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Room temperature SO$_2$ and H$_2$ gas sensing using hydrothermally grown GO–ZnO nanorod composite films

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Abstract

Graphene based 2D materials with a surfeit of active sites and advantageously high surface to volume ratio are effectively linked to well established nanostructured semiconducting metal oxides for development of nanocomposites with enhanced gas sensing properties. Graphene Oxide (GO), a sister material of graphene, is therefore a natural choice for development of room temperature operated gas sensors. In the current investigation hydrothermally grown GO and ZnO nanorods composite (GO–ZnO–NR) is utilised for room temperature gas sensing of H$_2$ and SO$_2$ gases. Room temperature detection of H$_2$ and SO$_2$ at sub-100 ppm levels with linear variation in response for different concentrations is demonstrated. Morphological and structural analyses are conducted using Scanning electron microscopy, Raman spectroscopy and X-ray diffraction. GO-ZnO-NR composite sensor is seen to exhibit robust sensing response of 5.82 and 5.45 for 100 ppm each of H$_2$ and SO$_2$ gases respectively at room temperature. Further, the delayed response and recovery times exhibited by the sensor for SO$_2$ gas are recognized to be due to formation of strongly adhering SO$_3$ species.

1. Introduction

Worldwide researchers are actively engaged in developing gas sensors with low operating temperature (preferably room temperature) not only due to demands of the industry to minimize power consumption but also favourably integrate the same with Si micromachining technology [1]. Room/low operating temperatures of gas sensors proffer opportunities for use of flexible substrates which in turn are envisaged to help in the rapid development of wearable gas sensors [2]. Available literature reports over the last five decades indicate extensive investigation in the preferred use of semiconductor metal oxides (SnO$_2$, ZnO, WO$_3$, TiO$_2$ etc) with additives, dopants, bilayer/heterostructures, nanostructures/layers for gas sensing applications with selectivity [3, 4].

Semiconducting metal oxide based gas sensors are seen to exhibit enhanced sensitivity, partial selectivity to target gases, fast response speed and recovery based on two mechanisms of catalyst control proposed by Morrison [5]. The two mechanisms of catalyst control were described as a) Fermi level energy control mechanism and b) Spillover mechanism. In Fermi-level energy control mechanism, the sensing gas is seen to affect the catalyst that in turn varies the barrier height at the inter-granular boundaries after exchange of electrons while in the spillover mechanism the catalyst is seen to dissociate the gas molecule, and reactive atoms spill-over onto the underlying semiconductor surface and influence its conductivity. Chowdhuri et al have advantageously utilized both the mechanisms in conjunction to realise a trace-level H$_2$S gas sensor with enhanced sensing and fast response speed [6]. Despite all the aforementioned advantages, semiconducting metal oxides have a major drawback in elevated temperature of operation. Further, their constraint in size reduction coupled with metal oxide grain growth leading to agglomeration during usage over extended periods of time has limited their commercial development.
Post discovery of electrical properties of graphene nanosheets [7] researchers quickly identified its benefit of high specific surface area and soon its gas sensing capabilities were reported [8]. Over the last couple of years, Graphene Oxide (GO), a graphene analogue, with its multitude of functional groups and unique chemical properties has been reported to advantageously exhibit room temperature gas sensing. Beginning 2010 literature reports indicate presence of review papers on gas sensing properties of GO and reduced GO (rGO) [9–11]. Researchers have since then focussed on plethora of processes to enhance sensing response and impart augmented selectivity to GO based gas sensors. Besides the above, researchers are actively engaged in improving GO synthesis through the use of green reduction technique for GO using Indian gooseberry (Ammla) extract [12]. For gas sensing applications while some groups are concentrating on fabrication of free standing GO films [13] others have tuned its electrical properties through nitrogen ion implantation [14]. Still others have performed IR studies and reported gas sensing by use of low-temperature thermally reduced GO films in ambient atmosphere [15]. Ultrasonensitive optical gas sensing through use of a facile fabrication of colorimetric GO reflecting films has also been reported [16] whereas effects of particle size have been investigated for chemoresistive gas sensing with graphene decorated with magnetic iron oxide nanoparticles [17]. Researchers while examining in detail have also observed a clear transition in gas detection behaviour in non-reduced GOs subjected to thermal annealing [18]. Due to suitable chemical, physical and electronic properties, semiconducting metal oxides like ZnO have been used in the sensing of various gases but they suffer from a major drawback of high operational temperatures in the range of 200 °C to 400 °C. Thus they have high power consumptions restricting their deployment in many applications [19]. Graphene and its derivatives like GO or rGO have been potential materials for gas sensing as they possess large specific area as well as sensitivity. But they also require high operating temperatures and have poor response and recovery times. It limits their usage in many domains. However, the composites of semiconducting metal oxides and GO/rGO exhibit unique structural and sensing properties like low operating temperatures, enhanced sensitivity, larger surface area, fast response and recovery times [20]. Toda et al have also published a review on recent progress in use of GO for gas sensing [21]. Studies in the review and other literature reports indicate a gradual shift in the work of the researchers towards use of semiconducting metal oxides/metal based heterostructures, bilayers, nanocomposites, nanofibres etc. While some have utilized G-WO3 nanocomposites, others have used strategic synthesis of α-MoO3−x nanorods boosted GO for gas sensing applications. Further, modulation of gas sensing properties of single-atom Pd supported on N-doped graphene sheets has been achieved along with PANI based GO nanocomposites. Gas sensing with both, column-shaped ZnO doped with graphene as well as graphene-ZnO based nanomaterials has been reported. To augment gas sensing capabilities viz; wafer-scale graphene growth on Cu/Ni films, three dimensional arrays of α-Fe2O3 nanorods on GO nanosheets and GO-multi-walled CNT composites have also been utilized. Literature reports indicate use of multi-pronged approach by researchers even for detection of the same gases. Ammonia adsorption study under varying humidity conditions has been reported on GO [22] with meta-toluic acid functionalized GO also being used [23] whereas selectivity has been imparted using GO functionalized with 2-amino pyridine [24]. Scientists also have detected ammonia using ZnO incorporated GO [25] and even fluorinated GO [26]. Gases like NO2 have been ultra-sensitively detected using band gap engineered GO [27] while CO detection is reported using UV-light enhancement of InGaN nanorods decorated with p-Phenylenediamine-GO composite [28]. GO with decorated porous silicon and GO/SnO2 nanowire composites have been utilized for H2 sensing also [29]. Gases like CH4, Acetone and H2S have also been detected using GO, GO-WO3 nanofibres and SnO2 quantum wire /GO. Researchers have investigated CO2, H2 and C2H2 sensing characteristics using nanoporous GO [30] and even compared CO2 sensing characteristics of graphene and graphene oxide nanoplatelets. Further, literature indicates presence of reports on sensing mechanism of layered reduced GO room thin films [31] as also experimental and theoretical studies on 2D graphene membranes exploring gas permeation mechanism [32].

Looking at the aforementioned reports it is noted that a systematic study exploring the gas sensing mechanism of GO films needs to be carried out. This study assumes importance since gas sensing properties of GO are critically influenced by the nature and abundance of edge sites wherein their concentration may be quite high in comparison to basal plane sites. The role of semiconducting metal oxide ZnO primarily as catalyst with GO films is yet to be investigated in detail. Sulphur Dioxide (SO2) is a hazardous greenhouse gas which has posed a serious environmental and health threat. It is mainly produced due to combustion of fossil fuels. It causes irritation of the respiratory tract and is very harmful to human health specially persons suffering from asthma and heart problems. It engineers chemical reaction and comes down as acid rain that has an adverse effect on water bodies as well as soil. Therefore, it is necessary to monitor SO2 emissions to reduce its catastrophic damages. Hydrogen (H2) has multifaceted uses as an alternate clean energy source because of zero harmful emissions, high calorific value, being inexhaustible as well as easily transportable or its utility because of its reducing properties in metallurgy, chemical, ceramic and semiconductor industry. But being very colourless, odourless, volatile and highly inflammable, it requires very sensitive handling. Any unwanted outflow even in lower quantities can be catastrophic. Therefore, there is a need to develop H2 gas sensors with excellent sensing
parameters at room temperature. Hence in the present study thin film of GO with ZnO nanorods (GO-ZnO-NR) have been used to sense SO₂ and H₂ to reconcile as to which kind of defect influences the sensing characteristics.

2. Experimental

2.1. Materials

All chemicals required for synthesis of GO films including graphite powder (flake size > 45 μm, purity 99.99 wt%) and hydrogen peroxide (H₂O₂) were procured from Sigma Aldrich, UK. Processing chemicals and those required for ZnO nanorods preparation including KMnO₄, (Zn(NO₃)₂,6H₂O), NaOH, HCl, H₂SO₄ and NaNO₃ were procured from Himedia Laboratories, India. Deionised (DI) water (Millipore, USA, 18.2 MΩ/cm) was used during the whole process of synthesis.

2.2. Fabrication of inter digital electrodes (IDEs)

IDEs of Platinum were used for measurement of SO₂ and H₂ gas sensing characteristics of GO-ZnO-NR thin films. Pt IDEs were patterned onto glass substrates of size 1.5 × 1.0 cm² using conventional photolithography, prior to coating of GO-ZnO-NR films. A thin buffer layer of titanium (≈10 nm) was initially coated over the glass substrate before deposition of platinum thin, film (≈90 nm) so as to enhance its adhesion on glass substrates. Details of fabrication protocol for IDEs have already been reported by Anjali et al [33]. The width and spacing of the Pt/Ti electrodes used in the present study were 0.5 mm.

2.3. Graphene oxide (GO) preparation

Graphene Oxide (GO) was synthesized following protocol outlined by Hummer’s method [34]. Primary chemicals including graphite powder (1 g), sodium nitrate (0.50 g) and concentrated sulphuric acid (23 ml) were taken in optimized proportions and mixed with constant stirring in an ice-bath maintained at 5 °C. Detailed preparation conditions are already reported in our earlier published work [35]. While potassium permanganate was subsequently added to inhibit any strong reactions, the whole mixture was subjected to enhanced heat treatment at 35 °C with sustained intense stirring. Thereafter, residual Mn³⁺ ions and acid in the solution were removed with sequential washing using dilute HCl (5%, 200 ml) and warm (70 °C) deionized water. Finally, GO solution was filtered out using vacuum filtration and dried in a glove box at 70 °C overnight.

2.4. Preparation of GO-ZnO-NR composite

GO-ZnO-NR composite was synthesized by hydrothermal method. In this process, Zinc nitrate hexahydrate was dissolved in DI water by continuous stirring and subsequently the GO solution (1 mg ml⁻¹) was added drop wise. The pH of prepared solution was adjusted to 12 by adding aqueous NaOH (1 M) solution. After that, the solution was transferred to Teflon hydrothermal container and it was kept at 200°C for 4 h. After the cooling down process, the solution was washed by DI water several times to neutralize the pH of solution. The solution was dried at 60°C in oven to convert it to the powder form. The wt. % of GO and ZnO was kept at 7:3.

2.5. Preparation of GO-ZnO-NR gas sensor

The prefabricated Pt/Ti IDEs were initially cleaned sequentially in tri-chloroethylene, acetone, methanol followed by isopropyl alcohol before being blow-dried using nitrogen gas. The same were drop-coated with the solution of GO-ZnO-NR composite (0.5 mg ml⁻¹ in DI water), while protecting the contact pads for electrical connections. Thereafter, GO-ZnO-NR coated IDE substrates were kept on a temperature controlled hot-plate initially at 50 °C for 30 min post which the temperature was ramped up to 70 °C and retained for another 30 min. This protocol was envisaged to be sufficient in stopping the ZnO nanorods from moving about too much thus preventing agglomeration and an almost uniform film of GO-ZnO-NR roughly of thickness of 500 nm could be obtained.

2.6. Characterization of GO-ZnO-NR composite

The synthesized GO-ZnO-NR composite was first characterized using X-ray diffraction (XRD) technique (BrukerD8 Discover High Resolution Diffractometer) with CuKα (λ = 0.154 nm) radiation source and the surface morphology of the composite was analysed using Scanning Electron Microscopy (SEM, ZEISSERT V40, Germany). Raman measurements were performed using Invia II Renishaw Laser Raman Spectrometer for optical characterization. The gas sensing measurements of GO-ZnO-NR composite sensor were undertaken in a customized gas sensing test rig (GSTR). In addition, change in sensor resistance on exposure to target gases was measured by means of Keithley 6487 picoammeter data acquisition module that was interfaced with the sensor.
3. Results and discussion

3.1. Characterization of GO-ZnO-NR composite sensor

SEM technique was used to investigate the surface morphology of the GO-ZnO-NR composite sensor structure and SEM images are shown in figures 1(a), (b). It can be clearly seen from figure 1 that there exists a compact structure of graphene oxide and ZnO nanorods. Existence of ZnO nanorods clearly points to the existence of an extra and enhanced surface area for the target gases to adsorb besides the basal plane of 2D graphene oxide.

Raman spectrum of GO-ZnO-NR composite sensor is shown in figure 2. It is seen to be comprised of two solid peaks, 1589 cm$^{-1}$ (G band) and 1343 cm$^{-1}$ (D band). The G and D bands assigned to graphene oxide are attributed to E$_{2g}$ phononic first-order dispersion of the sp$^2$ carbon bonds and structural defects respectively (distortion-induced mode) [36, 37]. ZnO related peaks in the nanocomposite sensor are also discernible at 563 cm$^{-1}$ (Peak 1) and 1093 cm$^{-1}$ (Peak 2) respectively [38, 39]. These are attributed to E$_1$ longitudinal optical (LO) mode phonons and 2A$_g$(LO) and 2E$_1$(LO) modes at the point of the Brillouin zone respectively. The 2D band is a defining feature for the thickness of graphene sheets and is sensitive to defects. The presence of a wider 2D band at 2420 cm$^{-1}$ for the GO-ZnO-NR composite ratifies the presence of reduced layers of graphene sheets [40].

Figure 1. SEM images of (a) GO-ZnO-NR composite and (b) Magnified image.

Figure 2. Raman Spectra of GO-ZnO-NR composite sensor.
X-ray Diffraction pattern obtained for the GO-ZnO-NR composite is shown in figure 3. The feature diffraction peak of GO at 2θ = 9° is observed and the same can be attributed to existence of oxygenated functional groups deposited on the carbon sheets. A small hump is also visible between 2θ = 23° to 26°. It is indicative of the presence of reduced graphene oxide (rGO) besides overriding presence of GO. It indicates partial restoration of GO in the form of rGO. All other diffraction peaks seen in the figure are related to the existence of ZnO structure and are observable at 2θ equalling to 31.6°, 34.5°, 36.4°, 47.6°, 56.6°, 62.9° and 67.9° values corresponding to ZnO hexagonal wurtzite (100), (002), (101), (102), (110), (103) and (112) planes respectively [39, 41]. The observed peaks match well with standard ZnO peaks (ICPDS 36-1451, a = 0.325 nm, c = 0.521 nm). The strong diffraction peaks are indicative of highly crystallized ZnO. In some of the previous work [42] on vertically aligned ZnO nanorods, typically the peak (002) in XRD pattern is much stronger than other peaks that is suggestive of the preferential growth of ZnO nanorods along c axis. In the present case, peak (002) is not as dominant as some of the other peaks at (101) or (100). It suggests that the ZnO in our sample is polydirectional. The obtained results clearly confirm successful fabrication of GO-ZnO-NR composite.

To understand the type of chemical bonding present in the synthesized GO-ZnO-NR composite, Fourier Transform Infra-red spectroscopy (Spectrum RXI, Perkin Elmer) was utilized in the current investigation. Figure 4(a) shows the FTIR spectrum in the range 400 to 4000 cm\(^{-1}\) for the GO-ZnO-NR composite. In the spectrum, the observed dips are at 3264 cm\(^{-1}\), 1545 cm\(^{-1}\), 1403 cm\(^{-1}\) and 1011 cm\(^{-1}\), which are readily attributable to O–H stretching vibration, (C–C) skeletal vibration of graphene oxide, O–H deformation of C–OH groups and C–O–C groups respectively [43]. Figure 4(b) shows the magnified view of the spectrum measured within the range of 400–600 cm\(^{-1}\). Some weak bonds are immediately noticeable in the range 400 cm\(^{-1}\) to 500 cm\(^{-1}\), which are part of the E\(_2\) mode of ZnO (Active Raman) with vibrating masses of ZnO [44]. The FTIR results further confirm the fabrication of GO–ZnO–NR composite structure.

### 3.2. Gas sensing results

The prepared GO–ZnO–NR composite sensor with underlying Pt/Ti IDEs was first mounted in a custom-built gas sensing test rig (GSTR) described elsewhere [6]. The GSTR provided controlled ambient for testing of the sensor and was interfaced with a picoammeter (Keithley 6487, USA) for data acquisition onto a computer. Calibrated leaks allowed for input of target gases (SO\(_2\) and H\(_2\)) within the GSTR and sensing characteristics of the sensor configuration could be logged as a function of varying concentration. Figures 5(a), (b) depicts the instantaneous variation in resistance of the sensor configuration at room temperature upon exposure to varying concentrations of H\(_2\) and SO\(_2\) gases (25, 50, and 100 ppm). Initially resistance of the GO–ZnO–NR composite sensor is seen to increase with introduction of the target gases (H\(_2\) and SO\(_2\)) into the GSTR. The graphs also depict resistance of the sensor configuration returning to its original state once fresh air (without target gas) is allowed to flow in a dynamic manner on the surface. The gas sensing response (S) is calculated as per the formula given in equation (1).
Where $R_g$ is the sensor resistance in presence of target gas and $R_a$ is the sensor resistance in air (without target gas). The estimated GO–ZnO–NR composite sensor parameters for SO$_2$ and H$_2$ gases are summarized in table 1 as also their respective sensing response values. Figure 6 depicts gas sensing response for GO–ZnO–NR composite sensor for SO$_2$ and H$_2$ gases as a function of gas concentration. It is clearly noted from the graph that sensing response exhibited by the GO–ZnO–NR composite sensor is almost linear in nature with respect to gas concentration. The average response and recovery times were also enumerated in table 1 and it is interesting to note that on average, response and recovery times for SO$_2$ gas sensing are longer in comparison to H$_2$ gas by the GO–ZnO–NR composite sensor while it exhibits similar sensing response values towards both SO$_2$ and H$_2$ gases. Figures 7(a) and (b) show our gas sensor response w.r.t time exposed to 25 ppm H$_2$ and SO$_2$ respectively at room temperature for three successive cycles. It is clearly seen that the sensor response for the three successive cycles is the replica of each other indicating that the system possesses good reproducibility. Similar results were observed for H$_2$ and SO$_2$ gas sensors for 50 and 100 ppm.

![Figure 4. FTIR spectrum of GO–ZnO–NR composite in the range (a) 400 to 4000 cm$^{-1}$ and (b) magnified view 600 to 400 cm$^{-1}$.](image)

![Figure 5. Gas sensing responses of GO–ZnO–NR composite sensor to varying (a) SO$_2$ and (b) H$_2$ gas concentrations.](image)

**Table 1.** Sensing characteristics obtained for GO–ZnO–NR composite structure towards SO$_2$ and H$_2$ gases in varying concentrations.

| Sensing Response | 25 ppm | 50 ppm | 100 ppm | Average Response time (s) | Average Recovery time (s) |
|------------------|--------|--------|---------|--------------------------|--------------------------|
| SO$_2$           | 2.97   | 4.09   | 5.45    | 80                       | 75                       |
| H$_2$            | 3.12   | 3.73   | 5.82    | 30                       | 40                       |

\[
S = \frac{R_g}{R_a}
\]

Where $R_g$ is the sensor resistance in presence of target gas and $R_a$ is the sensor resistance in air (without target gas).
In view of the aforementioned results, it was of interest to understand the mechanism of SO₂ and H₂ detection by the GO–ZnO–NR composite sensor as also investigate the obtained difference in their response and recovery times. The target gas (SO₂, H₂) sensing characteristics were initially thought to rely primarily on their interaction with reactive sites on graphene oxide surface only because of room temperature operation. Even semiconducting action of ZnO NRs leading to reversible adsorption-desorption of adsorbed oxygen species on their surface as well as depletion layer width modulation in the presence/absence of target gases was expected to be minimal. However, almost comparable sensing response values exhibited by the GO–ZnO–NR composite sensor indicated that both H₂ and SO₂ gas molecules with their small kinetic diameters of 0.289 nm [45] and 0.360 nm [46] respectively interact with adsorbed oxygen species at all active sites on graphene (armchair/zigzag/free edges) as expected. H₂ gas is a known reducing in nature however, upon exposure the GO–ZnO–NR composite sensor exhibited a rise in resistance. This indicated that H₂ molecules rather than interacting directly with carbon atoms reacted with adsorbed oxygen available. Further H₂ gas is also known to dissociate and reversibly adsorb on Zn²⁺O²⁻ pairs creating O⁻H and Zn–H species exhibiting well defined vibrational modes [47].

Photoemission and XANES studies carried out by Rodriguez et al on the adsorption of SO₂ gas on ZnO at room temperature (∼300 K) primarily indicates formation of SO₃ species on the oxide surfaces. Further, Zn-SO₂ interactions were seen to be very weak wherein no discernible decomposition of the adsorbed molecule could be observed [48]. This conversion of target SO₂ gas molecules to SO₃ species on the surface of GO–ZnO–NR composite at room temperature could be responsible for the observed rise in resistance exhibited by the sensor structure. Also, this augmented oxygen species of SO₃ in the case of SO₂ exposure and regeneration of the ZnO
surface post its removal can explain the relatively slow response speed and tardy recovery times observed vis-à-vis H₂ gas sensing. As seen from the Raman measurements, a dominant D peak indicate presence of sp³ defects along with partial restoration of GO to rGO. Also, GO adds to a larger specific surface area. This cumulative contribution augments the transfer of electrons that further facilitates faster absorption/desorption of the gas species.

The effects and changes on the surface occurring whence H₂ and SO₂ gas molecules are incident on GO-ZnO-NR composite sensor are shown in figure 8. As described above, the mechanism of H₂ and SO₂ gas molecule detection are seen to be quite different and same can be understood from the schematic of gas sensing mechanism (figure 8). It is known that ZnO is comprised of Zn²⁺ and O²⁻ and when H₂ gas molecules interact with it then 'spillover' occurs and H₂ molecule gets dissociated as 2H⁺. These H⁺ atoms get spilled over onto...
exposed GO surface and react with the present oxygen functional groups. The typical reaction occurring on the surface of ZnO nano-rods can be written as

\[
\text{ZnO} + \text{H}_2 \rightarrow \text{ZnO}_\text{solid} + \text{H}_2 \text{O}
\]

In the second case when the GO–ZnO–NR composite sensor is exposed to an environment rich in SO\(_2\), then the following reaction occurs

\[
\text{SO}_2\text{gas} + \text{ZnO}_{\text{solid}} \rightarrow \text{ZnSO}_3\text{solid}
\]

This indicates that there is formation of an over-layer of ZnSO\(_3\) on ZnO nanorods exposed to SO\(_2\) gas molecules on the surface [48]. Formation of this ZnSO\(_3\) on the surface indicates gain of extra O\(^{-}\) species which in turn is expected to lead to removal of electrons from the underlying GO–ZnO–NR composite sensor support. The same study reported that adsorption of SO\(_2\) occurred via preferential reaction with only oxygen centres on ZnO. In addition, when working with ZnO nanorods, the surfaces are exceptionally rich in oxygen adatoms which have a lower coordination number (<3) and a higher mobility compared to adsorbed oxygen on normal ZnO surface.

Table 2 shows comparison of sensing performance of our H\(_2\) and SO\(_2\) gas sensors based on various materials/hybrids. It can be clearly seen that overall performance of our H\(_2\) and SO\(_2\) gas sensors is much improved than some of the earlier reported work.

### 4. Conclusion

Hydrothermal synthesis of GO–ZnO–NR composite sensor was carried out in the present study. Room temperature SO\(_2\) and H\(_2\) gas sensing characteristics of the sensor configuration were investigated and sensing mechanism analysed. The fabricated GO–ZnO–NR composite sensor was found to exhibit linear response with varying concentrations for both H\(_2\) and SO\(_2\) gases in the range of 25–100 ppm. The tardy response and recovery times obtained during SO\(_2\) detection by the GO–ZnO–NR composite sensor are attributed to the formation of SO\(_2\) species on the ZnO surface that is known to be strongly attached. The obtained results are encouraging for fabrication of room temperature operated efficient SO\(_2\) and H\(_2\) gas sensors.

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