Room temperature detection of sulfur dioxide using functionalized carbon nanotubes

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The construction of a simple sensor structure sensitive to sulfur dioxide (SO_2) based on multi-walled carbon nanotubes (MWCNTs) functionalized by nitric acid is described in this study. The functionalized MWCNTs were comparatively analyzed by X-ray diffraction, Raman, and FTIR spectroscopy methods, and their morphology was observed by scanning electron microscope (SEM). The sensitivity to 5 ppm SO_2 gas is based on the change of resistance of functionalized MWCNTs. Tests on the fabricated sensor were performed at room temperature and defined that functionalized MWCNTs are sensitive to SO_2 gas compared with the pristine MWCNTs.

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1. Introduction

Sulfur dioxide (SO_2) is a colorless gas that is easy to identify by its strong smell and flavor. Like CO_2, it is mainly produced by burning fossil fuels and some industrial operations. Its high concentration may lead to respiratory issues, particularly in vulnerable populations like asthmatics. It also contributes to acid rain which can cause skin wounds and hair loss in human health, as well as destroy vegetation, appearance, and quality of buildings [1]. For that reason, there is a high demand for SO_2 sensors in our lives. The primary characteristics of the sensors are often their rapid response, selectivity, and quick recovery time. There are different materials and methods used for the detection of SO_2 gas. One of them is a vanadium tungsten titania (VWT) $V_2O_5/WO_3/TiO_2$-based resistive-type SO_2 sensor. VWT is a well-known catalyst material for good selective catalytic nitrogen oxide reduction with proven excellent durability in exhaust gases. The resistance of VWT decreases with an increasing SO_2 concentration. The best sensor response to SO_2 occurs at 400 °C using Au electrodes. The sensor response value is independent of the amount of added vanadium but dependent on the electrode materials at 400 °C [2]. There are other metals and metal-oxide nanostructures-based SO_2 sensors, such as CeO_2, WO_3, V_2O_5-TiO_2, MoO_3-SnO_2, and NiO sensors which contain these types of materials that operate at higher (<500 °C) than room temperature [3].

Another type of sensor is a carbon material-based sensor which has a great adsorption ability [4]. Carbon has many modifications, so one is Carbon nanotubes (CNT). It was discovered by the Sumio Iijima during fullerene syntheses with arc discharge method in 1991 [5]. Carbon nanotubes are needle-like tubes consisting of one or more rolled graphene layers [6]. CNT has special mechanical, electrical, and electromechanical features [7,8] and these make them interesting for many applications, especially for making sensors e.g., pressure sensors [9] and chemical sensors [10,11]. There are various techniques used for the growth of CNTs. Three popular methods are arc discharge [12,13], laser ablation [14,15], and chemical vapor deposition (CVD) [16,17]. Making sensors from synthesized CNT needs to be functionalized because functionalization enhances the reactivity, improves the solubility, and provides an avenue for

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further chemical modification of CNTs such as ion adsorption, metal deposition, and grafting reactions [18,19]. There are two types of functionalization: covalent functionalization and non-covalent functionalization [20]. Many covalent functionalizations demand much time and several chemical reactions [21].

This paper reports the one-step functionalization of MWCNTs by nitric acid and its application to the SO_2 gas sensor. The MWCNTs were characterized by the Raman scattering and the electrical properties were investigated by structuring electrodes onto the CNTs and measuring their change of resistance.

2. Experimental

2.1. Functionalization of MWCNTs

Commercial pristine MWCNTs synthesized by the chemical vapor deposition (CVD) technique were purchased from SWENT company (USA). The length and diameter of the MWCNTs were 1–25 μm and 10–40 nm, respectively, while the purity of MWCNTs is greater than 93% as stated by the supplier. Nitric acid (HNO_3) with 69-70% concentration was purchased from JT Baker (US). 1,25 gr of pristine MWCNTs was refluxed in 100 ml nitric acid solution by the MS-H280-Pro LED Digital Magnetic Hotplate stirrer. The stirring speed was kept stable at 500 rpm, the temperature was 150°C, duration of stirring was 2 hours. After refluxing, the solution was cooled to room temperature. MWCNTs were filtered out using a cellulose acetate membrane with a pore size of 22 nm and washed several times with deionized water until pH 7. At the end of the process, the solution was dried in a vacuum oven at 80°C overnight to remove water. To determine the functionalization of MWCNTs, they were added to distilled water and mixed in an ultrasonic bath for 5 minutes, the result is seen in the photo below. For preliminary controlling of functionalization, the product was mixed with distilled water and sonicated for 30 minutes.

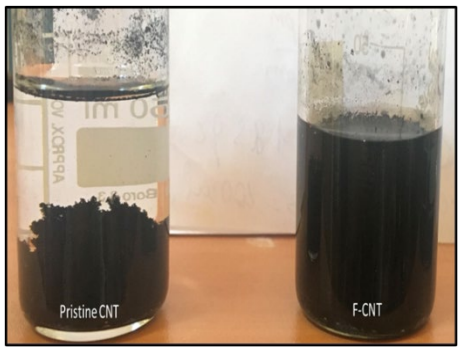


Fig. 1. Water dispersion of a) Pristine MWCNT; b) Functionalized MWCNTs.

Fig. 1 illustrates two kinds of MWCNTs solution in water. Solution A consists of pristine MWCNTs and distilled water after sonication, it agglomerates and settles to the bottom in a few minutes. However, after the sonication of solution B which consists of functionalized MWCNTs and distilled water, the CNTs are dispersed easily and stay for a long time (more than a month) without precipitation. This observation depicts that MWCNTs oxidized successfully.

2.2. Sensor structure design and test

Functionalized MWCNTs suspended in pure water at a concentration of 0.1 g/3 mL were dropped onto ceramic glass substrates and successively dried at 40 °C for 15 min. Afterward, silver paste contacts were deposited on ceramic glass substrates and dried at room temperature. The copper wire was adjusted with the silver contacts then the ends of the wire joined to the source

meter or analog-digital converter (ADC) connected to the computer. The test of the sensor sensitivity with the SO_2 vapors was carried out according to the scheme in Fig. 2.

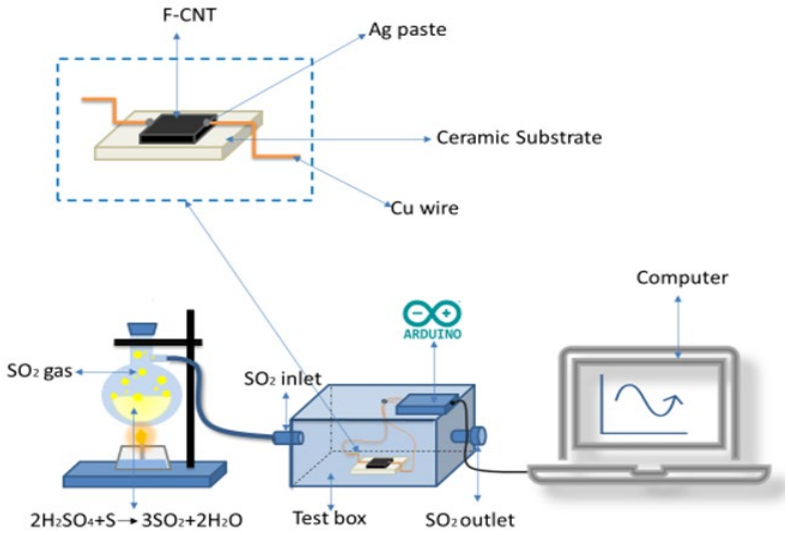


Fig. 2. Design of sensor structure and testing scheme.

SO_2 is obtained from the reaction of Sulfuric acid and Sulphur. According to the test box volume, the first reagent dosage for 5 ppm SO_2 gas was taken. The testing sample was placed in the test box so, that produced gas flowed into it and was removed from the box using a special pump.

3. Results and discussion

3.1. Structural and morphological analysis

X-ray diffraction patterns of pristine and functionalized MWCNTs are shown in Fig. 3. Three peaks at 26.5˚, 43.62°, and 53.5° are observed on both graphs a) and b), which corresponds to the interplanar spacing between the MWCNTs walls and is marked as CNT (002), (100), (101) and (004) indexes. The intensity of the 002-peak associated with CNT is stronger than other x-ray diffraction peaks due to the presence of the more tangled nanotubes in the analyzed sample. In addition, the X-ray analysis confirms that the functionalization doesn't damage the tubular structure of the nanotubes.

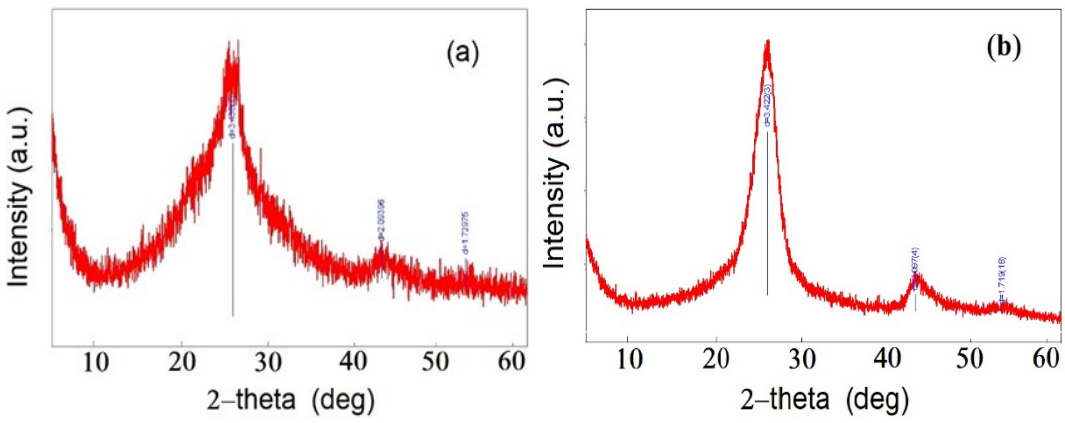
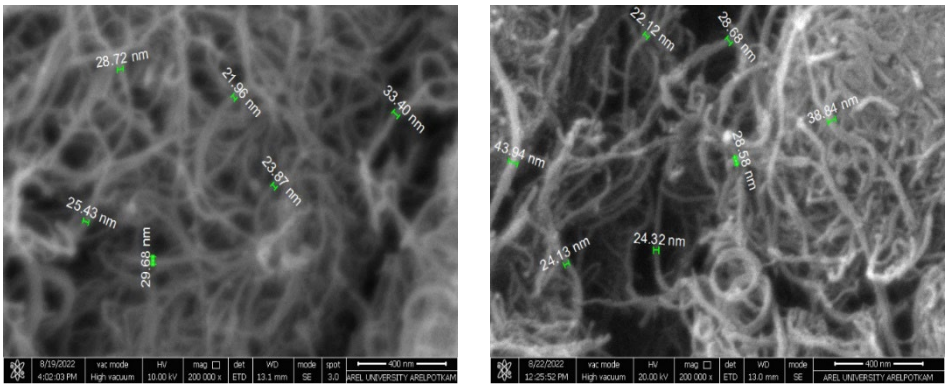


Fig. 3. X-Ray diffraction pattern of a) pristine and b) functionalized MWCNTs.

Fig. 4. illustrates the results of the SEM analysis. It can be seen from the images, pristine MWCNTs have a smooth surface thus, amorphous carbon or clusters are not observed. Regarding the result of the functionalization by a strong oxidant (HNO_3) the CNTs are not broken and their surfaces remained smooth. Eventually, both analysis results show that functionalization has no detrimental effect on the quality of CNTs.



a) *b)*

Fig. 4. FEGSEM images of MWCNTs before (a) and after (b) functionalization.

3.2. Raman spectroscopy

Raman spectra measured on pristine and functionalized MWCNTs network are given in Fig. 5 by the EnSpectr R532 Raman Spectrometer with 532 nm green laser in 400-4000 cm^{-1} range. Radial breathing mode (RBM) in the sample is not observed since the RBM signal from large diameter tubes, especially in multiwall carbon nanotubes is usually too weak to be observable [22].

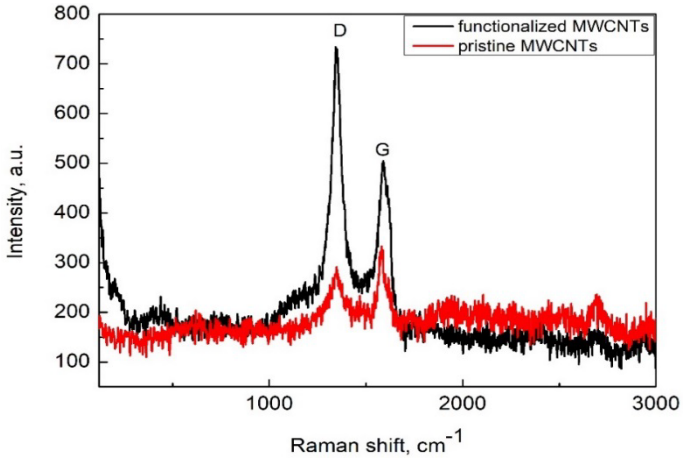


Fig. 5. Raman spectra of D- and G- mode of pristine and functionalized MWCNT.

The D band for pristine MWCNT is 1344 cm^{-1} and for functionalized MWCNT is 1349,6 cm^{-1}. It can be seen from the figure that, in addition to the spectral shift, the intensity of the D band in the functionalized MWCNTs has significantly increased compared to the G band. It would relate to the multiple graphite layers and sp^3 hybridized carbon atoms in MWCNT, which affect the intensity of the D band of the sample. G band for the pristine MWCNT is 1581 cm^{-1}, for the functionalized MWCNT it is equal to 1587 cm^{-1}, ID/IG = 0.885 cm^{-1} for pristine MWCNT, and

ID/IG=1.38 cm^{-1} for functionalized MWCNT. Further, it was observed that the Raman spectrum of functionalized MWCNTs is shifted towards the right concerning pristine MWCNTs spectra. This shift is symbolized by the -COOH attachment to MWCNTs.

3.3. FTIR spectroscopy

FTIR spectroscopy method is used for the analysis of functional (carboxyl-COOH, and hydroxyl -OH) groups, created during functionalization. Fig.4 shows the transmission spectra of pristine MWCNTs (a) and functionalized MWCNTs (b) in the 4000-500cm^{-1} wavelength range. It is observed that the intensities of the peaks between 3400-3560 cm^{-1}, which refers to the O-H stretching of the hydroxyl group from carboxyl groups (O=C-OH and C-OH) are significantly reduced as a result of the functionalization of MWCNTs, indicating a higher absorption compared to pristine MWCNTs [23,24]. The peaks at 1710 cm^{-1} and 1394 cm^{-1} appeared only in the spectra of f-MWCNTs and contributed to the existence of C=O and C-O and C-H stretching vibrations of the carboxylic groups (-COOH), respectively [23]. The intensities of the peak at 1620 cm^{-1} decreased compared with pristine MWCNTs probably due to C=C, C=O stretch modes. Other peaks between 2330-2360 cm^{-1} and 1136 cm^{-1} differ from pristine MWCNTs formed by vibrational absorption of C-O-C bonds and confirm the success of the functionalization process. The presence of oxygen-containing groups on the surface of pristine MWCNTs may be due to partial oxidation during purification, or water absorption from the environment.

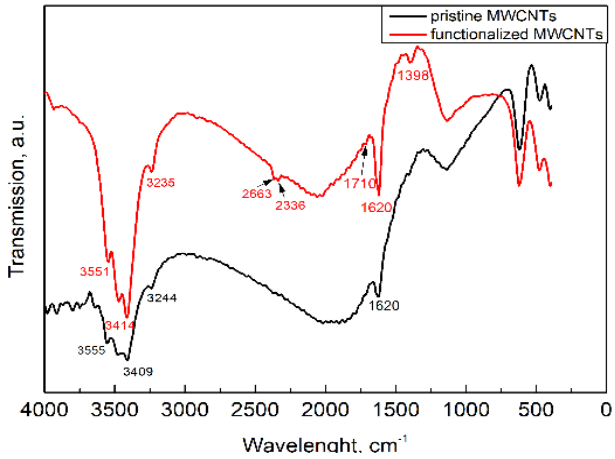


Fig. 6. Infrared absorption spectra of pristine (a) and functionalized MWCNTs samples.

3.4. Sensing characteristics

To investigate the performance and sensitivity of the CNT network as a sensing material, the detection of the SO_2 gas test was carried out, Sensor response (SR) of pristine MWCNT and functionalized MWCNT network during exposure to SO_2 gas was presented using the following equation:

$$\Delta R = \frac{(R-R_0)}{R_0} \quad (1)$$

where ΔR indicated the sensor response, R_0 of the initial resistance of the sensor, and R - indicated the sensor response of functionalized MWCNT. Fig 7. shows the curves indicating the comparative sensing response of pristine and functionalized MWCNTs-based structures to SO_2 gas at room temperature. As can be seen from the figure, the resistance of the pristine MWCNTs-based sensor structure is not changed in the mentioned gas ambient. However, after functionalization, the resistance of the f-MWCNTs sensor structure increases by 77% in 10 seconds.

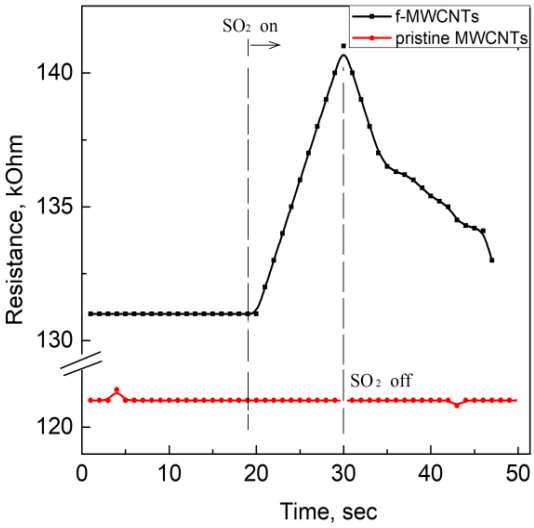


Fig. 7. Sensitivity to SO_2 gas of (a) Pristine MWCNT; (b) Functionalized MWCNT.

Resistance of functionalized MWCNTs starts to increase. Investigations show that the resistance increment is directly proportional to the concentration of SO_2 gas.

To evaluate the stability of the sensor response the testing is repeated consecutively. The results are demonstrated in Fig.8. The Sensor shows stability during initial tests. It should be noted that the recovery time of the sensor starts to lengthen, and its relative sensitivity starts to diminish when the tests are repeatedly performed over a short period of time. To reset the sensor, it is sufficient to heat it up to 50 degrees [25].

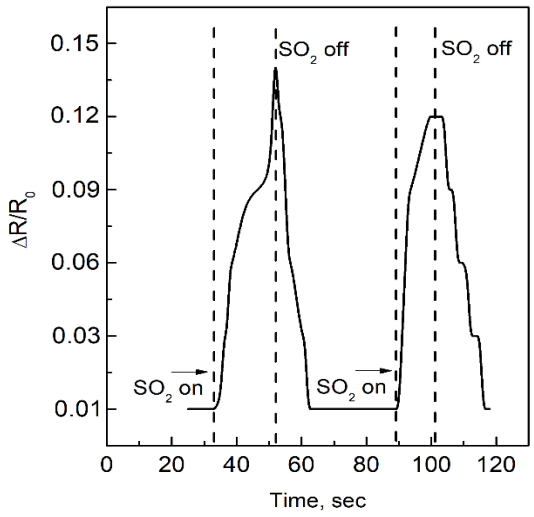


Fig. 8. Sensor response upon exposure to 5 ppm SO_2 gas for repeated testing.

4. Conclusion

MWCNTs are functionalized by refluxing a mixture of HNO_3 and MWCNT. During the chemical process, functional groups emerged on the MWCNT surface and enhanced the sensor response and sensitivity performance of the MWCNT network as a sensing layer. All the experiments and measurements were carried out at room temperature and under normal

atmospheric pressure which is very significant for detecting SO_2 gas in the industrial environment as well as public health concerns.

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