



GAS DETECTION USING SOLID-STATE ELECTRONIC SENSORS FOR CARBON DIOXIDE

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Abstract:

Carbon dioxide (CO₂) detection is crucial for uses in environmental protection, human health, and security, and even in outer space. Our group has investigated a new chemiresistive sensor for CO₂ detection using a nanocomposite of multiwall carbon nanotubes (MWCNTs) and iron oxide (Fe₂O₃). Sensors have been shrunk down to the size of a chip (1 cm²). As a result of the broad range of CO₂ concentrations within which the sensor performed well, it was concluded that the sensor had good sensing performance (100–6000 ppm). The sensing materials' structural characteristics were studied using techniques including field emission scanning electron microscopy, Fourier transform infrared spectroscopy, and Raman scattering. The creation of a depletion layer at the p-n junction in a MWCNT/iron oxide heterostructure is responsible for the substantially enhanced sensitivity of the composite materials to CO₂, and the concentration gradient attracts additional CO₂ gas molecules to the high surface area of MWCNTs. The CO₂ sensor was shown to have a broad dynamic detection range, high sensitivity, low power consumption, and a quick reaction time in the tests.

Key Words: Gas, Molecules, Fourier, Transform, Infrared, Spectroscopy.

Introduction

Global warming, "air quality management, healthcare, mining, and the food industry are just few of the areas that might benefit greatly from a reliable solid-state electronic device for monitoring carbon dioxide (CO₂). At concentrations below 0.04% (400 ppm), carbon dioxide (CO₂) in the atmosphere has no ill effects on humans; but, at concentrations beyond 1%, it starts to have such consequences [1, 2]. When the CO₂ concentration rises to 2-3%, headaches begin within hours. Symptoms of CO₂ poisoning, including lightheadedness, hypertension, and difficulty breathing, kick in at about 4-5%. When concentrations rise beyond 5%, workers experience impairment. At 17% CO₂, coma and death may ensue in a matter of minutes. The Occupational Safety and Health Administration sets the daily average CO₂ limit at 0.5% (5000 ppm) [3]. CO₂ poisoning poses a significant risk to personnel in closed situations like the space capsule, the mine, or the submarine. Because of the health risks associated with inhaling this gas, a sensor that can detect and precisely alarm when CO₂ concentrations approach dangerous levels is essential.

Nondispersive infrared (NDIR) sensors are now the gold standard in commercial CO₂ detection [4]. But their accuracy suffers in extreme conditions like high humidity, low temperature, and extreme pressure. The NDIR sensor measures atmospheric CO₂ content through a ratio of IR light emitted to IR light absorbed by CO₂. When the gas absorption lines start to become broader owing to local impacts of humidity, accuracy starts to become an issue. Absorption lines expand when pressure, temperature, and humidity rise because of increased radiating and collision time [5]. While NDIR sensors have shrunk in size recently, they still dwarf the chip-sized electronic sensors now available. Sensors for carbon dioxide (CO₂) are presently under development in nanotechnology research, with examples including silicon nanowires, Sn₂O₃ microspheres, and polymer nanofilms [6, 7, 8]. Commercial sensors have long made heavy use of metal oxides. They have a fast reaction time and a great sensitivity to various gases. Their high operating temperatures pose a risk in combustible situations and need a lot of energy to run [9]. Unfortunately, the swelling process used by polymer sensors to detect gases resulted in a lack of sensitivity. This demonstrates the need for a more dependable and adaptable sensor with a short reaction time, a large detection range, in-situ monitoring, low power consumption, room temperature functioning, and a compact design.

Due to their mechanical and thermal stability, electrical conductivity, and capacity to absorb gases, carbon nanotubes (CNTs) are a highly valuable sensing material [10]. Since it only has one dimension, almost all of its surface is accessible for the gas adsorption and charge transfer process [11]. This allows for very sensitive detection down to 1 part per trillion (ppb) and reactions to single molecules of foreign gases [12, 13]. Gases that give or take electrons have a significant impact on the electrical properties of CNTs [11]. Carbon dioxide (CO₂) is a weak oxidising gas that, when interacting with CNTs, will remove electrons from the material [14]. This will be reflected in a detectable shift in the nanotubes' resistance. Due to their high surface area to volume ratio [13], carbon nanotubes may be employed to boost sensitivity while requiring less material. Functional groups are required for selective gas adsorption, however these groups are not present in pure CNTs. In order to increase the selectivity, carbon nanotubes (CNTs) may be functionalized and/or doped, or CNT composite materials can be made that can adsorb just the molecules of a desired gas [13].

As a means of detecting carbon dioxide (CO₂), we have created a composite material out of multiwall-carbon nanotubes (MWCNTs) and iron oxide. Due to its huge surface area, carbon nanotubes are able to absorb

a greater number of CO₂ molecules, while the iron oxide nanoparticles serve as binding sites to engage with CO₂ and trigger the resistance change through charge transfer from the MWCNT/iron oxide to the CO₂. With a compact footprint and high sensitivity to CO₂, [12, 13] our MWCNT/iron oxide composite can operate at ambient temperature. Features that set our sensor apart include its tiny size (1 cm²), low power consumption (micro watts), and 2-terminal current-voltage measurement, which makes it ideal for multiplexing and integrating with existing circuits. Connectivity options for this item include both wired and wireless networks for sensing.

A chemiresistive sensor is described in this study that uses the selective characteristics of a MWCNT/iron oxide composite to detect CO₂ gas from 100 ppm to 0.5% CO₂ (OSHA exposure limit).

Materials and Methods:

Synthesis of Sensitive “Materials Nanostructured & Amorphous Materials, Inc. (Houston, TX, USA) supplied the multi-wall carbon nanotubes (MWCNTs), while US Research Nanomaterials, Inc. supplied the iron oxide (Houston, TX, USA). Nitric acid (HNO₃) and sulfuric acid were two of the many chemicals we purchased from Sigma Aldrich. First, mixed acid was used to oxidise MWCNTs. At a volume ratio of 3:1, MWCNTs were refluxed in concentrated sulfuric acid (98% H₂SO₄) and nitric acid (68% HNO₃) at 120 °C for 2 hours. Water was used to rinse it after many rounds of dilution, decantation, and centrifugation. After the MWCNTs were cleaned, they were dried in a programmed oven at 125 degrees Celsius for three hours. Oxidized MWCNTs were successfully dissolved in water to form solutions with uniform particle size distribution. Iron oxide (Fe₂O₃) was included into the MWCNTs at different ratios to create composite materials. Different composites with weight percentages of 5%, 4%, 3%, and 2% of iron oxide were made.

Preparing Sensor Chips. A one centimetre by two centimetre piece of printed circuit board of FR-4 grade serves as the substrate for the sensor chip (PCB). For this sensor chip, sixteen sets of interdigitated electrodes (IDE) were screen printed in gold onto a printed circuit board (PCB). Each paired IDE, also known as a sensor or channel, has the following dimensions: finger width of 70 m and finger gap widths of 100 m.

Drop casting using a micropipette was used to put the oxidised MWCNT/iron oxide composite sensing material onto the chips. There was a 0.3 L aqueous solution of the composite components in each IDE array. Two types of sensing materials were placed in a total of eight channels. Channels 1-4 on the sensors had an oxidised MWCNT/iron oxide nanocomposite coating, whereas channels 5-8 had a coating of oxidised MWCNTs without iron oxide. To determine which sensing material would work best, we employed all 16 channels on a second chip to install four distinct composites of MWCNT/iron oxide.

Trying out the sensors. Tests for CO₂ gas exposure were performed by connecting a sensor chip via adapt board to a Keithley 2700 (Keithley Instruments, Inc., Scottsdale, AZ, USA) to measure the electrical resistance value of each channel on the sensor chip. For the purpose of introducing CO₂ gas at adjustable concentrations in air, an Environics 2000 (Environics Inc., Tolland, CT, USA) gas blending and dilution system is employed. The provided certified gases included 10,000 ppm CO₂ (Matheson) and Zero Air (Praxair). The sensor chip adapt board and a Teflon cover with a nozzle served as a test chamber into which a stream of CO₂ gas was introduced. The CO₂ gas exposure and sensor testing made use of a gas stream of 400 cm³/min. The experiment began with a 10-minute dry air trial to calibrate the sensor chip for subsequent CO₂ exposure and dry air flush cycles. After the sensor chip had been exposed to the CO₂ in air gas stream for 1 minute, it was flushed with dry air for 5 minutes. Each concentration of CO₂ exposure lasted 1 minute, with a 5-minute dry air flush in between. Concentrations ranged from 100 to 6,000 parts per million. The same schedule was followed for a repeatability test, however the CO₂ content was held constant at 4000 ppm rather than gradually rising. Also performed was a step response test with progressively higher CO₂ concentrations” and a final air purge.

Optimization of Sensing Material:

First, four distinct “composite sensing materials with oxidised MWCNTs were created by altering the iron oxide weight % in order to maximise the ratio of the composite sensing material. These four substances were deposited using a sensor chip with 16 IDEs. Drop casting was used to put each material on each of the four channels. Channel resistances were measured after being dried at room temperature and then in a vacuum oven to eliminate any trace of moisture. Due to the presence of non-conductive iron oxide nanoparticles in the composite, channels 1-4, which were plated with 5% (by weight) iron oxide, exhibited no conductance (an open circuit). The average resistance of channels 5-8, which had 4% iron oxide formed on them, was 123 K. The average resistance of channels 9-12 deposited with 3% iron oxide was 3.8 K. The average resistance of Channels 13–16 deposited with 2% iron oxide was 0.7 K. Although the composite materials' sensitivity to CO₂ increased as the iron oxide percentage fell (from 4%, 3%, to 2%), all three performed well [5]. The 4% iron oxide sensor channels responded most strongly to CO₂ exposure, but their increased base resistance also made them noisier than the other three compositions. In light of these results, we settled on using 3.5% iron oxide for future experiments, since it demonstrated respectable sensitivity” and sustained base resistance.

Characterization of Sensor Elements:

Using a “FESEM Hitachi S-4800 SEM, we studied the morphology of oxidised MWCNT, iron oxide nanoparticles, and oxidised MWCNT/iron oxide nanocomposites. The sizes of MWCNTs were generally

between 4 and 10 nm [13]. The picture of iron oxide shows aggregates of spherical nanoparticles of iron oxide with diameters ranging from 5 to 50 nm that are strongly attracted to one another and stick together. Magneto static interaction between particles causes the iron oxide to aggregate into clusters. The MWCNT networks intertwine with the iron oxide nanoparticles in the oxidised MWCNT/iron oxide nanocomposites, as shown by scanning electron microscopy [8]. Using infrared spectroscopy, a study team revealed that they had found chemical connections between the carbon nanotubes and the inorganic covering layers, indicating that the composite material is more than merely a mechanical combination of the components. Iron oxide particles aggregate as free particles and also cling to the surface of oxidised MWCNTs. There seems to be no discernible pattern in the distribution of iron oxide nanoparticles over the MWCNT surface.

Sensing:

Using the described experimental set up, the electrical resistance of the sensors was measured both at baseline and as sensor responds to CO₂. In contrast to the oxidised MWCNTs/iron oxide (3.5% by weight) composite-based sensors, which have an average base resistance of approximately 13,000, the oxidised MWCNT-based sensors have a base resistance of around 1300. The sensor chip was subjected to 100, 200, 400, 800, 1600, 3800, and 6000 ppm of CO₂ at room temperature at the intervals described in the Experimental section. The sensor's response is the normalised resistance ($R - R_0 / R_0$), where R_0 is the resistance at time t without CO₂ exposure and R is the resistance at time t with CO₂ exposure. In response to exposure to increasing amounts of CO₂ gas, the sensor's resistance rose, as shown above. Variations in sensor responses to the same channels of sensing material are likely attributable to the hand-deposition procedure. Two sensor response curves, one for each sensing material. Our analysis of the response curves for the oxidised MWCNT sensor channels and the oxidised MWCNT/iron oxide channels revealed that the latter showed a significant improvement in sensitivity (5 times). This may be because the MWCNT surface and the iron oxide nanoparticles, each providing a unique sensing mechanism, are both present in the composite material and might be used to adsorb CO₂ molecules [9]. A process that produces a modification of surface charges in hybrid metal oxide coated carbon nanotubes has been shown to improve their performance as a gas sensing material. The semiconductor properties of metal oxide are mostly n-type, whereas those of MWCNT are primarily p-type. Due to these dissimilarities, such hybrid films exhibit two depletion areas. The first depletion zone may be seen on the metal oxide's surface, and the second can be found where the nanoparticle of metal oxide meets the MWCNT. Changes in the sensing layer's resistance may be traced back to CO₂ adsorption, which modifies the surface charges in a way that affects electron transmission between heterojunctions. Additionally, MWCNT may introduce nanochannels within the iron oxide matrix. The movement of gases is facilitated by these nanochannels [10]. These nanochannels make it simple for gas molecules to get into the gas-sensing layers, elevating the sensitivity of the sensors. Composite materials made of metal oxides and carbon nanotubes have shown similarly improved reactions. Furthermore, it seems that the sensor response range is expanded upon by the incorporation of iron oxide. The composite material sensor exhibited concentration dependency up to 6000 ppm CO₂, whereas the oxidised MWNT sensor was saturated at 1600 ppm CO₂ [11].

Conclusions:

A chemiresistive sensor made from oxidised MWCNT and nanoparticles of iron oxide was developed and tested in this work for CO₂ detection at ambient temperatures. It was discovered that by combining MWCNT with a small amount of iron oxide nanoparticles, we can increase the sensitivity to CO₂ by 5 times, increase the detection range of the CO₂ concentration from 100 ppm to 6000 ppm, have a quick response and recovery in 10 s, and have good repeatability from measurement to measurement and good reproducibility from sensor to sensor. Researchers have shown that the production of nano-heterojunctions at the interface between nanotubes and iron oxide nanoparticles is responsible for this increased sensitivity. Surface charges are changed by the presence of nano-heterojunctions. Gas adsorption is improved by both the presence of carbon and the nano-channels in the metal oxide. These two processes exponentially improve the sensor's sensitivity. We also used a commercial CO₂ analyzer to calibrate the sensor chip, and found that its detection capabilities were equivalent to those of our chemiresistive sensor, with the added benefits of its cheap cost, low power consumption, compact footprint, and ease of multiplexing and integration. Also, we have shown that a smartphone-based sensing device, suitable for both wireless and network-based sensing, may be utilised to detect carbon monoxide.

References:

1. Permentier, K.; Vercammen, S.; Soetaert, S.; Schellemans, C. Carbon dioxide poisoning: A literature review of an often forgotten cause of intoxication in the emergency department. *Int. J. Emerg. Med.* 2017, 10, 10–14.
2. Environmental Protection Agency (EPA). Carbon Dioxide as a Fire Suppressant: Examining the Risks, Report EPA430-R-00-002.
3. Occupational Safety and Health Administration (OSHA). Permissible Exposures Limits..

4. Delgado-Alonso, J.; Phillips, S.; Berry, D.; DiCarmine, P.; Chullen, C.; Quinn, G. Continued Development of Compact Multi-gas Monitor for Life Support Systems Control in Space. In Proceedings of the 46th International Conference on Environmental Systems, Vienna, Austria, 2016.
5. Wang, Y.; Nakayama, M.; Yagi, M.; Nishikawa, .; Fukunaga, M.; Watanabe, K. The NDIR CO₂ monitor with smart interface for global networking. IEEE Trans. Instrum. Meas. 2005, 54, 1634–1639.
6. Naama, S.; Hardjersi, T.; Keffous, A.; Nezzal, G. CO₂ gas sensor based on silicon nanowires modified with metal nanoparticles. Mater. Sci. Semicond. Process. 2015, 38, 367–372.
7. Michel, C.; Martinez-Preciado, A.; Parra, R.; Aldao, C.; Ponce, M. Novel CO₂ and CO gas sensor based on nanostructured Sm₂O₃ hollow microspheres. Sens. Actuators Chem. 2014, 202, 1220–1228.
8. Srinives, S.; Sarkar, T.; Hernandez, R.; Mulchandani, A. A miniature chemiresistor for carbon dioxide. Anal. Chim. Acta 2015, 874, 54–58.
9. Wang, C.; Yin, L.; Zhang, L.; Xiang, D.; Gao, R. Metal Oxide Gas Sensors: Sensitivity and Influencing Factors. Sensors 2010, 10, 2088–2106.
10. Wang, Y.; Yeow, J.T.W. A Review of Carbon Nanotubes-Based Gas Sensors. J. Sens. 2009, 2009, 1–24.
11. Tang, R.; Shi, Y.; Hou, Z.; Wei, L. Carbon Nanotube-Based Chemiresistive Sensors. Sensors 2017, 17, 882.
12. Zhang, Y.; Xu, M.; Bunes, B.R.; Wu, N.; Gross, D.E.; Moore, J.S.; Zang, L. Oligomer-Coated Carbon Nanotube Chemiresistive Sensors for Selective Detection of Nitroaromatic Explosives. ACS Appl. Mater. Interfaces 2015, 7, 7471–7475.
13. Penza, M.; Rossi, R.; Alvisi, M.; Cassano, G.; Signore, M.A.; Serra, E.; Giorgi, R. Pt-and Pd-nano clusters functionalized carbon nanotubes networked films for sub-ppm gas sensors. Sens. Actuators B Chem. 2008, 135, 289–297.