Study of Ink Paper Sensor Based on Aluminum/Carbon Nanotubes Agglomerated Nanocomposites

Marcos A. L. dos Reis¹, Augusto F. Saraiva², Manuel F. G. Vieira³, and Jordan Del Nero⁴,∗

¹Faculdade de Ciências Exatas e Tecnologia, Universidade Federal do Pará, Abaetetuba, PA 68440-000, Brazil
²Pós-Graduação em Engenharia de Recursos Naturais, Universidade Federal do Pará, Belém, PA 66075-110, Brazil
³Departamento de Engenharia Metalúrgica e de Materiais, Universidade do Porto, Porto, 4200-465, Portugal
⁴Departamento de Física, Universidade Federal do Pará, Belém, PA 66075-110, Brazil

Agglomerated nanocomposites based on Aluminum/Carbon Nanotubes (Al/CNT) were produced by an arc discharge technique under argon/acetone atmosphere and ultrasonically dispersed in distilled water to form an ink-like composite. This ink was spread onto commercial paper to produce a conductive thick film. Experimental results show that the electrical resistance of Al/CNT nanocomposite on paper changes when a mechanical stress and/or heat is applied. The multi-sensory properties obtained are the following: (i) piezoresistive effect, electrical resistance shows linear dependence with pressure intensity at room temperature; (ii) polynomial relationship between electrical resistance and temperature; and (iii) high accuracy thermal sensor compared to a K type thermocouple at 25 °C. The nanocomposite and paper morphology was analyzed by Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM/EDS) and a favorable surface for physisorption was observed. Transmission Electron Microscopy (TEM) was utilized for Al/CNT agglomerated indicating that the ink paper based on nanocomposite shows good performance as a thermo-piezoresistive sensor.

Keywords: Carbon Nanotubes, Al/CNT Agglomerated, Nanocomposite, Sensor.

1. INTRODUCTION

Carbon nanotubes (CNTs) were observed in 1991 by Iijima.¹ These nanomaterials have unique characteristics, as an electrical and thermal conductivity higher than copper and silver.²⁻³ This effect has motivated several researchers in developing CNT-based sensors to detect chemical analytical or physical properties such as temperature or pressure.⁴⁻⁵ These sensors are paper-like CNT films prepared by drop casting, dispersion or filtration of CNTs suspensions. Recently, Hu et al.⁶ reported a conductive paper of CNTs manufactured by Meyer rods coating method for energy-storage devices. Also, Wang et al.⁷ show CNT paper-like, also called buckypaper, with good performance in thermal conductivity, electrical conductivity and capacitance, where the sensors were prepared by macroscopic manipulation of aligned CNT onto the paper’s surface. Therefore, CNT-based sensors are more sensitive than usual sensors for temperature and pressure applications.³⁻⁷

The electric behavior of the sensor was changed when the nanocomposite is subjected to strains or temperature variation, i.e., the electric resistance was changed around room temperature or surface pressure. Moreover, one-step synthesis of nanocomposite and its manufacturing simplified led great advantage when compared with others carbon-based sensors, e.g., some carbon black-based sensors are prepared by ultrasonic mixing of polymer matrix and the carbon particles. This composite material is spun in wafers and structured by UV lithography increasing the manufacturing steps.⁸

Figure 1 shows a sensor made of nanocomposite film with 50 mm² of surface area and connected to copper wire using silver paint. This ink paper device, does not need an amplifier circuit other auxiliary electronic circuit because of its large active area. i.e., a commercial paper was used as substrate because of its porous fiber structures adsorbs strongly the molecules, for this reason Martins et al. and
Study of Ink Paper Sensor Based on Aluminum/Carbon Nanotubes Agglomerated Nanocomposites

Reis et al.

Fig. 1. The ink paper sensor based on nanocomposite. (a) Sensor array picture and (b) SEM image of the surface interface between nanocomposite film and paper fibers.

Kim et al., respectively made a memory transistor and papers actuators with cellulose substrate.9,10

2. EXPERIMENTAL DETAILS

2.1. Synthesis and Characterizations

The nanocomposites were produced by an arc discharge technique under argon/acetone (CH₃COCH₃) atmosphere and pressure from 375 Torr up to 750 Torr. The voltage and electric current of the arc discharge used, were 20 V and 85 A, respectively. The synthesis was made after three purges for introducing argon/acetone pressurized into the chamber. Figure 2 shows, schematically, the chamber built for the synthesis of nanocomposite, where the anode and cathode are pure graphite rod and pure aluminum plate, respectively. The anode was perforated at Ø2.0 mm and filled by Al-Si (99.94% wt pure aluminum) powder with 100 μm to 600 μm of particle size to increase plasma reaction between carbon and metal particles. After that, the anode was shifted to the cathode where kept a constant plasma to synthesize CNT directly from the metal matrix.

The Al/CNT agglomerated nanocomposites were characterized by Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM/EDS, FEI Quanta 400 FEG) and Transmission Electron Microscopy (TEM, JEM-2200 FS-200 kV).

2.2. Manufacturing and Measurements of the Ink Paper Sensor

The nanocomposite was ultrasonically dispersed in distilled water for 15 min to form an ink with CNT concentrations from 1.0 up to 5.0 mg/mL.6 Thereafter, the commercial paper was coated by drop-casting method and heated for 30 min at 50 °C. Finally, the ink paper was cut and the copper wire electrodes were placed using silver paint in order to assembly the sensor for measurements.

The ink paper sensors were electrically measured by two-point probe using MY-64 multimeter (accuracy at ±0.8%) and temperature was measured by MT-525 thermometer (accuracy at ±0.1%) with K type universal thermocouple (measure range from −50 °C to ∼200 °C, accuracy at ±0.75%). The electric responses were obtained for temperature and pressure at 73% of relative humidity. The morphology, as well as thickness was characterized by SEM/EDS.

3. RESULTS AND DISCUSSION

3.1. Morphology of the Nanocomposite

In general, Al-CNT composites have been made by various methods, such as spark plasma extrusion,11 semi-solid powder processing,12 plasma spraying technique,13 etc. In addition, ball milling14 and particle composite system (PCS)15 have been used to disperse the CNTs in the Al powder. However, we have made one-step production and obtained CNTs nucleated by aluminum, with particle size distribution from 4.85 μm up to 10.71 μm. Figures 3(a) and (c) show the agglomerated nanocomposites analyzed by SEM with X-ray microanalysis after purification by thermal oxidation at 500 °C of the as-prepared samples.16 Figures 3(b) and (d) show respectively electron backscattering and chemical elements obtained by EDS.

The TEM images of the nanocomposite structures show multi-walled carbon nanotubes (MWCNTs) with an inner diameter between 10 nm and 25 nm (corresponding to a wall number of 5–10), carbon nano-onion and aluminum particles. In Figures 4(a) and (b) show agglomerated nanocomposites with MWCNTs of various diameters (from 600 nm up to ∼8.0 μm) and metal particles inside nanotubes and nano-onion. The CNTs filled by metal-carbide particles can be explained by vapor-liquid-solid (VLS) growth model,17 which acts as a liquid metal-carbide for the nucleation and growth of CNTs. In general, metal particles inside CNTs in metal/CNT nanocomposites are related in the literature.18,19

The CNTs agglomeration can only reduce the thermal conductivity, but the behavior of the Al/CNT agglomerated nanocomposites is not reported. The alignment of the CNTs on the buckypaper surfaces can lead to better electrical and thermal conductive properties, because of the quantum transport and its relationship with electron-phonon scattering. However, agglomerated CNTs structures show potential applications as nanoelectromechanical systems (NEMS) and it was reported the cushioning effect of CNTs agglomerated with...
Study of Ink Paper Sensor Based on Aluminum/Carbon Nanotubes Agglomerated Nanocomposites

Reis et al.

3.3. Electrical Responses

Figures 6(a) and (b) show the thermal behavior of the ink paper sensor under temperature variation of ±17 °C. The electric resistance decreases as $T^3$ and it slowly increases when the room temperature returns. The hysteresis effect is observed in Figure 6(a) and is due to the great difference between thermal conductivity of the aluminum and CNTs, i.e., the MWCNT is 12 times higher than aluminum.

Figure 7 shows the operation of the ink paper sensor thermocouple-like compared with K type universal thermocouple at room temperature. The result indicates good performance of the nanocomposite film as a thermocouple, where the relative error was of ±0.04 °C when compared with mercury thermometer. The relative errors ($RE$) were calculated by Eq. (1):

$$RE (°C) = \frac{T_{\text{experimental}} - T_{\text{pattern}}}{T_{\text{pattern}}}$$

where $T_{\text{experimental}}$ was the temperature measured in degrees Celsius by ink paper sensor or K type universal

Fig. 5. SEM images of the ink paper sensor. (a) Transverse view shows nanocomposite film physisorbed on paper fibers and in (b) nano-agglomerated CNT on the paper surface.

Fig. 6. Electrical responses to temperature, where (a) the electric resistance changes with temperature variation and in (b) polynomial equation fit to $R(T)$ characteristics.
Fig. 7. The thermal behavior of K type thermocouple and ink paper sensor compared with mercury thermometer, where the relative errors were ±2.87 °C and ±1.04 °C, respectively.

The equivalent electrical resistance measured from the sensor was of 11.49 kΩ at room temperature. In the Figure 8 shows the overall resistance of the ink paper sensor that can be considered a quantum resistances \( nR_Q \) in parallel of \( M \) conduction channels associated in series with constant contact resistances \( R_c \) of the copper wire electrodes and silver paint. Note that, conduction channels as well as quantum resistance are responsible to determine the equivalent resistance as it is shown in the Eqs. (2) and (4). Moreover, the metal-filled structure does not change the ohmic behavior and contributes to the formation of heterojunctions.

The piezoresistive effect of the Al/CNT was studied: the resistance changes with applied pressure onto sensor surface exhibiting linear behavior. In this case, the resistance decreases when the pressure increases due to metal particles form more conduction channels. This behavior is a new concept compared to the other piezoresistive sensor based on polymer/CNT. The ink paper sensor was directly measured putting standard weights onto the surface and changing the electric resistance as a function of compressive stress. Theses effects are expected to CNT films under mechanical stress.

The micro-agglomerated at 10 μm was investigated by Yi Liu et al. This paper reports a great energy absorption by bulk MWCNT, with large volume of compression at 90% and recovery of the original form after pressure release. On this basis, we have tested the ink paper sensor for piezoresistive responses as shown in Figure 9, which obtained the reversible resistance without stress of 17.81 kΩ at 27.80 °C. See complemenary video presented in Ref. [29].

4. CONCLUSIONS AND FUTURE WORKS

In conclusion, we have made one-step syntheses of Al/CNT agglomerated nanocomposites and developed thermo-piezoresistive ink paper sensors. Results indicate that the nanocomposites have multi-sensory properties for temperature and pressures, where the electrical resistance decreases polynomially, while that the temperature increases as a relationship \( R \propto T^3 \). Also, the piezoresistive behavior shows linear dependence between resistance and pressure. These characteristics can be used as a thermocouple for monitoring environment temperature, touch and stress sensor or microbalance.

In future works, we will test other flexible substrates, high purified Al/CNT and others stress-strain relationship.

Acknowledgments: The authors acknowledge Rede nacional de pesquisa em nanotubos de carbono/CNPq, INCT Nanomateriais de Carbono/CNPq, Centro de
Engenharia Mecânica da Universidade de Coimbra/CeMUC and Euro Brazilian Windows for financial support (Erasmus Mundus mobility fellowship to M.A.L.R. at Universidade do Porto). M. A. L. R. and J. D. N. thank Brazilian financing agencies, CNPq and FAPESP. Fruitful discussions with Rúben Santos, Tito Garrido, Bruno Fragoso and Leandro Marzulo are gratefully acknowledged.

References and Notes

29. See at the following homepage for movies, in WMV format, of electrical responses discussed in this work. The video file is reachable at (http:// http://www.youtube.com/watch?v=FltrnXSiBH8)

Received: 6 October 2011. Accepted: 18 January 2012.