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Nano Layers of 2D Graphene Versus Graphene Oxides for Sensing Hydrogen Gas

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Abstract

Hydrogen is one of the most useful but dangerous gases because of its broad combustion range and small ignition temperature. Currently, there is a great need for hydrogen detectors with selectivity, high sensitivity and reliable operations in view of its safe production, storage, transportation and other applications. In this regard, nano thin films of two dimensional materials like graphene, graphene oxide (GO) and reduced graphene oxide (rGO) have immense promise because their material attributes can be exceptionally tuned to achieve the desired characteristics. Also graphene oxide and reduced graphene oxide serve as potential sensing hosts due to the presence of functional groups on their surfaces. In this chapter, an attempt has been made to compare the work done in the field of hydrogen sensors using pure graphene and graphene derivatives such as graphene oxide and reduced graphene oxide. The response parameters like sensitivity, stability, selectivity, response time, recovery time, detection limit, linearity, dynamic range, and working temperatures for various graphene based sensors have been elaborately compared. Finally, a conclusion and future outlook on nano scale thin film of graphene and graphene oxides for gas sensing have been briefly discussed.

Keywords: nano thin film, graphene, graphene oxide, reduced graphene oxide, hydrogen sensor, sensing mechanism

1. Introduction

Dimensionality plays a vital role in determining the structure of a nanomaterial. Nanomaterials fall in the range of nanoscale defined by at least one dimension (D), and categorized using the concept of quantum confinement. Quantum confinement may be defined as a state in which a nanocrystal is comparatively smaller as compared to Bohr exciton radius of that particular material for at least one dimension. When it is quantum confined in one direction, it is termed as a film (i.e., a 2D material). For two dimensional quantum confinement, rod (i.e., a 1D material) is the name given to it, and quantum dot (i.e., a 0D material) has all the three dimensions confined. All these have specific shapes for the density of states which arises due to difference in the degree of confinement of electrons. Bulk materials fall under the category of 3D materials in which none of the domains are confined. Graphene is a 1D confined material and is obtained from its bulk counterpart

graphite. The advantage of 2D materials is that they possess “all surface” properties that can be conveniently tuned by chemical functionalization and other surface treatments. It even beholds its magnificent properties when synthesized in the form of nano flakes. This is the reason why the field of 2D materials is growing at such a rapid pace [1–3].

The mechanical exfoliation method to obtain graphene from graphite using scotch tape is not scalable to industrial practice owing to its limited yield. Although the quality yield is lofty, yet the mass scale production is an issue. Since it is much easier to obtain graphene oxide using wet chemical method as compared to graphene, so a careful study of both graphene, graphene oxide and reduced graphene oxide would help in gaining more insights about this family as well as the hydrogen sensing attributes on a comparative scale.

2. About graphene and graphene oxide

Graphene is structured as 2D sheet of six carbon (sp^2 hybridized) ring and confined in a hexagonal lattice. Substituting some of the hexagons with pentagons, imparts a spherical curvature culminating into 0D structure known as fullerene. Rolling up graphene sheets form carbon nanotubes (1D), and racked up graphene sheets into layers results into 3D graphite [4, 5].

Graphene lattice holds two sub lattices involving atomic sites A and B which are arranged in a planar trigonal fashion. Putting together the A and B sites along parallel layers (similar to a multilayer graphene) can generate the unit cell. The normal separation between two carbon atoms is 1.42 Å. However, for a hexagonal carbon lattice, the parameters are $a = 2.46$ and $c = 6.7$ Å. Graphene forms two types of bonds viz. sigma (σ) bond (three in number) and pi (π) bond (one in number). The σ bond is a consequence of interaction of its hybridized s, p(x) and p(y) orbitals with the neighboring carbon atoms; likewise π bond being formed through its interaction with the p(z) orbital [5].

Owing to arduous extraction and production of graphene, several graphene derivatives took the limelight namely graphene oxide (GO) and reduced graphene oxide (rGO). Where graphene involves only oxygen and hydrogen bonds, and functional groups attached to them like CO, COOH, OH groups, it is known as graphene oxide. This possesses a partial aromatic nature as compared to graphene which is completely aromatic in nature. Due to addition of these functional groups, a band gap could be achieved. The reduced form of graphene oxide bears much resemblance with graphene rather than graphene oxide in respect that all the functional groups have been removed with some oxygen traces [6].

3. Device configurations used for graphene based sensors

There are various configurations present by which graphene based gas sensors can be fabricated. Some of these configurations are chemiresistor, field effect transistor (FET), capacitance sensor, surface acoustic wave (SAW), surface work function change transistor, optical fiber sensor, etc. (**Figure 1**).

In some transistor configuration, the surface work function of the sensing material can be tuned, while in optical fiber sensors the optical properties such as transmission/absorption are affected due to solid-gas interaction.

There are few technically uncommon sensor devices. For instance, Schedin and group fabricated a graphene device for selective gas sensing. Electrical contacts were made by using electron beam lithography on the mechanically exfoliated

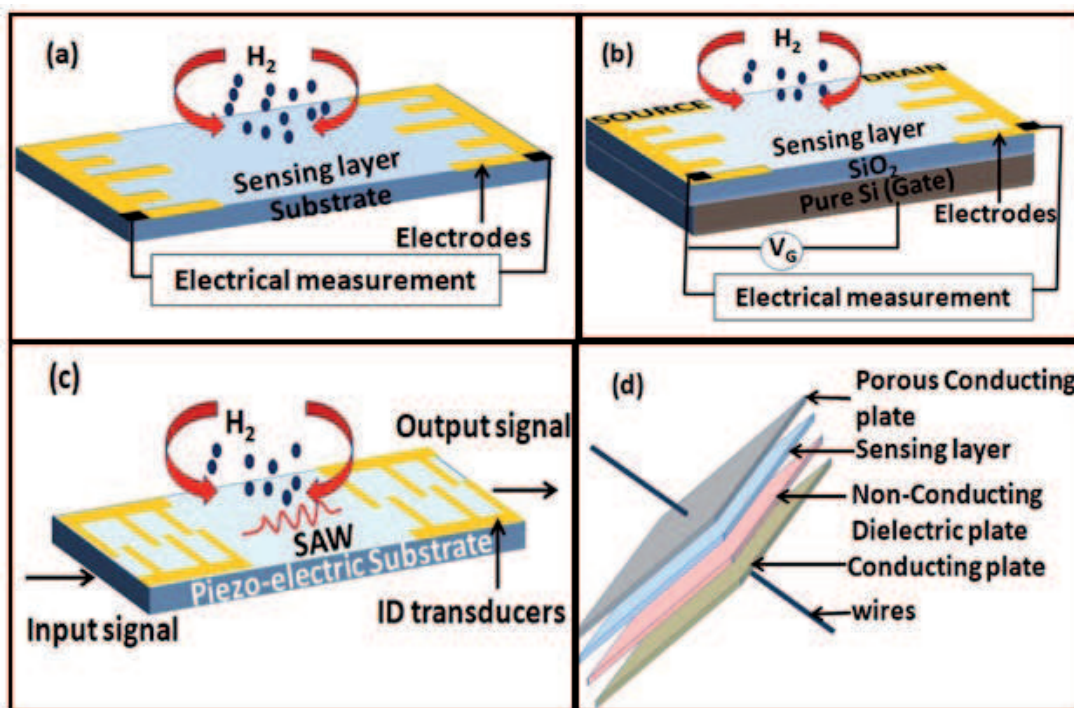


Figure 1.
 Schematic representation of gas sensors: (a) chemiresistor (b) field effect transistor, (c) surface acoustic wave and (d) capacitance sensor.

graphene sheets on the Si substrates. The as prepared sensing device was placed in a superconducting magnet and characterized using field effect measurements within a temperature range in order to calculate the value of mobility of charge carriers and no. of graphene layers [7]. Dutta and group fabricated a heterojunction by putting a TiO₂ layer on graphene synthesized by chemical vapor deposition method [8]. Prezoiso and group dispersed GO in water and deposited on the interdigitated Pt electrodes patterned on Si₃N₄ substrate by drop casting technique and dried at 50°C. Wang and group chemically synthesized GO and fabricated a hydrogen sensor by dielectrophoresis technique [9]. In 2014, Niu and group proposed a very simple method for the fabrication of phosphorus modified graphene based gas sensor. Doping was done by annealing graphene oxide with triphenylphosphine within a temperature range from 400 to 800°C under inert atmosphere. The sensing device was fabricated by spreading the phosphorus doped graphene powder on the ceramic substrate with Pd electrodes [10].

4. Tuning of the sensing layer

Pristine graphene have a poor response towards gas sensing, whereas graphene oxide and reduced graphene oxide shows good response towards gas sensing. A small gas molecule adsorbed on the GO or rGO surface brings change in the conductivity. When compared, rGO shows better sensing response than GO. Peng and Li [11] demonstrated adsorption of NH₃ on graphene and graphene oxide surfaces and reported that although the calculated adsorption energy of graphene is lower than GO, the presence of surface hydroxyl and epoxy groups in GO promotes the NH₃ adsorption on the electron deficient sites (or hole site). This leads to easy electron transfer from nitrogen to the hole site in GO matrix. Similarly a comparative study showed graphene with functional groups as better sensing host as compared to pristine graphene (Gr) (**Table 1**). This can be attributed to the fact that graphene

Sensing layer	Gr	RGO	RGO-Gr
Device resistance	Low	High	Low
Response (%)	0.48%	3.32%	4.7%
SNR	Moderate	Low	High

Table 1.
Comparison of various types graphene based material performance.

Sensing layer	t (°C)	C (k)	Response	τ_{res} (s)
Pd/Gr	RT	1	$\Delta G/G_{air} = 26\%$	40
Pt/Gr	30	10	$\Delta R/R_{air} = 1.6\%$	1
Pd/Ag/Gr	105	0.5	$\Delta R/R_{air} = 9.96\%$	102
MoO ₃ /Gr	RT	1	$R_{air}/R_{gas} = 20.5$	10
CuO/rGO/CuO	RT	0.1	$\Delta R/R_{air} = 4.2\%$	<80
Pd/WO ₃ /Gr	RT	1	$\Delta I = 12 \mu A$	17

t = temperature; C = concentration ($\mu L/L$); τ_{res}/τ_{rec} = response time/recovery time; RT = room temperature; k = 1000; Ref = references; G = conductance; R = resistance; I = current.

Table 2.
Graphene/nano-particle based gas sensors.

is perfect lattice with no functional groups hence no adsorption site for the gas molecules, while graphene oxide or reduced graphene oxide offer larger number of sites for the gases to adsorb on the surface. This efficiency was also confirmed from the high signal to noise ratio (SNR) [12].

Similar graphene based material tuning was done with metal or oxide nanoparticles to obtain interesting response with hydrogen (**Table 2**) [11, 13–18].

Gadipelli and Guo have clearly analyzed the graphene system for the uptake of carbon dioxide and hydrogen. They stated that more hydrogen can be adsorbed on modified porous structured graphene in comparison with normal chemically exfoliated graphene. Also, porous or doped graphene has been stated as a better host to adsorb carbon dioxide [15]. Hence porosity tuning is an important synthesis concern.

5. Electrical characteristics of graphene based materials in air

Due to the presence of oxygen functional group graphene oxide is insulating in nature which becomes electrically conducting on removal of oxygen by controlled reduction process. This results in the formation of reduced graphene oxide which on reduction still contains some of the oxygen groups. The remaining oxygen functional group is responsible for limiting the electron transport in rGO. The electrical characteristics can be analyzed by comparing parameters such as conductivity, barrier, etc., with respect to material doping, junction formation, material porosity, composite formation (with different concentrations), etc. The conductivity range for rGO is from 0.05 to 500 S/cm. This range depends on the reduction degree as this degree is related to the ratio of graphitic regions to that of oxidized regions. In one of the works, Jung et al. reported thermal and chemical combined reduction gave conductivity five times greater as compared to the samples that was reduced via thermal and chemical processes alone [16].

Gao et al. [19] synthesized sulfur doped graphene to study the electrical behavior of doped/undoped pristine graphene. The sheet resistance value S-doped graphene is $6.28 \times 10^3 \Omega/\square$, which is greater than that of pristine graphene. Hence doped system has lower conductivity. The presence of scattering centers (defects) in the doped sample is responsible for the lower conductivity (**Figure 2a**).

Jimenez and Dartora [17] gave a theoretical model which was successful in explaining the I-V characteristics of graphene based p-n tunnel junction. The study considered the effect of potential barrier of the junction and material doping (n- or p-type). It was concluded that the sign of potential barrier made no difference on the I-V characteristic and the conductivity increased with the increase in potential barrier (**Figure 2b**). This interesting fact is typical of graphene material which depicts unusual electronic properties in doped and undoped states. However, it needs further critical analysis.

Awasthi et al. [18] reported the I-V characteristics of multilayer graphene with polyaniline (mixed composite) at low temperature and room temperature with varying concentration. When the concentration of graphene nanosheets (GNS) was 3 wt%, the resistance came out to be 1.034 G Ω which decreased up to 4.106 M Ω on increasing the concentration to 6 wt% (**Figure 2c**). This increase in conductivity is attributed to the change in concentration of graphene only as all the other parameters were kept constant.

Haditale et al. [20] compared the I-V characteristics of graphene (G)/porous silicon (PS) hybrid structures with that of graphene/silicon (Si) by varying the graphene solution volume. The junctions were fabricated by taking 1 and 2 ml of graphene solutions, which were deposited on the substrates (Si or PS) by thermal spray pyrolysis. The G/Si junctions showed rectifying behavior and 1 ml devices showed higher values of current in comparison to 2 ml devices. Low volume (1 ml) resulted into low layered ordered structure of graphene which came out to be more conductive in nature. On increasing the volume to 2 ml, the structure became less ordered with lower conductivity value. On analyzing G/PS junctions following conclusions were drawn: (1) Reverse biased devices exhibited higher current values as compared to that of forward biased devices. (2) In reverse bias condition, G/Si have

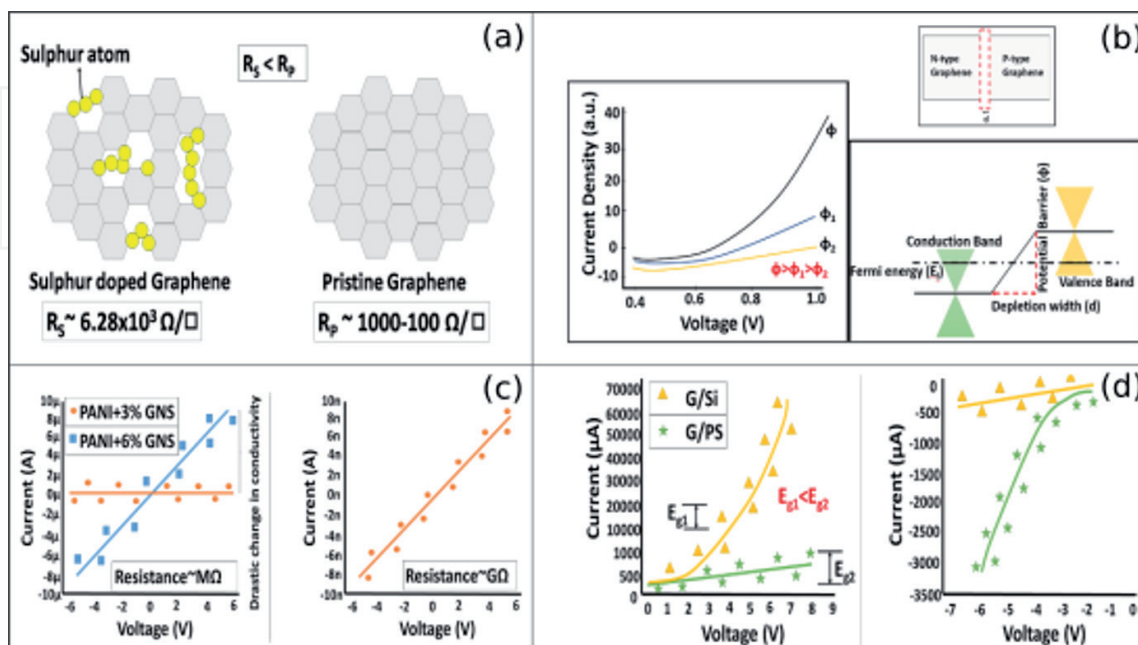


Figure 2. Electrical characteristics of graphene based material in air to highlight the (a) effect of doping, (b) effect of barrier, (c) I-V change due to incorporation of other components like polyaniline (PANI), and (d) I-V change due to porosity.

zero current values (for low bias) whereas G/PS devices have non zero and high current values (for low bias). (3) As the graphene volume increases, the current value increases in G/PS devices. (4) The forward current is high in G/Si and low in G/PS.

These differences are due to the porosity. PS surface have large surface which can easily accommodate tiny graphene flakes in large quantities. Hence, higher current is obtained with increase in graphene concentration. However the defects in PS is responsible for the enhancement of reverse leakage characteristics. Moreover, there are two effective junctions (G/PS and PS/Si) in G/PS devices, and only one in G/Si. The unique existence of multiple junctions is due to quantum confinement effect that increases the bandgap of PS which is responsible for creating the effective potential barrier of G/PS devices. So, probably the forward barrier is high in G/PS and low in G/Si. Hence the forward I-V characteristic of G/Si is superior in comparison to G/PS (**Figure 2d**).

6. Electrical characteristics of graphene based materials in hydrogen

Any solid-gas (oxidizing or reducing) interaction is known to change the conductance of the solid. When the sensor is exposed to some oxidizing gas, a reaction will be triggered which is given as Eq. (1):



where O_2 is the charge accepting molecule and takes up the electron from sensor surface. This will reduce the conductance due to reduction in electron concentration. Or else when exposed to reducing gas like hydrogen, the reaction given below will be triggered as shown in Eq. (2).



Here hydrogen will interact with oxygen ions adsorbed on the surface and result in increase in charge concentration. This will increase the device current [21]. The general experimental trend is to observe the device current/resistance variation at fixed bias. The I-V data in presence/absence of hydrogen can also be considered to evaluate various forward and reverse bias characteristics, and the voltage shift upon changing the ambient from air to hydrogen.

Temperature plays a crucial role in solid gas interaction and hence the electrical output can be tuned. In one report the concentration of hydrogen was fixed up to 10 ppm, and change in device current (from its value in air) was found to vary (initial increase and then decrease) with the increase in temperature [22]. The initial increase in the enhancement of adsorption while the later decrease is due to slow dominance of desorption over adsorption. The role of temperature was also reported by Dutta et al. in which the current of Pd/graphene junctions increased in hydrogen up to 100°C, beyond which the junction current decreased [23].

Composite morphology modulated the electrical output in hydrogen. As reported for graphene, the change in device current (from its value in air) was appreciably large for graphene/Pd nano-composite and negligibly small for the pure graphene matrix [24].

Similarly via other research effort it is well established that the electrical characteristics in presence of hydrogen not only depends on the gas concentration, but on parameters such humidity [25], catalytic modification [26], etc.

7. Parametric response analysis

Some of basic parameters that are considered for gas sensors are sensitivity (or response percent), selectivity, detection limit, dynamic range, linearity, response time, recovery time and working temperature. **Figure 3** presents pictorially some of the important parameters. All these parameters are very important to describe the properties of a sensing device or material. Sensitivity of a device is the ratio (per unit analyte concentration) of measured signal magnitude at a particular concentration limit of analyte and in absence of analyte. The response percent is the ratio of change in signal magnitude due to a particular concentration limit of analyte and the initial signal magnitude without analyte, which is expressed as a percentage Eq. (3):

$$\text{Response percent} = \frac{|I_g - I_a|}{I_a} \times 100 \quad (3)$$

Selectivity is the ability of a gas sensing device to act in response to a particular group of analytes or specifically to a single analyte. The lowest concentration of gas that can be detected by a sensing device at a specific temperature is known as detection limit. Detection range is the concentration range (minimum to maximum) that the sensor can detect. Linearity is nothing but a deviation from an ideal straight line to experimentally obtained calibration graph. Response time is the time needed by sensor to reach 90% of the final saturation value while responding to a concentration change, i.e., from zero to a certain value of concentration. Recovery time is the time the sensor signal takes to return to its 90% its initial baseline value. Working temperature is the temperature at which maximum sensitivity (or percent response) or minimum response time is achieved. High values of sensitivity, selectivity, and detection range while low values of detection limit, response time and recovery time are some characteristics of an ideal sensing

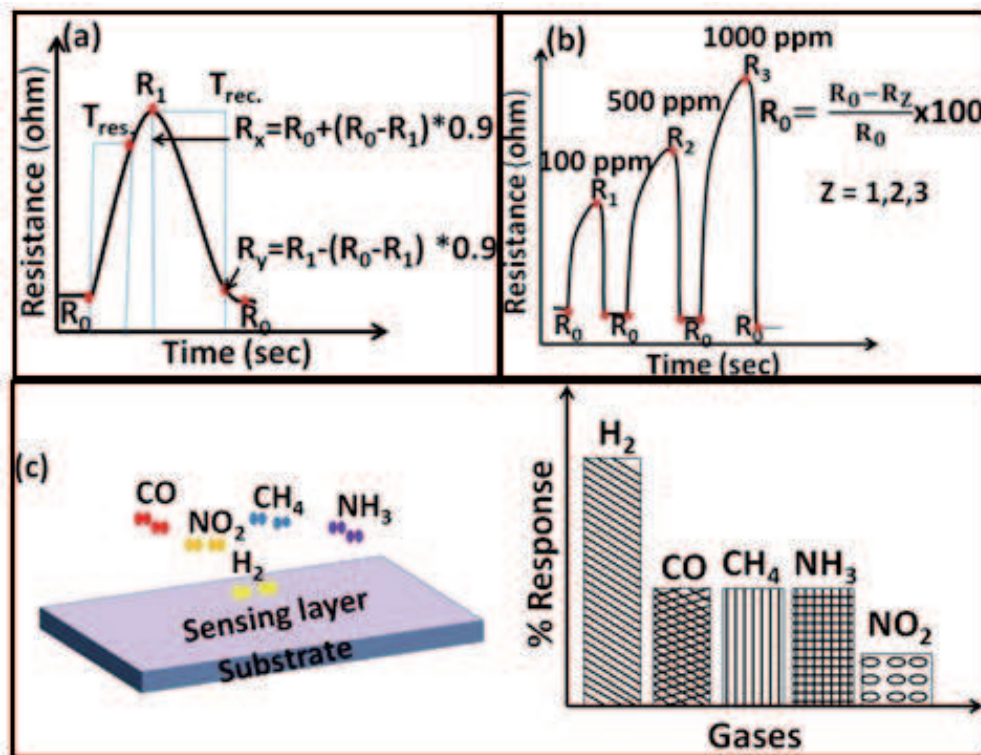


Figure 3. Schematic representation of (a) response time, and recovery time (b), sensitivity (c) selectivity of gas sensors.

device [27]. These parameters have been improved by various ways. For instance surface decoration improved the sensing parameters in an H₂ gas sensor based on reduced graphene oxide sheets decorated with nano-structured platinum [28]. The surface decorated graphene sensors showed higher sensitivity (of 16% at room temperature) than surface decorated carbon nanotubes. An extraordinary response to extremely low concentration of hydrogen was obtained with sensor based on rGO loaded ZnO nano-fibers [29]. They concluded that the properties

SL	OM	t	D	S	t _{res}	t _{rec}	Ref
Gr	—	50	—	69%	19 s	612 s	[34]
rGO	CuO	RT	10–1500 ppm	—	80 s	60 s	[35]
rGO	Pt	50	0.5%	8%	63 s	104 s	[36]
GO	—	RT	150 ppm	81%	—	—	[37]
Gr	Pd	RT	—	—	140 s	250 s	[38]
GO	Pd	RT	1%	~0.5%	—	—	[39]
rGO	PANI	RT	0.06–1%	16.57%	—	—	[40]
rGO	Pt-SnO ₂	50	0.5–3%	—	2–6 s	2–6 s	[41]
GA	Pt	—	10,000 ppm	1.6%	0.97 s	0.72 s	[42]
Gr	Pd	—	1000 ppm	32.5%	—	—	[43]
rGO	Ni-Pd	—	0.1%	11%	3 s	12 s	[44]
Gr	Pd	—	0.1%	7%	4 s	20 s	[45]
Gr	Pd	—	0.1%	33%	15 s	25 s	[46]
Gr	Pd	—	1%	50%	1 s	2 s	[39]
Gr	Pt-Pd	—	2%	4%	2 s	60 s	[47]
Gr	Pd-Ag	245	1 ppm	—	16 s	14 s	[48]
rGO	Pd -Pt	RT	6 ppm	—	3 min	1.2 min	[49]
rGO	Pd	RT	1%	—	1 s	9 s	[50]
GO	—	RT	200 ppm	6%	11 s	36 s	[51]
rGO	NiO	80	1%	1.58%	15 s	61 s	[52]
rGO	Pd	RT	100 ppm	1.6%	—	—	[53]
rGO	Pt	RT	4000 ppm	17%	—	—	[28]
rGO	Pt	RT	200 ppm	40%	—	—	[54]
rGO	Pd	RT	1000 ppm	13%	—	—	[55]
rGO	Pd	RT	1000 ppm	5%	—	—	[56]
rGO	SnO ₂	RT	10,000 ppm	1.8%	—	—	[41]
rGO	ZnO	150	200 ppm	3.5%	—	—	[57]
rGO	NiO	100	2000 ppm	24%	—	—	[58]
Gr	TiO ₂	125	5000 ppm	8%	—	—	[59]
rGO	MoS ₂	60	200 ppm	15.6%	—	—	[60]

SL = sensing layer; OM = other material (used); t = sensing temperature (°C); D = detection range; S = sensitivity; t_{res} = response time; t_{rec} = recovery time; RT = room temperature; G = graphene; GA = graphene aerogel; Ref = reference.

Table 3.
Detailed data of various graphene based hydrogen sensors.

of p type rGO sheets and semiconductor to metal transition in ZnO jointly are responsible for excellent sensing performance towards such a low concentration (100 ppb) of hydrogen. The selectivity of graphene based sensors was analyzed theoretically by Maity et al. by considering surface functional groups such as carboxyl, carbonyl, hydroxyl, epoxy and hydroxyl [30]. They reported that with GO nanoflakes, COOH group helps in selective NH₃ detection, while carbonyl group favors selective NO₂ detection. Other ways to improve the selectivity of graphene based sensors is to use filtration polymer based membranes, which was experimentally demonstrated by Hong et al. [31]. The PMMA (poly(methylmethacrylate)) polymeric coating on palladium/single layer graphene allowed only hydrogen molecules to pass through and reach the palladium surface. As a result, molecules like CH₄, CO, and NO₂ showed no response.

Another group in 2016 studied the properties of bimetallic-rGO based sensor for hydrogen detection under different working circumstances. Pt-Pd nano-particles were decorated on rGO surface via one step chemical reduction method and the sensor study was done by observing the resistance change upon exposure to different concentrations of hydrogen at room temperature. They concluded that the response percent was dependent on concentration and operating temperature but was independent of flow rate [32]. Moreover, the sensor recovery was faster in air than nitrogen, which were used as carrier gases. In 2009, the sensing properties of Pt decorated rGO sheets deposited on SiC substrates were studied by Shafiei et al. [33]. By studying the reverse I-V characteristics (while maintaining constant device current) in 1% of hydrogen in air, they observed a significant 100 mV shift at 100°C.

Similar other reports have also been tabulated in **Table 3**, which gives an idea about the variation of the response parameters in the field of graphene based hydrogen sensors.

8. Suggested mechanism of hydrogen sensing

A general overview or in particular few important hydrogen sensing highlights as proposed by research groups are compiled to explain the sensing mechanism of graphene based hydrogen sensors [13, 61]. Basically four factors critically influence the sensing mechanism: (a) relevance of material, (b) development of junction, (c) surface adsorbed species and (d) external perturbation during sensing.

8.1 Relevance of materials

Introduction of nanoparticles in the base matrix helps in preventing agglomeration of layered materials (such as graphene), and increase the surface area by forming three dimensional networks; an essential part to improve the base matrix performance during sensing [41]. Also, it is reported that catalytic metals such as palladium normally improves the adsorption/desorption kinetics [62]. Furthermore, synergistic effect (cumulative response) due to the presence of different sensing hosts is very important from gas sensor perspectives. Synergistic effect between copper oxide and graphene was the proposed mechanism by Zhang et al. [35]. Copper oxide (CuO) acts as good p-type semiconductor while graphene (rGO) acts as excellent conducting platform. Number of holes in the accumulation layer between CuO-rGO account for the electrical conductance change during hydrogen sensing (**Figure 4**).

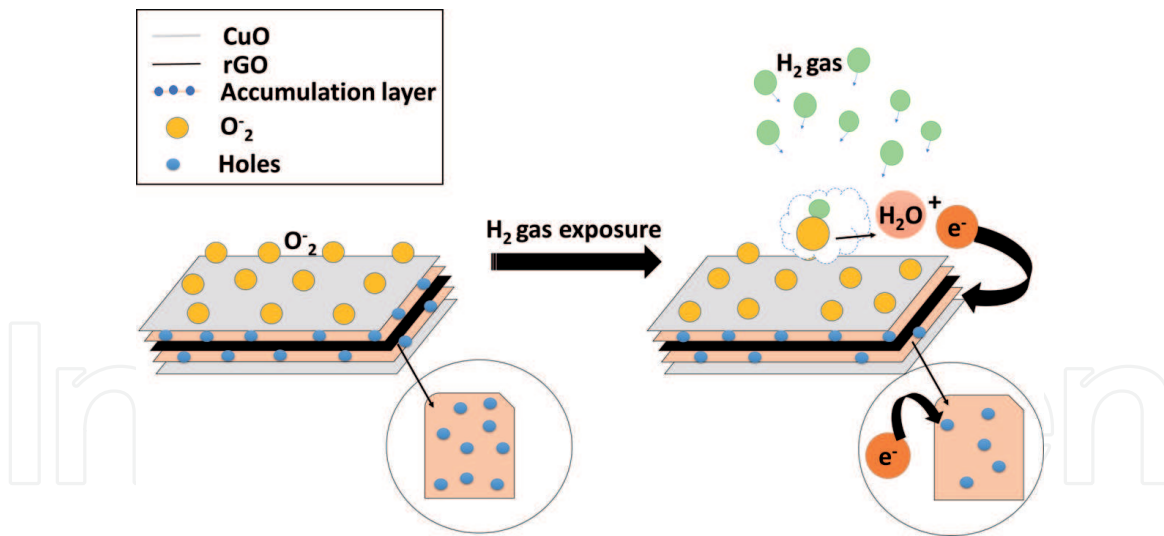


Figure 4.
Sensing mechanism graphene based material highlighting the role of accumulation layer.

8.2 Development of junction

The gas sensing properties can be enhanced by forming p-n heterojunctions between metal or metal oxide and graphene. Dutta and co-workers [59] have suggested a mechanism for p-TiO₂/n-graphene with palladium contacts. When this device was exposed to hydrogen gas due to interaction of palladium with the gas, dissociative adsorption took place as shown in Eq. (4):



Thereafter diffusion of atomic hydrogen into bulk palladium occur. A non-stoichiometric hydride PdH_x is formed which serves as dipole because of charge separation. Here hydrogen acts as positive center and palladium as negative center. An electron from diffusing hydrogen is now shared between the semiconductor and the palladium. Due to this an increase in concentration of electron at the interface leads to the reduction of work function of palladium. Shift in Fermi level is suggested due to which the heterojunction barrier changes. Change in this barrier during gas exposure is responsible for the change in device current. They observed that the current increased when exposed to hydrogen gas, implying reduction in barrier height. During recovery, the hydrogen gas desorb from the surface. This shows decrease in current in the circuit. Operating temperature has a major role in determining the adsorption and desorption of the gas molecules.

8.3 Surface adsorbed species

Adsorbed oxygen in hybrid materials that contain metal oxides such as SnO₂, CuO, ZnO, etc., tune the device resistance in presence and absence of test gas [13]. Sensing mechanism is based on the phenomenon of adsorption and dissociation of gas molecules on the host surface. Due to these interactions either a carrier is generated or a carrier is annihilated, which affects the resistance of the base matrix. Oxygen adsorbed on the graphene surface aids in good sensing. This oxygen accommodates an electron during its surface adsorption and stays in charged state on the surface of the sensing layer. During sensing there is interaction between the charged oxygen radical and the gas molecules and an electron is released. Hence, during gas exposure the surface oxygen gets removed from the surface, which is again recovered in sensor recovery process.

8.4 External perturbation during sensing

Tang and group in a sensing study with palladium and graphene discussed the formation of two phases, “ α ” and “ β ” in hydrogen adsorbed palladium [61] (**Figure 5**). At room temperature, pressure as low as 0.01 bar leads to the saturation of “ α ” phase. It results in 10% ratio of H/Pd. Their mechanism is based on the change in resistance of graphene which in turn is dependent on the Pd work function. Since Pd has higher work function (5.2 eV) than graphene’s (4.7 eV), therefore on Pd decoration, resistance of graphene tend to decrease. So considering p-type graphene, it is apparent that there is increase in hole density of graphene upon Pd decoration because the electron transfer occurs from graphene to palladium. During hydrogen exposure PdH_x is formed and its work function (3.2 eV) is less than graphene. Therefore in accordance to the previous argument, the resistance will increase and hole density will decrease. Also, the electron transfer is from PdH_x to graphene. This mechanism was more like a shark-fin (signal increase and decrease were slow and response percent low) curve, which were observed only in dark condition (without external light energy perturbation). Under light illumination (photon energy ~3.1 eV) square type (signal increase and decrease were fast and response percent high) response was observed (**Figure 5**). This difference is due to the extra energy provided by the external light source. During response, illumination energy is increasing the adsorption amount as well as accelerating fast dissociation of hydrogen molecules on the surface of palladium. During recovery, the low dissociation energy (2.96 eV) of PdH_x in comparison to incident photon energy helps in easy release of the adsorbed hydrogen, and the Pd work function slowly reverts back to its initial value. So the response parameters improved due to external perturbation [61]. Novoselov et al. also showed that it is possible to regenerate the sensor to its original state

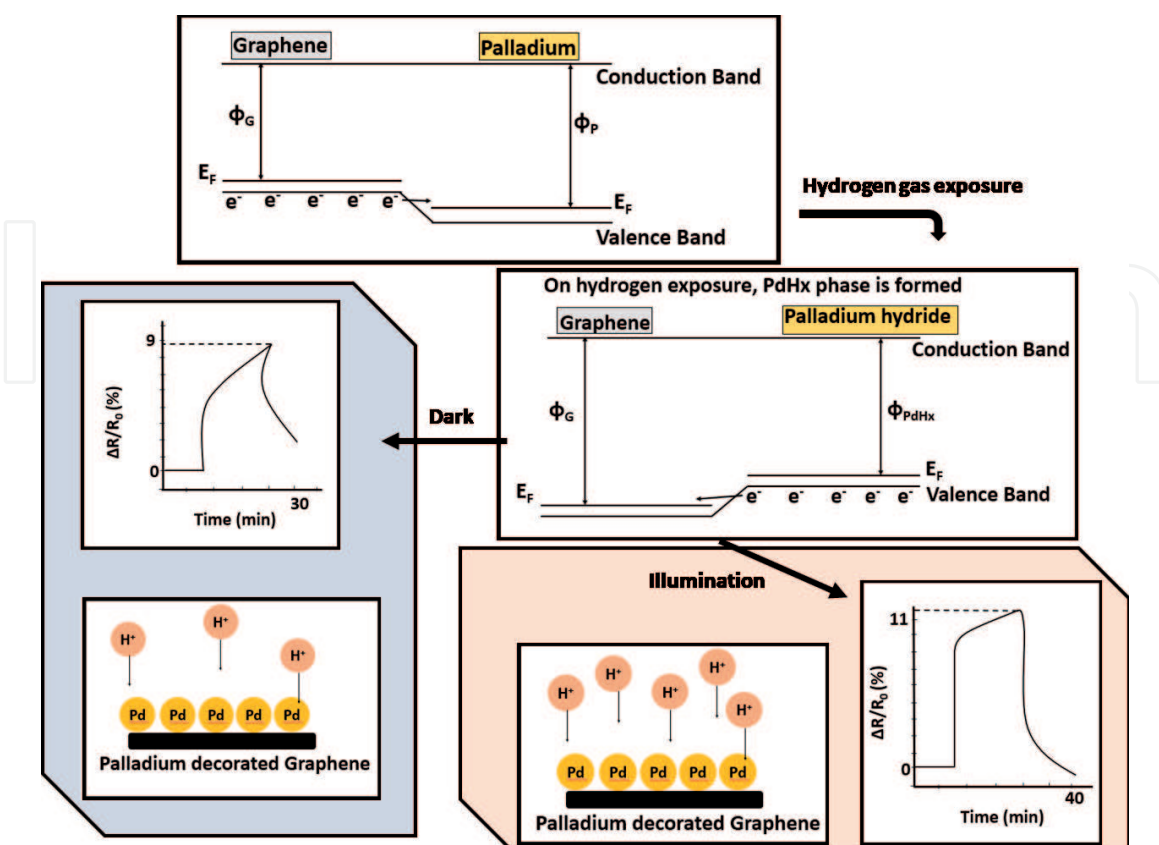


Figure 5.
 Effect of external perturbation (light illumination) during sensing.

by annealing at 150°C in vacuum or by short UV radiation exposure [7]. This can only be achieved within 100–200 s.

9. Performance rating

Graphene and graphene oxide based devices in sensing must have the following qualities such as (a) reliability, (b) reproducibility and (c) long term stability.

The accuracy and precision of a sensing device leads to its reliability in practical applications. The sensing system's capability to give same results when subjected to same or slightly distinct conditions is known as the reproducibility of the system. When same parameter is measured after a period of time, the ability of a sensing sensor to give the same output is known as its long term stability.

In order to test these qualities, the device is tested with respect to (a) the magnitude of response parameters within error limits under perturbed ambient conditions (such as high humidity or domestic/commercial/industrial locations), (b) the nature of response of a single device or multiple devices prepared under similar conditions and (c) time of aging (by continuous or repeated operation). Few notable experimental demonstrations in this regard are discussed below:

Dutta et al. have produced same results (with p-TiO₂/n-graphene heterojunction) in consecutive 3 days of sensor studies with 1% concentration of hydrogen in air [59]. The testing period can be extended from days to weeks or months for monitoring the response parameters. The reliability and reproducibility of graphene sensors were tested by Noll et al. by monitoring input characteristics continuously of a single device and then with large number of devices, respectively [63].

10. Conclusion and future outlook

Graphene and graphene oxides can be abundantly used as sensing materials due to their amazing properties, which are easy to tune. Reports regarding graphene and graphene oxide based gas sensors for hydrogen detection have proved that these materials can be used to selectively detect hydrogen. Hence there is possibility of fabrication of gas sensors with desired sensitivity, selectivity and stability with these materials. Furthermore, the possibility of doping or modification with other materials widens the future scope of graphene and graphene oxide based gas sensors. Reduced graphene oxide is also proven to be a tremendous sensing material for hydrogen along with graphene and graphene oxide. In fact the performance of reduced graphene oxide as a sensing material is better as compared to that of pristine graphene and oxidized graphene. Also, modification of graphene based layer with metal nano-particles have improved the response parameters. In addition to monometallic metal nanoparticles, bi-metallic or tri-metallic nano-particles also exhibit better catalytic properties due to synergistic effect between them. So it is apparent that graphene based layers modified with bi-metallic nano-particles or tri metallic nano-particles to form ternary or quaternary composites can be widely used as sensing hosts in near future. Hence within the purview of this review, it can be concluded that the potentiality of these materials is tremendous in the field of hydrogen sensing, which can further be cultivated to obtain desired selective response characteristics with other gases.

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