Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2012, Article ID 861591, 4 pages
doi:10.1155/2012/861591

Research Article

Field Emission Characteristics of SnO_2/CNTs Composites Prepared by Microwave-Assisted Wet Impregnation

Sreejarani K. Pillai,[1] Sarah C. Motshekga,[1,2] Suprakas Sinha Ray,[1,3] and John Kennedy[4]

[1] *DST/CSIR Nanotechnology Innovation Centre, National Centre for Nano-Structured Materials, Council for Scientific and Industrial Research, Pretoria 0001, South Africa*
[2] *Department of Chemical Engineering, Tshwane University of Technology, Pretoria 0001, South Africa*
[3] *Department of Chemical Technology, University of Johannesburg, Doornfontein, Johannesburg 2018, South Africa*
[4] *National Isotope Centre, GNS Science, 30 Gracefield Road, Lower Hutt 5010, New Zealand*

Correspondence should be addressed to Sreejarani K. Pillai, skpillai@csir.co.za and Suprakas Sinha Ray, rsuprakas@csir.co.za

Received 2 September 2011; Accepted 17 November 2011

Academic Editor: Chunyi Zhi

The SnO_2/CNT composites were prepared by microwave-assisted wet impregnation at 60°C. The process was optimized by varying the microwave power and reaction time. Raman analysis showed the typical features of the rutile phase of as-synthesized SnO_2 nanoparticles on CNTs, which was consistent with the results from X-ray diffraction. Enhanced field emission performance was observed for SnO_2/CNTs composite prepared by a microwave method when compared to pure CNTs and SnO_2/CNTs composite prepared by conventional wet impregnation. The dependence of emission current density on the electric field followed a Fowler-Nordheim relationship.

1. Introduction

Carbon nanotubes (CNTs) have remained in the forefront of intense research for more than a decade due to their exceptional physical, chemical, and electronic properties that have been inherited from the parent in-plane graphite [1]. The unique electronic properties of CNTs—due to the quantum confinement of electrons normal to the nanotube axis—make them ideal candidates for electron field emission. A significant enhancement in turn-on field, threshold field, and emission current stability can be attained by field enhancement effect due to their large aspect ratio, chemical inertness, high electrical conductivity, and mechanical strength. CNTs have been reported as excellent field emitters at low operating voltages [2]. Any surface treatments or modifications of CNTs can cause changes in the field emission (FE) characteristics of CNTs. It has been reported that by decorating the CNT surface with a metal having low work function leads to improvement in electrical conductivity [3], which is expected to enhance the field FE properties.

Tin dioxide (SnO_2) has long been recognized as an important n-type semiconductor. The wide bandgap (3.6 eV at 300 K) and high achievable carrier concentration (up to 6×10^{20} cm^{-3}) make it an excellent candidate for solid-state gas sensors [4], lithium ion batteries [5], solar cells [6], and cathode emitters of the FE device [7]. In the last few years, the FE measurement results of SnO_2 nanostructures such as nanobelts [7], nanowhiskers [8, 9], and beak-like nanorods [10] show that 1D and quasi-1D SnO_2 nanostructures have promising applications in FE devices. Hybrid structures of SnO_2 nanoparticles and CNTs could potentially display novel electronic properties other than those of individual components. This is based on the fact that the work function of CNTs is approximately equal to SnO_2, which makes the electrons travel through the SnO_2 grains to CNTs and then conduct in the CNTs with low resistance [11]. To date, various techniques have been used to prepare SnO_2/CNT hybrid structures, such as wet-chemical [12–15], sol-gel [16], gas-phase [17, 18], and supercritical fluid [19] methods. However, all those techniques are time consuming, expensive, and show relatively low capacity retention. Microwave assisted synthesis has recently shown remarkable advantages such as reduced reaction time, high reaction rate, small particle size, and homogenous and narrow size distribution of particles over the conventional synthesis routes [20].

In this work, FE performance of SnO_2/CNTs composite prepared by a simple and efficient microwave assisted wet impregnation is described. The FE characteristics of the prepared SnO_2/CNTs composite are compared with that of pure CNTs and similar composite prepared by conventional wet impregnation.

2. Experimental Details

The preparation and characterization procedures for the SnO_2/CNT composites are reported elsewhere [21]. The composites prepared by different procedures are denoted by SnO_2/CNTs-WI (conventional) and SnO_2/CNTs-MW (microwave). To investigate the FE property of materials, the powder samples were mounted onto a metallic substrate using silver conductive paste and electrically connected to a stainless steel block [22]. The assembly was placed in a vacuum chamber evacuated to a residual gas pressure of 2×10^{-7} mbar. The SnO_2/CNT composites were the cathode and a highly polished stainless steel rod with a circular flat tip of 4 mm diameter served as the anode. The anode was mounted on a microadjustment system (μm resolution) to set the anode-cathode separation. FE measurements were performed by applying different voltages across the stainless steel anode and the cathode in the vacuum chamber. A DC voltage was applied, and current was measured between the cathode and anode using a Keithley 237 source measure unit (Keithley Instruments Ltd., Reading, UK). The emission current was measured as a function of anode-cathode separation between 50 and 120 μm.

3. Results and Discussion

Microwave heating produced SnO_2/CNT composites with a different concentration of SnO_2nanoparticles. The density of nanoparticles on the CNT surface increased with increasing microwave power and exposure time. Based on the microwave process optimization results (not given here), the SnO_2/CNT sample prepared at 500 W for 5 min was chosen for FE studies. The formation of a considerable amount of SnO_2 nanoparticles on the CNT surface within 5 min of reaction time may be due to the strong microwave adsorption of CNTs [23]. The structural characterization results for the samples were published elsewhere [21].

HRTEM and SEM images showed heavy coating of the CNT surface with spherical SnO_2 nanoparticles in the size range of 2–5 nm for the sample prepared by microwave method. On the other hand, the sample from the conventional method showed the presence of spherical nanoparticles with smaller sizes (2-3 nm) on the surface with a larger interparticle distance (Figures 1(a) and 1(b)). Raman spectra of the composite samples (Figure 1(c)) showed additional peaks below 1000 cm^{-1}corresponding to SnO_2 nanocrystals [24, 25] other than those for the CNTs (G-band at 1585 and D-band at 1300 cm^{-1}). XRD patterns of the composite

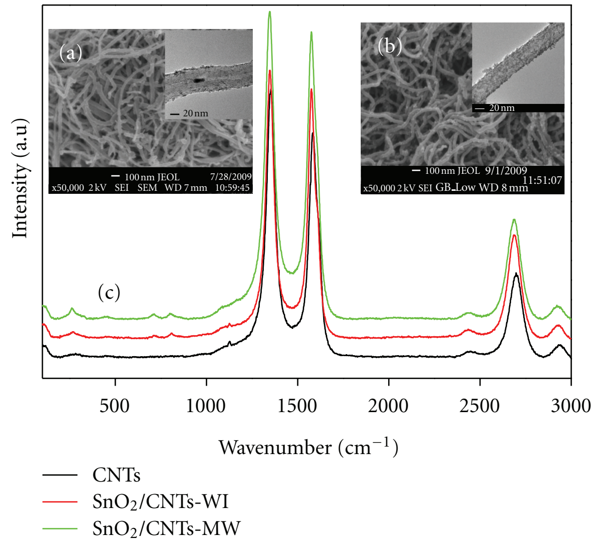

Figure 1: (a) SEM and TEM images of SnO_2/CNTs composite prepared by conventional wet impregnation method, (b) SEM and TEM images of SnO_2/CNTs composite prepared by microwave assisted wet impregnation method, and (c) Raman spectra for corresponding samples.

samples showed characteristic tetragonal SnO_2 phase along with C (002) and C (100) peaks (with d_{002} values of 0.34 nm) of CNTs.

Figure 2(a) shows the current density-applied electric field (J-E) characteristics of pure CNTs and those for the composites from conventional and microwave methods. The work function of the CNTs is assumed to be 5.0 eV (that of graphite) for comparison of the samples. The corresponding Fowler-Nordheim (F-N) plots are shown in Figure 2(b).

The values of turn-on field defined as the electric field required for extracting a current density of 10 $\mu A/cm^2$ and an emission current density of 1 mA cm^{-2} show an apparent decrease with microwave samples when compared to pure CNTs and composite prepared by conventional method as shown in Figure 2(a). The values obtained were 1.0, 1.3, and 1.49 V μm^{-1} for the composites from microwave, conventional methods, and pure CNTs, respectively. This demonstrates that the FE property for the obtained SnO_2/CNTs-MW hybrid has been improved significantly. TEM images show that the number of SnO_2 nanoparticles per unit surface area is higher for the sample prepared by microwave method, which results in the formation of many additional emitter tips on the CNT surface. The heavy coating of SnO_2 nanoparticles obtained by this method prevents the neighbouring CNTs from clustering together and hence reduces the possibility of electrostatic screening from aggregated dense CNTs [26].

The F-N property for all the samples is given in Figure 2(b). As per the figure, the F-N plots for pure CNTs and SnO_2/CNT composites that explain the tunnelling of electrons through a potential barrier show an exponential

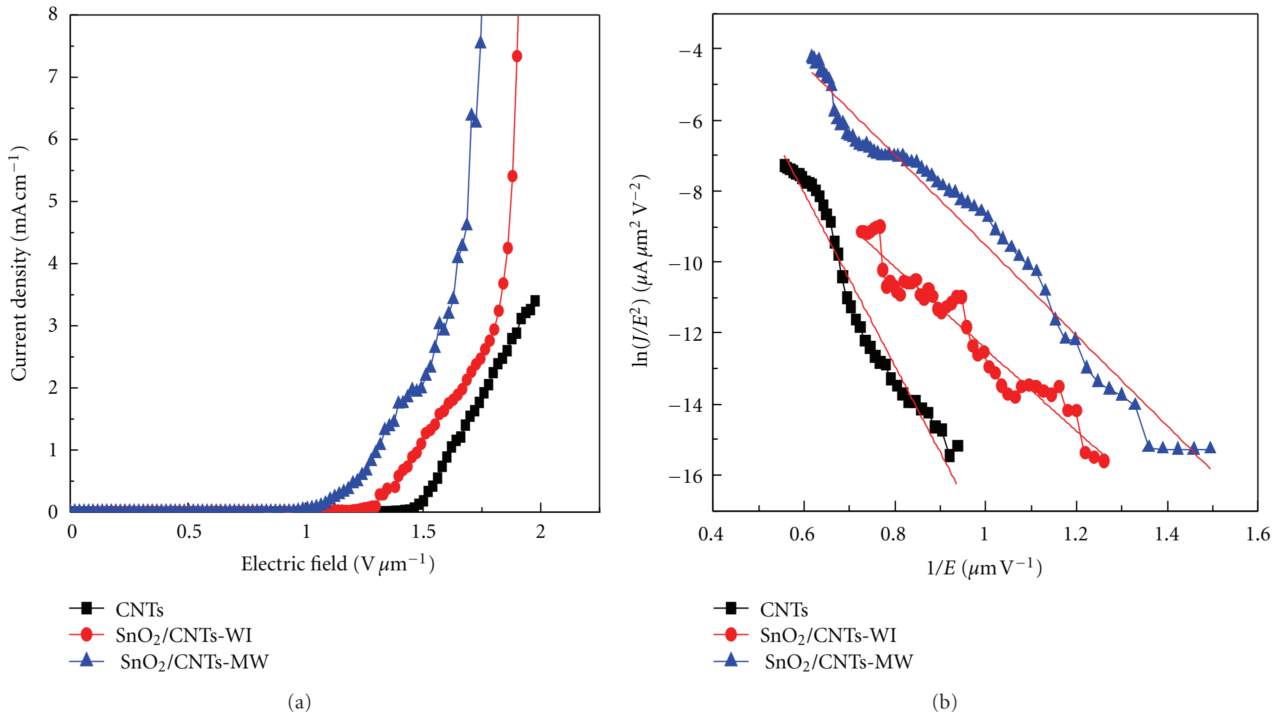

FIGURE 2: (a) Field emission plot for pure CNTs and SnO_2/CNTs composites prepared by conventional and microwave-assisted wet impregnation methods and (b) Fowler-Nordheim plots for the corresponding samples.

dependence between the emission current and applied field given by (1) [27]:

$$J = A\frac{\beta^2 E^2}{\phi}\exp\left(-\frac{B\phi^{3/2}}{\beta E}\right), \quad (1)$$

where $A = 1.54 \times 10^{-6}$ A eV V^{-2}; $B = 6.83 \times 10^3$ eV$^{-3/2}$ V μm^{-1}; $E = V/d$, where d is the separation between the anode and the cathode and V is the applied voltage, β is the field enhancement factor, and ϕ is the work function of emitters.

The FE enhancement factor β can be calculated from the slopes of the F-N plots. Generally, it has been identified that a significant increase in field enhancement factor β is strongly ascribed to the geometrical parameters of field emitter, mainly its surface morphology and high density of the substrate [28]. The β values calculated for various samples taking the work function (ϕ) of CNTs as 5.0 eV were 3.1×10^3, 6.1×10^3, and 6.7×10^3 for pure CNTs and SnO_2/CNTs composites from conventional and microwave assisted wet impregnation methods, respectively. The higher β values for the composite samples when compared to pure CNTs are attributed to the presence of spherical SnO_2 nanoparticles which act as additional independent emission centers other than the CNT tips. Ho et al. recently reported similar observations on ZnO/CNT hybrids with different ZnO layer density [29]. The SnO_2/CNT composite from the microwave assisted wet impregnation method shows significantly enhanced FE when compared to its counterpart from conventional method which may be due to the increased number of SnO_2 nanoparticles that contributes to the local field strengthening and emission current. In this case, the electron transport channels on the CNT surface are amplified by the presence of uniformly dispersed SnO_2 nanoparticles. The spherical SnO_2 particles on the CNT surface can act as additional emission sites in addition to the tip of CNTs. Moreover, similarity in the work function of CNTs and SnO_2 makes it easier for electrons to diffuse to CNTs resulting in high surface electron concentration.

4. Conclusions

The SnO_2/CNT composites were prepared by microwave method. Field emission properties of the composites were measured and compared with pure CNTs and similar composites prepared by conventional method. The microwave method efficiently produced more dense decoration of the CNT surface with SnO_2 nanoparticles in 5 min. The composites showed enhanced field emission properties over pure CNTs due to the presence of SnO_2 nanoparticles. SnO_2/CNT composite prepared by microwave-assisted wet impregnation method showed higher β value. This is attributed to the fact that the composite has a higher number of SnO_2 nanoparticles in the CNT sidewalls that act as independent emitters besides the CNT tips. The conventional method resulted in a composite with lower density of nanoparticles and higher interparticle distance. The results prove that CNT based hybrid materials with improved field emission properties can be prepared by a simple microwave-assisted wet impregnation method.

Acknowledgments

The authors (S. K. Pillai, S. C. Motshekga, and S. S. Ray) wish to thank DST and CSIR, South Africa, for the financial support.

References

[1] G. Dresselhaus, M. S. Dresselhaus, and Ph. Avouris, *CNTs: Synthesis, Structures, Properties and Applications*, vol. 80 of *Topics in Applied Physics*, Springer, Berlin, Germany, 2001.

[2] J.-M. Bonard, J.-P. Salvetat, T. Stöckli, L. Forró, and A. Châtelain, "Field emission from carbon nanotubes: perspectives for applications and clues to the emission mechanism," *Applied Physics A*, vol. 69, no. 3, pp. 245–254, 1999.

[3] B. K. Kim, N. Park, P. Sun Na et al., "The effect of metal cluster coatings on carbon nanotubes," *Nanotechnology*, vol. 17, no. 2, pp. 496–500, 2006.

[4] Q. Kuang, C. Lao, L. W. Zhong, Z. Xie, and L. Zheng, "High-sensitivity humidity sensor based on a single SnO_2 nanowire," *Journal of the American Chemical Society*, vol. 129, no. 19, pp. 6070–6071, 2007.

[5] R. Demir-Cakan, Y. S. Hu, M. Antonietti, J. Maier, and M. M. Titirici, "Facile one-pot synthesis of mesoporous SnO_2 microspheres via nanoparticles assembly and lithium storage properties," *Chemistry of Materials*, vol. 20, no. 4, pp. 1227–1229, 2008.

[6] S. Ferrere, A. Zaban, and B. A. Gregg, "Dye sensitization of nanocrystalline tin oxide by perylene derivatives," *Journal of Physical Chemistry B*, vol. 101, no. 23, pp. 4490–4493, 1997.

[7] Y. J. Chen, Q. H. Li, Y. X. Liang, T. H. Wang, Q. Zhao, and D. P. Yu, "Field-emission from long SnO_2 nanobelt arrays," *Applied Physics Letters*, vol. 85, no. 23, pp. 5682–5684, 2004.

[8] S. H. Luo, Q. Wan, W. L. Liu et al., "Vacuum electron field emission from SnO_2 nanowhiskers synthesized by thermal evaporation," *Nanotechnology*, vol. 15, no. 11, pp. 1424–1427, 2004.

[9] S. Luo, P. K. Chu, Z. Di et al., "Vacuum electron field emission from SnO_2 nanowhiskers annealed in N_2 and O_2 atmospheres," *Applied Physics Letters*, vol. 88, no. 1, Article ID 013109, 2006.

[10] J. H. He, T. H. Wu, C. L. Hsin et al., "Beaklike SnO_2 nanorods with strong photoluminescent and field-emission properties," *Small*, vol. 2, no. 1, pp. 116–120, 2006.

[11] J. Bai, Z. Xu, and Y. Zheng, "Microwave-polyol process for functionalizing carbon nanotubes with SnO_2 and CeO_2 coating," *Chemistry Letters*, vol. 35, no. 1, pp. 96–97, 2006.

[12] J. G. Zhou, H. T. Fang, J. M. Maley et al., "An X-ray absorption, photoemission, and raman study of the interaction between SnO_2 nanoparticle and carbon nanotube," *Journal of Physical Chemistry C*, vol. 113, no. 15, pp. 6114–6117, 2009.

[13] W. Q. Han and A. Zettl, "Coating single-walled carbon nanotubes with tin oxide," *Nano Letters*, vol. 3, no. 5, pp. 681–683, 2003.

[14] L. Zhao and L. Gao, "Coating of multi-walled carbon nanotubes with thick layers of tin(IV) oxide," *Carbon*, vol. 42, no. 8-9, pp. 1858–1861, 2004.

[15] L. Zhao and L. Gao, "Filling of multi-walled carbon nanotubes with tin(IV) oxide," *Carbon*, vol. 42, no. 15, pp. 3269–3272, 2004.

[16] J. Gong, J. Sun, and Q. Chen, "Micromachined sol-gel carbon nanotube/SnO_2 nanocomposite hydrogen sensor," *Sensors and Actuators B*, vol. 130, no. 2, pp. 829–835, 2008.

[17] G. Lu, L. E. Ocola, and J. Chen, "Room-temperature gas sensing based on electron transfer between discrete tin oxide nanocrystals and multiwalled carbon nanotubes," *Advanced Materials*, vol. 21, no. 24, pp. 2487–2491, 2009.

[18] Y. Fu, R. Ma, Y. Shu, Z. Cao, and X. Ma, "Preparation and characterization of SnO_2/carbon nanotube composite for lithium ion battery applications," *Materials Letters*, vol. 63, no. 22, pp. 1946–1948, 2009.

[19] G. An, N. Na, X. Zhang et al., "SnO_2/carbon nanotube nanocomposites synthesized in supercritical fluids: highly efficient materials for use as a chemical sensor and as the anode of a lithium-ion battery," *Nanotechnology*, vol. 18, no. 43, Article ID 435707, 2007.

[20] C. Hao, Y. Du, and L. Li, "Microwave-assisted heating method for the decoration of carbon nanotubes with zinc sulfide nanoparticles," *Journal of Dispersion Science and Technology*, vol. 30, no. 5, pp. 691–693, 2009.

[21] S. Motshekga, S. K. Pillai, and S. S. Ray, "Conventional wet impregnation versus microwave-assisted synthesis of SnO_2/CNT composites," *Journal of Nanoparticle Research*, vol. 13, no. 3, pp. 1093–1099, 2011.

[22] F. Fang, J. Kennedy, D. A. Carder, J. Futter, P. Murmu, and A. Markwitz, "Modulation of field emission properties of ZnO nanorods during arc discharge," *Journal of Nanoscience and Nanotechnology*, vol. 10, no. 12, pp. 8239–8243, 2010.

[23] D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato, "Chemistry of carbon nanotubes," *Chemical Reviews*, vol. 106, no. 3, pp. 1105–1136, 2006.

[24] K. N. Yu, Y. Xiong, Y. Liu, and C. Xiong, "Microstructural change of nano-SnO_2 grain assemblages with the annealing temperature," *Physical Review B*, vol. 55, no. 4, pp. 2666–2671, 1997.

[25] Y. Liu, C. Zheng, W. Wang, C. Yin, and G. Wang, "Synthesis and characterization of rutile SnO_2 nanorods," *Advanced Materials*, vol. 13, no. 24, pp. 1883–1887, 2001.

[26] Y. M. Ho, G. M. Yang, W. T. Zheng et al., "Synthesis and field electron emission properties of hybrid carbon nanotubes and nanoparticles," *Nanotechnology*, vol. 19, no. 6, Article ID 065710, 2008.

[27] C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh, and H. J. Lee, "Field emission from well-aligned zinc oxide nanowires grown at low temperature," *Applied Physics Letters*, vol. 81, no. 19, p. 3648, 2002.

[28] D. Temple, C. A. Ball, W. D. Palmer et al., "Fabrication of column-based silicon field emitter arrays for enhanced performance and yield," *Journal of Vacuum Science and Technology B*, vol. 13, no. 1, pp. 150–157, 1995.

[29] Y. M. Ho, W. T. Zheng, Y. A. Li, J. W. Liu, and J. L. Qi, "Field emission properties of hybrid carbon nanotube-zno nanoparticles," *Journal of Physical Chemistry C*, vol. 112, no. 45, pp. 17702–17708, 2008.