Polymer Nanocomposite based Chemiresistive NO_2 Gas Sensor

Divakara Meka[*], Linda George[**], Shalini Prasad*

* Department of Electrical and Computer engineering, Portland State University
** Department of Environmental Sciences and Management, Portland State University

ABSTRACT

Emission of harmful gases into the atmosphere pollutes the environment. These pollutants may have deleterious effects on ecosystems and affect human health. In order to control the emission of these harmful gases we first need to detect them.

We present here the development of a polymer nanocomposite based gas sensor for detecting trace gas emissions in ambient environment. This project aims to build a compact, readily deployable and cost-effective gas sensor that produces measurable electrical resistance changes due to interaction of NO_2 with a nanocomposite. Our sensor demonstrates parts-per billion (ppb) sensitivity with improved specificity into the ppb range through innovative functionalization and packaging of nanomaterial.

Keywords: nitrogen dioxide, gas sensor, chemiresistive, nanocomposite, selective.

1. INTRODUCTION

Human activity generates numerous gases and forms of particulate matter that either directly, or through the formation of secondary air pollutants, cause harm to human health or the ecosystem [1-10]. To minimize harm, the control of air pollution to attain regulatory standards is achieved through a combination of monitoring, modeling and emission control technology. Unfortunately, intensive monitoring of important air pollutants is severely limited due to the lack of cost-effective monitoring systems. Most air quality management districts monitor for regional air quality with only a handful of monitoring sites. This situation increases the reliance of air quality management on modeling and emission control, strategies which may not generate the most cost-effective approach to achieving regulatory standards. Furthermore, this limitation in monitoring capability is increasingly problematic as health studies document the importance of local scale impacts of elevated levels of air pollution. Clearly, the development of readily deployable, cost-effective sensors of air pollutants would address critical needs in air quality management.

We present here the development of a polymer nanocomposite based chemi-resistive gas sensor for detecting NO_2 in the ambient environment. This project aims to build a compact, readily deployable and cost-effective gas sensor that produces measurable electrical resistance changes due to interaction of NO_2 with a nanocomposite. This sensor demonstrates parts-per billion (ppb) sensitivity with improved specificity into the ppb range through innovative functionalization and packaging of nanomaterial. We achieve these improved performance parameters by incorporating carbon-based nanocomposites for improved electron transport that in turn amplifies NO_2 induced resistance changes in the composite. The performance of the prototype sensor has already achieved sensitivity to <200pbb but a factor 50 improvement in sensitivity will be necessary to meet ambient monitoring requirements. This improvement will be achieved through further design optimization.

2. CHEMIRESISTIVE NO_2 SENSOR

The principle of operation of the chemiresistive sensor is based on the measurement of resistance change associated with the adsorption/reaction of gaseous analyte by/with the nanomaterial matrix[11,12]. The prototype gas sensor functions based on the chemiresistive principle, where variations in the resistance of a NO_2 gas sensitive nanocomposite is observed and measured due to selective reaction between the nanocomposite and the NO_2 gas molecules that in turn decreases the number of free electrons resulting in a concentration dependant resistance increase. This chemiresistive NO_2 sensor mainly consists of a two parts:

2.1. Nanocomposite

Nanocomposites are materials that are created by incorporating nanoparticles into NO_2 sensitive material. After adding nanoparticles to the matrix material, the resulting nanocomposite exhibits enhanced electrical sensitivity to NO_2. The nanocomposite is packaged on to a miniature base platform. The base platform is comprised of a metallic interdigitated microelectrode structure (Figure 1). Coating the interdigitated electrode (IDE) with the nanocomposite will form an active sensing area, which is highly sensitive and selective towards NO_2.

The nanocomposite used here consists of an organic chemical compound which reacts with NO_2 and produces a new organic compound whose electrical properties are different to that of the original compound (Table 1). In addition to this organic compound the nanocomposite consists of Carbon Nanoparticles (CNPs) and surfactant. The carbon nanoparticles are employed for the enhancement of electrical and mechanical properties of the organic chemical

Clean Technology 2008, www.ct-si.org, ISBN 978-1-4200-8502-0

compound [13-17]. Since, the carbon nanoparticles are inert; they are incapable of reacting and electrically perturbing either the organic chemical of the nanocomposite or the NO_2 gas molecules. Hence the reaction between the organic compound and the NO_2 gas molecules will not be affected due to the carbon nanoparticles. But due to the addition of these nanoparticles the electrical activity from the nanocomposite, as well as the stability of the nanocomposite, are amplified due to the improved surface area to volume of the active sensing surface. The average size of the CNPs used in this nanocomposite is ~30nm. Surfactant is used to reduce the viscosity of the organic chemical compound in the nanocomposite and for the proper dispersion of CNPs.

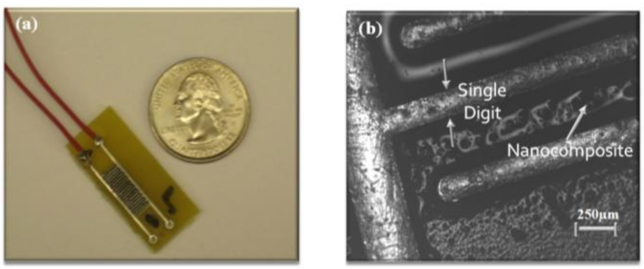

Figure 1 (a) The optical micrograph of the chemiresistive sensor chip with the interdigitated digits coated with polymer nanocomposite. Each sensor array is comprised of an interdigitated geometry with 20 digits. Each digit is ~200µm in width and 2mm in length with 300µm spacing. (b) The optical micrograph of the chemiresistive sensor comprised of an Interdigitated Electrodes (IDE) with the polymer nanocomposite forming a homogenous layer on the surface. Homogenous distribution of the polymer nanocomposite is accomplished with the addition of a surfactant in the polymer nanocomposite.

Component	Function
Polymer (Organic Chemical compound)	Responsible for NO_2 sensing
Carbon Nanoparticles (CNP's)	Improves nanocomposite's electrical and mechanical properties
Surfactant	Improves the dispersion of the nanocomposite

Table 1: Components of the nanocomposite which is used for the selective detection of NO_2 gas in the environment.

2.2. Electrical Circuitry

The organic compound, which is present in the nanocomposite, reacts with the NO_2 gas molecules and generates a new compound whose electrical properties are different from the original compound. Here, we employed a Wheatstone's bridge circuit, which can detect the change in the electrical resistance of the nanocomposite and generates an output voltage proportional to the change in the electrical resistance of the nanocomposite (Figure 2). In the entire circuit, the IDE pattern functions as an electrical resistor whose resistance changes depending on the reaction between the organic chemical compound and the NO_2 gas molecules.

The detection section is comprised of a base IDE platform (chip) with a polymer nanocomposite placed in a glass test chamber and the measurement section comprised of a ***Wheatstone's bridge*** to which the chip is connected. Change in the chip resistance is a result of chemical reaction of the polymer nanocomposite with NO_2 in the chamber.

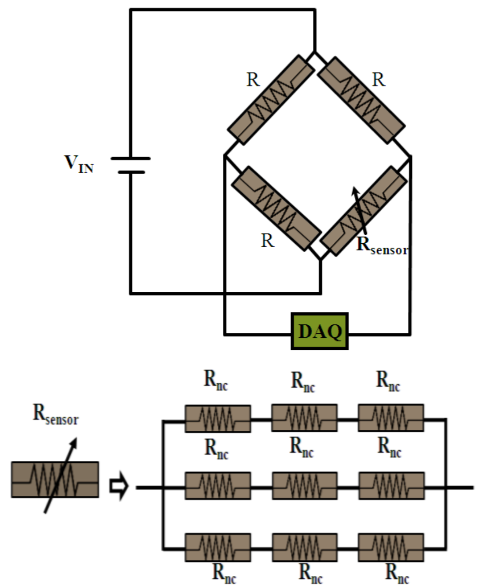

Figure 2. The equivalent circuit of the entire experimental setup and equivalent resistance of the nanocomposite. The resistor R_{sensor} in the Wheatstone bridge circuit is the resultant resistance of the nanocomposite.

3. EXPERIMENTAL TEST BED

The experimental test bed consists of a 200 liter glass chamber in which chips are placed and tested with all the gases. The chip in the chamber is connected to a simple wheat stone bridge circuit, which changes the voltage level at its output depending on the change in the resistance of the chip. The output of the Wheatstone bridge is connected to an analog to digital converter, which is connected to a PC using an USB cable. The DAC converts the analog signals from the Wheatstone bridge to a digital signal and send those digital signals to PC. Gas concentrations are monitored by standard air quality monitoring instrumentation. Signals from the Wheatstone bridge and gas monitoring instruments are fed into the data acquisition system and are continuously monitored.

When NO_2 is pumped into the test chamber, the active sensing area on the sensor reacts with the NO_2 gas molecules resulting in the change in electrical resistance of the chip. This change in the resistance causes an imbalance in the Wheatstone bridge which results in decrease in the voltage level at the output of the Wheatstone bridge.

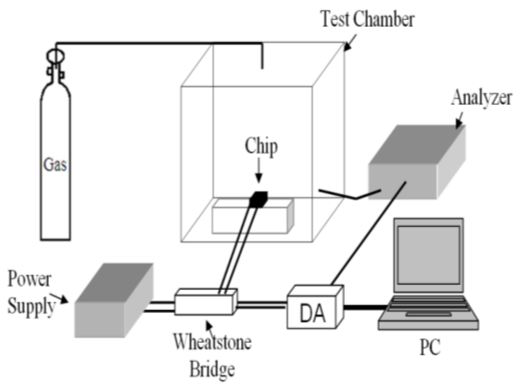

Figure 3 Shows the schematic of Experimental Test Bed. The test bed consists of glass test chamber in which the nanocomposite is tested, an chemiluminescence NOx analyzer which is used for monitoring the NO_2 concentration level in the test chamber and electrical circuit which is used for monitoring the change in electrical resistance of the nanocomposite when it is exposed to NO_2.

4. RESULTS

4.1. Control Measurements

The components of the nanocomposites have been optimized in order to improve the sensitivity of the nanocomposite towards NO_2. Table 2 shows the results of various combinations of nanocomposite variables. It was experimentally determined that the nanocomposite formed with the combination of 1 Wt% CNPs, 0.1 Wt% Surfactant and 1ml of polymer (20Vol %) /water has better sensitivity than any other combination.

CNPs (Wt %)	Surfactant (Wt %)	Quantity dispersed on sensor array (in µL)
0	0	0
1	0.1	10
2	0.2	20
4	0.5	--
↑ CNPs ↓ Response ↓ CNPs ↓ Mechanical Stability	↑ Surfactant ↓ Response ↓ Surfactant Improper dispersion	Entirely depends on the dimensions of the IDE Pattern

Table 2 Represents the various combinations of nanocomposites tried and it is experimentally determined that nanocomposite formed with the combination of 1 Wt% CNPs, 0.1 Wt% Surfactant and 1ml of polymer (20Vol %)/Water has better sensitivity than any other combination.

4.2. Sensitivity

Exposing the nanocomposite to various concentrations of NO_2 tests the sensitivity of the nanocomposite. It is observed that the resistance of the nanocomposite decreases with increase in the NO_2 concentration. The minimum sensitivity of the nanocomposite with the present electrical setup is <200ppb. The detection sensitivity can be improved by using electronic signal amplification circuitry in conjunction with the replacing the Wheatstone bridge circuit.

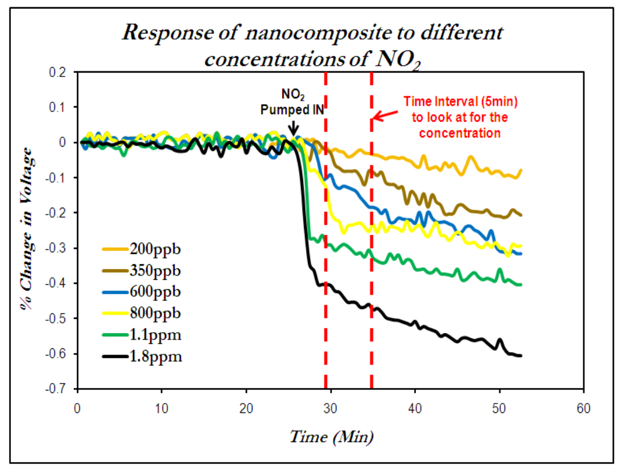

Figure 4 The response of nanocomposite to various concentrations of NO_2. It is observed that the resistance of the nanocomposite decreases with increase in the NO_2 concentration.

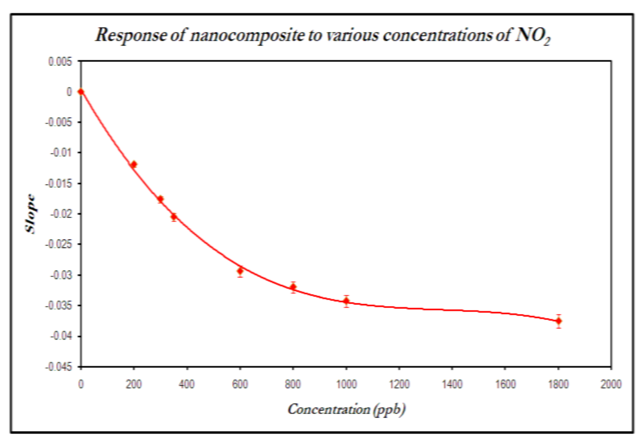

Figure 5 Slope vs. Concentration curve of the nanocomposite response to NO_2. From the curve it is inferred that there is a quadratic response of the nanocomposite to NO_2.

The signal produce by NO_2 interacting with the nanocomposite is cumulative and non-linear. The voltage decreases as a function of time exposure to NO_2. As the polymer reacts with NO_2 the product of this reaction

Clean Technology 2008, www.ct-si.org, ISBN 978-1-4200-8502-0

continues to change the resistive character of the nanocomposite. Therefore, the measurement of NO_2 is a function of the rate of change of the resistance (slope). The current prototype device also exhibits a highly reproducible non-linear response curve as well as saturation behavior at high NO_2 concentrations (Figure 5).

4.3. Selectivity:

The selectivity of the nanocomposite is tested by exposing the nanocomposite with various reactive gases other than NO_2 such as NO, SO_2, O_3, CH_4, CO, CO_2. It is observed that there are some transient responses from the nanocomposite but the steady state response (a period of 10 min) of the nanocomposite is negligible when compared to NO_2. This demonstrates that this nanocomposite is selective towards NO_2. But, in the real environment, there could be an issue with selective detection of NO_2 due to the presence of NO. This is one of the most important issues to be dealt with in the future.

Gas exposed and concentration	**Instant change in Voltage level**	**Steady state change (slope) in voltage level**
NO (1.3ppm)	+10mV	No significant change
NO_2 (0.8ppm)	-10mV	-1mV per 10min
SO_2 (2ppm)	-5mV	No significant change
CO_2 (9000ppm)	-10mV	No significant change
CO (0.8ppm)	-10mV	No significant change
CH_4 (1000ppm)	+5mV	No significant change
O_3 (10ppm)	No significant change	No significant change

Table 3 The response of the nanocomposite to various gases. From the table it can be observed that there will be steady change in the voltage only if the nanocomposite is exposed to NO_2 gas molecules.

5. FUTURE WORK

We anticipate improving the sensitivity by upgrading the electrical conditioning and amplifying circuitry, which can increase the signal to noise ratio as well amplify the response coming from the sensor prototype. The selectivity of the nanocomposite can be improved by compacting the nanocomposite to reduce stray electrical variations as well as modify the composition of the nanocomposite to enhance NO_2 detection.

6. REFERENCES

1. C. C. Yockey, B. M. Eden and R. B. Byrd, JAMA. **224**, 1221 (1980).
2. D. V. Hatton, C. S. Leach and A. E. Nicogossian, Arch Environ Health. **32**, 33 (1977).
3. F. E. Speizer, B. J. Ferris, Y. M. Bishop and J. Spengler, Am Rev Respir Dis **121**, 3 (1980).
4. H. D. Kerr, T. J. Kulle, M. L. McIlhany and P. Swidersky, Environ Res. **19**, 392 (1979).
5. J. Orehek, J. P. Massari, P. Gayrard, C. Grimaud and J. Charpin, J Clin Invest. **57**, 301 (1976).
6. J. Ramirez and A. R. Dowell, Ann Intern Med. **74**, 569 (1971).
7. K. Hedberg, C. W. Hedberg, C. Iber, K. E. White, M. T. Osterholm, D. B. Jones, J. R. Flink and K. L. MacDonald, JAMA. **262**, 3014 (1989).
8. M. T. Kleinman, R. M. Bailey, W. S. Linn, K. R. Anderson, J. D. Whynot, D. A. Shamoo. and J. D. Hackney, J Toxicol Environ Health. **12**, 815 (1983).
9. R. J. Melia, F. C. d. V, R. W. Morris, B. D. Goldstein, D. Clark and H. H. John, Int J Epidemiol. **11**, 155 (1982).
10. T. L. Guidotti, Environ Res. **15**, 443 (1978).
11. F. J. Ibanez, U. Gowrishetty, M. M. Crain, K. M. Walsh and F. P. Zamborini, J Anal. Chem. **78**, 753 (2006).
12. M. D. Wita, E. Vannestea, H. J. Geisea and L. J. Nagelsb, Sens. and Actua. B: Chem. **50**, 164 (1998).
13. B. C., B. C., Q. P., M. Y.L., L. J. and B. A. In *1996 IEEE International Symposium*, IEEE: Montreal, Quebee, Canada, (1996).
14. J. R. Li, J. R. Xu, M. Q. Zhangb and M. Z. Ronga, Carbon **41**, 2353 (2003).
15. C. X., J. Y., W. Z., L. D. and Y. J., Sens. and Actua. B: Chem. **66**, 37 (2000).
16. L. Quercia, F. Loffredo, B. Alfano, V. L. Ferrara and G. D. Francia, Sens. and Actua. B: Chem. **100**, 22 (2004).
17. F. Carmona and J. Ravier, Carbon **40**, 151 (2001).