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Thin film sensor materials for detection of Nitro-Aromatic explosives

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Abstract. Many countries have experienced terrorist activities and innocent people have suffered. Timely detection of explosives can avoid this situation. This paper targets the detection of Nitrobenzene and Nitrotoluene, which are nitroaromatic compounds possessing explosive properties. As direct sensors for detecting these compounds are not available, Polyaniline based thin film sensors doped with palladium are developed using the spin coating technique. The response of the developed sensors is observed for varying concentrations of explosives. It is observed that zinc oxide based sensor is more sensitive to Nitrotoluene exhibiting a relative change in resistance of 0.78. The tungsten oxide sensor is more sensitive to Nitrobenzene with a relative change in resistance of 0.48. The sensor performance is assessed by measuring the response and recovery time. The cross sensitivity of the sensors is evaluated for ethanol, acetone and methanol which was observed as very low.

1. Introduction

Every country is experiencing terrorist activities and the destruction caused by explosives is well known to all of us. Among hundreds of types of explosives, the use of nitroaromatic explosives is very common. Mixtures with Nitrobenzene (PubChem CID 7416), 4 Nitrotoluene (PubChem CID 7473), are found to be highly explosive of high sensitivity and detonation velocity. Also, mixtures with Nitrobenzene are spark detonable and pose a severe hazard to mankind. [1] The Ion Mobility Spectroscopy, Mass Spectrometry, Infrared Spectroscopy and Raman Spectroscopy are some of the common spectroscopic methods used for explosive detection in-house as described by several researchers [2, 3, 4, 5]. Though these methods are accurate, their use is confined to laboratories. These methods are time consuming and skilled personnel are required to handle these equipment. Though commercially available sensors exhibit a good sensitivity and selectivity, sensors for detecting Nitrobenzene (NB) and Nitrotoluene (NT) are not available. Considering the explosive properties of these compounds, this work aims at developing low cost laboratory developed sensors for detection of Nitrobenzene and Nitrotoluene.

For detection on the field, research on various sensors is being carried out. One of the popular sensors is the metal oxide sensors as suggested by Gardener [6]. Many scientists and engineers have studied metal oxide thin films as electronic materials due to their semiconducting behavior, structural simplicity and low cost [7, 8, 9]. These sensors exhibit change in its electrical properties (typically

conductance) when subjected to a gas. This phenomenon occurs due to adsorption and desorption of gas molecules on the gas sensitive surface. The selectivity of the sensor depends on the gas sensitive coating deposited on the sensor surface [10, 11]. The development of simple, low cost reliable sensors for detection of explosives in developing countries like India will accelerate the research towards timely detection of explosives. A critical study was performed to identify the materials to be used for sensor development in the laboratory using spin coating technique [12]. Alexy Tomchenko [13] designed a sensor array consisting of discrete thick-film sensors based on various semiconductor metal oxides (SMO) and fabricated it for ue gas analysis purposes. The selection of the sensitive materials for the array has been accomplished as a result of extensive studies of gas-sensitive properties of SMO. Sofian M. Kanan et. al. and Sergiu T. Shishiyanu [14, 15] presented a study of materials and systems used for detection of various chemical agents and nitro aromatic compounds. This study reveals the use of SnO_2, ZnO, WO_3, CuO, and In_2O_3 as potential materials for nitro aromatic detection. Dan Xie et al [16], developed Polyaniline based sensors for detection of NO_2 and studied the effect of thickness on the sensitivity of film.

2. Materials and Methods

2.1. Development of thin film sensors

After a detailed study of materials used for thin film sensors, sensors were developed with sensing materials of Tin oxide (Research Lab), Zinc oxide (Research Lab), Indium oxide (Research Lab), Polyaniline (Sigma-Aldrich), Lead phthalocyanine (Sigma-Aldrich), Tungsten Oxide (Research Lab). Selectivity is enhanced using palladium metal powder (Ottokemi) with 99.9% purity. The following procedure is adopted to develop the sensors. A micro balance is used to weigh the powders accurately. The weight of the powders depends on the pre-decided ratio of the mixture of powders to achieve a higher selectivity and sensitivity. The weight ratios decided for the sensor is a mixture of selective material powder (6%) and sensitive material powder (94%). The sensitive powder is a mixture of Polyaniline (65%) and metal oxide or phthalocyanine (35%). As the powders need to mix properly and micro or nano granules to form, severe pulverization of the mixture is done. Spin coating machine (Ambala SCM-6VT) is used to form thin film on the glass substrate of size 25mm x 25mm. The pulverized powder is mixed with 2-3 drops of glycerin which acts as a binding agent, before forming the thin film using spin coating machine. 1-2 drops of Dimethyl Sulfoxide are also added, which acts as a chemical agent. Sintering is the process wherein the formed films undergo heat treatment. This hardens the films and makes it quite sturdy. Sintering is carried out at a temperature of 80 degrees Celsius for 10 minutes. High conductivity copper alligator clips are used to generate contacts for the film. The clips are positioned on diagonally opposite sides to reduce contact resistance and thus enhance the response of thin film sensor.

Figure 1 shows a photograph of the developed sensors while figure 2 shows the box with copper alligator clips connected to the sensor. The sensors developed are tested using the Keithly 2110, five and half digit multimeter. The meter can be connected to a computer via USB and the response of each sensor can be stored for further analysis. The sensor response is calculated as the absolute value and expressed in equation (1).

$$\frac{\Delta R}{R} = \frac{R_a - R_g}{R_a} \tag{1}$$

where R_g is the resistance of the sensor when subjected to gas and R_a is the resistance of sensor in air.

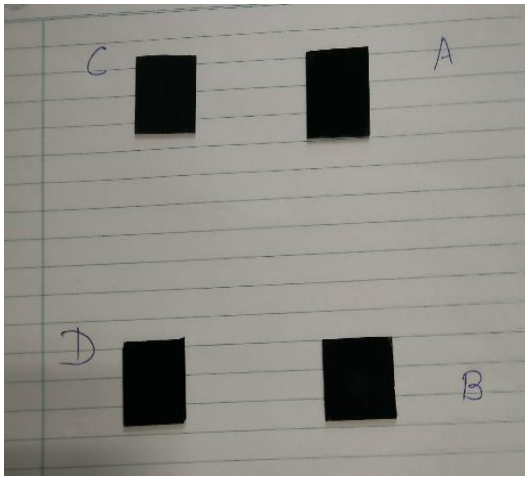

Figure 1. Photograph of some developed sensors.

Figure 2. Photograph of Sensor Box with Copper alligator clips.

2.2. Generation of gas from chemical

To generate the aroma of explosives, Nitrobenzene (LOBA Chemie Pvt. Ltd. Mumbai, India) and Nitrotoluene (Research Lab Fine Chem Industries, Mumbai, India) in chemical form are used. 6 concentrations each of Nitrobenzene and Nitrotoluene, from 1 mL to 30 mL are used as volumes beyond this are dangerous to handle. The nitroaromatic explosive was injected in a glass container of 1 litre capacity and allowed to stand for 25 minutes while covering it. The compound is allowed to mix with normal air and not with a pattern gas. After visually confirming the evaporation, the sensors are subjected to nitro-aroma of the compound through the pump and motor assembly for 60 seconds. Similar process is carried out for generating the volatile organic compounds (VOCs) of Ethanol, Acetone and Methanol (Research Lab Fine Chem Industries, Mumbai, India).

2.3. Experimentation

Experimentation is carried out using the system setup as illustrated in figure 3, while the actual photograph of the setup is shown in figure 4. After acquiring the sensor response for each sensor, the sensor box is purged with air for a pre-decided time interval to avoid interference of traces of earlier gas with the test gas. The sensor response was observed for nitrobenzene and Nitrotoluene using the Keithly multimeter. The cross sensitivity of the tungsten oxide and zinc oxide sensors to ethanol, acetone and methanol is observed using the same setup. The sensor response was also observed for nitro aromatic compounds of Ammonia and Nitric Oxide to study their selectivity towards the intended gas.

3. Results

Ten sensors were developed, out of which Polyaniline based 5 sensors with sensing material of Tin oxide, Zinc oxide, Indium oxide, Lead phthalocyanine and Tungsten Oxide displayed better sensitivity and selectivity towards Nitrobenzene and nitrotoluene. The response of each sensor was observed and recorded using the Keithly 2110, five and a half digit multimeter. An example of the observed response is illustrated in figure 5. The response of the sensors to NB and NT are illustrated in figure 6 and 7. It was observed that the Zinc oxide sensor exhibited maximum sensitivity towards Nitrotoluene and the tungsten oxide sensor showed maximum sensitivity towards Nitrobenzene. The cross sensitivity of the tungsten oxide and zinc oxide sensors is studied for Ethanol, Acetone and Methanol. The experimentation carried out followed the same procedure as that for nitrobenzene and nitrotoluene. It is observed that both the sensors were less sensitive to these VOCs. The response of these sensors is presented in figure 8 and 9. Table 1 shows the sensor performance in terms of response time, recovery time and sensitivity.

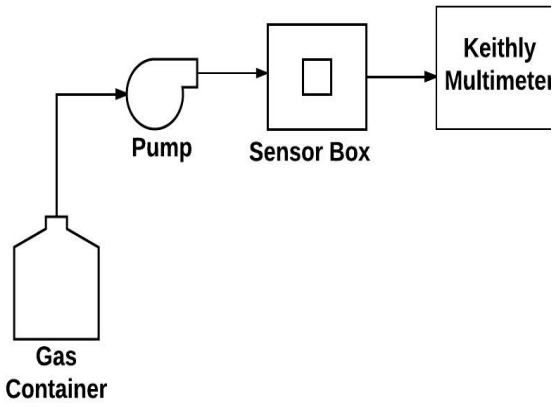

Figure 3. System schematic Diagram.

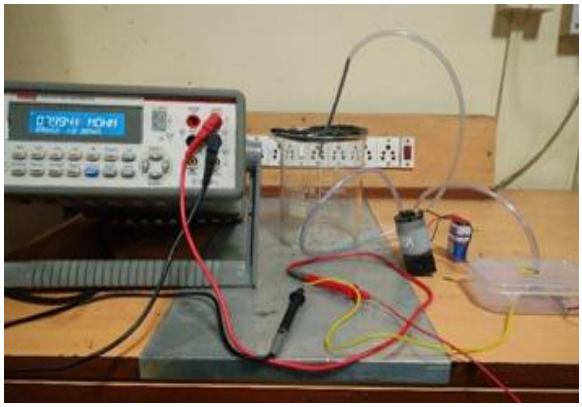

Figure 4. Photograph of the system.

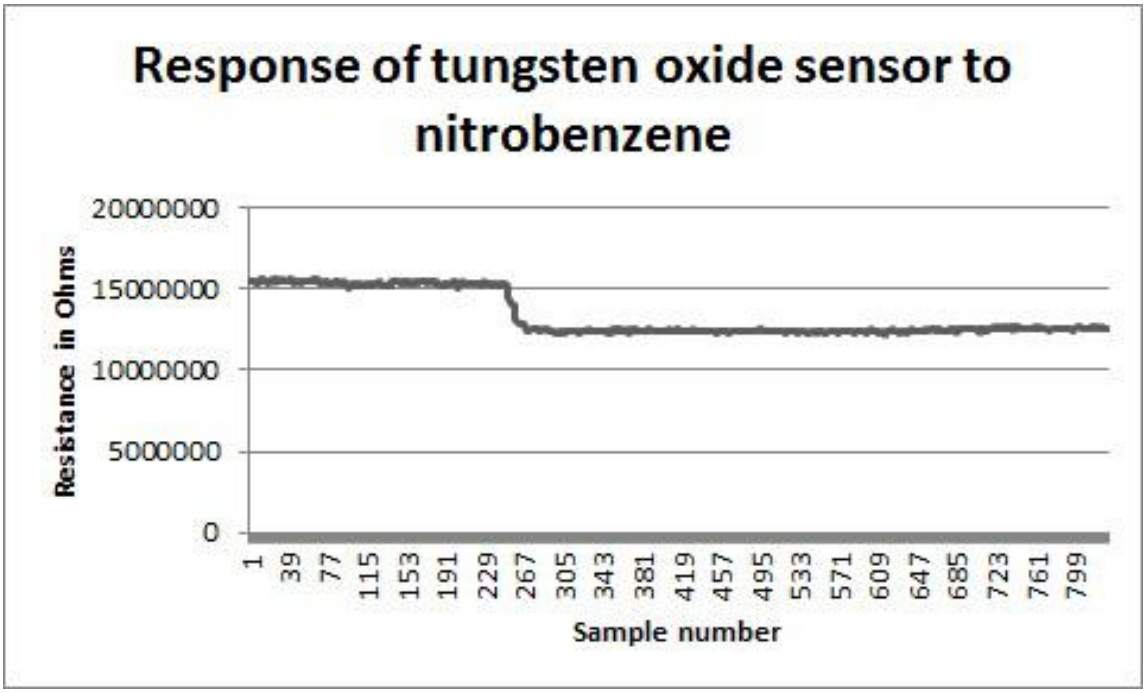

Figure 5. Response of tungsten oxide sensor to Nitrobenzene.

Table 1. Sensor performance.

Sensor Material	Response time (Seconds)	Recovery time (Seconds)	Percentage Sensitivity Nitrobenzene	Percentage Sensitivity Nitrotoluene
Tungsten Oxide	24	360	48	21
Indium Oxide	38	450	13	24
Zinc oxide	52	510	8.6	7.8
Lead Phthalocyanine	12	205	24	34.7
Tin Oxide	43	280	3	38

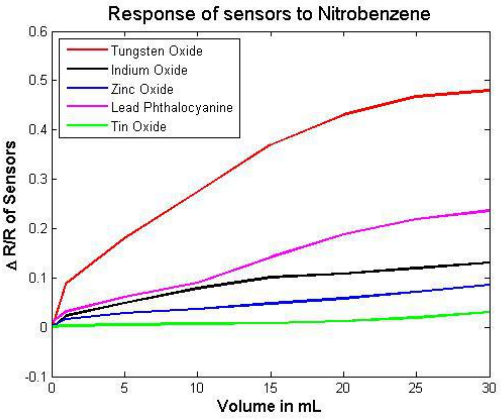

Figure 6. Response of sensors to Nitrobenzene.

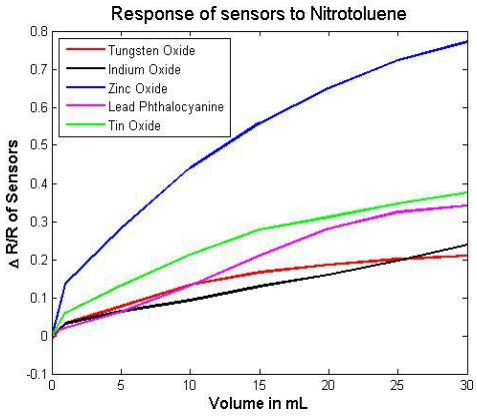

Figure 7. Response of sensors to Nitroluene.

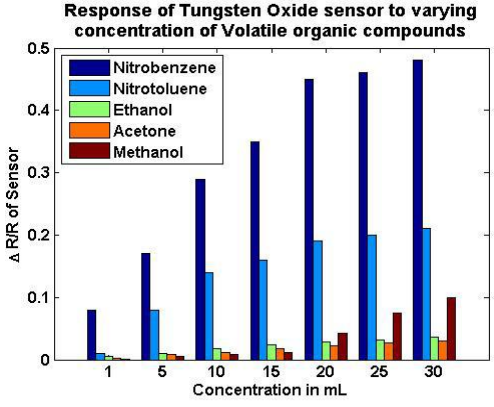

Figure 8. Response of Tungsten Oxide sensor to varying concentrations of Volatile Organic Compounds.

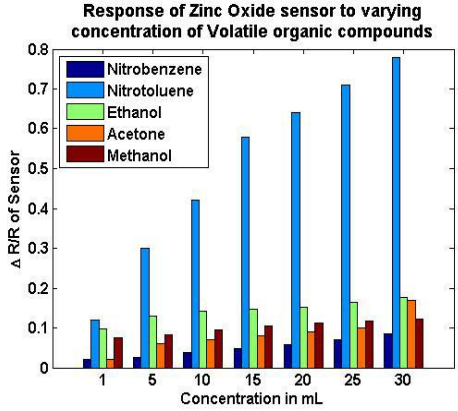

Figure 9. Response of Zinc Oxide sensor to varying concentrations of Volatile Organic Compounds.

4. Discussion and Conclusion

Study reveals the explosive properties of Nitrobenzene and Nitrotoluene and the literature reveals limited availability of sensors to detect these nitroaromatic explosive compounds. Thus thin film sensors are developed in the laboratory using the spin coating technique for detection of these compounds. Five sensors with sensing material of Tin oxide, Zinc oxide, Indium oxide, Lead phthalocyanine and Tungsten Oxide exhibited a measurable sensitivity towards these compounds. It was observed that though the sensors responded to both the compounds, their sensitivity was different. Also, it is observed that zinc oxide based sensor exhibited maximum sensitivity towards Nitrotoluene while tungsten oxide exhibited maximum sensitivity towards Nitrobenzene. Very low cross sensitivity was observed for the tungsten oxide and zinc oxide sensors towards ethanol, acetone and methanol. Extended work can be performed towards the study and improvement of repeatability of these sensors. The development of these sensors will help in the timely detection of explosives. As the method of developing these sensors is simple and of low cost, the sensor response can be acquired for various nitro aromatic compounds. These responses can be included in parametric models developed for explosive detection.

Acknowledgments

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