Chapter I Introduction

1.1 Introduction

1.2 Motivation

1.3 Types of gas sensors
   1.3.1 Optical gas sensors
   1.3.2 Surface Acoustic Wave (SAW) gas sensors
   1.3.3 Amperometric gas sensors
   1.3.4 Dielectric or capacitor-type gas sensors
   1.3.5 Catalytic gas sensors
   1.3.6 Metal oxide gas sensors

1.4 Tin dioxide (SnO\textsubscript{2}) and titanium dioxide (TiO\textsubscript{2})
   1.4.1 General properties
      1.4.1.1 SnO\textsubscript{2}
      1.4.1.2 TiO\textsubscript{2}
   1.4.2 Literature review on SnO\textsubscript{2} and TiO\textsubscript{2}-based metal oxide gas sensors

1.5 Green synthesis (Green chemistry)
   1.5.1 Green synthesis definition and principle
   1.5.2 Need of green synthesis
   1.5.3 Applications of green chemistry
   1.5.4 Advantages of green synthesis
   1.5.5 *Ganoderma Lucidum* (*G Lucidum*)

1.6 Characterization Techniques
   1.6.1 XRD (X-ray Diffraction)
   1.6.2 Scanning Electron Microscope (SEM)
   1.6.3 Energy Dispersive X-Ray Spectroscopy (EDAX)
   1.6.4 Ultraviolet/Visible Absorption Spectroscopy
   1.6.5 Transmission Electron Microscopy (TEM)
   1.6.6 X-ray Photoelectron Spectroscopy (XPS)
   1.6.7 Brunauer-Emmett-Teller Measurement

1.7 Objectives of Thesis

1.8 Thesis outline
   References
Chapter I Introduction

1.1 Introduction

Gas sensor is a device used to detect and quantify harmful, explosive and toxic gases in an area, often as part of a safety system. In the last decade, researchers have made a great efforts to fabricate the gas sensors of various types [1]. Gas sensors play an important and crucial role in several applications such as, a part of security or control systems, and to its leakage detection. In particular, monitoring of explosive and hazardous gases in the air is important challenge due to an increase in usage of different gases in industries. Owing to industrial applications, gas sensors are increasingly needed for industrial health and safety, environmental monitoring and process control. To meet industrial needs, considerable research into new sensors is ongoing, including efforts to enhance the performance of solid-state devices, in terms of sensitivity, selectivity, fast response/recovery and stability towards the target gas used. Currently, there are needs of gas monitoring systems which are divided in the following four broad categories [2].

(i) For oxygen, in connection with the monitoring of breathable atmospheres and for the control of combustion of processes i.e. in the boilers and internal combustion engines where, the desired concentration is required.

(ii) For the toxic gases in air, the exposure limit for the protection of human health is in between few parts per billion (ppb) to several hundreds of parts per million (ppm).

(iii) In case of flammable gases in air to protect against the unwanted fire or explosion, concentrations of these gases to be measured in the range up to lower explosive level (LEL). This level is up to few percent in some gases.

(iv) For the volatile organic compounds (VOCs), in connection with the monitoring of chemical atmospheres and for the control of organic and inorganic chemical reactions, the concentration of VOCs required is in between few ppb to few hundreds of ppm depending upon the type and nature of VOC.
1.2 Motivation

Gas sensors play crucial role in many important areas such as environmental monitoring, automotives, domestic safety, public security, air-conditioning in aeroplanes, space-crafts, etc. In 1984 more than 16000 people died, 5,58,125 people injured and 3,900 severely and permanently disabled in Bhopal disaster, also known as Bhopal gas tragedy. It was a gas leak incident in the Union Carbide India Limited (UCIL) pesticide plant which was occurred on the night of December 2-3, 1984 in Bhopal, Madhya Pradesh [3]. In Germany, every year approximately 600 people die, 6,000 seriously injure and 60,000 slightly injure in domestic fire accident. Most of them die due to the air pollution i.e. poisoning with smoke during night. The victims are unconscious in sleep and suffocate. Since the late 1970s, Europe’s main political concern is Air pollution. In 1996, the European Council adopted a Framework Directive on ambient air-quality assessment and management, Directive - 96/62/EC of September 27, 1996 [4], hence from 1996 in an automotive industry, metal oxide gas sensors are used to monitor the quality of vehicle exhaust. To analyze the air quality the sensors based on the change in resistivity of metal oxide semiconductors are primarily used. The metal oxide gas sensors have significant advantages over mass sensitive sensors or thermal conductivity sensors. High sensitivity, selectivity and stability, fast response and recovery time, low gas detection, a low dependence on humidity and temperature, a long service life and relatively low product costs are few advantages of the metal oxide semiconductor gas sensors. Taking these advantages into consideration, researchers are motivated towards metal oxide gas semiconductors.

In most of the chemical industries and fermentation plants, ethanol is the main product or by-product, to monitor the chemical reaction involved in this process; ethanol sensors play an important role. Moreover, for detecting ethanol vapours in human breath and to control drunken driving, breath analyser need to be highly sensitive and stable to ethanol [5]. Therefore, ethanol sensitive sensors are necessary and hence, further research on ethanol sensors is needed. Chlorine gas, when emitted into the environment, is very harmful. Conventionally, chromatography or chemical detecting tubes were used for the detection of Cl$_2$ gas. Therefore, the importance and demand of Cl$_2$ gas sensors capable of detecting low concentrations is increasing. The SnO$_2$-based ethanol gas sensor and TiO$_2$-based chlorine gas sensor properties, and
effect of noble metal sensitization (Ag, Au and Pd) on SnO₂ and TiO₂ sensor properties are attempted in the present work.

1.3 Types of gas sensors

Gas sensor is a device, which when exposed to a gas or a gaseous environment, changes one or more of its physical properties [6]. Sensors can be classified based on their operating principle as:

- Optical gas sensors
- Acoustic gas sensors
- Amperometric gas sensors
- Capacitor type gas sensors
- Catalytic gas sensors
- Metal oxide gas sensor

1.3.1 Optical gas sensor

Optical gas sensor is based on the absorption of light on the surface of target gas molecules in a specific wavelength [7]. The optical gas sensor consists of two main components; an infrared light source and an IR detector. Usually, the light source is an infra-red solid state LASER diode and an IR light detector is a semiconductor IR detector diode. The IR light source transmits a beam of light through gas environment towards the IR detector. According to the principle of optical gas detector, when light falls on the gas molecules, they absorb the light in a specific wavelength and thereby the intensity of light is get reduced, this decrease in intensity of light is detected by the detector, and sensing in the existence of particular gas is confirmed. The specific wavelength for different gases can be found in online database Figure 1.1 shows a schematic diagram of the optical gas sensor. Optical gas sensors have several advantages, such as good selectivity, sensitivity reproducibility and stability. Optical gas sensors have considerable durability compared to other detection methods. Due to the complexity in electronic circuits which includes IR source, detector and filters the cost of installation is very high. Also, it has a drawback of optical contamination over a period of time.
1.3.2 Surface acoustic wave gas sensor

Surface acoustic wave (SAW) gas sensors consist of an input acoustic transducer, and an output acoustic transducer on a piezoelectric substrate, typically quartz [8]. In between the input transducer and output transducer there is a gas sensitive chemical film. The input transducer produces an ultra-high frequency wave, typically 525 MHz that travels through the film and is detected by the output transducer. During the gas exposure, gas molecules absorb on the surface of the sensitive film, the velocity, phase change and attenuation of the signal can be recorded at the other transducer. The changes in parameters like, phase, velocity and attenuation of signal are calibrated in terms of the percentage of target gas [9]. The main advantage of the acoustic gas sensor is that, it has longer life and is less dependent to environmental contamination in the system. The schematic diagram of surface acoustic wave gas sensor is shown in Fig. 1.2.
1.3.3 Amperometric gas sensors

The principle of amperometric gas sensors is to record the change in ionic current due to oxidation and reduction reaction at the electrolyte. A typical amperometric sensor shown in Fig. 1.3 consists of counter, reference, electrolyte and working electrodes. The positions of the electrodes and electrolyte are shown in Fig. 1.3. The working electrode can be positioned behind electrolyte solution. The change in the current density is recorded due to the oxidation/reduction of target gas in contact with the working electrode and electrolyte. A constant high voltage bias is applied between the electrodes to detect measurable change in the current flow caused by the redox reaction between the gas molecules and working electrode. The sensitivity of the sensor depends on the diffusion rate of gas molecules onto the working electrode; since the diffusion rate of gas molecules in the diffusion chamber is slow, the response as well as recovery of the sensor is slow [10,11]. Amperometric sensors are generally used for the detection of different analysts, in the gas environment or liquid phase.

![Schematic diagram of amperometric gas sensors.](image)

1.3.4 Dielectric or capacitor-type gas sensors

The dielectric or capacitor type gas sensors can be fabricated by introducing a dielectric material between two parallel metal plate electrodes. It is well-known that, the electric capacitance of a condenser depends on the dielectric constant of the materials present in-between the electrodes. If the change in dielectric constant is
measured on exposure of target gas, the condenser can be a sensor for the gas. This type of sensors have already been developed for sensing the humidity, in which the water vapor present in the environment of sensor gives rise to a change in dielectric constant. Capacitive CO$_2$ gas sensor using polycrystalline CuO-BaTiO$_3$ ceramics has been reported [12]. This suggests that other metal oxide ceramics can also be used for the detection of all environmental gases other than CO$_2$.

1.3.5 Catalytic gas sensors

Solid state gas sensors based on catalytic activity can be used to monitor explosive mixtures like methane in air. The device known as ‘pellistor’ is essentially a catalytic micro-calorimeter consisting of a catalytic surface, maintained at a sufficiently high temperature to ensure rapid combustion of flammable gas molecules present there. The catalytic sensor has some limitations like low sensitivity, higher response time due to poisoning and burning out when exposed to high gas concentrations [13].

1.3.6 Metal oxide gas sensors

Brattain and Bardeen in 1956 first reported semiconductor type gas sensitive effects on germanium semiconductor [14]. Later Seiyama and Taguchi in the 1960’s developed semiconductor gas sensors of ZnO for the detection of Liquid Petroleum Gas (LPG) in homes [15]. In 1968, Taguchi (Figaro) revolutionized this field by identifying different metal oxide materials as gas sensing elements [16]. The gas-detection principle of metal oxide is based on the variations of the depletion layer at the grain boundaries in the presence of reducing or oxidizing gases, which lead to modulations in the height of the energy barriers for free charge carriers to flow, thus leading to a change in the conductivity (resistivity) of the sensing material. The operating temperature of the metal oxide semiconductor is generally above the ambient temperature i.e. $\geq$ 100 °C. The electrical resistance of metal oxide depends upon the operating temperature, composition of the surrounding atmosphere and the concentration of ambient gas i.e. oxygen [17]. A simple metal oxide gas sensor with electrical diagram is shown in figure 1.4.
The wide range of metal oxides is divided into two categories.

(1) Transition-metal oxides (\(\text{Fe}_2\text{O}_3\), NiO, Cr\(_2\text{O}_3\), etc.)

(2) Non-transition-metal oxides, which include

(i) pre-transition-metal oxides (\(\text{Al}_2\text{O}_3\), etc.) and

(ii) post-transition-metal oxides (\(\text{ZnO}\), \(\text{SnO}_2\), etc.).

Pre-transition-metal oxides like \(\text{Al}_2\text{O}_3\) and MgO, have large band gap so they fall in inert metal oxide category, hence they are rarely selected as gas sensor materials. The energy gap of transition metal oxides need to be essentially small, so they are preferred as sensor materials [19]. The classification of metal oxide based on the change in resistance on the exposure of oxidizing and reducing gases is shown in Table 1.1 and 1.2 show classification of metal oxides on the basis of conductivity.

**Table 1.1** Metal oxides classification of metal oxide-based oxidizing and reducing gas sensors.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Oxidizing Gas</th>
<th>Reducing Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-type</td>
<td>Resistance increase</td>
<td>Resistance decrease</td>
</tr>
<tr>
<td>(p)-type</td>
<td>Resistance decrease</td>
<td>Resistance increase</td>
</tr>
</tbody>
</table>

**Table 1.2** shows classification of metal oxides on the basis of conductivity

<table>
<thead>
<tr>
<th>Type of conductivity</th>
<th>Metal oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-type</td>
<td>ZnO, MgO, CoO, TiO(_2)WO(_3), SnO(_2), In(_2)O(_3), Al(_2)O(_3), Ga(_2)O(_3), V(_2)O(_5), ZrO(_2)</td>
</tr>
<tr>
<td>(p)-type</td>
<td>Yo(_2)O(_3), La(_2)O(_3), CeO(_2), Mn(_2)O(_3), NiO, PdO, Ag(_2)O, Bi(_2)O(_3), Sb(_2)O(_3)</td>
</tr>
</tbody>
</table>

When the surface of \(n\)-type semiconductor is exposed to the oxidizing gas, the decrease in resistance of metal oxide semiconductor is observed and vice a versa for \(p\)-type semiconductor, shown in Table 1.1. Table 1.2 enlists different \(n\)-type and \(p\)-type semiconductors.
1.4 Tin dioxide (SnO$_2$) and titanium dioxide (TiO$_2$)

1.4.1 General properties

1.4.1.1 SnO$_2$

A wide variety of metal oxides are used for the development of gas sensors for different oxidizing and reducing gases, but SnO$_2$ is investigated intensively over all other metal oxides due to its excellent sensitivity and stability towards the target gases. It is the first considered material for gas sensor, and till date using successfully for different toxic and explosive gases. SnO$_2$ is a wide band gap semiconductor and transparent in color of 3.6 eV band gap energy at 300K [20]. One can tailor its electronic and structural properties for making it useful in liquid crystal displays, photo-detectors, conductive filters and gas sensors [21]. The changes in the chemical behavior of SnO$_2$ are possible because of its multi-valence ability for specific applications. The rutile crystal structure of SnO$_2$, known as cassiterite, has a tetragonal unit cell with space-group symmetry of P42/mnm. The lattice constants are $a = b = 4.731$ Å and $c = 3.189$ Å. The crystal structure of cassiterite tin-oxide, shown in Fig. 1.5, confirms tin atoms of six fold coordination whereas oxygen atoms have three fold. The Sn with two oxidation states has stable SnO and SnO$_2$ oxide form. The rutile structure of SnO$_2$ is very popular due to its enhanced electronic and chemical properties, useful to gas sensor applications.

![Crystal structure of SnO$_2$](image)

**Fig. 1.5** Crystal structure of SnO$_2$

1.4.1.2 TiO$_2$

Titanium oxide is an intrinsic $n$-type semiconductor belongs to the family of transition metal oxides. Naturally occurred three polymorphs are known: anatase
(tetragonal), brookite (orthorhombic), and rutile (tetragonal) [22]. In this review, only the crystal structures (Table 1) [31-33] and the parameters and properties of the rutile, anatase and brookite polymorphs are shown in table 1.3.

(a) Rutile TiO$_2$

Rutile TiO$_2$ has a tetragonal structure and contains 6 Ti atoms per unit cell, as shown in Fig. 1.5. At the most of the temperatures and pressures up to 60 kbar, rutile TiO$_2$ phase is stable. Rutile phase is more stable than anatase for larger particles (~14nm). The structure of rutile is brukite with lattice parameters $a = b = 4.5933$ Å and $c = 2.9592$ Å with $c/a$ ratio of 0.6412, as shown in Fig. 1.5. Anatase and brookite structures can be transformed to the rutile phase at certain particle-size [23].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>$a = 4.5936$</td>
<td>$a = 3.784$</td>
<td>$a = 9.184$</td>
</tr>
<tr>
<td></td>
<td>$c = 2.9587$</td>
<td>$c = 9.515$</td>
<td>$b = 5.447$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 5.154$</td>
</tr>
<tr>
<td>Space group</td>
<td>P42/mnm</td>
<td>I41/amd</td>
<td>Pbca</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>4.13</td>
<td>3.79</td>
<td>3.99</td>
</tr>
<tr>
<td>Ti–O bond length (Å)</td>
<td>1.949</td>
<td>1.937</td>
<td>1.87–2.04</td>
</tr>
<tr>
<td>Molecule (cell)</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

(b) Anatase TiO$_2$

The anatase polymorph of TiO$_2$ is one of the two metastable phases (anatase and rutile). Anatase can be transformed into rutile by calcinations above 700 °C. At 0 °K the anatase phase is more stable than the rutile and the energy difference is very small, 2 to 10 kJ/mol [24]. The structure of anatase phase is tetragonal, with two TiO$_2$ formula units (six atoms) per primitive cell. Lattice parameters are $a = b = 3.7710$ Å and $c = 9.430$ Å with $c/a$ ratio of 2.5134, as shown in Table 1.3.

(c) Brookite TiO$_2$

Crystal structure of brookite TiO$_2$ belongs to the orthorhombic crystal system. Its unit cell consists of 8 formula units of TiO$_2$ and is formed by edge sharing TiO$_2$ octahedra, similar to rutile and anatase as shown in Fig. 1.5. The structure is more complicated and has a larger cell volume. Its density is smaller than other forms of TiO$_2$ thereby, is not used for experimental investigations [26].
The symmetry of brookite structure is very poor as compared to its counter morphs; the dimensions of the unit cell are unequal as shown in Table 1.3. Also the Ti-O bond lengths vary much than in the rutile or anatase phases as shown in Fig 1.5.

1.4.2 Review of research on SnO\(_2\) and TiO\(_2\) based metal oxide gas sensors

The first semiconductor based gas sensor was reported by Brattain and Bardeen in 1956. The experiments were carried out on germanium semiconductor [14]. Later in 1960's Seiyama and Taguchi developed ZnO based semiconductor metal oxide gas sensors for the detection of Liquid Petroleum Gas (LPG) [15]. Taguchi (Figaro) revolutionized this field by using different metal oxide materials as gas sensing elements. He filled Japanese patent in 1968 [16]. Since, then there has been numerous research carried on for new semiconductor materials and on the development of gas sensor technology in order to satisfy the best gas sensor performance. Klmokov et al. [26] explored the potentials and capabilities of several surface-sensitive microscopy approaches to demonstrate the properties of individual SnO\(_2\) nanowires and their networks. The results demonstrated in-situ electron transport properties of a nanostructured wires as an active element in chemiresistor gas sensing devices.

Law et al. [27] reported the development of photochemical NO\(_2\) sensors, at room temperature which are based on individual single-crystalline SnO\(_2\) nanoribbons. The strong photo conducting response of individual single crystalline SnO\(_2\) nanoribbons makes it possible to achieve favorable adsorption and desorption behavior at room-temperature by illuminating the material with ultraviolet (UV) light of energy near the SnO\(_2\) band gap. Klakov et al. [28] grown single-crystal SnO\(_2\) nanowires and nanobelts by thermal evaporation of SnO at 1000 °C into an argon carrier gas containing traces of oxygen. The H\(_2\) and O\(_2\) gas sensing abilities of
individual SnO$_2$ nanowires and nanobelts as gas sensors were measured before and after functionalization with Pd catalyst particles. Pd-functionalized nanostructures showed a dramatic improvement in sensitivity toward oxygen and hydrogen due to the enhanced catalytic activity of the molecular adsorbate on the Pd nanoparticles surfaces.

Liu et al. [29] developed hierarchical SnO$_2$ nanostructures using a simple hydrothermal method and used as an effective gas sensing material to examine volatile gases, such as ethanol, ammonia, benzene, acetone, toluene, methanol, diethyl ether, and methanol etc., where, as-prepared structures exhibited tremendous gas sensing performance toward ethanol.

Bulemo et al.[30] fabricated SnO$_2$ nanotubes (NTs) with numerous clustered pores (pore radius 6.56 nm) and high surface area (125.63 m$^2$/g) via selective etching of core (SiO$_2$) region in SiO$_2$-SnO$_2$ composite nanofibers (NFs). Investigation of gas-sensing performance of the porous SnO$_2$ NTs before and after decorating with Pt nanoparticles suggested exceptional selectivity and superior response (R$_a$/R$_g$) of 154.8 and 89.3 to 5 and 1 ppm of H$_2$S, respectively. Waitz et al. [31] reported the structural characterizations and gas sensing properties of mesoporous SnO$_2$ synthesized by structure replication (nanocasting) from ordered mesoporous KIT-6 silica with promising response to methane (CH$_4$) among several explosive gases. Yang et al. [32] synthesized SnO$_2$ hollow-microspheres by a one-pot hydrothermal method only using cheap Na$_2$SnO$_3$·3H$_2$O as starting material, without using any templates or surfactants. The SnO$_2$ hollow microspheres were employed to fabricate a gas sensor for detecting formaldehyde. The SnO$_2$ hollow microsphere sensor exhibited a high response, quick response/recovery characteristic, good reproducibility, and selectivity to ppm level of formaldehyde, suggesting its promising application as a formaldehyde gas sensor. Zang et al. [33] synthesized mesoporous SnO$_2$ microtubes using a facile and environmentally friendly solvothermal method. The gas sensors based on such SnO$_2$ microtubes showed the lower detection limit to detect formaldehyde and remarkable selectivity with the other various gases when operating at 92 °C. Li et al. [34] synthesized wormhole-like mesoporous SnO$_2$ via a facile evaporation-induced self-assembly method with gas-sensing properties measurement for different target gases. The effect of calcinations temperature on the gas-sensing properties of mesoporous tin oxide was investigated where SnO$_2$ sensor calcined at 400 °C demonstrated remarkable selectivity to ethanol vapors comparison to other target
gases. Kang et al. [35] demonstrated the synthesis and fabrication of thin film-based micro-gas sensors using undoped and Pt-doped SnO$_2$ thin films with thicknesses of 50 and 120 nm using RF sputtering and their sensing characteristics were investigated at 300-440 °C. The Pt-doped SnO$_2$ gas sensors with the thickness of 120 nm highlighted the selectivity to 1 ppm HCHO gas at 31.5 mW power consumption and to 25 ppm toluene gas at 45 mW. Pt-SnO$_2$ based gas sensors calcined at different temperatures for the detection of hazardous CO gas confirmed highest sensitivity for sensor sintered at 800 °C [36].

Pure and noble metal (Pt, Pd, and Au) doped TiO$_2$ nanoceramics have been prepared from TiO$_2$ nanoparticles through traditional pressing and sintering by Xiong et al. [37]. For those samples sintered at 550 °C, a typical premature sintering occurred, which led to the formation of a highly porous microstructure. At room temperature, Pt-doped sensors identified considerable response to H$_2$, with sensitivities as high as $\sim$500 for 1000 ppm at 300 °C. All samples showed good responses to CO, while the responses of noble metal doped samples were much higher than that of the undoped TiO$_2$ sensor. Gong et al. [38] first time reported an ultrasensitive nanostructured sensor which could detect 50 ppm of NH$_3$ gas in air. Specifically, nanograins of a p-type conductive polymer, polyaniline (PANI), were deposited on an electrospun n-type TiO$_2$ fiber surface with an improved sensitivity. The sensor fabricated in this work is 1000 times more sensitive than the best PANI sensor reported in the literature.

Moon et al. [39] synthesized pure and Pd-doped TiO$_2$ nanofiber-mats by electrospinning and subsequent calcination process. The sensors obtained using Pd-doped TiO$_2$ fibers showed promising gas sensing characteristics, such as low-operation temperature (180 °C) and sufficient gas response ($R/R_o = 38$ to 2.1 ppm NO$_2$). A new gas sensor using TiO$_2$ nanotube arrays fabricated by Lin et al. [40] was used for formaldehyde detection at room-temperature. Highly ordered TiO$_2$ nanotube-arrays were synthesized by using a simple electrochemical anodization process with a good response to different concentrations of formaldehyde from 10 to 50 ppm and a very good selectivity over other reducing gases such as ethanol and ammonia at room temperature.

Lee et al. [41] fabricated vertically aligned TiO$_2$ nanotube arrays for H$_2$ gas sensor by using atomic layer deposition combined with anodic aluminum oxide template. The TiO$_2$ nanotube sensors showed the highest magnitude of gas response of $\sim$100 toward 1000 ppm H$_2$/air at 100 °C. The sensor also showed a very short
response time (<1 s) and a high selectivity for H2 gas against several gases including NH3, CO, and C2H5OH.

Reduced graphene oxide (RGO) decorated TiO2 microsphere sensors, prepared by Li et al. [42] using simple hydrothermal method, obtained good sensitivity and excellent selectivity to different concentrations of ammonia from 5 ppm to 50 ppm at room-temperature. However, the response and recovery time of this sensor to ammonia was overwhelming and need further optimization.

Krško et al [43] presented a flexible H2 gas sensor prepared on 38 μm thick Kapton polyimide foil, based on a TiO2 thin. Under dry conditions, the sensor was highly sensitive even at room-temperature, with response (R0/RH2) reaching ~10^4 for 10000 ppm H2 in synthetic air and as low as ~30 ppm capability of sensing. The effect of humidity lowered the sensor performance at room-temperature. At 32% relative humidity the sensor response to 10000 ppm H2 decreased to ~10^3 and the lowest detected H2 concentration was ~300 ppm H2. Kim et al. [44] reported metal oxide semiconductor gas sensor fabricated by micromachining process that consisting of the micro-platform of Pt heater and electrode of 2.5 mm × 2.5 mm in dimensions. For hybrid sensing materials, SnO2 nanoparticles and TiO2 nanotube arrays were deposited on the micro-platform. Detection performances for CO and CH4 gases were investigated at operating temperatures of 100°C and 300°C, respectively. The power consumption of fabricated micro platform was 28 mW and 94 mW at 2 V and 4 V of heater voltages, respectively. High sensitivity and short response time towards both gases were noted.

Nikfarjam et al. [45] reported pure TiO2 and gold nanoparticles (GNP)-TiO2 using a novel electro-spinning procedure equipped with secondary electrostatic fields on highly sharp triangular and rectangular electrodes provided for gas sensing applications. The sol used for spinning nanofiber consisted of titanium tetraisopropoxide (C12H28O4Ti), acetic acid (CH3COOH), ethanol (C2H5OH), polyvinylpyrrolidone (PVP), and gold nanoparticle solution. Response of pure TiO2 single nanofiber sensor was measured for 30 for 200 ppm carbon monoxide gas. Addition of appropriate amounts of GNP decreased the operating temperature and increased the responses. CO concentration threshold for the pure TiO2 and GNP-TiO2 samples were about 5 ppm and 700 ppm, respectively. Park et al. [46] synthesized TiO2 nanoparticle-functionalized In2O3 nanowires by spin coating and a thermal
annealing process using In$_2$O$_3$ nanowires synthesized by VLS mechanism and hydrothermally synthesized TiO$_2$ nanoparticles. This sensor showed a high performance towards acetone gas detection at low-temperatures and ethanol gas detection at high-temperatures. Acetone sensors using TiO$_2$ nanoparticles functionalized In$_2$O$_3$ nanowires showed enhanced performance with good selectivity and responses.

1.5 Green synthesis (Green chemistry)

In modern era, the green synthesis has laid down to the novel approaches in the area of material designing because of its noteworthy principles of waste prevention, atom economy, use of less hazardous chemical synthesis approach, reduced derivatives, design in safer, energy efficiency, renewable feed stocks, superior catalytic reagents, design for degradation, real-time analysis for pollution prevention and inherently safer chemistry for accident prevention etc. [47]. The green chemistry is an exploitation of these principles leading to the reduction or elimination of the use or generation of hazardous substances in the design, manufacture and application of chemical products. Owing to this, green synthesis has become an advanced state of material modeling as compared to the prior state of art synthesis approaches. In the present study, green synthesis of SnO$_2$ and TiO$_2$ were carried out using biological species namely medicinal mushroom so called Ganoderma lucidum.

1.5.1 Green synthesis definition and principle

The approach that reduces or eliminates the use or generation of hazardous substances in designing, manufacturing and application chemical products is called green synthesis. It is also called as green chemistry or sustainable chemistry. The green chemistry works under the twelve principles as listed below [48].

1. Prevention - The synthesis process must be in such a way that the formation of waste must be prevented instead of cleaning or treating the already generated waste.
2. Atom economy- In a typical synthesis process all the chemicals used during the process must be converted into in final product.
3. Less hazardous chemical syntheses - The use or generation of the hazardous substances during the synthesis process should be prevented.
4. Designing safer chemicals - The end products of chemical processes must be less hazardous reagents.
5. Safer solvents and auxiliaries - The auxiliary substances, solvents, separation agents, etc., in any chemical reaction are avoided.

6. Design for energy efficiency - The synthesis methods should be carried out in an ambient temperature and pressure at optimum energy consumption.

7. Use of renewable feed stocks – The raw materials/feed stocks used in the synthesis process are renewable rather than depleting.

8. Reduce derivatives – The unnecessary derivatives and the steps having the requirement of additional reagents in a synthesis process should be minimum and to avoid the generation of waste.

9. Catalysis-catalytic reagents used should be in a way they should maintain the stoichiometry.

10. Design for degradation - The end product of chemical synthesis should be completely degradable and do not persevere in the environment at the end of their functioning.

11. Real-time analysis for pollution prevention - The analytical methodologies should be defined properly, so that it will help the real time analysis, in process monitoring and control of hazardous substances.

12. Safer chemistry for prevention of accident - The substances and the chemical materials used in a chemical process should be chosen properly for the minimization of chemical accidents.

1.5.2 Need of green synthesis

The several chemical approaches are being reported for the synthesis of different kinds of materials like metal, semiconductors, oxides, inorganic materials, organic materials etc. Often most of chemical approaches are costly and do not follow the basic principles of green chemistry as mentioned above. As a result, these approaches end up with the problems related to human health, environment pollution, economy and business. For example, usually chemical synthesis leads to the presence of some of the toxic chemicals absorbed on the surface that may have adverse effects in the medical applications. Hence, there is need to search the pathways that will overcome the problems associated with the prior-art approaches. The green synthesis offers the novel solution to the inherent problems of chemical and physical approaches because it is cost effective, environment friendly, useful for mass-production of chemicals.
Furthermore, during the designing of different materials by using green chemistry, high pressure, high energy, high temperature and toxic chemicals are not required. For example, the synthesis of nanomaterials/nanoparticles can be done by using the plant extracts or microbial enzymes with obeying the principles of green chemistry. With their antioxidant or reducing properties they usually are responsible for the reduction of metal compounds into their respective nanoparticles.

1.5.3 Applications of green chemistry

The green chemistry has number of applications which include inorganic nanomaterials, metal nano materials, polymers, pillared clays, coordination compounds, and inorganic–organic hybrid materials, metal–organic frameworks etc. They can be categorized into batter application-types for fuel cell, selective transformation, photocatalysis, and environmental related applications [49]. The pollution prevention, remediation of contaminated soils and water, and sensing and detection of pollutants etc., are some the noticeable green chemistry applications of the nanomaterials.

1.5.4 Advantages of green synthesis

There are number of advantages of the green chemistry in the various areas like human health, environmental issues, industry etc. The following advantages could be realized on employing the green approaches in day to day life [50].

1. Green chemistry leads a less release of hazardous chemicals waste. This reduces the air and water pollutions, which in turn provides less damage to human lungs and digestive system.

2. Less use or generation of the toxic materials in the chemical industry leads the less use of protective equipment and less potential for accidents like fires, release, explosion.

3. The safer consumer products will become available for purchase, products like medicine will be made with less waste and less safe products can be replaced with more safe products.

4. The safer food without toxic chemical in food chain can be used, safer pesticides that are toxic only to specific pests and degrade rapidly after their use can be made available.

5. Green chemicals either degrade to innocuous products or are recovered for further use.
6. Less harm to plants and animals from toxic chemicals in the environment.
7. Less potential for global warming, ozone depletion, and smog formation.
8. Less use of landfills, especially hazardous waste landfills and less chemical disruption of ecosystems.
9. Consumption of smaller amounts of feedstock to obtain the same amount of product (higher yields for green chemical reactions).
10. Faster manufacturing of products owing to fewer synthetic steps which allows increasing plant capacity, and saving energy and water.
11. Reduction in waste, eliminating costly remediation, hazardous waste disposal, and end-of-the-pipe treatments and replacement of a purchased feedstock by a waste product.
12. Less generation of product is needed to achieve the same function owing to better product performance.
13. Reduced use of petroleum products, slowing their depletion and avoiding their hazards and price fluctuation.
14. Reduced manufacturing plant size with improved competitiveness of chemical manufacturers and their customers.

1.5.5 *Ganoderma Lucidum* (*G. Lucidum*)

*G. lucidum*, a medicinal mushroom of Ganodermataceae family, also known as Lingzhi in China, Reishi in Japan and Youngzhi in Korea, is an oriental fungus and has been used over a long period of time in China and Japan as a traditional medicine to promote good health and lifestyle [51]. The photograph of medicinal mushroom is shown in Fig.1.6. The taxonomy of *Ganoderma lucidum* is as below [52]:

<table>
<thead>
<tr>
<th>Kingdom</th>
<th>Fungi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phylum</td>
<td>Basidiomycota</td>
</tr>
<tr>
<td>Class</td>
<td>Basidiomycetes</td>
</tr>
<tr>
<td>Order</td>
<td>Polyporales</td>
</tr>
<tr>
<td>Family</td>
<td>Ganodermataceae</td>
</tr>
<tr>
<td>Genus</td>
<td>Ganoderma</td>
</tr>
<tr>
<td>Species</td>
<td><em>Ganoderma lucidum</em> P. Karsten</td>
</tr>
</tbody>
</table>
G. lucidium mushroom consists of fruiting bodies, mycelia, and spores, which have traditionally been used for the treatment of various types of diseases, such as allergy, hypertension, arteriosclerosis, hepatitis, arthritis, nephritis, bronchitis, asthma, cancer and gastric ulcer [53]. It has also been recommended as an alternative medicine for treating chronic diabetes, hepatitis, carcinoma and in the treatment of viral, especially HIV infections [54-56]. Due to the applications of G. lucidum in medicine, human health and treating acute diseases, many commercial products are available in the form of powder, capsules, tablets and teas. These products are grouped into two types, non-extracted and extracted products [53]. The non-extracted products include dried powders obtained from fruiting bodies, mycelia and spores, while the extracted products are prepared by extracting contents of mushroom with hot water or ethanol from different parts of mushroom. The products available in the market are made from a mixture of these components. More than 300 bioactive compounds have been isolated from the fruiting body, spores and mycelia of G. lucidum. The major components in the G. lucidum cover triterpenoids, polysaccharides, glycoproteins, nucleotides, fatty acids, sterols, steroids and proteins or peptides [57, 58]. Among these molecules, polysaccharides and triterpenoids are used for treating cancer cells; polysaccharides play an important role in immunomodulation, while triterpenoids mainly helps in reducing cancer cell metastasis. Polysaccharides and triterpenoids are the major compounds of the G. lucidum. It is observed that the chemical structure of triterpenoid is similar to the highly oxygenated lanostane [59, 60].

Lanostane type triterpenoids can be classified, depending on the structural similarities and functional groups, including ganoderic acid (GA), ganosporeric acid, methyl ganoderate, ganoderenic acid, ganolucidic acid, ganoderiol, ganoderal, methyl lucidenate, lucidone and lucidumol. Most of the triterpenoids are GAs with a bitter
taste. Ganoderic acid-A and ganoderic acid-B are the first triterpenoids isolated from G. lucidum in 1982. Since then, more than 140 triterpenoids with definite chemical structures have been isolated from G. lucidum [60-62]. Few representative triterpenoids with their chemical structures are shown in fig. 1.7 [63].

![Fig. 1.7 chemical structures of ganoderic acids](image)

1.6 Characterization Techniques

According to the principle of nanotechnology, if the size of the material particles is at nano-meter size ($10^{-9}$m) level, the properties of the materials changes drastically. It is an emerging inter-disciplinary topic with wide range of applications in various branches of science and technology like mechanics, optics, material science, medicine, bio-technology, aero-space, etc. Researchers are synthesizing nanostructured materials with various chemical and physical methods. Besides, it is an emerging field posing lots of challenges to scientists and technologists. Thus, the nanotechnology has stimulated the research activities on the discovery and invention of sophisticated characterization techniques to investigate the morphology, size and dimensions of materials into a nano-range. The important characterization techniques used in the present study are discussed briefly in this section.

1.6.1 X-ray Diffraction (XRD)

The XRD technique is one of the most useful, nondestructive analytical techniques to study the structural properties of the materials [64]. With the help of
XRD technique, crystal size, lattice parameters, identification of the material and the type of crystal structure can be determined. Solid materials are generally appeared in the form of crystalline solids. The crystalline materials once interact with the X-rays, because of the occurrence of diffraction, finger print-like image of the substance is achieved. So, the powder diffraction technique is an ideal characterization method to determine phases of materials. The XRD is much faster technique, requires small sample and moreover it is non-destructive. The function of XRD is based on the measurement of the peak intensity of the scattered X-ray as a function of the angle between incident and scattered radiations. This X-ray diffraction analysis confirms the crystallinity type i.e. amorphous, polycrystalline and single crystal, state of chemical combination of the elements involved or the certain phase in which they are existing in the substance.

**Working principle**

XRD technique mainly works on the Bragg’s law which states that the path difference between two X-rays that are reflected from adjacent planes of a crystalline solid is an integral multiple of its wavelength ($\lambda$). It is mathematically expressed as given below:

$$2d\sin\theta = n\lambda$$  \hspace{1cm} (1.1)

where, $\lambda =$ wavelength of the X-ray, $n =$ an integer, $d =$ distance between the lattice planes and $\theta =$ the angle between the incident and scattered beams. In 1913, Prof. W. L. Bragg discovered that one could account for the position of the diffracted beams produced by crystallographic planes with an X-ray beam. By this simple model according to which, X-rays are diffracted from numerous planes of atoms in the crystal. The diffracted X-ray beams are found for situations in which the reflections from parallel planes of atoms interfere in the constructive fashion as shown in Fig. 1.8. When a monochromatic beam of X-rays is incident upon a regular crystalline material, then the beam will be scattered from the solid at definite angles. This produces an interference pattern called diffraction which is occurred between the X-rays from different atomic layers within the crystalline specimen.A crystal can be considered as a series of atomic planes (diffraction gratings) which are partly reflecting for radiation of wavelength ‘$\lambda$’ and are spaced equal to distances ‘$d$’.The reflected rays from adjacent planes have a path difference of ‘$2d\sin\theta$’.
The graph is drawn between $2\theta$ (the angle between the incident beam and the detector) and the intensity of diffracted X-ray beam (Fig. 1.9).

**Fig. 1.9:** Schematic diagram of an XRD beam showing the incident and scattered X-rays, from a pair of atoms in different planes

**X-ray diffraction technique limitations**

a. For mesoporous structured materials, only few higher-order peaks are appeared in the diffractograms, which makes it hard to define the internal structure without the support of additional methods of characterization.

b. Very smooth surface is required in case of large grained samples sizes, which otherwise is difficult to obtain.

c. The grinding of the sample is needed to reduce the size of the particles which might destroy the sample itself.
1.6.2 Field emission scanning electron microscopy (FE-SEM)

“The SEM works on the principle of interaction of an incident electron beam with the solid specimen [67]. When electrons are impinged on the specimen, numerous particles like secondary electrons, backscattered electrons, Auger electrons, X-rays, visible photons and so on are produced from the specimen. Well-concentrated mono-energetic (25 keV) beam is incident on the surface of the solid specimen to give the dissimilar signals as discussed above. Back-scattered and secondary electrons are extremely helpful in forming image in FE-SEM.

(a) Secondary electrons

When the incident electron collides with the surface atom, the atom being ionized and the electrons from the outermost orbital shell are emitted. The incident electron in each collision loses its energy. The incident electron has been left with no enough energy to free the secondary electrons in multiple collisions. Each secondary free electron possess a very small kinetic energy ($E_k$<0.050 keV), that is independent on the incident electron energy. The-as created secondary electrons are escaped and are collected by the detector. Resultantly, secondary electron imaging is strictly related with specimen topography.

(b) Backscattered electrons

When the incident electron collides with the nucleus of the surface atoms of the specimen, the electrons will bounce or scatter ‘backward’ out of the sample which is named as “backscattered electrons”. Backscattered electrons are high-energetic electrons, which carry the energy lying between 0.050 keV and that of the original incident electrons. Backscattered electrons are elastically scattered electrons. The backscattering probability varies proportionally with the atomic number $Z$ of the specimen. Since, the backscattered fraction is not a very strong function of $Z$ (varying very roughly as ~0.05 Z/2), elemental identification is impossible for primary electron beams employed in the SEM. There is much less topological dissimilarity in the images, since the escape depth for high-energy backscattered electrons is much greater than for low-energy secondary electrons.
Fig. 1.10: A photo-image of FE-SEM JEOL 6300 FEG microscope used in the present work.

(c) Auger electrons

The secondary electron generation leads to the creation of a vacancy in an ionized atom’s electron shell. An electron from a higher energy outer shell (from the same atom) can fall to fill this vacancy. Consequently excess amount of energy is produced in the atom which can be modified by emitting an outer most electron which is called, an Auger electron.

Auger electrons have a characteristic energy unique to the element from which (specimen) they are emitted. The compositional information about the specimen can be drawn by these Auger electrons. Fig. 1.11 shows the schematic diagram of a scanning electron microscope.

(c) Characteristic X-rays

When the primary electron beam is incident on the electrons of the inner shells of the atoms in the exposed sample, characteristic X-rays are emitted, resulting the analysis of X-ray spectrum. By calibration, elemental identification and elemental composition can be analyzed.
Difference between SEM and FESEM: There are two types of emission sources; thermionic emitter and field emitter. The main difference between the Scanning Electron Microscope (SEM) and the Field Emission Scanning Electron Microscope (FE-SEM) is its electron emitter type. The X-ray generation is also possible by the interactions of the incident electron beam with a specimen (like Auger electrons). The extra energy developed by reshuffling electrons to fill shell vacancies can also be released in the form of an X-ray, rather than Auger electrons that are similar to the Auger electrons generating process. Secondary electrons imaging and X-ray analysis are the primary functions used for SEM sample characterization. This system gives both high depth of field and spatial resolution. Furthermore, the technique is operated at smaller accelerating voltages reducing severe radiation sample damage. Electrical grounding and electrical conductivity of the sample material are most important for successful imaging and for optimal surface and signal resolution. To prevent the charging, in the case of insulating materials, a thin coating layer of a conducting material, generally platinum, gold or carbon are essential to be deposited onto the specimen surface. Two electron beams are controlled by the scan generator: one is the incident electron beam and the other is for the CRT display. Across the sample, the incident beam is scanned, line by line, where the signal collected from the secondary electrons is, detected, amplified are used to control the intensity of the secondary electron beam.

Fig. 1.11: Schematic diagram of a scanning electron microscopy
Thus, a map of intensity of secondary electron emission from the scanned area of the sample will be demonstrated by changing the brightness on the CRT screen and reflecting the surface morphologies of the specimen. Thermionic emitters use electrical current to heat up a filament ($I^2R$ rule); the two most common materials used for filaments are tungsten (W) and lanthanum hexaboride (LaB$_6$). When the heat is enough to overcome the work function ($\Phi$) of the filament material (W/LaB$_6$), the electrons can escape from the material.

Thermionic sources have few drawbacks including a low brightness, evaporation of cathode material and thermal drift during operation. Electrons can be generated by field emission can avoid these problems. A Field Emission Source (FES); also known as a cold cathode field emitter, does not heat the filament. The emission is generated by placing the filament in a huge electrical potential gradient. The FES is usually a wire of tungsten (W) in the form of a sharp point.

**Limitations**

(a) The diameter of the incident electron beam gets defocused due to demagnetization in a SEM system, using two or more electron lenses are required before it reaches the sample surface. At the same time, the effective diameter of the electron source is an important factor in determining the resolution of the SEM.

(b) To decrease the charging effect, samples used for SEM observation required to be sputtered with ~15 nm platinum or gold.

(c) The complete information about fine structure is lost, where coating is required as a result of clustering effects of the metal-particles in the case of porous materials.

(d) The spatial resolution of the SEM is strongly dependent on the diameter (spot size) of the electron probe beam at the specimen surface.
1.6.3 Energy Dispersive X-Ray Spectroscopy (EDAX)

An essential tool to confirm the chemical states of the elements of an unknown material is the Energy Dispersive X-Ray Spectroscopy (EDAX/EDS). “When the electrons with suitable energy are incident on the sample/target/material, then X-rays are emitted”, which is the basic principle involved in EDAX. The elements in the specimen are qualitatively identified by analyzing the characteristic wavelengths of X-ray beam using X-ray spectrometer. This is also known as microanalysis technique, because micro-volumes of the elemental content ranging one to several cubic meters can be analyzed. The EDS is a useful and powerful technique for those compositions greater than or about 1% and elements must be separated by few atomic numbers as the intensities are increased by about 100-fold [68]. When the specimen is irradiated by X-ray beam of sufficiently greater energy, it may emit fluorescent radiation. By analyzing this radiation in an X-ray spectrometer, the elements present in the sample can be found using their characteristics wavelengths. The areas of finding applications of this system are ferrites, composites, thin films, pharmaceutical samples and biological samples. The characterization capabilities of EDAX technique are due in large part to the fundamental belief of the periodic table that each element has a unique electronic structure corresponding to the electromagnetic waves [69]. The process of X-ray emission is given schematically in Fig. 1.12.

![Fig. 1.12 Schematic diagram of emission of X-ray](image)

While dropping from upper energy level to the lower energy level (E₂→E₁), energy difference of these energy levels gives rise to the emission of electromagnetic (Say L→K) radiation, which are basically X-rays (Fig. 1.11).
This vacancy created in the innermost shell is then filled by jumping an electron from upper energy shell in the atom.

![Fig. 1.12: X-ray microanalysis is based on electronic transitions between inner atomic shells.](image)

An energetic electron from an electron column knocks out an orbital electron from a shell of lower energy ($E_1$). Consequently, this vacancy can be filled by an electron jumping from higher energy level, losing energy in the process ($\Delta E = E_2 - E_1$) (Fig. 1.12). The energy loss ($\Delta E = E_2 - E_1$) may be seemed in the form radiation of energy and X-rays are emitted when high energy electron beams strike the material to be analyzed.

The emitted X-rays are thereby detected by a Si (Li) detector, calibrated with respect to cobalt metal emission (6.925 keV), which are further used to identify and analyze the elemental composition of the sample surface [70].

The elementary things involved in the EDAX analysis are given below:

(a) Production of X-ray beam,

(b) Detector [Si (Li) detector],

(c) Quantification (EDAX in SEM).

X-ray beam strikes a diode in the detector, a charge is produced. This charge further converted into opposite voltage pulse via a field effect transistor. Later, the pulse is converted into digital converter and then into a numerical value corresponding to the incoming energy of X-ray beams.
When an energy signal is then assigned to a particular energy channel and registered as a single count and these counts are collected to produce an energy dispersive spectrum. The several emission lines emitted from an atom associated with X-rays are named after the shell of the initial vacancy, i.e. K, L, M, N, O, etc. The shell of the electron that fills the gap is designated by a Greek letter. For example, when an electron from next highest shell (L) jumps to fill the vacancy in the K-shell, Kα-radiation is obtained. Kβ-denotes a K-shell vacancy filled by an electron from M-Shell. This is called K-series. In the similar manner when the vacancy is filled by the electrons of M, N, O-shells, the L-series is obtained. Thus K, L, M-series can be obtained. The basic rules which can be applied for the order and energy of the X-rays are:

a) The energies of the K-series > L-series. Thus for a given element, the lower line series has a greater energy,

b) Within a line series, the elements having higher atomic number emit greater energy X-rays i.e. the oxygen “K” lines are higher in energy than carbon “K” lines.

c) The K lines are simple, while the L and M lines get more complex and overlapping is occurred. Thus the lower line series may have simpler structures than the higher line series [71, 72].

Qualitative analysis determines the presence of elements in a sample by identifying the peaks in the spectrum. Quantitative analysis is helpful to derive the relative presence (abundance) of the elements present in the sample.

In succinct, EDAX analysis is mainly helpful to determine the bulk composition of the specimen.

1.6.4 Ultraviolet/Visible Absorption Spectroscopy

To determine the quantitative analysis of the amount of a compound known to be present in the sample, Ultraviolet/Visible Absorption Spectroscopy is highly useful. It is to be understood that molecules in a material have discrete electronic and transition levels from the ground to different excited states that can be affected by light (Fig. 1.13). As electronic levels in a particular chemical species are unique, these are employed as fingerprints for the identification of molecules. The phenomenon like absorption, transmission, scattering, reflection or fluorescence occurs when a beam of radiation strikes any substance.
In this technique, the sample has to be made thin enough because, the light passing through the sample to be analyzed undergoes reflection, transmission and absorption (Fig.1.13). Beer-Lambert law states that; “absorbance is directly proportional to the path length, L, and the concentration of the absorbing material, C”, and can be given as

$$A = \alpha LC$$  \hspace{1cm} (1.2)

where $\alpha$ is a constant of proportionality, called the absorptivity [73]. Using the Beer-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_1.13.png}
\caption{Electronic transitions of electron during the process of light absorption}
\end{figure}

\begin{equation}
A = -\log_{10} \left( \frac{I}{I_0} \right)
\end{equation}  \hspace{1cm} (1.3)

where, $A = \text{Measured absorbance}$,

$I_0 = \text{Intensity of the incident light at a given wavelength}$,

$I = \text{Intensity of the transmitted light}$.

Many spectrometers display the absorbance on the vertical axis, in the range from 0 (100 % transmittance) to 2 (1 % transmittance). The UV-Vis spectroscopic technique is highly helpful to measure the absorption spectra that are mainly due to the light absorption resulting from the excitation of electrons in atoms or molecules. When the specimen absorbs ultraviolet or visible (UV-Vis) light, the valence electrons of the substance are excited from their ground state to higher energy excited states. The generation of carriers due to optical absorption may disturb the stability state of the material used. When the sample is illuminated by the monochromatic light, the optical properties of a solid can be determined.
Transmittance or absorbance as a function of photon energy can be studied after this reflection. The major sources of absorption in solids are exactions, band-to-band transition, imperfections and free carriers. Out of which the band-to-band transition is an important contributor in absorption phenomenon. In crystalline substances; the electron shift from valence band to conduction band can be grouped into direct and indirect processes. In E-k space, in direct inter-band optical transitions; the wave vector “k” for elements remains constant in which momentum also remains the same, whereas, in indirect inter-band transition the wave vector “k” for electrons is altered.

Thus, in the Brillouin zone, vertical transitions are significant when the valence and conduction band extrema are located at the same point. For indirect transition, the band extrema differ in their positions in E-k space. By using classical relation, it is possible to differentiate the nature of optical transition as direct allowed or direct forbidden as expressed below:

$$\alpha = \alpha_0 \left[ \frac{hv - E_g}{h\nu} \right]^n$$

(1.4)

where;

n = Constant
E_g = Energy gap between the valence band and the conduction band
hν= Photon energy,
h = Plank’s constant,
ν = frequency of light

Here n = ½ for allowed direct transitions and n = 2 for allowed indirect transitions. Thus, the resultant graph drawn between (hν) and (αhν)^2 can be linear corresponding to the direct allowed transition. By extrapolating the linear portion of the curve to the energy axis at α = 0, the energy band gap (E_g) is generally determined, which is used for thin film type samples.

![Fig. 1.14: Schematic diagram of UV-Vis spectroscopy and output nature.](image-url)
Fig. 1.14 illustrates the schematic diagram of UV-Vis spectroscopy and the output nature.

1.6.5 Transmission electron microscopy (TEM)
The transmission electron microscopy (TEM) is an electro-optical instrument that uses electrons instead of light to view objects at very fine resolutions. In this technique a beam of electron is transmitted through an ultrathin specimen and interacts, when it passes through the sample, an image is formed by the electrons transmitted through the specimen, which is magnified and focused by electromagnetic lenses and appears on the CRT screen. The basic principle of operation of TEM is similar to the simple optical microscope but uses electrons instead of light.

![Figure 1.15: Schematic diagram of transmission electron microscopy.](image-url)
Generally, TEM is used for determining size, shape and arrangement of the particles, which forms the specimen. It is also useful for determination of the lattice planes and the detection of atomic-scale defects in areas of few nanometers in diameter with the help of selected area electron diffraction (SAED) technique [74].

The $d$- spacing between lattice planes of crystalline materials can be calculated from a SAED pattern using the relationship

$$ dr = \lambda L $$

(1.5)

where, $L$ is the distance between the specimen and the photographic plate, $\lambda L$ is known as the camera constant and $r$ is the radius of diffracted rings.

The schematic diagram of TEM is shown in Fig. 1.15. Generally, SAED pattern is more helpful as compared to XRD, due to the low detection limit of XRD instruments. In the present work, the TEM measurements were performed on a HR-TEM instrument operating at 300 kV and installed at SAIF IIT Bombay, Mumbai, whose actual photograph is shown in Fig. 1.16.

![Photograph of HRTEM-300kV at SAIF IIT Bombay.](image)

Before performing TEM measurements, the samples were dispersed in an isopropyl alcohol and sonicated for 30 minute and a drop of the solution was poured on carbon-coated Cu grids.
The film formed on the TEM grids was allowed to dry for 15 minutes and the TEM measurements were performed.

1.6.6 X-ray photoelectron spectroscopy (XPS)

XPS technique is primarily used to investigate the chemical and electronic states of the elements existing within the first few atomic layers of a material’s surface. The elemental analysis of the material surface such as, their chemical bonds, hence the chemical composition and stoichiometry can also be identified [75]. In this technique, a beam of X-ray strikes sample surface and interact with the electrons of an atom in the sample, mainly by photon absorption to produce the ejection of photoelectrons.

It is well-known that each element has a specific binding energy and this energy can be calculated using the following equation:

\[ E = h\nu - KE - \phi \]  

(1.6)

where \( E \) = electron binding energy (eV), \( h \) = Planck’s constant (eV/s), \( \nu \) = frequency of incident X-rays (s\(^{-1}\)), \( KE \) = kinetic energy of electron (eV), \( \phi \) = surface work function (eV). The X-rays used in XPS technique are generally emitted from magnesium or aluminum source and the intensity of the ejected photoelectron from the sample versus binding energy is plotted. The obtained spectrum is compared with the standard database. Material’s electronic configuration, and therefore, elements are analyzed using the peak positions and intensities. The schematic diagram illustrating photoelectron emission in X-ray photoelectron spectroscopy is shown in the Fig.1.17.

![Fig. 1.17 Photoelectron emission in X-ray photoelectron spectroscopy.](image)
1.6.7 Brunauer, Emmett and Teller Measurement

Physical adsorption of gas molecules on a solid surface is the basis of an important analysis technique (BET) for the measurement of the specific surface area of a material. Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published the first article in 1938, about the theory of BET [76]. The BET theory belongs to multi-layer adsorption, and usually adopts non-corrosive (inert) gases (like nitrogen, argon, carbon dioxide, etc.) as adsorbates to determine the surface area. It usually uses static volumetric principle, also has gas flowing technology can determine surface area data. The theory of BET is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses:

1. gas molecules physically adsorb on a solid in layers infinitely;
2. there is no interaction between each adsorption layer; and
3. The Langmuir theory can be applied to each layer.

The pore size or pore diameter is the space of converse particles. Pore-size is crucial for the application of materials. Materials are separated into microporous (diameter < 2 nm), mesoporous (2 nm < pore diameter < 50 nm), and macroporous (pore diameter > 50 nm) [77]. The porosity of materials can be characterized by gas adsorption evaluations. The adsorption of gas on the surface of the material permits faithful determination of the specific surface area, total pore-volume, and pore-size distribution of the substance. The Brunauer-Emmet-Teller equation is widely utilized for determination of the surface area of materials.

\[
\frac{1}{W(P_0/P)} = \frac{1}{C W_m} + \frac{C-1}{C W_m} \left( \frac{P}{P_0} \right)
\]  

(1.7)

where, W is the weight of the absorbed gas at relative pressure Po/P, C is a constant related to the energy of adsorption in the first adsorbed layer, and Wm is the weight of a monolayer of adsorbate.

The total surface area of the substance can be calculated by

\[
S_t = \frac{NA_{cs} W_m}{M}
\]

(1.8)

where,

N is an Avogadro number (6.023 \times 10^{23} molecules/mol), M is a molecular weight of the adsorbate, and A_{cs} is a cross-sectional area (16.2 Å at 77 K).
The specific surface area can be calculated from the total surface area and the weight of the substance:

\[ S = \frac{S_t}{W} \]  

(1.9)

The total pore-volume can be determined from the amount of vapor adsorbed at a relative pressure close to unity. Moreover, the pore-size distribution can be evaluated from the desorption branch of the isotherm. Pore-size is determined using the Kelvin equation: [78]

\[ \frac{r}{K} = \frac{-2yV_m}{RT\ln \frac{P}{P_0}} \]  

(1.10)

where,

\( \gamma \) is a surface tension of nitrogen at its boiling point (8.85 ergs/cm\(^2\) at 77 K), \( V_m \) is a molar volume of liquid nitrogen (34.6 cm\(^3\)/mol), \( R \) is a gas constant (8.314 \( \times 10^7 \) ergs/mol), \( T \) is a boiling point of nitrogen (77 K), \( P/P_o \) is a relative pressure of nitrogen, and \( r/K \) is a Kelvin radius of the pore.

Fig.1.18 Types of isotherms on the basis of porosity.

The inspection of gas adsorption over the surface of the material offers an information on the surface area, porosity and pore-size distribution etc.. The
adsorption isotherm is typically obtained by introducing known volumes of nitrogen and measuring the equilibrium pressure. The desorption isotherm is usually studied by measuring the amount of gas released from the materials as the relative pressure is decreased. The isotherms are classified into five types according to the type of adsorption of nitrogen takes place. The type I isotherm is related to micro porous materials where the adsorption of nitrogen is on the outer surface area and is limited by the convenience of the micro-pores [79]. Type II isotherm signifies nonporous as well as macro- porous materials where distinct multilayer of nitrogen can be absorbed. Type III isotherm is characterized by the heat of adsorption which is fewer than the heat of adsorbate. Type IV isotherm concerns mesoporous materials where the pores are filled at superior elevated pressures [80]. Finally, Type V isotherm is identical to the Type III isotherm though; this type is general for mesoporous materials. The adsorption and desorption branches in Type I, Type II, and Type III isotherms are the same and hysteresis occurs barely.

1.7. Objectives of Thesis

1) To use eco-friendly, cost-effective and green synthesis route for the synthesis of SnO$_2$ and TiO$_2$ nanoparticles.
2) To study the medicinal species, G. lucidum as an oxidizing and stabilizing agent.
3) To fabricate SnO$_2$ and TiO$_2$ films for gas sensing purpose by using ‘Doctor-Blade’ method.
4) To prepare noble metal sensitized SnO$_2$ and TiO$_2$ NPs thin films by using simple ‘Dip and Dry’ method.
5) To investigate phase formation, element analysis and surface morphology of metal oxide nanostructures using different characterization techniques.
6) To investigate ethanol (C$_2$H$_5$OH) gas sensor based on SnO$_2$ NPs and noble metal (Ag, Au and PD) sensitized thin films.
7) To study chlorine (Cl$_2$) gas sensor based on TiO$_2$ NPs thin film and noble metal (Ag, Au and PD) sensitized thin films.

1.8. Thesis outline

The present thesis comprises five chapters and is assembled in following order.

Chapter 1: Introduction

This chapter includes brief introduction of gas sensor, motivation of research, different synthesis techniques, theoretical background of green synthesis, literature
survey of SnO$_2$ and TiO$_2$ nanostructures as well as the sensitization of SnO$_2$ and TiO$_2$ nanostructures by noble metals Ag, Au and Pd. This chapter also includes theoretical background of aims and objectives of research, experimental techniques used and outline of thesis.

**Chapter 2: Experimental methods**

This chapter comprises of brief introduction to experimental methods, broth formation of medicinal mushroom *G. lucidum*, synthesis of active powder, substrate cleaning, and metal oxide film formation using ‘Doctor-Blade’ method. This chapter also contains a simple dip and dry technique used for the fabrication of noble metal (Ag, Au and Pd) sensitized SnO$_2$/TiO$_2$ films for ethanol and chlorine gas sensors.

**Chapter 3: Pure and Au, Ag & Pd sensitized SnO$_2$ films for ethanol gas sensor**

This chapter represents results and discussion, materials characterizations and conclusions. In results and discussion section, different properties of SnO$_2$ and Ag, Au and Pd sensitized SnO$_2$ nanostructures were discussed. For phase formation, element analysis and surface morphology of metal oxide nanostructures different characterization techniques such as XRD, XPS, FESEM, EDAX, TEM, UV-visible spectroscopy and BET measurements are discussed. Ethanol gas sensing properties of pure SnO$_2$, Ag- SnO$_2$, Au- SnO$_2$ and Pd- SnO$_2$ films such as sensitivity, selectivity, response time, recovery time, repeatability and stability factor are also discussed.

**Chapter 4: Pure and Au, Ag & Pd sensitized TiO$_2$ films as chlorine gas sensors**

This chapter contains results and discussion, materials characterizations and conclusions. In results and discussion different properties of TiO$_2$ and Ag, Au and Pd sensitized TiO$_2$ nanostructures were discussed. For phase formation, element analysis and surface morphology of metal oxide nanostructures, different characterization techniques such as XRD, XPS, FESEM, EDAX, TEM, UV-visible spectroscopy and BET measurements are discussed. Chlorine gas sensing properties of pure TiO$_2$, Ag-TiO$_2$, Au-TiO$_2$ and Pd-TiO$_2$ film sensors such as sensitivity, selectivity, response time, recovery time, repeatability and stability factor are also discussed.

**Chapter 5: Conclusions and Future Scope**

In this chapter, the results obtained related to the characterizations and gas sensor performances for both SnO$_2$ and TiO$_2$ sensors with Ag, Au and Pd sensitizations are discussed. The effects of variation of molar concentration of Ti and Sn - precursor on structure, morphology and optical properties of sensors are also discussed in this chapter. The influence of structural properties of SnO$_2$ film sensor on
ethanol gas sensing is discussed. Furthermore, the structural, morphological, optical and gas sensing properties obtained for these film sensors are compared and explored. From all these experimental results obtained, the final conclusions are drawn and presented. In last section of this chapter, the future scope and applications in continuation with the present research work done are also provided.

References
disaster.


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