Nanoscale heterojunctions of rGO-MoS₂ composites for nitrogen dioxide sensing at room temperature

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Abstract

Chemiresistive sensors, employing binary and ternary hybrids of reduced graphene oxide (rGO), are developed to detect nitrogen dioxide (NO₂) gas at parts per billion level (ppb) at room temperature. The sensors based on hierarchical structures of molybdenum disulphide (MoS₂) sheets decorated rGO and further integration of it with silver nanoparticles (Ag NPs) exhibit improved sensing responses with lower detection limits than the unary counterpart (rGO). An increase of nearly 500% in sensing response is observed in the ternary hybrid device over rGO alone at a concentration of 1 ppm and a 1145% increase in response is observed at 104 ppm. The ternary hybrid device outperforms the binary and the unary counterparts in terms of sensitivity to NO₂ over a wide concentration range from 1 ppm to 104 ppm. Additionally, the ternary hybrid device is highly selective to NO₂ amongst other atmospheric pollutants like ammonia, sulphur dioxide and carbon monoxide. An experimental detection limit of 50 ppb is further achieved with this device which is lesser than the 53 ppb permissible limit declared by Environmental Protection Agency (EPA). A synergistic effect was achieved with the binary and the ternary hybrids with the electronic modulations at the nanoscale interfaces at the nanoheterojunctions playing a key role in selective and enhanced adsorption of NO₂ at room temperature.

1. Introduction

Rapid industrialisation and a sudden surge of automobile usage, resulting from rapid growth of economic activities, has resulted in large scale emission of harmful hydrocarbons and other toxic gases [1]. Among those chemicals, NO₂ is one of the major pollutants of the atmosphere [1, 2] which plays a pivotal role in the formation of acid rain, ground level ozone and photochemical smog thereby being detrimental to both human life and the environment [1–3]. Chronic diseases such as acute respiratory illness may be developed as a result of continued and frequent exposure to NO₂ concentration higher than the EPA air quality standard EPA-456/F-11-003 (53 ppb) [4, 5]. Thus, selective detection of NO₂ gas at mild concentrations is of great importance for protecting environmental and human health.

Conventional metal oxide semiconductor based NO₂ sensors available in the market, need higher operating temperature (200 to 300 °C) in order to activate the chemisorption of ambient oxygen on the metal oxide surface and induce sensing [6]. Hence, it becomes difficult to deploy these power hungry sensors in oxygen starved areas or hazardous areas containing flammable species for continuous monitoring of NO₂. Hence, the quest for highly sensitive NO₂ sensors with low detection limit is in the process which will enable the sensors to operate at low or room temperature. Recently graphene and its derivatives (graphene oxide, rGO) along with other transition metal dichalcogenides like MoS₂, WS₂ etc have been studied extensively and have proved to be promising gas
sensing materials because of their high surface to volume ratio and excellent electronic properties [7–11]. In this regard, researchers are trying to focus on developing new novel nanomaterials hybrids out of these, in order to exploit the synergistic properties and develop high performance gas sensors. Development of hybrid structures renders multiple nanoheterojunctions and interfacial electronic modulations across such heterojunctions drastically enhance the sensing performances [8, 12]. For example, there can be electronic modulation of charge carriers and localised charge carrier densities resulting in modulation of Fermi level, effective charge carrier separation for efficient charge transport rendering fast and enhanced sensing [8, 12–14]. Thus, careful engineering of nanoheterojunctions allow tailoring of the electronic properties at the nanoscale interfaces which in turn contributes to different responses to external chemical perturbations. Thus, it is essential to design novel hybrid materials contributing to new sensing mechanisms for developing high performance NO₂ sensors.

In this work, we have developed chemiresistive sensors based on semiconducting MoS₂ nanosheets decorated rGO (rGO-MoS₂) and further integration of it with Ag NPs (rGO-MoS₂–Ag), synthesized by low cost hydrothermal routes. Surface functionalisation with Ag nanostructures is known to be an effective approach to improve the sensing performance of gas sensors because of the metal’s catalytic effect which reduces the energy required for reacting with gas molecules [14, 15]. Both the binary and ternary hybrid structures thus developed, allow improved response to NO₂ at room temperature than rGO and provide wide dynamic range of NO₂ sensing, enabling practical implementation of continuous monitoring sensors. Also, a low detection limit of 50 ppb is reached with the ternary hybrid which is lesser than the 53 ppb toxic limit implemented by the EPA. The importance of the interfacial electronic interactions at the nanoscale heterojunctions have been discussed thoroughly contributing to such enhanced sensing performances. This understanding further paves the way for developing novel hybrid sensors involving nanoheterojunctions with increased performance parameters.

2. Experimental details

2.1. Synthesis of rGO-MoS₂ and rGO-MoS₂–Ag

Graphene oxide (GO) was synthesized by simplified Hummers method [13, 16] using commercially procured pristine graphite powder (Superior Graphite. Co). In this method, a mixture of sulfuric: phosphoric acid (55:7) (by volume) was prepared to which 1 g of graphite was added and the solution was stirred constantly for 30 min in an ice bath. Then, 6.0 g of potassium permanganate was slowly added into the solution and the resulting mixture was stirred at 25 °C for 72 h. This resulted in the oxidation of graphite. Finally, hydrogen peroxide (20 mL, 30%) was added to inhibit the reaction until the colour transformed to bright yellow. The yellow precipitate of graphite oxide thus obtained was washed several times with 1.0 M aqueous hydrochloric acid and distilled water repeatedly until a pH of 4–5 was achieved. This process allowed the exfoliation of graphite oxide to GO, evident by the dark brown colour of the resulting solution [17]. The final brownish precipitate was again washed several times with large amount of deionized water and centrifuged at 10000 rpm for 30 min and vacuum dried.

The synthesis of rGO-MoS₂ was accomplished by using GO, sodium molybdate and sodium thiocyanate as precursors. A solution of GO was prepared by dispersing 20 mg of as prepared GO in 30 mL of DI water and sonicated well using a bath sonicator. Then, 1.21 g of sodium molybdate and 1.07 g of sodium thiocyanate salts were dissolved in this 30 mL of GO solution. Afterwards, the solution was poured into a Teflon lined stainless steel autoclave (60 mL volume), sealed tightly and then heated at 250 °C for 24 h in a vacuum oven (Lab Digital Instruments, India). The reduced black precipitate was filtered with Whatman filter paper 1 (11 μm pore size), washed and vacuum dried to obtain rGO-MoS₂ powder.

To prepare rGO-MoS₂–Ag, as obtained rGO-MoS₂ powder (20 mg) was dispersed in 30 mL of DI water by bath sonication. Silver nitrate (AgNO₃) with weight equivalent to 5 mM was dissolved in the dispersed solution. The solution was then heated to 80 °C and 20 μL of hydrazine hydrate was added to the solution which served as the reducing agent. This solution was stirred for 20 min. Finally, the black precipitate was collected, filtered and vacuum dried to get rGO-MoS₂–Ag powder.

For comparison, rGO was prepared by a similar approach by using sodium thiocyanate, which acts as a mild reducing agent, instead of hydrazine hydrate. For this, 20 mg of GO was dispersed in 30 mL of DI water. Then, 1.07 g of sodium thiocyanate was added to this well dispersed GO solution and stirred for five min. This solution was then transferred into a Teflon lined stainless steel autoclave, sealed tightly and heated to 250 °C in a vacuum furnace for 24 h. The final black solution obtained was vacuum filtered, washed and vacuum dried for 48 h to obtain rGO powder.

For evaluation of its bandgap, MoS₂ was synthesized using 1.21 g of sodium molybdate and 1.07 g of sodium thiocyanate salts dissolved in 30 mL of water. Afterwards, the solution was poured into a Teflon lined stainless steel autoclave, sealed tightly and then heated at 250 °C for 24 h in a vacuum oven. The reduced black precipitate was filtered, washed and vacuum dried to obtain MoS₂ powder.
2.2. Characterization

The morphology and microstructure of as-synthesized sensing materials were studied using scanning electron microscopy (SEM, Zeiss Ultra 55). The diffraction peaks for GO, rGO, rGO-MoS2 and rGO-MoS2-Ag were obtained using X-ray diffraction (XRD, Rigaku Smartlab) with Cu Kα radiation source (λ = 1.5418 Å) with a 2θ range of 10° to 90°. Raman spectroscopy (HORIBA JOBIN YVON LabRAM HR) was obtained using a 514 nm wavelength green laser as optical source for excitation. The chemical composition of rGO-MoS2 and rGO-MoS2-Ag was studied by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD). The work functions of rGO and MoS2 were measured using ultraviolet photoelectron spectroscopy (UPS), performed on the same instrument as XPS. The UPS spectra was obtained using He-I irradiation with hν = 21.22 eV. The Fermi level edge was calibrated against gold Fermi edge as 0 eV. The work function was evaluated from the difference between the exciting photon energy and the secondary electron edge cut off of the highest binding energy [13]. The secondary electron edge cut off is determined from the intersection point of the tangent to the threshold and straight line fitting of the binding energy axis [13].

2.3. Fabrication of gas sensing device and set up

As prepared rGO, rGO-MoS2 and rGO-MoS2-Ag powders (2.2 mg in each case) were dispersed separately in three glass vials, each containing 20 mL of dimethyl formamide, by bath sonication for 2 h. Then, 4 μL of each solution was dropcasted separately on three separate interdigitated electrodes (IDEs) respectively [Cr/Au (10 nm)/100 nm] on Si/SiO2 substrate. The sensors would henceforth be named as G, GM and GMA respectively. The IDEs were patterned by optical photolithography (lift off) process and the separation of the ‘fingers’ of IDEs was approximately 15 μm with squared contact pads of length 1000 μm. The IDEs were then dried under infrared lamp of 60 W to evaporate the residual solvent. All the devices were annealed under nitrogen (N2) flow for 2 h at 100 °C before electrical characterisation and gas sensing measurements, for providing better electrical contacts of the sensing materials with gold electrodes. The devices were fixed on a Printed Circuit Board (PCB) with epoxy glue and then aluminium wires were used to wirebond the devices to PCB contact pads. Deep ultraviolet light emitting diode (UV LED, 254 nm) that was used for obtaining better recovery characteristics was fixed in close proximity to the sensor with the tip of the LED being at a height of 1 mm from the sensor surface.

All the electrical characterisations and gas sensing experiments were performed in an inhouse built gas chamber provided with electrical feedthroughs and inlet and outlets for gases as depicted in figure S1 in the supplementary information (SI) available online at stacks.iop.org/NANOX/1/010003/mmedia. The device mounted inside the chamber was connected to Agilent B1505 semiconductor parametric analyzer via the electrical feedthroughs for measurement purpose and live data acquisition. Different concentrations of NO2 were achieved by mixing calibrated NO2 gas (104 ppm) with ultra-high pure nitrogen in specific flow rate ratios using respective mass flow controllers (Alicate make) as mentioned in our previous work [13]. In all the cases, the total flow rate was maintained to be 1000 sccm to nullify the effect of change in gas pressure on the sensor response.

3. Results and discussion

3.1. Morphological, elemental and structural analysis of synthesized sensing samples

Figure 1 depicts the synthesis procedure of rGO-MoS2 and rGO-MoS2-Ag and subsequent fabrication of the devices used for gas sensing. The morphology and microstructure of as prepared rGO, rGO-MoS2 and rGO-MoS2-Ag were investigated using SEM. Figure 2(a) shows well exfoliated, large but crumpled rGO sheets prepared by reduction of GO using sodium thiocyanate as discussed in the experimental section. Figure 2(b) depicts the rGO nanosheets decorated with interconnected and self-assembled nanosheets of MoS2 with various folds forming three dimensional MoS2. The average size of each unit varies between 4–5 μm as can be observed in figure 2(c). Such three dimensional structure of the MoS2 is attributed to the hydrothermal reaction conditions and precursors used in the synthesis process [18]. The plausible mechanism is as follows: MoO42− and sodium ions get released from sodium molybdate and sulphur gets released from sodium thiocyanate during the hydrothermal synthesis which act as sources for the formation of three dimensional MoS2. The MoO42− ions, possessing layered structure, react with sulphur ions to form MoS2 while the intercalating sodium ions prevents the stacking of the MoS2 structures, leading to the formations of self-assembled hierarchical MoS2 on rGO sheets [18, 19].

Thiocyanate also plays a role in the simultaneous reduction of GO to rGO. Figure 2(d) depicts the SEM image of rGO-MoS2-Ag. It is observed that Ag NPs are uniformly decorated on rGO sheets as well as MoS2. As can be observed in figure 2(d), the edges of the various folds of MoS2 act as active sites for Ag NPs nucleation.
XRD was further performed to study the crystallinity of the samples. The XRD patterns of GO and rGO, in the range of 2θ values from 10°–80°, are depicted in figure S2(a) in the SI. A sharp diffraction peak at 8.18° corresponds to the (002) plane of hexagonal graphene lattice with an interlayer distance of 10.80 Å. Because of the presence of oxygen functionalities such as hydroxyl, carbonyl, epoxy and peroxy groups in GO, water molecules intercalate between the GO layers, which result in the increase of the interlayer spacing from 3.40 Å in graphite to 10.80 Å in GO [17]. In contrast, a broad 2θ peak is obtained at 24.56° (corresponding to a d-spacing of 3.62 Å) indicating that GO has been reduced to rGO [17] using sodium thiocyanate indicating the removal of most of the oxygen-containing functional groups. Figure S2(b) in the SI depicts this peak in magnified view.

Figure 1. Schematic depicting the synthesis procedure of rGO-MoS2 and rGO-MoS2-Ag and the respective fabricated devices used for gas sensing.

Figure 2. SEM images of as-prepared (a) rGO nanosheets, (b-c) rGO-MoS2, (d) rGO-MoS2-Ag. XRD spectra of (e) rGO-MoS2 and (f) rGO-MoS2-Ag.

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Correspond to the D and G bands of rGO, respectively. The G band arises due to the in-plane bond stretching of rGO-MoS2. No other XRD peaks confirm the formation of few layer MoS2. Figure S5 shows the broad and weak sub peaks at 368.28 eV and 374.28 eV corresponding to Ag 3d5/2 and Ag 3d3/2 respectively. Figure 3 depicts the deconvoluted O 1s spectra confirming the presence of O=C–OH (531.65 eV), O=C–OH (532.95 eV) and Mo–O (530.51 eV) moieties. Furthermore, the deconvoluted spectra of Mo 3d shows two sub-peaks at 229.32 eV and 232.46 eV corresponding to the doublets of Mo 3d5/2 and Mo 3d3/2 respectively of metallic Ag. The peak at 235.46 eV corresponds to the Mo6+ oxidation state that arises due to slight oxidation of MoS2 in air. The high-resolution spectrum of S 2p peak in figure 3(e) is deconvoluted into two components located at 162.15 and 163.38 eV, representing the spin–orbit couple S 2p3/2 and S 2p1/2 of MoS2 phase respectively [29, 30]. Figure 3(f) represents the deconvoluted spectra of Ag3d which consists of two sub peaks at 368.28 eV and 374.28 eV corresponding to Ag 3d5/2 and Ag 3d3/2 respectively of metallic Ag (0 oxidation state). Moreover, the binding energy splitting of the 3d doublet of Ag is 6.0 eV which further confirms the formation of metallic Ag [23].

3.2. Gas sensing results and discussion

The I–V characteristics of as-prepared sensor devices (GM and GMA) were obtained by sweeping the voltage from −1 to 1 V in N2 atmosphere, as depicted in figure 4(a). A similar I–V scan was also performed for sensor G.
as depicted in figure S6 in SI. A linear behaviour was obtained for all the devices which indicated ohmic contacts of the sensing materials to the Au electrodes. The resistance of G was measured to be approximately around 80 $\Omega$ while that of GM was approximately around 65 k$\Omega$. A high resistance of the GM device is attributed to the semiconducting nature of the MoS$_2$ [31–33]. Further, the resistance of the GMA device was approximately around 15 k$\Omega$. The decrease in resistance in this device is plausibly due to the incorporation of metallic Ag NPs on the rGO-MoS$_2$ matrix forming shorter resistance pathways for some length. The gas sensing characteristics of the fabricated sensors (G, GM and GMA) towards various concentrations of NO$_2$ were then investigated at room temperature. A constant biasing voltage of 1 V was applied to measure the gas sensing characteristics of all the devices. The variation in current flowing across the respective sensing materials bridging the electrodes was monitored upon exposure to test gas. Cyclic experiments were performed to understand the dynamic sensor responses of the devices. A stable baseline under N$_2$ flow was obtained initially. Subsequently, in each cycle of exposure, specific concentration of NO$_2$ was exposed for 5 min and desorption was then allowed to occur under
$\text{N}_2$ flow for 5 min. Figure 4(b) shows the dynamic sensor responses of the devices (G, GM and GMA) to different concentrations of NO$_2$ gas ranging from 1 to 104 ppm. The sensor response, $S$, is defined as the relative change in conductance, $G$, given by ([13])

$$S(\%) = \frac{\Delta G}{G}(\%) = \frac{(I - I_0)}{I_0} \times 100$$

(1)

where $I$ is the electric current flowing through the respective samples when exposed to test gas and $I_0$ is the initial electric current in the sample during $\text{N}_2$ flow prior to the start of test gas exposure. It is evident from figure 4(b), that all the devices (G, GM and GMA) show increasing response with the increase in concentration of NO$_2$ exposure as the current in all the devices increases on NO$_2$ exposure. rGO in ambient conditions behaves as p-type due to unintentional doping from water and oxygen adsorbates ([13, 14]). Hydrothermally synthesized MoS$_2$ is also known to exhibit p-type semiconducting properties ([33, 34]). This is further experimentally confirmed later by work function and bandgap measurements by UPS spectroscopy and UV–vis spectroscopy and gas sensing behaviour of as synthesized MoS$_2$ on exposure to NO$_2$. As such, the hybrid GM also shows p-type transport behaviour. Further decoration of metallic Ag NPs onto rGO–MoS$_2$ matrix do not change the p-type conduction behaviour of the ternary hybrid GMA. Strongly electrophilic NO$_2$ accepts electrons from each sensor making it more p-type, as a result of which the number of hole carriers (majority carriers) and subsequently the hole current in the device increases, as can be observed in figure 4(b) ([14, 33]). However, the electron withdrawal ability of NO$_2$ varies in each kind of sensor, thus contributing to different levels of current change in the sensors upon NO$_2$ exposure. It is also observed in figure 4(b) that the sensors exhibit poor desorption rate at lower concentrations (1 and 3 ppm) such that when NO$_2$ gas is stopped at the end of each exposure cycle, the sensor response does not recover to its initial value. However, the rate of desorption increases at higher concentrations since the rate of desorption is directly proportional to the number of adsorbed gas molecules on the surface ([35]) which increases with each exposure cycle. This trend in desorption is further evident in figure 4(c) where the recovery percent in each cycle (at the specified concentration) is plotted for each kind of sensor. The percent recovery of the sensor is calculated as follows ([15]):

$$\text{Percent recovery (\%) } = \frac{I_f - I_r}{I_f - I_0} \times 100$$

(2)

where $I_f$ is the current value before exposure to target gas, $I_r$ is the current value after 5 min of gas exposure, $I_0$ is the recovered current value after 5 min of $\text{N}_2$ exposure. This incomplete recovery of current to the base value is attributed to the strong binding energy of the NO$_2$ molecules associated with the gas adsorption sites of G, GM and GMA ([5, 17]). As reported in literature for rGO and MoS$_2$ sensors, the adsorption of NO$_2$ molecules on these sensors can be divided into two parts: adsorption on low energy binding sites (such as sp$^2$ bonded carbon atoms) and on high energy binding sites (defects, vacancies and functional groups) involving energy of the several hundred meV/molecule ([5, 17, 36]). The partial recovery of the sensors as observed in figure 4(c) indicates high binding energy sites dominated adsorption ([5, 36]).

The sensitivity of the devices was further evaluated by calculating the sensor responses of all the devices corresponding to each concentration with error bars in figure 4(d). The individual sensor responses corresponding to each concentration are evaluated by subtracting the sensor response value at the start of exposure of respective concentration from that at the end of the exposure ([37, 38]). It is seen that at a concentration of 1 ppm, the mean sensor responses of G, GM and GMA sensors are 0.51%, 3.06% and 3.02% respectively. Hence, an approximate 500% increase in response is observed in case of GM and GMA sensors at an exposure of 1 ppm of NO$_2$. Similarly, at 104 ppm, the sensor responses of G, GM and GMA are 3.51%, 19.07% and 43.7% respectively. Thus, GM exhibits 443% increase in sensor response compared to that of G. Further, GMA exhibits 129% increase in response than GM and 1145% increase in response than G at 104 ppm. This manifold increase in response of the hybrid devices towards NO$_2$ compared to G device consisting of rGO alone suggests that the hybrid sensors have a wide dynamic detection range of concentration from few ppb to hundreds of ppm. Further, it is also observed that the responses of all the devices follow a Freundlich isotherm in the wide concentration range 1 to 104 ppm, as can be observed from the fitted curves in figure 4(d). The Freundlich equation based on adsorption on a heterogeneous surface is given by

$$S = K \times C^\frac{1}{n}$$

(3)

where $K$ is an indicative constant for the adsorption capacity, $C$ is the concentration in ppm and $I/n$ is an empirical parameter related to the adsorption intensity, which is affected by the heterogeneity of material. The value of $I/n$ ranges from 0 to 1, becoming more heterogeneous as its value gets closer to 0. This equation is valid for lower concentrations of the target gas ([13, 35]). The heterogeneity of the sensors is attributed to the multiple adsorption sites (sp$^2$ bonded carbon, defects, functional groups) which possess different activation energy of adsorption ([39]). The fitting parameters, including the correlation coefficient ($R^2$), for all the sensors are provided in table 1.
Amongst the three sensors, GMA exhibits strongest adsorption capacity \((K = 3.30)\) and higher than GM \((K = 2.90)\) and G \((K = 0.46)\) sensors. Hence a higher sensor response is observed in case of GMA than GM and G for all the concentrations. The variation in \(I/n\) values, indicating the heterogeneity of the three sensors, is attributed to different contribution of the multiple adsorption sites to overall adsorption depending on surface defects, functional groups etc in case of each sensor \([39]\).

Further, sensitivities and detection limit of each sensor are evaluated by a straight line fitting of the sensor response values corresponding to lower concentrations (1 ppm to 10 ppm), as depicted in figures 4(e) and (f) and S7 in SI, yielding consistent percentage sensitivities of 0.08, 0.56, 0.83 for G, GM, GMA sensors respectively. The high error bars in case of G sensor as depicted in figure S7 at all concentrations from 1 to 10 ppm indicate poor resolution capability of the sensor in detecting the different low concentrations. Again, the error bars of 3 ppm and 5 ppm responses of the GM device overlap indicating poor distinction capability between the two concentrations. This is resolved in case of GMA sensor as depicted in figure 4(f) indicating high sensitivity to both the concentrations. At low NO\(_2\) concentrations, when most of the adsorption sites were available, the charge transfer was directly proportional to the gas concentration \([36]\) as observed from the linear fitting of the response curve versus concentration. However, at higher NO\(_2\) concentrations, the sites become occupied with gas molecules during the gas exposure, and thus the response reaches a saturation point as observed in figure 4(d). The detection limit of each sensor is calculated theoretically using the information extracted from the sensor signals as described in SI. The detection limit of the three sensors G, GM and GMA are calculated to be 1.36 ppm, 147 ppb and 70 ppb approximately. Thus the hybrid sensors GM and GMA exhibit very low detection capability, far below the detection standards of NIOSH (CAS’ No. 10102-44-0). To validate the theoretical detection limit, the GMA sensor was also tested for 50 ppb of NO\(_2\) gas to which it responded (figure S8 in SI) which indeed confirms the low detection capability of the sensor. Moreover, the wide range detection capability of the sensors indicates that the sensors are highly beneficial for continuous environmental monitoring applications. The different parameters involved in calculating the detection limit of the three sensors and the detailed procedure of calculation is provided in the SI.

It is to be noted that because of strong adsorption of NO\(_2\) on MoS\(_2\)/rGO surfaces, the recovery rates of the GM and GMA sensors are very slow. Since GMA provided lowest detection capability, an external energy is used in the form of photon energy to accelerate the recovery rate of the sensor so that it can be used for practical gas sensor applications as thermal heating incurs increased cost and would affect the electronic properties of the sensor in the long run \([13]\). Deep UV LED with wavelength 254 nm was used continuously during the sensing and desorption cycle. Figure 5(a) shows the response of the GMA device to 1 ppm of NO\(_2\) exposure for four cycles. Though there was a slight drift in the baseline, but the recovery percentage improved to ~52% (in 5 min interval) than previous 2.94% making it suitable for practical sensing applications. In 10 min, there is a 72% recovery of the sensor response. Also, the sensor response (1.7%) remained constant for four cycles indicating a repeatable response of the sensor. Selectivity is another important sensor parameter to evaluate the ability of the sensor to discriminate a specific gas in presence of other interferents. This is addressed in figure 5(b) where it is observed that the sensor is highly selective to NO\(_2\) amongst other atmospheric pollutants like NH\(_3\), SO\(_2\), CO making it suitable for selective NO\(_2\) sensing at room temperature.

Table 2 compares the operating temperatures, detection limits, sensor responses and the detection range of various rGO—nanostructures hybrids towards NO\(_2\) and highlights that the present work involving GM and GMA devices detect NO\(_2\) at room temperature over a range of 50 ppb – 104 ppm.

### 3.3. Gas sensing mechanism

The results thus obtained, indicate that both the binary and the ternary hybrids of rGO, GM and GMA show improved sensing responses compared to rGO alone. Further, GMA showed the best response out of the three sensors with very low detection capability and excellent selectivity. The increased sensor performance in GM hybrid compared to G can be attributed to the following factors: (1) The defect dominated adsorption of NO\(_2\) molecules on rGO and MoS\(_2\) as explained previously \([5]\), (2) the 3D morphology of MoS\(_2\) as evident from the SEM images indicate the interconnected 2D lamellas which expose the basal plane of MoS\(_2\) with rich active gas

| Sensor | \(K\) | \(1/n\) | \(R^2\) |
|--------|-------|--------|--------|
| G      | 0.46 ± 0.07 | 0.47 ± 0.04 | 0.95   |
| GM     | 2.90 ± 0.52 | 0.39 ± 0.06 | 0.90   |
| GMA    | 3.30 ± 0.27 | 0.52 ± 0.04 | 0.93   |
adsorption sites. These 2D sheets of MoS₂ are assembled into a 3D morphology thus increasing the effective surface area for gas adsorption. The presence of Mo–C bond in XPS indicates the strong coupling between the MoS₂ sheets and rGO which facilitates rapid charge transfer, (3) further, modulation of accumulation region at the p-p heterojunction between rGO and MoS₂ (denoted by RM) is another factor contributing to increased response. Such modulation of accumulation region on NO₂ exposure leads to greater change in resistance thus contributing to enhanced sensitivity. Similar homojunction between two types of materials leading to enhanced resistance change has been reported previously [54]. The p-type nature of the MoS₂ is further confirmed from the gas sensing behaviour of MoS₂ synthesized hydrothermally and work function and valence band maxima (VBM) position evaluation by UPS technique. Figure 6(a) shows the gas sensing characteristics of MoS₂ towards 3 ppm of NO₂ at 80 °C for 3 cycles. The current increases on exposure of electrophilic NO₂ confirming p-type behaviour of MoS₂.

UPS spectra was obtained to evaluate the work function and VBM position of MoS₂. Figure 6(b) shows the high binding energy part of the UPS spectra with the secondary electron edge cut off at 17.29 eV. Thus the work function of MoS₂ is (21.21–17.29) eV = 3.92 eV. Additionally, the work function of rGO as measured by UPS is

| Materials       | OT (°C) | Experimental detection range (ppm) | Detection limit (ppm) | Sensor response | References |
|-----------------|--------|-----------------------------------|-----------------------|-----------------|------------|
| rGO (2D)        | RT     | 10–100                            | 10                    | 9.15 (R_/R₀) at 10 ppm | [40]       |
| rGO (3D)        | RT     | 1–100                             | 1                     | 10% at 10 ppm | [17]       |
| NiO nanosheet/rGO | 200 °C | 1–15                             | 1                     | 200% at 1 ppm | [41]       |
| WO₃ NPs–rGO     | 250 °C | 1–20                             | 1                     | 1.28% at 1 ppm | [42]       |
| Ag-S–rGO       | RT     | 0.5–50                           | 0.5                   | 45% at 50 ppm | [43]       |
| Au–rGO         | 50 °C  | 0.5–5                            | 0.5                   | 1.3 (R_/R₀) at 5 ppm | [44]       |
| ZnO NPs–rGO (2D) | RT    | 1–25                             | 1                     | 25.6% at 5 ppm | [45]       |
| ZnO spheres–rGO (3D) | RT    | 10–200                           | 10                    | 2.5% at 10 ppm | [46]       |
| α-Fe₂O₃/rGO    | RT     | 0.18–90                          | 0.18                  | 150.63% at 90 ppm | [47]       |
| rGO–MoS₂       | 60 °C  | 2–8                              | 5.7 ppb               | 59.8% at 2 ppm | [36]       |
| WS₂            | 150 °C | 0.1–1                            | 0.1                   | 10 at 1 ppm | [48]       |
| MoS₂/rGO aerogel | 200 °C | 0.50–1                           | 0.014                 | 9% at 0.5 ppm | [5]        |
| MoS₂/rGO composites | 160 °C | 0.1–3                           | 0.1                  | 1.16 (R_/R₀) at 1 ppm | [49]       |
| MoS₂/rGO fibre | RT     | 50–1000                          | 0.05                  | 80% at 50 ppm | [50]       |
| MoS₂/rGO composites | 90 °C | 0.15–5                          | 0.15                  | 5% at 5 ppm | [51]       |
| SnO₂/rGO (2D)  | 50 °C  | 0.5–5                            | 0.5                   | 3.31% at 5 ppm | [52]       |
| 3D MoS₂/rGO    | 80 °C  | 0.1–10                           | 27.9 ppb              | 2483% at 10 ppm | [53]       |
| rGO–MoS₂       | RT     | 1–104                            | 0.147                 | 5.84% at 5 ppm | This work |
| rGO–MoS₂–Ag    | RT     | 1–104                            | 0.05                  | 7.53% at 5 ppm | This work |

OT: Operating temperature; RT: Room temperature.
4.5 eV (figure 6(c)). Further, figure S9 shows the low binding energy part of the UPS spectra close to the Fermi energy $E_F = 0$ eV. The VBM was determined from the cut-off of the lowest binding energy [55]. The VBM of MoS$_2$ is located at 0.7 eV below the Fermi level. Further the indirect band gap of MoS$_2$ synthesized hydrothermally was evaluated from the Tauc’s equation using the optical absorption data near the band edge [56]

$$\frac{(\alpha_{hv})^{1/2}}{A} = A(hv - E_g)$$

(4)

where $\alpha$ is the absorbance, $hv$ is the incident photon energy, $A$ is a constant. Plotting $(\alpha_{hv})^{1/2}$ against photon energy $hv$ and extrapolating the tangent to the linear region of the curve to the x-axis gives the optical band gap as shown in figure 6(d). The band gap of MoS$_2$ thus calculated is approximately 2.04 eV which is close to the reported values [57]. This further confirms the p-type nature of MoS$_2$. Thus, having known the values of work function of rGO and MoS$_2$, on contact, to equilibrate the Fermi level due to work function differences, hole transfer occurs from rGO to MoS$_2$ thus creating a hole accumulation region at MoS$_2$. On NO$_2$ exposure, due to further extraction of electrons, the hole accumulation region further widens, and facilitates easy charge transfer.
of holes to rGO which provides a rapid charge transfer pathway, thus enhancing the sensor response. This mechanism is elucidated in figure 6(e).

The increased sensitivity in GMA hybrid can be attributed to the following factors: (1) number of active gas adsorption sites increases due to functionalisation of GM hybrid with Ag NPs leading to increased adsorption of NO₂, (2) secondly, the uniformly distributed Ag NPs on rGO and MoS₂ provide catalytic effect by providing more active intermediate species like NO⁻ and O⁻ between gas phase NO₂ and NO₂ adsorbed on rGO and MoS₂ [15]. These intermediate species have high adsorption energy compared to NO₂ and facilitates the reaction, (3) further on functionalisation with Ag NPs, two additional kinds of heterojunctions are formed namely (a) the junction between rGO and Ag, further denoted as RA junction, and (b) the junction between MoS₂-Ag, further denoted as MA junction. In case of RA junction, the work function differences between rGO and Ag lead to electron transfer from Ag to rGO thus shifting the Fermi level of rGO upwards thus making it less p-type. This process further facilitates more electron withdrawal by electrophilic NO₂. The work function of Ag NPs is 4.2 eV [58]. The work function of rGO varies over a wide range due to the different degree of reduction. In this work, the work function of rGO as obtained from UPS measurement is 4.5 eV which also matches with the reported values [59]. Thus electron transfer readily occurs from Ag to rGO. This has been previously reported for Ag-graphene heterostructures [58]. A similar interfacial electron transfer occurs at the MA junction. This is evident from the binding energy shift of the XPS core level 3d and S 2p spectra of MoS₂ in GMA hybrid sensor. The binding energy of Mo 3d₅/₂ and 3d₃/₂ shift from 228.82 eV and 231.92 eV in rGO-MoS₂ to 229.32 eV and 232.46 eV in rGO-MoS₂-Ag respectively. Similarly, the binding energy of S 2p₁/₂ and S 2p₃/₂ shift from 161.85 eV and 163.05 eV in rGO-MoS₂ to 162.15 eV and 163.38 eV in rGO-MoS₂-Ag respectively. This upward shift in the binding energy (blueshift) can be attributed to the n-type doping effect of Ag NPs as a result of interfacial electron transfer [15]. This binding energy shift is depicted in figures 7(a) and (b). Thus, we see the significant contribution of the electronic interactions at the various interfaces of the nanoscale heterojunctions contributing to enhanced sensor performances. This further paves the way for rational designing of heterostructures and implementing engineering at the nanoscale interfaces in order to achieve high performance NO₂ sensors.

4. Conclusion

In conclusion, chemiresistor devices based on rGO-MoS₂ hybrid and rGO-MoS₂-Ag have been developed for selectively detecting NO₂ over a wide concentration range from 1 to 10⁴ ppm at room temperature. Both the devices show much higher sensor responses than rGO alone. The sensors GM and GMA exhibit 443% and 1145% increase in sensor response compared to that of G at a concentration of 10⁴ ppm. Further, GMA exhibits 129% increase in response than GM at the same concentration. Also, both the devices show an approximate 500% increase in response to NO₂ exposure than device G at a concentration of 1 ppm. Moreover, the detection limits of the G, GM and GMA sensors calculated theoretically are 1.36 ppm, 147 ppb and 70 ppb respectively. Such a low detection limit is far below the detection standards of NIOSH. Thus, the sensors GM and GMA possess wide range detection capability at room temperature. The increased sensor performance of GM hybrid compared to G can be attributed to the defect dominated adsorption of NO₂ molecules on rGO and MoS₂.
Further, the hierarchical morphology of MoS2 provide increased adsorption sites for NO2 and effectively increase the surface area for adsorption. Also, modulation of accumulation region at the p-p heterojunction on NO2 exposure provide enhanced sensitivity. Further, on integration of Ag NPs onto rGO-MoS2 matrix, interfacial electron transfer occurs from Ag to rGO and MoS2 induced by work function differences due to which modulation of Fermi level occurs locally. Such an upshift in Fermi level fills the conduction band with more electrons thus facilitating electron withdrawal by NO2. Also the Ag NPs provide catalytic effect due to which more active intermediate species like NO− and O2− are formed that get adsorbed on rGO and MoS2 that lead to enhanced sensitivity. Thus, interfacial electronic interactions at the junctions of the hybrids allow us to achieve high performance NO2 sensors and can pave the way for future sensing technology.

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