Development of Acetone Gas Sensor Based on Metal Oxide-Graphene Composite

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Abstract. Nowadays, various technologies have been developed to facilitate human tasks or activities, such as the use of volatile organic compounds (VOCs). VOCs are a diverse group of chemical compounds emitted as gases from various sources, including industrial processes, vehicle emissions, and household products. These compounds can have a significant impact on indoor air quality and outdoor air pollution, raising various health and environmental concerns. Engineers have developed air quality monitoring technologies; however, the current sensors often come with high costs, power consumption, and low selectivity. Therefore, this study aims to develop a VOC gas sensor based on metal oxide-graphene composite, which exhibits good stability, selectivity, and response, even at low temperatures. The sensor is designed to be simple, cost-effective, and efficient. The SnO_2-rGO sensor was developed using a reduction method and tested using Cellkraft P-10 mass flow controllers. In an enclosed chamber, a sensor on a heater stage was maintained at room temperature by a Nextron Temperature Controller, with compressed dry air and acetone flow rates controlled by, relative humidity kept constant at 5 ± 1% and a direct voltage of 2V applied while monitoring electrical resistance changes with a Keithley 2410 source measuring unit.. OriginPro 2019b software was used to analyze the raw data obtained from the sensor testing. The focus of this study is on testing the stability, selectivity, and response of the developed acetone gas sensor. This chemoresistive sensor produced good results for detecting acetone gas at a concentration of 6 ppm at room temperature. The sensor gives a good response and recovery time, low detection limit, and exhibited good selectivity when exposed to acetone and toluene gases. Therefore, SnO_2-rGO sensor is a promising candidate for acetone gas detection

Keywords: SnO_2-rGO; VOC; Acetone sensor

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1 Introduction

Acetone is a reagent commonly used in industry and laboratories. Acetone has an organic compound with the formula $(CH_3)_2CO$. It is a colorless, volatile, flammable liquid, and is the simplest ketone. Acetone is a man-made chemical that also occurs naturally in the environment. Acetone is also easily known as dimethyl ketone, 2-propanone, and beta-ketopropane. These acetone-type VOCs are used to dissolve plastics, clean paraffin, and dehydrate tissues in pharmacy. Acetone also occurs naturally in plants, trees, volcanic gases, forest fires, and as a result of the breakdown of body fat. These volatile organic compounds are also found in vehicle exhaust, tobacco smoke, and landfills. It is very unstable and very dangerous to human health and biology.

Graphene is an unusual material formed by a thick layer of sp2 hybridized carbon atoms arranged in a honeycomb lattice. (Raslan et al. 2020; He & Fang 2016). This causes the atoms found on one layer of graphene to be considered as surface atoms and graphene can interact with even one molecule (Schedin et al. 2007; Majhi et al. 2021). However, graphene has no band gap or functional groups, limiting its gas sensor applications (Chatterjee et al. 2015). Therefore, rGO, which is synthesized by the reduction of GO, is a better choice for gas sensing applications because it has many functional groups and defects.

Table 1 shows some existing studies that produce acetone sensors using different methodologies and types of sensitive materials. There are many studies that use rGO, metal oxide, and metal oxide-rGO materials as sensitive materials to develop acetone gas sensors. Studies that use metal oxide-graphene-based sensitizers give better results than studies that use metal oxide or rGO alone as sensitizers. However, this study of metal oxide-graphene still operates at high temperatures and uses complex and expensive methods. Therefore, this study was conducted to develop an acetone gas sensor based on metal oxide-graphene that has a high level of stability, selectivity and sensitivity at low gas concentrations and uses a cheap method.

This study will focus on the development of sensitive materials based on metal oxide-graphene by using the reduction method. This method is implemented with the aim of achieving the overall objective of synthesizing a sensitive material using a simple and cheap technique that can operate at room temperature, producing an acetone gas sensor that has high responsiveness and sensitivity at low gas concentrations, as well as the level of selectivity, response and better gas sensor stability compared to existing gas sensors.

Table 1. Table captions should be placed above the tables.

Sensing material	Type of gas detected	Operating temperature (°C)	Concentration of gas (ppm)
Metal Oxide (Wang et al. 2019)	Acetone	248	300
Metal Oxide (Hassan et al. 2019)	Acetone	300	10,000
rGO (Tiwary et al. 2021)	Ethanol	RT	100
Metal Oxide-rGO (Shanavas et al. 2021)	Acetone	RT	500
Metal Oxide-rGO (Gao et al. 2021)	Acetone	160	100

2 Methodology

2.1 IDE Fabrication

Interdigitated electrode (IDE) was made on 1 cm^2 Si/SiO_2. The Pt/Ti (100/10 nm) IDE geometry consists of 3 pairs of finger electrodes and each electrode has a width and length of 0.1 mm and 2 mm, respectively. The distance between the fingers between the electrodes is 0.2 mm. These test structures were built using lithography, metallization, and standard lift-off processes. Therefore, the coverage of the sensing area is close to 6 mm^2. The prepared gas sensing device was dried overnight in a desiccator. The preparation method of this device was done by MIMOS researchers

IDE must be clean before use. The IDE cleaning process begins by undergoing an ultrasonication process using IPA for 20 minutes. Then, IDE will undergo the ultrasonication process again using DI for 20 minutes. Next, this wet IDE will be dried using a nitrogen stream. The process of heating the IDE on a hotplate in a short period of time to ensure that the IDE has completely dried referring to Figure 1, the cleaned IDE will be used in the sensor development step.

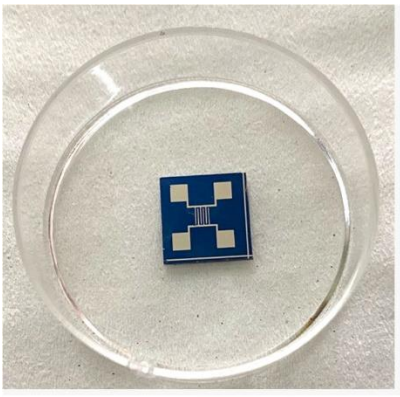

Fig. 1. Cleaned IDE

2.2 Preparation of SnO_2-rGO hybrid composites.

Among the materials and reagents used to synthesize SnO_2-rGO sensing materials are graphene oxide solution (4.0 mg/ml), tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$), ethylene glycol ($C_2H_6O_2$), and ammonium hydroxide (NH_4OH). Figure 2 shows the hybrid composite, SnO_2-rGO synthesized through the reduction method. 1 ml of graphene oxide (GO) was dissolved in 40 mL of deionized water (DI) in beaker A and underwent ultrasonication for 1 hour. The ultrasonication process was performed to achieve homogenization in the GO and DI solutions. Then, 1.7611g of tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$) was dissolved in 10 ml of ethylene glycol ($C_2H_6O_2$), in beaker B and stirred vigorously at room temperature for 1 hour. Next, the solutions in beaker A and beaker B were mixed and stirred for 8 hours at a temperature of 120 °C. After the rest of the solution cooled naturally, the centrifugal process or the English term centrifugation process was done 4 times at a speed of 4000 rpm. The resulting SnO_2-rGO solution is washed using DI and ammonium hydroxide (NH_4OH) to remove residual contaminants such as unwanted ions.

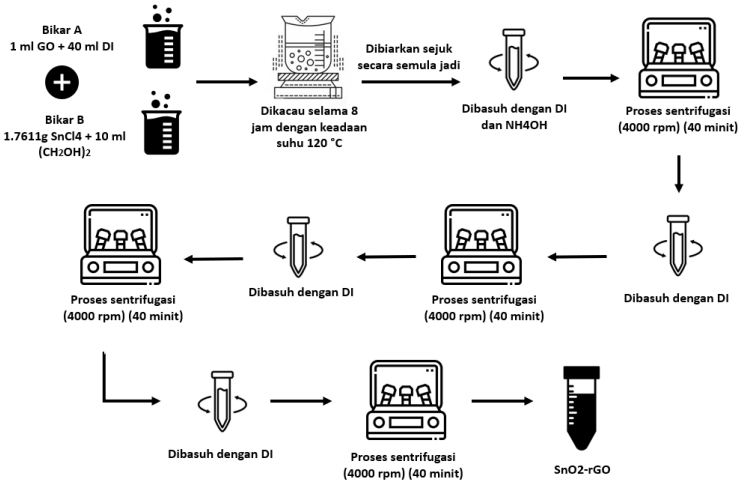

Fig. 2. Illustration of the preparation of SnO_2-rGO composites

2.3 Sensor Development and Testing.

The gas sensor was established by dropping 300 µl of an aqueous dispersion of the sensitized material that had been synthesized using a micropipette to produce a thin film on the interdigitated electrode (IDE). Figure 3 shows the dropcast activity onto the electrode (IDE). Sensitive materials must be allowed to dry first before being used during the testing of sensitive materials.

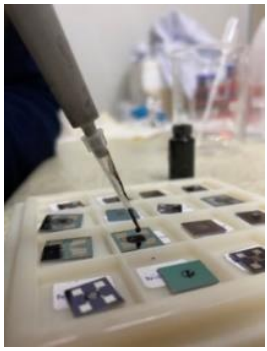

Fig. 3. Dropcast over the IDE using a micropipette

Figure 4 shows a schematic of the measurement setup used to investigate the sensing performance of three different composites towards C_3H_6O. The sensor will be placed on a heating stage in a closed chamber and controlled by a Nextron Temperature Controller. The temperature was set at room temperature. The flow rate of compressed dry air or its English term, compressed dry air (CDA) and C_3H_6O is controlled by the mass flow controller of the humidifier system (Cellkraft P-10). The relative humidity is set as a constant at 5±1% using a closed loop control system. Tests are performed by applying a direct voltage of 1 V and the change in electrical resistance is monitored (using a Keithley 2410 source measuring unit).

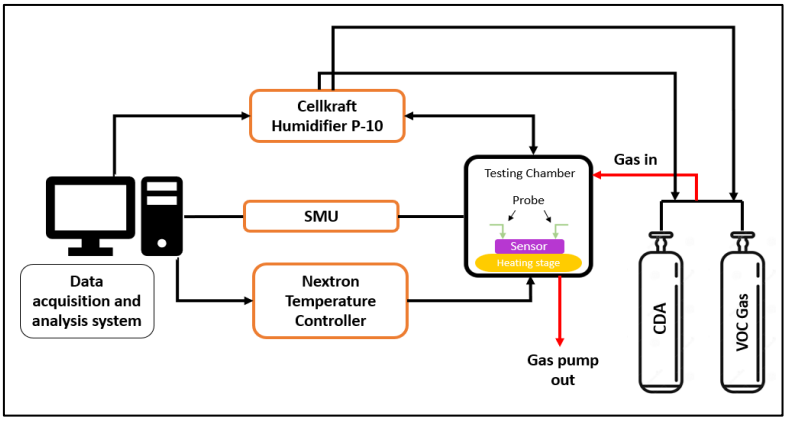

Fig. 4. Schematic illustration of testing C_3H_6O

2.4 Characterization of Sensing Materials.

Among the tests that will be performed on the sensor are Raman Spectroscopy, Field Emission Scanning Electron Microscope (FESEM) and X-ray Diffraction Analysis (XRD). The crystal structure and phase composition of each sample (composite) prepared was evaluated by an X-ray diffraction (XRD) system. The vibrational modes of

each composite were investigated using 473 nm laser Raman spectroscopy (NTEGRA Spectra MT-MDT). The microstructure and morphology of SnO_2-rGO composites were examined by transmission electron microscopy (TEM).

Response and recovery time, are considered the main parameters of chemical resistivity type sensors. This response and recovery time is measured and defined as the time taken by the sensor to reach 90% of its maximum resistance during changes in the adsorption and desorption process. An ideal gas sensor should have a fast response and recovery time. The sensor response is calculated using Equation (1), where 'Ra' is the electrical resistance of the sensor in air and 'Rg' is the presence of gas in the experiment.

$$S\% = (Ra - Rg)/Ra \times 100 \quad (1)$$

3 Result and Discussion

3.1 Field Emission Scanning Electron Microscope (FESEM)

FESEM is used to identify the morphology or nanostructure of the composite sensitive material that has been synthesized. Figure 5 and Figure 6, shows the morphology of the composite sensitive material with a magnification of 30,000 and 100,000 with an area of 100 nm. FESEM characterization results show that the SnO_2-rGO sensitive material composite has a nanocrystalline shape.

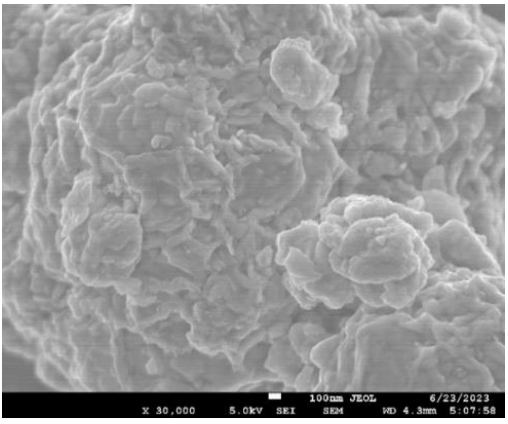

Fig. 5. Magnification 30,000

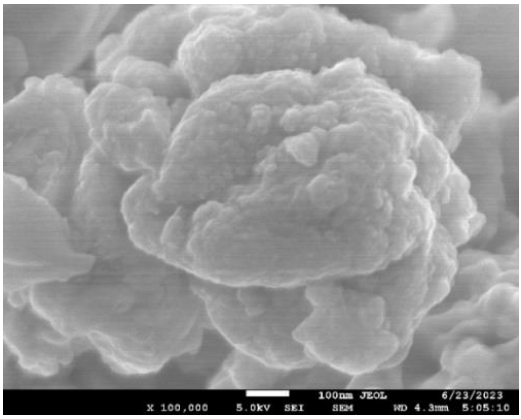

Fig. 6. Magnification 100,000

3.2 X-ray Diffraction Analysis (XRD).

XRD is used to determine the level of crystallinity and the proportion of crystalline and amorphous areas and to determine the type of material present in the sensitizer that has been synthesized. The resulting diffraction peaks will be analyzed to obtain the intensity plane position of each peak. The XRD diffraction pattern of the SnO_2-rGO material synthesized using the reduction method was analyzed. Referring to Figure 7, the XRD diffraction pattern of the SnO_2 sample on the (110), (101), (200), (211), (220) and (301) planes with diffraction angles of 27.8°, 33.9°, 42.6° respectively, 47.7°, 56.5°, and 64.8°.

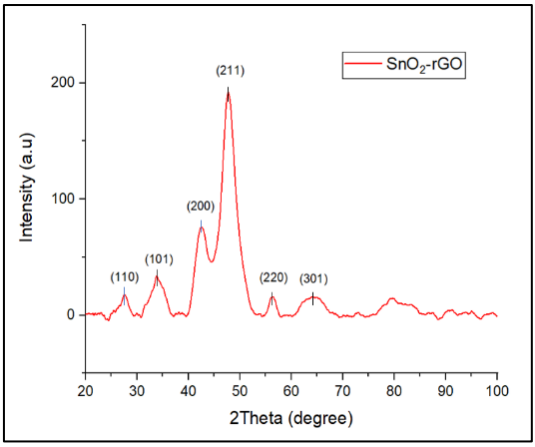

Fig. 7. XRD diffraction patterns of the SnO group.

This diffraction peak shows that the synthesized sensitive material composite has a cassiterite crystal phase with a tetragonal rutile structure. The type of mole number for SnO cannot be identified accurately, however the resulting XRD pattern successfully

proves the presence of SnO composite in the synthesized sensitive material. This is also proven by the study of Li et al. 2020 with his study on Tin dioxide (SnO_2) as an acetone gas sensor synthesized using the solvothermal method. The XRD results for this study is more or less the same as the XRD pattern for this study.

3.3 Raman Spectroscopy

Raman spectroscopy was performed to confirm the graphene-type material present in the composite of the sensitive material that had been synthesized. Referring to Figure 8, the results of Raman spectroscopy for the SnO_2-rGO sensitive material sample show spectral peaks at 1358 and 1593 cm^{-1} with an intensity of 1769.6 a.u. and 1218.5 a.u, which respectively accommodate the Defect band (D-band) and Graphitic band (G-band). The ID/IG ratio between D-band and G-band indicates the degree of drift and disorder for the SP2 area. The SnO_2-rGO sensitizer composite produced an ID/IG ratio of 1.45.

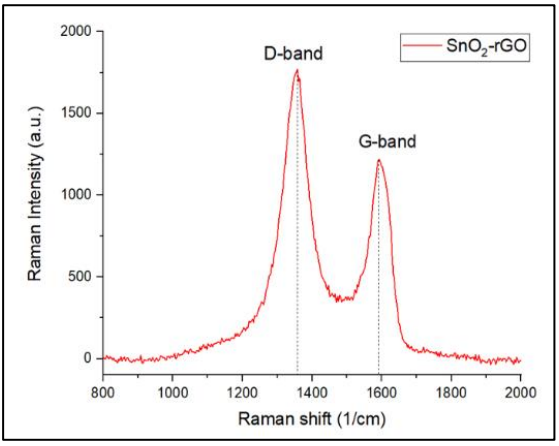

Fig. 8. Raman spectroscopy of SnO_2-rGO sensors

3.4 IV Characteristic of Sensor

Current-Voltage (IV) characterization was performed on the SnO_2-rGO sensor with a voltage range between -1V to 1V. This characterization is done to identify the electrical conductivity between the sensitive material and the IDE. Current versus voltage graphs have been generated to better show the IV characterization. Referring to Figure 9, the results show that the developed sensor has a good ohmic electrical contact with the IDE.

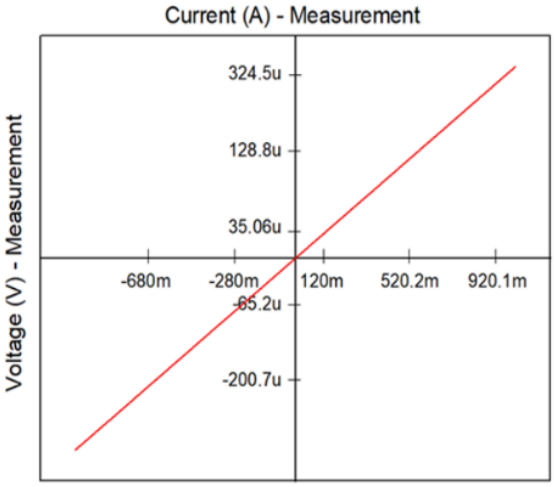

Fig. 9. IV Characterization of SnO_2-rGO sensors

3.5 Response Rate of SnO_2-rGO Sensor to VOC gas

Sensor response rate testing was performed against acetone gas. The response time and recovery time of the sensor will be measured using a count of 90% of the maximum resistance during changes in the adsorption and desorption process. Referring to Figure 10, the SnO_2-rGO sensor takes 22.93 seconds to respond when acetone gas at a concentration of 6 ppm is present and takes 32.76 seconds to recover after acetone gas is stopped. In addition, the sensitivity of the developed SnO_2-rGO sensor to acetone gas is 1.126 %.

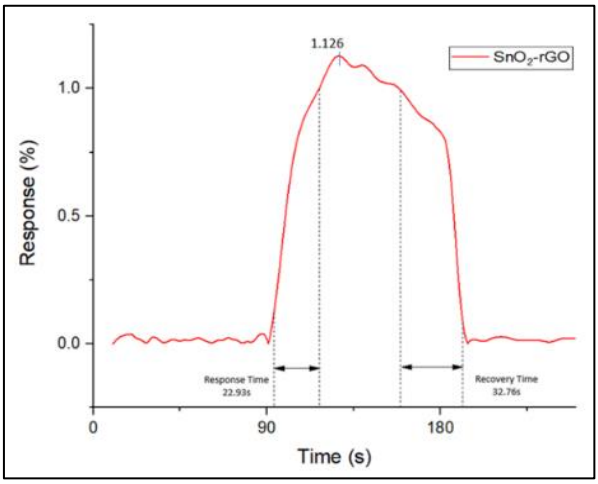

Fig. 10. Sensitivity of SnO_2-rGO sensor to acetone gas (6 ppm)

3.6 Selectivity of Sensor

A good level of sensor selectivity means that the sensor is able to identify different types of gas. Sensor selectivity testing was done against two different types of VOC gases, namely acetone and toluene. Figure 11 shows the sensitivity of the developed SnO_2-rGO sensor to toluene gas which is 0.767 %. Referring to Figure 12 the developed SnO_2-rGO sensor gives significant sensitivity values for these two different types of gases. The SnO_2-rGO sensor is sensitive to acetone gas with a value of 1.126 % while the sensitivity of the sensor to toluene gas is 0.767 %. This clearly shows that the developed SnO_2-rGO sensor has a good level of selectivity.

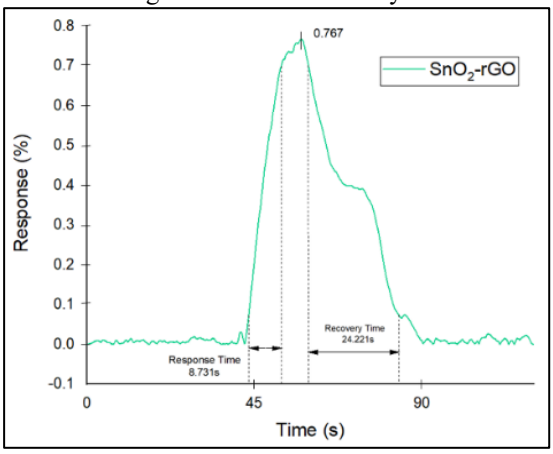

Fig. 11. Sensitivity of SnO_2-rGO sensor to toluene gas (6 ppm)

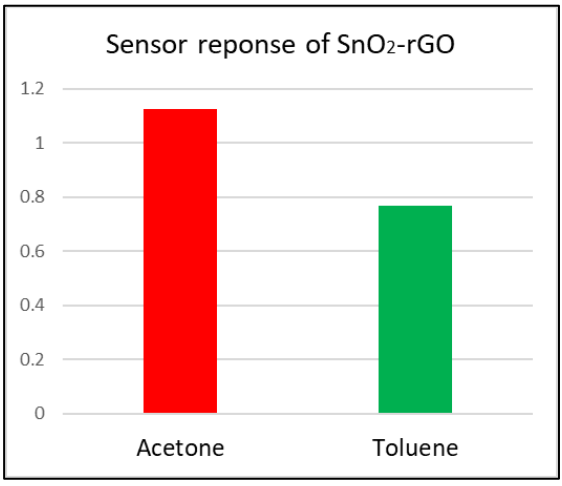

Fig. 12. Selectivity of SnO_2-rGO sensor towards acetone and toluene gas

3.7 Stability of Sensor

Testing of the SnO_2-rGO sensor against acetone gas at a concentration of 6 ppm was carried out for 3 cycles. Each cycle starts with Gas Off and is followed by Gas On. In the No Gas condition, only CDA will flow into the IDE test chamber, and no VOC gas will flow. Next, in the condition of Gas On, the flow of CDA will be stopped and the VOC gas will be flowed into the IDE testing room. Cycles of Gas and No Gas are performed 3 times. Referring to Figure 13, the sensor has gone through 3 testing cycles and managed to give approximately the same sensitivity values of 1.126 %, 1.135 % and 1.034 % in each cycle. Therefore, the developed SnO_2-rGO sensor has good stability.

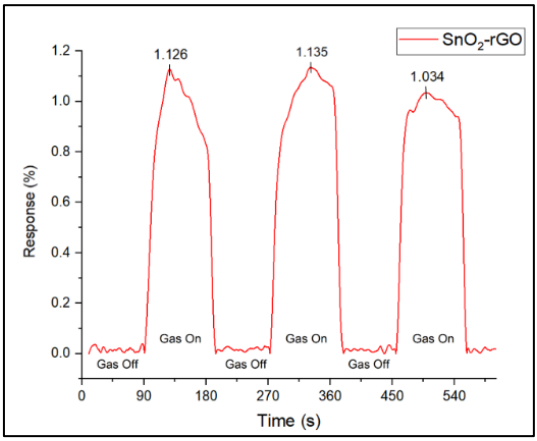

Fig. 13. Stability of SnO_2-rGO sensor towards acetone gas (6 ppm)

3.8 The detection Limit of Sensor

The detection limit of the sensor was measured using different acetone gas concentration values at 6, 4, 3, 2, 1, 0.5, and 0.3 ppm. The Gas and No Gas cycle is performed 7 times. The concentration of acetone gas decreases with each cycle to see the detection limit for the SnO_2-rGO sensor. Referring to Figure 14, the SnO_2-rGO sensor has undergone 7 testing cycles with decreasing concentrations of acetone gas. The SnO_2-rGO sensor successfully provided a good response rate up to 1 ppm acetone gas concentration. This is so because, there is no significant change in resistance that can distinguish between the presence of VOC gas and the absence of VOC gas at acetone gas concentrations of 0.5 ppm and 0.3 ppm. Therefore, the detection limit of the developed SnO_2-rGO sensor is 1 ppm.

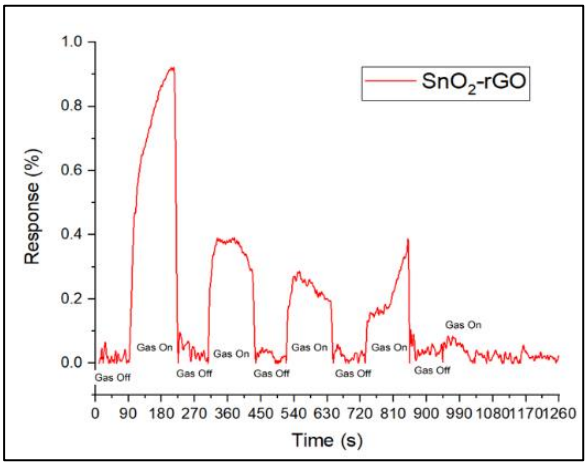

Fig. 14. Detection limit of SnO_2-rGO sensor towards acetone gas

4 Conclusion

The developed SnO_2-rGO sensor gave a good response rate to acetone gas at a concentration of 6 ppm at room temperature. When the detection limit was tested against the SnO_2-rGO sensor, it managed to give a good response down to 1 ppm at room temperature.

The SnO_2-rGO sensor has excellent sensitivity to acetone gas at 1.126 %. In addition, this sensor also has a good level of selectivity because it managed to produce different sensitivity values when exposed to 0.767 % toluene gas. The significant difference in the sensitivity value of the sensor to two different types of gases proves that the developed SnO_2-rGO sensor has an excellent level of selectivity.

The level of stability that the SnO_2-rGO sensor has is also very good because the sensor shows approximately the same response rate when tested with several acetone gas cycles. Next, the reduction method used to develop the SnO_2-rGO acetone gas sensor is also a cheap and simple method. This is because, this method does not require the use of high power and expensive machines.

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Disclosure of Interests. It is now necessary to declare any competing interests or to specifically state that the authors have no competing interests. Please place the statement with a third level heading in 9-point font size beneath the (optional) acknowledgments[1], for example: The authors have no competing interests to declare that are relevant to the content of this article. Or: Author

A has received research grants from Company W. Author B has received a speaker honorarium from Company X and owns stock in Company Y. Author C is a member of committee Z.

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