Porous reduced graphene oxide (rGO)/WO3 nanocomposites for the enhanced detection of NH3 at room temperature†

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Incorporation of reduced graphene oxide (rGO) modifies the properties of semiconducting metal oxide nanoparticles and makes it possible to tune the surface area and pore size to optimum values, which in turn improves their gas sensing properties. In this work, to improve the ammonia (NH3) gas sensing characteristics, reduced graphene oxide (rGO) was incorporated into tungsten oxide (WO3) nanospheres using a simple ultrasonication method. The rGO–WO3 nanocomposites exhibited porous nanosheets with nanospherical WO3 as observed with field-emission scanning electron microscopy (FE-SEM). The oxidation state of the rGO–WO3 nanocomposite was determined using X-ray photoelectron spectroscopy (XPS). Three ratios of (1, 5 and 10% rGO/WO3) nanocomposites and pure WO3 showed good selectivity towards NH3 at 10–100 ppm, and more remarkably at room temperature in the range of about 32–35 °C and at a relative humidity (RH) of 55%. The limit of detection (LOD) of the synthesized rGO–WO3 nanocomposites was 1.14 ppm, which will highly favour low detection ranges of NH3. The sensor response was 1.5 times higher than that of the bare WO3 nanospheres. The sensors showed excellent selectivity, ultrafast response/recovery times (18/24 s), reproducibility and stability even after one month of their preparation. We believe that metal oxides using the rGO modifier can improve the sensitivity and reduce the LOD towards NH3 and can be used effectively in real-time environmental monitoring.

1 Introduction

Today’s fast industrial development and intense use of vehicles have caused severe air and water pollution. Volatile organic compounds (VOCs) like acetone, ethanol and formaldehyde and toxic gases such as, ammonia (NH3), hydrogen sulfide (H2S) and nitrogen oxide (NO2, NO and N2O) are the major pollutants, which have hazardous effects on both human health and the environment. These toxic compounds are released every day from different sources into the environment and it is very essential to detect them to minimize their harmful effects. NH3, accounted to be a very toxic gas, has been identified as the origin for many serious respiratory diseases. With the rapid developments in technology, the use of NH3 has become unavoidable, especially in applications like production of explosives employed in defense, fuels for automobiles, fertilizer and in food processing. The long-term acceptable exposure limit of NH3 is around 50 ppm, as reported by the occupational safety and health administration (OSHA). Exposure to NH3 above this limit may lead to serious health issues. Thus, selective and sensitive detection of NH3 is a vital safety measure for a pollution-free ecosystem. In this regard, it is essential to develop a reliable, cost-effective and ultrasensitive NH3 sensing device, which can work at room temperature.

A number of studies based on metal oxide semiconductor nanoparticles, like zinc oxide (ZnO), tin oxide (SnO2), indium oxide (In2O3), tungsten oxide (WO3), molybdenum oxide (MoO3) and vanadium oxide (V2O5) were conducted towards the development of NH3 gas sensors. Among these metal oxides, WO3, an n-type semiconductor, is considered as a forefront material for chemiresistive gas sensing application. The sensing effects of WO3 nanoparticles are determined by the capability of tungsten ions to change their valence state upon oxidation/reduction. The oxygen vacancy sites, related to substoichiometric WO3–x, act as active sites for chemisorption and easily regulate the sensing effects of the WO3 nanoparticles as well as the changeable sensibility of these particles with respect to analyte molecules. However, most of the WO3 nanoparticle based NH3 sensors work in the high temperature range of about 50–350 °C and other factors like high response and recovery times, high resistivity and low surface area restrict...
the use of WO3 in practical sensing applications. But, the need of the hour is room temperature (RT) sensors with fast response/recovery times and selectivity.12

The hurdles in the usage of semiconducting metal oxides (SMOs) in sensors can be surmounted by compositing them with carbon-based materials. In particular, the outstanding properties of graphene such as, its large specific surface area, chemical functionalities and fast electron transportation kinetics at room temperature ensure that it can be combined very well with SMOs for the fabrication of RT gas sensors. Moreover, SMO/graphene based nanocomposites are being continuously explored in different fields such as electroluminescent smart windows, gas and biosensors and photocatalytic and energy storage applications.13-18

Jinjin Shi et al. synthesized graphene oxide/hexagonal WO3 nanosheet composites for the detection of H2S and the sensors employing these nanocomposites showed a low detection limit of 10 ppb at a temperature of about 330 °C.19 Tarcisio M. Perfecto et al. explored WO3-0.33H2O nano-needles and their composites with rGO for detecting isopropanol down to 1 ppm at room temperature.20 Xiaqian et al. successfully employed the one-step hydrothermal method to prepare WO3 nanorods/graphene nanocomposites, which exhibited sensitivity towards NO2 up to 25 ppb at 300 °C.21 Ruma Ghosh et al. developed rGO/SnO2 hybrid-sensing layers by ultrasonication mixing and studied their sensing performance towards NH3 at room temperature.22 Huiling Tai et al. designed ZnO/rGO bilayer films, which offered excellent NH3 (10–50 ppm) detection at room temperature with fast response/recovery times.23 All these studies indicate that the incorporation of porous rGO into WO3 could lead to ultrasensitive NH3 sensing properties making WO3 an ideal candidate for gas sensing. To the best of our knowledge, no previous reports are available on NH3 sensing using porous rGO/WO3 nanocomposites at room temperature. For confirmation, previously reported literature is listed in ESI Table 1 (ST1†).

In the present work, porous rGO/WO3 nanocomposites were prepared via the ultrasonication method and examined for effective sensing and selective trace level detection of NH3 at room temperature. The WO3 nanospheres were uniformly distributed on the porous rGO sheets and the sheets showed good affinity towards WO3 nanospheres. The obtained sensing results were compared with those of pure WO3 nanospheres. The porous rGO/WO3 nanocomposite sensor revealed outstanding enhancement in NH3 sensing when compared with the pure WO3 sensor. Structural, morphological and electrical measurements were carried out. The possible sensing mechanism was elucidated in detail. The present work will make a major impact on the room temperature sensing of NH3.

2. Experimental section

2.1 Synthesis of WO3 nanostructures and GO

The detailed synthesis methodology and scheme for the preparation of pure WO3 nanospheres are reported in the ESI (Fig. S1 and ST2†). The preparation of GO and rGO has already been reported in our earlier studies.15,25

2.2 Synthesis of rGO/WO3 nanocomposites

Three different weight percentages (1%, 5% and 10%) of rGO were loaded into the prepared WO3 nanospheres. In a typical synthesis process, the required quantities of the prepared WO3 nanospheres were dispersed using ethanol and sonicated for 20 min. Next, 1% of rGO was dispersed using water and sonicated for 30 min to obtain a homogeneous dispersion. The dispersed rGO solution was then slowly added into the WO3 solution and the mixture was kept in an ultrasonic bath for 1 h to exfoliate a few layers of reduced graphene oxide, which resulted in the formation of a 1% porous rGO/WO3 nanocomposite. Changing the amount of rGO suitably resulted in the formation of 5% and 10% rGO/WO3 nanocomposites. The as-obtained products were labeled as 1% rGO/WO3, 5% rGO/WO3 and 10% rGO/WO3.14,25 The schematic representation of the formation of porous rGO/WO3 nanocomposites is shown in Fig. 1.

2.3 Characterization

The structural analysis was done using X-ray Diffraction techniques (XRD, Rigaku Smart Lab) with Cu-Kz radiation (1.5406 Å). The elemental and morphological analyses were done using field emission scanning electron microscopy (FESEM, FEI Quanta 250 FEG). Raman spectra of the prepared nanostructures were recorded using a Horiba Jobin Yvon LABRAM-HR 800 spectrometer with an argon laser at an excitation wavelength of 514 nm. The photoluminescence (PL) spectra were obtained by using a FLUORLOG, Horiba Jobin Yvon spectrophotometer. The composition and electronic state of the material were recorded using X-ray Photoelectron Spectroscopy (XPS) Kratos analytical, ESCA-3400, Shimadzu) with an X-ray source (Mg Kz, 1253.6 eV). BET surface area analysis was performed using a BELSHORP MINI II (BEL Japan).

2.4 Fabrication of nanocomposite thin films by spin coating

The prepared materials were ultrasonicated and thin film deposition of these materials was done using the spin coating technique. The obtained nanocomposites (1% rGO/WO3, 5% rGO/WO3 and 10% rGO/WO3) were subjected to uniform dispersion by ultrasonication for 10 min. The deposition of uniform rGO/WO3 nanocomposite thin films on pre-cleaned glass substrates (1 × 2 cm) was carried out using a spin coater.26,27

2.5 Gas-sensing capacity measurements of the fabricated sensors

For sensing measurements, highly conductive silver paste and copper wire were used to establish contacts on the spin coated thin film samples. The copper wires were connected to a high resistance electrometer (Keithley 6517B) interfaced with a computer using RS232 cable for recording the resistance. Room temperature sensing studies were done using a customized sensing chamber. The schematic diagram of the gas
3. Results and discussion

3.1 Synthesis and characterization of rGO/WO3 nanocomposites

XRD analysis was performed to study the purity and crystal structures of the prepared samples. XRD spectra of pure WO3 nanospheres, GO and rGO are shown in Fig. S2(A & B†). The typical diffraction peaks obtained (Fig. S2A† and 2) in this study indicate the monoclinic phase of WO3 and they are in good agreement with the Joint Committee of Powder Diffraction Standards (JCPDS card no. 89-4476). The characteristic peaks at 23.12°, 23.59° and 24.38° correspond to (0 0 2), (0 2 0) and (2 0 0) orientations respectively. The peaks of all the samples (1%, 5% and 10% rGO/WO3 nanocomposites) occur at nearly the same angle, indicating the successful replication of material formation. No noticeable peak corresponding to rGO is seen and this is owing to the lower percentage of rGO incorporation into WO3. This result is in agreement with earlier reports.18 We further performed Raman spectroscopy, XPS analysis and FESEM to confirm the presence of porous rGO in the obtained rGO/WO3 nanocomposites. The sharp and high intensity reflection peaks obtained for all three samples indicate their highly crystalline nature as well as the phase purity of the prepared samples, which means that the rGO incorporation does not change the phase of WO3.25 The average grain sizes were calculated for all the samples (1%, 5% and 10% rGO/WO3 nanocomposites) using the Scherrer formula and were found to be in the ranges from 42 to 45, 46 to 50 and 39 to 43 nm for 1%, 5% and 10% rGO/WO3 respectively.

In the present study, five Raman active modes have been observed experimentally for pure WO3 and D, G, and 2D bands for GO and rGO as shown in Fig. S3(A and B†). In Fig. 3, the sharp intense peaks at 709 and 807 cm⁻¹ correspond to the stretching vibration of O=W=O, whereas the peaks at 264 and 328 cm⁻¹ relate to the bending vibration of W–O–W. The peak at 131 cm⁻¹ is assigned to the lattice vibration of crystalline WO3 and the additional low intensity peaks belong to D and G bands, which denote the presence of porous rGO in the nano-composite.25 The D band at 1346 cm⁻¹ corresponds to the defect originated in the graphene structure and the G band at 1535 cm⁻¹ is due to the scattering of sp² carbon atoms from the graphene lattice. The disordered crystal structure of graphene is strongly indicated by the intensity ratio (I_D/I_G) between the D and G bands. The value of I_D/I_G for the 10% rGO/WO3 is the highest (1.0), while its values are 0.9 and 0.7 for 5% and 1% rGO/WO3 respectively. This is due to the decrease in the C (sp²) area for the lower concentrations of rGO. In addition to this, the improved intensity of D and G bands for higher percentages of rGO confirms the formation of different weight percentages (1%, 5% and 10%) of rGO/WO3 nanocomposites.

Detailed confirmation about the size, typical morphologies and elemental percentage of the synthesized WO3, GO and rGO nanostructures was obtained by FESEM and EDAX analyses.
ultrathin porous graphene sheet and the average diameter of WO3, which are in agreement with the previous report. The agglomeration of WO3 nanospheres and therefore maintains a high surface area.

The chemical binding states of rGO/WO3 nanocomposites and the stoichiometry of tungsten and surface elements of the nanocomposites were studied using the X-ray photoelectron spectra (XPS). The phase and chemical structure of all the nanocomposites were similar (confirmed by XRD, Raman and EDAX), except the percentage of rGO incorporation (1%, 5% and 10%) at low and high magnifications. The rGO/WO3 nanocomposite reveals uniform dispersion of WO3 on the ultrathin porous graphene sheet and the average diameter of the WO3 nanospheres is about 120–130 nm. During ultrasonication, the rGO sheets are well dispersed. Transparent thin layered and wrinkled sheets are uniformly incorporated into WO3 due to a strong Van der Waal’s interaction occurring between rGO and WO3. Besides, rGO incorporation prevents agglomeration of WO3 nanospheres and therefore maintains a high surface area.

The W 4f and O 1s core level spectra are shown in Fig. 5(a–c). The W 4f core level corresponds to binding energies 35.7 and 37.9 eV for W 4f7/2 and W 4f5/2 respectively with a spin-orbit quantum confinement effect in WO3. The photoluminescence (PL) spectra are used to study the structural defects and to understand the transfer and recombination processes of photoexcited charge carriers of the prepared nanocomposites. The strongest PL emission peaks appear at 328, 326 and 325 nm (Fig. 7) for WO3, and 1% and 5% rGO/WO3 nanocomposites respectively and they are associated with near-band edge emission (UV-emission). The other small peaks appearing at 414, 409 and 405 nm are attributed to the abundant incorporation of oxygen defects into the prepared WO3 and rGO/WO3 nanocomposite. The PL intensity obtained for 5% rGO/WO3 is six times lower than that for pure WO3 nanospheres and 3 times lower than that for the 1% rGO/WO3 nanocomposites showing a drastic quenching after the introduction of rGO, which is clearly observed in Fig. 7(a–c). When the samples were excited at 290 nm, the PL peak intensities for the three samples were in the following order: WO3 > 1% rGO/WO3 > 5% rGO/WO3. The quenching effect in the nanocomposite is due to the large contact between the WO3 nanospheres and rGO nanosheets, which might be due to the 2D and π–π conjugated structure of rGO. The rGO/WO3 nanocomposites can efficiently hinder the recombination of electron–hole pairs and strongly support the electron transfer from the conduction band of WO3 to the electronic states of rGO. Various researchers have reported similar results on metal oxide/rGO nanocomposites. The emission peaks are observed to be blue shifted when compared with earlier reports. This might be due to the influence of quantum confinement effect in WO3.

3.2 Gas sensing performance

As previously reported, the rGO/WO3 nanocomposite is a promising candidate for detecting many toxic gases such as NO2, H2S, acetone and so on. In the present work, sensing of
NH₃, as the target vapour is demonstrated using rGO/WO₃ nanocomposites. So far, there are no specific reports on the use of rGO/WO₃ nanocomposites towards NH₃ sensing at room temperature. Fig. 8(a–d) show the influence of different percentages of rGO (1%, 5% and 10%) in the rGO/WO₃ nanocomposite based chemiresistive-type sensor towards the detection of different concentrations (10, 20, 40, 60, 80 and 100 ppm) of the reducing vapour NH₃ at 35 °C (RH: 54%). For comparison, different morphologies (nanorods, nanospheres and aggregated nanoparticles) of pure WO₃ towards the detection of NH₃ were also tested and their dynamic response cure, response and recovery times, sensitivity and selectivity characteristics of the samples are shown in Fig. S6(a–f).† Increase in the percentage of rGO content leads to an increase in conductivity and therefore a noticeable change (decrease) in the resistance value (Fig. 8), which clearly confirms the incorporation of different percentages of rGO into the WO₃ nanospheres. When the rGO/WO₃ nanocomposite is exposed to different concentrations (10–100 ppm) of NH₃, an increase in the resistance value is observed (Fig. 8(a–c)). This indicates the p-type behavior of the sensing element. However, the resistance of the pure WO₃ based sensor decreased (Fig. S6(a–c)†) when exposed to NH₃ indicating the n-type behavior of WO₃. The sensing response of rGO/WO₃ nanocomposites towards NH₃ is shown in Fig. 8(d). The 5% rGO/WO₃ nanocomposite shows the maximum response when compared with the other two percentages of the nanocomposites and pure WO₃. The response values of the 5% rGO/WO₃ nanocomposite are 4.50, 5.22, 7.53, 9.69, 12.88 and 15.83 for different concentrations of NH₃ such as 10, 20, 40, 60, 80 and 100 ppm, respectively. The sensor response value is in the following order: 5% rGO/WO₃ > 1% rGO/WO₃ > WO₃ > 10% rGO/WO₃ as seen from Fig. 8(d) and S6(d).† To evaluate the sensing performance of rGO/WO₃ nanocomposites, the sensitivity (S) was calculated using the formula,
\[ S = R_b - R_a/R_a, \]

where \( R_a \) is the baseline resistance of the sensor in air and \( R_g \) is the resistance of the sensor after exposure to the test vapour/gas.

Further, the single transient response/recovery times of all the prepared rGO/WO\(_3\) sensors on exposure to 40 ppm NH\(_3\) are displayed in Fig. 9(a–c). The response and recovery times of the sensor are respectively defined as the times taken to reach 90%
of its stable resistance value on exposure to target vapour and to reach 10% of its baseline resistance value when exposed to an air atmosphere.\textsuperscript{37-49}

The pure WO\textsubscript{3} sensor shows a response time of 165 s and recovery time of 132 s, which are shown for comparison in Fig S6(e).\textsuperscript{†} However, the response and recovery times of the prepared sensor are 18 s and 24 s respectively. From these observations, one can confirm that this trend is due to the influence of concentration. Increased NH\textsubscript{3} concentration results in faster adsorption on the nanocomposite surface, which leads to a decrease in response time; on the other hand, adsorption of a higher concentration of NH\textsubscript{3} slightly prolonged the desorption at room temperature.

It is important to study the selectivity of the prepared material. In this work, ten different compounds, such as, ammonia (NH\textsubscript{3}), ethanol (C\textsubscript{2}H\textsubscript{6}O), methanol (CH\textsubscript{3}OH), isopropyl alcohol (C\textsubscript{3}H\textsubscript{7}OH), formaldehyde (CH\textsubscript{2}O), acetone (C\textsubscript{3}H\textsubscript{6}O), triethylamine (C\textsubscript{6}H\textsubscript{15}N), dimethylamine (CH\textsubscript{3})\textsubscript{2}NH, xylene (C\textsubscript{8}H\textsubscript{10}) and n-butanol (C\textsubscript{4}H\textsubscript{10}O) vapours at 100 ppm concentration have been tested. From Fig. 9(d), it is evident that all the rGO/WO\textsubscript{3} nanocomposites and pure WO\textsubscript{3} selectively detected NH\textsubscript{3}. Details of the size of each molecule and the dipole moments of all the probable interfering compounds are listed in Table 1. It is evident that the molecular sizes of all the other gases are large when compared to NH\textsubscript{3} and this is the reason for its higher permeation ability and hence a higher response and selectivity. NH\textsubscript{3} molecules rapidly donate electrons to the rGO/WO\textsubscript{3} nanocomposite surface even at room temperature compared to other vapours. This might be another important reason for its selectivity. Especially, the 5% rGO/WO\textsubscript{3} nanocomposite has a good selectivity and the highest response to NH\textsubscript{3}, when compared to the other two percentages of rGO/WO\textsubscript{3} nanocomposites and pure WO\textsubscript{3}. The response values of WO\textsubscript{3}, and 1%, 5% and 10% rGO/WO\textsubscript{3} towards 100 ppm NH\textsubscript{3} are 10.5, 14.53, 16.0 and 0.60 respectively.

The 5% rGO/WO\textsubscript{3} nanocomposite exhibited an excellent sensing capacity towards NH\textsubscript{3}, which is 1.5 times higher than that of WO\textsubscript{3} nanostructures. Moreover, the rGO/WO\textsubscript{3} nanocomposite has a high surface area, which leads to more active reaction sites and an obvious increase in the sensor performance.\textsuperscript{35} However, the sensing properties are strongly

Fig. 7 PL spectra of pure WO\textsubscript{3}, 1% rGO/WO\textsubscript{3} and 5% rGO/WO\textsubscript{3}.

Fig. 8 (a) Dynamic response and recovery curve of the 1% rGO/WO\textsubscript{3} nanocomposite on exposure to 10–100 ppm of NH\textsubscript{3}. (b) Dynamic response and recovery curve of the 5% rGO/WO\textsubscript{3} nanocomposite on exposure to 10–100 ppm of NH\textsubscript{3}. (c) Dynamic response and recovery curve of the 10% rGO/WO\textsubscript{3} nanocomposite on exposure to 10–100 ppm of NH\textsubscript{3}. (d) The response curve of the rGO/WO\textsubscript{3} nanocomposite on exposure to different concentrations of NH\textsubscript{3}. 
influenced by the rGO content; increasing the rGO content beyond 5% decreases the sensor response. The increase in rGO content beyond 5% leads to an increase in the graphene layer, which fully covers the WO3 surface by wrapping the active sites. Therefore, there is a significant reduction in the electrical resistance and an extreme decrease in the sensor response. A similar result is reported by Perfecto et al. towards detection of isopropanol down to 1 ppm. Based on the above discussions, the NH3 sensing properties of the 5% rGO/WO3 nanocomposite and its basic sensor characteristics such as, LOD, RH, reproducibility, and stability were studied.

In addition to high sensitivity and selectivity, a good gas sensor needs a good limit of detection (LOD), relative humidity value (RH%), reproducibility and stability. When the NH3 concentration increases, the response value of the sensor proportionally increases. The 5% rGO/WO3 nanocomposite sensor shows (Fig. 10(a)) a linear response on increasing the concentration of NH3. The sensor has an $R^2$ (coefficient of determination) value of 0.9907 as illustrated in Fig. 10(a). The LOD of the 5% rGO/WO3 nanocomposite is calculated using the following formula,

$$\text{LOD} = 3\sigma/S$$  \hspace{1cm} (2)

where $\sigma$ and $S$ are the standard deviation and the slope respectively. The LOD for the developed sensor is found to be 1.14 ppm. Fig. 10(b) shows the response of the 5% rGO/WO3 nanocomposite sensor on exposure to 100 ppm NH3 with a change of 15%, 41%, 54%, 72%, and 88% in the RH percentage. A decrease in sensor resistance with an increase in RH% is observed. The standard deviation of 100 ppm NH3 with the change in humidity values is <5%. The developed sensor material provides good reproducibility towards sensing of NH3 (60 ppm). Also the sensor resistance recovered to its initial baseline value after four cycles indicating the outstanding reproducibility of the prepared material (Fig. 10(c)). Measuring the response value of the sensor over a period of time helped in checking the stability of the device. Fig. 10(d) shows the variation in response of the 5% rGO/WO3 nanocomposite towards 10 and 100 ppm concentration of NH3 for a period of 30 days. The response values of the 5% rGO/WO3 nanocomposite for 10 and 100 ppm concentrations of NH3 on

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**Table 1** Molecular size and dipole moment of NH3 and all interfering compounds

| Different compounds | Dipole moment (D) | Molecular size (nm) | Ref. |
|---------------------|------------------|---------------------|------|
| Acetone             | 2.88             | 0.66                | 50   |
| Formaldehyde        | 2.33             | —                   | 51,52|
| Ethanol             | 1.69             | 0.44                | 53   |
| Isopropanol         | 1.66             | 0.47                | 7    |
| Methanol            | 1.70             | 0.43                | 53   |
| Trimethylamine      | 0.87             | 0.78                | 7    |
| Dimethylamine       | 1.12             | —                   | 54   |
| Ammonia             | 1.4              | 0.32                | 7,50,52|
10th, 20th and 30th days were observed as 4.5, 4.1 and 3.9 and 15.8, 15.3 and 15.1 respectively. The observed response values confirm the stability of the sensing element throughout the 30-day period with an allowable error value of <5%. To prove the validity of the results obtained from the present work, the observed room temperature NH3 sensing properties of rGO/WO3 nanocomposites are compared with the earlier reports and the data are presented in ST3.† The present work on rGO/WO3 confirms superior sensing properties, ultrafast response and recovery, selectivity and stability towards NH3 specifically at room temperature. Three possible reasons have been proposed, which might be responsible for the enhancement in the sensor response.

(i) The porosity and specific surface area have a significant impact on the gas–solid interaction and provide more active sites for reactions. The obtained BET results proved that the enhancement in sensing performance of the 5% rGO/WO3 nanocomposite is due to the improved specific surface area and pore size of the 5% rGO/WO3 nanocomposite when compared to pure WO3.20

(ii) In gas sensing, the depletion layer formation is directly related to the available number of oxygen vacancies in the rGO/WO3 nanocomposite surface, because oxygen vacancies act as electron capturers, which result in a decrease in the recombination process and they also act as preferential adsorption sites for VOCs and gas molecules.16,21 On the basis of the PL intensity quenching, we conclude that the 5% rGO/WO3 nanocomposite leads to a reduction in charge recombination and this might be another reason for the enhancement in sensing performance of the 5% rGO/WO3 nanocomposite.

(iii) Finally, the p–n heterojunction facilitates electron transfer from the conduction band of WO3 to the electronic states of rGO and strongly hinders the recombination of electron–hole pairs. In addition to this, the ohmic contact helps in the continuous convenient flow of charge carriers at the interfaces of rGO and WO3.43–46,56–58 This ohmic contact formation is the additional reason for the enhanced sensing performance of the 5% rGO/WO3 nanocomposite. The pore size, specific surface area, p–n heterojunction and ohmic contact formation were studied from the BET, PL and I–V analyses of the prepared rGO/WO3 nanocomposites and the pure WO3 and the results support the enhancement of the sensor response (Fig. 6 and 7). These three characteristics function together to improve the response of rGO/WO3 nanocomposite based NH3 sensors at room temperature.

3.3 Gas sensing mechanism

Based on the above results, it can be said that the vapour sensing mechanism of metal oxide/rGO nanocomposites is governed by many factors, such as sensor porosity, specific surface area and heterojunction formation. Semiconductor metal oxide based sensors work on the principle of the change in resistance owing to the reaction among gas molecules and the sensitive surface. This involves surface reaction, gas adsorption, and desorption processes.29 This process is completely temperature dependent. At temperatures below 100 °C or at room temperature, a single molecular oxygen absorbs only one electron and forms a molecular ionic oxygen species (O2−), but above 100 °C, it is capable of absorbing two electrons to form atomic oxygen species (O− and O2−).47
The possible room temperature sensing mechanism of pure WO₃ towards NH₃ is as follows,

\[ \text{O}_2 \text{(atmosphere)} + e^- (\text{WO}_3 \text{ surface}) \rightarrow \text{O}_2^- (\text{WO}_3 \text{ surface}) \]  

Initially when the WO₃ surface is exposed to an air atmosphere, the oxygen molecules are adsorbed on the WO₃ surface by capturing the electrons, which modulates the surface carrier concentration, leading to the formation of an enlarged electron depletion region. This results in a stabilized baseline resistance. Moreover, on exposure of the WO₃ surface to the NH₃ reducing vapour, the pre-adsorbed oxygen reacts with NH₃ to produce N₂ and H₂O at room temperature. The resistance of the sensing element decreases due to the removal of chemisorbed oxygen, which obeys the n-type behaviour of WO₃. As a result, the trapped electrons are released into the conduction band of WO₃, thus improving the carrier concentration. As a consequence, the baseline resistance decreases, leading to a decrease in the width of the depletion region.

The main reaction between WO₃ and NH₃ based on the above discussions is given below:

\[ 4\text{NH}_3 + 3\text{O}_2^- (\text{WO}_3 \text{ surface}) \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} + 6e^- \]  

However, in the case of rGO/WO₃ nanocomposites, WO₃ is an n-type semiconductor and rGO behaves like p-type. It is well known that the n and p type materials are dominated by electrons and holes respectively. Once they come into contact with each other, a depletion layer is formed at the interface which is a p-n heterojunction. The rGO/WO₃ sensor shows p-type behavior towards NH₃ detection. rGO possesses a higher work function and defects in the prepared nanocomposite surface, which provide many adsorption centers for NH₃. Therefore, when the sensor surface is exposed to NH₃, the NH₃ molecules are adsorbed on the composite surface, and the interaction between adsorbed O₂⁻ and NH₃ releases free electrons and neutralizes the holes in the rGO which contributes to reduction in the width of charge conduction channels, leading to the increase in the width of the electron depletion layer (as shown in Fig. 11) and hence an increase in sensor resistance.

The results of the present work on NH₃ sensing are of immense importance due to the highly improved sensor response of rGO/WO₃ nanocomposites at room temperature when compared to the earlier report. These results are in concurrence with those of Zhang et al.

4 Conclusions

Porous and conductive rGO/WO₃ nanocomposites were fabricated by a simple ultrasonication method. The structural, morphological, vibrational, compositional and optical properties confirm the formation of the nanocomposite. The 5% rGO/WO₃ nanocomposite shows enhanced sensing performance towards NH₃, which is attributed to the increased surface area and pore size of the nanocomposite when compared to pure WO₃ nanospheres. The voids in the graphene sheet may provide excellent permeability to NH₃ due to physisorption. Moreover, the incorporation of WO₃ into 2D structures provides a greater number of reactive sites for selective and sensitive detection of NH₃. Additionally, the 5% rGO/WO₃ nanocomposite sensor was found to be highly selective towards NH₃ in the presence of possible interfering gases and exhibited remarkable stability and repeatability at room temperature. The obtained data clearly show that the surface area, pore size, p-n heterojunction and ohmic contact play important roles in the enhancement of sensor performance towards NH₃ detection.

Conflicts of interest

There are no conflicts to declare.

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