DETECTION OF HAZARDOUS SO_2 BY MWCNTS-BASED GAS SENSORS A NEW APPLICATION FOR MONITORING IN MUSEUMS

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This study aims to investigate advance material and develops a technique that detects the smallest traces of hazard gases for the instantaneous rate of atmospheric corrosion of archaeological materials indoor and outdoor. This article describes the advance and use of multiple-walled carbon nanotubes (MWCNT) with carbon nanoparticles and spheres as a network to investigate it as resistive gas nanosensors for SO_2 detection. The responses of the sensors based on the MWCNs in various concentration to SO_2 responses, in SO_2 ambient air, performed by resistance measurements from room temperatures of 25 °C to 250 °C, more than 400 °C the structure will. SO_2 gas concentration from 0.5 to 20 ppm to find new application, particularly application in Museums to conserve cultural heritage materials from deterioration caused by hazard gases.

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1. Introduction

This paper presents ideas about the role of scientific methods, to conserve tangible cultural heritage such as monuments, landscapes, and artifacts in museums and for supporting the continuity of the intangible items such as languages, art, music which exist in books in museum and art galleries and so forth. It focuses on the primary errands of the museums which are taking care of artifacts, handling objects, and restoring them when needed to the appropriate condition, providing the proper environment. Museum describes the place where societies house and preserve the essential element of their cultural heritage; it is also a center for learning about cultural heritage. Over the past decades, several sorts of gas sensors developed. Accordingly, the gas sensors classified as electrochemical, catalytic, combustion, thermal conductive, infrared, ultraviolet, paramagnetic absorption, solid electrolyte, carbon nanostructure, and metal oxide semiconductor sensors [1-5]. MWCNTs consist of grapheme co-cylindrical graphene layers, grapheme layer itself is an excellent electrode material with the advantages of conductivity and electrochemistry of sp^2 carbon but without the disadvantages related to carbon nanotubes, such as residual metallic impurities [6].

Gas sensors for hazard gases like SO_2, NO_x, and volatile solution like acetone are increasingly required not only for ensuring human health, but also for the conservation of human cultural heritage, indoor and outdoor. These types of sensors consist of nanosized MWCNT composites, whose properties have attracted considerable technological interest due to their potential application when detecting the harmful agents of pollution and corrosion of human cultural heritage materials, both indoor and outdoor [7-13].

The concept of museology distinction research is focusing on collecting, conserving, and exhibiting objects in the museum and art galleries. The conservation of archaeological materials needs quantitative and qualitative monitoring process for hazardous, harmful gases such as COx, NOx, SO_2, and hydrocarbons (HC) is of great importance to several application areas such as toxic gas alert, industrial and environmental pollution [14-16].

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The paper aims to present some meaningful application of nanosensors that could highlight the innovation potential of the nanomaterials in the field of Cultural and Natural Resources. However, it is also relevant to note that the sustainability of monitoring of hazardous gases concentration, is considered necessary to compare the natural decay of the archaeological metal corrosion, which may be accelerated by unwanted environmental conditions due to pollution or poor conservation practices [17-20].

The main causative hazardous is Sulfur dioxide (SO_2) which is produced by combustion of fossil fuels and petroleum products; it is a corrosive acid gas, power plants, and automobiles have been of concern for a clean environment. Various approaches have been performed to detect SO2 gas. Conventional gas sensor types usually made of thin, sensing layers of semiconducting oxide films deposited directly over a substrate and composites, which generally require a heating system to enhance SO_2 detection [20-22].

The use of MWCNTs attributed as a functional device such as gas sensors, which has excellent performance and reduced size due to the extremely high specific area -surface-to-volume ratio material. The sensitivities of Multiple wall carbon nanotube (MWCNT) make it an attractive composite for chemical and physical sensing devices, especially for nanoscale gas sensors due to their unique physical and chemical properties [23]. Researchers have been making lots of efforts to develop the MWCNTs-based gas sensors in the last few years due to their display of high response, quick response, low power consumption, small size, and low operating temperature. Gas nanosensors built by MWCNTs and carbon nanoparticles and nanospheres as well as multiple walls (MWCNTs), and aligned CNTs intensely explored, and the modification of MWCNTs with functional groups and polymers for gas sensors were also considered [24-26].

It reported that MWCNTs used as sensitive nanomaterials for surrounding ambients like SO_2, NH3, NO_2, and other (VOCs) volatile organic compound recognition. The absorption of hazard gaseous molecules can significantly stimulate the matrix to produce electrons, and holes affect the conductivity by donating and withdrawing the MWCNTs, changing their electrical properties. The high and fast response of the MWCNTs gas sensors has been positive. The drawback of these sensors, however, is their slowness and partial recovery. To date, there has been a variety of attempts to overcome this limitation. It reported that the electrical conductance of semiconducting multiple-wall tubes dramatically changes when the MWCNTs exposed to SO_2, O_2, and NH_3 [27-29]. Theoretical work has revealed how the electronic properties of CNTs vary when the MCNTs exposed to reducing or oxidizing hazard gases in the MWCNs-SO2 system [27, 30, 31].

MWCNT films reported showing a p-type semiconducting system with decreasing resistance upon exposures to sub-ppm concentrations of hazard gases as SO_2. Also, Gas sensor devices usually use metal oxide semiconductors like TiO_2, and ZnO, as sensing materials because of their excellent electrical properties. Therefore, to increase the permeability of the material to absorb more gases, the MWCNTs are usually mixed with clusters of iron nanoparticle, unlike the MWCNT. Chemical functionalization is a method used to improve both processibility and sensing performance of MWCNTs. Firstly, it allows the unique properties of MWCNTs joined to other materials, such as nanoparticles, and nanospheres, to generate a hybrid sensing system with enhanced sensitivity, selectivity, and faster response time Conducting and semiconducting organic films with MWCNTs are promising gas sensing [32-36].

Secondly, it can improve the dissolution and dispersion of MWCNTs in various solvents, which opens the door to cost-effective methods to construct sensors with simple techniques. Theoretical studies on using the nanoparticles-functionalized MWCNTs reported that these tubes and nanoparticles act as reactive locations to target the gas molecules leading to an alteration in electrical conductivity of the system due to the absorption of gas molecules [37, 38].

Recently, it reported that MWCNTs/metal oxides composites, based on either pure MWCNTs or MWCNTs with metal impurities could be used to detect SO_2 at room temperature and higher temperatures with relatively high sensitivity. Nevertheless, additional efforts are still required to optimize the production processes and the operational circumstances of the system to create a system with various applications in nanoelectronics. The synthesis and fabrication of highly sensitive MWCNTs- SO_2 nanosensor accessible [32, 37, 39, 40].

2. Experimental details

2.1. Synthesis of materials

The gas sensing materials properties characterized by scanning electron microscopy (SEM), and direct current (DC) electrical resistance at different gas concentrations and varying temperatures.

MWCNTs obtained from Rice University, Houston. The MWCNTs mixed with carbon nanoparticles as a matrix to absorb the hazard gases. It is necessary to have open tubes and opened side nanospheres to enrich the porosity of the matrix to produce more surface to interact with SO_2 gas molecules, which are typically closed directly after the synthesis to purify it from the other carbon cluster it heated by 400 °C degree. The solution of deionized water and MWCNTs centrifuged to separate the amorphous carbon from the carbon nanotubes. They are then sonicated by an ultrasonic finger several times to crack the structure in the solution. The process of sonication is prepared with an ultrasonic probe (Finger ultrasonic generator Up 200S) with 40 Watt at full cycle for one minute, the process cut the tubes to make them smaller with more porosity. The sonication also increases the material porosity this leads to trapping more gas molecules inside the composite as well, it observed that too long sonication make the stability of the composite solution worse and inferior.

2.2. Fabrication of Gas Nanosensor

The ultrasonic treatment cuts the multi-walled carbon nanotubes. Figure (1): SEM images of MWCNTs. MWCNT gas sensor was fabricated by a conventional lithography process using a sapphire substrate. The gas sensor is composed of a sensing layer, a particular pair of hair comb-shaped gold-plated electrodes for I-V measurements. A sensing layer, composed of a gas sensor and a Cr heater resistor. Casein films prepared with the spin-coating technique of aqueous casein solutions on glass surfaces. Thick films with an equal weight ratio of MWCNT composite 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 700 rpm/min, and the period of the coating was 30 seconds.

After that, the coating layers heated in the air using an Infra-Red source, drying at approximately 150°C for one hour, to evaporate the solvents in the coating layers. Then, the sensor connected with copper wires to the electrometer and the temperature controller. The sensor located inside a programmable 3- zone tube furnace used as a sealed cylindrical chamber filled by compressed SO_2 gas. The sensor characteristics observed from the resistance varying in air and SO_2 atmosphere with gas different concentration of gas 0.5, 1, 2, 5, 10 and 20 ppm and at a temperature varying from 25–250°C. The response and recovery, as a function of time, monitored and recorded via an interfaced personal computer, the temperature does not exceed .412 °C, after this temperature the structure of MWCNT will be damaged as shown is a thermogravimetry diagram in Figure 1, it is due to the burning of amorphous carbon. Weight loss between 412 and 600 °C attributed to the oxidation of MWNTs. Final residual weights of 7, respectively, revealing a purity of about 90% for the purified MWCNTs. Itis due to the burning of amorphous carbon. Weight loss between 412 and 600 °C attributed to the oxidation of MWNTs. Final residual weights of 7, respectively, revealing a purity of about 90% for the purified MWCNTs.

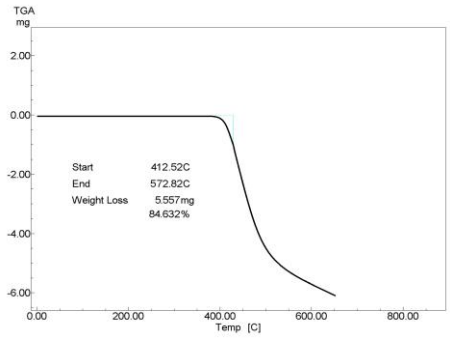

Fig. 1. The initial weight loss for MWNTs sample at 412 °C.

The response and recovery time defined as the time for the sensor to reach 90% of its total resistance variation. For SO_2 gas sensing, the sensor was loaded in the chamber and then dry air pumped for 5 min to make a base measurement line steady until the sensor's response reached a constant value. When the sensor reacts with SO_2, the response is measured; and the chamber pumped by a rotary pump for five minutes. Furthermore, the process repeated for a higher concentration and higher temperatures.

3. Results and discussion

3.1. Structural characterization

The morphology of the MWCNTs and Carbon nanoparticles networks, in figure 2. However, the MWCNTs composite image shows an entirely different morphology in which the nanotubes are well dispersed and their surfaces decorated with Carbon Nanoparticles. Some clusters of Carbon nanoparticles also observed in at nanotube interjunctions and surface defects.

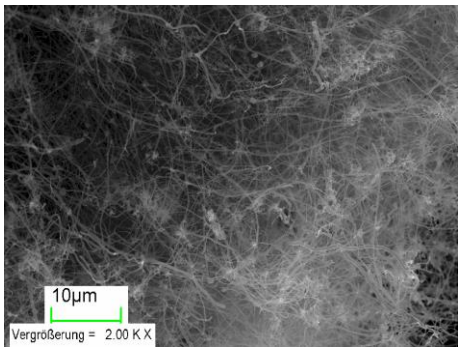

Fig. 2. SEM (scanning electron microscope) images of (a) multi-walled carbon nanotube (MWCNT) bundles.

SEM Figures (3 left and right) represent a high abundance of pure MWCNTs bundles with different chirality which is forest-like and twisted around each other, forming multiple tube robes of the average diameter of 140 nm and about ten µm length. Figure (3, L, and R). SEM images of MWNTs / Nanoparticles and nanospheres.

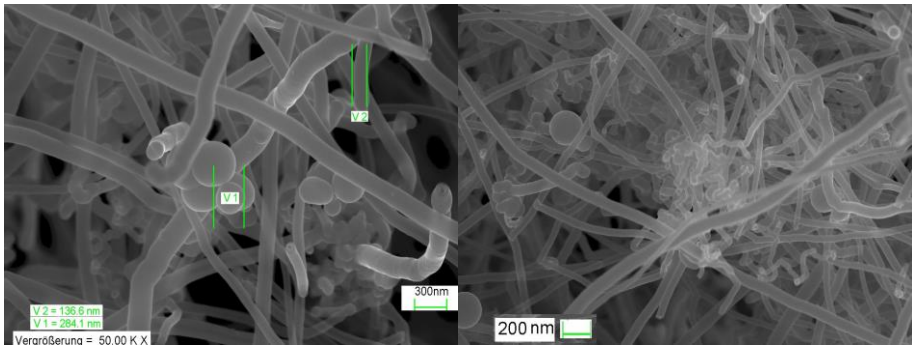

Fig. 3. left and three right. Show a SEM (scanning electron microscope) images of (a) multi-walled carbon nanotube (MWCNT) bundles and Nanoparticles and Nanospheres, twisted nanotubes on the right image.

To further clarify the electronic nature of the nanotube, more detailed electrical mapping of the junction region has been obtained via (CITS) Current Image Tunneling Spectroscopy in which a (current-voltage) I–V spectra was acquired at each pixel in the imaging mesh, providing 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 shown in Fig. 4.

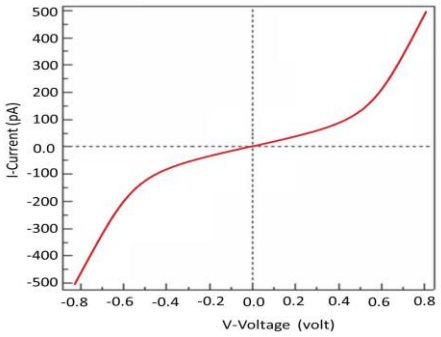

Fig. 4. I–V curve recorded over MWNTs sample at a point on the junction.

These spectra considered the semiconducting of wall carbon nanotubes. It should be noted that the most brilliant feature of carbon nanotubes is the coexistence of metallic and semiconducting properties of MWCNT's and how difficult it is to distinct it. It is possible that the tunneling of electrons somewhat explains the junction twisted in the considered case between MWCNT's in a bundle or between the MWCNT bundle and Carbon nanoparticles on a highly cleaned oriented pyrolytic graphite HOPG substrate. Comprehensive information about the surface topography and conductivity of multiple-walled carbon nanotubes can be attained by high-resolution scanning tunneling microscopy (STM) images in the nanoscale, which is beyond the scope of this study [41, 42].

MWCNT composite can be applied in many types of sensing devices, achieving a good dispersion at a sizeable specific area it might seem like a primary composite of materials and have significantly influenced the sensing performance of the composite films. From the STM and SEM results, it observes that the sonication considerably reduces the baseline noise of the sample without appreciable changes in the amplitudes of responses [41, 42]. Namely, the response and recovery characteristics depend on how MWCNT bundles can untangle to utilize the side surface area of MWCNTs. Also, MWCNTs are generally in a bundle from where interaction is through weak van der Waals forces or a transient hydrogen bond; this phenomenon makes them gather. Namely, it is needed to consider the objectionable reduction of the specific area due to the

formation of bundles. However, the agglomerates of MWCNTs breaks down by the intensive sonication, which cause baseline fluctuations and well-dispersed samples are likely to provide sensor signals with reduced noise.

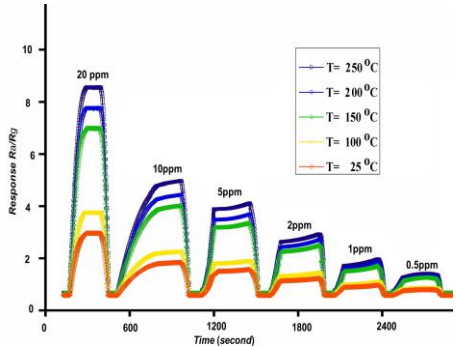

Fig. 5 shows the time response of the gas sensitivity defined as the ratio (Ra/Rg) of electrical resistance for the MWCNT sensor at different temperatures and SO_2 gas concentrations where Ra and Rg are the resistances of the sensor in air and gas under similar conditions at the same temperature. The gas concentration defines as the ratio (Ra/Rg) of electrical resistance for the MWCNT sensor at different temperatures.

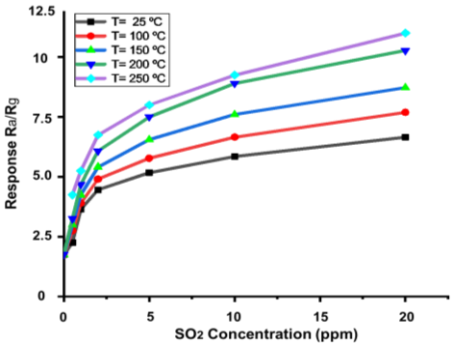

Fig. 6 shows the SO_2 gas concentrations sensitivity of MWCNTs.

The calibration curves of the complete response of the MWCNT sensor versus SO_2 gas concentrations plotted in figure 6 at different working temperatures. As it is, the sensor exhibits considerable enhancement in the response in the whole gas concentration range, which examined. When the pure MWCNTs sensor exposed to SO_2, The resistance of the matrix decreases, this decrease explained by the conventional p-type semiconductor theory of the tubes electronic gaps structure. An electron charge transfer forms acceptor to the p-type semiconductor electron-accepting molecules upon exposure to the electron-accepting gases such as SO_2 resulting in the Fermi level shift of the MWCNT closer to the valence band density of states of an MWCNT. This shift developed the hole carriers in the matrix and decreased its resistance. It considered now that MWNTs tend to conduct at room temperature, while MWCNTs act as semiconducting materials. However, MWCNTs can contain some semiconducting tubes among vast metallic ones [41, 43]. The semiconducting MWCNTs utilized as materials of gas sensors, but the molecular interaction effects over metallic and semiconducting tubes. Similarly, the inner tubes in MWCNT films blocked from interacting with SO_2 because the molecules are not expected to diffuse into MWCNT films [41, 44, 45].

The maximum response is about eleven achieved at higher temperatures (250ºC) and higher gas gas concentration (20 ppm). However, at room temperature (25 ºC) and low gas concentrations (0-2 ppm), the sensor shows a maximum ratio of response of about four, while the reaction is about six at 250 ºC for the same gas concentration.

It is noted that response and recovery times are estimated at 100 seconds and 170 seconds, respectively. The response time at higher temperatures and gas concentrations becomes slightly more extensive. The smaller the concentration of SO_2, the higher the response time. This occurs because it takes some time for the SO_2 target gas to have the specific area on the sensing surface when it flows into the gas chamber toward the target. The fewer the molecules that come in, the longer it takes for the gas-sensitive surface to be covered and saturated with adsorbed molecules. On the other hand, negligible fluctuations in the sensor baseline observed during the gas evacuation process. Figure 6 (above) shows the SO_2 gas concentrations sensitivity defined as the ratio (Ra/Rg) of electrical resistance for the MWCNT sensor at different temperatures. Figure 6 (down) shows the time response of the SO_2 gas as the ratio (Ra/Rg) [33, 41]. The SO_2 gas responses from the MWCNTs sensor presented in figure 6 (above) at different temperatures and different SO_2concentrations. Carbon is well known to be an n-type semiconductor, and the very strongly electrophilic SO_2 gas molecule acts as an electron acceptor when it adsorbs on the surface. Therefore, when Carbon is exposed to SO2 gas, the resistance increases according to the increased number of SO_2 gas molecules adsorbed by the surface. However, the presence of the MWCNT network, which p-type semiconductors, play a predominant role in the overall change in the resistance of the sensor. Also, 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 MWCNT sensor observed in our results, which is larger than that of the MWCNT sensor.

Fig. 6 (above) illustrates the maximum responses of the MWCNT sensor versus gas concentrations at different working temperatures. The baseline resistance in an air of this sensor changes from 1.5 kiloOhms at room temperature to 3.7 kiloOhms at 250 °C. 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 a relatively high-temperature range (150-250 ºC) and set B represents that for lower temperatures (25-100 ºC). The average response changes from 1 to 4.5 for set A and from 0.5 to 1.3 for set B, which is much higher than that of pure MWCNT sensor. It is worth pointing out that the response and recovery times for MWCNT sensor considerably reduced to almost half of that for the MWCNT sensor. This indicates that the role of temperature is more pronounced for large gas concentration. On the other hand, for the MWCNTs nanosensor, the temperature found to be nearly ineffective throughout the entire temperature range, except between 100 ºC and 160 ºC where a considerable increase of sensitivity is observed, but at a temperature smaller than 90 ºC and larger than 160 ºC the sensitivity remains almost constant. This recommends that the addition of specific amounts of Carbon nanoparticles and nanospheres to the (MWCNTs) matrix predictable to play a significant role in tuning the sensitivity to the gas molecules during gas adsorption and desorption and optimizing the sensors working temperatures. Compared to conventional polymer-based gas and solid-state and sensors, that operate at higher temperatures with limited sensitivities [46]. This composite MWCNT 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 [13].

Hence, better results obtained by controlling the Carbon to MWCNT weight ratio to have suitable material with a more specific area, the nanotubes dispersion, and alignment, which is still under investigation. It recommended that the recovery time was relatively long because of the higher surface energy between MWCNTs and SO_2 reacted with SO_3 molecules with the catalytic surfaces of the bundles of nanotubes.

4. Conclusions

A new composite of MWCNT gas sensor was developed here with high sensitivity and favorable response properties in detecting SO2 gas at different temperatures and gas concentrations with changed temperature responses ranging from room temperature to 250 °C. The experimental MWCNT/ Carbon nanosphers sensor was able to detect Sulfur dioxide molecules at levels of just 0.5 ppm.

This study aimed to assess the possibility of using MWCNT-based composite as an innovative SO_2 nanosensor for monitoring applications in the conservation of cultural heritage. Scarce, valuable archaeological materials are consisting of inorganic materials like marble, calcite, calcareous materials, and organic materials like paintings, canvases, and other art materials, both outdoor and indoor, to regulate the museums and galleries environment from harmful gases like SO_2.

Improvement of the sensor's performance at lower gas concentration and temperatures is still under extensive investigation to find other innovative methods to increase the porosity of the new nanomaterial, to use it as a filter for harmful gases. Moreover, this is a capable step toward the progress of smart devices with extensive analytical capabilities.

At room temperature, MWCNTs with equal weight ratio has shown quite high sensitivity to SO_2 with levels as low as 0.5 ppm; this allows it as a nanosensor to control the setting of the places where the artifacts found. Considerable increases in the sensitivity of the matrix are at higher temperatures, up to 250°C in comparison to MWCNT free MWCNTs. All tested sensors exhibit high stability and a relatively low response and recovery time. The primary response values of the composite attained at temperatures ranging between 100 and 250 °C and gas concentrations higher than 2 ppm. For all gas concentrations, the MWCNT sensor shows an impressive performance at temperatures higher than 100 °C compared to the pure MWCNT nanosensor.

The results of the work show that this type of material is surprising, revealing that the measured sensitivity upon exposure to SO_2 strongly depends on the changing matrix of the microstructure and the preparation conditions of the MWCNT. The hazard gases detection mechanisms, as well as the optimal gas sensing parameters, were discussed.

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