/MWNT on the graphitised carbon cloth.

Field emission properties of the resulted film as cathode were studied using an indigenously fabricated experimental set up as explained in our previous work [8]. The dependency of the emission current on the applied voltage was measured. The field emission measurements were carried out in a vacuum chamber at the base pressure of 2×10^{-5} Pa. Gold coated copper rod was used as an anode, and the distance between anode and cathode was 400 μm with an emission area of 0.0314 cm^2. Field emission measurements were repeated by changing the distance between the anode and cathode and

reproducible *J–E* plots were obtained. Each time, for a particular separation the field emission characteristics were measured for several times in order to ensure the reproducibility of the results. The electron emission turn-on field in the experiment is defined as the electric field (E) for a current density (J) of $10\,\mu A\,cm^{-2}$.

3. Results and discussion

The XRD pattern of SnO_2/MWNT nanocomposite material shows the reflections of SnO_2 along with that for graphitic carbon. The broad peaks reveal the presence of nanostructured crystalline metal oxides. This result has been explained in our previous work [13]. Figure 1 shows the SEM image (FEI; QUANTA Scanning electron microscope) of PANI/SnO_2/Sn/MWNT composite spin coated over the graphitised carbon fabric substrate. From this image, it is very clear that the homogeneous layer of PANI covers the surface of individual MWNTs. Also, it is clear that the packing density of PANI/SnO_2/Sn/MWNT composite material over the carbon substrate is very high.

Transmission electron microscopy image (Philips CM12 transmission electron microscope, acceleration voltage 120 KV) of purified MWNT is shown in Figure 2(a). The TEM micrograph shows that the nanotubes have an average outer diameter of about 30 nm and an inner diameter of about 10 nm. Eventhough, CNTs were almost unaffected by the acid and oxidation treatment because of their higher thermal stability, the purification process has resulted in cutting open of the nanotube edge. The TEM images (JEOL, JEM-3010 Electron Microscope with an acceleration voltage of 200 KV)

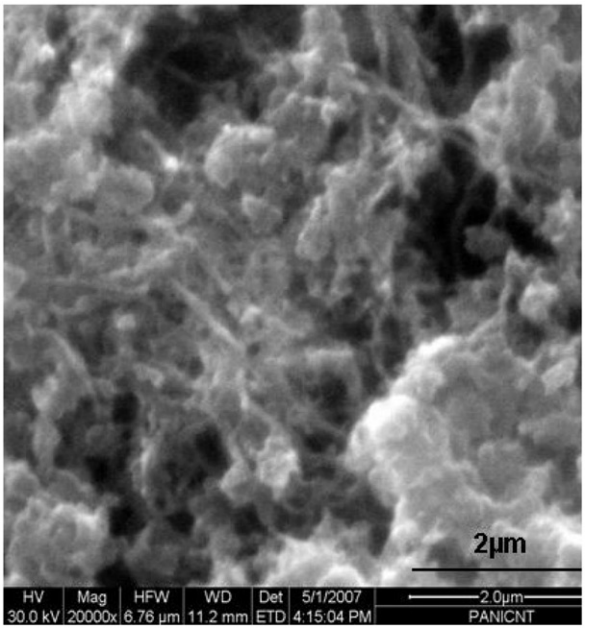


Figure 1. SEM image of PANI/SnO_2/Sn/MWNT over graphitised carbon cloth.

of SnO_2/Sn/MWNT and PANI/SnO_2/Sn/MWNT composites are shown in Figure 2(b) and (c), respectively. Figure 2(b) shows the encapsulation of Sn particles throughout the inner cavity of the nanotube. From Figure 2(c), it is very clear that there is a significant increase in the outer diameter of the MWNT after polymer coating. It also indicates that the composite has a thick layer of polymer on the surface of SnO_2/Sn/MWNTs. For PANI/SnO_2/Sn/MWNT the average outer diameter is found to be 60–80 nm. Figure 2(b) clearly indicates the uniform distribution of nanocrystalline metal oxide particles of size of about 3–5 nm on the surface of MWNT. The lattice planes of Sn nanoparticles are seen clearly in the HRTEM images (Figure 2(d)) of Sn/PANI/MWNT indicating crystalline nature of metal oxide particles. Also the size of crystalline metal oxide particles was found to be in the range of 3–5 nm.

The EDX of Sn particle encapsulated inside the MWNT and that of SnO_2 particle present on the surface of MWNT are shown in Figure 3(b) and (c), respectively. For ensuring the nature of the nanoparticle present inside the nanotube EDX pattern were taken for different particles and in all those, the intensity of oxygen peak was lesser than that of Sn peak. Where as, for the particles outside the nanotube, the intensity of oxygen peak was higher than that of Sn peak. So, we concluded that only those Sn particles on the outer surface of the nanotubes are undergoing oxidation upon calcinations. In this case, the loading was fixed as 50%. EDX measurements helps only in ensuring the presence of the particular metal oxide on the surface of the MWNT and it gives only its local concentration.

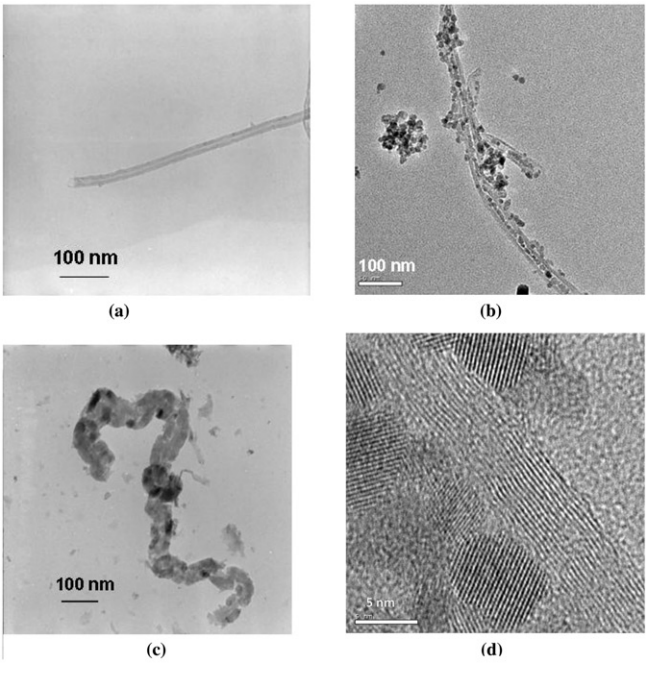
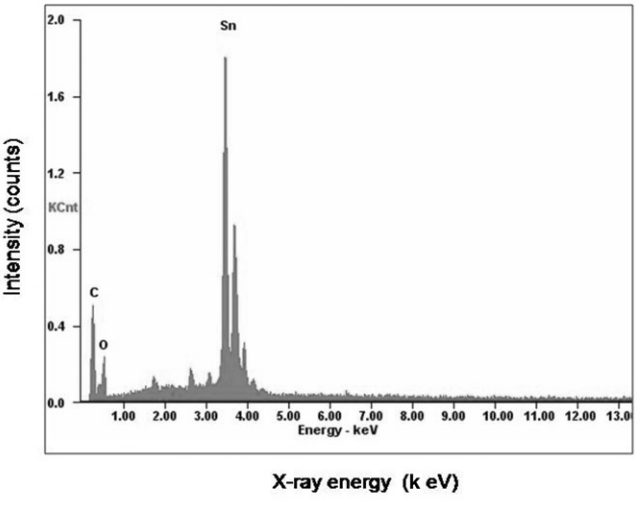
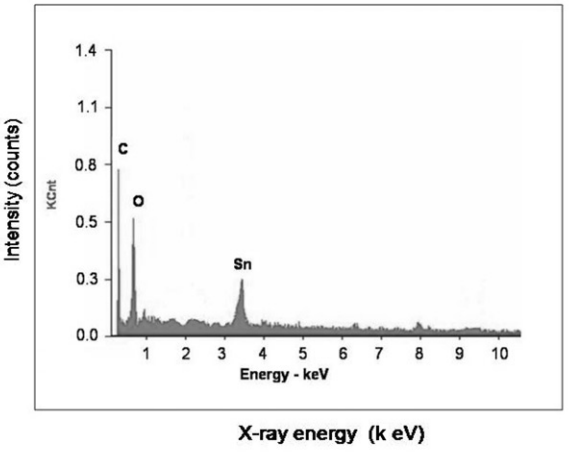


Figure 2. TEM image of (a) purified MWNT, (b) SnO_2/Sn/MWNT, (c) PANI/SnO_2/Sn/MWNT and (d) HRTEM image of SnO_2/Sn/MWNT.



(a)



(b)

Figure 3. EDX pattern of (a) Sn particle encapsulated inside the MWNTs, (b) SnO_2 particle on the surface of the MWNT.

Generally, the field emission is described using the Fowler–Nordheim (FN) equation [14],

$$j = \frac{AE^2}{\phi}\exp\left(-\frac{B\phi^{3/2}}{E}\right)$$

where j is the current density, $A = 1.56 \times 10^{-6}\,\mathrm{A\,eV\,V^{-2}}$, $B = 6.83 \times 107\,\mathrm{eV^{-3/2}\,V\,cm^{-1}}$, Φ is the work function, and the applied electric field (E) is defined as $\beta V/d$, where V is the voltage between the anode and the CNTs emitters, d is the distance between them, and β is the field enhanced factor. It is well known that the emission density is primarily dependent on the field enhancement factor of the CNTs and work function [15]. It has been already

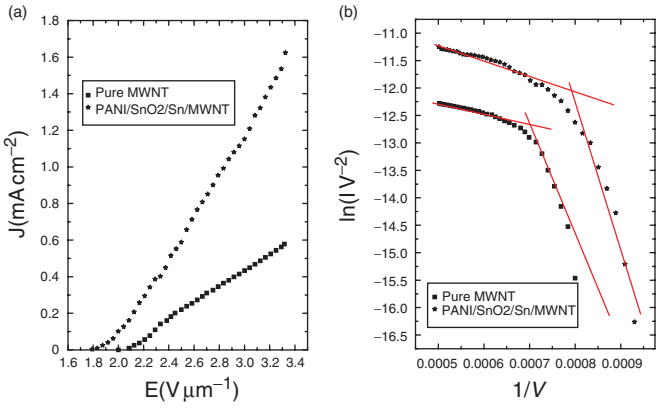


Figure 4. (a) Field emission current density–electric field (J–E) characteristics of purified MWNT [8] and PANI/SnO_2/Sn/MWNT based field emitters. (b) Fowler–Nordheim plot.

reported that the work functions of PANI, SnO_2, and Sn are 4.1, 4.3, and 4.4 eV, respectively. The work function of MWNT is assumed to be ~5.0 eV (that of graphite) for comparison of the samples.

Figure 4(a) shows the current density–electric field (J–E) characteristics of purified MWNT [8], and PANI/SnO_2/Sn/MWNT-based field emitters. The corresponding Fowler–Nordheim (FN) plots are shown in Figure 4(b). In the FN plot obtained by plotting $\ln(I/V^2)$ *versus* $1/V$, a straight line can generally be drawn through a slope, which is dependent on Φ, β, and d. The value of β has been determined from the slope of the FN plot using the relation [16]

$$\beta = \frac{B\Phi^{3/2}d}{\text{slope}}$$

Actually, the exact analysis of field emission characteristics of the samples is difficult as the work function of the individual emitters will be different. For both the samples, measured current is an average of currents due to individual emitters as the emission occurs from multiple emitters. In order to remove the emission noise and instability, the high-voltage annealing for all the five samples was carried out until the fluctuation of emission currents was less than 2% [17].

It is clearly seen from Figure 4(b) that for both the samples, the FN plot has two distinct slopes. The slope in the high-field region is much less compared to that in the low-field regime. This behavior at high-field regime may be attributed to a number of mechanisms [18,19]. Among them are vacuum space charge effect, changes in local density of states at the emitter's tip, solid state transport, interaction among adjacent tubes and adsorption/desorption of gaseous species even under high-vacuum conditions due to emission assisted surface reaction processes. However, the complicated properties of MWNT, have prevented researchers from developing a complete understanding of the exact nature of such deviation from FN theory [20,21]. The field enhancement factor in the high-field region is denoted as β_H and that in the low-field regime as β_L. The turn-on field, i.e., the applied field at which emission current density becomes 10 μA cm^{-2}, the threshold field at an emission current density of 0.5 mA cm^{-2} and the field enhancement factor β, for

Table 1. Comparative field emission characteristics of randomly oriented purified MWNT [8], and PANI/SnO_2/Sn/MWNT field emitters spin coated over graphitised carbon substrate.

Serial No.	Sample	β_L	β_H	Turn-on (1 μA cm^{-2}) field(V μm^{-1})	Threshold field at 0.5 mA cm^{-2} (V μm^{-1})
1	Purified MWNT	1000	5032	2.1	3.03
2	PANI/SnO_2/Sn/MWNT	612	4800	1.8	2.41

Table 2. Comparison of the field emission performance of Ni/MWNTs with literature results.

Sample	β	Turn-on (10 μA cm^{-2}) field(V μm^{-1})
PANI/SnO_2/Sn/MWNT (present)	4800	1.8
Directly grown pure MWNT [22]	170,000	3
Ru coated MWNT [8]	5000	2.10
ZnO/SWNT [23]	3200	1.8

the samples are listed in Table 1. In the present study, as the obtained field emission data shows deviation from the F-theory, we are using the FN theory only as a guide for the analysis of field emission parameters.

A comparison of the field emission performance of Ni/MWNTs with literature results has been presented in Table 2 [8,22,23]. Emission performance of PANI/SnO_2/Sn/MWNT is found to be comparable to that of ZnO/CNT field emitter. There is improvement in the field emission characteristics of pure MWNT upon loading of polymer and nanocrystalline metal clusters having low work functions. There is a decrease in the β-values of PANI/SnO_2/Sn/MWNT field emitters, which can be attributed to the increase in their diameter upon coating.

4. Conclusions

Chemical reduction method followed by calcination procedure is a simple and effective technique for the preparation of Sn encapsulated SnO_2/MWNT composite. *In situ* polymerisation technique helps for the deposition of conducting polymer PANI on the surface of SnO_2/Sn/MWNT. PANI/SnO_2/Sn/MWNT field emitters fabricated over graphitised carbon fabric substrate exhibit excellent field emission properties with a very low turn-on field of 1.8 V μm^{-1} and useful from the practical field emission application point of view. The field enhancement factor of the composite material decreases due to the increased diameter on polymer coating.

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