Reduced graphene oxide-zinc oxide nano-composites for gas sensing applications

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Abstract

Nowadays, gas sensors are fast becoming an imperative part of modern life with extensive applications in domestic safety, environmental monitoring, industrial process control, public security, medical applications and chemical warfare assessment amongst many others. The detection of minor gas leaks has been a challenging area of research, particularly in view of the hazards to human health and safety posed by toxic gases like NO_2, NO, CO, NH_3 etc and combustible gases like methane, hydrogen gas and some volatile organic compounds. Thus it is imperative to evolve and employ simple yet reliable gas sensing mechanisms with optimum response and selectivity towards even low concentration of analyte gas at room temperature. Most of the conventional gas sensors are based on metal-oxide semiconductors which are low-cost, exhibit good sensitivity and fast response/recovery. Zinc oxide is one such n-type semiconducting oxide, which has been widely studied for gas sensing response due to its ease of fabrication, high sensitivity and environment-friendly nature. However, the operating temperature of such sensors is usually high (>200°C) owing to the wide band-gap (3.37 eV) and high electrical resistance (kΩ-MΩ), which limits their practical utilization. In order to be used in hazard monitoring and home/workplace safety, the gas sensors need to be sensitive to gas exposure in mild operating conditions. As an alternative, more recently, graphene and its derivatives like pristine graphene (PG), reduced graphene oxide (rGO) etc. have been studied for sensing applications owing to their exceptional electronic and physical properties such as high carrier mobility at room temperature, good thermal stability, high mechanical strength, ballistic conductivity and large specific surface area. These sensors show high sensitivity at low operating temperatures (down to room temperature) towards low concentrations of analyte gas. However most of these rGO based sensors exhibit relatively longer response/recovery times than metal-oxide based gas sensors. Hence, nanocomposites formed by hybridizing graphene or its derivatives with metal-oxide nanoparticles are being explored as gas sensing materials. Combining reduced graphene oxide with zinc oxide to form hybrid nanostructures is particularly interesting because not only do they display the individual properties of the metal oxide NPs (faster response/recovery times) and of graphene (high electronic conductivity leading to efficient room temperature gas response), but may also have synergistic effects leading to better sensitivity as a gas sensing material. Here we present a review of the recent progress in rGO-ZnO nanocomposites based gas sensors. Copyright © 2018 VBRI Press.

Keywords: Reduced graphene oxide, zinc oxide, gas sensor, grapheme.

Introduction

Gas sensors are fast becoming an imperative part of modern life with extensive applications in domestic safety, greenhouse gas monitoring for environmental studies, industrial process control such as methane detection in mines, in automotive industry for evaluating the exhaust of cars for pollution control check, public security, medical applications such as electronic noses simulating human olfactory system and chemical warfare assessment. They are being progressively employed in mass-market applications, such as in indoor air quality control as well as the more conventional areas of explosive and toxic gas detection. In view of the hazards to human health and safety posed by toxic gases like NO_2, NO, CO, NH_3 etc and combustible gases like methane, hydrogen gas, and some volatile organic compounds, it is imperative to evolve and employ simple yet reliable gas sensing mechanisms with optimum response and selectivity towards even low concentration of analyte gas at room temperature.

An efficient gas sensing technique is characterized by certain performance parameters such as: (i) High sensitivity (ii) Low detection limit i.e. the minimum volume of target gas concentration at which response is generated should be low (iii) Good selectivity which means that the sensor should be able to detect a particular gas from a given gas mixture (iv) Faster response time (v) Short recovery time (vi) Operating Temperature should be ambient (vii) Reversibility i.e. the sensing material should return to its original state after detection is complete (viii) Good Adsorptive capacity (ix) Low Fabrication cost (x) Stability of Operation.

Common conventional gas sensors use either polymers or metal-oxide semiconductors as active materials while the techniques used for sensing are calorimetric, optoelectronic, gas chromatography, mass spectrometry and acoustic methods. These methods are usually very costly with high power consumption, bulky devices and poor miniaturization due to which they are limited for real-time use. Chemiresistive gas sensing technique has been gaining popularity in sensor research due to its easy device fabrication. Gas sensors based on polymers have been shown to exhibit (i) high sensitivities, (ii) short response times and (iii) low operating temperatures but they also offer some major drawbacks such as (i) irreversibility, (ii) poor selectivity and (iii) long-term instability[1,2,3]. In order to be employed in practical applications, the sensors need to be reversible, i.e. it should be usable over many sensing cycles. Also, for practical use, the sensors need to be thermally stable and their operation should not be significantly affected by ambient conditions.

Metal oxide semiconductors, due to their (i) low cost (ii) large specific surface area (iii) high sensitivity (iv) good chemical stability and (v) simple fabrication techniques, are widely used for gas detection. However, the operating temperature of these sensors are quite high (>200°C) which limits their practical utilization. In order to be used in hazard monitoring and home/workplace safety or as wearable sensing alarms, the sensors need to be sensitive to gas exposure at room temperature in mild operating conditions. The high temperature working conditions require high power consumption which in turn affects the long-term stability of the sensor[4]. High working temperatures may also lead to sample degradation or cause ignition of explosive or inflammable gases, evoking safety hazards.

As an alternative, carbon nanostructure based gas-sensing materials have been gaining significant attention[5]. Various carbon materials such as carbon nanotubes, carbon fibers, graphene, graphene oxide etc. have been shown to have chemical, gas as well as bio-sensing capabilities[6]. More recently, graphene and its derivatives like pristine graphene (PG), reduced graphene oxide (rGO) etc. have been studied for sensing applications owing to their exceptional electronic and physical properties such as (i) high carrier mobility at room temperature, (ii) good thermal stability, (iii) high mechanical strength, (iv) ballistic conductivity, (v) low electrical noise due to honey-comb lattice and (vi) large specific surface area. These sensors have not only exhibited a good response to gas exposure, but have also shown high sensitivity at low operating temperatures (down to room temperature). However most of these rGO based sensors have shown relatively longer response/recovery times and poor selectivity as compared to the metal oxide nanostructures.

Therefore, combining reduced graphene oxide with metal oxides to form hybrid nanostructures is particularly interesting because they display the individual properties of the metal oxide NPs i.e. faster response/recovery times and of graphene i.e. high electronic conductivity leading to efficient room temperature gas response. In addition to this they may also give rise to synergistic effects leading to better sensitivity as a gas sensing material. Here we present a review of the recent advances in the synthesis and performance of rGO/ZnO nanocomposites in gas sensing. An overview of the gas sensing performance of zinc oxide nanostructures as well as those of reduced graphene oxide has also been made in order to understand the advantages and drawbacks of both materials and how their nanohybrids overcome these limitations.

Zinc-oxide based gas sensors

Zinc oxide is an n-type semiconducting oxide with a wide band gap (3.37 eV). It has been widely studied for gas sensing response due to its ease of fabrication, high sensitivity and environment-friendly nature. Hierarchical nanodisks of zinc oxide have been reported by Alenezi et al[7] to not only exhibit a good response towards acetone but fast response/recovery (2s/4s) however the operating temperatures were quite high (175°-450°C) with the optimum temperature being 425°C with 5 ppm detection limit. Ahn et al[8] demonstrated the NO_2 sensing ability of their ZnO nanowire gas sensor with good detection limit (0.5-3 ppm) and high sensitivity with the response being maximum at 225°C. Both response time and recovery time were short, 44s/5s respectively. Calestani et al[9] have developed ZnO tetrapods with high sensitivity to various analyte gases such as ethanol (20 ppm), NO_2 (50 ppm) with the best response of 25% being towards 1 ppm H_2S while the operating temperatures in all cases ranged from 200°C-400°C. The ZnO nanopillar gas sensors by Bei et al[10] showed good sensitivity to even 50 ppm ethanol at 200°C with the response and recovery times being less than 10 s and 20s respectively. Similar reported works by Zhang *et al*[11], Wei *et al*[12], Ahmad *et al*[13] and Hsueh *et al*[14] the fabricated ZnO sensors have been used to sense various VOCs with high sensitivity and selectivity at high operating temperatures. A similar performance of ZnO based gas sensors has been reported in the reviews by Fine *et al.*[15] and Liu *et al.*[16]. The High operating temperature of zinc oxide based gas sensors limit their practical utilization due to their high electrical resistance (kΩ-MΩ) at room temperature.

Reduced graphene oxide based gas sensing materials

Graphene, as a single planar sheet of sp^2-bonded carbon atoms, tightly packed in a two-dimensional honeycomb crystal lattice, was described theoretically by P.R. Wallace[17]. In 2004 a stable 2D sheet of carbon atoms was isolated by using the technique of micromechanical cleavage by Novoselov *et al.*[18]. Novoselov *et al.* reported the first graphene based gas sensor in 2007[19]. Their device was a micrometer-size sensor which was capable of detecting individual gas molecules adsorbed on the sensing surface. Subsequently, several research groups have reported gas sensors based on intrinsic graphene obtained by micromechanical cleavage, chemical vapour deposition and epitaxial growth as reviewed by Basu *et al.*[20].

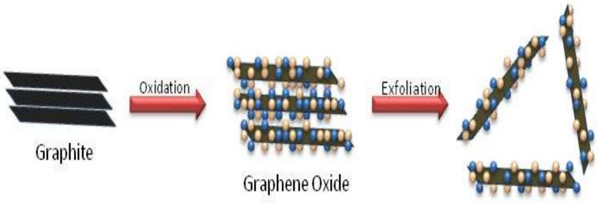

Fig. 1. Schematic of graphite to graphene oxide conversion.

Although intrinsic graphene boasts of high quality and good control, there are certain limitations too, in view of practical gas sensing applications. Intrinsic graphene is (i) not suitable for mass production (ii) production is costly (iii) it has no functional groups to provide active sites for gas/vapour adsorption and (iv) is relatively inert to atmosphere due to lack of functional groups. The functionalization of graphene is tedious which reduces the possibility of performance enhancement. Therefore reduced graphene oxide, which is a form of graphene obtained by reduction of graphene oxide (GO), is a promising material as it is easy and cheap to produce at large scale. This is one of the most promising and cost-effective mass production routes of graphene[21]. As per the Lerf-Klinowski model[22], GO contains two kinds of regions: aromatic regions with flat unoxidized benzene rings and wrinkled regions with alicyclic six-membered rings bearing C-C, ether and hydroxyl groups with the GO sheets terminating with carboxyl and hydroxyl groups. So GO can be considered as an insulating and disordered analogue of the highly conducting crystalline graphene.

Due to the presence of many functional groups and defects, RGO can be readily functionalized, the band gap can be tuned and it is hydrophilic due to which it can be easily dispersed in order to form composites. RGO has been widely explored for gas sensing as reviewed by Toda *et al*[23]. Kumar *et al*[24] reported a response of 9.8% to 25 ppm NH_3 at room temperature with response/recovery times as 163s/200s. A chemical sensor was prepared by Papazoglau *et al*[25] by laser printing GO onto gold electrodes using LIFT technique to sense water vapours, ethanol and xylene vapours at room temperature. They recorded a response of 0.22% towards 5000 ppm water vapour with response/recovery time being 3min/50min, while 0.5% response towards 700 ppm p-xylene and 0.3% towards 10,000 ppm ethanol. An NO_2 gas sensor reported by Lu *et al*[26] exhibited good response to different NO_2 concentrations at room temperature with a response time of about 10 minutes and recovery time of nearly 25 minutes. Wang *et al*[27] demonstrated the gas sensing ability of reduced graphene oxide sheets formed using two different routes of reducing GO, by hydrazine vapours and by pyrole vapours. The sensors exhibited a good response towards 50 ppm NH_3 gas with the effective response time as 12 min.

rGO/Zinc oxide nanocomposites as gas sensing material

The hybridization of metal oxide NPs with rGO leads to more number of active sites such as vacancies, defects, oxygen functional groups as well as sp^2-bonded carbon and thus increases the overall active sensing surface area, subsequently enhancing the gas molecule adsorption during the sensing process. Furthermore, Lu et al.[28] have explained that the hybridization of p-type graphene sheets with an n-type metal oxide (ZnO) can lead to the formation of heterojunctions which modify the potential barrier at the ZnO/rGO interface. **Fig. 2** shows the schematic sensing mechanism.

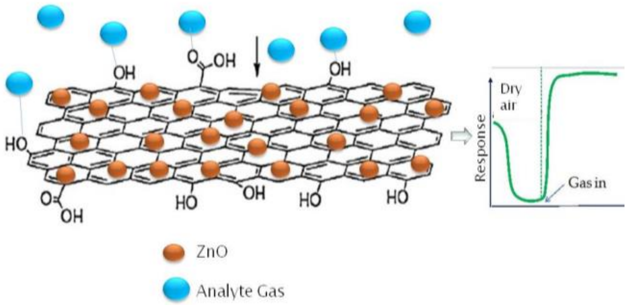

Fig. 2. Sensing Mechanism of rGO/ZnO Nanocomposites.

Synthesis of rGO/ZnO nanocomposites

GO is prepared by the oxidation of graphite and the exfoliation of the generated graphite oxide via Hummer's method[29] or by its improved alternative route suggested by Marcano *et al*[30]. The exfoliation is facilitated by the oxygenous functional groups as they expand the gap between the graphite layers. In this method, Graphite flakes (1 wt equivalent) are the precursors which are strongly oxidized by adding potassium permanganate (6 wt equivalent) in the presence of a 9:1 mixture of conc. H_2SO_4/H_3PO_4. The solution is stirred at 50°C for 12h. It is then cooled at RT and poured on ice with H_2O_2 (30%). The supernatant is removed from the oxidized graphite flakes by successive steps of centrifugation, decantation and washing the solution with 200 ml water, 200 ml 30% HCl, 200 ml ethanol and 200 ml ether alternately. The solid obtained after washing is vacuum-dried overnight at room temperature to obtain graphene oxide.

GO reduction can be effected by various external stimuli such as heating (annealing) or chemical treatment(using hydrazine hydrate) [21, 31]. It yields reduced GO (rGO) that resembles pristine graphene structure and is electrically conductive (due to restoration of graphene sp2 network). Depending on reduction extent, a partly restored sp2 lattice may be generated while also retaining some oxygen bearing groups. So rGO can find applications as a mass-producible graphene alternative[32].

The metal oxide nanoparticles can be prepared using some metal-organic precursor such as zinc acetate in suitable acidic or basic conditions to yield NPs of controlled size. The NPs can also be prepared using metallic powders as the precursors, for e.g., metallic zinc powder in an alkaline medium (KOH or NaOH), wherein the intermediate metal hydroxide loses its water to form the resulting zinc oxide[33, 34, 35].

In order to synthesize the composite materials, there are two approaches - *in situ* or *ex situ*. In the *ex situ* approach, the graphene oxide aqueous dispersions and the metal oxide nanoparticles are synthesized separately. The substrates coated with reduced graphene oxide sheets are immersed in the zinc oxide dispersion to form the oxide-rGO composite. The *in situ* approach involves the hydrothermal technique wherein the zinc oxide precursors are added to a dispersion of graphene oxide followed by the reduction within the mixture to form the resulting nanocomposite.

General mechanism of chemiresistive gas sensing

When a sensing material is exposed to air, adsorption of oxygen ions occurs at the sites of defects or functional groups on the sensing surface. They form chemisorbed oxygen species as per equations (1) and (2), by capturing free electrons from the matrix leading to reduced surface activity[36].

$$\tfrac{1}{2} O_2 + e^- \underset{ads}{\Leftrightarrow} O^- \qquad (1)$$

$$\tfrac{1}{2} O_2 + 2e^- \underset{ads}{\Leftrightarrow} O^{2-} \qquad (2)$$

when exposed to the sensing gases, the oxygen ions interact with the analyte gas and release the trapped electrons. The target gas then interacts with the surface of the rGO/metal oxide film (generally through the surface adsorbed oxygen ions), which causes a change in the charge carrier concentration of the material. This in turn serves to alter the conductivity (or resistivity) of the material[37].

In an n-type semiconductor electrons are the majority carriers, so upon interaction with a reducing gas (electron donor) like NH_3, CO, ethanol, acetone etc., an increase in conductivity occurs. On the other hand, an oxidizing gas (electron acceptor) like NO_2, H_2O, iodine etc., causes depletion of electrons in the sensing layer, which results in a decrease in conductivity.

In p-type semiconductor, positive holes are the majority charge carriers so the effects observed are opposite to that of n-type. The conductivity increases in the presence of an oxidizing gas. A conductivity decrease is observed in case of a reducing gas, due to the depletion of hole concentration by the negative charge introduced in to the material.

The high operating temperature of metal oxide gas sensors is mainly due to the reaction temperature of O–[4]. It is required to heat the sensing layer to a high temperature so as to effect an increase in the probability of adsorption of gas molecules on the sensing surface, consuming the ions of the sensing material[16]. The conductivity of the film increases as the ions are consumed, thus realizing the sensing function.

Reduced graphene oxide-zinc oxide gas sensors

Recent years have witnessed a fast-growing research interest towards fabrication of cost-effective gas sensors with high sensitivity and selectivity using zinc-oxide loaded graphene or rGO nanocomposites.

Singh *et al.*[38] reported the detection of common industrial toxins like CO, NH_3 and NO for concentrations as low as 1ppm at room temperature. They used zinc acetate as the precursor for metal oxide and $Li(OH)_2$ as the precipitating agent. The composites were synthesized hydrothermally using a suspension of the synthesized GO in ethanol. They also investigated the effect of ZnO/GO molar ratio on gas sensing response. The sensing response was studied using the films deposited on ITO glass substrate in dc four-probe measurements. The bare ZnO sensor was not sensitive to either of the gases at room temperature while showed a fast response to 1ppm NO_2 at 350°C. On the other hand, the ZnO-rGO films showed a good response and selectivity to electron donor gases like CO (24.3%, 22ppm) and NH_3 (24%, 1ppm) at room temperature. According to them, the enhanced response is attributed to the formation of heterojunctions. The adsorbed gas molecules affect two different depletion layers- one at the surface of ZnO and the other at the ZnO/rGO interface thus leading to better response magnitude.

Liu *et al.*[39] demonstrated the higher sensitivity, shorter response and recovery time of ZnO-rGO based gas sensors than those of the gas sensors based on rGO for NO_2 detection. The sensors were fabricated by coating the DMF dispersion of ZnO-rGO hybrids onto the substrates, over which two pairs of micro-electrodes were printed on each side. The fabricated ZnO-rGO sensors exhibited a response of 25.6% to 5ppm of NO_2 at room temperature with fast response and recovery times, 165s and 499s respectively. The rGO sensor was not sensitive to 5ppm concentration of NO_2. On exposure to 25ppm NO_2 at room temperature, the rGO sensor exhibited a response of 12% with slower response and recovery, 14.4min and 18min respectively. They also studied the variation of response with operating temperature and the long-term stability of the samples was examined as well.

A ZnO nanowire/rGO based novel portable gas sensing electronic device was reported by Sun *et al.*[40] for ammonia gas sensing at room temperature. While the pure rGO sensor gave a response of 0.8% to 50 ppm gas with slow response/recovery (600s), the ZnO/rGO sensor showed an optimum of 7.2% to 1ppm gas with faster response/recovery (50s/200s) at room temperature. A detection limit of 500ppb could be achieved at RT with good response (3%). They also studied the effect of target gas concentration on sensing response and reported that as the concentration is increased from 500 ppb to 500 ppm, the response first increases and then saturates.

Li *et al.*[41] developed hierarchical flower-like ZnO structures by one step hydrothermal synthesis. While both pure rGO and rGO/ZnO films show response to HCHO at room temperature, the response towards 2-10 ppm HCHO is enhanced in case of rGO/ZnO hybrid films in comparison with pure rGO.

Table 1. Gives a comparison of the key parameters obtained by various research groups.

Table 1. Key Parameters of ZnO, rGO and rGO/ZnO nanocomposites.

Material	Analyte Gas	Operating Temp	Conc. (ppm)	Response	Response/ Recovery time	Reference
ZnO nanodisks	Acetone	425°C	100	25%	2/4 sec	[7]
ZnO nanowires	NO_2	225°C	5	~50%	44/5 sec	[8]
ZnO nanopillar		200°C	50	-	10/20 sec	[10]
rGO	NH_3	RT	25	9.8%	163/200 sec	[24]
rGO	NO_2	RT			10/25 min	[26]
ZnO/rGO	NO_2	RT	5	25.6%	165/499 sec	[39]
ZnO/RGO	CO	RT	22 in dry N_2	24.3%	5/2–5 sec	[38]
	NH_3	RT	1 in dry N_2	24%		
	NO	RT	5 in dry N_2	3.5%	25/–	
ZnO/RGO	NH_3	RT	1	7.2%	50/200 sec	[40]

Scope of further research

Most of the published works on metal oxide/graphene based sensors have focused on detection of polar gases such as NO, NO_2, H_2S, NH_3 etc. at room temperature with high sensitivity and shorter response/recovery times. There are fewer reports on exploring the ability of these nanohybrids sensors to sense nonpolar gases (like hydrogen, methane, pentane, propane, butane etc.) and volatile organic compounds (such as acetone, methanol, ethanol, propanol, aldehyde etc.) which appear in environment from various sources and contaminate the atmosphere. Most of these gases are highly inflammable and thus pose a potential risk of disastrous leaks and accidents. RGO/metal oxide based gas sensors for combustible gas detection is an area much needed to be explored widely. For widespread application of these sensors, they must be able to detect polar as well as non-polar gaseous molecules.

Also, for real life applications one needs to note that the performance of the gas sensors can be influenced strongly by the relative humidity of the surroundings. The ability of gas detection can get screened depending upon the level of humidity, which may reach up to thousands of ppm in the real world environment. Mostly the reports on metal-oxide/graphene nanohybrids sensors are based on measurements in dry air (or inert gas) and vacuum. The success of these sensors largely depends upon their sensitivity to humidity. There have been reports of graphene and graphene-metal oxide based humidity sensors, which implies that these nanostructures do exhibit sensitivity to humidity (water vapor) even at room temperature[42,43,44,45]. Thus there is a need to explore the influence of humidity on the sensing response of such sensors to various gases and work needs to be done to quantify and control it. One of the very few references dedicated to investigate the influence of humidity on a graphene based sensor is the one by Kim *et al.*[46] who used CVD grown single layer graphene to detect gases such as NO_2 and NH_3 under the influence of humidity and ambient temperature. They found that NH_3 reacted with humidity to form NH_4OH which acts as a donor on graphene and decreases the current. This clearly indicates the importance of humidity in the context of graphene based sensors, and thus needs to be investigated as a parameter affecting sensor response.

Conclusion

Reduced graphene oxide/zinc oxide nanocomposites are a promising material for the development of efficient gas sensors owing to their high sensitivity, selectivity, fast response/recovery, resistance to wear and tear, thermal stability and ease of miniaturization. These hybrid materials have been shown to exhibit better gas sensing response than pure ZnO or rGO films as well as they overcome the drawbacks of both the materials to a considerable extent, which is attributed to the increased surface area per unit volume as well as the formation of heterojunctions. Some of the latest studies on rGO-metal oxide nanohybrids have also demonstrated appreciable response at room temperature thus opening the possibilities of their practical utilization. Although in order to take these materials to manufacturing level, further research needs to be done on certain pragmatic aspects such as mass production of high quality sensitive films, sensor performance in adverse weather conditions, screening of sensor response by humidity, eco-compatibility etc.

To conclude, graphene based nanocomposites have immense potential in the coming decade. These nanohybrids are the next generation materials that shall manifest not only excellent chemical sensitivity with fast response and recovery, but also develop a unique configuration with versatile applications in a combined sensor platform. Lastly it is expected that more sophisticated sensing mechanisms will explain the operations of these superior chemical sensor devices.

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