Mediterranean Archaeology and Archaeometry, Vol. 14, No. 1, pp. 25-35

NANOSIZED ZINC OXIDE DEPOSITED ON SINGLE WALL CARBON NANOTUBES COMPOSITES FOR NITROGEN DIOXIDE-SENSOR IN MUSEUMS AND ART GALLERIES MONITORING

Wassef Al Sekhaneh[1], Habiba Dahmani[2]

[1]Faculty of Archeology and Anthropology, Yarmouk University, Irbid 2111-63, Jordan
[2]Badji Mokhtar University, Annaba Algeria Electronics Department

Received: 05/01/2012
Accepted: 03/03/2013
Corresponding author: sekhaneh@yahoo.de

ABSTRACT

The aim of this investigation is to develop a material and technique for detects the smallest traces of poison gases and for the instantaneous rate of atmospheric corrosion of archaeological materials indoor. This paper describes the development and use of a single walled carbon nanotubes with ZnO (SWCNT/ZnO) composites as a Networks to investigate it as resistive gas sensors for NO_2 detection. Sensor film was coated on an sapphire substrate by spin coater. At room temperature, SWCNT/ZnO composites with equal weight ratio have shown quite high sensitivity to NO_2 concentrations as low as 1 ppm, this gives the opportunity to us it as a sensor to control the environment of the places where the cultural heritage materials are found. All ZnO (SWCNT/ZnO) tested sensors exhibit high stability and relatively low response and recovery time. The highest response values of the composite were achieved at temperatures ranging between 100 and 300°C and gas concentrations higher that 50 ppm. For all gas concentrations, the SWCNT/ZnO sensor shows much impressive performance at temperatures higher than 100°C compared to pure SWCNT sensor. The results show that this type of material is surprising, revealed that the measured sensitivity upon exposure to NO_2 strongly depends on the changing matrix of the microstructure and the preparation conditions of the composite material. The gas detection mechanisms as well as the optimal gas sensing parameters were discussed.

KEYWORDS: Zinc Oxide, nanotubes, SWCNT, gas sensors, NO_2, Cultural Heritage, Museums, art Galleries

1. INTRODUCTION

This paper presents an idea about the role of scientific cultural heritage to conserve the tangible objects such as monuments, landscapes, and artifacts in the Museums for supporting the continuity of the intangible items as arts, music, etc. It focuses on the main tasks of the museums, which are taking care of artifacts, handling the object and restoring them when needed in the appropriate store, providing the proper environment. These type of sensors are consisting of nanosized SWCNT/ZnO composites, whose properties have attracted considerable technological interest due to their potential application mainly is the detection of the harmful agents of pollution and corrosion of the human cultural heritage materials indoor and outdoor (Johansson et al., 1991; Malaga-Starzec, 2003; Gysels, et al, West, et. al; 2004; Odlyha, et al., 2000).

Museum, means the place where societies house and preserve the most important element of their cultural heritage also its a center of learning. The concept of the museum emphasis on research and focusing most of that research on collecting, preserving and exhibiting objects (Solinger, 1990).

The conservation of cultural heritage elements needs quantitative and qualitative monitoring of hazardous and harmful gaseous substances such as CO, NO, NO_2 and hydrocarbons (HCs) is of great importance in several application areas such as toxic gas alert, industrial and environmental pollution. The present paper intends to present some meaningful application of nanosensors that could highlight the innovation potential of the nanotechnology in the field of cultural heritage. However, it is also relevant to note that the continuous monitoring of gases is considered necessary to contrast the natural decay of the archaeological objects, which may be accelerated by undesirable environmental conditions due to the pollution or poor conservation practices.

The major causative hazardous is nitrogen dioxide (NO_2) which is produced by combustion of fossil fuels, power plants and automobiles has been of concern for clean environment. Various approaches have been performed to detect NO_2 gas. Conventional gas sensor types are usually made of thin sensing layers of semiconducting oxides films deposited directly over a substrate and composites which usually require a heating system to enhance the NO_2 detection (Koshizaki et al., 2000; Baratto et al., 2004; Wang et al., 2006; Hyodo et al., 2003; Tamaki et al., 2004; Jun et al., 2009). The use of SWCNTs has been attracted to be a functional device such as gas sensors, which has an excellent performance and reduced size due to the extremely high specific area -surface-to-volume ratio material.

The sensitivities of Single wall carbon nanotube (SWCNT) make it an attractive composite for chemical and physical sensing devices, especially for nanoscale gas sensors due to their unique physical and chemical properties. The development the CNTs-based gas sensors display a high response, prompt response, low power consumption, small size and low operating temperature. Gas sensors based on pristine CNTs as well as single wall and multiwall carbon nanotubes (SWCNTs and MWCNTs), and aligned CNTs are intensively investigated , and the modification of CNTs with functional groups, metal oxides, metals and polymers for gas sensors were also considered (Valentini et al., 2003; Kong et al., 2000; Pengfei et al., 2003; Lucci et al., 2006; Zhang et al., 2006; Nguyen et al., 2006; Shi et al., 2003; Suehiro et al., 2005; Cho et al., 2006; Chiang et al, 2001).

It has been reported that SWCNTs are used as sensitive nanomaterials for surrounding ambient like SO_2, NH_3, NO_2, and other volatile organic compounds (VOC) detection. The adsorption of gaseous molecules can significantly affect the conductivity by e*lectron donating* and *withdrawing* in the SWCNTs, changing their electrical properties. The high and fast response of the SWCNTs gas sensors has been confident. The drawback of these sensors is slow and partial recovery.

It has been reported that the electrical conductance of semiconducting single-wall tubes dramatically changes when the tubes are exposed to NO_2, O_2, and NH_3 (Baratto et al., 2004; Hyodo, et al., 2003). Theoretical work has revealed how the electronic properties of CNTs vary when the CNTs are exposed to oxidizing or reducing gases. More recently, MWCNT films have been reported to show a p-type semiconducting character with decreasing resistance

upon exposures to sub-ppm concentrations of NO_2 (Valentini, et al., 2003).

Also Gas sensor devices usually uses metal oxide semiconductors like TiO2, ZnO, and SnO_2 as sensing materials because of their excellent electrical properties. Therefore, to increase the porosity of the material in order to absorb more gases, the SWCNTs are usually mixed with metal oxides (ZnO) as SWCNTs/ZnO matix.

Chemical functionalization is a method to improve sensing performance of SWCNTs. First, it allows the unique properties of SWCNTs to be joined to other materials, such as metals, metal oxides and polymers, to create hybrid sensing nanomaterials with enhanced sensitivity, selectivity and faster response time. Second, it can improve dissolution and dispersion of SWCNTs in various solvents, which opens the door to cost-effective methods to fabricate sensors by simple techniques. Theoretical studies on using the nanoparticles-functionalized CNTs reported that these nanoparticles act as reactive sites to target the gas molecules leading to a change in electrical conductivity due to absorption of gas molecules (Barsan, et al., 2000; Peng, et al., 2004). Newly, it has been reported that CNTs/metal oxides composites, based on either pure SWCNTs or pure MWCNTs can be used to detect NO_2 and NH_3 at room temperature (RT) and higher temperatures with relatively high sensitivity. Nevertheless, additional efforts are still required to optimize the production processes and the operation circumstances of these composites to make them *useful* in many *applications* in electronics. Here the synthesis and fabrication of highly sensitive SWCNT/ZnO. NO_2 gas sensor will be presented. The gas sensing properties were characterized by X-ray diffraction (XRD), scanning tunneling microscopy (STM), scanning electron microscopy (SEM), and direct current (DC) electrical resistance at different gas concentrations and different temperatures.

2. EXPERIMENTAL DATA

2.1 Purification of the-Single-wall carbon nanotubes from the iron clusters

The single walled carbon nanotubes are close from both side after the production, we have to open the purification of the single-wall carbon nanotubes magnetic clusters is necessary to this study. Mainly the metal clusters or metal nanoparticles catalysts that hinder the investigations of SWCNTs. It is necessary to remove as many clusters as possible. For CNTs functionalization with nanoparticles it is necessary to open the tubes to enrich the porosity of the materials, which are normally closed directly after the synthesis to purify it from the metal cluster inside the tubes. SWCNTs are produced by catalytic conversion of high pressure CO over Fe particles process in a flow of gas by using CO as the carbon feedstock and $Fe(CO)_5$ as an iron-containing catalyst precursor at CNI, Houston, TX, and have been used as delivered. Nanotubes produced have a significant amount of Fe impurity (figure 1A), but Fe nanoparticles are not encased in heavy graphitic shells as in arc or laser production but are relatively easy to remove (Cunibertiet al., 2007; Loiseau, 2006; Nikolaev, et al, 1999 Kong, et. al; 1998).

The raw samples were stepwise purified by controlled thermal oxidation in air atmosphere at about 360°C for three hours or until 25% weight loss to remove the amorphous carbon by converting carbon into carbon oxides. The sample is dispersed in deionised water in 1% of surface-active agents SDS (sodium dodecyl sulfate) then the SDS can modify the particle-suspending medium-interface and prevent the aggregation of particles for a long time. The solution was centrifuged to separate the metal clusters from the carbon nanotubes followed by acidic treatment using concentrated hydrochloric acid (HCl) to remove the metal clusters (Rinzler, et al., 1998; Vázquez, et al., 2002; Duesberg, et al., 1999; Zimmerman, et al., 2000).

The solution was sonicated by ultrasonic finger several times to fracture the structure in the surfactant solution. The process of sonication is prepared with an ultrasonic probe (Finger ultrasonic generator Up 200S) with 50 Watt at full cycle for one minute, with US (ultra sound) the tubes are cut to make them smaller with more porosity (see Fig. 1C). Therefore, too long sonication times should be avoided to prevent destruction of nanotubes. The ultrasonic treatment decomposes the metal nanoparticles.

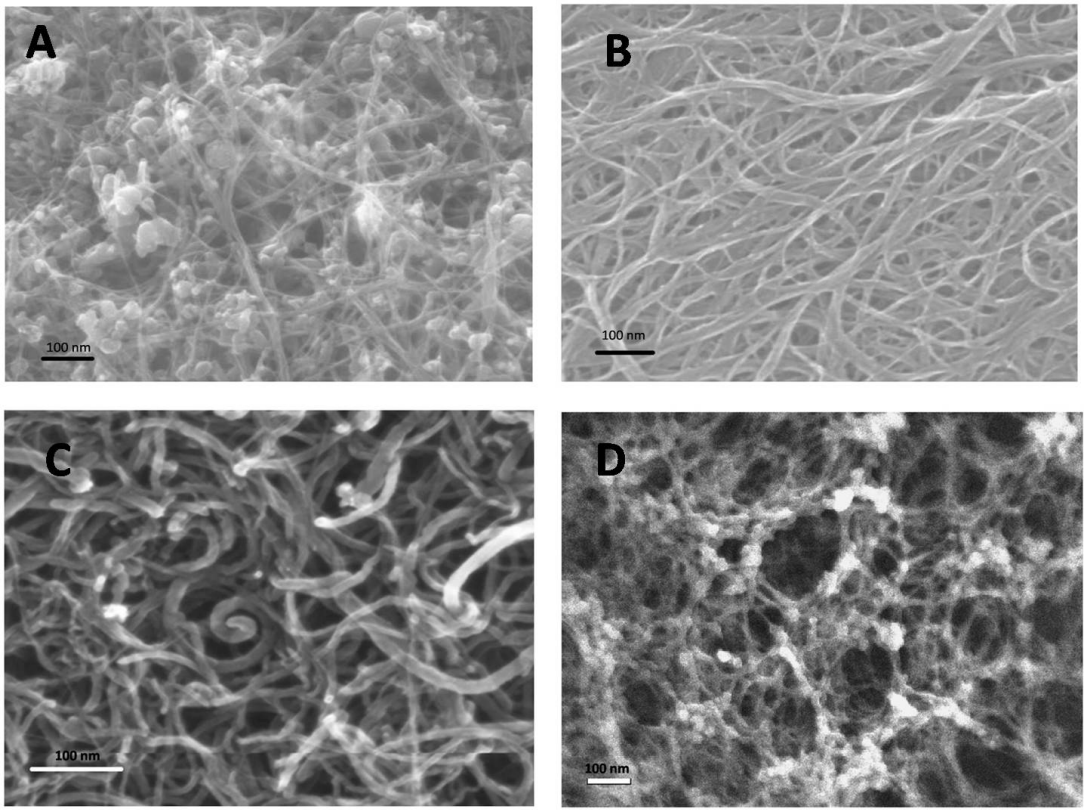

Figure 1. SEM images of hypco pure SWCNTs after treatment at 370°C to delete the amorphous carbon from the matrix. (A) centrifugation with acidic solution treatments for several times to delete the iron cluster from the matrix, (B) Sonication to make the tube shorter this will produce more porosity to the system, (C) SWCNT/ZnO composite, and, (D) The matrix of single wall carbon nanotubes and nitrogen dioxide.

The average diameter of individual SWCNT is about 1 nm, measured with Raman Breathing Modes (RBM). Figure (2: A, B, C, D) gives a view of Raman spectra from the SWCNTs sample. The Raman spectrum of SWCNTs has an important region. It is related to RBM Raman breathing modes, This region is dominated by a low-frequency band ranging from 173 to 214 cm^{-1} that originates from a radial (RBM) and is unique for SWCNTs to determine the diameter of the tubes (Rao et al., 1997).

In this figure there are four peaks at 173, 162, 186 and 214 cm^{-1}, from which we can calculate the distribution of the diameters d of single wall carbon nanotubes from the relation $\omega^{RBM} = C/d$ with C = 218 cm^{-1}nm. This leads to d= 0.79 nm, 0.83 nm, 0.89 nm and 1.03 nm. Different groups have used different values for the constant C = 218 (Jishi et al., 1993), 223.75 (Bandow et al., 1998), 234 (Kurti et al., 1998), 232 (Sanchez-Portal et al., 1999), 248 (Jorio et al., 2001), and 223.5 (Bachilo et al., 2002), all in cm^{-1} nm.

2.2 Preparation of SWCNT/ZnO Nanocomposite

A suitable amount of SWCNTs are dispersed in 10 mL of a 10 mM of zinc acetate dehydrate ($Zn(O_2CCH_3)_2(H_2O)_2$), (98%, from Aldrich), Zinc acetate is a precursor via a sol-gel route to the transparent semiconductor zinc oxide. The material immersed in ethanol solution which was loaded into a vessel of 25 mL. The solution was subjected to magnetic stirring at 25◎C for 30 min. Subsequently, it was moved to a water bath and maintained at a temperature of 90◎C for about 2 hours with magnetic stirring. Then, the vessel was slowly and gradually cooled to room temperature. As a final point, the gray solution was sonicated for 5 hours. Before the deposition, the obtained composite was studied with several methods like STM, SEM and XRD.

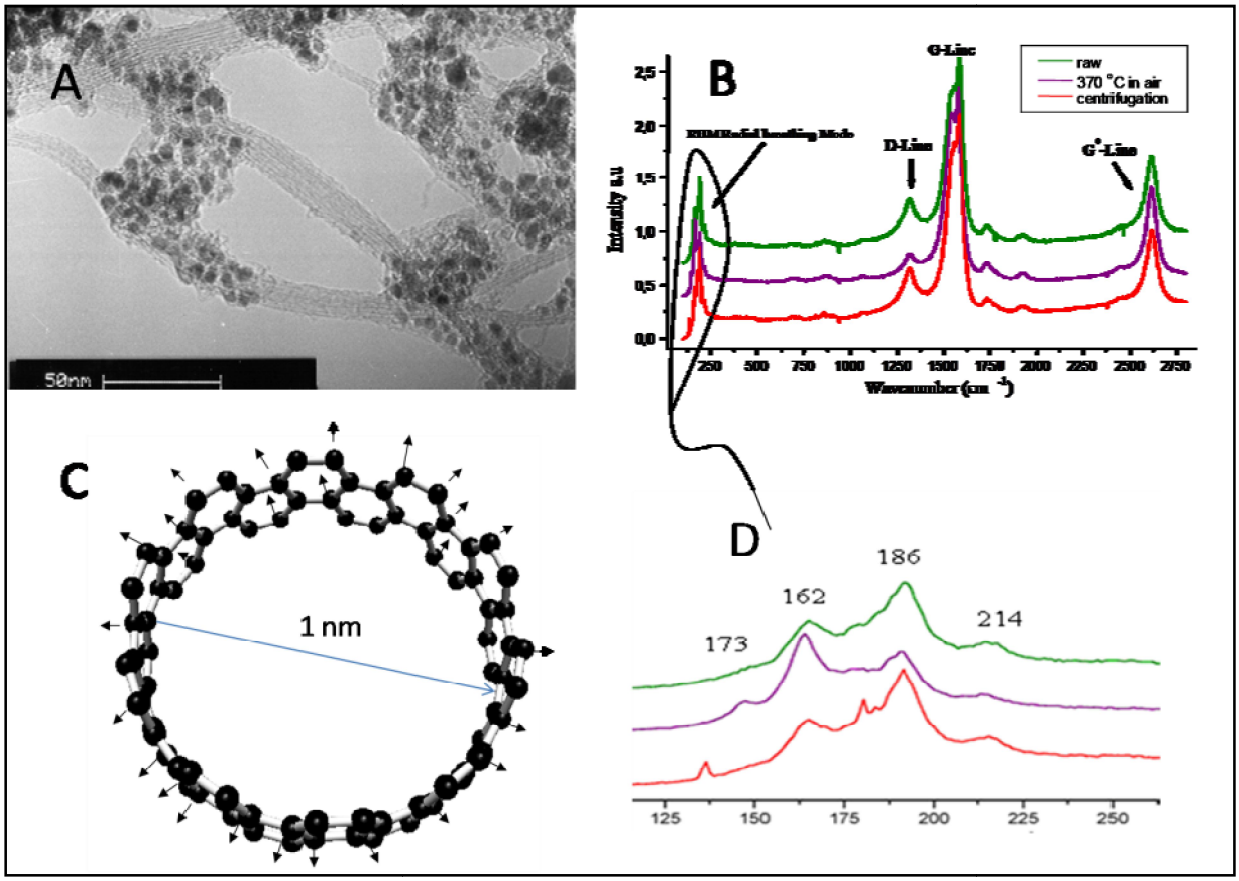

Figure 2. The diagram shows the Single wall carbon nanotube without deposition of ZnO particle: (A) TEM images of SWCNTs (Fe impure); (B) Raman Breathing Modes of single wall carbon nanotubes (C) Shows RBM of SWCNT (D) four peaks represent the diameter of SWCNT, d= 0.79 nm, 0.83 nm, 0.89 nm and 1.03 nm

2.3 Sensor fabrication

The SWCNT/ZnO gas sensor was fabricated by a conventional lithography process using sapphire substrate. The gas sensor is composed of sensing layer, a special pair of hair *comb shaped gold*-plated *electrodes.* A *sensing layer, composed* of a gas sensor and a Cr heater resistor. Casein films were successfully *prepared* with the *spin-coating* technique of aqueous casein solutions on base-treated glass surfaces.

Thick films with equal weight ratio of SWCNT/ZnO composite were successfully prepared with the spin-coating technique of a drop of the aqueous composite just on the top of the sensing layer. The spinning was at 1000 rpm/min and the period of coating was 20 s. After that, the coating layers were heated in air using an Infra-Red drying at approximately 150◎C for 30 minutes, to evaporate the solvents in the coating layers. Then, the sensor was connected with copper wires to the electrometer and the temperature controller. The sensor was located inside a programmable *3-Zone Tube Furnace* used as a sealed cylindrical chamber filled by a compressed gas. The sensor characteristics were observed from the resistance varying in air and in NO_2 atmosphere with gas different concentration of gas 1, 10, 50, 250, 500 and 1000 ppm and at optimum temperature changing from 25–300°C. The response and recovery as a function of time were monitored and recorded via an interfaced personal computer. The response and recovery time is defined as the time for the sensor to reach 90% of its total resistance change.

For NO_2 gas sensing, the sensor was loaded in the chamber and then dry air pumped for 5 min to make base measurement line stabilize until the sensor's response reached a fixed value. When the sensor reacts with NO_2, the response has been measured, then the chamber was pumped by a rotary pump for 5 minutes. Furthermore the process is repeated for higher concentration and higher temperatures.

3. RESULTS

The morphology of the SWCNT and ZnO/SWCNT networks on sapphire substrate is shown in Fig. 3A. However, the SWCNT/ZnO composite image (Fig. 3A) shows a quite different morphology in which the nanotubes are well dispersed and their surfaces are decorated with ZnO nanoparticles. Some clusters of ZnO nanoparticle are also observed in (Fig. 3A) at nanotubes interjunctions and surface defects. Fig. 3C represent a high abundance of pure SWCNTs bundles with different chairality which are forest-like and twisted around each other forming multiple tube robes of average diameter of about 10 nm length.

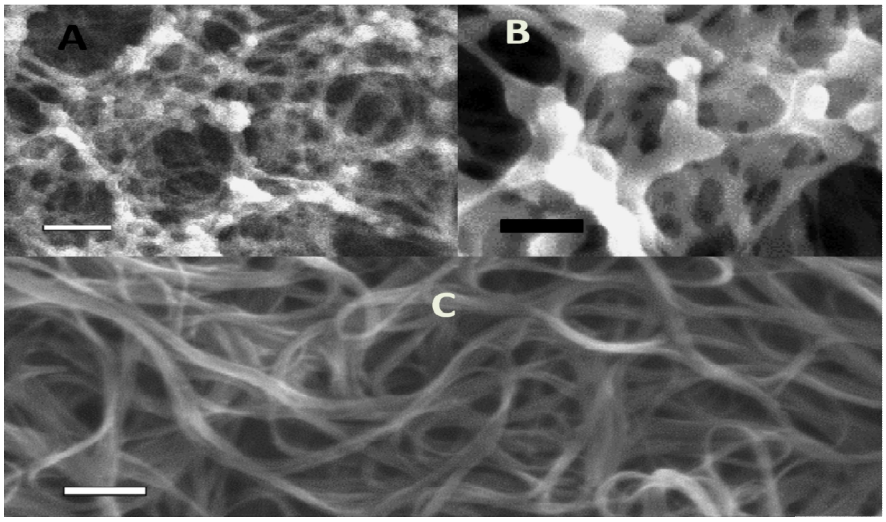

Figure 3. SEM images of single wall carbon nanotube with 1 nanometer diameter (A): ZnO/SWNTs composite (scale 50 nm); (B): ZnO/SWNTs(scale bar 5 nm); (C): SWNTs (scale bar 50 and 5 nm).

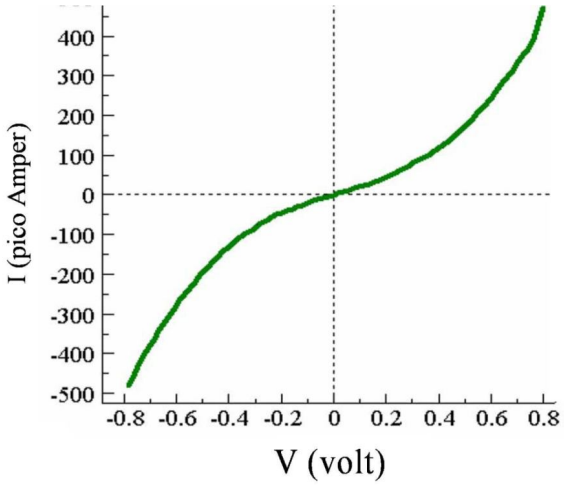

Figure 4. I–V curve recorded over ZnO/SWNT sample at a point on junction (Albiss et al., 2010).

To further clarify the electronic nature of the nanotube, more detailed electrical mapping of the junction region has obtained via (CITS) current image tunneling spectroscopy in which an (current-voltage) I–V spectra was acquired at each pixel in the imaging mesh, provided a dense array of both electronic and topographical features linked with the complete scanned area. A typical I-V curve at a point on the junction is shown in Fig. 4.

These spectra were considered to the semiconducting wall carbon nanotubes. It should be noted that the most wonderful feature of carbon *nanotubes is* coexistence of metallic and semiconducting properties SWCNT's and difficult to separate it. It is possible that the junction formed in the studied case is somewhat explained by the tunneling between SWCNT's in a bundle or between the SWCNT bundle and ZnO nanoparticles on a highly cleaned oriented pyrolytic graphite HOPG substrate. Comprehensive information about the surface topography and conductivity of single walled carbon nanotube can attain by high resolution scanning tunneling microscopy (STM) images in the nanoscale which is beyond the scope of this study (Albiss et al., 2010).

SWCNT/ZnO composite can be applied in many types of *sensing* devices, achieving good dispersion and large specific area are might

seem *quite* crucial composite materials and had significantly influenced the sensing performance of the composite films. From the STM and SEM results, it is observed that the sonication considerably reduces the baseline noise of the sample without appreciable changes in the amplitudes of responses (Albiss, et al., 2010). Namely, the response and recovery characteristics depend on how SWCNT bundles can untangle to utilize the side surface area of SWCNTs. Also, SWCNTs are generally in a bundle form where interact only through weak *Van der Waals forces* or through transient hydrogen bond, this phenomena make them gathering. Namely, it is needed to consider the objectionable reduction of specific area due to the formation of bundles. However, the agglomerates of SWCNTs breaks down by the intensive sonication which cause baseline fluctuations and well-dispersed samples are likely to provide sensor signals with reduced noise, the sonication increase also the material porosity this leads to trap more gas molecule inside the composite. As well as, it had been also observed that too long sonication make the stability of the composite solution worse and inferior in character.

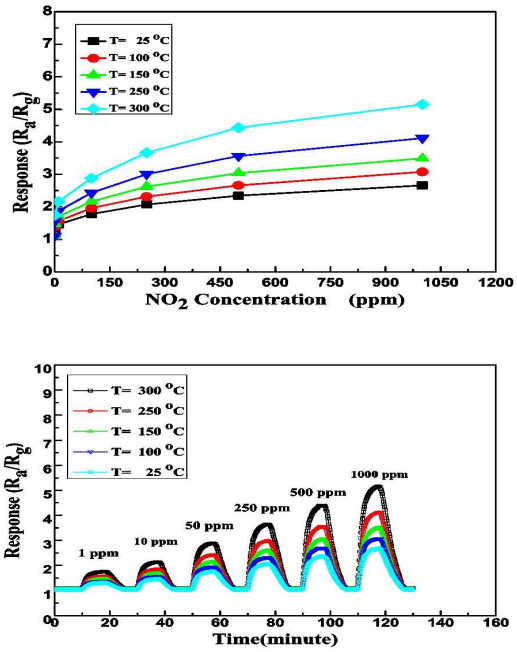

Figure 5 (above) shows the NO_2 gas concentrations sensitivity defined as the ratio (*Ra*/*Rg*) of *electrical resistance* for the SWCNT sensor at different temperatures and. Figure 5 (down) shows time response of the NO_2 gas as the ratio (*Ra*/*Rg*) (Albiss et al., 2010).

Fig. 5 shows the time response of the gas sensitivity defined as the ratio (*Ra*/*Rg*) of *electrical resistance* for the SWCNT sensor at different temperatures and NO_2 gas concentrations. Where, R_a and R_g are the resistances of the sensor in air and gas under similar conditions at same *temperature*.

When the pure SWCNTs sensor is exposed to NO_2 the resistance decreases. This decrease can be explained by the conventional p-type semiconductor theory. An electron charge transfer forms electron acceptor to the p-type semiconductor electron-accepting molecules upon exposure to the electron-accepting gases such as NO_2 resulted in the Fermi level shift of the nanotube closer to the valence band. This shift enriched the hole carriers in the nanotube and decreased its resistance. It is well known now that MWNTs tend to conduct at room temperature, while SWCNTs act as semiconducting materials. However, MWCNTs can contain some semiconducting tubes among predominant metallic ones (Albiss et al., 2010). The semi conducting MWCNTs can also be utilized as materials of gas sensors, but the molecular interaction effects are averaged over metallic and semi conducting tubes (Albiss et al., 2010). In addition, the inner tubes in MWCNT films are blocked from interacting with NO_2 because the molecules are not expected to diffuse into MWCNT films. This explains the small response of the MWCNT films by gas exposure, unlike the quite large response of in the case of semiconducting SWCNT. The calibration curves of the maximum response of SWCNT sensor versus NO_2 gas concentrations are plotted in Fig. 5 (above) at different working temperatures. As it is, the sensor exhibits considerable enhancement in the response in the whole gas concentration range which was examined. The maximum response of about 4 has been achieved at higher temperatures and gas concentration. However, at room temperature (25°C) and low gas concentrations (0-100 ppm), the sensor shows a maximum response of about 0.7, while the response is about 2 at 300°C for the same gas concentration. It is noted that the response and the recovery times are estimated at about 5 min and 8 min, respectively. The response time at higher temperatures and gas con-

centrations becomes slightly larger. The smaller is the concentration of NO_2 the higher is the response time. This occurs because it takes some time for the NO_2 target gas to reach the sensing surface when it flows into the gas chamber. The fewer the molecules that come in, the longer it takes for gas-sensitive surface to be covered and be saturated with adsorbed molecules. On the other hand negligible fluctuations in the sensor base line were observed during the gas evacuation process (Albiss et al., 2010).

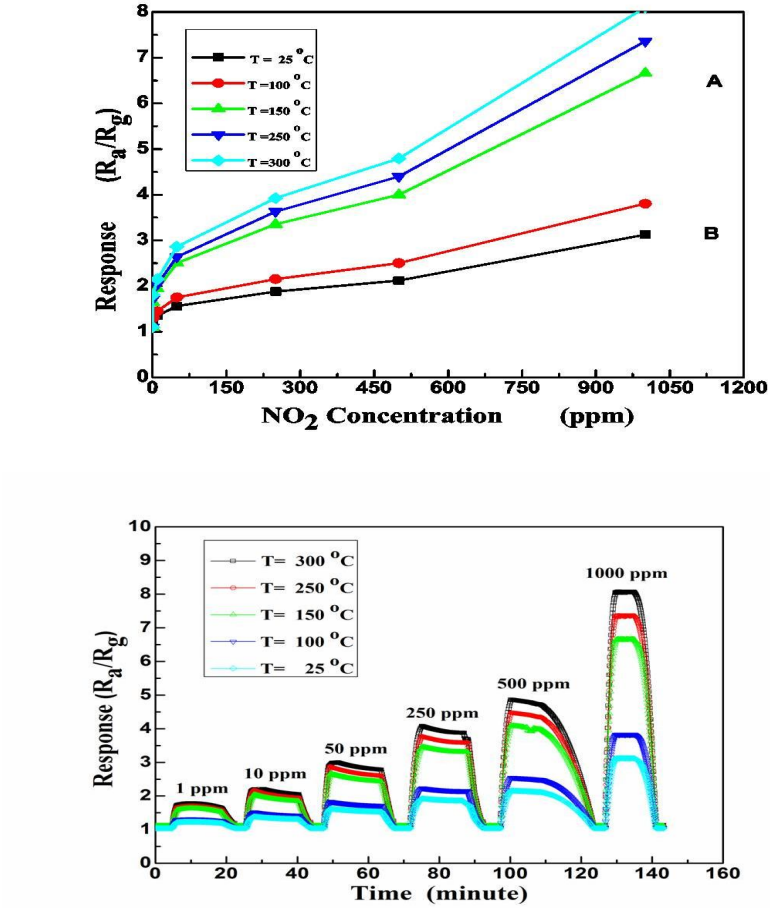

Figure 6 (above) shows the NO_2 gas concentrations sensitivity defined as the ratio (*Ra*/*Rg*) of *electrical resistance* for the SWCNT/ZnO sensor at different temperatures and. Figure 6 (down) shows time response of the NO_2 gas as the ratio (*Ra*/*Rg*) (Albiss et al., 2010).

The NO_2 gas responses from the SWCNT/ZnO sensor are presented in figure 6 (above) at different temperatures and gas concentrations. ZnO is well known to be an n-type semiconductor, and the very strongly electrophilic NO_2 gas molecule acts as an electron acceptor when it adsorbs on the surface. Therefore, when ZnO is exposed to NO_2 gas, the resistance increases according to the increased number of NO_2 gas molecules adsorbed by the surface. However, presence of the SWCNT network, which are p-type semiconductors, play a predominant role in the overall change in the resistance of the sensor. In addition, in the composite networks, the metallic and semiconducting molecular interactions are averaged and thus affect the conduction mechanism in the sensing material. This may explain the decrease in the resistance response of the SWCNT/ZnO sensor observed in our results which is larger than that of the SWCNT sensor. Fig. 6 (above) illustrates the maximum responses of the SWCNT/ZnO sensor versus gas concentrations at different working temperatures. The base line resistance in air of this sensor changes from 2.5 kΩ at room temperature to 5.3 kΩ at 300°C. In order to make the

recognition of these results easier, the sensor response curves are separated into two sets A and B. Set A represents the responses at relatively high temperature range (150-300°C) and set B represents that for quite low temperatures (25-100°C). The average response changes from 1 to 6.5 for set A and from 0.5 to 1.5 for set B which is much higher than that of pure SWCNT sensor. It is worth pointing out that the response and recovery times for SWCNT/ZnO sensor were considerably reduced to almost half of that for the SWCNT sensor. Comparing Fig. 5 (above) with Fig. 6 (above), the rate of the increase of the response as the NO_2 concentration increases is larger for the SWCNT/ZnO. This reflects the important role of the ZnO addition on the sensitivity (Albiss et al., 2010).

It can be seen that sensitivity factor of SWCNT increases with temperature for temperature range from 25°C to 300°C. This acting indicates that the role of temperature is more pronounced for large gas concentration. On the other hand for the SWCNT/ZnO sensor, the temperature is found to be nearly ineffective throughout the whole temperature range, except between 100°C and 150°C where a large increase of sensitivity is observed. But at temperature smaller than 100°C and larger than 150°C the sensitivity remains almost constant.

This suggests that the addition of specific amounts ZnO nanoparticles to the (SWCNTs) network is expected to play an important role in tuning the sensitivity to the gas molecules during gas adsorption and/or desorption and optimizing the sensor working temperatures. Compared to conventional polymer-based gas and solid-state and sensors, that operate at higher temperatures with limited sensitivities (Langmaier et al. 1997).

This composite SWCNT/ZnO increases the porosity of the material then it is expected that the sensing devices can exhibit much better sensitivity and quick response at temperatures close to room temperature (RT). Hence, better results can be obtained by controlling the ZnO to SWCNT weight ratio to have suitable material with more specific area, the nanotubes dispersion and alignment which is still under investigation.

It is suggested that the recovery time was relatively long because of the higher surface energy between SWCNTs and NO_2 and the presence of the reacted NO_3 molecules with the catalytic surfaces of the bundles of nanotubes.

4. CONCLUSIONS

A new composit of SWCNT/ZnO gas sensor was developed herein with high sensitivity and favorable response properties in detecting NO_2 gas at different temperatures and gas concentrations with different temperature response response ranging from room temperature to 300 Celsius degree. The experimental SWCNT/ ZnO sensor was able to detect nitrogen dioxide molecules at levels of just 1 ppm.

The goal of this work was to assess the possibility of using SWCNT-based composite as an innovative NO_2 sensor for environmental applications conservation of very rare valuable archaeological materials consist of inorganic materials like limestone, marble, dolomite, calcareous cemented sandstone and organic materials like pictures, canvases and other Art materials indoor and outdoor to control the museums and galleries from harmful gases like NO_2.

Improvement of the sensors performance at lower gas concentration and temperatures is still under our extensive investigation also to find novel methods to increase the porosity of the new nanomaterial to use it as filter to harmful gases. Moreover, this is a promising step toward the development of miniaturized devices with extensive analytical capabilities.

REFERENCES

Johansson, L.G., Lindqvist, O., Mangio, R. (1991) Corrosion of calcareous stones in humid air containing SO_2 and NO_2. *Durability of Building Material 5*, 439–449.

Malaga-Starzec, K., Panas, I., Lindqvist, J.E., Lindqvist, O. (2003) Efflorescence on thin sections of calcareous stones. *Journal of Cultural Heritage 4*, 313–318.

Gysels, K., Delalieux, F., Deutsch, F., Van Grieken, R., Camuffo, D., Bernardi, A., Sturaro, G., Busse, H., Wieser, M. (2004) Indoor environment and conservation in the Royal Museum of Fine Arts, *Journal of Cultural Heritage 5*, 221–230, Antwerp, Belgium.

Odlyha, M., Cohen, NS., Foster, GM., West, R. (2000) Dosimetry of paintings: determination of the degree of chemical change in museum exposed test paintings (lead white tempera) by thermal analysis and infra-red spectroscopy. *Thermochim Acta 53*, 365.

Solinger, Janet W., (1990) *Museums and universities Choices*, New York.

Koshizaki, N., Oyama, T. (2000) Sensing characteristics of ZnO-based NO_x sensor. *Sensor Actuators B 66*, 119–121.

Baratto, C., Sberveglieri, G., Onischuk, A., Caruso, B., di Stasio, S. (2004) Low temperature Selective NO2 sensors by nanostructured fibres of ZnO. *Sensor Actuators B: Chem. 100*, 261–265.

Wang, J.X., Sun, X.W., Yang, Y., Huang, H., Lee, Y.C., Tan, O.K., Vayssieres, L. (2006) Hydrothermally grown oriented ZnO nanorod arrays for gas sensing application. *Nanotechnology 17*, 4995–4998.

Hyodo, T., Abe, S., Shimizu, Y., Egashira, M. (2003) Gas-sensing properties of ordered mesoporous SnO_2 and effects of coatings thereof. *Sensor Actuators B: Chem. 93*, 590–600.

Tamaki, J., Hayashi, A., Yamamoto, Y. (2004) Highly sensitive detection of dilute nitrogen dioxide using tungsten oxide thick film sensor. *Journal of the Ceramic Society of Japan*, vol. 112(1305), 546–549.

Jun, H., Yun, J., Cho, K., Hwang I., Lee, J., Kim, S. (2009) Necked ZnO nanoparticle-based NO_2 sensors with high and fast response. *Sensors and Actuators B 140*, 412–417

Valentini, L. Armentano, I., Kenny, J.M., Cantalini, C., Lozzi, L., Santucci, S. (2003) Sensors for sub-ppm NO_2 gas detection based on carbon nanotube thin films, *Appl. Phys. Lett. 82*, 961–963.

Kong, J., Franklin, N.R., Zhou, C.W., Chapline, M.G., Peng, S., Cho, K.J., Dai, H.J. (2000) Nanotube molecular wires as chemical sensors. *Science* 287 (5453), 622–625.

Pengfei Q.F., Vermesh, O., Grecu, M., Javey, A., Wang, O., Dai, H.J., Peng, S., Cho, K.J. (2003) Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection, *Nano Lett.* 3 (3), 347–351.

Lucci, M., Reale, A., Di Carlo, A., Orlanducci, S., Tamburri, E., Terranova, M.L., Davoli, I., Natale, C., Di D'Amico, A., Paolesse, R. (2006) Optimization of a NO_x gas sensor based on single walled carbon nanotubes. *Sensor Actuators B: Chem.* 118 (1–2), 226–231.

Zhang, J., Boyd, A., Tselev, A., Paranjape, M., Barbara, P.(2006) Mechanism of NO_2 detection in carbon nanotube field effect transistor chemical sensors. *Appl. Phys. Lett.* 88 (12), 3.

Nguyen, H.Q., Huh, J.S. (2006) Behavior of single-walled carbon nanotube-based gas sensors at various temperatures of treatment and operation. *Sensors and Actuators B*, vol. 117, no. 2, 426–430.

Shi, W., Johnson, K. (2003) Gas adsorption on heterogeneous single-walled carbon nanotubes bundles. *Phys. Rev. Lett. 91* (1), 015504.

Suehiro, J., Zhou, G., Imakiire, H., Ding, W., Hara, M. (2005) Controlled fabrication of carbon nanotube NO_2 gas sensor using dielectrophoretic impedance measurement. *Sensors and Actuators B*, vol. 108(1-2), 398–403.

Cho, W.S., Moon, S.I., Paek, K.K., Lee, Y.H., Park, J.-H., Ju, B.K. (2006) Patterned multiwall carbon nanotube films as materials of NO_2 gas sensors. *Sensors and Actuators B*, vol. 119(1), 180–185.

Chiang, I.W., Brinson, B.E., Smalley, R.E., Margrave, J.L., Hauge, R.H. (2001) Purification and Characterization of Single-Wall Carbon Nanotubes, *J. Phys. Chem. B*, 105, 1157-1161.

Barsan, N., Weimar, U. (2001) Conduction model of metal oxide gas sensors. *J. Electroceram.* 7, 143–167.

Peng, S., Cho, K., Qi, P., Dai, H. (2004) Ab Initio study of CNT NO_2 gas sensor. *Chem. Phys. Lett.* 387, 271–276.

Cuniberti, G., Fagas, G., Richter, K. (2007) *Introducing Molecular Electronics, (Lecture Notes in Physics),* Springer-Verlag. Berlin.

Loiseau, A., Launois, P., Petit, P., Roche, S., Salvetat, J.P. **(**2006) *Understanding Carbon Nanotubes: From Basics to Applications, (Lecture Notes in Physics),* Springer.

Nikolaev, P., Bronikowski, M.J., Bradley, R.K., Rohmund, F., Colbert, D.T., Smith, K.A., Smalley, R.E. (1999) Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chem. Phys. Lett.,* 91, 313.

Kong, J., Soh, H.T., Cassell, A.M., Quate, C.F., Dai, H. (1998) Synthesis of Individual Single-Walled Carbon Nanotubes on Patterned Silicon Wafers. *Nature*, 395, 878.

Rinzler, A.G., Liu, J., Dai, H., Nikolaev, P., Huffman, C.B., Rodriguezmacias, F.J., Boul, P.J., Lu, A.H., Heymann, D., Colbert, D.T., Lee, R.S., Fischer, J.E., Rao, A.M., Eklund, P.C., Smalley, R.E. (1998) Large-scale purification of single-wall carbon nanotubes: process, product, and characterization. *Appl. Phys. A*, 67, 29-27.

Vázquez, E., Georgakilas, V., Prato, M. (2002) Microwave-assisted purification of HIPCO carbon nanotubes, *Chem. Commun.,* 2308–2309.

Duesberg, G.S., Blau, W., Byrne, H.S., Muster, S., Burghard, M., Roth, S. (1999) Chromatography of Carbon Nanotubes. *Synth. Met.,* 103, 2484.

Zimmerman, J.L., Bradley, R.K., Huffman, C.B., Hauge R.H., Margrave, J.L. (2000) Gas-Phase Purification of Single-Wall Carbon Nanotubes. *Chemistry of Materials*, 12, 1361-1366.

Rao, A.M., Richter, E., Bandow, S., Chase, B., Eklund, P.C., Williams, K.W., Menon, M., Subbaswamy, K.R., Thess, A., Smalley, R.E., Dresselhaus, G., Dresselhaus, M.S. (1997) Infrared and Raman spectroscopic studies of single-wall carbon nanotubes. *Science*, 275, 187-191.

Jishi, R.A., Venkataraman, L., Dresselhaus, M.S., Dresselhaus, G. (1993) Phonon Modes in Carbon Nanotubules. *Chem. Phys. Lett.,* 209**,** 77-82.

Bandow, S., Asaka, S., Saito, Y., Rao, A.M., Grigorian, L. ,Richter, E., Eklund, P.C. (1998) Effect of the Growth Temperature on the Diameter Distribution and Chirality of Single-Wall Carbon Nanotubes. *Phys. Rev. Lett*., 80, 3779-3782.

Kurti, J., Kresse, G., Kuzmany, H. (1998) First-principles calculation of the radial breathing mode of single-wall carbon nanotubes. *Phys. Rev., B* 58, 8869.

Sanchez-Portal, D., Artacho, E., Soler, J.M., Rubio, A., Ordejon, P. (1999) Ab initio structural, elastic, and vibrational properties of carbon nanotubes, *Phys. Rev. B*, 59**,** 12678.

Jorio, A., Saito, R., Hafner, J.H., Lieber, C.M., Hunter, M., McClure, T., Dresselhaus, G., Dresselhaus, M.S. (2001) Structural (n;m) determination of isolated single-wall carbon nanotubes by resonant Raman scattering, *Phys. Rev. Lett.,* 86, 1118.

Bachilo, S.M., Strano, M.S., Kittrell, C., Hauge, R.H., Smalley, R.E., Weisman, R.B. (2002) Structure-assigned optical spectra of single-walled carbon nanotubes. *Science*. 298, 2361.

Albiss, Borhan A., Sakhaneh, Wassef A., Jumah, Inshad and Obaidat, Ihab M. (2010) NO_2 Gas Sensing Properties of ZnO/Single-Wall Carbon Nanotube Composites. *IEEE sensors journal,* vol. 10(12), 1807-1812.

Langmaier, J., Opekar, F., Samec, Z. (1997) Amperometric solid-state NO_2 sensor based on plasticized PVC matrix containing a hydrophobic electrolyte. *Sensors and Actuators B* 41, 1-6.

West, R.H., Odlyha, M., Pratt, K., Roberts, A., Hutton, S. (2004) Monitoring the environmental degradation of paint dosimeters used to assess risk for fine art paintings on display by XPS. Surf. *Interface Anal. 36*, 862–865.