Synthesis of nano-carbon structures with functionalized metal oxides and their sensing applications

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Utkarsh Kumar

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Under the Supervision of

Prof. Bal Chandra Yadav

Department of Applied Physics

School for Physical Sciences

Babasaheb Bhimrao Ambedkar University (A Central University)

Lucknow -226025, U.P., India

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Currently environmental pollution has become a severe problem towards the whole world and its prevention is very challenging for us. Many sensors have been designed and fabricated to detect the levels of various toxic gasses in order to avoid disasters. From the literature, it is observed that presently available sensors have two major shortcomings; first, low sensitivity and second, high operating temperature [1]. We have to compromise with either sensitivity or operating temperature. A highly sensitive gas sensor mostly works at a very high operating temperature which increases the power consumption. Thin film-based sensors operated at room temperature are one of them [2] and such type of gas sensors have been established as an emerging technology in the field of environmental sensing. In the present work, we have focused on carbon nanotube (CNT) based thin film gas sensors because carbon nanotubes (CNTs) [3] have extraordinary physical, chemical, structural and mechanical properties [4, 5]. These are an ideal quantum system for exploring the one-dimensional physical application in nanoscale devices [6]. The growth of CNTs may be done by using the chemical vapour deposition method for having one-dimensional growth with high aspect ratio and unique structural properties [7]. Catalysts such as Au, Ag, Pt, Fe, Mn, Mo and Mg may be used for the growth of CNTs but the best growth was found by using metal catalysts like Co, Ni and Fe. These catalysts may be easily filtrated from the nanotubes by the distillation process [8].

The burning of fossil fuels from the industries, motor vehicle and volcanic eruption are the resources of major environment pollutant like carbon monoxide and carbon dioxide. The continuous increase in the concentration of CO_2 in the natural environment has raised the temperature of the earth causing global warming which is further liable for the melting of glaciers and rising sea levels. Also, the excessive presence of CO_2 in the ambient environment causes suffocation and creates unconsciousness in human beings. Therefore, precise measurement and control of CO and CO_2 are necessary. In the sensor technology, metal oxides are widely used for good sensing behaviour but these materials have a high operating temperature (200-400℃) [9]. Thus CNT based sensors which may be operated at room temperature with fast recovery and response times are highly desirable.

The development of portable CO_2 and LPG sensors that are robust, small-sized, have long lifetimes, are quick in response and have sufficient sensitivity in the ambient environment is necessary and demanded in order to prevent the explosion accidents in homes and industries for safety requirements. Solid-state CO_2 and LPG sensors using carbon nanomaterials are the most promising for the detection of such toxic gas because of their compact structure, high selectivity, low cost, and the ability of continuous monitoring [10]. The need for reliable, cheap and user-friendly gas sensors for the detection of CO_2 and LPG is industrially important and has led to a considerable expansion in the field of sensor research and development. For this reason, efforts are made nowadays by scientific research communities in leading laboratories all over the world to focus on the investigation of novel LPG sensitive materials suited for solid-state gas sensors. Consequently, their performances have to be improved dramatically by adopting preparation conditions and by controlling deposition processing. Several types of CO_2 and LPG sensors such as chemical sensors, the resistive and conductive type sensors using semiconductors and sensors based on metal-polymer complexes have been investigated by different research groups in various parts of the world. Therefore, great attention has been recently paid to the development of new material “architectures” at the nano-scale.

Carbon nano-materials can enhance the performance of gas and humidity sensor because of their much higher surface-to-volume ratio as compared to micro grained materials [8]. In addition to the enhanced sensitivity demonstrated by the nanostructured material based sensors, the sensors can give a quick response too. Tubular shape and crosslinked structure have a major effect on the gas-sensing properties of polycrystalline materials and their full characterization should be the first step in the study of materials.

Ability to synthesize one-dimensional carbon nanostructure with extremely high aspect ratios makes them attractive in gas and humidity sensor fabrication [6-8]. The space charge layer control of nanostructures makes them particularly interesting since conduction can change drastically with the expansion and contraction of the layer in the presence of different gases. In spite of these observations at the nano-scale, many of the mechanisms responsible for conduction at the nano-scale are still poorly understood [9, 10]. Room temperature gas sensing may be achieved by modifying several different material parameters with modifications available when dealing with materials at the nanoscale. First, achieving a high non-equilibrium amount of oxygen vacancies in the oxide sensor material will help in achieving this goal. A high non-equilibrium amount of oxygen vacancies would serve to contribute in the more effective movement of charge across the sensor material. The term non-equilibrium is used here because thermodynamics at room temperature does not predict the number of vacancies required for this at low operating temperatures. Second, increasing the number of surface sites for gas interaction will help in achieving this goal; so that even a low concentration of the gas can be detected at room temperature. Use of nanomaterials is significant for this due to their high surface to volume ratio. This can be increased by changing the shape of the nanoparticle from spherical to one dimensional, by creating rods or hollow tubes. The third change that can be made to the sensor material is modification of the space charge layer. This is done in order to get the maximum signal change in the presence of the target gas. Modification of the space charge layer can be done by: (i) reducing the crystallite size, (ii) changing the defect chemistry within the space charge layer and surface of the material, and (iii) changes in the particle shape may play a significant factor. Another interesting aspect of nanomaterials that make them a candidate for room temperature gas sensor applications is the fact that the changes in the bandgap have been reported at extremely small sizes. The possibility to modify this bandgap may be another way to improve room temperature gas sensing by changing the potential barrier energy required for charged species to conduct. Another enhanced feature of nanocrystallites is their conduction of electrons from the surface reaction. These conduction electrons have to overcome a potential barrier induced by the space charge layer. The magnitude of this space charge layer is dependent on the crystallite size (D) as well as the space-charge layer thickness (L). It has been shown that when $D < 2L$, the sensitivity of a gas sensor is enhanced drastically. This $D < 2L$ limit can be reached when employing nanostructures.

Carbon is an exceptional and extraordinary element ever discovered. It has the capability to form different types of bonds with C atoms having varied bond lengths and strengths. This enables its presence in a variety of allotropes corresponding to the various geometries of C atoms. Carbon Nanotubes (CNTs), which consist of single or multiple cylindrical graphene layers, have received much attention due to their novel structural and electronic properties in current years [11]. Based on their excellent properties, many fabulous applications have been suggested [12]. Large quantities of CNTs are necessary for industrial applications. Especially, because the electronic structures of carbon nanotubes (CNTs) depend strongly on diameter and chirality, thus CNTs with a narrow distribution of diameters are highly desirable for the investigation of physical properties and future application in nanoelectronics.

CNTs behave as p-type semiconductor without having any type of doping. A number of interpretations were made for its p-type behaviour including with atmospheric oxygen or metal electrode or due to impurity or defects introduces during the synthesis process. They have very high absorptive property due to the very large surface to volume ratio. CNTs based sensors also gave very high sensing response to gases e.g. NH_3, NO_2, CO_2 etc. [13]. The sensing mechanism of through these nanotubes is based on the chemisorption and physisorption process. Also, CNT-based thin film may also be used for the fabrication of solar cells having high efficiency. The chemical sensors [14] fabricated by using carbon nanotubes (CNTs) have created a great interest in the research community and it was demonstrated that these can be used to detect toxic gas such as CO_2 and CO with low concentration level at room temperature [19, 20].

Requirements of a LPG, CO_2 and Humidity Sensor

Liquefied petroleum gas is one of the most hazardous gases due to its inflammable and explosive nature which presents much harm to humans as well as environment. Also, it is one of the extensively used gases. Therefore the leakage of LPG is a serious problem. So nowadays the LPG sensor has become a very interesting topic in view of the fundamental research as well as industrial applications.

CO_2 is one of the major pollutants which causes so many problems and so hazardous for us. Hence, it is crucial to detect it in its early stages of the leakage and to perform the active suppression.

Humidity refers to the water in gaseous form whereas moisture refers to the water in liquid form. Therefore, humidity obeys gas laws. Humid air being less dense is one of the fundamental biotic factors that decide the habitat of a particular plant or animal. Humidity measurement is required for climate monitoring, human health, food preservations, packaging, weather forecasts etc.

For designing a robust gas/humidity sensor, the sensor material should possess the following qualities given as under:

(i) The material should have high sensitivity over a wide range of humidity and temperature.

(ii) It should quickly respond to any fast changes in the ambient.

(iii) The sensor material should have a rapid response to the variation of gas concentration and good reproducibility of the electrical signal.

(iv) The sensitivity should be independent of the ambient temperature.

(v) The material should not react with any chemical contaminants present in the application ambient.

(vi) It should show stable characteristics for a long time.

(vii) The construction of the sensor should preferably be simple using IC technology and of low cost.

(viii) The device should be operated at low voltage.

LPG gas sensor working principle

The gas sensing mechanism is based on the surface controlled phenomenon of thin-film sensor. Such a phenomenon depends on the open surface area of the thin film at which the gas reacts and adsorbed with pre-adsorbed oxygen molecules. The centre of oxygen chemisorption is localized donor and acceptor states, oxygen vacancies and defects formed on the surface of nanomaterial which is formed during synthesis. These pores are filled with oxygen when exposed in the air. For achieving the equilibrium state between atmospheric oxygen and oxygen of the sensing element the gas sensing film has been put inside the sensing setup. So the equilibrium has been formed due to chemisorption process occurred at room temperature. The stabilized resistance at this state is known as the resistance in the presence of air (R_a).

The chemisorption kinematics at room temperature may be explained by the following reactions:

$$O_2\,(gas) \leftrightarrow O_2\,(ads) \ldots\ldots\ldots\ldots(1)$$

$$O_2\,(ads) + e^- \rightarrow O_2^- \ldots\ldots\ldots\ldots(2)$$

When the LPG is exposed to the thin film then the increase in resistance has been found. This is because the chemisorbed oxygen captures the free electrons from the conduction band so the electron concentration at the film surface starts decreasing and higher resistance has been observed. Thus, the sensor resistance was used for determining the surface reaction occurred by the charge transfer mechanism at the surface of the sensing element. When the thin film is exposed to the reducing gas molecule such as LPG, it reacts with the chemisorbed oxygen. The adsorbed oxygen is removed and gaseous species are formed in interaction with the hydrocarbons (C_nH_{2n+2}) of LPG. Then the resistance of the film has been changed, which is imputable to the alteration in the width of the depletion layer after exposure to LPG. The reaction of hydrocarbons with oxygen species is given as Eqn. 5:

$$C_nH_{2n+2} + O_2^- \rightarrow C_nH_{2n}O + H_2O + e- \ldots\ldots\ldots\ldots\ldots..(3)$$

Where C_nH_{2n+2} represents the hydrocarbons present in LPG. When the LPG reacts with the sensing element, then the surface ions interact with LPG and formed water and developed a potential barrier. Initially, the film surface was dry and when the gas is let out along the film then the condensation of the water vapour takes place in the pores so the resistance of the film becomes constant [15, 16].

CO_2 sensor working principle

The gas sensing mechanism depends on the oxygen chemisorption centers which are localized donor and accepter states, oxygen vacancies and defects formed on the nanomaterial surface during the synthesis. When the film was exposed in air, the O_2 of air was adsorbed on the nanotube surface and ionized to oxygen ion by trapping the free electron and built a thick space charge layer, which increases the potential barrier. At lower concentration of gas, the CO_2 molecules interact with oxygen species and form a metastable compound CO_3 and release electrons which attenuate the potential barrier and the resistance starts decreasing.

$$O_2 \text{ (ads)} + e- \longrightarrow O^{2-} \text{ (ads)} + O^- \ldots\ldots\ldots\ldots\ldots..(4)$$

When interacting with CO_2

$$CO_2 + O^- \rightarrow CO_3 + e \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Humidity sensor working principle

The mechanism to interpret the electrical response of MWCNT based materials to humidity is based on the physically and chemically adsorbed water molecules as well as capillary condensation of water inside the walls of the nanotube and also on the tiny pores found in the film. The nanostructure and the surface reactivity with water are fundamental parameters for the performance of MWCNT based humidity materials [17]. Due to having the tubular structure of sensing element and highly porous film with large surface to volume ratio is the key elements for humidity sensing. Water was absorbed by nanotubes when they were exposed to humidity leading to an increase in their electrical conductivity [18, 19]. Water adsorption inside the walls and surface functionalization of nanotubes are important for electrical conduction, being dominant for low relative humidity. Adsorbed water condensed on the surface of materials and protons were conducted in the form of aquatic layers. The larger is the surface area, the larger is the content of adsorbed water and, consequently, larger is the density of charge carriers, usually protons.

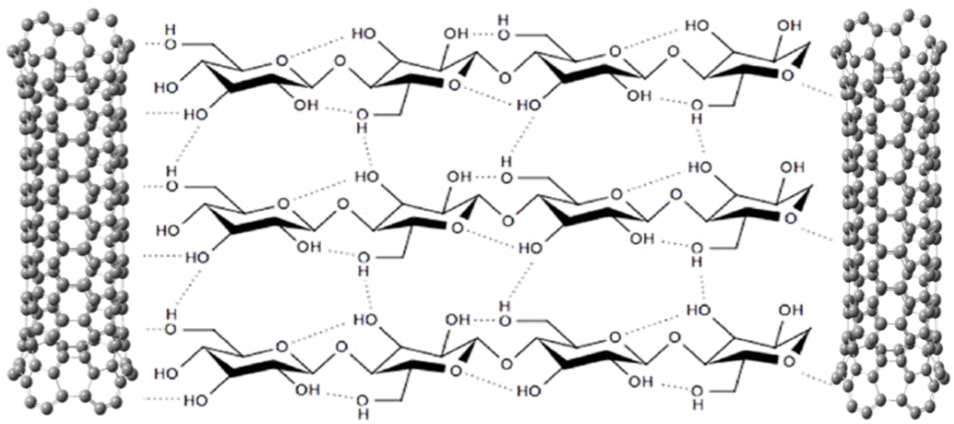


Fig. 1 Grotthus chain reaction in MWCNT based thin film.

The operation of the sensor is based on the conductivity of the tubular and highly porous films due to having high surface area are preferred for the humidity sensing investigation. The mechanism of the humidity is based on the physisorption and chemisorption of hydroxyl ion on the surface of MWCNTs. When the film interacts with the water molecule then physisorption of water molecule with MWCNTs are formed. Physisorbed water dissociates into H_3O^+ and OH^- because of high electrostatic fields at the interface between the surface and adsorbed layer. Transportation of charge occurs by movement of a proton from H_3O^+ ion to an adjacent water molecule and so on. Now, protonic conduction is set up on the surface. This mechanism of charge transport is known as Grotthuss chain reaction mechanism as shown in Fig. 8. Protonic conduction causes the observed drop in impedance in the humid atmosphere. At low humidity, only the surface protonic conduction causes the change in resistance. However, at higher values of humidity, water may condense and be polarized on the sensing surface; hence, electrolytic conduction also occurs, causing a large change in impedance [20].

The present thesis is divided into seven chapters. Chapter 1 contains the introductory part of the synthesis of carbon nanomaterials and application in various fields. It also focuses on the detailed description of synthesis of carbon nanotube and its sensing applications. A detailed investigation including synthesis, characterization and application as field emitter and photosensor on multiwall carbon nanotube is depicted in chapter 2. In chapter 3, the synthesis, characterization and humidity sensing property of modified MWCNT are reported. Chapter 4 describes the fabrication of f-MWCNT thin film using ethanol as a carbon precursor and its application as CO_2 sensor at room temperature. Chapter 5 reports the synthesis of MWCNT/PPY nanocomposite using oxidation polymerization method and its application as CO_2 and humidity sensor at room temperature. Chapter 6 reports the effect of LPG on the resistance of MWCNT/ZnO based thin film at room temperature it also reports the enhanced sensitivity and sensor response of the sensor by doping of MWCNT with TiO_2. A study of the synthesis, characterization with gas, photo and humidity sensing properties of MWCNT, f-MWCNT and its different nanocomposite is summarized in chapter 7. This chapter also gives the guidelines for further research work in the field of gas and humidity sensing.

Chapter 1: This chapter contains the basic introduction of different type of carbon nanostructures and their roles in a different type of sensing application have also been discussed. This chapter also provides detail information for the synthesis of carbon nanomaterial and the advantage of a chemical vapor deposition method over other synthesis methods. The chapter provides the application of carbon nanotubes in various fields like humidity sensing, gas sensing, photo sensing and field emission devices. The chapter also introduces the detailed information about the ongoing research on carbon nanomaterial in the field of sensors. For this, carbon nanomaterials are the best suited. However, obtaining high sensitivity, good reproducibility, negligible ageing effect with fast response and recovery time at room temperature are the major concern which is not yet reported in the literature. Carbon nanomaterials symbolize an increasing asset in numerous productions, particularly due to their sharp chemical, physical, and electronic properties and have versatile applications like environmental monitoring, health and personal care, energy, water treatment. Also, as the crystallite size of these materials reduces, great enhancement in their properties is observed. This diverted the research community towards the low dimensional metal oxides, while ensuring that their properties remain stable even at high operating temperature.

In present investigations synthesis and characterization of carbon nanomaterials like Multiwall Carbon Nanotube (MWCNT), Functionalized Multiwall Carbon Nanotube (f-MWCNT), Modified Multiwall Carbon Nanotube, MWCNT/PPY nanocomposite, MWCNT/ZnO nanocomposite and MWCNT/TiO_2 nanocomposites have been carried out. Thin film of various carbon nanomaterials have been fabricated using spin coating technique. Further they were employed as gas, humidity and photo sensor.

Chapter 2: This chapter includes the synthesis of MWCNTs at temperatures 650 ℃ and 750 ℃ and the investigations on the field emission and photosensing property. The synthesized material was then investigated using SEM, XRD and UV-visible absorption technique. The dilute solution of the material was analyzed using TEM and particle size analyzer. Field emission current of both the sample was calculated. The emission of photocurrent at room temperature through thin film was also calculated. Sensitivity along with response and recovery time was calculated. The experiment was repeated from time to time to check the repeatability, response and recovery times. The material was employed in a field emission device to observe the field emission capability of the material. Experimental data were verified by theoretical data using DFT calculations.

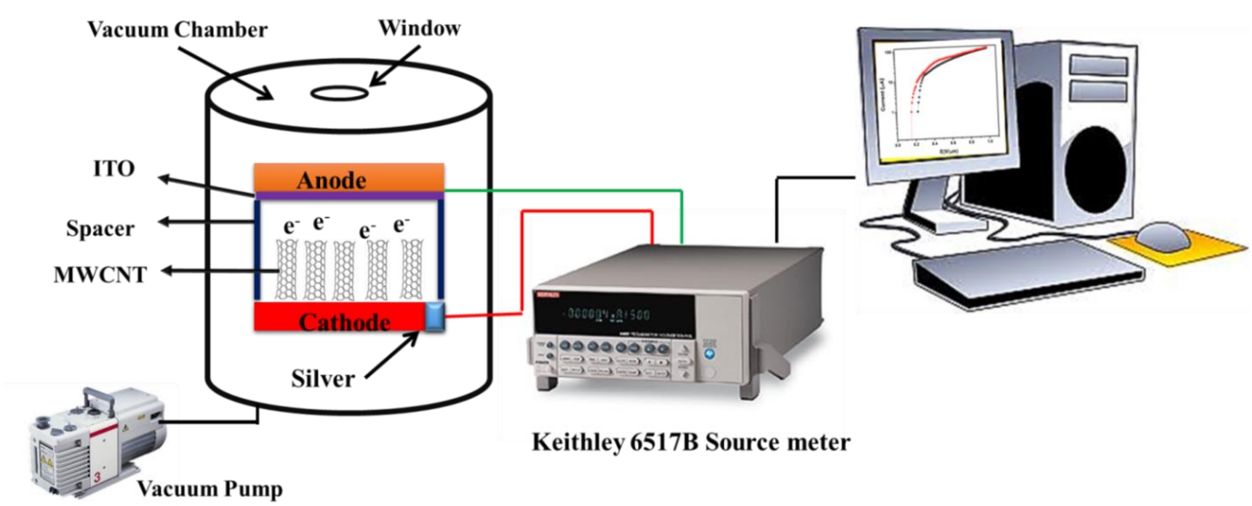
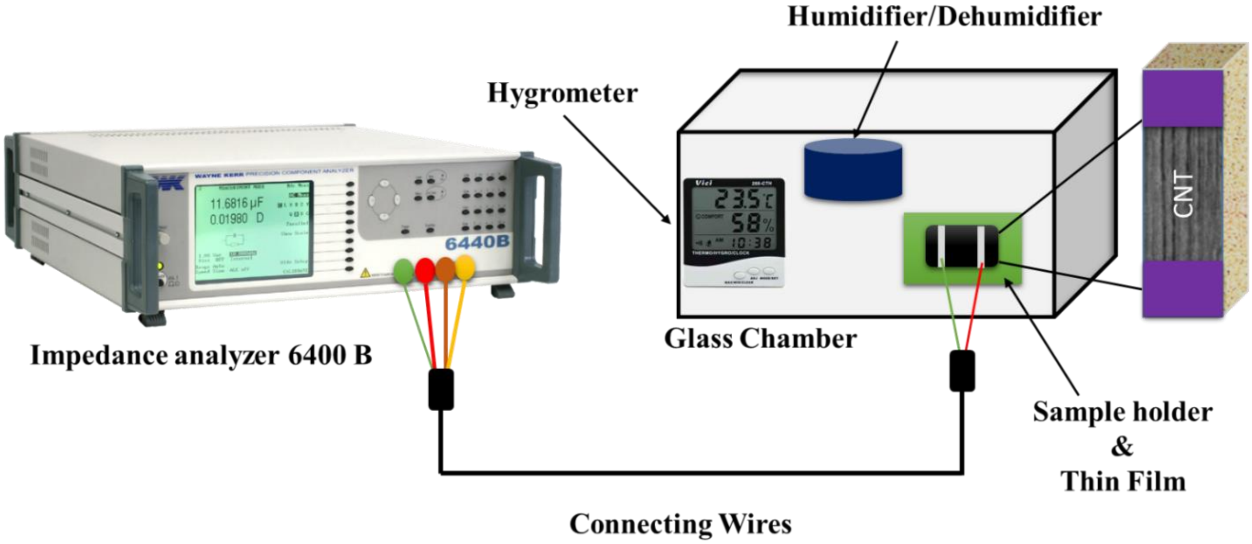


Fig. 2 Graphical abstract of Chapter 2

Chapter 3: One-dimensional carbon nanostructures e.g. Carbon nanotubes (CNTs) possess outstanding physical properties owing to their unique structure and atomic arrangement. High electrical conductivity, highly exposed surface area and stability of these carbon nanostructures introduce them as the leading choice of nanomaterials for a number of electrical and industrial applications like humidity and gas sensing. The conductance or capacitance of CNTs varies greatly with the adsorption-desorption of molecules such as hydroxyl (OH-) ions. In this paper, we report the preparation of carbon nanotubes based thin film using CVD technique which has been characterized by using Scanning Electron Microscopy (SEM), UV-visible microscopy and X-ray diffraction method. The characterized film was investigated as a humidity sensor. In the experimental part, the variations in the impedance of film were observed by Impedance Analyzer 6440 B on varying the humidity levels. In the theoretical part, we have simulated the CNTs using Ab initio density functional theory (DFT) calculations to investigate the formation of endohedral complexes among CNTs and OH- groups. The binding energy, dipole moment, electronegativity and HOMO-LUMO gaps were monitored by increasing the hydroxyl group levels which results in its better use in developing a robust and cost-effective humidity sensor.



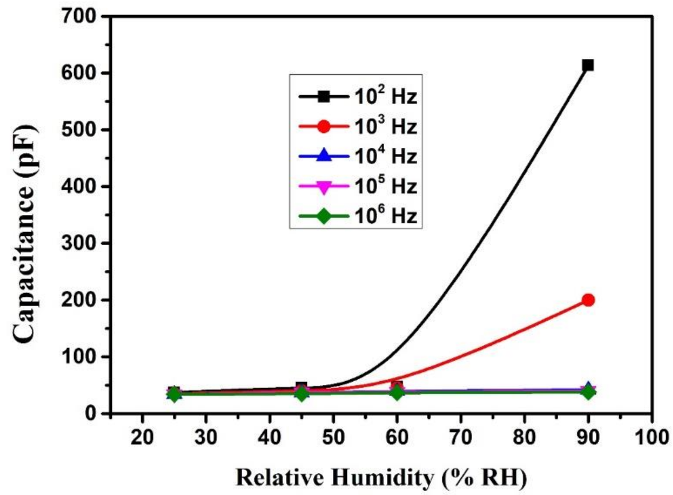


Fig. 3 Graphical abstract of Chapter 3

Chapter 4: This chapter reports the synthesis and characterization of Multiwall Carbon Nanotube (MWCNT) based thin film and its application as a CO_2 gas sensor. The MWCNT was prepared by direct liquid injection chemical vapor deposition method (DLICVD) using ethanol as a precursor in the presence of argon gas atmosphere and furnace temperature at 750 °C. The thin film of MWCNT was prepared by using the spin coating technique and characterized using Scanning electron microscope (SEM), UV-Visible spectrometer, Particle size analyzer and X-ray diffractometer (XRD). The vibrational and rotational spectra were observed through Fourier Transform Infra-Red Spectroscopy (FTIR) and Raman Spectroscopy. The SEM image of the thin film exhibited the tubular structure grown throughout the surface. From XRD, the minimum crystallite size was found to be 14 nm. The optical energy band gap of the nanotube-based thin film was found as 3.6 eV. The synthesized CNT-based thin film was employed for the CO_2 sensing at room temperature. The sensor response of the sensor was found as 2.1 and the results were found 98% reproducible. The response and recovery times were found to be 30.2 and 49.6 sec respectively. Theoretical calculations were also performed in the support of CO_2 sensing through the MWCNT.

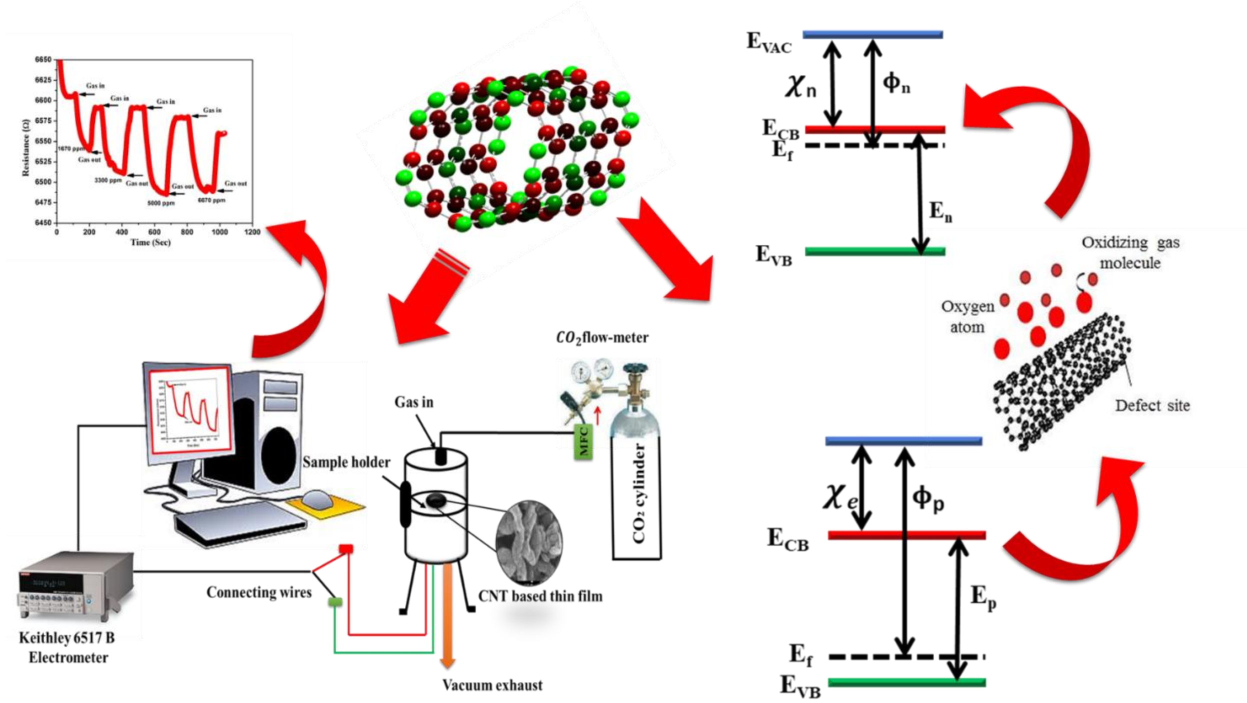


Fig. 4 Graphical abstract of Chapter 4

Chapter 5: This chapter includes the synthesis of multiwall carbon nanotube (MWCNT) and polypyrrol (PPY) nanocomposite and its characterizations along with the applications. The MWCNT was prepared by using direct liquid injection chemical vapour deposition technique (DLICVD) and MWCNT/PPY based nanocomposite was synthesized by the oxidation polymerization method. The thin film of MWCNT/PPY was prepared by spin coating technique and characterized using Scanning electron microscope (SEM), Transmission electron microscope (TEM), Particle size analyzer and X-ray diffractometer (XRD). The vibrational and rotational spectroscopies were observed through Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy. The optical band gap was found to be 3.2 eV and the minimum crystallite size was found to be 8 nm. The synthesized MWCNT/PPY has been used for CO_2 and humidity sensing. The sensor response of thin-film towards CO_2 was found to be 7.2 at 1000 ppm and minimum response and recovery time at 250 ppm were found to be 30 sec and 37 sec respectively. The sensitivity of thin-film towards humidity was found to be 41.3 kΩ/%RH. The theoretical calculation was also performed in support of experimental data.

Chapter 6: In this chapter, the synthesis of MWCNT based nanocomposite used as a room temperature LPG sensor was investigated. The first part precepts the effect of LPG on the resistance of MWCNT/ZnO based thin film at room temperature. The film was then investigated using SEM, TEM, FTIR and UV-visible spectroscopy. The average particle size of the material was calculated by using particle size analyzer. The highest sensor response was found as 60 at 2 vol%. In the second part, we enhanced the sensitivity and sensor response of the sensor by doping of MWCNT with TiO_2. This film was further analyzed by using SEM, TEM, XRD, FTIR and Raman spectroscopy. The average pore size and surface area were calculated by using BET. These films were employed as room temperature LPG sensor to observe the LPG sensing potential of the film. Sensor response along with response and recovery time was calculated. Experimental data were verified by theoretical data using DFT calculations.

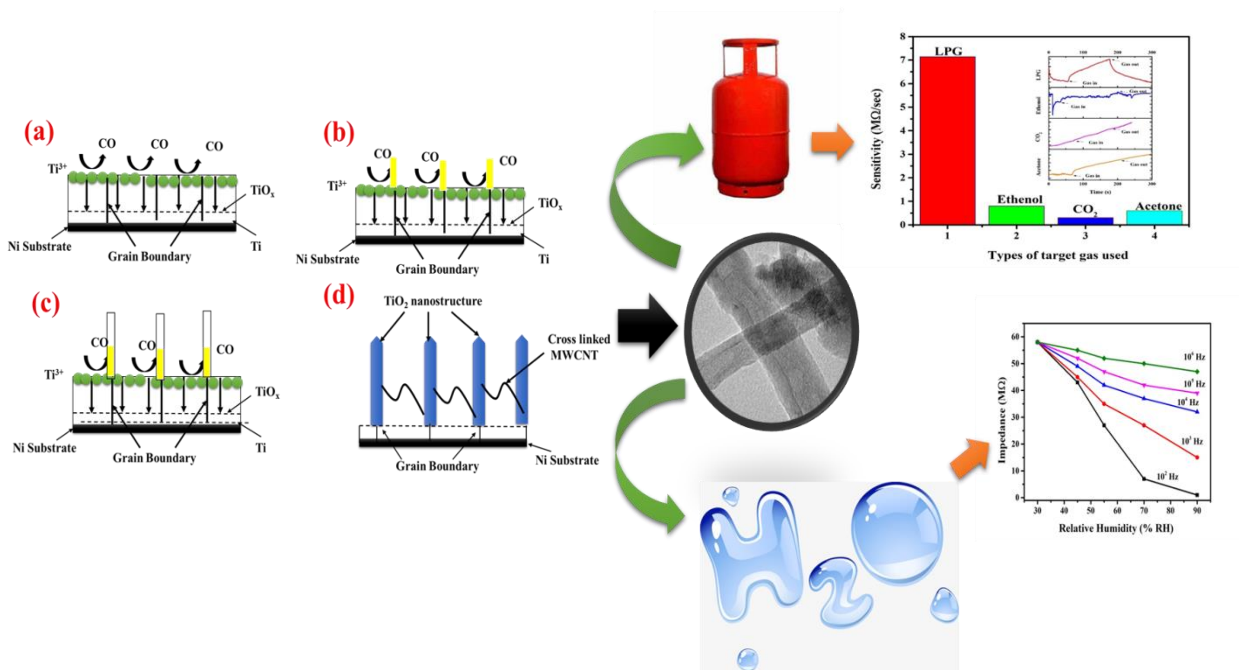


Fig. 5 Graphical abstract of Chapter 6

Chapter 7: A study of synthesis, characterization and sensing properties of carbon nanostructure and its nanocomposites is summarized in the present chapter. This chapter also gives the guidelines for further research work in the field of carbon nanostructure and its nanocomposite films as efficient humidity, gas and photosensor.

The complete overview of the Thesis including the sensing materials, dopants, bandgap, sensitivity, crystallite size, average grain size, pore size is depicted in Table 1. The main target of our research work was to design and fabricate the different type of sensors using carbon nanomaterials which would be robust, cost-effective and more sensitive than previously reported sensors.

Table 1: A chapter-wise sketch of the Thesis.

Chapters	**Materials**	**Methods**	**Types of sensing application based on the best selectivity**	**Sensitivity/Sensor response**	**Response time**	**Recovery time**
Chapter 1	**Introduction**					
Chapter 2	MWCNT	DLICVD	Photosensor	4.4 µA/sec	34 m sec	38 m sec
Chapter 3	MWCNT modified with NMP	DLICVD	Humidity	6.41 pF/%RH	24 sec	30 sec
Chapter 4	MWCNT functionalized with HNO_3 & H_2SO_4	DLICVD	CO_2	1.9 Ω/sec & 2.1	30 sec	49 sec
Chapter 5	MWCNT/PPY	DLICVD/Oxidation polymerization	CO_2	81.3 Ω/sec & 7.2	30 sec	36 sec
Chapter 6	MWCNT/ZnO	DLICVD/Chemical precipitation	LPG	3.8 MΩ/sec & 35.8	475 sec	491 sec
	MWCNT/TiO_2	DLICVD	LPG	4.2 MΩ/sec & 429	36 sec	20 sec
Chapter 7	**Conclusions**					

From the Table 1 we conclude that the pure MWCNT, Modified MWCNT, CNT/PPY and MWCNT/TiO_2 synthesized by DLICVD method are excellent materials for photo-sensing, humidity, CO_2 and LPG sensing applications respectively. After optimization, these materials may be useful for a commercialized model of sensor applicable for both indoor and outdoor detection of gas/ humidity and photon. Thus various configurations/systems described in the thesis and the detailed specifications given for each of them are expected to prove useful in fabricating a sturdy, robust and cost-effective sensor suitable for operation at room temperature.

7.7 Scope of Further Research

- Future investigations that would be fruitful in further understanding the role of carbon nanomaterials for more applications at and below room temperature are needed. These include incorporation of the recovery aspects achieved from the incorporation of catalyst onto the surface of carbon nanomaterials being used to detect a reducing gas. Growth simulations and reconstructions of the different surface species under different synthesis conditions would give rise to even more specific engineering of nanomaterials than what is currently known to the world of research within nanotechnology. Spectroscopic evaluation and surface nanoscale engineering of the sensing mechanism would be very fruitful in the selection of the material to be used for the fabrication of cost-effective sensors in future.
- Detailed analysis of the evolution of the surface reactions with respect to the temperature needs to be carried out, in order to exactly understand the reaction products from the surface interaction. Temperature Programmed Desorption (TPD) experiments give valuable information on the formation and desorption of reaction products on the surface. Controlled TPD experiments, at the sensing temperatures, need to carry out for understanding the surface chemistry.
- The occurrence of crystallographic defects affects the sensing mechanism of gas sensors. An in-situ XPS with gas atmosphere control would give a better idea as to what happens to the electronic structure of the carbon nanomaterials and its nanocomposite during high-temperature gas interaction and also an idea of how the shear planes grow and whether this leads to an increase in the density of states in the gap.
- Carbon nanostructured materials may be very useful in biomedical applications such as drug delivery system, cancer cell detection and treatment etc. The related physics may be studied.

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