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Research Article

Synthesis, characterization and ethanol vapor sensing performance of SnO_2/Graphene composite films

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Abstract

High performing sensor consisting of SnO_2/Gn nanocomposite was fabricated using a novel one-step *in-situ* sonochemical method. The reducing properties of $SnCl_2$ was used to reduce graphite oxide (GO) so that $SnCl_2$ could be transformed to SnO_2 on the basal plane of graphene. The combined characterizations including X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transformed Infra-Red spectroscopic data (FTIR) indicated the successful formation of SnO_2/Gn composites. Current-voltage (I-V) characteristics of the gas sensor showed ideal ohmic behavior having low resistance. To demonstrate the product on sensing application, gas sensors were fabricated using SnO_2/Gn composites and used in detecting ethanol vapor at room temperature (27˚C).The results indicate that the SnO_2/Gn composite exhibits a considerably high sensing performance of 17.54% response at 150 ppm ethanol vapor, rapid response and reproducibility. Furthermore, the performance of the gas sensor based on SnO_2/Gn is very stable for a long period of time under normal operating conditions. Therefore, it is suggested that SnO_2/Gn can be considered as an excellent sensing material which also has a potential for wider range of applications on sensors.

Keywords: SnO_2/Graphene; ethanol vapor sensing

1. INTRODUCTION

Throughout the world, research on electronic sensors has become an important activity because of their importance, especially in applications involving human breath quality, wine quality, food, oil, and coffee quality. The sensor activity in the vicinity of

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different gases makes the resulting output pattern to appear differently. Sensors can be mainly classified as solid electrolyte detectors, catalytic detectors, electrochemical detectors, infrared gas detectors, solid-state sensors, paramagnetic gas sensors etc. Out of these, the semiconductor gas sensors provide the most promising application for the purpose of detecting gases. The response from the semiconductor (p- or n-type) is not only a function of the doping and material extrinsic properties, but is also dependent on the concentration of the gas exposed to the semiconductor[1].The main identification factors of these sensors are the resistance variation of the semiconductor provided that the gas is exposed to the semiconducting material.

Recently, graphene has evolved as an interesting material due to its unique physical and electrical properties[2]. Graphene is different from the conventional semiconductors because it is identified as a zero band-gap semiconductor[2-10]. Graphene based materials are suitable for gas sensing device fabrication because of their high surface to volume ratio[10,11]. Moreover, since it is a low resistance material (typically few hundred ohms~(10^2-10^3 Ω)), gas sensors based on graphene do not require high impedance circuits. However, the relatively poor performances such as low response, long response time and recovery times should be further improved for effective applications[16]. Gas sensing applications of tin oxide nano structured materials have been investigated for which moderate results were obtained[19]. Recently, high performing sensors have been constructed using graphene and metal oxide nanocomposite overcoming the above limitations[17,18]. However, the operating condition of most of these sensors is at elevated temperatures.

The present work reveals the performance of a Graphene/ SnO_2 sensor which can be operated at room temperature. An *in-situ* method was followed to synthesize the composite using graphite oxide (GO) and $SnCl_2$, wherein, $SnCl_2$ acts as a strong reducing agent. The present novel one step reaction method is identified as an economical approach for mass scale production of these sensors.

2. METHODOLOGY

2.1 Synthesis of graphite oxide

Bogala graphite flakes of 97% purity were oxidized using Modified Hummers method[15]. 1.0 g of natural graphite was added to 20 cm^3 of Conc. H_2SO_4 at 0°C. 3.0 g of $KMnO_4$ was added gradually to the mixture while stirring. The mixture was then stirred at room temperature for 30 min and 50 cm^3 of water was added slowly. Subsequently, 150cm^3 of distilled water was added followed by 10 cm^3 of 30% H_2O_2 solution. The solids were separated by centrifuging and washed repeatedly with 5% HCl until sulphate could not be detected with $BaCl_2$.The product was washed with acetone and dried in an oven at 90°C for 2 h.

2.2 Synthesis of SnO_2/Gn Composite

$SnCl_2.2H_2O$ and graphite oxide (GO) were mixed at a ratio of 15:8 by weight with water and sonicated for 3 hours. In this process, $SnCl_2$ is used to reduce GO and concurrently produced SnO_2 on the graphene basal plane through the reaction given below:

$$SnCl_2 + GO + H_2O \rightarrow SnO_2/Gn + HCl \quad (1)$$

The resulting reaction mixture was washed with distilled water to remove impurities and dried at 60^oC for 12 hours.

2.3 Fabrication of SnO_2/Gn thin film gas sensor

Gold was deposited on a SiO_2 glass substrate by using sputtering process. The Shadow mask method was used in developing the electrode plate where gold sputtering was enhanced by the EMITCH K 550 instrument. The SnO_2/Gn composite was mixed with ethanol using an agate mortar and transferred on the pre-prepared gold electrode. The average area of the gold film is ~1 cm^2 and developed electrode plate was annealed in a vacuum oven at 70˚C for 3 hour. The sensor fabricated as described above was then used for characterization purpose and to study gas sensing properties.

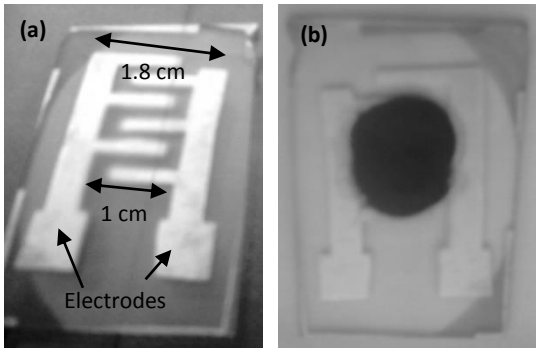

Figure 1: (a) Developed gold electrodes on the SiO_2 glass substrate (b) Fabricated SnO_2/Gn gas sensing composite on the gold electrodes

3. CHARACTERIZATION

X-ray powder diffraction (XRD) analysis was conducted to identify the crystalline phase composition of the prepared SnO_2/Gn composite at the range of 5^o–100^o with Cu Kα1 radiation (λ = 1.5406 Å) at 40 kV and 40 mA using Regaku ultima IV X-ray diffractometer. The morphology of SnO_2-Gn was characterized by LEO 1420vp scanning electron microscopy (SEM). Functional groups attached to GO and SnO_2/Gn composite were characterized using BRUKER Tenor 27 FTIR-ATR spectrometer. The optical band gap of the composite was measured with SHIMADZU UV-1800UV-Vis spectrometer, I-V characteristics were also measured to study the ohmic behaviour of the gas sensor using BioLogic sp-150 potentiostat.

The static measuring system was used to test gas sensing properties. The investigation was done under laboratory conditions (room temperature - 27^{o}C and humidity - 75 %). The relative variation of the gas sensor resistance (gas response) was calculated by applying a constant current of 1 mA and obtaining the corresponding voltage variations in subsequent time periods. Further Response (S) was calculated by equation $S = (R-R_{air})/R_{air}$, where R and R_{air} represent the resistances of the sensor in corresponding gas and the initial resistance of the gas sensor in air, respectively.

4. RESULTS AND DISCUSSION

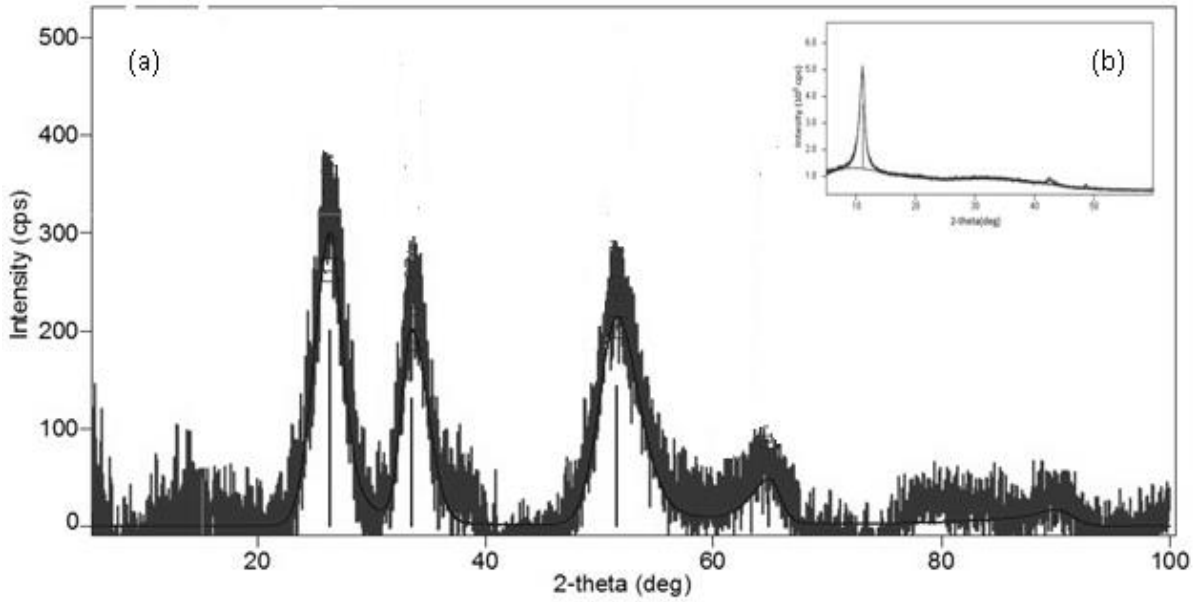

Figure 2: X-ray powder diffraction (XRD) patterns of (a) SnO_2/Gn composite (b) GO

Figure 2(b) shows the XRD patterns of GO. A strong peak at 2θ of 11.03˚ corresponding to the (0 0 2) interlayer d spacing of 8.01 Å of GO was observed, indicating the successful conversion of GO from graphite by oxidation of graphite. Figure 2(a) shows the XRD patterns of SnO_2/Gn. Several strong peaks are observed at 2θ of 26.49˚, 33.48˚, 51.59˚ and 64.42˚, which are attributed to the (1 0 0), (1 0 1), (2 1 1) and (1 1 2) planes of tetragonal rutile SnO_2, indicating the formation of SnO_2 crystals. However, no diffraction peaks can be ascribed to graphene, probably due to relatively low intensity of the peak which corresponds to graphene.

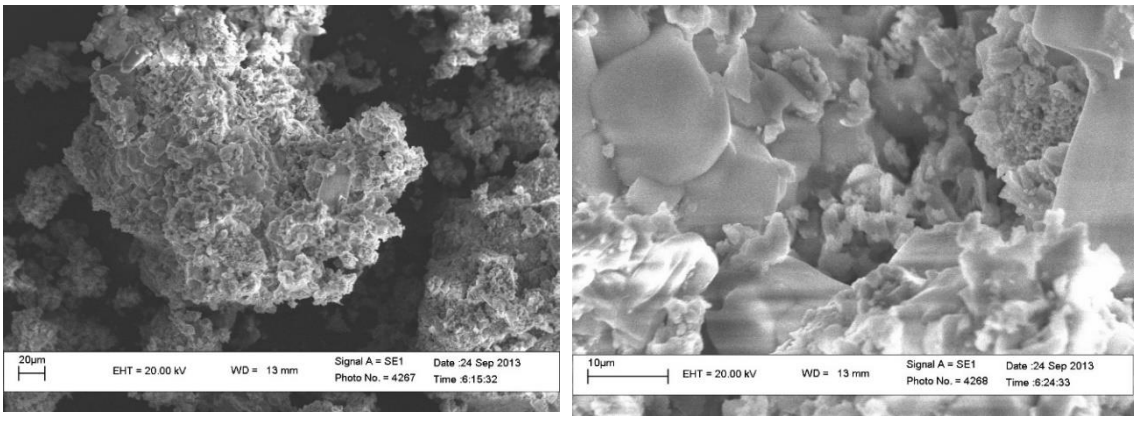

Figure 3: Scanning Electron Microscopy (SEM) images of the SnO_2/Gn composite

Figure 3 shows the scanning electron microscopy images of the SnO_2/Gn composite. As illustrated in the figure, the micron size cavities can be visualized clearly which obviously results in high surface area. The probability of adsorbing gas molecules in these cavities is also high and therefore the morphology is favorable for gas sensing.

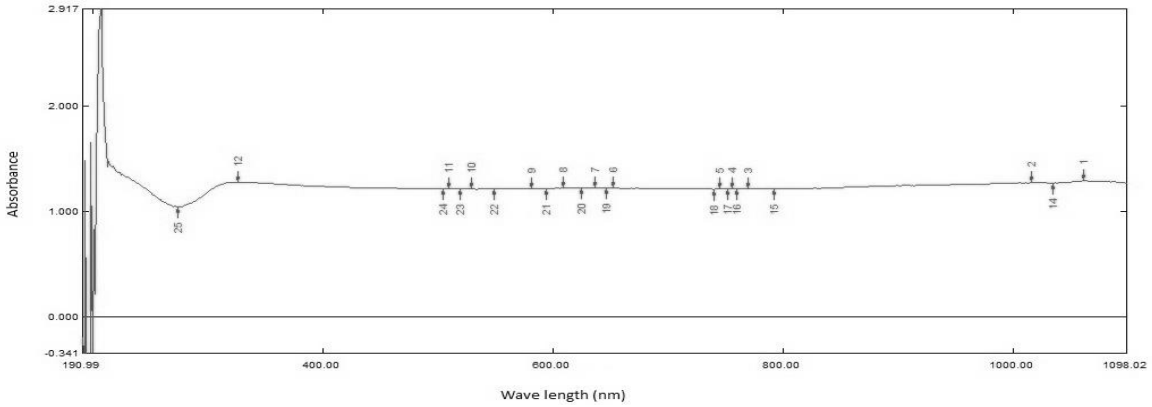

Figure 4: UV – Visible Spectrum of SnO_2/Gn composite

The optical band gap of the SnO_2/Gn composite was investigated using UV-visible absorption spectrometer. The UV-visible spectra of the composite showed an absorbance with relevant to the rising edge of the sharp peak which is 334 nm (Figure 4) and the corresponding band gap energy of the composite is ~ 3.71 eV.

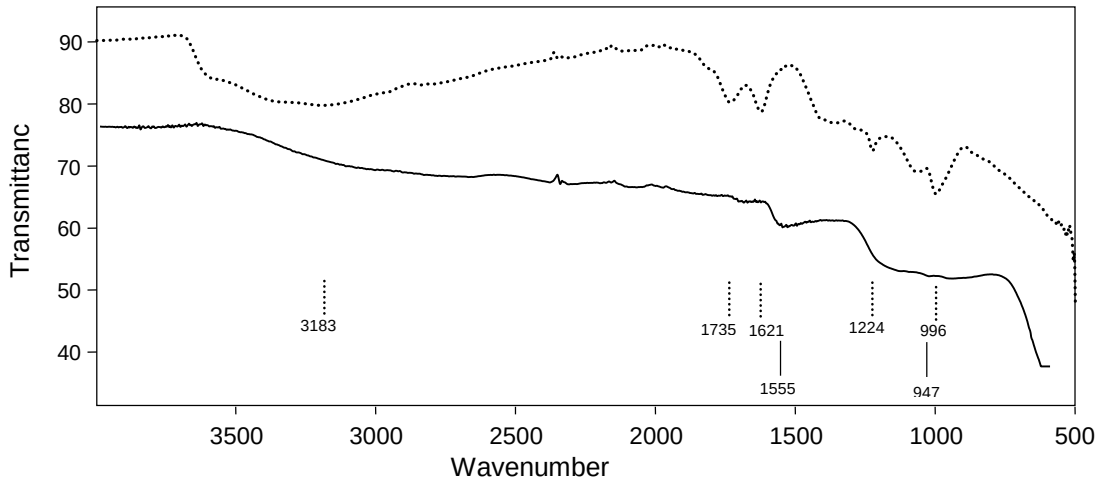

Figure 5: FTIR spectra of GO (dotted line) and SnO_2/Gn composite (solid line)

Figure 5 shows the FTIR spectras of GO (dotted line) and SnO_2/Gn composite (solid line). It is found that different types of oxygen functionalities are present in graphite oxide confirming various oxygen configurations. Epoxides (C–O–C) and structural hydroxyls (C–OH) attributed bands can be seen at 996 cm^{-1} and 1224 cm^{-1}, and carboxyl (COOH), ketonic species (C=O) and C–O attributed bands can be seen at 1621 cm^{-1} and 1735 cm^{-1}. Band around 3183 $cm^{-1}$are attributed to free hydroxyl (C–OH) from water vapor. In this process, $SnCl_2$ is used to reduce GO to graphene and it is found that sp^2-hybridized C=C peak of reduced graphene at the band 1555 cm^{-1}. Band at 947 cm^{-1} is attributed to remaining epoxide (C–O–C) attached to the graphene basal plane. Sn-O bond should lie below the band of 500 cm^{-1}.

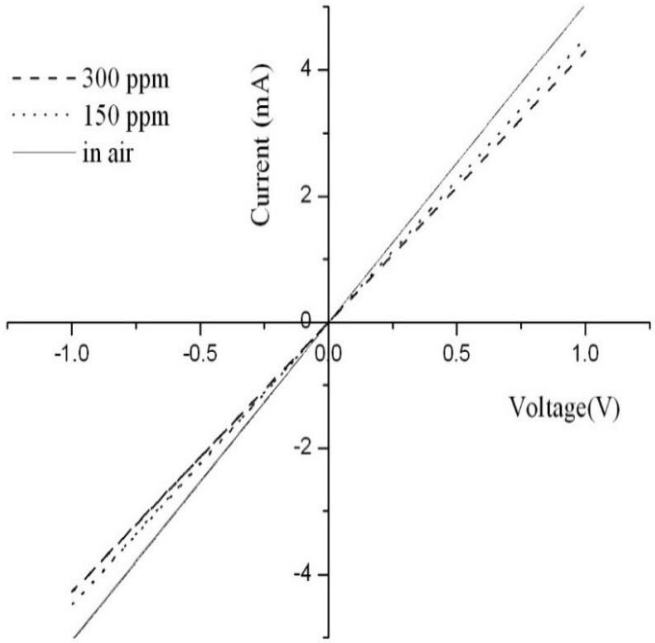

Figure 6: Current-voltage (I−V) characteristics of the gas

Figure 6 represents the current-voltage (I−V) characteristics of the gas sensor in air and at different ethanol concentrations. The I−V curve of the fabricated sensor produced ideal ohmic behavior. The ohmic behavior is a very important gas sensing property, because the sensitivity of the gas sensor is affected by contact resistance. It was found that the resistance of SnO_2/Gn composite was 197.6 Ω in air at room temperature and when exposed to ethanol concentrations of 150 ppm and 300 ppm the corresponding resistance increased to 222.2 Ω and 233.3 Ω consecutively. The highlighted property of the present sensor is the low resistance which is few hundred ohms. Therefore sensors developed based on this material will not require high impedance measuring circuits. Therefore, the present gas sensing device can have promising applications due to their integration capability in electronic devices.

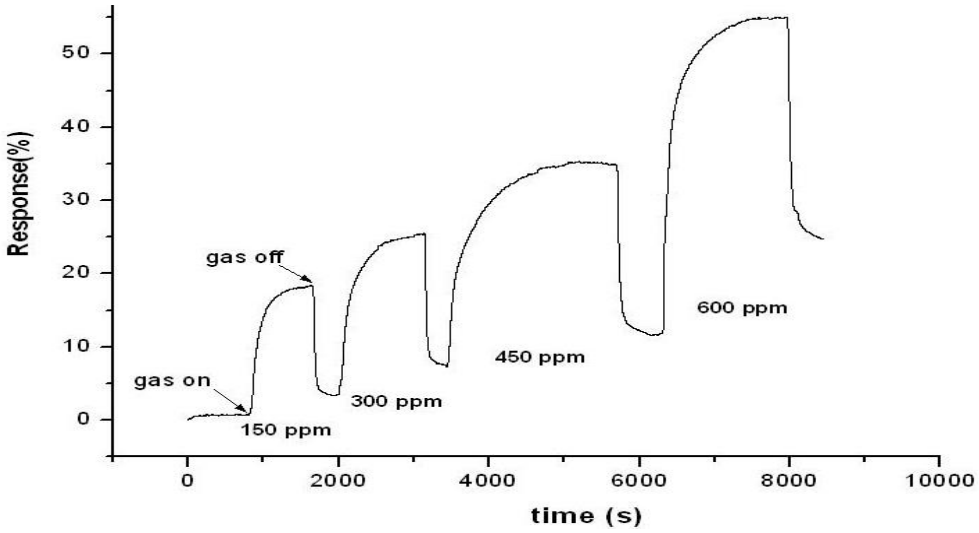

Figure 7: The response of the SnO_2/Gn sensor exposed to different concentrations

Figure 7 shows the response of the SnO_2/Gn sensor exposed to different concentrations of ethanol vapor at the operating temperature of 27°C and humidity as 75%. The response is about 17.54, 21.06, 25.44 and 38.58 to 150, 300, 450, 600 ppm respectively, In addition, the sensor demonstrated are relatively fast response times as revealed by the rapid changes in resistance and recovery (to original resistance)when exposed to the target gas and then air, respectively. Moreover, we observed an increase in the resistance of the SnO_2/Gn sensor with exposure to ethanol vapor. The polarized C_2H_5OH is adsorbed to SnO_2/Gn composite and free electrons on the surface are bonded with $H^{+\delta}$. Therefore, the decrease of free electrons causes an increase of the sensor resistance.

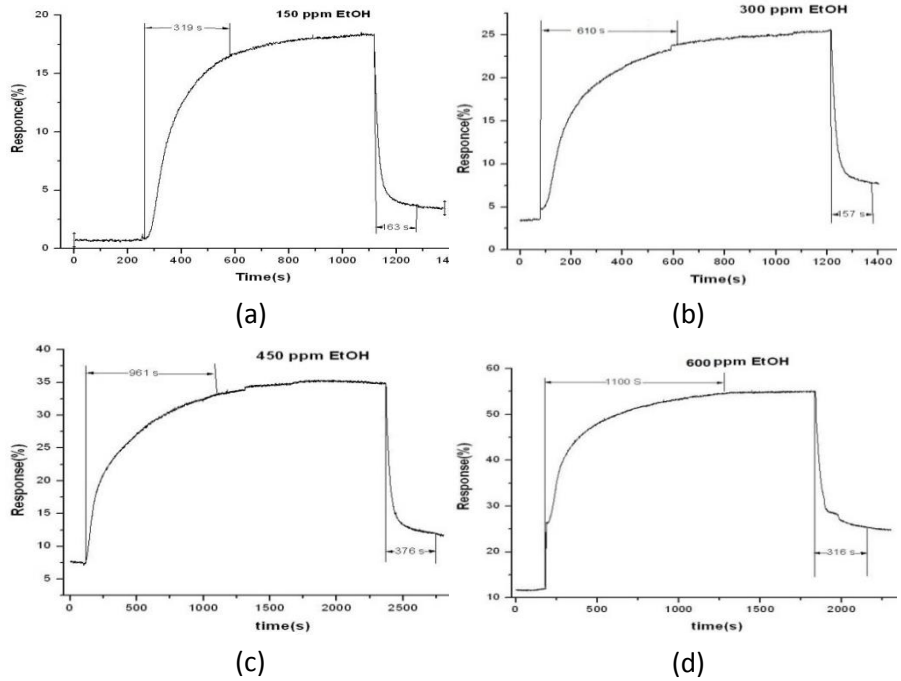

Figure 8: The response time and recovery time of the SnO_2/Gn sensor exposed to different concentrations of ethanol vapour

The response time and recovery time of the SnO_2/Gn sensor exposed to different concentrations of ethanol vapor is demonstrated in Figure 8. It is clearly seen that when the ethanol vapor concentration was increased to the level 150, 300, 450 and 600 ppm the percentage response was also increased to 17.54, 21.06, 25.51 and 38.58 consecutively. It is also related to 319, 610, 961 and 1100 of the response time in seconds. When the recovery time is concerned all the four cases had lower deviation in data and mean average of 253 seconds was produced.

The percentage variation of response due to various ethanol concentrations is demonstrated in Figure 9. Further the plot on response (S) vs concentration gave an exponential curve fitted with a matching equation of $S=S_o+A.e^{(C/t)}$ where S_0, A and t are constants having values of S_0 = 15.98 A = 0.8496 and t = 183.066, it produced a definite variation type in a mathematical form.

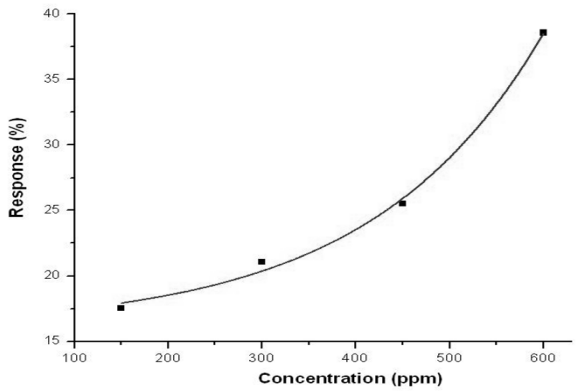

Figure 9: The response curve for different concentrations of ethanol vapour

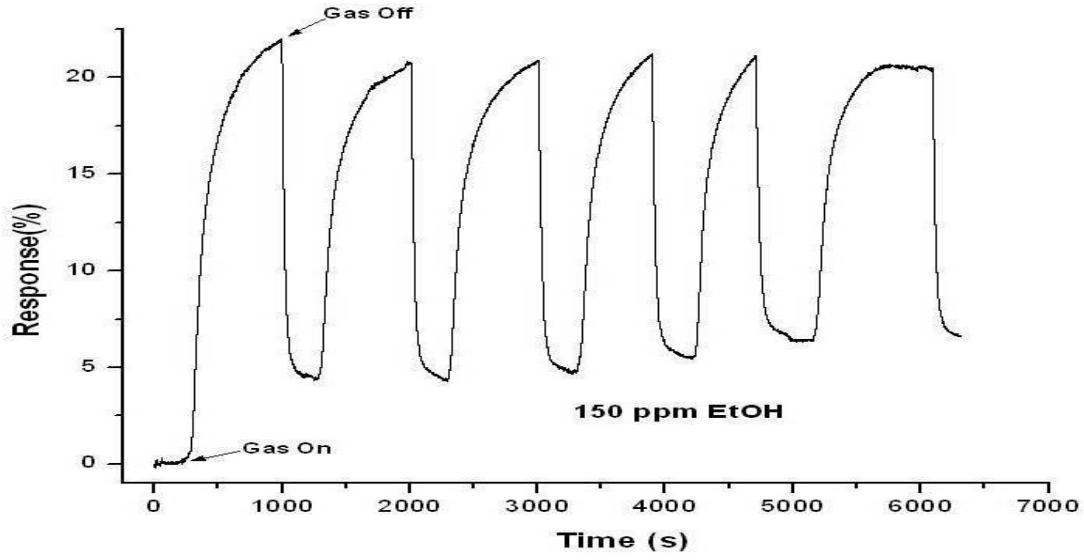

Figure 10: The repeatability of the gas sensor when exposed to 150 ppm concentration of ethanol vapour

The repeatability of the gas sensor was also studied and the results are, as shown in Figure 10. Six cycles of responses to ethanol vapors were executed through exposure of the SnO_2/Gn based sensor to 150 ppm ethanol vapor repeatedly. We found that the response levels of the sensor are maintained even after repeated cycles of exposure to ethanol vapor and recovery, suggesting that the SnO_2/Gn based gas sensor exhibits a high repeatable characteristic. The performance of the gas sensor based on SnO_2/Gn was found to be very stable for a long period of time under normal operating conditions.

5. CONCLUSIONS

$SnCl_2$ is effective in reducing graphite oxide and synthesizing in-situ SnO_2/graphene nano composite. The gas sensing results indicate that the SnO_2/Gn composites exhibit a considerably high sensing performance, 17.54% response at 150 ppm ethanol vapor level at room temperature ($27^{\circ}C$), with rapid response and reproducibility. Furthermore, the performance of the gas sensor based on SnO_2/Gn is very stable for a long time under normal operating conditions. Therefore, it is suggested that SnO_2/Gn has an immense potential in application as a sensor.

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