Modified WO$_3$ nanosheets by N-GO nanocomposites to form NO$_2$ sensor

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ABSTRACT
In this work, WO$_3$ nanosheets were synthesised and decorated with different percentages of N-GO nanocomposites to study gas sensing assets. The X-ray diffraction (XRD) and Raman spectra showed fine crystal quality. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) illustrated nanosheets morphology for WO$_3$ and confirmed its decoration. The variation of the sensor electrical resistance was studied at various gas concentrations in the range of temperature intervals. The optimal operational temperature was 200 $^\circ$C. The optimum response signal and recovery time for WO$_3$–N-GO 6% at 200 ppm concentration were 90 s and 205 s, respectively. The selectivity of the WO$_3$–N-GO samples was 53%, 46% and 60% for WO$_3$–N-GO 3%, WO$_3$–N-GO 6% and WO$_3$–N-GO 9%, respectively at 200 $^\circ$C. The highest response was found for WO$_3$–N-GO 9% to NO$_2$ (58%) and WO$_3$–N-GO 6% to CO (28%) at 200 $^\circ$C. Therefore, by selecting the optimum percentage of N-GO nanocomposites, the sensors can be fabricated with the highest response to NO$_2$ or CO.

1. Introduction
Among the air pollutant species, nitrogen dioxide (NO$_2$) has a higher share in the air pollution which has a distinctive biting odour. The origin of this pollutant comes typically from the fuel combustion in the vehicles which causes numerous ecological effects, like tropospheric ozone formation, acid rain precipitation and photochemical smog [1–4]. Persistent exposure to the NO$_2$ with the concentration exceeding 4 ppm increases the chance of respiratory symptoms and impairing lung function [5]. Therefore, on-line monitoring of the NO$_2$ concentration and determining the possible leakage are critical for human health and environmental protection to be controlled. Up to the present time, several procedures, including electrochemical techniques, spectroscopic methods and chemiresistive sensors, have been exploited for NO$_2$ detection in the form of gas species [6–9]. Yan Zhao et al studied electrical properties and sensitivity of WO$_3$ for NO$_2$ gas.
sensor [10]. You et al. fabricated the WO₃ sensor that exhibited superior sensing performance to low concentration NO₂ [11]. The mesoporous WO₃ thin film properties as a NO₂ gas sensor were investigated by Teoh et al. [12]. Shendage et al. demonstrated the fabrication of 2D WO₃ nanoplates by using the hydrothermal method for the NO₂ gas sensor [13]. Meng et al. reported the synthesis of WO₃ nanoparticles and their application to NO₂ sensor [14]. Hua et al. studied NO₂ sensing properties of pure WO₃ ceramics [15].

Tungsten trioxide (WO₃) is a wide bandgap (2.6 eV) n-type semiconductor material which reported for gas sensing applications and explosive gases monitoring [16–19]. The WO₃ sensors function suffering from poor selectivity and consequently low sensitivity during extended response time with high resistivity. Thus, methods such as metal or non-metal doping in the WO₃ structure, changing the morphology and particle size of WO₃ and combining with semiconductors have proposed [20–28]. These methods enhance WO₃ sensing properties yet some contributions have been made to decrease the high resistivity of these sensor products [29,30]. Heterojunction structure of WO₃/g-C₃N₄ with a well-defined morphological structure reported by Liu et al. [31]. A novel photocatalyst system based on the WO₃/multi-walled carbon nanotube studied by Dinari et al. with the higher photodegradation rate compare to the pristine WO₃ [32]. The composite of semiconductor nanostructure with the graphene oxide (GO) has engrossed extensive attention [33–35].

GO with the sp²-hybridized orbitals has a two-dimensional honeycomb structure [36]. There are plentiful potential applications of GO-based composites considered in the fields of catalysis, fuel cells, sensors and lithium-ion batteries [37–44]. At first, Williams et al. [45] proposed graphene as an electron transfer medium. The high adsorption capacity of the rGO–WO₃ composite reported by Prabhu et al. [46]. Introducing the graphene in the band structure of the semiconductor, alter the bandgap energy and interfacial charge transfer in the semiconducting materials. Few studies have described the hybrid nanocomposite of tungsten oxide and graphene thick-film as gas sensors to date [47–49]. According to the provided reasons, a theoretical basis for the combination of nitrogen-doped GO and WO₃ is expected to obtain an ideal sensor.

In this study, we synthesised WO₃ nanosheets and decorated them by nitrogen-doped graphene (N-GO) using the hydrothermal method. The morphology analysis and gas sensing tests were applied to investigate the advantage of these sensors. The results showed improvement in response time. In addition, it is possible to manufacture sensor for CO and NO₂ by changing the amount of the N-GO.

2. Experimental details

2.1. Synthesis of WO₃ nanosheets and WO₃ decorated by nitrogen-doped GO

The chemicals in this experiment were bought from Merck Company. In order to synthesise WO₃ nanosheets, a solution of 20 mL deionised water, Na₂WO₄ 2H₂O (0.825 g) and NaCl (0.29 g) were prepared by stirring. Then it was gradually titrated by HCl to obtain pH = 2. The obtained milky solution was transferred into a 150 mL Teflon lined stainless steel autoclave and heated to 180 °C for 24 h. After cool down to room temperature, the obtained powder was washed with distilled water (2 times) and dried at 30 °C. The next step, graphene was synthesised by using Hummer’s method [50]. Then 0.25 g graphene was dispersed in 100 mL ethanol and stirred for 10 min. (NH₃) 2CO (7.5 g) slowly was added to the solution and stirred for 30 min. The obtained solution was transferred into a 150 mL Teflon lined stainless steel autoclave and heated to 180 °C for 12 h. After cool
down to room temperature, the obtained powder was washed with ethanol and distilled water (two times) and dried in vacuum at 70 °C for 3 h. N-GO nanocomposite was synthesised. In the last step, a solution of 50 mL ethanol and 0.58 g WO₃ was prepared, then N-GO nanocomposites with 3% (0.018 g) mass percentage was added to the solution and stirred for 2 h. The final solution was transferred into a 150 mL Teflon lined stainless steel autoclave and heated to 180 °C for 18 h. After cool down to room temperature, the obtained powder was washed with distilled water (two times) and dried at 30 °C (WO₃–N-GO 3%). The same process was repeated with 6% and 9% mass percentage separately to fabricate three different samples (WO₃–N-GO 6% and WO₃–N-GO 9%).

2.2. Sensing setup

The working mechanism of metal oxide sensors is the variation of surface electrical conductance in the presence of a gaseous environment. The setup has been proposed to measure the gas response of different gases by changing the electrical resistance of the sensing element (Figure 1). The sensing property of the samples can be measured at different temperatures using the setup. A gas sensor was fabricated as follows: the WO₃ decorated N-GO nanocomposites were mixed with DI water (0.1 M), and then coated on a previously cleaned glass substrate by drop cast method at room temperature. Then a pair of interdigital gold thin-film electrodes deposited by e-beam deposition. Then the sample was transferred to the controlled temperature chamber (up to 400 °C) to investigate the sensing properties. A calibrated digital multimeter was used to record the electrical resistance of the samples. The resistance of the fabricated samples was measured in air (step 1). The gas concentration was adjusted using the dry air mixture controlled by mass flow controllers in the chamber. Again, the resistance of the fabricated samples was measured in the presence of gas (step 2). Steps 1 and 2 were repeated at different temperature in various gas concentrations. The variations in electrical resistance was explored in the presence of different gases species and air at different concentrations and temperatures in the chamber (Figure 1).

Figure 1. Schematic of the experiment.
The response of n-type semiconductor sample for the reducing gas and the oxidising agent is defined, respectively, as:

\[
\text{Response (\%) } = \frac{R_a - R_g}{R_a} \times 100 , \text{ for reducing gas (1)}
\]

\[
\text{Response (\%) } = \frac{R_g - R_a}{R_g} \times 100 , \text{ for oxidising gas (2)}
\]

where \( R_a \) is the sample resistance at ambient temperature, while \( R_g \) is the resistance under the examination gas species. The examination period in which the resistance of the sensor changes to 90% of the original base resistance is defined as the response time. Accordingly, the required time to record 90% of the signal is defined as the recovery time [51]. To study the operational parameters attributed to the sensor quality, response time, recovery time, optimum working temperature and lower limit of detection were investigated and reported as the main performance parameters of a sensor.

2.3. Characterisation

Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu radiation (\( \lambda = 1.54178\text{Å} \)). The 2\( \theta \) range used in the measurement of tungsten oxides was from 10\( ^o \) to 70\( ^o \) in steps of 0.02\( ^o \) with a count time of 1 s. The morphology of the samples was investigated by scanning electron microscopy (SEM, XL30). The transmission electron microscopy (TEM) observations were carried out on a Tecnai 20 operating 200 kV. Energy-dispersive X-ray spectroscopy (EDX, (VEGA/TESCAN-XMU)) illustrated the elements of the nanocomposite. Raman spectroscopy was performed with a Thermo Nicolet Almega XR model spectrometer with laser excitation 633 nm.

3. Results and discussion

Figure 2 shows the XRD patterns of the WO3–N-GO samples. All the diffraction peaks of the pure WO3 match with the hexagonal structure (JCPDS card no. 33-1387) [52]. There were no additional peaks detected, indicating single-phase synthesised WO3 with high purity. The main diffraction peaks of WO3–N-GO samples (2 0 0) are presented at different weight percentages. No diffraction peak for GO was detected, representing the considerable reduction of GO. Since hydrothermal doping leads to a reduction of GO, it can be reduced by heat treatment, under the process called thermal annealing reduction. The fast increase in the temperature rate makes the species with the functional oxygen attached to the carbon plane, which later decomposes into gases that create immense pressure among the stacked layers. Besides exfoliating graphite oxide, the rapid heating process decomposes oxygen-containing groups and reduces the functionalised graphene sheets at elevated temperatures [53,54].

It has been reported, heating up to 100\( ^o \)C in a thermal reduction process deoxygenate GO sheets [55]. Surface accessibility and active gas diffusion between matching layers of graphene enhances by the introduction of WO3 nanosheets, which also avoids the GO sheets from restacking. To estimate the crystallite size of the nanocomposites, the Williamson–Hall plot was used [56]. The data are collected in Table 1.

There are many factors that can origin strain in the nanoparticles, which are particle size, shape and twinning. The lattice mismatch induced by the lattice distortions in the
supporting substrate through the strained layer structures between metals in multimetallic core–shell can also raise the strain in nanoparticles. As a result, defects will be generated by the strain between oxide films and substrates [57–59]. The complex hybridizations between the W and O atoms are changed in W–O bond lengths by strain [60]. Besides, it can be noticed that an increase in N-GO content enhances strain, which is due to the substitution of nitrogen dopant and as a result disturbs the crystallinity and makes more strain in the structure.

The size, shape and morphology of the resulted nanostructures of WO₃ and WO₃–N-GO samples are characterised by SEM (Figure 3(a–d)). It is observed that the WO₃ nanostructure is mostly nanosheets with uniform size distribution. The nanosheets have a ribbon morphology with a quadrilateral cross-section. From Figure 3(b–d) it is evident that the WO₃ nanosheets are surrounded by the N-GO nanocomposites. It is obvious that by increasing in N-GO content, the more N-GO are attached on the surface of WO₃ nanosheets. It is evident that a highly ordered three-dimensional nanoporous is formed over the entire samples.

EDX analysis was applied to identify the elemental composition of the samples (Figure 4). The data from Figure 4 are collected in Table 2, which shows an increasing extent of C and N for the WO₃–N-GO samples.

In the TEM images, it is obvious that the WO₃ nanosheets are well decorated with N-GO nanocomposites (Figure 5(a–c)). Both N-GO nanocomposites and WO₃ nanosheets can be clearly observed. By the enhancement of N-GO, more nanocomposites are attached to WO₃ nanosheets.

The lattice and phonon vibration modes were obtained from the Raman scattering spectrum, which is shown in Figure 6. The spectra contain some sharp and strong peaks related to WO₃ and two soft peaks related to N-GO nanocomposites. The peaks appear at

Table 1. Crystallite size and strain of the samples calculated from XRD analysis.

| Sample       | Crystallite size | Strain          |
|--------------|------------------|-----------------|
| WO₃–N-GO 3%  | 181.06           | 5.92E–03        |
| WO₃–N-GO 6%  | 191.56           | 4.92E–03        |
| WO₃–N-GO 9%  | 272.19           | 2.50E–02        |
249 and 471 cm\(^{-1}\) ascribe to W – O – W bending vibration. Other peaks at 780 and 936 cm\(^{-1}\) are related to W – O – W stretching vibration [61]. In addition, the peaks associated with N-GO are also seen, which marked with a dotted point and displayed with larger magnification.

The first-order scattering of the \(E_{2g}\) mode in the sp\(^2\) carbon domains appears in the G band, while the D band is allied with sp\(^3\)-hybridized carbon derived from the structural defects, amorphous carbon or the edges that can disrupt the structural symmetry. The intensity of the D band to the G band ratio (\(r = \frac{I_D}{I_G}\)) can be used to evaluate the defect and disorder of the graphitised structure besides the fraction of sp\(^3\)/sp\(^2\)-bonded carbon [62]. The calculation results are \(r = 0.47, 0.67\) and 0.83 for WO\(_3\)-N-GO 3\%, WO\(_3\)-N-GO 6\% and WO\(_3\)-N-GO 9\%, respectively. This indicates that the highest density of defects can be found in WO\(_3\)-N-GO 9\%, while the lowest density of defects is in WO\(_3\)-N-GO 3\%, which is due to the substitution of nitrogen dopants.
3.1. Gas sensing

The sensitivity of the WO$_3$–N-GO samples sensor was determined by measuring the electrical resistance in a dried-atmosphere exposing to the toxic gases and vapours (50–300 ppm), in the temperature range of 50–300 °C. The stable zero levels for the electrical resistance of the semiconductor metal oxide films were maintained and carried out before the measurements, as it is one of the critical limits for gas sensing applications.

The adsorbed oxygen has a practical impact on the surface states of the sensors related to the operating temperature and determining the gas sensing properties of the products.

According to the oxygen-adsorption model [63]; in the presence of oxygen species, oxygen anions will form by the capture of electrons from semiconductors, which can undergo with various reactions at the different operating temperatures as shown below:

\[
\begin{align*}
\text{O}_2 \text{(gas)} & \rightarrow \text{O}_2 \text{(ads)} \\
\text{O}_2 \text{(ads)} + e^- & \rightarrow \text{O}_2^- \\
\text{O}_2 \text{(ads)} + 2e^- & \rightarrow 2\text{O}^- \\
\text{O}_2 \text{(ads)} + 4e^- & \rightarrow 2\text{O}^{2-}
\end{align*}
\]

In the case of the n-type semiconductors, the width of the electron depletion layer increases as the electrons incessantly swipe the semiconductor surface when exposed to oxidising gases. This phenomenon causes an escalation of electrical resistance. Contrarily,
reducing gas species act as electron donors, reducing the width of the depletion layer, which decreases the resistance of the sensor [64].

In the case of p-type semiconductors, oxidising gases reduce the resistance as the width of the hole accumulation layer increases where electrons capture from the surface of a

Figure 5. TEM images of (a) WO$_3$–N-GO 3%, (b) WO$_3$–N-GO 6% and (c) WO$_3$–N-GO 9%.

Figure 6. The Raman spectra of the WO$_3$–N-GO samples.
Figure 7. Work function and Fermi level of the WO$_3$ and N-GO nanocomposites.

Figure 8. The electrical response of the WO$_3$–N-GO samples to 250 ppm of different alcohols at various temperatures.
semiconductor. Accordingly, the resistance of the sensor increases as the width of the hole accumulation layer decreases by the exposure of the semiconductor surface to the reducing gases [64].

As the operational temperature influences the kinetics, conductivity and electron mobility, the sensing acts of semiconductors sensors are strongly dependent on the working temperature [65].

The presence of functional groups on the GO surface results in the most substantial impact on WF (6.7 eV) relative to all other groups [66]. For the n-type WO₃, the Fermi energy ($E_F$) has to be 0.39 eV smaller than the conduction band [67]. Therefore, direct electron transfer from the conduction band of WO₃ to the N-GO is energetically favourable when WO₃ nanosheets are attached to the N-GO nanocomposites [68].

**Table 3.** Sensors’ response to 250 ppm of different alcohols species at 200 °C.

| Sample        | Response to ethanol (%) | Response to methanol (%) | Response to propanol (%) | Response to ammonia (%) |
|---------------|-------------------------|--------------------------|--------------------------|-------------------------|
| WO₃–N-GO 3%  | 8.5                     | 10.6                     | 7.3                      | 5.7                     |
| WO₃–N-GO 6%  | 14.2                    | 13.8                     | 9.2                      | 6.6                     |
| WO₃–N-GO 9%  | 11.3                    | 11.8                     | 6.5                      | 7.9                     |

**Figure 9.** The electrical response of the (a) WO₃–N-GO 3%, (b) WO₃–N-GO 6% and (c) WO₃–N-GO 9% to NO₂ and CO gases at different temperatures.
Besides, graphene offers conductive pathways that boost the efficiency of charge-carrier transfer in the samples, which enhances the response. In summary, most of the electrons are carried by N-GO nanocomposites (Figure 7).

Figure 8 represents the sensor response in the bar diagram of the WO$_3$–N-GO samples. The samples exposed to different alcohol species relating to the operational temperature. As a result, the temperature dependence with the sensing intensity of different alcohol species can be determined. As seen, the highest response values for 250 ppm at 200°C are obtained according to the following order; ethanol (14.2%), methanol (13.8%), propanol (9.2%) and ammonia (7.9) (Table 3). This tendency comes from the fact that there are different adsorption/desorption rates as well as different energy levels for these

**Figure 10.** Dynamic gas analyses to NO$_2$ in various concentration at optimum temperature 200 °C (a) WO$_3$–N-GO 3%, (b) WO$_3$–N-GO 6% and (c) WO$_3$–N-GO 9%.

**Table 4.** Collected data from Figure 10.

| Concentration (ppm) | WO$_3$–N-GO 3% | WO$_3$–N-GO 6% | WO$_3$–N-GO 9% |
|---------------------|----------------|----------------|----------------|
|                     | Response time (s) | Recovery time (s) | Response time (s) | Recovery time (s) | Response time (s) | Recovery time (s) |
| 50                  | 180             | 202            | 170             | 190             | 160             | 240             |
| 100                 | 130             | 210            | 122             | 215             | 110             | 230             |
| 150                 | 146             | 210            | 114             | 230             | 106             | 220             |
| 200                 | 121             | 220            | 90              | 205             | 110             | 256             |
| 250                 | 110             | 260            | 103             | 270             | 81              | 260             |
| 300                 | 92              | 273            | 86              | 260             | 77              | 290             |
species. Outcomes from this phenomenon relate to the optimum operating temperature for the sensors as a critical factor for the different gaseous species.

Figure 9 shows the response of the samples at different operating temperatures to NO₂ and CO. The strong dependence of the temperature with the sensing intensity of different alcohol species was also achieved. The maximum response is found for WO₃–N-GO samples to NO₂ (58%) and CO (28%) at 200°C.

The capability of a sensor to differentiate various gases in a mixture defines as selectivity, which is related to the operational temperature. One of the main drawbacks of metal oxide gas sensors is constant conductivity value for various gases. That is why this type of sensor suffers from a lack of selectivity [69]. There are some costly techniques reported for enhancing sensor selectivity [70]. The selectivity is calculated from the equation:

$$\text{Selectivity} = \frac{S_g(1) - S_g(2)}{S_g(1)}$$

where $S(\text{NO}_2) = S_g(1)$ and $S(\text{CO}) = S_g(2)$. The selectivity of the WO₃–N-GO samples is 53%, 46% and 60% for WO₃–N-GO 3%, WO₃–N-GO 6% and WO₃–N-GO 9%, respectively at 200°C (Figure 9).

The gas–response transient curves of the samples as a function of the dynamic behaviour are displayed in Figure 10 and the data are collected in Table 4. Results from this study confirm the strong dependence of the responses to the NO₂ concentration.

The n-type WO₃–N-GO semiconductor sensors adsorb oxygen molecules at the surface. Transferring of the electrons from the conduction band to the adsorbed oxygen, form the ionic oxygen species (i.e. as O⁻, O²⁻ and O²⁻). A depletion layer will form as the electrons consume at the surface. NO₂ molecules inject electrons back to the conduction band as they adsorb onto the WO₃–N-GO surfaces. The resistance of the WO₃–N-GO sensor reduces as the depletion width decreases by releasing of the electrons.

The fabricated sensor exhibited good sensing behaviour to NO₂, while the pure WO₃ and graphene samples are not a suitable sensor for NO₂ [64]. Decoration with N-GO nanocomposites distinctly decreases the response time. The reason for the high sensing of the nanocomposite sensor is the effective charge transfer between graphene and WO₃ nanosheets by chemical bonds, which suggests that the decoration of N-GO nanocomposites enables the high-response gas detection sensor.

The reported results for WO₃-based sensor in literature are collected in Table 5. A significant reduction in the response and recovery time for the samples was prepared in this study is noticeable.

### 4. Conclusion

In summary, decorated WO₃ nanosheets with different percentages of N-GO nanocomposites were synthesised. The XRD, SEM, TEM and Raman spectra were applied to study crystal structure and morphology of the samples. The response of the WO₃–N-GO 9% to NO₂ was two times the response for WO₃–N-GO 6% to CO. The optimum response time of 90 s and recovery time of 205 s were achieved for WO₃–N-GO 6%. The sensors
exhibited suitable sensing and selectivity to NO₂, while the pure WO₃ and graphene sensors have no response to NO₂. The response time decreased after decoration by N-GO nanocomposites due to effective charge transfer between graphene and WO₃ nanosheets. This suggests that the decoration of N-GO nanocomposites enables the sensor to perform high-response gas detection. Therefore, it is possible to fabricate a sensor to detect NO₂ or CO by choosing a suitable percentage of N-GO nanocomposites.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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