**Chapter-1**: **Carbon–based nanosized hybrid materials: Introduction and Applications**

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**Abstract**

In this chapter, the significance of nanosized hybrid materials and their applications have been introduced. The general structural and electrical properties of the hybrid materials in the bulk and their gas sensing mechanism have been discussed. Comprehensive pictures of different types of carbon based materials, properties and their applications have been also included in this chapter. The relevant research on the Graphene based hybrid materials in past years is also discussed in literature review sections. Literature survey based on Fe/Rb based sensors finally the objective of the work also outlined.

# Introduction to Nonmaterial and Nanotechnology

A nanomaterial represents a revolutionary path for material Science and technological growth that concerns the organization of material at the nanometer scale (one billion times smaller than a meter). Nanotechnology exactly means any equipment on the nanoscale that has various applications in the real world. Nanotechnology literally include the manufacture and relevance of chemical, physical, and biological systems at scales ranging from individual molecules or atoms to submicron level, and also the assimilation of these resulting nanomaterials into bigger structure. It has the potential to change our point of view and outlook to provide us with the capability to resolve global issues. **[1-2]** The innovation and use of carbon nanomaterials has allowed foreword of many new areas of technology in biosensors, and bioelectronics. In recent years, nanotechnology has emerged as a multidisciplinary field, in which gaining a basic understanding of the electrical, optical, magnetic, and mechanical properties of nanostructures pledge to deliver the next creation of well-designed materials with sweeping relevance. Nanostructures can also provide solutions to scientific and ecological challenges in the areas of catalysis, solar energy renovation, and water management.

The creation of a new field with strange phenomena, there are new kinds of possibilities and effects become possible in composite circumstances at small scales was proposed by Feynman in his classic lecture “There’s Plenty of Room at the Bottom" in 1959 **[1].** This small scale material opened up the possibility of an huge number of technological application at miniature sizes. Over the past half century, electronic industry, especially silicon-based, has been continuously driven by the process of efficiency that has revolutionized the electronic field by providing compact, faster, power-efficient electronic devices and eventually low cost integrated circuits. These advances have found applications in infrastructure, computing, hauling, healthcare, and many more that affect every aspect of human life.

As a result of miniaturization, it has now become possible to shrink the complicated giant electronic devices such as computing machines to the size on the order of nanoscale making devices more powerful by integrating more and more transistors in a given chip area which is possible by making each transistor extremely small**[2]**. In the 21st century, the efficiency of modern equipment is well improved by the influence of great advance technology named as “nano”. Nanotechnology connects a bridge between atomic, molecular and bulk systems. Nanoscience primarily deals with synthesis of nanosized materials and characterization, exploration of nanostructured materials. The researchers can produce a variety of new material in the range of about 10-9 to 10-7 m, which possess different novel properties within the same material compared to their corresponding macro particles. New materials with outstanding mechanical, optical, electrical and magnetic properties are rapidly being developed for using in information technology, bioengineering and energy and environmental applications. The particle size has reduced to nanometer scale, impurities are eliminated, and perfections of particles are increased. The higher level of atomic homogeneity in the nanosized particles may enhance their structural, mechanical, optical, electrical, and magnetic properties of materials, would be better than the bulk materials.

Furthermore, the quantum size effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviors (**Manikandan et al., 2013; Zhang et al., 2011**). By the influence of nanoscience and nanotechnology, the size of devices in semiconductor industry is rapidly shrinking. At recent time, nanoscale devices are available which include tunneling junctions carbon nanotube transistors, single molecular transistors etc. The research being undertake on the interface between nanotechnology, biology and medicine.

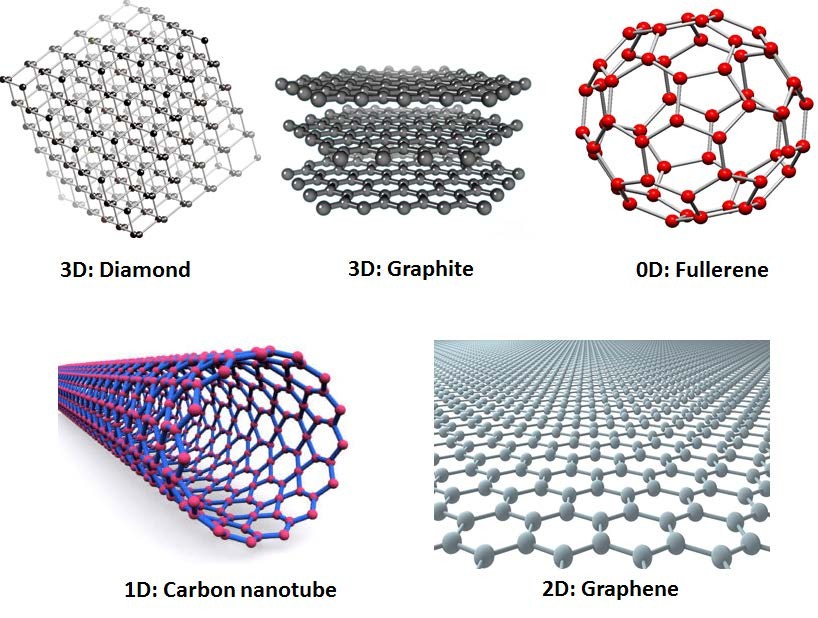
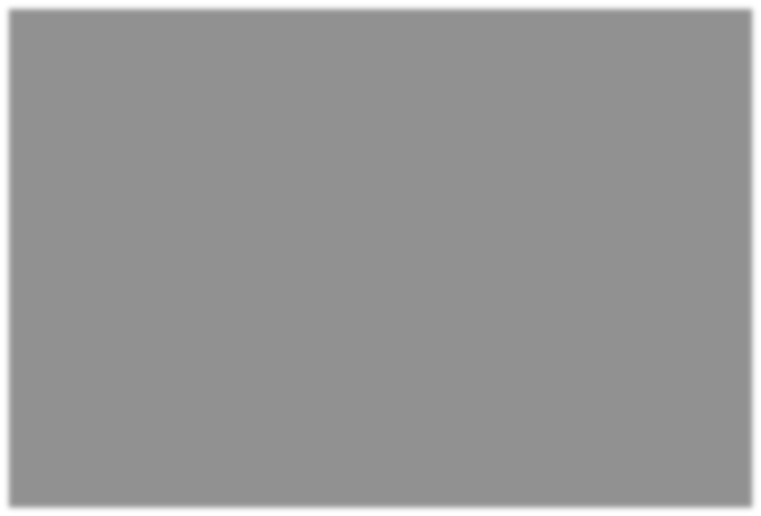
# Dimension of nanomaterials

The nano materials are in a selection of composition like wires, powders, tubes, fullerenes, nanofibers, crystallites, needles, particles, pillars, thin films, rods, quantum dots etc. based on their dimensionality, The given nanostructures fall in the following four categories: namely, 0D, 1D, 2D or 3D. Nanoparticles, quantum dots having all the dimensions in the nanometer range, are listed in 0D. Nanowires, nanorods, nanotubes are listed in 1D category because their diameter is in the nanometer range and length is outside the nano range. Similarly, the thickness of coatings, thin-film-multilayers is in the nanorange and length is outside the nanorange. These kinds of materials are fall in 2D. All dimensions of 3D materials are outside the nano meter range. These include bulk materials composing of the individual blocks, which are in the nanometer scale (1-100 nm). In terms of nanocrystalline composition, bulk nano materials can be composed of a multiple array of nanosized crystals, most typically in diverse orientations. The most versatile and promising materials that have made significant contributions in the field of nanotechnology, both from a fundamental point of view as well as for potential technological applications are novel low-dimensional carbon based materials: fullerenes **[3]**, carbon nanotubes (CNTs) **[4, 5]** and graphene **[6]**.

# The origin of different forms of carbon

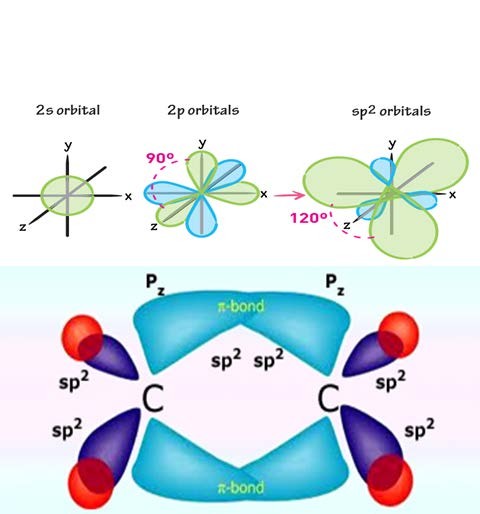
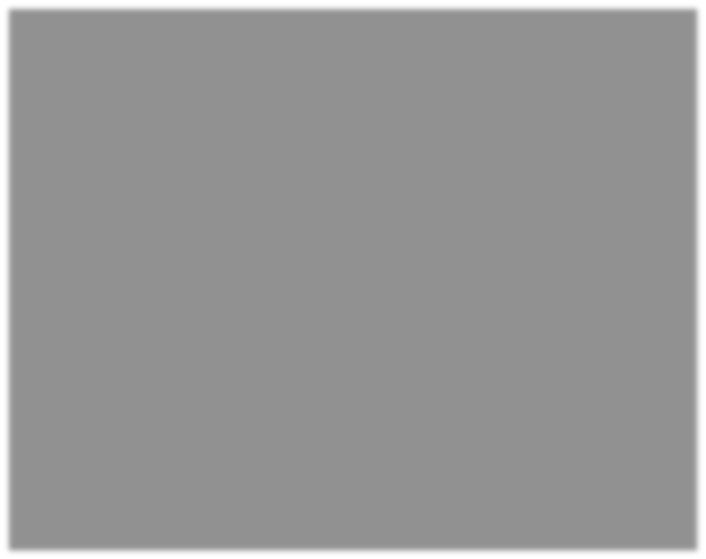
Carbon is one of the popular abundant elements in the earth’s shell and in the world. It is a essential element for the living world because of its chemical properties. Carbon has four valence electrons which make it a really versatile element as it can bind itself or to other atoms to form complicated networks **[7]** which is the basis of all known life. It is the only element in the periodic table that emerges in different forms with varying dimensions from zero-dimensional to three-dimensional. The three-dimensional forms of carbon, diamond and graphite, have been well known materials for centuries. Diamond has been used as jewelry and is known as an electrical insulator, whereas graphite has been used in pencils and is known as a good conductor of electricity. Moreover, the zero-dimensional fullerene (Bucky ball) discovered in 1985 by Kroto et al. **[3]**started the modern era of carbon materials, followed up with the discovery of one- dimensional multi-walled carbon nanotubules (MWCNTs) in 1991 by Iijima **[4]** and two years later single-walled carbon nanotubes (SWCNTs) by Iijima and Ichihashi **[5]**. The latest two-dimensional form of carbon named graphene was obtained by Geim and Novoselov in 2004 **[6]**. Graphene is the most studied material from a theoretical point of view **[8, 9, 10]** which is used to describe properties of various other carbon materials **[11]**. The electronic structure of graphene was predicted by Wallace in 1947 **[8]**. Initially, many scientists believed that two- dimensional crystals were too unstable to exist **[11-16]** due to thermal fluctuations. This argument was even supported by experiments **[17, 18].**Suddenly in 2004, the experimental discovery of free standing graphene **[6]** followed by the discovery of the other two-dimensional crystals **[19]** removed this belief. **Figure 1.1** illustrates the different allotropes of carbon. These structural differences in carbon allotropes can be understood from the fact that carbon is the sixth element of the periodic table and each carbon atom has six electrons occupying 1s2 2s2 and 2p2 atomic orbitals.

# Figure 1.1: Different allotropes of carbon. Adapted from reference [20].



The four electrons in the outer shell (2s and 2p orbitals) having similar energies can mix to form three types of hybrid orbitals. The process of mixing of different orbitals of nearly equal energy of an atom to form equal number of new hybrid orbitals is called hybridization. For example, the mixing of a 2s orbital with n=1, 2, 3 2p electrons results in spn hybridization. Therefore, a carbon atom can form four sp3, three sp2 or two sp hybrid orbitals as found in diamond, graphite and ethyne (C2H2), respectively. Graphene has sp2 hybridization, whereas fullerene and CNTs have deformed sp2 hybridization due to the circular curvature **[21-23]** which causes quantum confinement and the shifting of the three σ bonds, lying in the sp2 plane, to be out of plane. This results in more delocalized π orbital **[23]**. **Figure 1.2** shows (a) the sp2 hybridization of carbon **[24]** and (b) the deformed sp2 hybridization of carbon nanotubes **[25].** This symmetry change in the sp2 orbital makes CNTs more reactive, strong, and conductive as compared to graphite **[22, 23].** Among these carbon allotropes this thesis is focused on graphene.

**Figure 1.2: Schematic representation of sp2 hybridization of carbon and its derived materials. The three sp2 hybridized orbital are in-plane, with 2p orbital orthogonal to the plane. Reproduced from reference [24].**



* 1. **Background and Discovery of Graphene**

Graphite of which the term was consequent from the Greek word “graphein” (to write) in, is a layered planar configuration composed of carbon atoms that are given in a honeycomb network. The separation between carbon atoms in the lattice is 0.142 nm, and the distance between planes is 0.335 nm in graphite arrangement. In graphite, isolated single sheet that is composed of sp2 hybridized carbon atoms is called graphene. The term of graphene invent from the mixture of graphite and suffix–ene that is previous used in the classification and terms of polycyclic aromatic hydrocarbons **[26]**. The possibility of wrapping up graphene into 0D fullerenes, rolling it into 1D carbon nanotubes (CNTs) and stacking of it into 3D graphite makes graphene the central building block of all graphitic materials **[27]**. Despite the discovery of fullerenes in 1985 by Kroto, Curl, and Smalley **[28]** and shortly thereafter of CNTs in 1991 by Iijima **[29]**, graphene had already been studied theoretically for the first time in 1947 by P.R.Wallace

**[30]**, later in 1956 by J.W. McClure **[31]** and in 1984 by G.W. Semenoff **[32]**. The isolation of graphene was thought to be not possible thermodynamically according to Peierls **[33]**, Landau, and later Mermin **[34]** reported that a 2D lattice melts due to thermal fluctuations and long range crystalline order is prevented.

However, A.K. Geim and K. Novoselov in 2004 isolated the graphene by bonding agent put an end to masking tape and characterized it successfully **[35]**. They used mechanical exfoliation method to produce single graphene sheet from graphite. Then, graphene was transferred onto silicon dioxide substrate, characterized by optical microscopy and AFM as well as electrical measurements were conducted for it. These two Russian scientists both from Manchester University were awarded the 2010 Nobel Prize in Physics for these “groundbreaking experiments regarding the two-dimensional material graphene”. However, it should be noted that graphene like structures (graphite intercalation compounds GICs, graphite oxide GO and reduced graphene oxide rGO) have been already known since 1840s by German scientist Schafhaeutl who describe the addition of acid or alkali metal between the carbon lamellae (intercalation) and exfoliation of graphite with sulfuric and nitric acids **[36]**. After Schafhaeutl, Brodie (in 1859) **[37]**, Staudenmaier (in 1898) **[38]** and Hummers (in 1958) **[39]** also produced GO by exfoliating the graphite via high oxidizing reagents. In 1962, Boehm (he originally coined the term “graphene” in 1986) and coworkers for the first time reported slight, lamellar carbon containing small quantity of hydrogen and oxygen via chemical reduction of dispersions of GO in dilute alkaline media with hydrazine, hydrogen sulfide, or iron(II) salts. Just after this report, thermal reduction of GO was also published by the same group in 1962.

Boehm et al. made an assumption that thinnest lamella consisted of a single carbon layer and tried to prove that the thinnest lamella by transmission electron microscopy (TEM) micrograph densitometry measurements. Experimental error due to the thickness calibration standards however prevented the exact identification of monolayer carbon at that time **[40]**. It is worth to note that graphene (reduced graphene oxide rGO or chemically derived graphene CDG) not pristine graphene (without heteroatomic contamination) was for the first time described by H. P. Boehm and coworkers. Besides RGO sample synthesized by Boehm, ultrathin graphitic films and even monolayer pristine graphene was grown epitaxially on metal substrates (Ru, Rh and Ni in 1970) **[41, 42]**, on insulating carbides (SiC in 1975 and TiC, TaC in 1993) **[43]** and on graphite in 2001 **[44].**

# Table 1.1: Timeline of graphene showing attempts for research, isolation, and classification [35].

|  |  |
| --- | --- |
| **Year wise innovation concerning graphene** | |
| **1840-1958** | **Graphite oxide prepared by Schafhaeutl, Brodie, Staudenmaier,**  **Hummers and others.** |
| **1962** | **Boehm and co-workers prepared reduced graphene oxide (r-GO)**  **by chemical and thermal reduction of graphite oxide.** |
| **1968** | **Morgan and Somorjai obtain LEED patterns produced by small**  **molecule absorption ontp Pt (100).** |
| **1969** | **May interprets the data collected by Morgan and Somorjai as the**  **presence of monolayer of graphite on Pt surface.** |
| **1970** | **Blakeiy and co-workers prepared monolayer graphite by**  **segregating carbon on the surface of Ni (100); several subsequent reports follow.** |
| **1975** | **Van Bommel and co-workers prepare monolayer graphite by**  **subliming silicon from silicon carbide.** |
| **1986** | **Boehm and co-workers recommended that the term ‘graphene’ be**  **used to describe single layer of graphite-like carbon.** |
| **1997** | **Ruoff and co-workers micromechanically exfoliate graphite into**  **thin lamellae comprised of multilayer of graphene.** |
| **1999** | **IUPAC formalizes the definition of graphene: ‘The term graphene**  **only use when the reactions, structural relations or other properties of individual layers are discussed’.** |
| **2004** | **Geim and co-workers prepare graphene via micromechanical**  **exfoliation; numerous reports follow.** |

Not only was the production of pristine graphene known by epitaxial development in graphene research **[45]**. After peeling optically thin layers of graphite from highly ordered pyrolytic graphite (HOPG) with apparent strip, carrier dynamics of the sample was studied as well. Then after, visualization of few-nm thick graphite was reported in 1995 using atomic force microscopy (AFM) on top of HOPG **[46]** and using a scanning electron microscope (SEM) in 1999 **[47].** Besides production and visualization of ultra- thin graphite samples, electrical properties were also analyzed for the samples with thickness down to 60 layers in 1997-2001 **[48]**.Graphene monolayers for their cleavage on top of HOPG in 2003 **[49]** by STM and ultrathin epitaxial growth of graphite films composed of typically 3 graphene sheets from SiC in 2004 were reported by W. A. de Heer and coworkers **[50]**.

Geim declared his awareness of such earlier reports on the ultra-thin graphitic films and even the monolayers of graphene production, visualization and measurements. However; he finds all the previous reports as observational with the lack of reporting distinguishing properties of graphene **[41]**. He explains further that not only the ease of method (Scotch tape) that they have used to produce graphene, but also the isolation, identification, characterization and electronic measurements showing the astonishing electronic quality of graphene took researchers by surprise. Therefore their work did not disappear into oblivion to previous literature. Graphene is a single two-dimensional layer of carbon atoms densely packed in a hexagonal arrangement. Graphene’s structure gives rise to unusual properties. The strong sp2 bonding in graphene makes it 100 times stronger than steel, yet flexible due to its single layer, two-dimensional structure.

Graphene exhibits linear dispersion at low energies. Thus, charge carriers in graphene behave in a unique manner, they move as if they have zero effective mass and a velocity which is about 300 times slower than the speed of light **[51-55].** Graphene reveals ambipolar electric field-effect where the charge carriers can be electrons or holes with their density proportional to gate voltage **[56-58]**. Graphene possesses extremely high carrier mobility, a measure of how fast charges travel, **[59, 60]** leading to ballistic transport **[61]**, and also exhibits quantum hall effect **[62-66]**. In addition to these properties graphene also has low electrical noise and high thermal conductivity. These exceptional properties of graphene to be promising building blocks for next-generation

Electronics such as transistors **[67-77],** transparent electrodes including displays and touch screens **[78-81]**; chemical **[82-97]** and biological **[98-112]** sensors; and hydrogen storage devices **[113-120]**, to name a few.

From a wide range of applications of graphene, this thesis addresses the application of graphene for chemical (gas) sensing. The peculiar structural and electronic features of graphene that make it the most promising candidate for gas sensing are:

1. Its 2D structure with only surface and no volume, which maximizes the interactions between surface adsorbates and graphene,
2. Its metallic conductivity and hence low Johnson noise,
3. A little change of charge carrier density can result in detectable changes in electrical conductivity and
4. Few crystal defects which ensures a low level of 1/f noise caused by their thermal switching.

All these properties along with the immense mechanical robustness made graphene an excellent candidate for gas sensing applications **(Table 1.2)**. The target gas species act as dopants to the graphene layer and change the localized charge carrier concentration by inducing either electrons or holes that can be recorded by change in electrical conductivity.

# Table 1.2 Properties of graphene useful for gas sensors.

|  |  |
| --- | --- |
| **Property of Graphane** | **Reported value** |
| **Young modulus 1.05 TPa** | **1.05 TPa** |
| **Density** | **0.77 mg/m2** |
| **Carrier density** | **1013/cm2** |
| **Resistivity** | **10-6 Ωcm** |
| **Electron mobility at room**  **temperature** | **10, 000 cm2/Vs** |
| **Thermal conductivity at 27 °C** | **2000-5000 W/mK** |

* 1. **Chemo-resistive sensors**

A sensor is a tool that detects the transform in a variety of types of quantities and generates a analogous output, generally as an electrical or optical signal read by an observer or an device. Sensors are broadly classified into physical sensors and chemical sensors. Physical sensors measure various physical quantities like sound, pressure, temperature, velocity, flow, liquid level, electric field etc. As per IUPAC classifications (Hulanicki et al. (1991)), “A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information, mentioned above, may invent starting a chemical reaction of the analyte or from a physical property of the system investigated.”

Chemical sensors possess two basic functional parts, a receptor and a transducer. “In the receptor component of a sensor the chemical information is transformed into a form of energy which may be considered by the transducer.” while “The transducer part is a device capable of transforming the energy carrying the chemical information about the sample into a useful analytical signal. The transducer as such does not show selectivity.”(Hulanicki et al. (1991)).

# Need for a Gas Sensor

Gas sensor is a type of chemical sensor capable to translate the chemical properties of a volatile gas into electrical signals. Gas sensors have been a subject of interest ever since it was observed that semiconductor’s conductivity is affected by reducing or oxidizing ambience and eventually their successful exploitation for environmental monitoring, home safety and chemical controlling. In this regard, numerous materials such as metal oxides, sensitive organic layers, conducting polymers etc. have been extensively explored for their gas sensing behavior. A sensor is a device that detects a physical or chemical species and converts it into a measurable electrical signal output. A good and efficient sensor is characterized by parameters such as high sensitivity, selectivity, stability, fast response time and recovery time. Gas sensors thus find a vide applicability in several areas, some of which are as follows (Parthangal (2007)):

1. Detection of carbon monoxide, nitrous oxides, ammonia and volatile organic compounds (VOCs) like LPG for domestic and industrial safety.
2. Breath analysis for diabetes, gastro intestinal disorders and alcohol detector for checking drunken drivers.
3. Detectors for chemical and biological warfare agents like phosgene, chlorine, sarin, tabun etc.
4. Freshness monitors for medical diagnostics of food processing units and aroma sensors for baking, roasting processes etc.
5. Detectors for chlorofluorocarbons and greenhouse gases for air quality measurement based on industrial and automobile wastage with the purpose of environmental safety.

# Sensor Specification and Characteristics

The desired specifications of any sensor material are:

* **Sensitivity-** it is a measure of the ability of a gas sensor to detect changes. Sensitivity is expressed as the ratio of the change in current or resistance of the sensor in the presence of the gas to the original current or resistance in air at a fixed temperature:

S = 𝐈gas

𝐈𝐚𝐢𝐫

# x 100 (1.1)

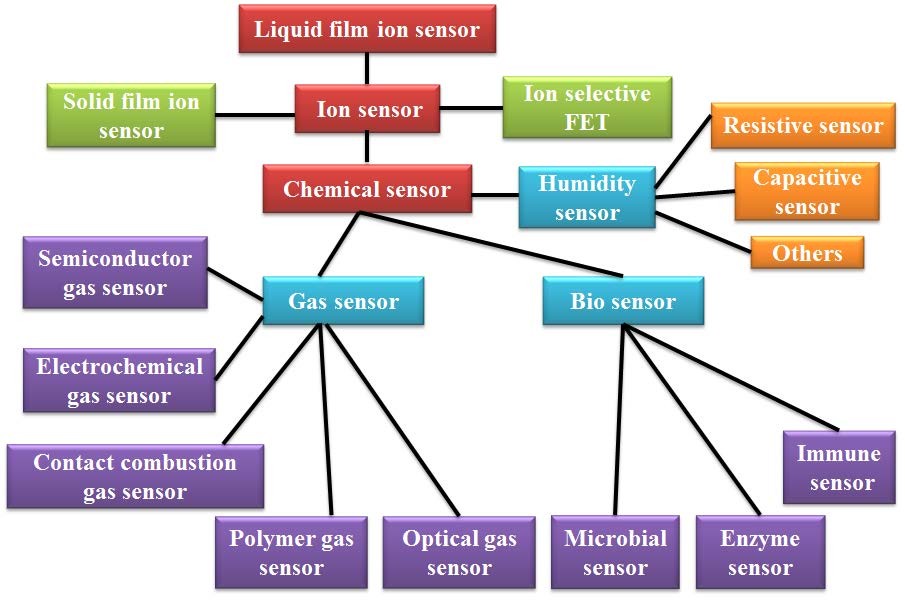
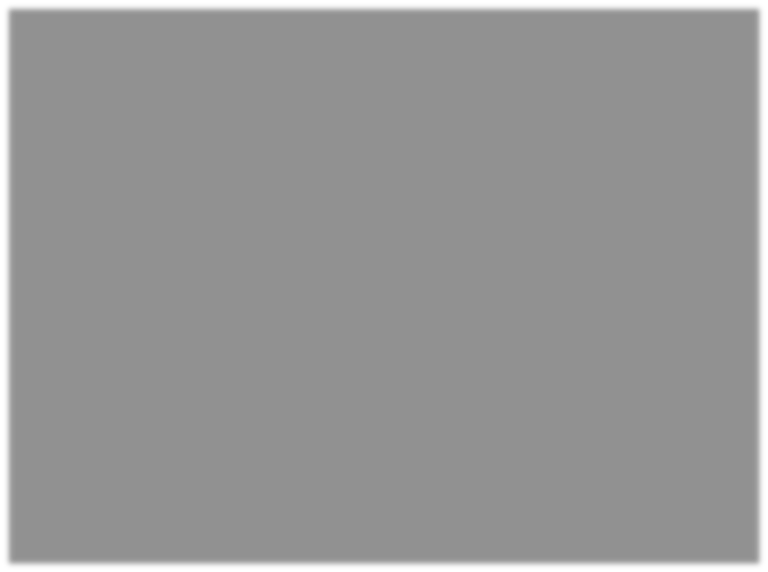
* **Selectivity-** it indicates the ability of a sensor to measure only a particular target gas.
* **Response time-** the time for a sensor to respond to changes in the environment.
* **Recovery time-** the time for a sensor to come back to baseline (original) value after the elimination of the measured gas.
* **Stability-** it is the ability of a sensor to provide reproducible results over a certain period of time, retaining all the above defined parameters. In addition, sensors should be economical, low power consuming and reliable (Parthangal (2007)).
* **Repeatability-** Repeatability is the degree to which test results are consistent when gas sensors are continuously tested in the same test environment. Repeatability can affect the working life of the sensor.
* **Limit of detection (LOD) -** The LOD is the minimum gas concentration that gas sensors can detect. The concentration requirements of the detection limit will be different for different application areas. LOD is usually defined on the basis of signal to noise ratio (S/N), that is, the signal measured by the low level sample is compared with the signal measured by the blank sample to calculate the minimum concentration that can be reliably detected. The detection limit is generally determined by an S/N of 3:1.
* **Optimum temperature -** The Optimum temperature is the temperature that can gives the gas sensor its highest sensitivity. The adsorption and desorption rate of gas depends on the reaction temperature, and different sensing characteristics are obtained at different operating temperatures

# Chemical Gas Sensors

The Chemical gas sensor is a device that dealings a change in its conductivity upon interface with chemical vapor or gas. All chemical gas sensors detect, identify and measure gas concentration through electrical or optical signals. Human nose generally employs sensory panels for assessing the quality of the substances through odour, but they suffer a major limitation of being affected by certain physical and biological factors and hence this method is extremely subjective (Pearce et al. (2003)). Also, it is unable to sense very low concentration of certain gas species as well as odourless gases. This necessitates the employment of a gas sensing device to fulfill the requirements.

# Types of Chemical Gas Sensors

Chemical gas sensors are broadly classified as catalytic bead, solid state, electrochemical, piezoelectric and infrared sensors (Korotcenkov (2007)). Catalytic bead sensors belong to thermometric sensor devices which convert the temperature changes generated by chemical reactions into electrical signals. In the presence of hot catalyst, oxidation occurs in a chemical reaction, releasing heat and consequently causing the increase in the temperature of the catalyst when exposed to a flammable gas or vapor. Solid state sensors employ the use of a semiconducting material deposited between two metallic electrodes on a substrate embedded with a heater which detect adsorbed gases on the surface of sensing element. Electrochemical sensors usually detect electroactive species involved in chemical recognition processes, making use of charge transfer from a solid or liquid sample to an electrode or vice versa. They generally consist of three active gas diffusion electrodes viz. sensing, counter and auxiliary electrodes immersed in a common electrolyte, where interaction of gas molecules with the sensing electrode leads to a change in the measured current between the electrodes. Sensors based on piezoelectric effect undergo a change in surface mechanical oscillation frequency upon interaction with gases. Infrared sensors use IR radiation to thermally excite gas molecules and sense gases based on their absorption or transmission spectra. Each sensor type has its own advantages and disadvantages depending upon the application. Catalytic bead sensors having advantage in high temperature and harsh environment; solid state sensor for domestic and industrial safety; electrochemical sensors for toxic gas detection; infrared sensors for volatile organic compound (VOC) and surface acoustic wave (SAW) devices for chemical warfare agents etc. (Parthangal (2007)).



# Figure 1.3: Classification of sensor.

**Table 1.4: Comparison of the five types of gas sensors [121].**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sensor Type** | **Detectable Gases** | **Linearity** | **Power consumption** | **Response Time** | **Life Expectan cy** |
| **Electrochemical** | **Gases which are electrochemically active, about 20**  **gases** | **Linear at room temperature** | **Lowest, very little power consumption** | **<50s** | **1-2 years** |
| **Catalytic** | **Combustible gases** | **Linear at 400**  **°C to 600 °C** | **Large, need to heat up to 400**  **°C to 600 °C** | **<15s** | **Up to 3**  **years** |
| **Solid-state** | **About 150 different gases** | **Linear at operational temperature** | **Large, need heating element to regulate temperature** | **20s to 90s** | **10+ years** |
| **Non-dispersive infrared** | **Hydrocarbon gases and carbon dioxide** | **Nonlinear, need**  **linearized procedure** | **Small, mainly consume by infrared source** | **<20s** | **3 to 5 years** |
| **Photo-ionization** | **Volatile organic compound (VOCs)** | **Relatively linear** | **Medium, mainly consume by ultra-violet source** | **<3s** | **Depends on ultra-violet source,**  **normally 6000h** |

# Graphene as gas sensors

Sensors have a considerable impact in daily life which has revolutionized the recent development. Gas or chemical sensors are drawing great attention because of their broad range of applications from environmental, industry monitoring, homeland protection to space exploration, and many more. Detection of environmental pollutants and hazardous gases has always been a serious concern, especially with the increasing concerns of global warming. There is a strong demand of highly efficient gas sensors capable of monitoring and controlling the ambient environment. High-performance sensors are also required for detection of explosive and toxic gases in industries, and for nerve agent sensing for homeland security. Identification of atmospheric components of various planets is another application of gas sensors **[122]**. A tremendous progress in nanotechnology has created the potential to build highly sensitive, compact sensors with low cost and low power consumption. Graphene have a large surface area **[123-125]** with every carbon atom on their surface in direct contact with surrounding atmosphere, making their electronic and mechanical properties extremely sensitive to small changes in their environment **[126]**. Hence, enabling the fabrication of miniaturized sensors capable of detecting a number of molecular species with high sensitivity, excellent selectivity, and fast response and recovery time. Sensing properties of graphene are based on the local changes in their electrical properties induced by charge transfer from molecules adsorbed on their surface. Such changes can be easily detected by measuring electron current signals. The important effect is the charge transfer between adsorbed molecules and graphene which actually causes a shift in the position of the Fermi level, thus affecting their electrical properties. The nature of doping, whether it is p-type or n-type, is determined by the direction of charge transfer **[126]**. The p-type doping of devices is caused by electron-accepting adsorbents that shift the Fermi level downwards toward valence band, whereas the n-type doping is achieved by electron-donating adsorbents that up shift the Fermi level away from the valence band **[82, 126].**

Recently, the possible use of graphene as a highly sensitive gas sensor is also reported **[88-97]**. The sensing characteristics of graphene have been attributed to its two- dimensional structure and the extraordinary mobility of charge carriers **[88, 92]**. Since graphene is all surfaces, no bulk, thus there is a huge scope for studying the surface dependent gas sensing phenomenon on its surface. The large surface area gives very high sensitivity and the high electron mobility gives ultra-fast response times. Graphene is superior because of its high electrical conductivity (even if there are few carriers) as well as low noise properties **[31, 39, 50, 88]** which make the local change in its electrical properties, due to adsorption of gas molecules on its surface, detectable. Schedin et al.

**[88]** have reported that the adsorption of gas molecules (NO2, NH3, H2Oand CO) on graphene surface induces a change in the local carrier concentration and hence changes its resistivity. This helps in the fabrication of highly sensitive gas sensors, even for single molecule detection. Motivated by these findings Leenaerts et al. **[89]** have presented their theoretical study to investigate the adsorption of NH3, H2O, NO2, CO and NO on graphene using first principle calculations. The charge transfer between the adsorbents and graphene was investigated and found to be almost independent on the adsorption site but it depends strongly on the orientation of the adsorbate with respect to the graphene surface.

Dan et al. **[90]** have reported on experiments where the sensor response of graphene monolayer was measured for analytes such as water vapor, nonanal, octanoic acid, and trimethyle amine (TMA). They have observed that the contamination layer (resist residue due to conventional nanolithography) on graphene surface chemically doped the graphene and acted like an absorbent layer that absorbed vapor molecules at the graphene surface, thereby increased the sensor response. They have also demonstrated a cleaning process which removed the contamination layer and allowed the measurement of intrinsic chemical responses of the graphene monolayer. These intrinsic chemical responses were found to be small, even when the device was exposed to strong vapor such as NH3. These findings still indicate a number of desirable characteristics of graphene sensors. Studies on sensing performance of graphene have also been presented by Fowler et al. **[91]**, Arsat et al. **[92]**, Ko et al. **[93]**, Joshi et al. **[94]**, Yoon et al. **[95]**, and Rumyantsev et al. **[96]** for detection of NO2, NH3, H2, CO, O2, CO2 gases and different chemical vapors (chloroform, acetonitrile etc.).Graphene have shown their potential for detection of various molecular species with high sensitivity in ambient conditions. However, their performance is limited to those molecular species that get adsorbed on their surface causing a detectable sensor response. On the other hand, the sensor response of clean graphene (without resist residue on the surface) to water vapor, TMA, octanoic acid **[90]**, as discussed above, and to DMMP and PA **[127]** was found to be very small. To overcome this limitation of graphene, functionalization is a genuine approach to tune their electronic properties.

The functionalization can be simply divided into a chemical (covalent) and physical (noncovalent) interactions between adsorbed molecules and graphene. Chemical functionalization relies on the covalent bonding between carbon surface and functional groups and involves a change of hybridization from sp2 to sp3 disturbing the π conjugation system of the graphene sheet which alters the physical properties of graphene strongly. This functionalization can be achieved by reaction with highly chemical reactive molecules. In contrast, noncovalent functionalization does not destroy the π conjugated system which allows no change in graphene and preserves their intrinsic structure and properties. Noncovalent functionalization includes interaction with aromatic compounds and polymers, employing van der Waals, π − π stacking or hydrophobic interactions **[128, 129, 130].**The effect of functionalization of graphene with polymers and metal nanoparticles on their sensing properties in terms of enhanced reactivity and sensitivity towards various inert molecular species have been reported in the literature by Lu et al. **[127]**, Kong et al. **[131]**, Kauffman et al. **[132, 133]**, and many other groups **[134-140]**. Despite continuing experimental progress in gas sensing applications of graphene the underlying mechanism of gas adsorption and detection is not very clear and needs an in-depth understanding. The path breaking experiments on functionalized graphene have raised challenging issues for theory and modeling, especially, on how to describe the dynamics in the presence of dopants for electronic transport measurements. To address these issues a quantitative and detailed understanding of the basic molecular interaction and electronic transport in such nanohybrids is needed.

# Advantages of graphene-based gas sensors

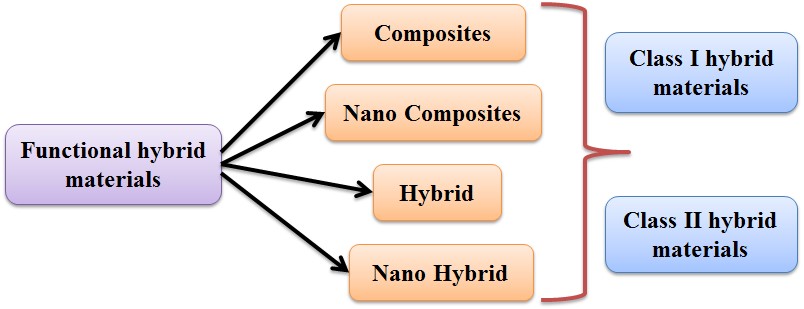
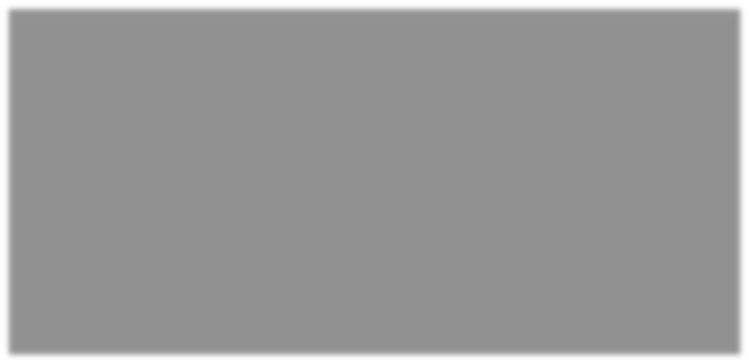
Graphene proves to be a good candidate for the development of highly sensitive gas sensors due to its advantageous properties such as:

* + - 1. The extremely high surface-to-volume ratio of graphene with all atoms exposed to surface adsorbates allows this nanomaterial to detect even the lowest concentration of target species i.e. sensitivity down to single atom or molecule.
      2. The electronic and mechanical properties of graphene can be easily utilized for sensing signal transduction.
      3. The interaction of graphene with specific molecules can be enabled by its functionalization with polymers, metals or other modifiers thereby improving the selectivity dramatically.
      4. A notable variation in carrier concentration could be recorded even with few charge carriers induced by the target species, due to low intrinsic noise of graphene. **(e)** Four-probe devices can be fabricated using graphene monocrystals.

**(f)** Compared to other graphitic materials like CNTs, graphene and its oxide can be produced economically.

# Functional hybrid materials for gas sensing application:

The last decade has witnessed a paradigm shift of focus for sensor development from traditionally used materials like glass, silicon etc. to bio-origin or environmentally benign materials. This will result in achieving the ambitious goals of sustainability. Homeland security/Environmental monitoring is an important issue in terms of national security and safeguarding the lives of people. In this regard, designing bio-derived sensing platforms are of outmost importance fulfilling the dual targets of detection of explosive materials and subsequently helping in the control of soil, water and air. The **Figure 1.4** depicts the classification of functional hybrid materials. The field of functional hybrid materials is widely recognized as one of the forefront areas with implications in research areas like optics, ionics, electronics, energy, mechanics, environment, biology and medicine. Such hybrid materials find extensive applications in various fields which particularly depend on the properties and functional characteristics of these materials.



# Figure 1.4: Classification of functional hybrid materials

In this regard, chemical composition, morphological and structural parameters play fundamental roles. These materials find wide applications as smart membranes, separation devices, new generation of photovoltaic and fuel cells, functional smart Coatings, photocatalysts, new catalysts, sensors, smart microelectronics, photovoltaic and micro-optical components etc. Different types of functional hybrid materials are reported in the literature namely-

1. **Nanoclay hybrid materials:** These are expected to have a potential as nanoscale fluorescent reporters and optical probes for photoluminescence based analytical and diagnostic applications. Specifically, diagnostic applications include bio imaging of disease related biomarkers. An important example is attachment of target specific biomolecules like proteins to Si (OH) x groups etc.
2. **Polymer-nanoparticles hybrid materials:** The integration of inorganic nanoparticles as an additive to enhance polymer properties has led to the emergence of polymer- nanoparticles hybrid materials**.** The addition of small amount of nanoparticles (1-10) % provides property enhancement compared to larger conventional loadings of (15-40) % of micrometer-scale inorganic fillers**.**
3. **Polymer-cluster hybrid materials:** These hybrid materials are formed via assembling metallic oxo-clusters into macroscopic networks**.** Such metallic oxo-clusters are also encountered extensively in MOFs.
4. **Nanohybrids:** These are atomic or molecular level mixture of two or more materials formed via chemical bonds. Extensive research is underway for the synthesis and development of nanohybrids materials for varied applications. Khan et al. has prepared nanohybrid materials based on poly propylene carbonate (PPC) for chemo sensing applications toward ethanol.
5. **Composites:** These are mixture of materials comprising of matrix and micron- level dispersion**.** Composite hybrid materials have recently emerged as an important class of materials having wide applicability.
6. **Nanocomposites:** These refer to sub-micron level mixture of similar kinds of materials**.** Sure et al. has reported the development of iron oxide-Polypyrrole nano-composites for gas and humidity sensor**.** Another study reports the development of Ni/SiNWs for capacitive humidity sensors**.**

# Literature survey based on additive materials:

Noble metals are most preferred elements as an additive for sensors and catalytic applications. These cations support the adsorption of gaseous molecules, increase sensor sensitivity and enlarge the amount of reagent converted by the catalyst and aid in formation of adsorbing centers. There are several literature for improving the sensor performance in the view of operating temperature and selectivity such as addition of metal/metal oxides. The addition of noble metal catalysts (Pt, Pd, Rb etc.) on the sensor surface improves the sensitivity of the sensor. The catalyst increase the active surface site on the sensor surface for the adsorption of test gases as well as lowers the activation energy required for the sensing reactions to take place and in turns improves its sensing performance. The influence of Alkali metal cations on the catalytic or sensing properties of Rb is recognized with the carbonate characteristics of the oxides concerned (Yamauret al., 2004). The basic characteristics of Alkali metal oxides may support some sensing (or) catalytic aspects, such as gas adsorbing midpoint. It is therefore expected that the concomitant use of noble metals and Alkali metal cations can create some kind of synergetic effect, resulting in high performance metal oxide-based sensors (or) catalysts.

# Literature survey based on Fe Modified Sensors

Ning Lv et al. **[152]** reported that the preparation of N-type Fe2O3 nanobelts and P-type LaFeO3 nanobelts by electros pinning. They observed that the at optimum operating temperature of the gas sensors fabricated from Fe2O3 nanobelts is 285 ◦C, whereas that from LaFeO3 nanobelts is 170 ◦C. Under optimum operating temperatures at 500 ppm ethanol, the response of the gas sensors based on these two materials is 4.9 and 8.9, respectively. The results show that LaFeO3nanobelts exhibit good selectivity to ethanol, making them promising candidates as practical detectors of ethanol.

Mane et al. **[153]** described that the Graphene oxide (GO), iron oxide (Fe2O3) and GO@Fe2O3 composite sensors, achieve at 0.1, 1.0,10 wt% concentrations of GO in Fe2O3, of dissimilar structure, morphologies, porosities, surface areas, and charge transfer resistances, etc. have been produce via a easy, economic, solid-state synthesis approach and predict as an efficient room-temperature (27 °C) liquefied petroleum gas(LPG) sensors. The electrical conductivity of the composite sensor decreases due to production of a variety of charge transport channels with increase of GO wt% concentration. However, for absorption more than 1 wt% of the GO both pore-size and surface area ofGO@Fe2O3 decreases. The 1 wt% GO@Fe2O3 composite sensor reveals∼35% room-temperature (27 °C) LPG sensitivity @100 ppm level over pure GO (∼15%) and Fe2O3 (∼25%), and also otherGO@Fe2O3 composite sensors (20%–30%), recognized to their enlarged specific surface area and condensed charge transfer resistance, which, in general, have more surface active surface sites for adsorbing LPG molecules than those of individual and other low-surface area sensors.

Park et al. **[154]** reported that flute-like porous a-Fe2O3 nanorods and branched nanostructures such as pentapods and hexapods through dehydration and recrystallization hydrate thermally produce b-FeOOH precursor. TEM and high- resolution TEM and selected area electron diffraction analyses reveal that the nanorods, which grow along the [110] direction, have nearly hollow cavities and porous walls with a pore size of 20–50 nm. These distinctive iron oxide nanostructures offer the first opportunity to study their magnetic and gas sensing properties. The nanostructures exhibited unusual magnetic behavior, with two different Morin temperatures under field- cooled and zero field-cooled conditions, owing to their shape anisotropy and magneto- crystalline anisotropy. Furthermore, the a-Fe2O3 nanostructures demonstrate much better sensing performance towards ethanol. In addition, the a-Fe2O3 nanostructure based sensor can selectively identify formaldehyde and acetic acid among other toxic, corrosive and irritant vapors at a low working temperature with rapid response, high sensitivity and good strength.

Jing et al. **[155]** reported that the creation of Ni-doped and un-doped γ-Fe2O3 nanopowders by anhydrous solvent method, using lauryl alcohol as anhydrous medium. The rod-like products, 15 mol% Ni-doped γ-Fe2O3 Nano powders with the length of ∼140 nm and the width of ∼13.3 nm, are seen by TEM. The untried results reveal that both the undoped and the 15 mol% Ni-doped γ-Fe2O3 sensors exhibit good sensitivity to acetone and ethanol, whereas poor sensitivity to petrol, CH4, H2, and CO at working temperature of 240 and 270 °C, respectively. Compared with the undoped sensor, the 15 mol% Ni- doped γ-Fe2O3 sensor presents high sensitivity, less response–recovery time and good long-time stability, indicating that it might be a promising sensor for detecting acetone and ethanol gases. The synthesis method and doping environment can profoundly control the morphology as well as the gas sensing properties of the sensors. Safa et al. **[156]** described that synthesized Encapsulated ZnO nanorod arrays are on glass substrate by a two-step route, hydrothermal followed by dip coating. They found that the encapsulating process increases the rod diameters from ∼20 to ∼40 nm without any significant effects on the microstructure, even with a Fe-doped ZnO encapsulated layer. Their optical studies had shown a reduction in the band gap of the encapsulated nanorods. The electrical measurements had shown a remarkable reduction in resistance due to the encapsulation process, especially in the encapsulated ZnO nanorod film with a Fe- doped-ZnO shell layer. The gas-sensing properties of the sensors observed to different concentrations of ethanol vapor at temperatures up to 270 ◦C. An optimum operating temperature was found for each sensor in which high sensitivity and fast recovery were achieved. The response was enhanced from 11.7 to 19 by Fe doping on the ZnO encapsulated nanorod at a constant 500 ppm concentration of ethanol.

Neri et al. **[157]** reported that the synthesized Ag@α-Fe2O3 nanocomposite having a core– shell structure by a two-step reduction-sol gel approach, together with Ag nanoparticles mixture by sodium borohydride as the reducing agent in a first step and the consequent mixing with a Fe+3solfor α- Fe2O3 coating. The synthesized Ag@α- Fe2O3 nanocomposite has been distinguish by various techniques, such as SEM, TEM and UV- Vis spectroscopy. The electrical and gas sensing properties of the synthesized composite towards small concentrations of ethanol have been estimated. The Ag@α- Fe2O3 nanocomposite showed improved sensing characteristics than the pure α- Fe2O3. The peculiar hierarchical nano-architecture and the chemical and electronic sensitization effect of Ag nanoparticles in Ag@α- Fe2O3 sensors were assumed to play a key role in modulating gas-sensing properties in association to pure α- Fe2O3 sensors.

Patil et al. **[158]** reported that the α- Fe2O3 nanorods were successfully synthesized without any pattern by calcining the α–FeOOH precursor in air at 300 ◦C for 2 h and their LPG sensing characteristics were inspected. The α –FeOOH precursor was organized through a easy and less cost wet chemical route at low temperature (40 ◦C) using FeSO4·7H2O and CH3COONa as starting materials. The formation of α-FeOOH precursor and its topotactic transformation to α- Fe2O3 upon calcination was established by X-ray diffraction measurement (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) investigation. In case of α-Fe2O3 nanorods exhibited excellent gas sensing characteristics such as, more gas response (∼1746–50ppm LPG at 300◦C), extremely fast response (∼3–4 s), relatively less recovery (∼8–9 min), outstanding repeatability, excellent selectivity and lower operating temperature (∼300 ◦C). Furthermore, they can be reliably used to monitor the attention of LPG over the range (5–60 ppm). The untried results clearly demonstrate the potential of using α- Fe2O3nanorods as sensing material in the invention of LPG sensors. Plausible LPG sensing mechanism of the α-Fe2O3nanorods is also discussed.

Yang et al. **[159]** synthesized Porous ZnFe2O4 double-shell, york-shell, and solid microspheres using a grouping of hydrothermal technique and thermal treatment (carried out at appropriate temperature determined via gravimetric). The definite surface area is mixed by adopting different heating rates during the thermal treatment; double-walled structure is formed at advanced heating rates. Gas sensors based on ZnFe2O4 double- shell microspheres illustrate a promising response when tested with ~20 ppm acetone (Rair /Rgas = 13.6). The gas sensors clarify an almost linear response to acetone concentration and a low detection limit for acetone of 0.13 ppm. The observed gas sensing performance suggests that the ZnFe2O4 double-shell microspheres obtainable to them are prospective sensing materials for acetone detection.

Liu et al. **[160]** reported that an ultrasensitive methanol gas sensing device based on the quasi-molecular imprinting machinery. They applied the sol-gel method and combustion synthesis to arrange Ag-LaFeO3 based sensors. The morphologies and structures of the Ag-LaFeO3materials were inspect via various detection method. The ALSM and ALCM sensor fabricated using the sol-gel technique and combustion synthesis combine with quasi-MIT exhibit excellent gas sensing properties to methanol, in contrast with the two devices without the use of quasi-MIT. The results show that quasi-MIT establish the target gas in the fabrication method of the device, in performance an important role in the intend of the ultrasensitive methanol gas sensor. The sensing reaction and the optimum working temperature of ALSM and ALCM gas sensor are obtain 52.29 and 155°C and 34.89 and 155 °C, respectively, for 5 ppm methanol, and the highest reaction to other gases is 8. The ALSM and ALCM gas sensors make known excellent selectivity and response for methanol.

# Literature survey of Rb Modified Sensors

Yamazoe et al. **[161]** reported that among various single-metal oxides, In2O3, SnO2 and ZnO were establish to exhibit rather enhanced sensitivities to CO at 300°C and above. particularly In203 appeared to be most smart in view of the selectivity to CO over H2. It was further observed that the change of In203 with the addition of alkali metal carbonates, particularly Rb2CO3, were very effective for enhancing the sensitivity and the selectivity to CO. The sensor element using Rb-ln203 could notice 500-4000 ppm CO in wet air at 300oC adequately, while it’s cross sensitivities to other gases such as H2, CH4, C3H6, and NO were comparatively less. Catalytic activity test and TPD measurements showed that, as a reason for the supporting effects, the addition of Rb2CO3 to In203 improve the catalytic activity of CO oxidation. In addition, XPS data point out that, as another reason, Rb2CO3 forms the strongest p-n junctions with In203 among alkali metal carbonates.

Long et al. **[162]** proposed work on a novel strategy to make highly-stable NO2 sensor based on a pyro chlore-phase Gd2Zr2O7 oxygen performer. The incorporation of alkaline-earth metals distinctly improve the sensing performance of the Gd2Zr2O7 based sensors. The excellent sensor based on Gd1.95Ca0.05Zr2O7+δ shown rapid response- recovery characteristics with the maximum response current value (ΔI = 6.4 μA), tremendously short 90% response (3 s) and 90% recovery (35 s) time towards 500 ppm NO2 at 500 °C, which is better than that of commercial YSZ under the same condition. The ΔI value towards NO2 is much elevated than those towards other gases (CH4, C3H6, C3H8, CO, NO, SO2, C2H4, CO2 and C2H6), exhibiting outstanding selectivity for notice NO2. The response signal basically maintains a stable value of 6.4 μA after the sensors was stored for half a month and a month. The excellent selectivity and highly stability of the NO2 sensors based on Gd2−xMxZr2O7+δ are expected to a promising application in automotive vehicles.

Hirai et al. **[163]** reported that the synthesized Sr and Ba-aluminas in a single phase were in the MO-MgO-Al2O3 (M=Sr and Ba) arrangement by a solid state sintering technique. The electrical conductivity was measured at 873 K to 1473 K by an A.C. impedance technique. The electrical conductivities of Sr-alumina and Ba-alumina were 1.2x10-2 Sm- 1 and 6.7x10-4 Sm-1 at 1473 K, respectively. The activation energies of gradually cooled Sr and Ba-aluminas are 103.1 kJ mol-1 and 173.8 kJ mol-1 respectively. The EMF of the cell using Sr-alumina improved with increasing temperature and CO2 partial pressure. The cell with Sr-alumina could be used as a CO2 gas sensor at high temperatures. The sensor could be used at more than 1000 K. Shi et al. **[164]** shown that fabricated One-dimensional alkaline-earth metals composited SnO2 (Ae/SnO2) nanofibres were via electro spinning method, followed by thermal action at 600 °C for 5 h. Transmission electron microscopy (TEM) studies illustrate that the nanoparticles size of Ae/SnO2 was 5–7 nm, which was lesser than the pristine SnO2 nanorods attached by 20 nm nanoparticles. The Sr/SnO2 nanotubes shown an excellent sensing response toward NH3 gas at room temperature, lesser detection limit (10 ppm), higher response time (6 s towards 2000 ppm 16 s towards 10 ppm) and improved reversibility compared to the pristine SnO2 nanorods. The enhanced sensor performances were attributed to the enhanced conductivity of the Sr/SnO2. Mott–Schottky plots (M–S) and electrochemical impedance spectroscopy (EIS) measurements shown that the carrier density of Sr/SnO2 nanotubes was 3 fold of that pristine SnO2.

Docampo et al. **[165]** reported that Rubidium and cesium cations have been newly known as performer for perovskite solar cell performance. However, the impact of these inorganic cations on the permanence of the (FA0.83MA0.17) Pb (I0.83Br0.17)3 perovskite crystal lattice has not been fully understand yet. During the perovskite film mixture, RbPb (I1−xBrx) 3 is formed, while introduction to humid air leads to the rapid development of another hitherto unreported side phase (RbPb2I4Br). The formation of the Rb-rich side phases not only results in a loss of light incorporation but also extracts bromide ions from the photoactive perovskite phase, thereby reducing its band gap. In association, the moisture-assisted formation of a CsPb2I4Br phase upon Cs-addition occurs on a considerably longer time scale than its Rb analog. While the incorporation of Cs+ remains attractive for high-performance solar cells, the severe moisture-sensitivity of Rb-containing mixed halide perovskites may create further engineering challenges.

Matsuzawa et al. **[166]** reported that a CO gas sensor composed of rare earth metal oxide added to alkaline metal carbonate and alkaline earth metal compounds has been recently prepared. In their study, the effect of various additives to the rare earth metal oxide on the gas sensitivity was observed. They that Na2CO3 and CaO additives are effective in increasing the gas sensitivity and the Na2CO3-CaO-BaCO3-Y2O3 system has the maximum gas sensitivity among the samples observed. In case of XFUY study, it is observed that the CO2 gas sensitivity of the sensor is closely associated to the crystal structure of the gas-sensing materials.

Deng et al. **[167]** reported that Rubidium, cesium and its compounds play an significant role in traditional and high-tech fields. Rubidium and cesium property are rich in saline lakes and its useful investigation received subsequent achievement in high-tech fields. Solvent extraction method for the separation and extraction of brine with low concentration rubidium and cesium achieves the resultant laboratory research outcome, but the industrial creation has not been reported yet up to now. The method using t- BAMBP shows the superiority compared with other methods. However, the results are not ideal with the brine haveing high potassium. Gao et al. **[168]** reported that highly sensitive sensors for alkali metal ions based on complementary-metal-oxide semiconductor- compatible silicon nanowires SiNWs with crown ethers covalently immobilized on their surface are discussed. A densely packed organic monolayer ended with amine groups is commence to the SiNW surface via hydrosilylation. Amine-modified crown ethers, acting as sensing elements, are then immobilized onto the SiNWs through a cross-linking response with the monolayer. The crown ether–functionalized SiNWs recognize Na+ and K+ according to their complexation ability to the crown ethers. The SiNW sensors are highly selective and competent of achieving an ultralow sensing limit down to 50 nM, over three orders of magnitude lower than that of conventional crown ether–based ion-selective electrodes.

Dryuchkov et al. **[169]** reported that the fabrication of a highly sensitive sensor based on single-walled carbon nanotubes surface adapted with functional amino groups (-NH2). The report described the sensor potential for sensing of alkali (sodium, lithium, and potassium) metals. The results of computer simulation of the interaction process between the sensor and an arbitrary surface of the modified tube hold atoms of the studied metals are discussed in the report.

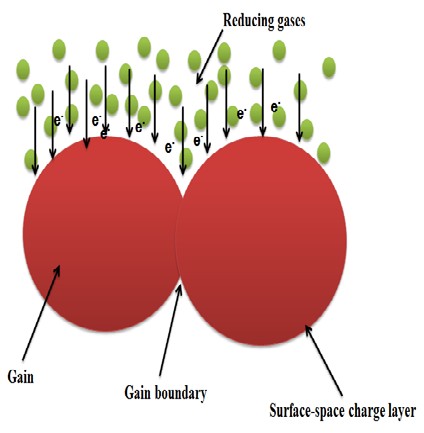
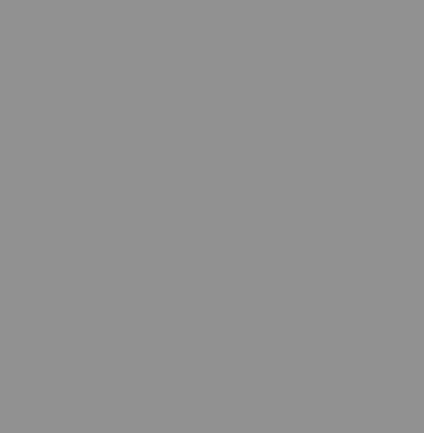
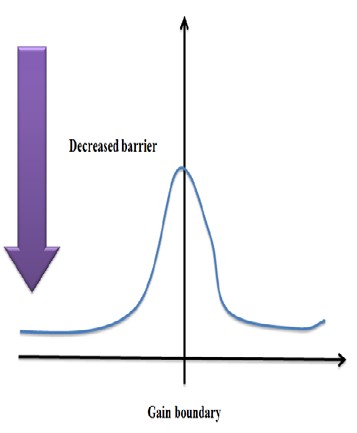
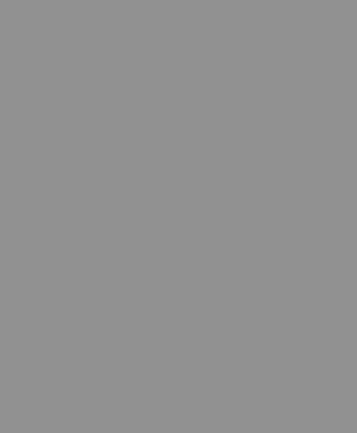
# Gas Sensing Mechanism for graphene based gas sensor

In view of that the gas-sensing mechanism of graphene is unsure and related research is exceptional here we just give a recognized point of view as a general introduction of the reference of other related literatures **[170–173].**

Graphene is intrinsically inert and nonselective, its great capability to conduct electricity and distinguishing features of ballistic transport of charges decide that this two-dimensional material is an best candidate to serve as a platform or a supporter, in which we can realize many specific functions by doping or compositing with other materials. Once combined with other materials physically or chemically, graphene can show the characteristics of the semiconductor in normal conditions, of which conductivity is determined by carriers’ concentration. For chemo-resistive type sensors, sensing materials show response to externalities by the change of conductivity, that is the variation of concentration of hole or electron carriers. Bulk porous materials usually have a large precise surface area, hence gas molecules can be easily adsorbed, following by the interaction between gas molecules and specific groups in the graphene surface, and then the gas molecules capture or donate electrons from the sensing material, which changes concentration of the semiconductor’s carriers.

Different doping and reaction conditions may guide to different types of graphene- based semiconductors (p-type or n-type). As we all know, p-type semiconductors refer to those who have a larger hole concentration than electron concentration. In p-type semiconductors, holes are the majority carriers and electrons are the minority carriers. As opposed to p-type semiconductors, n-type semiconductors have a larger electron concentration than hole concentration. In n-type semiconductors, electrons are the majority carriers and holes are the minority carriers. For example, one doped graphene shows characteristic of n-type semiconductors: when it is exposed to a reducing atmosphere, such as LPG and Hydrogen, it would get electrons from the gas molecules, leading to an increase of the electron concentration, i.e., a decrease of graphene’s resistance occurs. Likewise, when it is exposed to an oxidation atmosphere, such as CO2, it will deliver electrons to the gas molecules, leading an increase of hole concentration, leading to an increase of graphene’s resistance.

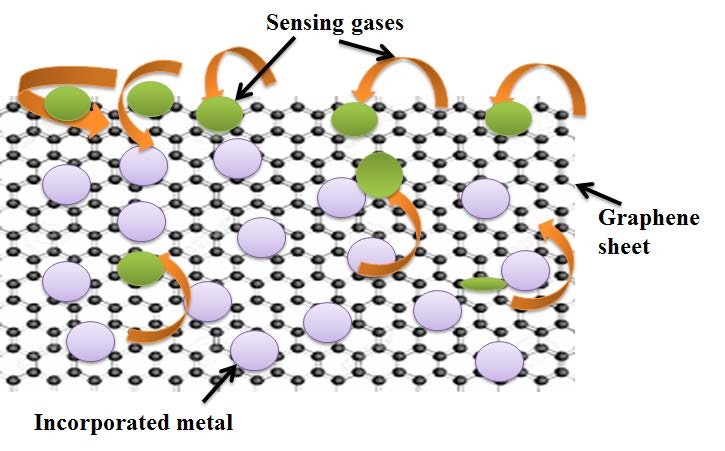
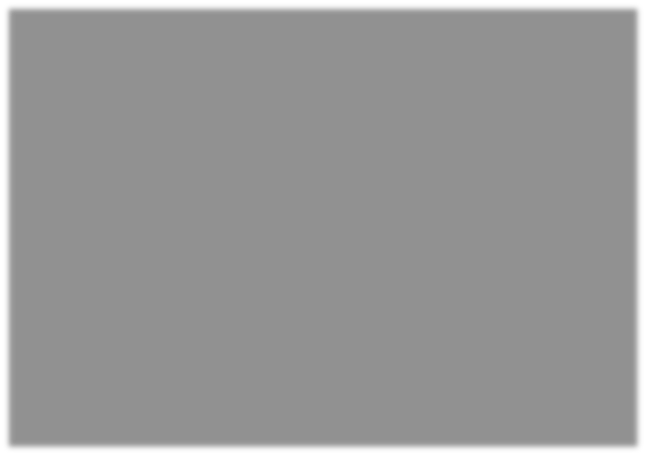
**Figure 1.5** demonstrates a general progress of gas sensing, which has been described above. This is the old and universal theory called “Oxygen anion barrier model,” which used to illustrate the mechanism of gas-sensing progress based on metal- oxide semiconductors **[174–177].**



# Figure 1.5 Oxygen Anion Barrier Model for reducing gases.

Schedin et al. reported that the graphene gas sensor can effectively detect the adsorption or dissociation behavior of a single gas molecule on the surface of graphene, due to the fact that the change of carrier concentration of graphene leads to the change in electrical conductivity (Schedin et al., 2007). Meanwhile, due to the existence of oxygen functional groups, GO and rGO usually show better sensing properties than graphene. When GO or rGO are exposed to the air, the oxygen functional groups of them mainly combine H2O molecules with hydrogen bonds and the adsorbed H2O molecules are transferred to H3O+, further encouraging the formation of ion channels on the surface of the sample. When they are in contact with adsorbed molecules, the hydrogen bonds will be destroyed, which inhibits the ionization reaction between oxygen functional groups and H2O molecules and leads to step-like changes in resistance (Ozcan et al., 2018). Prezioso et al. (2013) prepared a p-type gas sensor through GO drop-cast on standard interdigitated Pt electrodes and their sensing property to NO2 was analyzed. They also presented the sensing mechanism of the gas sensor: when NO2 molecules adsorbed on the oxygen functional groups, the electrons of the adsorption sites are transferred to NO2 molecules, which leads to the decrease of electron concentration in the surface of the sensing materials, giving a reason for the p-type behavior. In general, the sensing mechanisms of graphene hybrid are analyzed from the following three aspects.

* First, the introduction of nanoparticles can effectively prevent the aggregation of graphene sheets, thereby the graphene hybrid material is more favorable to form a 3D porous nanostructure with higher specific surface area, and more adsorption sites, vacancies, defects, and sp2-bonded carbon, which are beneficial to the adsorption of gas molecules (Russo et al., 2012; Zhang et al., 2015a).
* Secondly, the formation of p-n heterojunctions between graphene and metal/metal oxide enhances the gas sensing properties. Once the target gas molecules are in contact with these interfaces, the depletion layers at the heterojunctions will be modulated, the electron state will be changed, and the phenomenon of charge transfer is more active, which lead to a larger relative change of resistance of graphene hybrid material (Tran et al., 2014).
* Thirdly, when hybrid materials contain metal oxide (e.g., SnO2, ZnO, CuO, Co3O4), the sensing behavior can be explained by the surface-adsorbed oxygen (Bai et al., 2015). For n-type metal oxide material, the oxygen molecules O2 (gas) will capture electrons from the surface of metal oxide to form chemisorbed oxygen species (O−, or O2−), which leads to a high resistance of the sensor, as observed in the experiments (Jin et al., 2016).



# Figure 1.6 Scheme of the mechanism of the gas sensing property of metal incorporated graphene.

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