Chapter 1

Literature survey, objectives and scope of work

1.1 Introduction

The world we abide by, is highly influenced by sensors. In our daily life, we are surrounded by a wide variety of sensors. The food we eat in the breakfast is processed by using timing devices and temperature sensors. Commuting to the office in an automobile vehicle which is full of sensors, aiding in the operation and regulation of the vehicle. We encounter a wide variety of sensors in our homes, offices, market and cars etc. which are making our lives easy. Many different automatic tasks are possible due to the use of sensors [1].

Sensors are also an essential part of our life counting the safety, control, scrutiny, detection and awareness in general. Sensors are also becoming very important for disease diagnosis, and public care. Sensors are very well indulged in various industrial applications like process monitoring [2]. Various eloquent innovations and inventions are made on a daily basis. Nanotechnology involved new materials that are smarter, smaller and efficient for the fabrication of electronic devices to play a key role in future of sensor technology. To accomplish the development of ubiquitous sensors that possess high sensitivity, improved selectivity, greater stability at low cost and all other advantages are gained through miniaturization [3].

Nanotechnology has been the key reason behind the various breakthroughs in the technology till now and also assures to alter the changes in the technology in future in every aspect of life. [4]. Ever since the discovery of a variety of nanomaterials, their fascinating properties with supreme molecular geometry has not only encouraged the field of nanotechnology but has activated the attempts for advancement in physics, biology, chemistry and indeed the field of material science [5].

The term nanotechnology has been acknowledged from the fact that the particles having low dimensions, particularly less than 100 nm present themselves as nanostructures with totally modern characteristics and behaviour. The facts and observations confirmed that the nanostructures with low dimensions than usual often exhibit new physics and chemistry and thus escorting a unique behaviour confining upon the dimensions [6].

Sensors are the devices that respond to a stimulus and can be classified depending upon different criteria. Sensors can be classified or can be grouped further depending upon the mode of operation (optical, resistive, capacitive mass, piezoelectric etc.), kind of applications (environmental and food monitoring, medical diagnosis etc.) and recognition technique (molecular, DNA etc.) [4],[5]. Among various sensors like pressure sensor, temperature sensor, biosensors, weather sensor, acoustic sensor etc., gas/vapor sensor is one of the popular category where resistance or capacitance of sensing layer changes in the exposure of different gases and vapours [7]. Vapor sensors have a variety of applications in many fields such as- leakage detection of explosive gases (hydrogen), real time detection of toxic or pathogenic gases in industries, monitoring of environment, domestic safety, public security, indoor air quality monitoring, automobile applications, air conditioning in air planes, spacecraft etc. [8],[9]. Due to various applications, gas/vapor sensors have evolved over the years and various factors affecting the performance of the sensors have been improved. These factors include low cost, low power consumption, stability in performance, low operating temperature, high sensitivity, selectivity, fast response and recovery time. By improving these parameters, performance of gas/vapor sensors can be improved significantly [10].

One of the primary concerns in the present scenario is the establishment of new ways and fabrication of advanced devices for the detection of minimum volume of target species in user friendly and cost effective ways. Different methods and techniques have been proposed by researchers for the recognition and detection, but the nanomaterial based devices have come into the view as the dominant group of ultrasensitive electrical sensors for tracking down the chemical species or physical quantities.

One peculiar property of nanomaterials is high surface to volume ratio which has enabled them to be used as a sensitive layer in biomedical or chemical sensors by observing the changes in the electrical properties as induced by surface based chemical alteration. The surface to volume ratio enhances appreciably when the size of the structure is reduced and the surface phenomena dominates powerfully over the physics and chemistry of the bulk [11],[12].

Yamazoe in 1991, represented that minimizing the crystallite size improvises the sensor performance [13]. Nanostructured metal oxide possess carriers that are trapped in surface states and a few carriers are accessible for conduction. In this configuration, transition of electrons between surface and target vapour species is highly dominant, which has a great effect on sensor performance. Since then it was highly demanding to synthesize nanostructures that are beneficial for sensing for long time periods [14].

A number of metal oxides (both *p* type and *n* type) like SnO_2 [15], WO_3 [16], TiO_2 [17], ZnO [18], Fe_2O_3 [19], Cr_3O_4 [20] etc. have been extensively used as a sensing material by many researchers as they are easy to be synthesized and provide an acceptable response to different volatile organic compounds (VOCs) with good response and recovery characteristics. A stable structure, flexibility in production and low cost of metal oxides makes them more favourable for real time detection of various harmful VOCs [14],[21]. Therefore, semiconducting metal oxides have been known as a good sensing material since decades [22].

The extraordinary and adjustable electronic, physical and substance characteristics of carbon nanostructures allow new innovations and trends that can be applied in various applications. Carbon nanostructures e.g. the zero-dimensional (0-D) fullerene, one-dimensional (1-D) carbon nanotubes (CNTs) and two-dimensional (2-D) graphene, possess excellent mechanical and electrical properties. These emerging nanoforms of carbon are also being considered as the valuable backbone for sensing nanocomposites with different dimensions and geometrical shapes [23],[24]. Graphene can be used as a model system for studying two-dimensional physics and chemistry because of its excellent physical and chemical properties. Graphene, nowadays, is used for many applications as it is providing an unprecedented advantage in different fields with better results. The remarkable sensitivity of graphene-based sensors with different VOCs have made the graphene and its derivatives suitable for convenient applications related to the gas/vapor sensing [25], [26]. Exceptional geometry and morphology of CNT with good thermal and electrical properties make it popular for the variety of applications in the field of nanotechnology. The one-dimensional structure of CNT with nanopores has led to it being used as a nanofiller to synthesize the nanocomposite with improved mechanical and electrical characteristics [24],[27]. The simple configuration of CNT based resistive devices and field effect transistors are utilized for sensing applications [28]. Fullerene, the third allotrope of carbon, has fascinated a number of researchers. Its cage-like structure nearly spherical in nature with good mechanical strength, strong electron affinity, easy functionalization, many redox states and luminescent behaviour have promoted the interest of researchers for various applications [29], [30].

1.2 Importance of VOC sensing

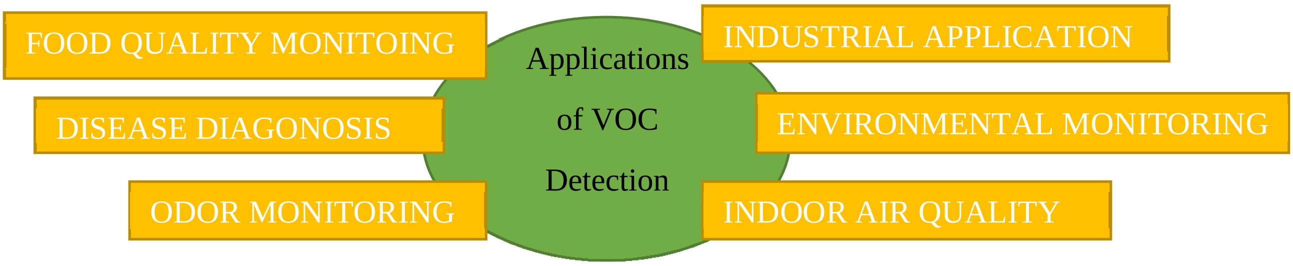

Fig1.1. Overview of the various applications of VOC sensing.

The presence of VOCs is pervasive in nature. The existence of VOC in the atmosphere is evident from the daily activities such as car driving, house painting, grass cutting, using pesticides or the straight forward breathing. Different activities are responsible for the emission of organic compounds such as alcohols, alkenes, carbides, alkanes, ethers, carbonyls, amides and aromatic compounds. The release of toxic volatile organic compounds in the atmosphere is deteriorating the air quality, which is a further threat to environmental and human health. Different practices involving petroleum refining, water separation, wastewater treatment, production of paints, automobile vehicles etc. produce a huge amount of VOCs [31],[32]. Fig 1.1 depicts the various applications of VOC sensing.

National Institute of Occupational Safety and Health (NIOSH), European agency for safety and health at work, Environmental protection agency or other safety organisation have entrenched various rules and regulations to restrain the subjection of VOC to humans in indoor and workplace environments due to their negative impact on human health. Some VOCs cause numerous health issues due to the carcinogenic nature [33-36]. Major examples of such VOCs are benzene and formaldehyde which are declared as hazardous air pollutants (HAP) by US Environmental Protection Agency (EPA). The exposure to benzene for continuous short intervals causes dizziness, headaches, nausea, cough and eye irritation [31][37].

Formaldehyde on the other hand is an extensively used important raw material in chemical industries for various purposes such as building material and coatings, adhesives. Therefore, furniture and building material are a great cause of indoor pollution as they release a good amount of formaldehyde [38]. Incomplete combustion of hydrocarbon leads to the emission of formaldehyde as an intermediate product at the rate of 700 mg/l gasoline. The main concentration of formaldehyde (4×10^{11} kg annually) is accumulated in the troposphere, as a result of photochemical oxidation of emitted hydrocarbons [39].

Formaldehyde assembles in the atmosphere over the cities and causes asthma in human beings. Presently, there is huge demand for timely and precise formaldehyde detection as subjection to 60 mg/m^3 because formaldehyde causes damage to nervous system, immune system sense, organs (blindness) and respiratory systems. It is also responsible for causing leukaemia, memory loss and headaches as an indoor pollutant. An exposure to 0.08ppm of formaldehyde for approximately 30 minutes is declared as a safety standard by World Health Organisation (WHO) [40].

Alcohols, a dominant category of volatile organic compounds, also have a wide variety of applications in different fields. Methanol or methyl alcohol is a highly potential organic compound which is utilized in automobile fuel, wastewater denitrification, and electricity generation. Methanol is used in the production of perfumes, dyes, colours and drugs. The exposure to 200 ppm or above of methanol 1hour/day is extremely harmful to human health. Continuous vulnerability to methanol causes blindness, acidosis, headaches, blurredness, shortness of breath and dizziness. Skin contact with methanol results in dermatitis or scaling and eye contact results in vision destruction [41],[42].

Ethanol, one of the most important members of the alcohol group, has numerous applications. It is a colourless volatile organic compound with a sweet smell and taste. However, the exposure to ethanol is not at all harmful. But with the extensive drinking of alcoholic beverages, car accidents in the world is one of the main concerns which needs to be resolved by quantitative detection of ethanol vapours in exhaled human breath [43],[44].

Detection of ethanol with the range of 5 – 100 ppm is essential with a designed blood alcohol tester. The concentration of alcohol in blood is 2100 times higher than in the breath [45]. The blood alcohol concentration (BAC, grams of alcohol/100 ml of blood) level can be depicted as vapor alcohol concentration (grams/210 litre of breath) level by maintaining the blood : breath ratio as 2100 :1. In many European nations, the BAC limit at the time of car driving is confined in the range of 0.2 mg/g to 0.5 mg/g which is equivalent to 42 ppm to 103 ppm of vapor alcohol concentration range (using the conversion formula - gm/210 litre × 2605 = ppm (34 °C, 760 torr)) [44],[46].

Other different VOCs (acetone, toluene, propanol, naphthalene and tetrachlorethylene etc.) utilized enormously for many applications have some harmful effects on environment and human health both. Continuous exposure to VOCs causes sick building syndrome (SSB) which is an essential health issue that causes potential damage to human health [31]. Along with the threat to human health, VOCs are also the cause of extinction of the ozone layer. Halogenated VOC (Polychloromethanes) after participating in stratospheric photocatalysis process liberate ozone destroying carriers that has caused stratospheric ozone layer depletion and Antarctic ozone layer depletion [47]. Due to the continuous increase of VOC in the atmosphere and their dangerous effects on human health and environment, Goteborg protocol with stringent emission regulation has been imposed which states that half the sum of the amount of VOC released in 2000 should have been in 2020 [48]. Therefore, continuous and real time monitoring of VOCs is a very important task for human well-being and environmental safety.

VOC released by the human body gives reliable and important information about human health. Medical diagnosis can be performed by identification of a particular pattern of VOCs within the limits [49]. Numerous VOCs are generated by human breath which can be dealt as VOC biomarkers for detection of different diseases like diabetes militias. VOC detection has become a benchmark for quick and selective noninvasive disease diagnosis as it provides a better and alternative way than blood sampling [50]. One of the advantages of VOC detection is non-invasive analysis and medical diagnosis of disease.

Different methods have been developed by the researchers to monitor VOC such as high performance liquid chromatography (HPLC), gas chromatography (GC) and mass spectrometry (MS). However, these techniques require costly equipment, no portability, and huge power. Also, these machines need highly professional operators and consume a lot of time. These techniques do not provide a real time detection of toxic volatile organic compounds which is of high concern these days [32]. Therefore, there is a huge demand for portable, low cost, speedy and reliable VOC sensing devices. Researchers have developed a number of VOC sensors based on different sensing techniques like capacitive, resistive, optical and electrochemical etc. This large scale research has led to the development of a wide variety of nanostructured material for VOC sensing.

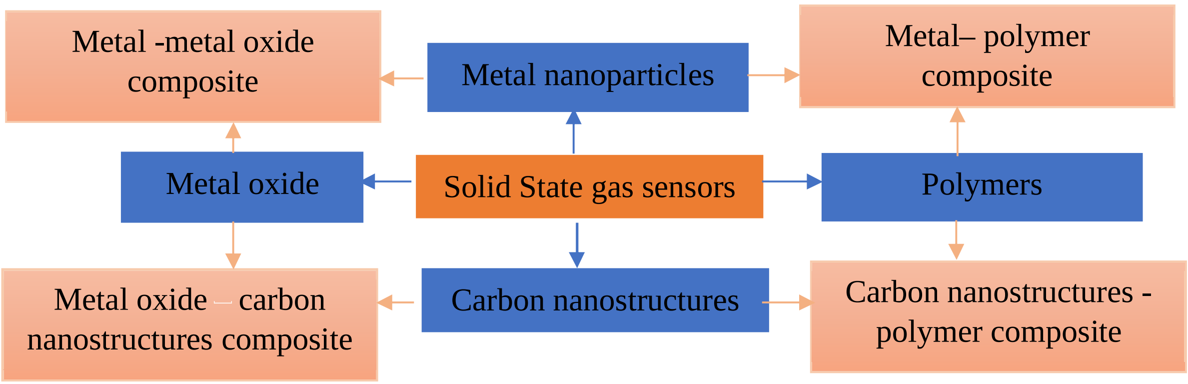

Fig.1.2. Different nanomaterials utilized to fabricate solid state sensors for VOC detection.

The sensing material is a key component of the VOC sensors. Researchers have proposed different sensing materials that include metal oxide semiconductors, metal nanoparticles, doped metal oxide, carbon based nanomaterial, metal oxide composite and polymers etc (Fig 1.2). Metal oxide semiconductor based VOC sensors are highly acceptable due to their low cost, high sensitivity, ease of use, nano dimensional structure and quick response etc. Carbon nanostructures are also promising sensing materials that can be applied independently or in composite form to fabricate VOC sensors.

Nowadays, the urgency to develop a novel sensor with more peculiar properties is increasing at an alarming rate. High performance characteristics like stability, sensitivity, fast response and recovery are much needed in the modern VOC sensors.

1.3 Carbon nanostructures for VOC sensing

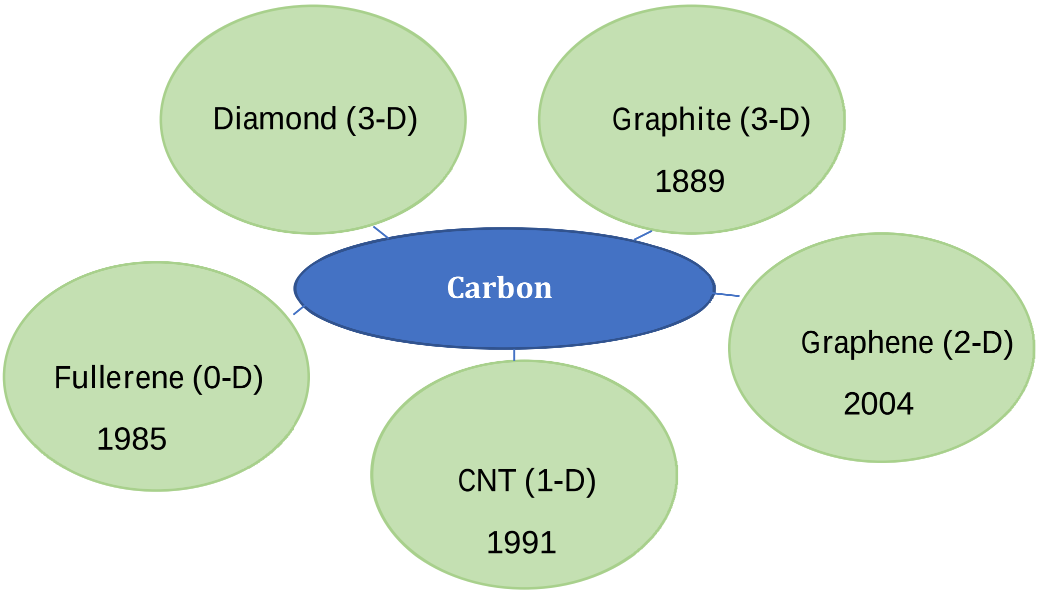

Fig. 1.3. Different allotropes of carbon and year of their invention

Within the short intervals of time a novel nanomaterial emerges with totally unique and outstanding properties which attracts the scientific society. Carbon is one such star nanomaterial whose allotropes are being discovered time to time depicting outstanding properties. Fig. 1.3 represents the different allotropes of carbon with their year of invention. Most known allotropes of carbon are diamond and graphite. However, 35 years back, the world of allotropes of carbon was totally changed with the discovery of two new nanoforms of carbon – fullerene and Carbon nanotubes (CNT). After that an elusive two dimensional nanoform of carbon was discovered - graphene in 2004 by Geim and group in Manchester university [51]. Carbon is the nontoxic abundant element present in nature that has aroused as crucial nanomaterial in different domains of nanoscience.

Nanocarbons indeed represent unique physical and chemical properties and can be considered as good alternative options to the available highly expensive sensing materials. Simple manufacturing with high scale production and minimum defects makes carbon a powerful sensing material [52]. One of the major advantages of carbon nanostructures is that they can be easily hybridized with different nanomaterials like metal oxides, noble metals and polymers etc. This leads to the development of sensors with improvised characteristics. Unique carbon nano structures like graphene or its derivatives, CNT and fullerene have allured a lot of researchers in the field of vapor sensing. Moreover, nanocarbons possess easy functionalization and have the capability to be miniaturized which makes them highly reactive and catalytic in nature. Other advantages can also be enlisted for carbon nanostructures (CNS) based sensors-

i. Carbon nanostructures based sensors are less affected by temperature fluctuations. Also, they are steady and reliable in harsh situations like elevated temperatures or acidic ambience. Therefore, they can be implied in coarse conditions for toxic vapor sensing.
ii. CNS based sensors perform well at low temperature or room temperature, whereas metal oxide based sensors perform at elevated temperatures (100 -1000 ˚C).
iii. CNS based sensors exhibit huge electrical mobility and conductivity and therefore provides good sensitivity towards toxic VOCs.

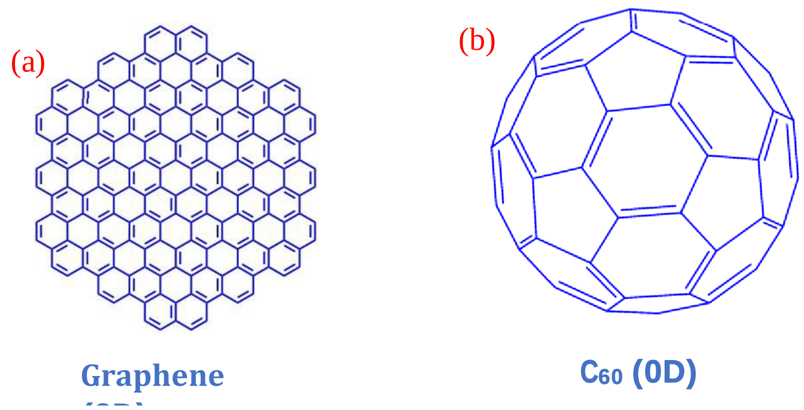

Fig.1.4. Structure of nanocarbons; (a) graphene (2-D), (b) fullerene (0-D) (source: chem draw 19.0)

Graphene is the most fascinating two dimensional nanostructure of carbon which can be enclosed in zero dimensional fullerene nanoparticles, curved in one dimensional nanotubes and stacked in three dimensional graphite structure. The one atom thick honeycomb structure of graphene is the fundamental building block of other nanoforms of carbon (Fig 1.4(a)). Graphene interestingly can be considered as the mother of all carbon nanostructures. Graphene and its derivatives (graphene oxide and reduced graphene oxide) have been extensively applied in gas sensing applications. Graphene, undoubtedly, is an astonishing material with extravagant properties like high carrier mobility, ballistic transport, high thermal stability and very low 1/f noise [53].

In 2007 Novoselvo and co workers synthesized a graphene based gas sensor for the first time that has the capability to detect the single gas molecule [54]. In 2010, Andre Gein and Konstantin Novoselvo at University of Manchester was awarded with Nobel prize for physics for demonstrating revolutionary experiments on 2-D graphene. After that, many researchers have utilized the two-dimensional structure of graphene and its derivatives to fabricate gas/vapour sensing devices. Moreover, extremely high surface area and high conductivity of graphene have attracted the attention of the researchers worldwide. A few literature surveys are depicted in Table 1.1 indicating the VOC sensing performance of graphene and its derivatives. Another outstanding property of graphene is the ambipolar current transport which is observed due to the field effect [55]. A few reports have been published depicting the vapour sensing properties of graphene field effect transistors (GFET) [56]. One drawback of pure graphene based sensors is elongated response and recovery time which further limits its application [57].

Table 1.1 Performance of carbon nanostructures based VOC sensors

Carbon nanoforms	**VOCs**	**Concentration**	**Response Magnitude**	**Temperature**	**Response/ Recovery Time**	**Ref**
Graphene oxide	C_2H_5OH	25 ppm	-	RT	20/75	[58]
Graphene	C_7H_8	3 ml vacuum filtration	$(R_a-R_g)/R_a$ % = 13	RT	10/15	[59]
rGO	C_2H_5OH	-	17 %	-	300/-	[57]
C_{60}	$C_{15}H_{16}O_2$	3.7nM	.23 µM	RT	-/95%	[60]
C_{60}	$C_6H_5NH_2$	-	310 Hz	-		[61]

RT: Room Temperature, R_a: Resistance in air, R_g: Resistance in reducing vapor or gas.

Another transpiring low dimensional (0-D) allotrope of carbon is fullerene which exhibits new principles and patterns in the research due to its unique physical and chemical properties that are different with other allotropes of carbon like diamond and graphite [62],[63]. Fullerene was discovered in 1985 by Kroto and group. Fullerene is a very well known electron acceptor with other fascinating properties like multiple redox states, low lying triplet states etc. Its cage-like structure nearly spherical in nature with good mechanical strength, strong electron affinity, easy functionalization, many redox states and luminescent behaviour have promoted the interest of researchers for various applications. Moreover, C_{60} has a unique closed shell configuration having 12 pentagons and 20 hexagons (Fig. 1.4(b)) [64]. Considering these unique charge transfer and electron accommodation properties, Buckminsterfullerene has been used in various applications like photoconductors [65], biosensors [66], photovoltaics [67], gas sensors [68] etc. Fullerene is relatively less explored carbon allotropes for VOC sensing. Two reports are found and shown in Table 1.1 depicting the detection of Bisphenol [60] and Aniline [61].

Although the nanocarbon implied VOC sensors are ubiquitous, they have certain issues which lack their use in real time applications. Issues such as poor stability, slow response and recovery characteristics, and poor selectivity have been reported by many researchers [69]. Individual nanocarbon based sensors are not good performers for VOC sensing as they depict poor sensitivity. These parameters need to be improvised to encounter the technical demands of real time gas sensors.

1.4 Metal oxide semiconductors for VOC sensing

Metal oxide semiconductors are the most explored and reported materials for gas/vapor sensing applications. Since 1960, solid state gas sensors established on metal oxide semiconductors have gained substantial recognition in both practical and scientific manner. Heiland [70], Bielanski [71] and Seiyama [72] provided the very first reports describing the gas -metal oxide semiconductor interaction and after that Taguchi established metal oxide semiconductor based gas sensors as an industrial product. Figaro, FIS, MICS, Applied sensor and Citytech etc. are the leading companies that provide metal oxide-based sensors that act as toxic gases or vapours alarms [73-75].

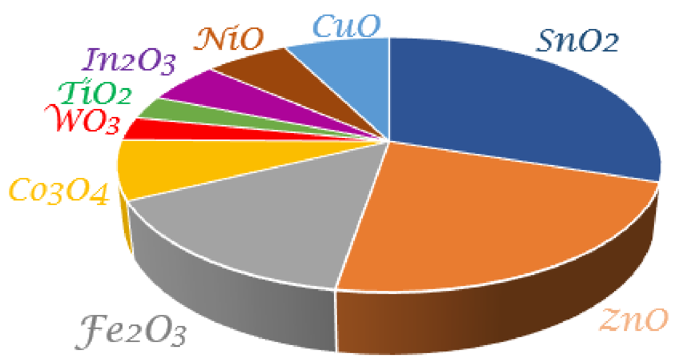

Fig.1.5. Pie chart representing the extensive utilization of different metal oxide semiconductors as sensing material [15],[18],[19],[79],[80], [94],[95],[97].

Nanoscale metal oxide semiconductors (MOS) have established their dominance in the field of gas or vapor sensing since considerable decades. Minimum cost, flexibility, easy fabrication, and high congruence with silicon microfabrication made MOS popular. Moreover, the mechanical stability and environmental friendly nature makes the metal oxides more favourable for real time detection of hazardous and toxic gases and VOCs [76- 77]. Therefore, traditional sensors are mostly based on semiconducting metal oxides [78]. Fig. 1.5 represents the pie chart depicting the extensive utilization of metal oxide semiconductors as sensing material.

Table 1.2 Performance of metal oxide semiconductor based VOC sensor

Nanoscale metal oxides	**VOCs**	**Concentrations (ppm)**	**Response Magnitude (%)**	**Temperature (°C)**	**Response Time/ Recovery Time**	**Ref**
SnO_2 film	CH_3OH	10-500	4.5 - 40	320	10/9	[79]
SnO_2	C_2H_5OH	10-1000	10-140	240	10/5 (20 ppm)	[80]
SnO_2 microspheres	HCHO	1–200	1.7 – 9	300		[81]
SnO_2 nanosheets	HCHO	200	207.7	200	30/57	[82]
SnO_2 nanobelts	C_2H_5OH	250	$\Delta G/G \times 100 = 4160$	400	-	[83]
ZnO nanofiber	C_3H_6O	1–200	R_a/R_g = 7.1-87.9	220	11-17/7-15	[84]
ZnO nanowire	C_2H_5OH	1-200	R_a/R_g = 1.9 – 47	300	-	[85]
ZnO nanotube	C_2H_5OH	1-500	R_a/R_g =2.5-59	300	3/30	[86]
WO_3 films	C_2H_5OH	10-50	$(R_a-R_g)/R_a \times 100$ =29-70	240	68/75(50ppm)	[87]
WO_3	C_3H_6O	100-300	34 -70	200	-	[88]
WO_3 nanoflowers	C_2H_5OH	10-400	$(R_a-R_g)/R_a \times 100$ =30-90	27	19/27 (400 ppm)	[89]
V_2O_5 nanowire	C_2H_5OH	1000	R_a/R_g = 9.09	330	50/100(50 ppm)	[90]
α-Fe_2O_3 microspheres	C_3H_6O	10–1000	R_a/R_g = 3 – 17	250	5/17 (100 ppm)	[91]
α-Fe_2O_3 nanoparticles	C_2H_5OH	100	R_a/R_g = 10	250	10/70	[92]
Co_3O_4 nanosheets	C_3H_6O	100	6.1	160	98/7	[93]
NiO nanowires	HCHO	5-100	2-19	200	19/17 (200 ppm)	[94]
In_2O_3 mesoporous	C_3H_6O	50	R_a/R_g = 29.8	300	0.7/14	[95]
α-MnO_2 nanoparticles	C_2H_5OH	200	R_a/R_g = 30.6	300	30/40	[96]
TiO_2 nanotube	HCHO	10- 50	$(R_g-R_a)/R_a \times 100$ = 8 - 37	RT	3min	[97]
TiO_2 powder	C_3H_6O	500	R_a/R_g = 25.97	370	13/8	[98]
TiO_2 nanoparticle	C_2H_5OH C_3H_6O	20-200	I_{vapour}/I_{air} = 6-12	350	----	[99]
TiO_2 nanotubes	C_2H_5OH CH_3OH	10-1000	$(R_a-R_g)/R_a \times 100$ =15-45	RT	34/130	[100]

RT: Room Temperature, R_a: Resistance in air, R_g: Resistance in vapours or gas.

Metal oxide semiconductors have a major advantage of having the capability to be synthesized in different nanoforms like nanotubes, nanobelts, nanoparticles, nanorods, nanoclusters, nanowires [14]. As a consequence, different 0-D (nanoparticles and nanodots), 1-D (nanotubes, nanowires, nanorods etc.) 2-D (nanosheets and nanofibers etc.) and 3-D (nanospheres and nanoflowers) nanoforms of various metal oxides like SnO_2, ZnO, WO_3, Fe_2O_3 Co_3O_4, CuO and TiO_2 etc. have been extensively investigated by the researchers for VOC sensing. SnO_2, ZnO and Fe_2O_3 etc. are the conventional and mostly investigated metal oxide semiconductors for gas or vapour sensing whereas TiO_2 and WO_3 etc. are relatively least investigated in the field of sensing. These nanostructured metal oxide semiconductors naturally possess a high surface to volume ratio which obviously accounts for the huge number of surface sites to the target gases/VOCs. MOS nanomaterial thus provides an enlarged sensing layer for interaction.

Table 1.2 illustrates different metal oxide semiconductors (*p*-type and *n*-type) based VOC sensors operating in the resistive mode. Metal oxide semiconductors have dangling bonds on their surface that are the key component which participate in the formation of ionized oxygen species via adsorption on the surface of metal oxide in the air ambient. The electrical resistance of the MOS (*n*-type) in air is increased due to the reduction of free electron concentration available on the surface of metal oxide via adsorption. On exposure to the reducing VOC, resistance of MOS is thereby decreased due to the release of free electrons during interaction of vapours and adsorbed oxygen species. This phenomenon is reversed in *p*-type MOS where holes are the majority carrier concentration and the resistance is increased in exposure to reducing VOC.

One of the major drawbacks of metal oxide semiconductor sensors is high operating temperature to obtain high sensitivity, which in turn consumes a lot of power. Also, high operating temperature reduces the life of the sensor material as high temperature causes maturing of sensing material. Different metal oxide based sensors (ZnO, SnO_2, In_2O_3 and MnO_2 etc.) have been observed with operating temperature higher or equivalent to 300 ˚C [85],[86],[90],[95],[96] and some being reported at or above 200 ˚C [80],[82],[84],[92],[94]. Also, low level detection till ppb is also very difficult to achieve with pure metal oxide semiconductor. Multiple metal oxide semiconductor sensors have been observed with a detection limit above 300 ppm which is not very beneficial for most of the real time applications [80],[90],[91],[98]. A few researchers reported detection till 1 ppm but at high operating temperature and with low response magnitude [81],[84],[85],[86].

1.5 Carbon-metal oxide nanocomposites-based VOC sensors

The above discussion envisages that the nanocarbon has its own benefits while on the other hand metal oxides are the traditionally developed sensing nanomaterial posses several advantages. Nanocomposite of metal oxide and nanocarbon provide a novel sensing material having synergistic effects of both the nanomaterials. Considering the recent survey, the nanocomposites of metal oxides and carbon nanostructures have opened new opportunities for the researchers to improve VOC sensing. The nanocomposites offer a high specific area, enhanced carrier mobility, low intrinsic noise, abundant functional groups and lower activation energy [101]. Also, the carbon nanostructures act as a strong substrate in the formation of nanocomposite [102]. The metal oxides can be synthesized in different nanoforms like 0-D, 1-D, 2-D and 3-D and then can be decorated or arranged in different patterns on carbon nanoforms like graphene and fullerene. Nanocomposites of metal oxides and carbon nanoforms provide varieties of dimensional framework which are advantageous for sensing. Researchers have explored different forms of carbon-metal oxide nanocomposites to examine the abilities of 0-D, 1-D, 2-D and 3-D structures to boost up their performance towards VOC sensing. Carbon nanomaterials and metal oxides nanohybrids alter the properties of the pure material (either metal oxide or carbon nanostructure) and obtain the superior combined properties of both materials. The formation of heterojunctions (*p-p, p-n* or *n-n*) in the hybrid structure is responsible for enhancing the sensitivity and selectivity of the sensors towards a particular VOC [103]. The metal oxide-based sensors have a drawback of being operated at a high temperature that can be overcome in the nanocomposite of carbon-metal oxides which can operate at relatively lower temperature [104],[105].

The VOC sensing performance of graphene and its derivatives composite with various metal oxides on the basis of response magnitude, operating temperature, response time and recovery time has been depicted in Table 1.3.

The p-SnO_2-rGO nanocomposite exhibited efficient acetone sensing in the concentration range 10 ppm - 2000 ppm at room temperature. The response magnitude was recorded almost double in case of SnO_2-rGO as compared to the bare rGO. SnO_2-rGO sensor also showed a very stable response for a long period of time (30 days) [107]. 1 ppm acetone sensing was achieved by Graphene-WO_3 hemitubes at 300 ˚C with a very fast response and recovery time of 8.5 s and 19 s respectively [108]. SnO_2-rGO nanocomposite exhibited phenol detection down to 10 ppb with fast response and recovery at room temperature. Selectivity of the SnO_2-rGO nanocomposite towards phenol was tested in comparison with ammonia, methanol, oxygen, benzene, methyl benzene and ethanol [109]. α-Fe_2O_3-graphene nanocomposite showed quite a good response magnitude towards 1 ppm of ethanol with fast response and recovery [112]. ZnO quantum dots decorated graphene composite depicted a good response magnitude in 100 ppm of formaldehyde at room temperature. The nanocomposite was selective towards formaldehyde compared to methanol, acetone, benzene and toluene [115]. ZnO nanosheets-graphene oxide composite sensor exhibited highly selective nature towards acetone in comparison to other VOCs and the sensing was down to 1 ppm [118]. TiO_2 nanotubes-rGO composite sensor was reported with a very high response magnitude of 98.6% towards 800 ppm methanol at room temperature [120].

Table 1.3 Performance of graphene (and its derivatives)-metal oxide nanocomposite based VOC sensor

Graphene/ Metal oxide nanocomposites	VOCs	Concentration (ppm)	Temperature (°C)	Response Magnitude (%)	Response/Recovery Time (s)	Ref
rGO-ZnO nanorods	C_2H_5OH	5-50	260	R_a/R_g = 1.1 – 27	7/8	[106]
rGO/ SnO_2 film composite	C_3H_6O	10 - 2000	RT	R_a-R_g/R_a ×100 = 2.1 - 72%	107/95 146/141	[107]
Graphene- WO_3 hemitubes	C_3H_6O	1 – 5	300	R_a/R_g = 2.8 - 7	13.5/25 8.5/19	[108]
rGO/SnO_2 aerogel	C_6H_6O	.01 – .08	RT	0.5 - 1.7	2.43/1.06	[109]
Graphene- SnO_2 nanocomposite	C_6H_6	.05 - .1	RT	(I_g– I_a/I_a) × 100 = 1.87-94.3	2/8	[110]
rGO/α-Fe_2O_3 nanofiber	C_3H_6O	100	375	R_a/R_g = 8.9	3/9	[111]
Graphene α/Fe_2O_3 nanostructure	C_2H_5OH	1 - 1000	280	R_{air}/R_{gas} = 5 - 30	10/12	[112]
Graphene/ZnO	C_2H_5OH	200	340	(R_a-R_g/R_a) ×100 = 97	5/20	[113]
rGO- ZnO Nanoparticles	C_2H_2	30-1000	250	R_a/ R_g= 0.5 - 143	100/28	[114]
Graphene-ZnO quantum dot -	HCHO	25 – 100	RT	(G_g–G_a)/G_a = 0.42 - 1.1	30/40	[115]
rGO/ SnO_2 nanoparticles	C_2H_2	0.5 – 50	180	R_a/R_g= 2 – 12.43	54/23	[116]
rGO/Co_3O_4	C_7H_8	0.5 - 5	110	1-11.3	80/90	[117]
GO-ZnO nanosheets	C_3H_6O	100	240	R_a/R_g= 35.8	3/6	[118]
rGO/SnO_2 nanoparticles	C_2H_5OH	5-500	300	R_a/R_g= 2.7-297.8	11/20	[119]
rGO /TiO_2 nanotubes	CH_3OH	10- 800	RT	ΔR/R_a×100 = 24 -96.93	18/61	[120]
Graphene-ZnO film	HCHO	9	RT	R_g-R_a/R_a = 52	36	[121]
rGO/ZnO flower hybrid	HCHO	2-10	RT	ΔR/R_a × 100 = 2-.5%	39/50	[122]
rGO-MoO_3 Nanoflakes	C_2H_5OH	100 - 8000	310	R_a/R_g= 53 - 702	6/54	[123]
GO/SnO_2 nanofibers	HCHO	5 - 100	120	R_a/R_g = 4.2 - 32	66/10	[124]
Graphene/ SnO_2 mesoporous	HCHO	1- 400	120	R_a/R_g =5 - 80	1/85- 1/90	[125]
Graphene-ZnO nanorods	C_2H_5OH	10-50	300	R_a/R_g =9-90	8/20	[126]
Graphene loaded Ni-SnO_2	C_3H_6O	200	350	R_a/R_g =169.7	5.4	[127]
Graphene-MoS_2	CH_3OH	10 - 50	RT	R_g-R_a/R_a = 1.6-4.9	210/220	[128]
GO/WO_3	C_2H_5OH	100 - 2000	317	R_a/R_g = 5.8 – 40.9	-	[129]

RT: Room temperature, R_a: Resistance in air, R_g: Resistance in vapours or gas.

The rGO-Fe_2O_3 nanocomposite showed ethanol sensing down to 1 ppm at room temperature with a high response magnitude and fast response/recovery time [101]. SnO_2-graphene nanocomposite was reported with a high selectivity and good sensitivity towards formaldehyde. It showed a response magnitude of 35% on exposure to 100 ppm formaldehyde at 260℃ [130]. MoO_3 nanoflakes-rGO composite reported with high sensitivity and selectivity towards ethanol at the operating temperature of 310 ℃ [123] Graphene-$ZnFe_2O_4$ nanocomposite sensor detects acetone with high selectivity. However, it was a general observation that the increase of graphene content in the nanocomposite lowered the operating temperature [131]. Therefore, the overall discussions and summarized sensing performance in Table 1.3 confirmed that the incorporation of graphene and its derivatives in metal oxides enhanced the selectivity of the sensor towards a particular VOC with increased sensitivity at low operating temperature.

Table 1.4 Fullerene – metal oxide nanocomposite-based VOC sensing performance.

Fullerene/ Metal oxide nanocomposites	VOCs	Concentration (ppm)	Temperature ℃	Response Magnitude (%)	Response/Recovery Time (s)	Ref
C_{60}-Al	C_2H_5OH	3-5 Hz	-	Frequency shifts -208Hz	-	[132]
C_{60}-ZnO	C_2H_5OH	100	RT	32%	80/15	[133]
C_{60}cryptand 22 coated quartz crystal	CH_3OH C_2H_5OH	0.80 mg/l 0.70 mg/l	RT	73.2 Hz/ ($mgml^{-1}$) 750 Hz/ (mgl^{-1})	-	[134]

Relatively, less quantity of work was reported on fullerene and metal oxide nanocomposite for VOC sensing as listed in the Table 1.4. C_{60}-ZnO nanocomposite sensors with various levels of C_{60} depicted a good response magnitude toward ethanol. C_{60}-ZnO nanocomposite sensor with highest concentration of fullerene (6 mg) showed a strong selectivity toward ethanol with the highest response magnitude [133]. C_{60}-cryptand coated surface acoustic wave (SAW) quartz crystal sensor was also reported for the organic vapour sensing. The fabricated fullerene C_{60}-cryptand 22 was utilized as a sensing material which was further plated on SAW crystal. This sensor provided much better results as compared to conventional QCM sensors for various organic vapours with short response time and great reproducibility [134].

1.6 TiO_2 nanostructures for VOC sensing

TiO_2 has turned up to be one of the most wonderful materials in this present-day scenario. Chemical inertness or non-toxicity, environmentally friendly, photostability and corrosion free nature has made TiO_2 extremely popular in almost every field covering -drugs, cosmetics, dyes, food items, solar cells, sun blockers, paints. The amazing optical, ionic and electronic properties of this metal oxide has attracted material researchers, physicists, chemists, biologists and engineers for different purposes [135],[136].

TiO_2 is a wide bandgap metal semiconductor that exists in three different forms- anatase (~3.2 eV), rutile (~3 eV) and brookite (~3.1-3.5 eV). The ground or highly stable state - rutile is easily synthesized and utilized in numerous industries whereas the least known unstable or highly reactive brookite state is utilized these days for the fabrication of valuable organic compounds and performs high photocatalytic activity. Anatase and brookite are the metastable states that change into rutile on being calcined at elevated temperatures [137]. Anatase having higher catalytic activity is preferred more over the rutile phases. Anatase is highly preferred in the sensing field due to the following features :-

i. The higher bandgap of anatase promotes easy electron transfer from TiO_2 to adsorbed molecules with higher oxidation capability of electrons. Thus makes anatase highly suitable for vapor sensing [138].
ii. Anatase depicts higher indirect bandgap which in turn facilitates longer carrier life that enables the charge carriers to participate in surface reactions.
iii. Anatase promotes operation at lower temperature than rutile.
iv. In general, micro or macro crystalline rutile TiO_2 is the more stable phase at higher temperature and it does not come back to anatase phase. It is also established that rutile TiO_2 is permanently an n-type semiconducting material. But the anatase phase may be very stable when the crystals are few nanometers in diameter [138],[139]. It has also been analyzed that the thermodynamic phase stability of the nanocrystalline anatase titania is more as compared to the rutile phase.

Major advantage of TiO_2 is that it can be tailored into different nano dimensions~ 0-D (nanoparticle), 1-D (nanotubes, nanorods), 2-D (nanofiber) and 3-D (nanosphere) and then can be applied for diverse applications like purification of contaminated water, biomedical coating, solar cells and lithium-ion batteries and sensors [140]. It is very important to escalate the surface area for some applications in order to obtain the overall efficiency. Thus, the nanoparticulated forms of TiO_2 are highly utilized.

Different TiO_2 nanostructures with different morphology have been acknowledged by VOC sensing community due to their electrical and chemical properties. The zero-dimensional TiO_2 nanoparticle are synthesized via sol gel method [141]. The fabrication of one dimensional nanoforms of TiO_2 is done by different routes like electrochemical anodization, hydrothermal method and template assisted methods [142]. 2-D TiO_2 nanostructures can be synthesized by atomic layer deposition [143].

Zero-dimensional (0-D) nanomaterial is one of the most promising materials with its unique nature. Excessive small size with highly functioning edge sites per unit mass and also the edge and quantum confinement effect of 0-D materials makes them supreme among other nanomaterials [144].

The 1-D TiO_2 nanotube array obtained by simple method of electrochemical anodization is considered the most promising nanostructure for VOC sensing [140],[145]. These self-organized TiO_2 nanotube layers have gained a lot of attention from several years for vapor sensing as nanotubes allow much higher control over the chemical and physical behaviour. The discovery of carbon nanotubes by Iijima, inspired the researchers to explore the transition metal oxide synthesized in 1-D nanoform. 1-D morphology possesses high mechanical strength, uniformity, one dimensional electron flow, highly crystalline nature, high surface to volume ratio and huge electron mobility [146].

Generally, all the metal oxide semiconductors have two major types of defects present e.g. oxygen vacancy which acts as a donor and metal vacancy which acts as an acceptor. For TiO_2, oxygen vacancy is the donor type defects and titanium vacancy is the acceptor type defects. The conductivity of TiO_2 can be altered significantly by varying the donor types defects or acceptor type defects via external treatments. *n*-type TiO_2 sensor devices exhibit higher mobility, whereas *p*-type TiO_2 sensor devices exhibit several advantages like low humidity dependence and rapid recovery kinetics etc [147],[148].

1.7 Structure of sensors

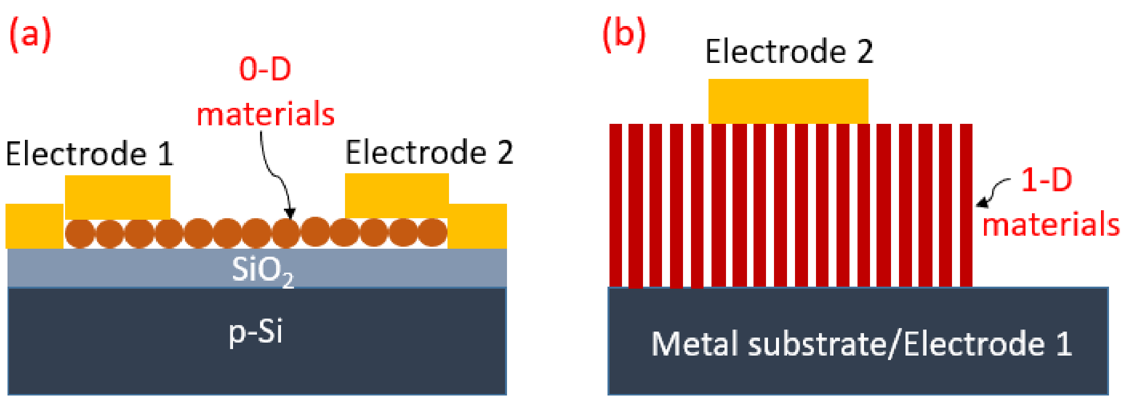

Fig.1.6. (a) Planar structured sensor, (b) Vertical structured sensor.

Sensing device structure is one of the important concerns. Different device structures have already been proposed for gas/vapour sensing. Selection of proper device structure for different nanostructures is an important task. Three device structures have been proposed here for three different nanostructures- 0-D, 1-D and 2-D

Planar device structure

In planar structure electrodes are taken from the same plane of the sensing layer. 0-D nanostructures like nanoparticles of one or few layer deposit over the substrate like Si/SiO_2, glass, aluminium etc. Two top metal (gold/platinum/palladium) electrodes are deposited on the sensing layer (Fig. 1.6a) following any deposition route. The resistance or conductivity is measured from these two electrodes deposited on the same plane of the sensing layer.

Vertical device structure

For 1-D nanostructures, vertical or metal-insulator metal (MIM) device can be fabricated where highly aligned and oriented nanostructures like nanotubes, nanorods can be sandwiched between electrodes. For TiO_2 nanotubes which are grown by electrochemical anodization on Titanium substrate can be used in vertical structured sensor. One top electrode is deposited on the sensing layer and metal (Ti) substrate is taken as the bottom electrode (Fig. 1.6(b)). A very fast one dimensional electron transport takes place vertically between the two electrodes (top and bottom).

Field effect transistors device structure

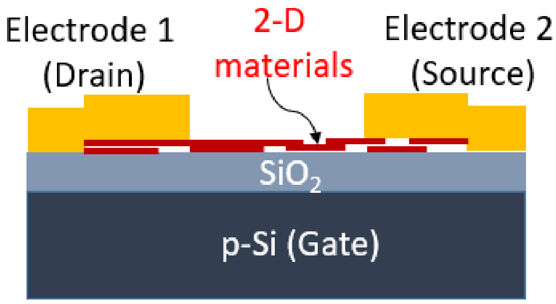

Fig1.7. FET structured sensor

FET structure is quite popular in gas/vapour sensing application [149]. It is preferred in back gate structure where sensing layer is exposed to the environment. In this structure 2-D materials like graphene or graphene derivatives like GO, rGO are deposited on the Si/SiO_2 substrate. Two metal top electrodes (source and drain) are deposited on the top of sensing layer (Fig. 1.7). Back gate contact is taken from *p*-Si substrate as shown in Fig 1.7.

The proposed device structure are well suited for the synthesized nanoforms. The device structures are highly synchronized with the morphology of the nanostructures of the sensing layers.

1.8 Gaps in the research

The literature review reveals that most of the VOC sensors suffer from several drawbacks. Sensors have a drawback of being operated at high temperature (300-500ºC). Most of the sensors does not show a high response magnitude and a great sensitivity. Sensing of toxic VOC down till ppb level is still a difficult task for researchers. Sensors also suffer from a high response time and recovery time.

A significant number of the reports are based on pure metal oxides or any other pure nanomaterial which are not suitable for low temperature sensing. Individual nanomaterial based sensors are incapable of providing high response magnitude and detection till ppb level. Selectivity is one of the important issue faced by researchers. All these problems can be solved by using nanocomposites based sensing material.

It has been observed from the literature, sensing material is given much more importance than device structure. Different nanomaterials undoubtedly perform very well. But there is a significant opportunity to improve the sensing performance by choosing appropriate sensor device structure.

After considering all these short comings of the sensor research, composites of two nanoscale material-based sensors have been proposed in the present research proposal. Nanocarbon along with TiO_2 nanostructures have been chosen to develop advanced VOC sensors in different device structures. Major objective is to develop low temperature sensor that detects the ppb level of VOC. Also, emphasis for developing first responding devices for different VOC to develop naturally selective sensors. Nanocarbon -TiO_2 nanocomposite also enabled sensing with ultra-fast response and recovery time.

1.9 Objectives

- Synthesis of TiO_2 nanostructures (1-D TiO_2 nanotubes and 0-D TiO_2 nanoparticles) hybridized with variable nanocarbons (2-D graphene and 0-D fullerene)
- Structural, morphological and chemical characterizations of developed nanocomposite or nanocarbon functionalized TiO_2 nanostructures.
- Fabrication of vertical, planar and field effect transistor type sensor devices.

- Testing and characterizations of sensors in the exposure of volatile organic compounds (VCOs).
- Optimization of sensor performance to improve sensitivity, operating temperature, response time, recovery time and stability.

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