Electrochemical Sensing of H_2S Gas in Air by Carboxylated Multi-walled Carbon Nanotubes

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ABSTRACT: *The electrochemical sensor for detecting of hydrogen sulfide was fabricated. H_2S gas molecules pass through polytetrafluoroethylene membrane with 0.22 μm pore size. Carboxylated multi-walled carbon nanotubes (MWCNTs-COOH) were used to fabricate working and counter electrodes. It can be seen from Field Emission Scanning Electron Microscopy (FESEM) images of working electrode that MWCNTs-COOH are distributed fairly uniform on the hydrophobic membrane. Quantitative results of Energy Dispersive X-ray (EDX) analysis show the presence of carbon (85.95 wt %) and oxygen (12.95 wt %) on the working electrode. The cyclic voltammetry results show the MWCNTs-COOH respond to H_2S. The sensor response up to 56 ppm of H_2S gas was measured by chronoamperometry. The sensor showed linear behavior up to 16 ppm. The detection limit of the sensor is 310 ppb and its sensitivity 48 hours after assembling is 0.1436 μA/ ppm. The averages of response and recovery times for 10 ppm of H_2S were obtained 6.06 and 4.13 minutes respectively. The sensor with functionalized carbon nanotubes has many advantages than the sensor with raw carbon nanotubes; include more uniformity of fabricated electrodes, the greater response and less noise. Using functionalized carbon nanotubes with respect to raw nanotubes increase the response of the sensor by 14.8 times at 10 ppm of H_2S. Also the response of the sensor to 250 ppm concentration of carbon monoxide gas was 4.35 nA that is very low with respect to sensor response for hydrogen sulfide (1.64 μA for 10 ppm of H_2S).*

KEYWORDS: *Hydrogen sulfide; Electrochemical sensor; MWCNTs-COOH; Hydrophobic polytetrafluoroethylene membrane; Sulfuric acid.*

INTRODUCTION

Hydrogen sulfide is a colorless, flammable, extremely hazardous gas with a rotten egg smell. Low concentrations irritate the eyes and respiratory system. H_2S gas affects both oxygen utilization and the central nervous system. A level of H_2S gas at or above 100 ppm is Immediately Dangerous to Life and Health (IDLH) [1]. Exposure to 500 -700 ppm concentrations causes staggering, collapse in 5 minutes, serious damage to the eyes in 30 minutes and death after 30-60 minutes. Exposure to 700 -1000 ppm causes rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes and for higher concentrations immediate death [2]. The H_2S exposure inhibits cytochrome oxidase enzyme and prevents oxygen

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absorption [3]. The detection and monitoring of H_2S is very important, because of its extensive sources such as crude oil, natural gas, hot springs, bacterial decomposition of organic materials and industrial activities, and its serious health effects.

Carbon Nano Tubes (CNTs) are cost-effective nanomaterials for many applications such as pollution detection and environmental remediation that has attracted considerable attention [4]. It is quite reasonable that increasing the contact interfaces between the gases and sensing materials, can significantly enhance the sensitivity. Thus CNTs based gas sensors have attracted a great interest [5]. CNTs can play substantial role in sensors development because of great adsorptive capacity due to large surface area to volume ratio, better electrical characteristics upon exposure to gases due to greater interaction zone over the cross-sectional area, improvement possibility of properties by adjusting the composition, geometry and size of the nanostructures [6]. In spite of the fantastic characteristics of CNTs, there are some properties such as insolubility in all organic solvents, tendency to aggregate together because of high surface energy of CNTs and strong van der Waals attraction between them, and about the gas sensing the lack of specificity to different gases and the low sensitivity to some of them, that may limit their applications [6, 7]. The functionalization of chemical reactants on the sidewalls of the CNTs can compensate its weaknesses and increase conductivity of them which leads to improve sensors. Different types of functionalization are considered by researchers including CNTs functionalized via metal nanoparticles, metal oxide nanoparticles, polymers and CNTs decorated with functional groups [6].

A variety of sensor types are used for detection of hydrogen sulfide in the air. Semiconducting metal-oxide sensors are widely used for sensing hydrogen sulfide. As the reaction of a target gas on the metal-oxide surface alters its electronic properties, the resistance of the metal-oxide semiconductor also changes to operate the sensing system [8]. Many metal oxides have been investigated for H_2S-gas sensing, for example SnO_2 (or doped SnO_2) has been used most widely {e.g., CeO-doped SnO_2 thin film (prepared by the sol–gel technique)} was investigated for the detection of H_2S at room temperature [9]. The CeO – SnO_2 thin films can detect as low as 5 ppm of H_2S. Also resistive sensor was fabricated using single-walled carbon nanotubes decorated with silver nanoparticles at room temperature in a background of nitrogen that showed irreversible response to H_2S, due to the formation of Ag_2S. Furthermore, the sensor is not selective [10]. Also Au-decorated SWCNTs were used for detecting H_2S at room temperature in air. The sensor was fabricated by electrodepositing gold nanoparticles on single-walled carbon nanotube networks. Sensor arrays were micro fabricated on a silicon substrate using standard lithographic patterning that operated as resistive films. The detection of H_2S at concentration as low as 20 ppb was shown. This sensor is very sensitive to other gaseous species such as NO_2 [11, 12].

The Co_3O_4-SWCNT composite was used for detecting H_2S at 250 ºC as a resistive sensor too. The small amount of CNTs within the nanocomposite makes the sensor more sensitive to hydrogen sulfide and small cross-sensitive to ammonia, methane, and hydrogen [13]. Mass change sensing base devices or piezoelectric devices are a type of gas sensors. Quartz Crystal Microbalance (QCM) apparatus and Surface Acoustic Wave (SAW) devices are two kind of piezoelectric devices. Detection of H_2S has been performed by a quartz crystal microbalance [14]. Surface Acoustic Wave (SAW) based H_2S gas sensor was developed by using single-walled carbon nanotube decorated with copper nanoparticles (Cu NP-SWCNT). The optimum operating temperature of 175 ºC was obtained that resulted in the largest frequency shift after exposure to H_2S in air ambient. The sensor is sensitive to H_2S at ppm levels and does not have cross-sensitivity to hydrogen, ethanol or acetone. A 40% relative humidity level destroys room temperature sensitivity and for this reason, the temperature must be above 100 °C for operating the sensor [15, 16]. Also optical chemical sensors based on attenuation of light waves are one of the effective chemical gas sensors that can be categorized into direct and reagent mediated types [17]. As an example of direct optical sensing of H_2S, a compact, rugged and portable fiber-optic evanescent field laser sensor was developed for simultaneous detection of H_2S, CO_2, and H_2O in the gas streams of volcano fumaroles located at Solfatara, Italy [18].

Conducting- polymer sensors are used to gas sensing, due to easy fabrication. The basic idea is to mix

conducting materials with polymers selected for the target gas to form a conducting-polymer-composite sensing material. For instance remarkable responses to hydrogen sulfide have been shown by polyaniline nano fiber composites with transition-metal chlorides. This sensor measured H_2S upon exposure to 10 ppm H_2S in a humid environment [19].

The electrochemical sensors are inexpensive and able to measure a wide range of gas concentration and their selectivity can be obtained by proper selection of filter, working electrode and electrolyte [16]. Moreover they have low power consumption, good linear behavior, relatively good life time and repeatability. Thus it can be said that the electrochemical sensors have considerable benefits. Electrochemical sensors are also used to detect H_2S and other gases. Liquid and solid electrolyte sensors based on electrolyte type, amperometric and potentiometric sensors based on working principle are a variety of electrochemical sensors [20].

As an example electrochemical reactivity and direct determination of sulfide at CNT modified glassy carbon and carbon fiber electrodes in buffer phosphate solution with a detection limit of 9 ppb [21].As mentioned above, electrochemical sensors have several advantages in order to detect hydrogen sulfide such as possibility of performance in ambient temperature and being not vulnerable in a humid environment in a relatively broad range of moisture. Also the use of nanomaterials to reduce the price, minimize the size of the sensor and improve sensor specifications. Since the multi-walled carbon nanotubes have not been studied in electrochemical sensors for measuring hydrogen sulfide in the air, we decided to do this. And for improvement of the sensor, we used functionalized MWCNTs. Therefore according to these reasons, the present study aims to investigating the construction of H_2S gas electrochemical sensor in air by use of COOH-MWCNTs.

EXPERIMENTAL SECTION

In order to measure the concentration of H_2S gas in air we designed and fabricated an electrochemical sensor. The sensor contains: body of the sensor, working electrode, reference electrode, counter electrode, electrolyte container, electrolyte, hydrophilic separators, o- ring, capillary diffusion barrier, and connection wires. The body of sensor was made of polytetrafluoroethylene (PTFE). Electrodes were connected to the galvanostat- potentiostat system with three Platinum-Rhodium (9:1) wires (Johnson Matthey Co., 0.35 mm thickness). Working electrode made using hydrophobic PTFE membrane (Merck Millipore Co., pore size: 0.22 μm). We used PTFE tape for fabricating reference and counter electrodes.

Carboxylated carbon nanotube was purchased from US Research Nanomaterials Inc. COOH functionalized MWCNTs (>95%, OD: 20-30 nm) were used to fabricate working and counter electrodes. At first 21 mg/mL of the mixture of COOH functionalized MWCNTs in N, N-Dimethylformamide (DMF- Titrachem, >99.5%) was prepared and then it was sonicated for 15 minutes. Next 230 μL and 120 μL of suspension were poured on the substrates of the working and counter electrodes respectively, and then were allowed to dry at ambient temperature. The substrate of the working electrode was 2.5 cm×2.5 cm hydrophobic PTFE membrane and the substrate of the counter electrode was 2.3 cm×1.4 cm PTFE tape.

To fabricate reference electrode the 60 nm gold layer was sputtered on PTFE tape (DSR1 Desk Sputter Coater Nanostructured Coatings Co.). Dimensions of PTFE tape were 2.4 cm×1.7 cm. The rate of coating was 10 nm/ minute, the coating time was 300 s, the final vacuum pressure of rotary pump was 40 mTorr, the operating pressure was 70 mTorr, the target diameter was 50 mm, the thickness of target was 0.1 mm, the distance from target to substrate was 60 mm and the coating current was 20 mA. The applied potential between reference and working electrodes was selected 0.01 V for doing measurements. Electrodes were separated with cellulose papers that moistened with 1 mM sulfuric acid (Merck, 97%) electrolyte (2.75 pH). To maintain electrolyte content of the cellulose papers, the electrolyte container at the bottom of the sensor was embedded. Also the diameter of the capillary diffusion barrier aperture was 4.2 mm. The fabricated sensor is shown in Fig. 1.

In order to measure the response of the electrochemical sensor, a suitable system was developed that was shown in Fig. 2 schematically. In this system the specific concentration of H_2S gas enters in the chamber and after influencing on the sensor exits from it. The electrical current due to gas influx is measured and recorded.

The sensing system equipped to three mass flow controllers (MFCs) for controlling exact values of H_2S, N_2 and CO. MFCs of H_2S and N_2 were prepared from

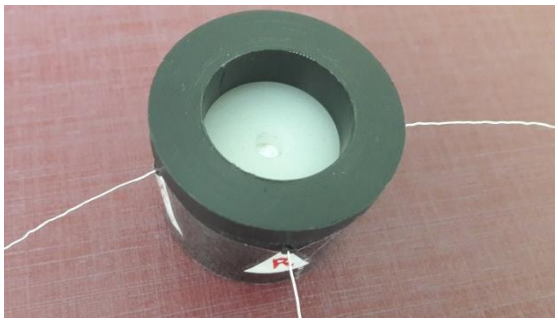


Fig. 1: The image of fabricated sensor.

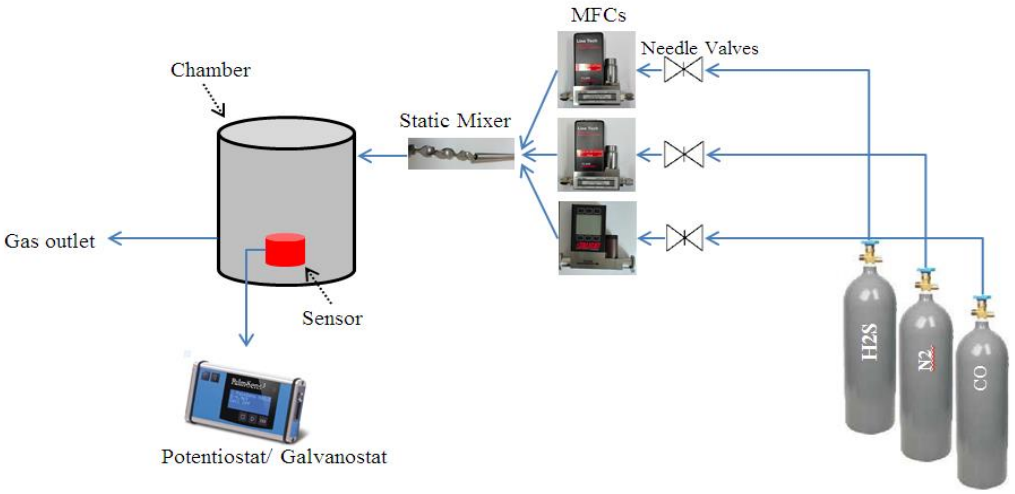


Fig. 2: Schematic image of the fabricated system for measuring sensor response.

Line Tech Co. and the other was purchased from Alicat Co. Also a static mixer for uniform mixing of these gases was designed and fabricated and then placed after MFCs. The measurements were done using chronoamperometry and cyclic voltammetry. We used a PalmSense 3 galvanostat- potentiostat to measure the current and adjust the bias potential of working electrode to reference electrode. The concentration of H_2S gas cylinder was 500 ppm and MFC of H_2S was calibrated for this concentration. The purity of N_2 gas was >99.9995%.

SEM images of working electrode and PTFE membrane were taken with TESCAN MIRA2 and their EDX analysis was done by SAMx. Also SEM image of reference electrode was taken with Hitachi SN3500 and its EDX analysis was done by Ametek Octane Prime.

RESULTS AND DISCUSSION

In order to detect of H_2S gas, carboxylated MWCNTs have been used to fabricate working and counter electrodes. The working electrode acts as hydrophobic permeable barrier that allows the gas molecules pass into the sensor and prevents water loss of electrolyte. The working electrode creates the possibility of contact between gas, electrocatalyst and electrolyte. H_2S oxidation in working electrode produces current which is proportional to the gas concentration within a specific range depending on the sensor's characteristics.

Fig. 3a and Fig. 3b show the SEM images of a PTFE hydrophobic membrane which allows H_2S gas molecules pass through its pores. Pore size of this membrane is 0.22 μm. Fig. 3c and Fig. 3d show the SEM images of working electrode surface. It can be seen that the MWCNTs-COOH are distributed fairly uniform on the hydrophobic membrane. It should be mentioned that the interior surface of working electrode allows the connection of gas with electrocatalyst and electrolyte to create a three phase gas, liquid, and solid interface, that oxidation of hydrogen sulfide occurs on it.

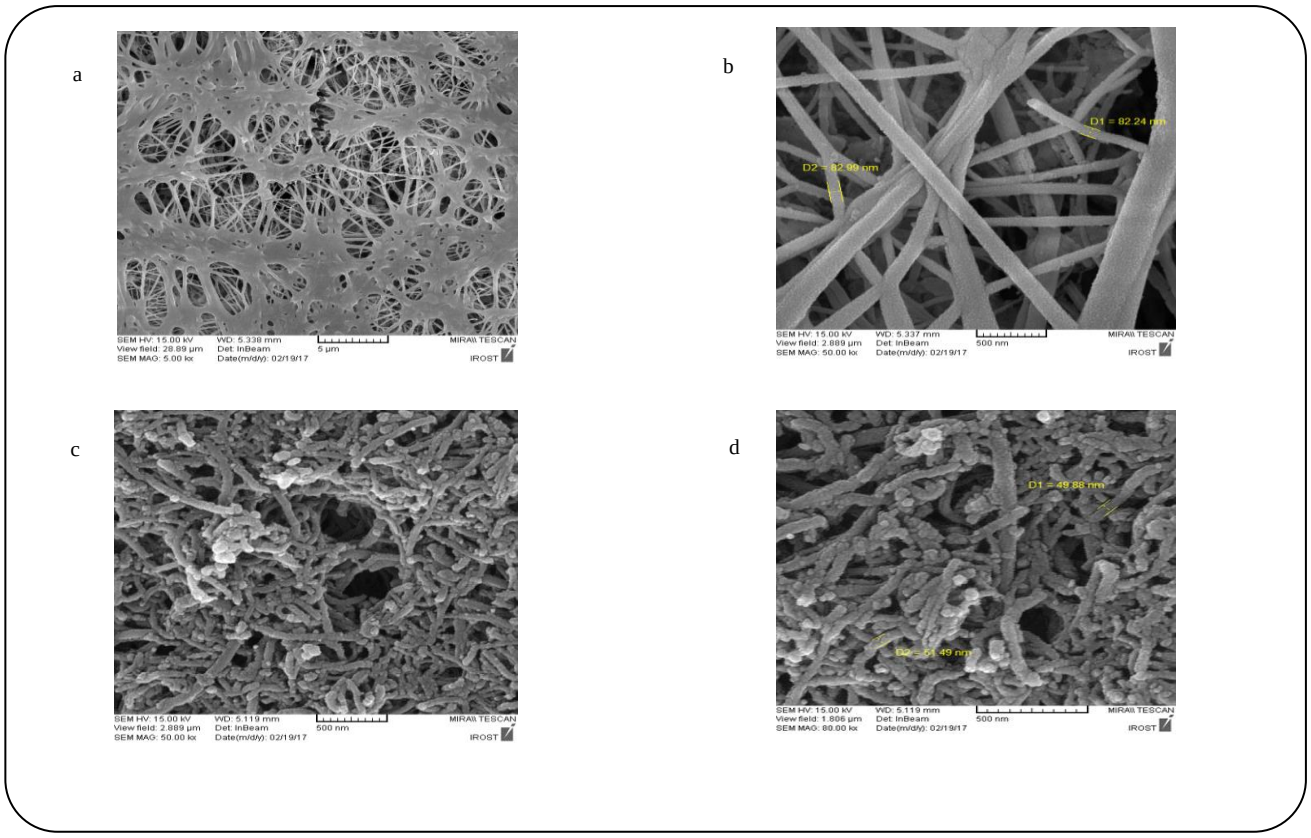


Fig. 3: (a,b) SEM images of a PTFE hydrophobic membrane; (c,d) SEM images of carboxylated carbon nanotubes on the membrane surface.

The hydrophilicity of the electrode coating makes better contact of the aqueous electrolyte (sulfuric acid solution 1 mM), gas and electrocatalyst in microscopic dimensions. Thus the presence of carboxyl group and consequently, the better hydrophilicity of carbon nanotubes facilitate this process. This is while that the outer surface and the thickness of the membrane that is not coated still remain hydrophobic and prevent excessive evaporation.

There are important differences between using MWCNTs-COOH and raw MWCNT: electrode fabrication using MWCNTs-COOH generates more uniform electrodes than use of MWCNT, the other is the difference in performance that includes the much larger output signal and less noise using MWCNTs-COOH than the use of MWCNT. The sensor response when using raw carbon nanotubes to 10 ppm of H_2S is 0.11 µA and that's while the sensor response with MWCNTs-COOH to 10 ppm of H_2S is 1.63 µA.

Fig. 4 shows EDX analysis of a PTFE hydrophobic membrane and EDX analysis of the working electrode. Quantitative results of EDX analysis of membrane and working electrode has been shown in Table 1. Quantitative results of EDX analysis show the presence of carbon (85.95 wt %) and oxygen (12.95 wt %) on the working electrode as expected. While according to Table 1, before stabilization of carboxylated MWCNTs on PTFE membrane, the wt % of carbon was 27.98 and wt % of oxygen was zero. Fig. 5a shows SEM image of reference electrode which was fabricated by coating gold layer on PTFE tape and EDX analysis of reference electrode has been shown in Fig. 5b and its quantitative results have been presented in Table 2.

EDX analysis according to Fig. 5b and Table 2, shows the presence of gold in the deposited layer on PTFE tape and the presence of fluorine and carbon of the tape.

It should be noted, the simplest form of the sensor operating on electrochemical principles has two electrodes. They are working (sensing) and counter electrodes. The current due to oxidation or reduction of gas that is proportional to gas concentration can be measured across a load resistor in the external circuit. As the gas concentration increases so does the current flow,

Table 1: Quantitative results of EDX analysis of PTFE hydrophobic membrane and working electrode.

	Element	Weight%
Membrane*	C	27.98
	F	62.73
	Cu	1.26
	Hf	0.59
	Au	7.44
*These results were obtained after Au coating for SEM analysis		
working electrode	C	85.95
	O	12.95
	F	0.45
	Ti	0.65

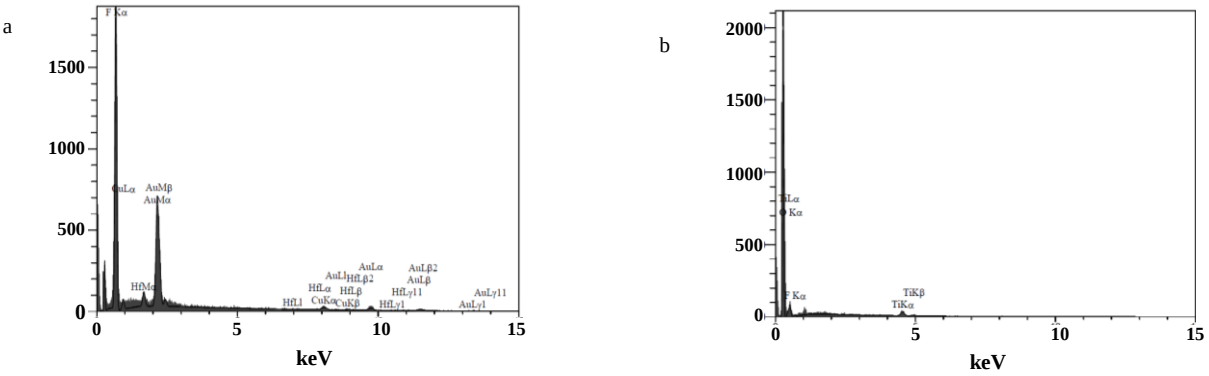


Fig. 4: (a) EDX analysis of a PTFE hydrophobic membrane; (b) EDX analysis of the working electrode.

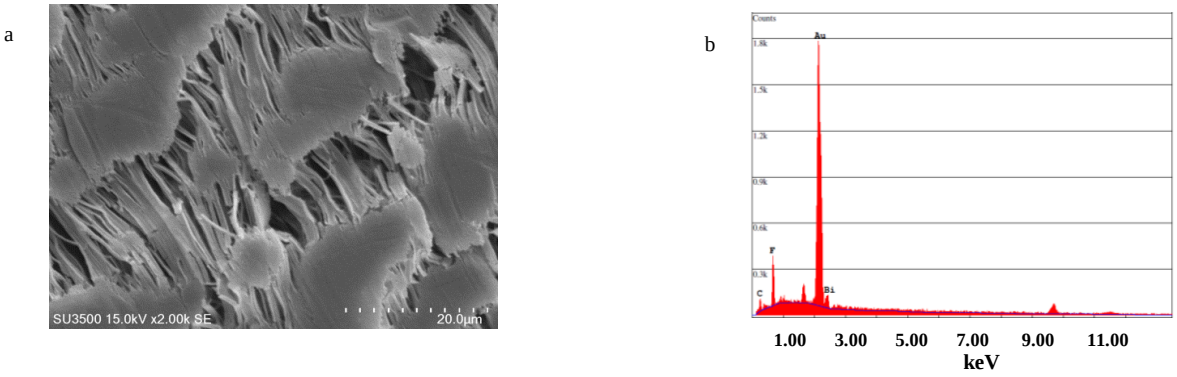
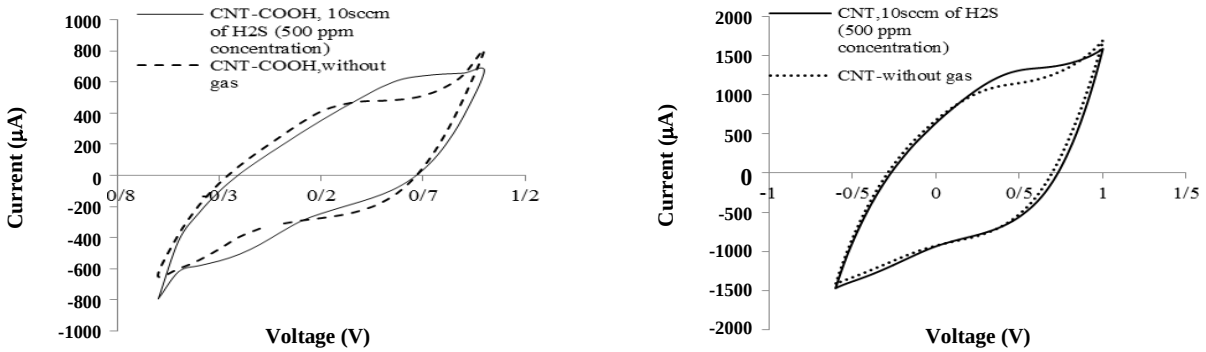


Fig. 5: (a) SEM image of reference electrode; (b) EDX analysis of reference electrode.

causing a change in the potential of the counter electrode (polarization). With the electrodes connected together by a simple load resistor, the working electrode potential follows that of the counter. If the gas concentration continues to rise, the working electrode potential will eventually move outside its permitted range. The limitation imposed by counter electrode polarization can be avoided by introducing a third, reference electrode, and using an external potentiostatic operating circuit. With this arrangement the working electrode is held at a fixed potential relative to the reference electrode and no current flows from the reference electrode.

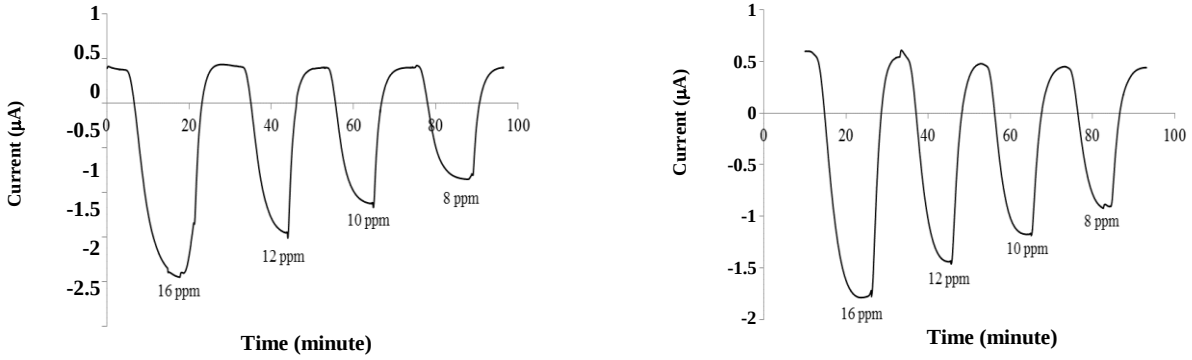
Table 2: Quantitative results of EDX analysis of reference electrode.

Element	Weight%
C	6.86
F	11.13
Au	82.01



a b

Fig. 6: cyclic voltammogarms of the fabricated electrodes, (a) by use of MWCNTs-COOH and (b) by use of raw MWCNTs. Dashed lines indicates voltammograms before exposure to hydrogen sulfide.



a b

Fig. 7: Response of sensor to 16 ppm, 12 ppm,10 ppm and 8 ppm of H_2S in (a) the first and in (b) the second experiment.

Since the main functions of the reference electrode is only to prevent polarization of counter electrode and holding the working electrode at fixed potential, the uniform layer of gold particles can do these functions very well. For this reason we used reference electrode fabricated by sputtering of gold particles on PTFE tape.

Fig. 6.a shows the cyclic voltammogarms of the fabricated working electrode by use of MWCNTs-COOH. The solid and dashed curves indicate cyclic voltammogarms after and before exposure to 500 ppm of H_2S respectively. Also Fig. 6b indicates the same results for the working electrode fabricated by raw MWCNTs. In these voltammograms the scan rate was 0.1 V/s. As it can be seen, both raw and functionalized MWCNTs respond to H_2S, with the functionalized CNTs responding better than the raw MWCNTs.

We measured sensor response up to 56 ppm of H_2S gas in two experiments. The first experiment was done after 48 hours after assembling the sensor and the second experiment was done 24 hours after the first one.

Fig. 7 shows the response of sensor when exposed to 16 ppm, 12 ppm, 10 ppm and 8 ppm of H_2S in two experiments.

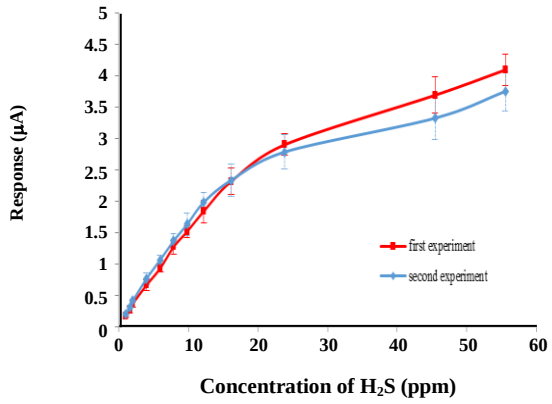


Fig. 8: Calibration curves of the sensor in the first and the second experiments

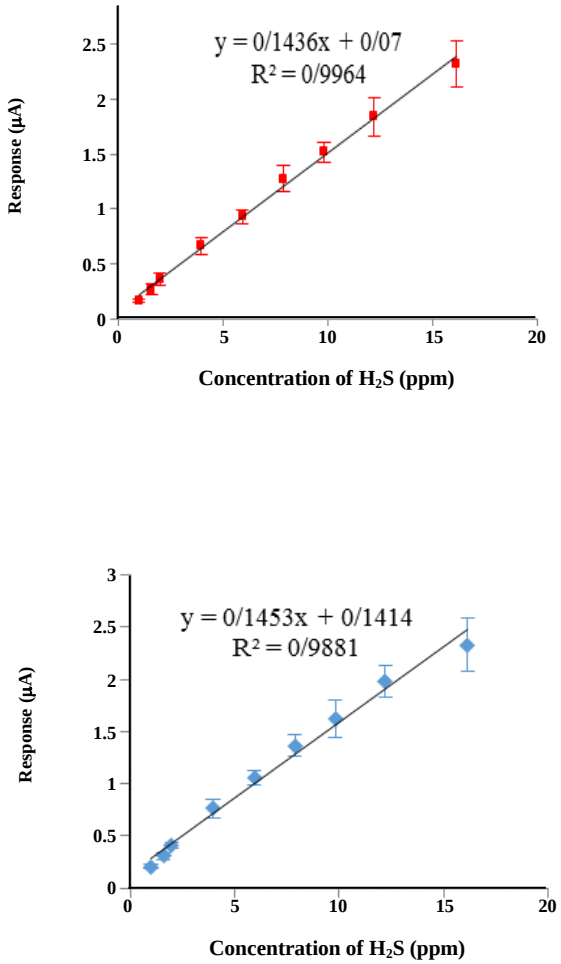


Fig. 9: Linear range of the sensor in (a) the first, and (b) the second experiments

Fig. 8 shows calibration curves of the sensor in the first and the second experiments. As shown in this figure, there is relatively good agreement between the curves in two experiments.

As shown in Fig. 9, the sensor has linear behavior up to 16 ppm during two experiments.

Sensitivity of the sensor is the ratio of the incremental change in the sensor's output (Δy) to the incremental change of the measurand in input (Δx). Therefore the sensitivity of the sensor in linear range is 0.1436 µA/ppm in the first experiment and 0.1453 µA/ppm in the second one.

The detection limit (DL= 3 σ/S, σ is the standard deviation of the sensor response before gas entry and S is the slope of linear range of calibration curve) of sensor 48 hours after sensor assembly is 310 ppb.

The measurement of the sensor response to 10 ppm concentration of H_2S gas was repeated four times, 72 hours after sensor assembly. The averages of response and recovery times for 10 ppm were obtained 6.06 and 4.13 minutes respectively. The average of response for this concentration was 1.64 µA and its standard deviation was 0.036 µA. Also the response of the sensor to 250 ppm concentration of carbon monoxide gas was 4.35 nA that is very low with respect to sensor response for hydrogen sulfide (1.64 µA for 10 ppm of H_2S).

The constructed sensor is a non-consuming sensor that the material of the working electrode is not consumed. Thus carboxylated MWCNTs of working electrode which have metallic behavior, transfer electrical charges and do not consumed. H_2S gas is oxidized at working electrode, therefore electrons and hydrogen ions are generated at this electrode. The counter electrode balances reaction of working electrode by reduction of oxygen molecules that are produced from the air. Since the counter electrode requires oxygen molecules in order to complete the process, insufficient oxygen impairs the performance of the sensor. The current of the sensor is function of H_2S gas concentration in accordance with the following reactions.

$$H_2S + 4H_2O \rightarrow \qquad (1)$$

$$H_2SO_4 + 8H^+ + 8e^- \quad (\text{working electorde})$$

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O (\text{counter electrode})$$

CONCLUSIONS

In recent years a variety of sensors such as gas sensors has been highly regarded. Electrochemical sensors have a special situation among them. They have several advantages in order to detect hydrogen sulfide such as possibility of performance in ambient temperature and being not vulnerable in a humid environment in a relatively broad range of moisture. We have successfully built an electrochemical sensor for hydrogen sulfide gas detection in the air using MWCNTs-COOH as sensing material and PTFE membrane for passing gas and preventing the evaporation of electrolyte water. The use of MWCNTs-COOH makes the electrodes more uniform, much larger output signal and less noise than using MWCNTs. The measurements were done using chronoamperometry and cyclic voltammetry. Using amperograms, calibration curve was drawn which showed linear behavior up to 16 ppm. The sensor response to carbon monoxide is very low.

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