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RESEARCH ARTICLE

PEDOT:PSS/GO NANOCOMPOSITE FOR INDOOR CO_2 SENSOR

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Abstract

Carbon dioxide (CO_2) which is a colourless and odourless gas, requires an efficient detection, as excessive amount in the environment would possibly leads to global warming. This work discusses on an environmentally friendly and non-toxic CO_2 sensor for indoor air monitoring. The fabricated sensor is developed by using poly(3,4ethylenedioxythiophene):poly(4styrenesulfonate)/ graphene oxide (PEDOT:PSS/GO) nanocomposite. Nanocomposite characterisations are performed by using field-emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) to confirm excellent properties of PEDOT:PSS and GO as suitable materials for CO_2 sensor development. Fabrication of one layer PEDOT:PSS/GO nanocomposite on environmentally friendly kaolin-coated paper substrate via dip coating method shows good electrical conductivity of 0.25 S. At room temperature, at fixed CO_2 flow rate of 0.05 l/min, the fabricated sensor response time is 32 s, with sensor response and sensitivity of 0.8 and 16/l/min respectively. With fast chemiresistive response towards CO_2 molecules, the fabricated sensor provides promising results for indoor CO_2 monitoring.

Introduction:-

Since the discovery of organic conducting polymers, the identified remarkable properties and precision structures have been widely used in the fields of chemistry and materials science. However, structural, and chemical properties should be further enhanced for use in various practical applications.Conductive polymers currently have an extensive range of applications, especially in the inventory of gas sensors, in numerous fields of electronics. Conducting polymers are also well known to have an edge due to their chemical and structural diversity in achieving high sensitivity and selectivity. These conducting polymers, however, are of low sensitivity as a gas sensor and have a comparatively high working temperature limit. Thus, a nanostructured material that also has strong conducting property to provide better miniature sensor efficiency compared to their bulk counterparts will boost the receptive time of conducting polymer-based sensors further. The manufacturing of electrode on an environmentally friendly paper substrate can also be accomplished by using the dip coating and inkjet printing methods. Currently, the existing conducting polymer-based gas sensors are pricey for their cost production and their technique of synthesizing required high surfactant concentration which leads problem in terms of environmental pollution. Proper ventilation is required to regulate air flow in a confined room. Air monitoring in a closed room is usually limited to temperature and humidity. However, there are many variables that influence air quality. High concentration of CO_2 which is colourless and odourless in a poorly ventilated area would be deadly. In addition, during coronavirus

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pandemic, poor air quality would possibly contribute to easier infection spreads. Therefore, in this work, polymer-based sensor is fabricated, to detect CO_2 hence provide indication for the best time to ventilate. Therefore, by using the preferable cost-effective method and organic conducting polymer nanocomposite and substrate, may along lead to long term uses and environmentally friendly solution.The ever-increasing quantity of toxic gases in the atmosphere is a major source of concern in modern life. As a result, detecting, collecting, and lowering CO_2 is becoming extremely important, sparking interest in novel technical solutions for CO_2 monitoring. Because of their excellent selectivity and sensitivity, nondispersive infrared (NDIR) sensors are commonly used to monitor atmospheric CO_2 concentrations. However, the reduction of NDIR technology's potential is limited and its use in small, portableelectronic devices is limited. Moreover, it is incompatible for use in battery powered devices with significant power consumption, and usually need multiple hundreds of microwatts. As a result, attempts are being made to create alternative or superior CO_2 detection systems.

Gas sensors have been shown to be useful devices in our everyday life for environmental control, manufacturing processes control, diagnosis of disease and control of protection. In recent years, a great deal of attention has been paid in developing miniaturized, reliable, and highly sensitive gas sensors that can be built into portable devices like smart phones and wearable devices. Gas sensors based on conducting polymers (CPs) have attracted the attentions of researchers due to their microelectronic batch manufacture compatibility, stability, and ability to create multilayer device architectures.

CPs are polymers that have significant conductivity levels and are also nanostructure materials. The conduction of polymers is due to the presence of free electrons in the body of the sample. CPs have a reversible redox behaviour and rare mixture of metal and plastics as a replacement for a metal conductor and semiconductor. These materials have special mechanism of state and strong environmental stability of oxygen and water. Due to the chemical flexibility, stability, process ability, low specific gravity, extended life cycle and low cost, these polymers may be very promising for many technical uses. Variety types of gas sensors are based on polymers, such as electrochemical sensors, electrical sensors, optical sensors and mass sensor systems. Conducting polymers combines with other materials, forming functional nanocomposites result in several desirable characteristics such as high electron mobility, superior thermal conductivity and optical transmission [1].There are many reported works on the use of PEDOT: PSS in sensor development [2-5], due to incredibly high susceptibility and quick reaction to gas molecules, owing in large part to a high surface-to-volume ratio [3]. One of PEDOT benefits is that the monomer is extremely economical, whereas possess optical durability, and is soluble in water with polystyrene sulfonate (PSS) [4]. Each type of conducting polymers varies in the values of conductivity [6]. The factors that affect the conductivity are:

1. Density of charge carriers.
2. Charge carriers' mobility.
3. The direction.
4. Presence of doping materials (additives that facilitate the polymer conductivity).
5. Temperature.
6. Conjugation length of the polymer chain.
7. Doping level.
8. Frequency of current.

In addition, several inexpensive, modest CO_2 gas sensors based on electrical response of the active material have been presented. Alternatively, nanostructured materials can be used to allow gas sensors to work at room temperature or to improve CO_2 reactivity [7]. An orthogonal strategy is to employ polymeric active materials such as CPs, which have good electrical, chemical, and structural optimization and facilitate sensor production. One of the best conducting polymers used in sensor development is PEDOT:PSS. Nonetheless, it has inadequate structural and chemical properties which limit its effectiveness in real applications. These drawbacks can be overcomed by combining with carbon nanomaterials [8]. GO, a two-dimensional monolayer of carbon atoms organized in a honeycomb lattice, has grabbed the researchers' interest due to its high surface area, excellent electrical conductivity, and excellent mechanical properties [9]. There is a large number of oxygens containing feature groups on the surface of GO, that enhances solvent dispersibility as well as decreases aggregation and increases the connection of nanocomposite fillers to polymers. Many thin films based on GO nanocomposites for transparent and versatile electronic devices have been investigated [10-13]. PEDOT:PSS and GO are both hydrophilic, which allows them to be uniformly deposited as thin films onto sensor substrates, which is essential for sensor technology applications. Despites their large abundance, high crystallinity and high purity, only single example of kaolinite intercalation with

organic polymers are described compared with other natural clays [14]. Kaolinite and bentonite are one of the most prevalent clay minerals in the world and is one of the most significant raw materials used in the industry, especially in the soils, sediments, and sedimentary rocks. This mineral has an ideal composition $Al_2Si_2O_5(OH)_4$, a hydrated aluminum disilicate.

Kaolinite is a mineral made of physically asymmetric layers, 1:1 dioctahedral clay. One side of the layer is gibbsite-like with octahedrally coordinated aluminum atoms and hydroxyls. The other part of the layer consists of a structure of a silicate layer, where the silicone atoms are tetrahedrally coordinated with oxygen. Thus, the structure of kaolinite mainly comprised of one silica sheet of tetrahedral fusing a single alumina of the oxygen sheet on one side and hydroxyls on the other of the oxygen planes [15-17]. Therefore, in this work, kaolinite and bentonite are chosen to intercalate with CP and carbon nanomaterials. To the best of our knowledge, however, PEDOT:PSS/GO composite has not been exploredfor CO_2 gas sensing applications. As a result, incorporation of GO into the commercially available PEDOT:PSS matrix is investigated in the current study to improve the conductivity of the PEDOT:PSS/GO composite, which is then investigated for sensitive, selective, fast, and repeatable detection of CO_2 gas molecules at room temperature.

Materials and Methods:-

Sample preparation can be divided into coated paper substrate preparation and nanocomposite sensor fabrication via dip coating. Firstly, the type of suitable clay to coat paper substrate is determined. Bentonite and kaolinite of 5 ml respectively are diluted in 7.5 ml distilled (DI) water, yielding a ratio of 1:1.5, are stirred well for 25 minutes. Each diluted solution was then used to coat a 125gsm paper via dip coating technique. Bentonite and kaolin coated papers were then left to dry at room temperature. Surface morphology of the prepared paper substrate was then further analysed though FESEM, to determine the most excellent coating and surface to be used in sensor fabrication.

Next, suitable ratio of PEDOT:PSS to DMSO solvent was determined. DMSO is one of the solvents used to dilute thick PEDOT:PSS solution, to ease stirring process and to achieve excellent dispersion with other materials. In this work 0.8 ml and 1.2 ml of PEDOT:PSS were added to 2 ml DMSO. Later the number of nanocomposite coating layer was determined. PEDOT:PSS/ GO solution was prepared by stirring process at room temperature as portrayed in Fig. 1. After that, XRD spectra of 1, 5 and 7 layers were observed for any change in material structure with increasing coating layers. Based on characterisation analysis obtained by using FESEM and XRD, nanocomposite ratio and the number of nanocomposite coating on paper substrate to be used in sensor fabrication was determined.

Figure 1:- Stirring process of PEDOT:PSS and GO.

Dip coating is a simple, low-cost, reliable and reproducible method which involves the deposition of a wet liquid film by immersion of the substrate into a solution. It also involves the deposition of a liquid film via the precise and controlled withdrawal of a substrate from a solution using a dip coater.

Experimental set up to test the developed sensor performance is shown in Fig. 2. CO_2 detection takes place in an acrylic gas chamber shown in Fig. 2, which prototypes a closed room. CO_2 detection was measured by using two electrode methods by using a multimeter, to obtain sensor resistance value. At room temperature, without CO_2 gas

released, the baseline resistance, R_0 was measured. Then CO_2 was released at constant flow rate, Δf and resistance values increases until saturation, R_1.

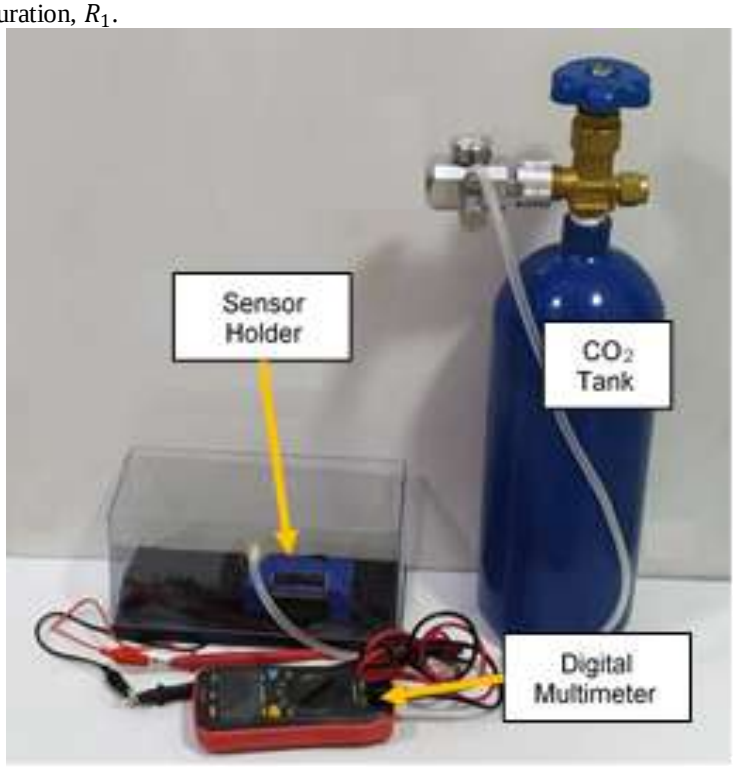


Figure 2:- CO_2 measurement set up.

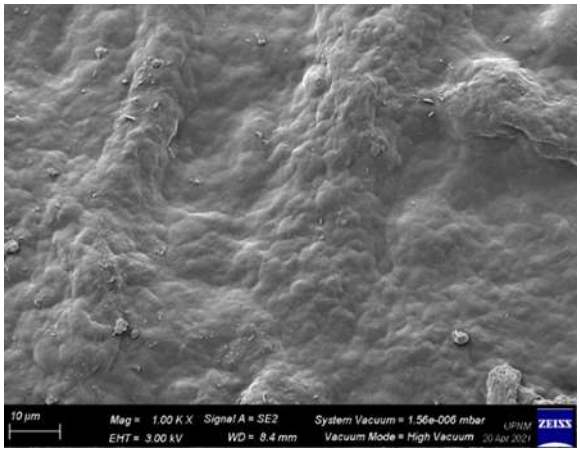
Results and Discussion:-

In this work kaolinite and bentonite were used because the structure and good electrical properties, when these clays being implemented in polymer-clay nanocomposites. In spite of its great abundance, high crystallinity and high purity are advantageous when compared with other mineral clays. Besides, both clays could interact with molecules that contain silane groups. The clays were mixed with DI water with the same ratio and were stirred well. The ratio of DI to kaolinite and bentonite was chosen to ensure complete wetting and to prevent separation of the suspension and to obtain a homogeneous system.

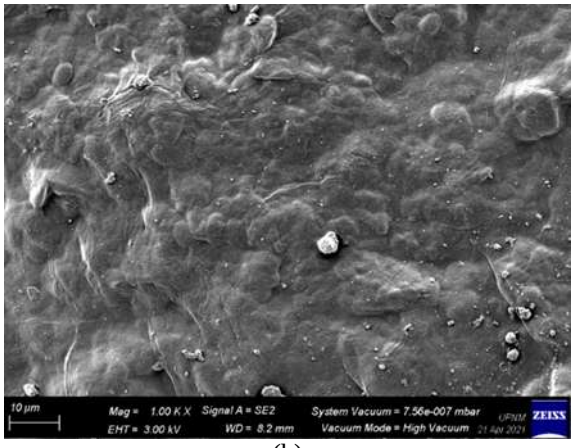
The same ratio of DI water to kaolinite and bentonite of 1.5:1 was used in this work. Bentonite solution was stickier and thicker compared to kaolinite solution, so it was hard to spread the solution uniformly on the paper substrate. The first attempt of dip coating by using this clay solution was made on 0.5 x 6 cm, 60 gsm paper substrate, but it was very hard to hold the substrate since it was very thin and light. After that, thicker paper substrates of 125 gsm was used, and the size was also changed to 1 x 4 cm. Then the substrate was used in dip coating process.

Next, both coated substrates were left to completely dry for 3 days at room temperature. FESEM images of coated paper are shown in Fig. 3, where kaolin coated paper surface is seen better than bentonite coated paper substrate. Surface morphology and roughness of kaolin provide smoother layer than bentonite. It can be clearly seen (Fig. 3(a)) that the swelling of kaolin molecules on the paper substrate is adequately uniform.

Consequently, water molecules are desorbed and transferred into the bulk phase leading to swelling. While for bentonite coated substrates (Fig. 3(b)), swelling of the clay is not uniform This is due to thicker solution causing the material to not easily stick on paper substrates and dry subsequently. Other than that, it can be seen that there are a lot of impurities present on the surface, due to non-well dispersion of the bentonite solution. Consequently, based on FESEM results, bentonite was not used in this work. Kaolin coated paper was then prepared to be used in sensor fabrication.



(a)



(b)

Figure 3:- FESEM images of paper substrate coated with different clays. (a) Kaolinite. (b) Bentonite.

Preparation of nanocomposite solution was done by stirring process. The stirring process was completed after 2 hours, and there was no agglomeration formed in the solution during stirring. Fig. 4 shows the XRD pattern of PEDOT:PSS/GO with different layered dip-coating. Based in Fig. 5(a), there are two obvious peaks present at 15.5° and 22.5° diffraction angle. The development of hydroxyl, epoxy, and carboxyl groups on the surface of the carbon network was linked to this interlayer gap. Because of the elimination of the oxygen-containing functional groups, the interlayer distance of the GO was predicted to decrease [17]. Based on XRD spectra, increasing PEDOT:PSS/GO coating thickness cause no further modification to the structure compared to thinner layer. Increasing the number of coating layer was not causing any peak shift in XRD spectra too. Hence, the next stages in nanocomposite film fabrication was used is 1 layer on the coated paper substrates. Previous studies also reported that the small different number of layers will not give a high affect and intense different in the analysis [18]. Based on the attained results, absorption peaks are not shifted by increasing PEDOT:PSS ratio in the solution. Therefore, in this work, equal ratio of PEDOT: PSS to DMSO and GO was selected.

In addition, increasing number of coating layers are not affecting the XRD spectra of PEDOT:PSS nanocomposite, suggesting that the structure is not changed with more layers. Therefore, in this work, one layer of PEDOT:PSS/GO is used to coat kaolin coated paper substrate. The fabricated kaolin coated paper substrate and PEDOT:PSS coated paper are shown in Fig. 5 (a), whereas one layer of PEDOT:PSS/GO coating on kaolin coated paper substrates are represented by Fig. 5 (b).

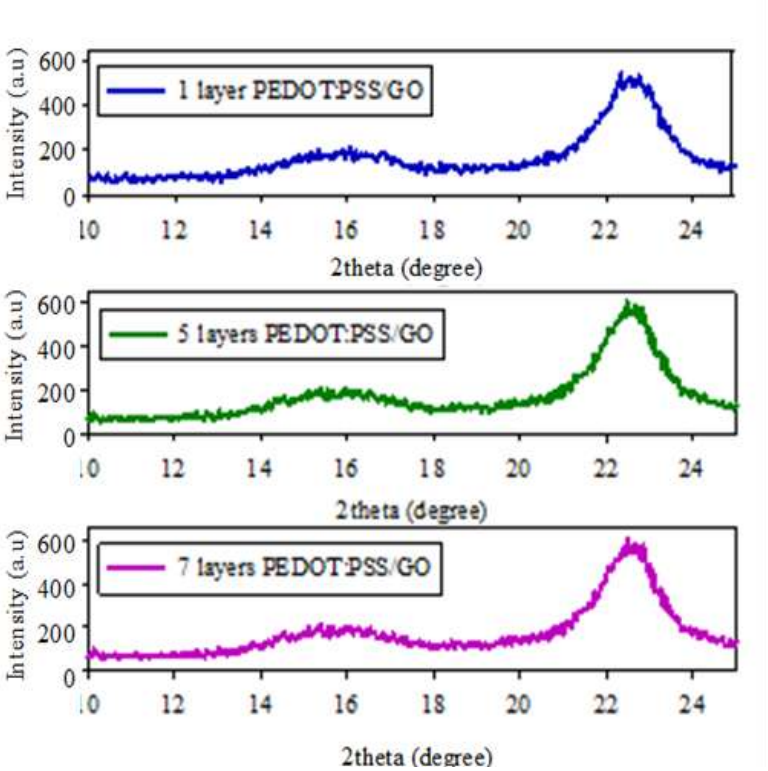


Figure 4:- XRD spectra of PEDOT:PSS/GO coating layers(1, 5 and 7 layers).

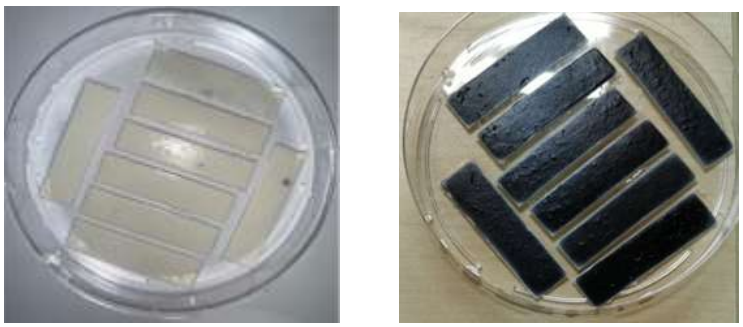


Figure 5:- Samples prepared by using dip coating method.(a) Kaolin coated paper substrate. (b) PEDOT:PSS/GO.

After every process of dip coating on the substrates, the kaolin coated paper substrates prepared via dip coating method are used in surface resistance measurement, shown in Fig. 6. Resistance in inversely proportional to electrical conductance, as expressed mathematically by equation (1).

$$G = 1/R \qquad (1)$$

where G is the conductance and R is surface resistance.

Based on this equation, the lower the resistance of the tested coated substrate the better, as this will cause higher conductivity. Dried kaolin coated substrate possess high surface resistance. The lowest resistance of three selected samples shown in Fig. 6 is 0.737 MΩ, which is quite high, thus resulting poor conductivity.

This is evident and straightforward due to the fact that kaolin is not an electrical conductor. Conversely, resistance is further reduced after PEDOT:PSS/GO is coated on kaolin layer. The reduction in resistance value indicate excellent coating as PEDOT/PSS/GO penetrates into intercalated layered kaolin structures.

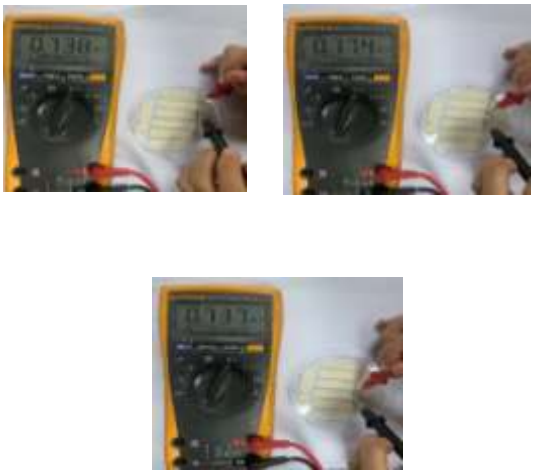


Figure 6:- High surface resistance of kaolin coated paper substrates. (a) 0.738 MΩ. (b) 0.774 MΩ. (b) 0.737 MΩ.

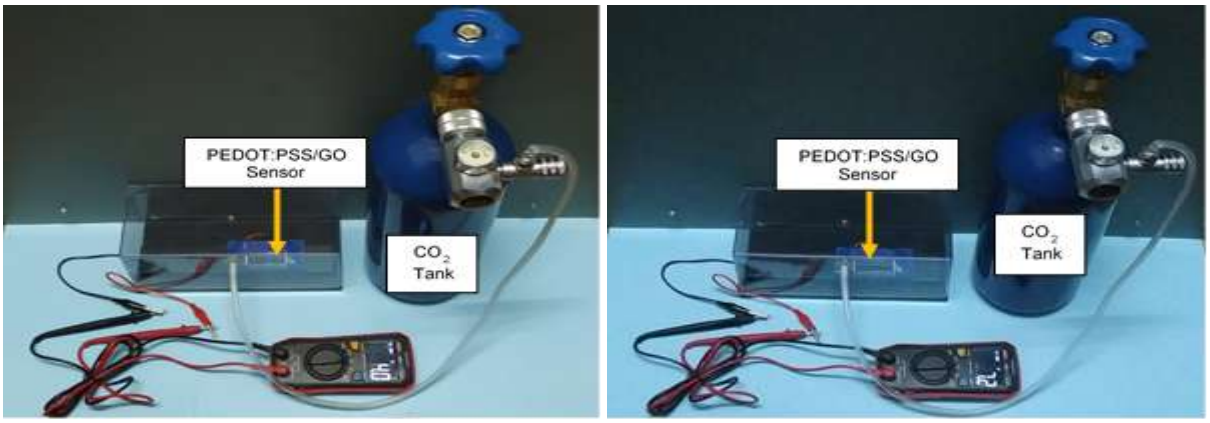
Equation (2) and (3) describes sensing response, ΔR and sensitivity, ΔS of developed PEDOT:PSS/GO sensor towards CO_2 gas detection.

$$\Delta R = \frac{R_1 - R_0}{R_0} \qquad (2)$$

$$\Delta S = \frac{\Delta R}{\Delta f} \qquad (3)$$

where R_0 is the baseline resistance of the PEDOT:PSS/GO sensor and R_1 is the resistance of the PEDOT:PSS/GO sensor in the presence of target gas at constant flow rate, Δf .

Measurement of R_0 and R_1, at 0.05 l/min flow rate is shown in Fig. 7. In CO_2 detection, the rise of resistance value is due to chemoresistive response of the PEDOT:PSS/GO towards CO_2 gas molecules [19]. Carbon nanomaterial, GO inclusion into PEDOT:PSS has led to a significant increase in charge carrier concentration. Furthermore, high density of chemical groups on GO, particularly hydroxyl and carboxylic, enhance surface adsorption of CO_2 in hydrogen bonding as well as other chemical interactions, potentially leading to substantially improved CO_2 detection sensitivity [20]. Besides, electron-drawing CO_2 gas molecules attach on graphene surface, give rise to graphene's doping level, causing higher conductance [21].



(a) (b)

Figure 7:- CO_2 sensor detection testing. (a) R_0 of 4 Ω.(b) R_1 of 7.2 Ω.

As seen in Fig. 7 (a), with no CO_2 flow, R_0 is 4 Ω. Later, constant CO_2 gas flow of 0.05 l/min is released into the testing chamber, causing resistance values to increase. After 32 seconds resistance increases to 7.2 Ω, and the value keeps constant for 8 seconds, Resistance values continue to decrease to baseline value of 4 Ω, as the gas flow is terminated and released as represented in Fig. 8.

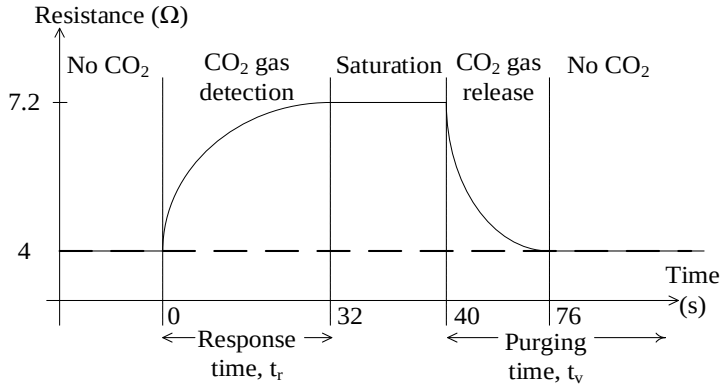


Figure 8:- Resistance and response time measurement.

Sensor response time, t_r is 32 s with response value of 0.8. Sensor's sensitivity at 0.05 l/min CO_2 flow is 16/l/min. Fast response time is successfully achieved by utilizing the fabricated PEDOT:PSS/GO. Therefore, the stability and fast response of the fabricated PEDOT:PSS/GO are quite promising to be utilized as an one of the available alternatives to non-toxic and environmentally friendly indoor CO_2 detection in the future. The observed response and resolution make the device a practical low-cost sensor for CO_2 detection. In the future, the developed non-toxic and environmentally friendly PEDOT:PSS/GO CO_2 sensor, fabricated on kaolin coated paper substrate can be used for smart real time indoor air quality monitoring, through the integration with microcontrollers and Internet of Thing (IoT).

Conclusion:-

CO_2 gas sensor is successfully fabricated by using PEDOT-PSS and GO nanocomposites. One layer PEDOT:PSS/GO on kaolin coated paper substrate is fabricated by using dip coating method. At room temperature and fixed CO_2 flow rate of 0.05 l/min, chemiresistive response of the developed nanocomposite towards CO_2 molecules causes baseline resistance, R_0 of 4 Ω to increase to 7.2 Ω. The developed sensor also achieves fast response time, t_r of 32 s, with sensor response and sensitivity of 0.8 and 16/l/min respectively. These promising results suggestthat the developed PEDOT:PSS/GO CO_2 sensor offers significant stability and selectivity as one alternative for non-toxic, environmentally friendly and sustainable indoor air quality monitoring solution. In addition, for future development, PEDOT:PSS/GO CO_2 sensor is possible to be integrated with microcontrollers and IoT platform for smart real time indoor air quality monitoring.

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