

# A Review on Graphene & its Derivatives for Gas Sensors

<sup>1</sup>Anil B. Patil\*, <sup>2</sup>Umesh. J. Tupe, <sup>3</sup>Arun V. Patil

<sup>1,2,3</sup>Department of Electronic Science and Research Center, L.V. H. College, Nashik, India.

## Abstract:

This review summarizes the present scenario and research on Graphene and its derivative based gas sensors and its application as gas sensors. Graphene-based gas sensors have attracted much attention in recent years due to their variety of structures, unique sensing performances, room-temperature working conditions, and tremendous application prospects, etc. Graphene-like properties make reduced graphene oxide a highly desirable material to be used in gas sensor, biological, environmental or catalytic applications as well as optoelectronic and storage devices.

In this article, we summarize firstly the basics of gas sensors, various sensing material, need and properties of graphene, various synthesis methods of graphene based materials. Structure of gas sensors and review on application of graphene and its derivatives as gas sensor. The review provides important reference for follow-up research work for the future.

**Keywords:** Pollution, Gas sensors, Graphene, Reduced Graphene Oxide (rGO), Sensitivity.

## I. INTRODUCTION

Modern industrialized society has brought a series of problems to our world. Many industrial and commercial activities makes it necessary to constantly monitor and control pollution in the environment, chemical factories, and food processing plants, laboratories, homes, hospitals, and technical installations in general, with applications ranging from domestic gas alarms and medical diagnostic apparatus to safety, environmental and chemical plant instrumentation.

Nowadays, Gas sensor technology has played an important role in various fields such as in the automation of industrial processes, in the emission control for automobiles, and in gas leakage detection in the home and workplace, and so on. Without sensors, significant advances in control and instrumentation will not be possible.

Nitrogen and oxygen are main components of air out of a mixture of several gases. Other components of air usually showing small concentrations are argon, other inert gases, carbon dioxide and hydrogen. The composition of air is constantly varying due to the interchange of atoms and molecules between air and the surrounding bodies and also, because of the diffusion and interaction of the particles in the gas phase. This makes atmosphere a fully open system, spatially in-homogeneous and with rich internal dynamics. Some other constituents usually sensed in changing concentrations are ozone, carbon monoxide, sulphur or nitrogen oxides and several VOC compounds. Also important is noting that very small solid (smoke, dust) or liquid particles (the clouds, the fog) can be carried in suspension by air.

Also, Hydrocarbon gases, including liquid petroleum gas (LPG) find useful applications, as a clean source of energy at both fuels for domestic and industrial purposes [1]. Major constituents of LPG include butane-(C<sub>4</sub>H<sub>10</sub>) (70%-80%), propane-(C<sub>3</sub>H<sub>8</sub>) (5%-10%) and propylene-(C<sub>3</sub>H<sub>6</sub>), butylenes-(C<sub>4</sub>H<sub>8</sub>), ethylene and methane (1%-5%). They are not pure chemical hydrocarbons, but commercial quality products marketed as butane and propane, which also contain trace quantities of other similar gases. But they are potentially hazardous and combustible gases which might cause explosion if any leaks of these gases occur accidentally or by mistakes.

Gases are the key targets in many industrial and domestic activities requiring improved level of measurement or control. This has been stimulated by a series of clean air laws [2], which have or are being legislated on the international, national, state and local levels.

At present, gaseous pollution is mainly caused by rapid industrialization which increasingly involves the use and manufacture of highly dangerous substances. Particularly nitrogen oxides and other gases toxic and combustible gases are released in large amounts to the environment from combustion sources and automobiles. Inevitably, occasional escapes of gas occur which leads to environmental imbalance and global

warming. It is well known that Therefore, The detection of gas molecules such as NO, NO<sub>2</sub>, NH<sub>3</sub>, CO, and HCHO is necessary in various areas from environmental control to everyday monitoring of such activities as public safety, engine performance, medical therapeutics, and many more due to their toxicity and associated risk to the ecosystem. The detection of NO and NO<sub>2</sub> has attracted considerable concern because NO and NO<sub>2</sub> are harmful to plants and the respiratory systems of human beings and animals[3].

The development of the modern society requires the development and improvement of devices (sensors) able to transform physical or chemical phenomena into electrical signal for further treatment using transducer systems. Our society requires gas sensors for domestic, automotive and industrial applications due to the implication of gases in environmental control or dangerous emissions. So, major reasons for the need of gas sensors are monitoring of environmental pollutants and controlling their emission. At this respect, the market, based on the new regulations, demands a higher reliability in domestic and environmental gas sensors for the detection of combustible and toxic gases. Different kinds of sensing devices for gas monitoring can be used.

Gas sensor means the device which detects the presence of various gases within an area, usually as part of a system to warn about gases which might be harmful to humans or animals especially the combustible and hazardous gases like liquefied petroleum gas (LPG), CO<sub>0</sub>, CO, SO<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>, Ar, N<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O and several organic vapours such as methanol, ethanol, isopropanol, benzene and some amines, among others, because of their toxicity, their relation with atmospheric composition.

Chemo resistive gas sensor was invented by Seiyama et.al. [4] for gas detection in 1962 and was able to demonstrate that gas sensing is possible with simple electrical devices. The working principle of the chemo resistive gas sensors is based on conductivity changes produced when the sensing material is exposed to the target gases. The magnitude of change in electrical resistance gives a direct measure of the concentration of the target gas present. Taguchi [5] developed and patented the first practical chemiresistive gas sensor using tin dioxide (SnO<sub>2</sub>) as the sensitive material for real life applications in 1970. Since then, semiconductor gas sensors have been widely used as domestic and industrial gas detectors for gas-leak alarm, fire alarm, process control, pollution control.

Since the pioneering works of Seiyama, the research into gas sensors based on semiconducting metal oxides has made remarkable progress in detecting various kinds of gas molecules such as H<sub>2</sub>, CO, hydrocarbons, NO<sub>x</sub>, SO<sub>x</sub>, CO<sub>2</sub>, VOCs, and odors. With the development of science and technology, the development of gas sensors towards high sensitivity, high selectivity, fast response, low cost, low power consumption, stability and portability has led to the search for new and superior gas-sensing materials [6, 7, 8].

The demand for developing simple and reliable gas sensors is urgent for applications in various areas, including environmental monitoring, agriculture, and medical diagnosis, building indoor environments, national defense, and in various industries such as chemical and petrochemical industries, food and drinks processing, semiconductor manufacturing, agriculture, fabrication industries, including the motor, ship, and aircraft industries, power generation, etc., where control and analysis of process gases are necessary.

## II. NEED OF GRAPHENE BASED SENSING MATERIALS

Sensing materials play a key role within the successful implementation of gas sensors. However, the multidimensional nature of the interactions between function and composition, preparation method, and end-use conditions of sensing materials often make their rational design for universe applications very challenging.

Moreover, the planet of sensing materials is extremely broad and practically all well-known materials may well be used for the chemical sensors elaboration. Therefore, the selection of optimal sensing material for gas sensor is complicated and multivariate task, with stability and functionalizing of gas sensing materials, selection of optimal sensing materials and promotes an understanding of the fundamentals of sensor functioning and development of the technological route of their fabrication play major role for applications in various types of gas sensors.

Beside conventional gas sensing materials such as metal oxides[9], polymers, metal films, and semiconductors, new trends in gas sensing materials include analysis of, among other materials, 1D metal oxide nanostructures, carbon nanotubes, fullerenes, graphene, semiconductor quantum dots, and metal nanoparticles used in the development and fabrication of gas sensors for the sensor market.

Recent developments in nanotechnology [10] have created huge potential to build highly sensitive, low-cost, portable sensors with low power consumption. Therefore, gas sensors based on nanomaterials have been widely investigated. From the literature survey, there are primary three nanomaterial-based gas sensing materials which are metal oxide (MO<sub>x</sub>) nanoparticles, carbon nanotubes (CNTs), and graphene[11].

### III. PROPERTIES OF GRAPHENE AND ITS DERIVATIVES

In recent years, one of the most known carbonic materials is graphene and its derivatives like pristine graphene, graphene oxide (GO), and reduced graphene oxides (RGO) have been reported to be promising in sensing application. Graphene which was first isolated discovered by Geim and Novoselov using micro-mechanical peeling of graphite in received the Nobel Prize in Physics since the pioneering works in 2010 [12, 13, 14] which has been then the target material for extensive theoretical and experimental research.

Graphene is a two-dimensional (2D) carbon-based nanomaterial crystal made of a basal monolayer of sp<sup>2</sup> hybridized carbon atoms disposed in a hexagonal packing that was theoretically predicted long time ago[15] and produced only in 2004. It is a building block of many other carbonic materials such as fullerene buckyballs, carbon nanotubes or 3D graphite [16].

In particular, among existing nanomaterials graphene has a large surface area (2630 m<sup>2</sup>/g) and high charge carrier mobility (15000 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>) at room temperature is attractive for various electronic applications. The charge transport and electronic properties [17] of graphene are due to its unique electronic  $\pi$  band structure with high electrical conductivity. Its unique structure leads to astonishing mechanical properties resulting from strong planar  $\sigma$  bonds[18]. Graphene is considered the thinnest stretchable crystal possessing good thermal conductivity and high electron mobility[19].

GO properties can be further tuned using chemical engineering[20] and can lead to a plethora of applications [21]. It quickly became essential in a wide range of applications such as optoelectronic devices[22], sensors[23, 24], supercapacitors[25], biomaterials and bionics[26], solar cells[27], energy storage[28] and batteries[29], electrochemical performance[30], thermal management[31], armor material[32], generation of neurons[33], cellular migration[34], drug delivery[35], water purification[36] and many more.

### IV. SYNTHESIS METHODS OF GO AND rGO

In order for graphene's potential to be fully accomplished and to satisfy requirements for applications, convenient methods for its synthesis should be developed. There are primarily four methods to synthesize single layered or few-layered graphene: chemical reduction, micromechanical exfoliation, epitaxial growth, and vapor deposition [37–40].

The top-down and bottom-up approaches for graphene synthesis originating from different carbon sources are considerable. There are two main categories of synthesis of GO as:

- Top-down methods where layers of graphene derivatives are extracted from a carbon source, typically graphite [41, 42] which approaches involve breaking apart the stacked layers of graphite to produce single graphene sheets (micromechanical cleavage, electrochemical exfoliation, solvent-based exfoliation, exfoliation of graphite intercalation compounds, unzipping carbon nanotubes).
- Bottom-up methods where simple carbon molecules are used to construct pristine graphene, and involve synthesis of graphene from alternative carbon containing sources (epitaxial growth on silicon carbide, chemical vapour deposition on, substrate-free methods, graphene synthesis via the ash pyrolysis of the solvothermal product of sodium and ethanol, etc). Bottom-up synthesis (such as chemical vapor deposition, epitaxial growth on silicon carbide wafers, etc.) has been shown to be time-consuming and faces challenges to scalability [43].

It is possible to produce graphene sheets from a stacked layered graphite sheet, if the interplanar van-der-Waals is broken. The most popular top-down method is via the oxidative exfoliation of graphite. Graphite oxide is usually synthesized by either the typical method proposed by Hummer et.al. [44] which is becoming the most popular approach to synthesize GO by virtue of its merits, including rapid, easy and relatively safe properties some modification of this method. Various modified Hummers methods have been reported to promote the progress of GO preparation [45-48]. In this, graphite oxide synthesized was exfoliated into graphene oxide sheets by few hours of ultrasonication in water to form a stable aqueous dispersion of graphene oxide.

Marcano et al. [49] reported improved technique which greatly increases the efficiency of oxidizing graphite to GO using KMnO<sub>4</sub> as the only oxidant and an acid mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> (9:1) as the acidic medium. Shen et al. [50] oxidized graphite using benzoyl peroxide at 110°C for 10 min in an opened system to GO. This technique provides a fast and efficient route to synthesis of graphene oxide.

The graphene oxides are then reduced into graphene by means of thermal annealing, solvothermal reduction, electrochemical reduction [51], hydrogen plasma treatment or radiation-induced reduction etc.

Among other methods, the most customarily used method is chemical reduction using reductants such as hydrazine. The above-mentioned various reduction methods available result in with a relatively perfect

structure and excellent properties of reduced GO, which in turn affect the final performance of device materials composed of rGO. The schematic illustration of synthesis of rGO using this method is shown in following figure 1 shows different routes of graphene synthesis.

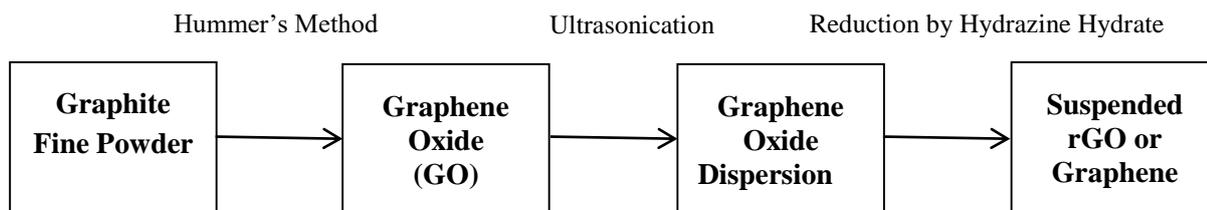


Figure 1: Synthesis of rGO [52]

## V. STRUCTURE FOR GAS SENSORS

According to different forms of reaction with external atmospheres, gas sensors can be classified into chemiresistor, field-effect transistor (FET), surface acoustic wave (SAW) change transistor, surface work function (SWF) change transistor, optical fiber sensor (OFS), capacitance sensor (CS), and so on [53].

Among them, chemiresistor is the extensively used in the construction of gas sensors for practical applications, due to distinctive features like simple structure, convenience to implement, room-temperature operation, and relatively low cost [54].

Most gas sensors reported so far are operated in a resistive mode is shown in figure 2. The gas concentration is analyzed by direct test sensor with the change of resistance under the interaction with the detection gas [55], by applying voltage on both electrodes of the device, and detect the present fluctuating over time when gas composition changes. The substrate is formed of insulant like ceramic or silicon oxide, and also the graphene material or various graphene composite materials is coated or grown on the surface of the substrate as gas-sensing materials. The electrodes are drawn at both ends of the gas-sensitive material. When the detected gas and gas-sensitive materials to bear, gas molecules adsorbed on the surface of gas-sensitive materials leading to resistance changes. The gas can be measured qualitatively and quantitatively according to the change of resistance [56].

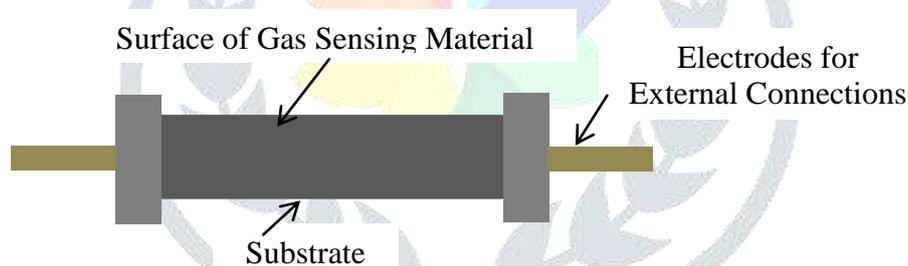


Figure 2: Chemiresistor structure

## VI. GAS SENSORS USING GRAPHENE AND ITS DERIVATIVES

Metal oxide semiconductor (MOS) gas sensors are the most widely used gas sensors in the world for production and use due to its high sensitivity and fast response time, but, short life, poor selectivity and high operating temperature are the disadvantages of MOS.

The key indicator of material gas sensitivity is the specific surface area, which is the total surface area of a material per unit of mass [10]. The large specific surface area facilitates the adsorption of gas molecules in nanomaterials, thereby improving the sensitivity of gas sensors. Over the last fifty years, novel sensing materials others than metal oxides have been proposed.

Organic materials are far more easily modified than inorganic materials with reference to such characteristics as sensitivity, working temperature, and selectivity. Long-term instability may be a main drawback of the sensors supported conducting polymers as they're thermally unstable, so it's often impossible to use them at temperatures at which gas-solid interactions proceed rapidly and reversibly. The gas-sensing properties of conducting polymers were first reported in 1983. To fully use all the potential advantages of organic and inorganic materials, hybrid composites have also been introduced as sensing elements for resistive sensors [57] with new functionalities and properties such as increased room-temperature sensing capability when exposed to low-concentration gases such as NO<sub>2</sub>, H<sub>2</sub>, and CO, because of size effects and interfacial interactions.

Nanomaterials synthesis have provided enormous advantages for gas sensing because their extremely high surface-to-volume ratio, large specific surface area, high aspect ratio, excellent electronic properties, and simple fabrication [58]. for ideal condition of gas molecule adsorption. The successful synthesis of nanoparticles, nanowires, nanotubes and other shapes has generated a lot of work to use these nanostructured materials in gas sensing [59-61]. Important examples are that of conductive carbon, carbon nanotubes (CNTs), or graphene which are currently receiving a great deal of interest in gas sensing.

Graphene, a two-dimensional monolayer of carbon atoms, has been identified to be a promising sensing material because it has unique and excellent electrical and mechanical properties [55] in 2007., Graphene appears to be more suitable than CNTs since graphene's planar nanostructure makes it advantageous for integration into devices used in standard fabrication techniques, suitable for depositing and stabilizing small metal and/or metal oxide nanoparticles, which is of remarkable interest for use in gas sensors.

Theoretical and experimental results showed that [11] graphene and its derivatives, like graphene oxide (GO) and reduced graphene oxide (rGO), exhibit large specific area, excellent conductivity, and straightforward adsorption of gas molecules, and also the surface can easily be modified by functional groups, so it's good gas sensing properties.

Graphene and its derivative based devices have shown excellent sensing properties toward  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and volatile organic compounds (VOCs). For evaluating the performance of gas sensors, there are a few critical parameters including component resistance, measure resistance, sensitivity and selectivity, limit of detection, response time, and recovery time.

In the present review, a comprehensive overview on the recent advances in the development of graphene and its derivatives based gas sensors are done. The key difficulties and future points of view in this quickly emerging field going for Graphene and its derivatives, gas sensing devices for future applications are given.

Schedin et al [62] reported that mechanically-exfoliated graphene can potentially detect gaseous species down to the single molecular level. The gas-sensing mechanism of graphene is generally ascribed to the adsorption/desorption of gaseous molecules (which act as electron donors or acceptors) on the graphene surface, which leads to changes in the conductance of graphene.

Sen Liu et al. [63] fabricated ZnO nanoparticles and Au nanoparticles modified reduced graphene oxide gas sensors by using wet chemical method. The developed sensing materials were used as a for  $\text{NO}_2$  sensing at relatively low operating temperature ( $80^\circ\text{C}$ ). Author reported ZnO-rGO-Au hybrids exhibits fast response and recovery rate, as well as good selectivity to nitrous dioxide gas.

Choi et.al. [64] reported a highly sensing  $\text{NO}_2$  gas sensor based on multilayered graphene films synthesized by a CVD method on a microheater-embedded flexible substrate. The multilayered graphene had a very low detection limit of  $\text{NO}_2$  at sub-ppm ( $\backslash 200$  ppb) levels which when exposed to 1 ppm  $\text{NO}_2$  at room temperature, presented high responses and a short response time.

Lu et al. [65] studied the thermally-reduced GO which can be used to fabricate molecular adsorption-type gas sensors and demonstrated transport characteristics typical of a p-type semiconductor and showed room-temperature sensing properties under atmospheric pressure. The electrical contact between the GO and the metal electrode makes the sensing response more complex and deserves further investigation. The simple and low-cost manufacturing process and the wide availability of GO could lead to cost-effective graphene-based gas sensors and other opportunities for graphene.

Novoselov et al. [66] used the mechanical exfoliated graphene for detecting gases in 2007. They claimed that this graphene-based gas sensor had a limit of detection (LOD) as low as parts per billion (ppb), and this value is equivalent to those of the foremost sensitive gas sensors ever reported. so as to be told the basic LOD of graphene-based gas sensors, they further optimized the sensing device by using the Hall geometry to supply the strongest response to the change accountable carrier density near the Dirac points

S. Khojin et.al.[67] compared the sensing response of pristine graphene and polycrystalline graphene with wrinkles. They confirmed that the sensitivity of a graphenebased gas sensor depended on the type and geometry of graphene defects for detecting the vapors of organic compounds. Pristine graphene with only a few point defects is insensitive to the vapors of 1,2-dichlorobenzene and toluene. By introducing line defects to graphene sheets, the sensing responses can be greatly enhanced. This is because of reducing the conduction paths around such defects.

Lu et al. [68] developed a high performance gas sensor using partially reduced GO prepared by low temperature (e.g.  $200^\circ\text{C}$ ) annealing as sensing layer. This device showed a sensitivity of 1.41 ( $\text{Gg}/\text{Ga} - 1$ , where  $\text{Ga}$  and  $\text{Gg}$  are the conductance in air and target gas, respectively) to 100 ppm  $\text{NO}_2$ , and a full recovery was achieved after 30 min exposure to dry air. The high response of partially reduced GO upon exposure to  $\text{NO}_2$  is due to the restoration of  $\text{sp}^2$ -graphitic carbon atoms as active sites for  $\text{NO}_2$  adsorption. Moreover,

vacancies or small holes were possibly created in the thermal treatment and these defects can also serve as adsorption sites for gas.

Yi et. al. [69] synthesized thin metal layers as the top electrodes of vertically aligned ZnO NRs (ZnO NRs–Gr/M) by using CVD-graphene sheets. The hybrid architecture can maintain sufficient space between NRs for maximizing their surface area to contact with target gas, allowing a fast and easy gas transport. The hybrid based sensor exhibited a response of 9 or 90 to 10 or 50 ppm ethanol

Zopf et. al. [70] revealed that the electrical conductivity of rGO increases upon NO<sub>2</sub> gas adsorption which is caused by the electron withdrawing effect of the adsorbed NO<sub>2</sub>, which leads to more positive charge carriers (or holes) in p-type rGO, whereas the adsorption of hydrogen gas (H<sub>2</sub>) and methane gas (CH<sub>4</sub>) decreases the electrical conductivity of rGO, since H<sub>2</sub> or CH<sub>4</sub> is neither an electron donor nor an electron acceptor which are not able of charge transfer. Instead, the gas molecules from synthetic air that previously physisorbed on the surface of rGO are replaced by H<sub>2</sub> or CH<sub>4</sub> molecules, which are responsible for the observed electrical changes. The same goes for the decreases in resistance when NO<sub>2</sub> and ammonia (NH<sub>3</sub>) are adsorbed on graphene as they both induce hole and electron conduction, respectively.

Ao Z. M. et al. [71] found that the adsorption of CO on aluminium-doped (Al-doped) graphene by using density functional theory and CO could strongly adsorb on Al-doped graphene by forming Al–CO bonds. This strong interaction further induced significant changes in the electrical conductance of graphene, indicating a great sensitivity for CO detection.

Pandey et. al.[72] showed that the resistance of a palladium (Pd)-doped GO-based sensor changes because of the shift in the work function of Pd upon H<sub>2</sub> gas adsorption due to dissociative chemisorption process.

Cui et. al. [73] doped metal nanoparticles into RGO to improve the selectivity of graphene-based gas sensors and a sensor was fabricated by using RGO/Ag nanoparticle composite as the sensing material improving its selectivity of NH<sub>3</sub> gas.

Zhanget. al. [74] developed SnO<sub>2</sub>/graphene three-dimensional frameworks with 3 different morphologies and a flower-like SnO<sub>2</sub> nanostructure have been used for fabricating gas sensors. In comparison, pure SnO<sub>2</sub> flowers without graphene substrate showed a relatively weak signal. This is due to diameters and distribution uniformity of metal oxide NRs can significantly influence the sensing performances of the gas sensors based on their composites with graphene.

Denget. al. [75]studied immobilized Cu<sub>2</sub>O nanowire mesocrystals on RGO sheets and developed their applications in gas sensors for the detection of NO<sub>2</sub>. The response ( $I_g/I_0 - 1$ , where  $I_g$  and  $I_0$  are the current in target gas and in N<sub>2</sub>, respectively) of Cu<sub>2</sub>O mesocrystal/RGO hybrid material was 67.8% for 2 ppm NO<sub>2</sub>, much higher than that of RGO (22.5%) or Cu<sub>2</sub>O nanowires (44.5%) alone.

Al-Mashatet. al. [76] used a graphene/polyaniline (PANI) nano- fibre composite for the detection of H<sub>2</sub>.The composite-based sensor showed a strong response of 16.57% (DR/R<sub>0</sub>) to 1% of H<sub>2</sub>. In comparison, the responses of the graphene- and PANI-based sensors were measured to be only 0.83% and 9.38%, respectively. According to the response direction of the composite-based sensor, it is reasonable to conclude that the PANI sensing mechanism is dominant. The presence of graphene increased the specific surface area of the sensing layer because of the formation of PANI nanofibers with larger porosity.

Efforts have been made to summarize and discuss performance parameters and related works in the development of new sensor technologies in the following table 1.

Table 1: A summary of some recent researches about graphene based gas sensors

Sensing Material	Structure of sensor	Target gas	Response Time (s)	Recovery Time (s)	LOD	Ref.
GO	Chemiresistor	NO <sub>2</sub>	3000	3000	4 %/100ppb	77
RGO+ SnO <sub>2</sub>	Chemiresistor	NO <sub>2</sub>	75	300	3.31%/5 ppm (50 <sup>0</sup> C)	78
PrintedRGO/ S+ Ag	Chemiresistor	NO <sub>2</sub>	12	20	74.6%/50 ppm	79
GR + PANI	Chemiresistor	NH <sub>3</sub>	50	23	0.7 %/1 ppm	80
GO	Chemiresistor	H <sub>2</sub>	270	306	6 %/800 ppm	81
Few-layered GR	Chemiresistor	CO <sub>2</sub>	11	14	3 ppm	82
GR/PANI	Chemiresistor	CH <sub>4</sub>	85	45	10 ppm	83
GR	FET	SO <sub>2</sub>	120	120	100 %/50 ppm	84
RGO/Fe <sub>2</sub> O <sub>3</sub>	Chemiresistor	H <sub>2</sub> S	500	<30	15 ppm (190 <sup>0</sup> C)	85
Few-layered GR	Chemiresistor	LPG	5	18	4 ppm	82

RGO	FET array	Ethanol	300	-	17 %	86
RGO/Ag	Optical fiber sensor	Ethanol	11	6	1 %	87
rGO-ZnO	Chemiresistor	NO <sub>2</sub>	165	-	5 ppm	88

GR – Graphene, GO – Graphene Oxide, RGO - Reduced Graphene Oxide

## VII. CONCLUSIONS:

This review summarizes the present scenario and research on Graphene and its derivative based gas sensors and its applications. To meet the demand of high sensitivity, selectivity, and stability and to detect the pollutant gas before its flammability limit, considerable research into the development of graphene based gas sensing materials with novel design using tailored material properties is underway.

The excellent property of graphene such as high conductivity, the surface-rich and easily modifiable functional groups gives it great advantage as a chemo resistive sensor. Through summarizing the performance parameters of the gas sensor, it can be seen in Table 1 that the main gases detected by the graphene gas sensor are NO<sub>2</sub>, NH<sub>3</sub>, organic gases such as ethanol and acetone and other important industrial gases.

## VIII. FUTURE PERSPECTIVE:

In recent years, graphene, polymer, metal and metal oxide composite obtained by the new composite materials emerge within the field of gas detection, which greatly enhances the performance, indicating that grapheme composites within the gas sensitive material features a superb potential for development. Due to the benefits in sensitivity, selectivity and small-size, the long run of graphene gas sensors have an honest application prospect in industrial and agricultural production, and environmental monitoring. However, this large-scale application of graphene still has difficulties.

There are two main bottlenecks. Firstly, there's no method for large-scale preparation of graphene gas sensors. Secondly, graphene has to be further treated to enhance its response sensitivity to specific gases. Judging from this development trend, the advance of latent period could also be from the subsequent aspects: (1) increasing specific area by modifying surface and compositing with other nanomaterials specifically; and (2) designing appropriate structure. Improved graphene-based sensitive materials will occupy a vital position within the way forward for gas-sensitive materials and show greater advantages because the research progresses.

But, there are still many critical limitations and tremendous research work continues to be done before these technologies will be used at industrial stage, thus providing great potential for practical applications even in unfavorable environments within the market within the future. Thus, there's a scope for further study of graphene based materials towards pollutant gas sensing to boost the sensitivity, selectivity, fast response and recovery time of gas sensor to attain largely enhanced sensing performance.

## References:

- [1] DivyaHaridas, Vinay Gupta and K.Sreenivas, 2008, "Enhanced catalytic activity of nanoscale platinum Islands loaded on SnO<sub>2</sub> thin film for sensitive LPG gas sensors", Bull. Mater. Sc. (India) 31:1-4.
- [2] U.S. Environmental Protection Agency, Air Trends 1995 Summary, <http://www.epa.gov/oar/aqtrnd95/no2.html>.
- [3] Atkinson, R., 2000, Atmospheric Chemistry of VOCs and NO<sub>x</sub>. Atmos. Environ, 34: 2063–2101.
- [4] Seiyama, T.; Kato, A. Fujiishi K. and Nagatani M., 1962, A new detector for gaseous components using semiconductor thin film. Anal. Chem., 34 (11): 1502–1503.
- [5] Taguchi, N., 1971, Gas Detecting Devices. U.S. Patent 3: 631- 436.
- [6] Zhang, T.; Mubeen, S., 2008, Recent progress in carbon nanotube-based gas sensors. Nanotechnology, 19: 332001.
- [7] Zhang, X.; Wang, Y., 2013, Research and Development of Gas Sensors Based on Nanomaterials. Sens. Microsyst, 32: 1–5.

- [8] Wang, T.; Huang, D.; Yang, Z.; Xu, S.; He, G.; Li, X.; Hu, N.; Yin, G.; He, D.; Zhang, L., 2016, A Review on Graphene-Based Gas/Vapor Sensors with Unique Properties and Potential Applications. *Nano Micro Lett.*, 8: 95–119.
- [9] Govardhan, K.; Grace, A.N., 2016, Metal/Metal Oxide Doped Semiconductor Based Metal Oxide Gas Sensors - A Review. *Sens. Lett.* 14: 741–750.
- [10] Mohammadi, M.R.; Fray, D.J., 2009, Development of nanocrystalline  $\text{TiO}_2\text{-Er}_2\text{O}_3$ , and  $\text{TiO}_2\text{-Ta}_2\text{O}_5$ , thin film gassensors: Controlling the physical and sensing properties. *Sens. Actuators B Chem*, 141: 76–84.
- [11] He, Q.; Wu, S.; Yin, Z.; Zhang, H., 2012, Graphene-based electronic sensors. *Chem. Sci.*, 3: 1764–1772.
- [12] Zhang, S.; Shao, Y.; Liao, H.; Engelhard, M.H.; Yin, G.; Lin, Y., 2011, Polyelectrolyte-induced reduction of exfoliated graphite oxide: A facile route to synthesis of soluble graphenenanosheets, *ACS Nano*, 5: 1785–1791.
- [13] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, 2004, *Science* 306: 666.
- [14] *Physics Today*: 2019, <https://physicstoday.scitation.org/doi/10.1063/PT.4.0866/full/>
- [15] P. R. Wallace, 1947, *Phys. Rev.*, 71: 622-634.
- [16] A. K. Geim and K. S. Novoselov, 2007, *Nat. Mater.*, 6 : 183-191.
- [17] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim and H. L. Stormer, 2008, *Solid State Commun.*, 146 : 351-355.
- [18] C. Lee, X. Wei, J. W. Kysar and J. Hone, 2008, *Science*, 321: 385-388.
- [19] A. K. Geim, 2009, *Science*, 324: 1530-1534.
- [20] G. Eda and M. Chhowalla, 2010, *Adv. Mater.*, 22: 2392- 2415.
- [21] S. Sajjad, S. A. Khan Leghari and A. Iqbal, 2017, *ACS Appl. Mater. Interfaces*, 9:43393-43414.
- [22] R. Garg, S. Elmas, T. Nann and M. R. Andersson, 2017, *Adv. Energy Mater.*, 7: 1601393.
- [23] M. Xu, J. Qi, F. Li, X. Liao, S. Liu and Y. Zhang, 2017, *RSC Adv.*, 7: 30506-30512.
- [24] J. Liu, M. Xu, B. Wang, Z. Zhou and L. Wang, 2017, *RSC Adv.*, 7: 1432-1438.
- [25] Z. Li, S. Gadipelli, Y. Yang and Z. Guo, 2017, *Small*, 13: 1702474.
- [26] B. C. Thompson, E. Murray and G. G. Wallace, 2015, *Adv. Mater.*, 27: 7563-7582.
- [27] A. Agresti, S. Pescetelli, L. Cinà, D. Konios, G. Kakavelakis, E. Kymakis and A. D. Carlo, 2016, *Adv. Funct. Mater.*, 26: 2686-2694.
- [28] X. Shuai, Z. Bo, J. Kong, J. Yan and K. Cen, 2017, *RSC Adv.*, 7: 2667-2675.
- [29] C. Tang, B.-Q. Li, Q. Zhang, L. Zhu, H.-F. Wang, J.-L. Shi and M. F. Wei, 2016, *Adv. Funct. Mater.*, 26: 577-585.
- [30] E. Kecsenovity, B. Endrődi, P. S. Tóth, Y. Zou, R. A. W. Dryfe, M. K. Rajeshwar and C. Janáky, J., 2017, *Am. Chem. Soc.*, 139: 6682-6692.
- [31] D. G. Cahill, P. V. Braun, G. Chen, D. R. Clarke, S. Fan, K. E. Goodson, P. Keblinski, W. P. King, G. D. Mahan, A. Majumdar, H. J. Maris, S. R. Phillpot, E. Pop and L. Shi, 2014, *Appl. Phys. Rev.*, 1: 011305.
- [32] J. H. Lee, P. E. Loya, J. Lou and E. L. Thomas, 2014, *Science*, 346: 1092-1096.
- [33] S. Baek, J. Oh, J. Song, H. Choi, J. Yoo, G.-Y. Park, J. Han, Y. Chang, H. Park, H. Kim, S.-G. Cho, B.-S. Kim and J. Kim, 2017, *Small*, 13: 1601993.
- [34] X. Tian, Z. Yang, G. Duan, A. Wu, Z. Gu, L. Zhang, C. Chen, Z. Chai, C. Ge and R. Zhou, 2017, *Small*, 13: 1602133.
- [35] M. Zhang, N. Zhou, P. Yuan, Y. Su, M. Shao and C. Chi, 2017, *RSC Adv.*, 7: 9284-9293.
- [36] C. Zhu, P. Liu and A. P. Mathew, 2017, *ACS Appl. Mater. Interfaces*, 9: 21048-21058.

- [37] Z. Yang, R.G. Gao, N.T. Hu, J. Chai, Y.W. Cheng, L.Y. Zhang, H. Wei, E.S.W. Kong, Y.F. Zhang, 2012, The prospective two-dimensional graphenenanosheets: preparation, functionalization, and applications. *Nano-Micro Lett.* 4(1): 1–9.
- [38] K.S. Subrahmanyam, L.S. Panchakarla, A. Govindaraj, C.N.R. Rao, 2009, Simple method of preparing graphene flakes by an arcdischarge method. *J. Phys. Chem., C* 113(11): 4257–4259.
- [39] K.S. Subrahmanyam, S.R.C. Vivekchand, A. Govindaraj, C.N.R. Rao, 2008, A study of graphenes prepared by different methods: characterization, properties and solubilization. *J. Mater. Chem.* 18(13): 1517–1523.
- [40] R. Paola, H. Anming, C. Giuseppe, 2013, Synthesis, properties and potential applications of porous graphene: a review. *Nano-Micro Lett.* 5(4): 260–273.
- [41] C.K. Chua, M. Pumera, 2014, Chemical Reduction of Graphene Oxide: A Synthetic Chemistry Viewpoint, : 291–312.
- [42] Z. Wang, J. Liu, W. Wang, H. Chen, Z. Liu, Q. Yu, H. Zeng, L. Sun, 2013, Aqueous phase preparation of graphene with low defect density and adjustable layers, *Chem. Commun.* 49 (92): 10835–10837.
- [43] X.-Y. Wang, A. Narita, K. Müllen, 2017, Precision synthesis versus bulk-scale fabrication of graphenes, *Nature Reviews Chemistry* 2 (1):0100-0100.
- [44] W.S. Hummers, R.E. Offeman, 1958, Preparation of graphitic oxide. *JACS* 80(6): 1339–1339.
- [45] J.Y. Cao, L.Z. Song, J.L. Tang, J. Xu, W.C. Wang, Z.D. Chen, 2013, Enhanced activity of Pd nanoparticles supported on Vulcan XC72R carbon pre-treated via a modified Hummers method for formic acid electrooxidation, *Appl. Surf. Sci.* 274: 138–143.
- [46] C. Botas, P. Alvarez, P. Blanco, M. Granda, 2013, Graphene materials with different structures prepared from the same graphite by the Hummers and Brodie methods. *Carbon*, 65 : 156–164.
- [47] T. Chen, B. Zeng, J.L. Liu, J.H. Dong, X.Q. Liu, Z. Wu, X.Z. Yang, Z.M. Li, 2009, High throughput exfoliation of graphene oxide from expanded graphite with assistance of strong oxidant in modified hummers method, *J. Phys. Conf. Ser.*, 188: 01205.
- [48] C.I. Chang, K.H. Chang, H.H. Shen, C.C. Hu, 2014, A unique two-step Hummers method for fabricating low-defect graphene oxide nanoribbons through exfoliating multiwalled carbon nanotubes. *J. Taiwan. Inst. Chem.*, E 45(5): 2762–2769.
- [49] Daniela C. Marcano, Zhengzong Sun, Alexander Slesarev, Lawrence B. Alemany, Wei Lu, and James M. Tour, 2010, *ACS Nano*, 4 (8): 4806–4814.
- [50] B. Shen, et al., 2012, Influence of different buffer gases on synthesis of few-layered graphene by arc discharge method, *Appl. Surf. Sci.*, 258(10): 4523e4531.
- [51] H. L. Guo, X. F. Wang, Q. Y. Qian, F. B. Wang, X. H. Xia, 2009, A green approach to the synthesis of graphenenanosheets, *ACS Nano*, 3: 2653–2659.
- [52] Zhu, Y.; Murali, S. 2010, Graphene and Graphene Oxide: Synthesis, Properties, and Applications. *Adv. Mater.* 41: 3906–3924.
- [53]. W.J. Yuan, G.Q. Shi, 2013, Graphene-based gas sensors. *J. Mater. Chem., A* 1(35): 10078–10091.
- [54] P.J. Shaver, 1967, Activated tungsten oxide gas detectors, *Appl. Phys. Lett.*, 11(8): 255.
- [55]. Pearce, R.; Iakimov, T. 2010, Epitaxially grown graphene based gas sensors for ultra-sensitive NO<sub>2</sub> detection. *Sens. Actuators B Chem.* 155: 451–455.
- [56] Sun, F.; Xu, S. 2013, Application of Graphene Material in Gas-Sensor, *J. South China Norm. Univ.* 6: 93–98.
- [57] Jiang, T.; Wang, Z.; Li, Z.; Wang, W.; Xu, X.; Liu, X.; Wang, J.; Wang, C. 2013, Synergic effect within n-type inorganic–p-type organic nano-hybrids in gas sensors, *J. Mater. Chem. C*, 1: 3017–3025.
- [58] Tang X, Mager N, Vanhorenbeke B, Hermans S, Raskin JP, 2017, Defect-free functionalized graphene sensor for formaldehyde detection, *Nanotechnology*, 28:055501.
- [59] Lu, J.G.; Chang, P.; Fan, Z. 2006, Quasi-one-dimensional metal oxide materials—Synthesis, properties and applications. *Mater. Sci. Eng. R*, 52: 49–91.

- [60] Cao, G. 2004, Nanostructures and Nanomaterials; IC Press: London, UK.
- [61] Comini, E. 2006, Metal oxide nano-crystals for gas sensing. *Anal. Chim. Acta*, 568: 28–40.
- [62] Schedin F, Geim A K, Morozov S V, Hill E W, Blake P, Katsnelson M I and Novoselov K S 2007, *Nat. Mater.* 6: 652–5
- [63] Sen Liu, Ziyang Wang, Yong Zhang, Zhuo Dong and Tong Zhang, 2015, *RSC Adv.*, 5:91760–91765
- [64] H. Choi, H.Y. Jeong, D.S. Lee, C.G. Choi, S.Y. Choi, 2013, Flexible NO<sub>2</sub> gas sensor using multilayer graphene films by chemical vapor deposition. *Carbon Lett.*, 14(3): 186–189.
- [65] Ganhua Lu, Leonidas E Ocola and Junhong Chen, 2009, *Nanotechnology*, 20: 445502.
- [66] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, 2007, *Nat. Mater.*, 6: 652–655.
- [67] A. Salehi-Khojin, D. Estrada, K. Y. Lin, M. H. Bae, F. Xiong, E. Pop and R. I. Masel, 2012, *Adv. Mater.*, 24: 53–57.
- [68] G. H. Lu, L. E. Ocola and J. H. Chen, 2009, *Appl. Phys. Lett.*, 94: 083111–083113.
- [69] J. Yi, J. M. Lee and W. I. Park, 2011, *Sens. Actuators, B*, 155: 264–269.
- [70] A. Zopfl, M. Lemberger, G. Ruhl, F. Matysik, and T. Hirsch: 2014, *Faraday Discuss.* 173: 403.
- [71] Z. M. Ao, J. Yang, S. Li and Q. Jiang, 2008, *Chem. Phys. Lett.*, 461: 276–279.
- [72] P. A. Pandey, N. R. Wilson, and J. A. Covington: 2013, *Sens. Actuators B* 183: 478.
- [73] S. M. Cui, S. Mao, Z. H. Wen, J. B. Chang, Y. Zhang and J. H. 2013, *Chen, Analyst*, 138: 2877–2882.
- [74] Z. Y. Zhang, R. J. Zou, G. S. Song, L. Yu, Z. G. Chen and J. Q. Hu 2011, *J. Mater. Chem.*, 21: 17360–17365.
- [75] S. Deng, V. Tjoa, H. M. Fan, H. R. Tan, D. C. Sayle, M. Olivo, S. Mhaisalkar, J. Wei and C. H. Sow, 2012, *J. Am. Chem. Soc.*, 134: 4905–4917.
- [76] L. Al-Mashat, K. Shin, K. Kalantar-zadeh, J. D. Plessis, S. H. Han, R. W. Kojima, R. B. Kaner, D. Li, X. Gou, S. J. Ippolito and W. Wlodarski, 2010, *J. Phys. Chem. C*, 114: 16168–16173.
- [77] F. Yavari, E. Castillo, H. Gullapalli, P.M. Ajayan, N. Koratkar, 2012, High sensitivity detection of NO<sub>2</sub> and NH<sub>3</sub> in air using chemical vapor deposition grown graphene. *Appl. Phys. Lett.* 100: 203120.
- [78] H. Zhang, J.C. Feng, T. Fei, S. Liu, T. Zhang, 2014, SnO<sub>2</sub> nanoparticles- reduced graphene oxide nanocomposites for NO<sub>2</sub> sensing at low operating temperature. *Sens. Actuators B*, 190: 472–478.
- [79] L. Huang, Z. Wang, J. Zhang, J. Pu, Y. Lin, S. Xu, L. Shen, Q., Chen, W. Shi, 2014, Fully printed, rapid-response sensors based on chemically modified graphene for detecting NO<sub>2</sub> at room temperature. *ACS Appl. Mater. Interface*, 6(10): 7426–7433.
- [80] Z.Q. Wu, X.D. Chen, S.B. Zhu, Z.W. Zhou, Y. Yao, W. Quan, B. Liu, 2013, Enhanced sensitivity of ammonia sensor using graphene/ polyaniline nanocomposite. *Sens. Actuators, B* 178: 485–493.
- [81] B. Singh, J. Wang, S. Rathi, G.-H. Kim, 2015, Alignment of grapheme oxide nanostructures between microgap electrodes via dielectrophoresis for hydrogen gas sensing applications. *Appl. Phys. Lett.*, 106: 203106.
- [82] K. R. Nemade, S.A. Waghuley, 2013, Chemiresistive gas sensing by few-layered graphene, *J. Electron. Mater.* 42(10): 2857–2866.
- [83] Z. Wu, X. Chen, S. Zhu, Z. Zhou, Y. Yao, W. Quan, B. Liu, 2013, Room temperature methane sensor based on graphene nanosheets/ polyaniline nanocomposite thin film. *IEEE Sens. J.*, 13(2): 777–782.
- [84] Y. Ren, C. Zhu, W. Cai, H. Li, H. Ji, I. Kholmanov, Y. Wu, R.D. Piner, R.S. Ruoff, 2012, Detection of sulfur dioxide gas with grapheme field effect transistor. *Appl. Phys. Lett.*, 100: 163114.
- [85] Z. Jiang, J. Li, H. Aslan, Q. Li, Y. Li et al., 2014, A high efficiency H<sub>2</sub>S gas sensor material: paper like Fe<sub>2</sub>O<sub>3</sub>/graphenenanosheets and structural alignment dependency of device efficiency. *J. Mater. Chem.*, A 2(19): 6714–6717.

- [86] B. Chen, H. Liu, X. Li, C. Lu, Y. Ding, B. Lu, 2012, Fabrication of a graphene field effect transistor array on microchannels for ethanol sensing, *Appl. Surf. Sci.* 258(6): 1971–1975.
- [87] A. Aziz, H.N. Lim, S.H. Girei, M.H. Yaacob, M.A. Mandi, N.M. Huang, A. Pandikumar, 2015, Silver/graphenenano-composite modified optical fiber sensor platform for ethanol detection in water medium. *Sens. Actuators, B* 206:119–125.
- [88] Liu, S.; Yu, B. 2014, Enhancing NO<sub>2</sub> gas sensing performances at room temperature based on reduced graphene oxide-ZnO nanoparticles hybrids, *Sens. Actuators B Chem.*, 202: 272–278.

