Semiconductor Nanostructures for Device Applications

A thesis

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Abstract

This thesis demonstrates a synthesis and device application of some semiconductors nanostructure.

**Section 1**, layered hexagonal disks of CuO was synthesized on a large scale via low-temperature hydrothermal growth process. The detailed morphological investigations by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The detailed structural characterizations of the hexagonal CuO disks were done by high-resolution TEM (HRTEM) and X-ray diffraction (XRD) which confirmed that the synthesized structures possessing well nanocrystalline nature and monoclinic structure. The purity and composition of the synthesized products were examined by using energy dispersive spectroscopy (EDS), elemental mapping and Fourier transform infrared spectroscopy (FTIR). Using UV-Vis spectroscopy at room temperature we obtained indirect and direct band gap values slightly blue shifted to the bulk values. Finally, a plausible growth mechanism has been proposed for the formation of CuO layered hexagonal disks.

**Section 2** reports the fabrication of highly-sensitive, robust, reliable and reproducible 4-nitrophenol (4-NP) chemical sensor based on CuO nanocubes. The structural characterizations confirmed the nanocrystalline nature and monoclinic structure for as-synthesized nanocubes. The optical property of CuO nanocubes exhibits indirect and direct band gap values examined by UV-Vis spectroscopy at room-temperature. The as-synthesized CuO nanocubes were used as efficient electron mediators for the fabrication of 4-nitrophenol chemical sensor by simple I-V technique. High-sensitivity of ~132.84 ± 0.02 mA.cm$^{-2}$.mol L$^{-1}$ and detection limit of ~5×10$^{-9}$ mol L$^{-1}$ in a short response time of ~10.0 s were observed for the fabricated 4-nitrophenol sensor. This work shows that simply synthesized CuO nanostructures have great potential for the fabrication of efficient and reliable chemical sensors.

**Section 3**, we reported the high-yield facile synthesis, detailed characterization and photocatalytic application of α-Fe$_2$O$_3$ nanoparticles. The UV-Vis absorption spectrum of the synthesized nanoparticles demonstrated the existence of two optical band gaps which correspond to direct and indirect transitions, respectively. The as-synthesized
α-Fe₂O₃ nanoparticles exhibit good photocatalytic properties on photocatalytic degradation of methylene blue.

**Section 4**, reports the facile synthesis of α-Fe₂O₃ nanoellipsoids by low-temperature hydrothermal process and effectively utilized for the fabrication of highly sensitive aqueous ammonia chemical sensor by *I-V* technique. The detailed structural and optical properties confirmed the rhombohedral α-Fe₂O₃ structure and indirect (1.87 eV) and direct (2.15 eV) band gap, respectively, for synthesized nanoellipsoids. The fabricated aqueous ammonia sensor based on nanoellipsoids exhibits very high and reproducible sensitivity of ~4.678 µA.cm⁻².mM⁻¹ and detection limit ~0.04 nM with correlation coefficient (R) of 0.995 in short response time (10.0 sec). The presented work demonstrates that simply synthesized iron oxide nanostructures can efficiently be used for the fabrication of reliable and reproducible chemical sensors.

**Section 5**, this section demonstrates the successful and facile large-scale synthesis and characterizations of SnS₂ nanoflakes. The photocatalytic properties of SnS₂ nanoflakes towards the photocatalytic degradation of Rhodamine B under visible light irradiation showed reasonably good degradation of ~61%. Moreover, the as-synthesized SnS₂ nanoflakes were used as efficient electron mediators for the fabrication of nitroaniline chemical sensor by simple *I-V* technique. Very high-sensitivity of ~ (505.82 ± 0.02) mA.cm⁻².(mole/L)⁻¹ and experimental detection limit of ~15*10⁻⁶ (mole/L) in a short response time of ~10.0 sec with LDR in the range of 15.6*10⁻⁶ (mole/L) to 0.5*10⁻³ mole L⁻¹ were observed for the fabricated nitroaniline chemical sensor. The observed results indicated that the SnS₂ nanoflakes can efficiently be used as visible-light-driven photocatalysts and the fabrication of ultra-high sensitive chemical sensors.

**Section 6**, in this section a heterojunction device was fabricated with solution processed SnS nanosheets (p-type)/TiO₂ nanoparticles (n-type) and a top Pt thin layer to form Pt/SnS/TiO₂/FTO diode assembly. The fabricated heterostructure device presented considerably improved electrical properties with high current of 0.78 mA at 1V, reasonable ideality factor of 31 and relatively high effective barrier height of 0.634 eV.
**Keyword(s):** Semiconductor nanostructure, Copper oxide, Iron oxide, Tin sulphides, Hydrothermal process, Optical band gap, chemical sensors, Photocatalytic degradation, Heterojunction diode.
Περίληψη

Στην παρούσα διατριβή παρουσιάζεται η σύνθεση ημιαγώγιων νανοδομών και η εφαρμογή τους σε διατάξεις.

Μέρος 1 Παρουσιάζεται η σύνθεση επιταξιακών εξαγωνικών δίσκων οξειδίου του Χαλκού CuO μέσω μίας υδροθερμικής διαδικασίας ανάπτυξης χαμηλής θερμοκρασίας. Η μορφολογική μελέτη καθώς και ο δομικός χαρακτήρισμός έχουν γίνει με τις μεθόδους FESEM, TEM, HRTEM και XRD αντίστοιχα. Οι οπτικές ιδιότητες μελετήθηκαν μέσω UV/VIS φασματοσκοπίας σε θερμοκρασία δωματίου, όπου υπολογίστηκαν τα έμμεσα και άμεσα χάματα τα οποία είναι ελαφρώς μετατοπισμένα προς το μπλε σε σχέση με τις τιμές του μακροσκοπικού υλικού. Επίσης η καθαρότητα και η σύσταση των δειγμάτων μελετήθηκαν μέσω EDS και FTIR. Τέλος, έχει προταθεί ένας μηχανισμός ανάπτυξης για τον σχηματισμό των επιταξιακών εξαγωνικών δίσκων οξειδίων του χαλκού.

Μέρος 2 Αναφέρεται στην παρασκευή υψηλής ευαισθησίας χημικών αισθητήρων 4-nitrophenol (4-NP) που βασίζονται στους νανοκύβους του CuO. Ο δομικός χαρακτήρισμός επιβεβαίωσε την νανοκρυσταλλική φύση και μονοκλινή δομή των δειγμάτων. Οι οπτικές ιδιότητες των νανοκύβων μελετήθηκαν με UV-Vis φασματοσκοπία σε θερμοκρασία δωματίου, και παρουσίασαν έμμεσο και άμεσο χάσμα. Οι νανοκύβοι CuO χρησιμοποιήθηκαν για την παρασκευή χημικών αισθητήρων 4-nitrophenol (4-NP) μέσω μίας απλής I-V τεχνικής. Οι αισθητήρες αυτοί παρουσίασαν υψηλή ευαισθησία ~132.84 ± 0.02 mA.cm⁻².(mol L⁻¹)⁻¹ και όριο ανίχνευσης ~5×10⁻⁹ mol L⁻¹ σε μικρό χρόνο απόκρισης ~10.0 s.

Μέρος 3 Παρουσιάζεται υψηλής απόδοσης σύνθεση, λεπτομερής χαρακτηρισμός και η εφαρμογή στη φωτοκατάλυση νανοσωματιδίων α-Fe₂O₃. Το φάσμα απορρόφησης UV-Vis παρουσίασε δύο οπτικά χάσματα που αντιστοιχούν σε άμεσες και έμμεσες μεταβάσεις αντίστοιχα. Τα νανοσωματιδία α-Fe₂O₃ εμφανίζουν καλές φωτοκαταλυτικές ιδιότητες στη καταλυτική υποβάθμιση του methylene blue.
Μέρος 4 Παρουσιάζεται η σύνθεση νανοελλειψοειδών α-Fe₂O₃ μέσω μίας υδροθερμικής μεθόδου χαμηλής θερμοκρασίας και η χρήση τους για την παρασκευή χημικών αισθητήρων αμμωνίας υψηλής απόδοσης, με την I-V τεχνική. Οι λεπτομερείς δομικές και οπτικές ιδιότητες επιβεβαιώσαν την ρομβοεδρική δομή και τα άμεσα ενεργειακά χάσματα αντίστοιχα. Οι αισθητήρες αυτοί παρουσίασαν υψηλή ευαισθησία ~4.678 μΑ.επιτομή -2, μΜ.-1 και όριο ανίχνευσης ~0.04 nM με συντελεστή συσχέτισης (R) 0.995 σε μικρούς χρόνους απόκρισης (10.0 sec).

Μέρος 5 Παρουσιάζεται η ευρείας κλίμακας σύνθεση νανονιφάδων SnS₂ καθώς επίσης και ο χαρακτηρισμός τους. Οι φωτοκαταλυτικές ιδιότητες των νανονιφάδων SnS₂ παρουσίασαν υποβάθμιση 61% της Rhodamine B υπό ακτινοβολία ορατού φωτός. Επιπλέον οι SnS₂ νανονιφάδες χρησιμοποιήθηκαν για την παρασκευή χημικών αισθητήρων υποβάθμισης μέσω της I-V τεχνικής. Οι αισθητήρες παρουσίασαν υψηλή ευαισθησία ~ (505.82 ± 0.02) mA.επιτομή -2, (mole/L) -1 και πειραματικό όριο ανίχνευσης ~15*10⁶ (mole/L) σε μικρό χρόνο απόκρισης ~10.0 sec.

Μέρος 6. Παρασκευάστηκε διάταξη ετεροδομής με νανοφύλλα SnS(p-type)/TiO₂ νανοσωματίδια (n-type) επάνω σε γυαλί FTO με λεπτή επιφανειακή επίστρωση Pt δημιουργώντας μία διάταξη διόδου Pt/SnS/TiO₂/FTO. Η ετεροδομή αυτή εμφάνισε βελτιωμένες ηλεκτρικές ιδιότητες με υψηλό ρεύμα 0.78 mA στο 1V, παράγοντα ιδεατότητας 31 και σχετικά υψηλό φράγμα δυναμικού 0.634 eV.

Λέξεις κλειδιά: Ημιαγώγιμες νανοδομές, Οξείδιο του χαλκού, Οξείδιο του σιδήρου, Σουλφίδια του κασσιτέρου, Υδροθερμική διαδικασία, Οπτικό ενεργειακό χάσμα, Χημικοί αισθητήρες, Φωτοκαταλυτική υποβάθμιση, Δίοδος ετεροεπαφής.
To my Parents and my Small family
Preface

Semiconductor nanomaterials have attracted considerable research interest over recent decades due to their unique physical and chemical properties and potential applications in the fields of engineering, science and technology. Due to the size effect, the properties of semiconductor nanomaterials can be tailored and particular properties of these nanomaterials could be achieved for specific applications. Semiconductor nanomaterials are not only used for catalysis, sensing, and electronic devices but also for biomedical and environmental applications and other fields. Due to the high-efficient applications, researchers have developed several synthesis methods to synthesize semiconductor nanomaterials with desired morphologies for specific applications. Because of the exceptional properties and wide applications of semiconductor nanomaterials, there is still a wide gap to work on the nanomaterials to be utilized them for specific applications.

This thesis focuses on the synthesis, characterizations and specific applications of three semiconductor nanomaterials. The investigated copper oxide (CuO), iron oxide (α-Fe₂O₃) and tin sulfide (SnS) semiconductor nanomaterials were synthesized by facile and simple hydrothermal process, then characterized by SEM and used in applications as photocatalysis and electron mediator. The photocatalysis application was used to degrade organic dyes such as methylene blue and Rhodamine B, and also used as efficient electron mediator for the fabrication of highly sensitive and reproducible chemical sensors.

This thesis is divided into several chapters. Chapter 1 starts with a brief introduction of the semiconductor nanomaterials and their various synthesis methods. In addition to this, a short review on the studied semiconductor nanomaterials and their applications are also discussed in this chapter. In addition, this chapter also describes the objectives and importance of the thesis.

Chapter 2 gives a detailed overview on the synthesis and characterization techniques used in this thesis. All the investigated semiconductor nanomaterials were prepared by facile and simple hydrothermal process. Moreover, the prepared nanomaterials were examined by variety of techniques in terms of their general.
morphologies using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). For the structural properties, the prepared nanomaterials were characterized by high-resolution TEM (HRTEM) and x-ray diffraction (XRD) pattern. The elemental and chemical compositions of prepared nanomaterials were investigated by energy dispersive x-ray spectroscopy (EDS) and Fourier transform infrared (FTIR) spectroscopy, respectively. The optical properties were examined by UV-visible spectroscopy at room-temperature. The prepared nanomaterials were used for various applications such as sensing, photocatalytic, and heterojunction diodes. This chapter also provides all the detailed procedures for the synthesis, characterizations and applications of investigated nanomaterials in this thesis.

Chapter 3 describes the main results and discussion of the thesis. This chapter is divided into several sections and each section describes the synthesis, detailed characterizations and particular application of a particular semiconductor nanomaterial. Section 1 describes the synthesis and detailed characterizations of special kind of CuO structure, namely CuO layered hexagonal disks prepared by low-temperature hydrothermal process. Section 2 demonstrates the simple and facile hydrothermal synthesis of CuO nanocubes and their utilization as electron mediators for the fabrication of highly-sensitive 4-nitrophenol chemical sensor. High-yield synthesis, characterization and photocatalytic applications of well-crystalline α-Fe$_2$O$_3$ nanoparticles are presented in section 3. Fabrication and characterization of highly sensitive ammonia chemical sensor based on α-Fe$_2$O$_3$ nanoellipsoids are presented in section 4. Section 5 demonstrates the visible-light-driven photocatalytic and chemical sensing properties of SnS$_2$ nanoflakes prepared by simple and facile hydrothermal process. A heterojunction device was fabricated with solution processed SnS nanosheets (p-type)/TiO$_2$ nanoparticles (n-type) and a top Pt thin layer to form Pt/SnS/TiO$_2$/FTO diode assembly and the detailed results are presented in section 6.

Chapter 4 briefly highlights the overall conclusion and future work for further investigations suggested by the work undertaken here in this thesis.
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I especially thank my mom Khadiga, dad Eisa- brothers and sisters. My hard-working parents have sacrificed their lives for my sisters’ brothers and provided unconditional love and care. I love them so much, and I would not have made it this far without them. I know I always have my family to count on when times are rough.

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I dedicate this thesis to the soul of my brother Nazar and My family, my Wife Muram, son Mossab and daughters Malak and Mihad for their constant support and unconditional love.

I love you all dearly.

Mohamed Eisa Abaker Adam
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Abbreviations

FESEM: Field Emission Scanning Electron Microscopy

TEM: Transmission Electron Microscopy

HRTEM: High Resolution Transmission Electron Microscopy

XRD: X-ray Diffraction

EDS: Energy Dispersive x-ray Spectroscopy

SAED: Selected area electron diffraction

FTIR: Fourier Transform Infrared spectroscopy

UV-Vis: Ultraviolet –visible

0D: Zero dimensional

1D: One dimensional

2D: Two dimensional

PVD: Physical Vapor Deposition

CVD: Chemical vapor deposition

PLD: Pulsed laser deposition

MOCVD: Metal organic chemical vapor deposition

HMADA: Hexamethylenediamine

GCE: Glassy carbon electrode

RhB: Rhodamine Blue
CHAPTER-1

Chapter 1 deals with a brief introduction of semiconductors and semiconductor nanomaterials, their general synthesis techniques, applications and importance. Short descriptions of the targeted semiconductor nanomaterials and aimed applications, such as sensing, photocatalytic and heterojunction diodes, are also demonstrated in this chapter. Finally, the chapter describes the objectives and importance of the thesis.
1 INTRODUCTION

1.1 Semiconductor materials

Materials are characterized in terms of their electrical properties i.e. their ability to conduct electrical current. In general there exist three types of materials in this regard, conductors, semiconductors, insulators. The electrical conductivities of semiconductor materials lie between conductors and insulators, in the range of $10^4$ and $10^{-6}$ (W$^{-1}$ cm$^{-1}$). Furthermore, the so called band gap is the term that can be used to determine the material category, for conductors there is no band gap due to the overlap between the conduction and valence bands.

For semiconductors the band gap lies between $0 - 4$ eV. The band gap separates the valence and conduction bands; Figure (1.1) shows the bands arrangement for the three types of materials.

![Energy Bands Diagram](image)

Figure 1.1 shows the energy bands of conductors, semiconductors and insulators.

It's clear that the energy band gap for semiconductors is smaller than that of insulators. Therefore, relatively small energy is needed by the valence electrons to cross over to the conduction band. Even at room temperature some of the valence
electrons may acquire sufficient amount of energy to enter the conduction band, and thus become free electrons.

Semiconductors and insulators as well, have the same band criterion but with different energy band gap size; where in semiconductors a small gap exists compared to insulators. The temperature effect on semiconductors is in general essential for the electron transport across the bands. However, the temperature variation can also affect the electrical properties of the semiconductors, this is very significant behavior. At absolute zero temperature all electrons are tightly held by the atoms. The inner orbits are bound whereas the valence electrons are engaged in a co-valent bonding; this means that there are no free electrons. Consequently, the semiconductor behaves as a good insulator, i.e. no electron transport. As mentioned the materials consist of valence and conduction bands separated by the forbidden gap within which the so called Fermi level lie in the middle of the band gap for semiconductors. Furthermore, the formation of the band gaps is the result of the atoms arrangements in a crystal causing to the modification of energy levels due to the interaction between atoms in the crystal lattice. Above absolute zero some of the band break due to thermal energy gained, hence electrons are released free and constitute a tiny current if a potential difference is applied across the crystal. In general the band structure play a central role in the controlling the materials properties, i.e. at absolute zero the highest completely filled band (valence band).

The most famous semiconductor material is elemental silicon (Si) and germanium (Ge), which dominate for long time in fabrication of semiconductor devices due to their abundance and versatile properties. They have been utilized in a variety of applications for decades such as solar cells, switching, lasers, light emitting diodes and solid state electronic devices etc. Nonetheless, due to the rapid development in science and technology, the so called compound semiconductors materials have emerged to the surface, this include for example GaAs, GaP, and In As. These type of semiconductors exhibit several behavior such as magnetic characteristics of $Cd_{1-x}Mn_xTe$ or ferroelectric in $Sb SI$, others become superconductors when doped with sufficient carriers like ($GeTe$ and $SrTiO_2$).
Semiconductor materials research began in the early nineteenth century which lead to the discovery of the transistor in the late 40's, by the time the numerous materials have been developed for the utilization in such device. However, semiconductors research became the field of interest for a huge number of scientists due to its attracting properties and applications. Therefore, fabrication of new materials and new fabrication techniques are rapidly increasing due to market demand.

1.1.1 Electrical properties

The electrical conductivity of a solid material varies over many orders of magnitude. This property differentiates whether the material can conduct electricity or not. The electrical conductivity of a conductor can be given in terms of its electrical resistivity as:

\[ \sigma = \frac{1}{\rho} \] 

Where \( \rho \) is the resistivity of the material.

Since materials have been classified according their ability of electrical conduction, so metals have a large conductivity in this regard, while it decreases as we go to the semiconductors and insulators. However, the most important issue of semiconductors is to control their conductivity by implementing the doping process to maintain suitable conducting properties. Nevertheless, semiconductors are capable of conducting due to the temperature effect, by decreasing the resistivity of the material. The temperature dependence of the resistivity is shown in Figure (1.2). Thus, the resistance of a pure high quality semiconductor material increases upon decreasing the temperature. The exact behavior of the resistivity in the presence of temperature dependence is the same as in metals depends on the parity and on the number of defects, Figure (1.2), displays the resistivity changes with temperature.
The conductivity of a semiconductor is given in terms of the carrier concentration as follows:

\[ \sigma = \frac{n_e e^2 t_e}{m_e^*} \]  \hfill (1.2)

Where: \( n_e \), \( e \), \( t_e \), and \( m_e^* \) are the carrier concentration, charge, relaxation time and the effective mass of the electron, respectively. One of the most important properties of semiconductors is its electrical properties; this can be enhanced by doping with a relevant impurity. The improvements of the electrical character of a semiconductor lead to enrich the functionality of the electronic devices.

### 1.1.2 Optical properties

Excitation of an electron from the valence band to conduction band can occur when a photon of energy \( h \nu \) greater than \( E_g \) passes through a semiconductor and absorbed. The average energy of the electron in the conduction band is about \( \frac{3}{2} k_B T \).
above $E_c$. If the photon energy is much larger than $E_g$, then the excited electron is not near $E_C$ and has to lose the extra energy $(h\nu - E_g)$ to reach thermal equilibrium. The excess energy is lost to lattice vibrations as heat as the electron is scattered from one atomic vibration to another. This process is called thermalization. For a photon with energy less than $E_g$, the photon cannot be absorbed and the semiconductor is now transparent to wavelengths larger than $\frac{hc}{E_g}$ this indicates that there are no energy states in the energy band gap. If the intensity of the incident light of $I_o$ then the transmitted intensity can be expressed by the Beer-Lambert law as:

$$I(x) = I_o e^{-\alpha x} \quad \text{.................. (1.3)}$$

Where: $\alpha$ is the absorption coefficient of the semiconductor, whose magnitude depends on the photon energy, $I(x)$ is the transmitted intensity. The distance of $x = 1/\alpha$, over which the light intensity falls to a value of $I_o/e$, is called the penetration depth $\delta$. The absorption coefficient depends on the photo absorption processes occurring in the semiconductor. In the case of band-to-band (interband) absorption, $\alpha$ increases rapidly with the photon energy $h\nu$ above $E_g$. The representation of the absorption coefficient vs. $h\nu$ generally tend to behave like the corresponding density of state $D(E)$, which increases from the band edges and usually exhibits peaks and troughs. Generally $\alpha$ increases with the photon energy greater than $E_g$ because more energetic photons can excite electrons from populated regions of the valence band to available states deep in the conduction band. For direct gap semiconductor the maximum of the valence band and minimum of the conduction band fall at the same place in k-space.and the absorption coefficient is proportional to $(h\nu-E_g)^{1/2}$. On the other hand, the situation for the indirect gap semiconductor the maximum of the valence band and minimum of the conduction band fall in different points in k-space where a lattice vibration (phonon) is involved in the electronic excitations, this results in decreasing the absorption coefficient $\alpha$ and it is related to the energy as $\alpha (h\nu - E_g)^2$. The most widely used materials for the fabrication of semiconductor devices is silicon because of its variety of rich properties and abundance. Over the years many semiconducting materials have been studied, while silicon (Si) has been and remains the dominant material due to the high quality silicon dioxide, which is a very good
insulator that is thermally, be grown on silicon. In addition, Si in the form of silica and silicates comprises 25% of the earth crust, which make the material very cheap in comparison to other alternatives. Silicon is one of the group four members in the periodic table of elements, where each atom possesses four valence electrons, i.e. half filled, and the crystalline type for this group is the diamond structure.

Semiconductors have been utilized in a variety of applications since their breakthrough. A large range of device applications, semiconductor industry introduced itself as the heart of the modern industrial field due to its versatile applications. Moreover, semiconductor chips are the essential core of the mobile phones computers, flat monitors, a wide range of medical procedures including CT scans, ultrasound, and X- rays imaging, they play an enormous role in today's sophisticated cars and air craft.

1.2 Semiconductor Nanostructure

The term nano world is simply referred to a kind of materials with reduced size down to a tiny scale less than 100 nm in one or more dimensions and exhibit novel physical properties that are not possessed by their bulk forms. In 1959 Feynman Noble prize winner in physics came with a brilliant concept of the nano when he said "There is a plenty of room at the bottom". Furthermore, G. Moore suggested that the number of transistors for the same surface doubles every 18 months and it has been under his name "Moore's Law". Consequently the technology market need accelerates the development of materials and methods of device fabrication. This results in the replacement of silicon devices with new fabricated materials such as thin epitaxial film and multilayered structure (2D) with versatile properties. These structures have led to the development of field effect transistors; such as quantum well, lasers, optical modulators, quantum well photo-detectors, etc. In this regard the so called quantum size effect plays a significant role in enhancing the properties of the 2D systems, compared to the properties of their bulk structure.

Semiconductor materials based on nanoscale range have attracted considerable research interest over recent decades due to their unique physical and chemical properties and potential applications in the fields of engineering, science and
technology. Due to the size effect, the properties of these new materials could be extremely different in comparison to the bulk crystals of the same material. In general speaking the optical and electrical properties of semiconductor nanostructures can be tailored to a large extent by the dimensions of the crystals. Various effects that occur due to spatial confinement of electrons/ phonons in such structure can be very important for a specific application. Since their emergence, semiconductor nanostructures were adapted in a variety of electronic devices in numerous fields of applications including opto-electronic industry, solar cells technology, information technology, environments, health and medical treatments, etc. Several materials have been synthesized for device applications in the above mentioned fields. Among various semiconductor nanostructures, metal oxide nanostructures stand out as one of the most versatile materials, due to their diverse properties and functionalities. Their nanostructures not only exhibit the exclusive properties which can be used in a variety of applications for the fabrication of novel and efficient nanodevices but also possess exotic properties associated with their highly anisotropic geometry and size confinement.

The size dependent properties of semiconductor nanostructures allows controlling the possible energy states available within a semiconductor device through dimension induced band structure change, while electrons appear to have a quasi-continuum of available states within bulk materials, electronic states can be further quantized by controlling the size of the nanostructure. However, in low dimensional device carriers are no longer moving in a three dimensional crystal, but they are confined within a two-, one-, or zero- dimensional space. This is realized by fabricating devices where carriers are confined within a thin crystal such as quantum wire, or in a low dimensional potential well such as quantum well devices. Though the reduction of the dimensionality of an electronic system modifies its density of states (DOS) as presented in Figure (1.3) shows how the reduction affects the size. Thus when an electron is confined in a volume as a small as quantum dot (QD) whose typical size is 2 ~ 10nm, (10- 50 atoms). Size reduction to 1D produces the so called quantum wires and 2D generates quantum wells systems.
Figure 1.3 Schematic representation of: (a) three-dimension (3-D), (b) two-dimension (2-D), (c) one-dimension (1-D) and (d) 0-dimension (0-D). The corresponding density of states (DOS) (a–d) plots for each type is also presented.

It’s clear that the 0D has the shape of delta function. The following equations describe each dimensional system from 3D down to 0D.

For 3D
\[ \frac{dN}{dE} \propto \frac{d}{dE} E^3 = E^2 \]

For 2D
\[ \frac{dN}{dE} \propto \frac{d}{dE} \sum_{E_i \leq E} (E - E_i) = \sum_{E_i \leq E} 1 \]

For 1D
\[ \frac{d}{dE} \propto \frac{d}{dE} \sum_{E_i \leq E} (E - E_i)^{1/2} = \sum_{E_i \leq E} \frac{1}{(E - E_i)\sqrt{2}} \]

For 0D
\[ \frac{d}{dE} \propto \frac{d}{dE} \sum_{E_i \leq E} (E - E_i) = \delta(E - E_i) \]

Where \( E_i \) are the discrete energy levels, \( \theta \) is the Heaviside step function and \( \delta \) is the Dirac delta function.
1.3 Synthesis techniques of Semiconductor Nanostructures

Nanostructured materials have attracted much attention due to their unique properties and functionality in a variety of applications. However, to enhance their functionality, and reduce energy consumption, the major focus of the development of semiconductor devices was on the synthesis techniques. In this regard, the development of different synthesis methods capable of realizing high crystallinity and purity of materials is an enabling step toward making such nano-devices a reality. There are two basic approaches for the synthesis of nanostructured materials, top-down approach, which involves breaking down the bulk material into particles with nanometer sized grains, and the bottom-up approach in which individual atoms or molecules are put together to form the nanoparticles. The fabrication method is of significant importance because it determines the particle composition, structure, size and size distribution. There are two basic approaches to the synthesis of nanostructured mate-rials. The first is the “top-down” approach, which involves breaking down the bulk material into particles with nanometer-sized grains. The other approach is the “bottom-up” approach, in which individual atoms or molecules are put together to form the required nanoparticles. In the “top-down” methods we have mechanical processes such as mechanical alloying, high-energy ball milling, equal channel angular pressing, high pressure torsion, and accumulative roll bonding [1]. Among these bottom up methods of synthesizing metal oxide nanomaterials, such as hydrothermal, [2, 3] combustion synthesis [4], gas-phase methods [5, 6], microwave synthesis and sol-gel processing [7].

1.3.1 Physical Vapor Deposition (PVD)

Physical methods produce the atoms that deposit on a substrate. This process is also called vacuum deposition process as the whole process is usually done in an evacuated chamber. The physical vapor deposition of metal films is used for preparation of nanostructures. It is important to prepare the thin layers with absolutely known properties. Two methods of PVD namely magnetron sputtering and thermal evaporation are widely studied in the literature. The PVD has been known and performed for very long time [8]. However the magnetron sputtering is widely used in
the fabrication process techniques [9]. In magnetron sputtering method the plasma is used and acceleration of ions towards a target; material “sputtered” from the target and deposited on the wafer; extensively used in Si technology. On the other hand thermal evaporation is still important for some thin layer preparations. The deposition of a thin film on a wafer occurs as the result of the metal vapor condensation at high vacuum. Physical vapor deposition process has been successfully used for synthesizing a variety of oxide and non-oxide nanobelts and nanowires. An example of materials that have been synthesized using PVD such as: ZnO, Cuprous oxide (Cu$_2$O), and TiO$_2$.

1.3.2 Chemical Vapor Deposition (CVD)

Chemical vapor deposition is widely used in materials processing technology. The majority of its applications involve applying solid thin-film coatings to surfaces, but it is used also to produce high-purity bulk materials and powders, as well as to fabricate composites. CVD has been used to deposit a wide range of materials in many different areas. Intentionally, in this method the source materials can be heated up to their gaseous form under vacuum and the reacted species are deposited on solid substrates. The deposition can be done through a chemical reaction so that the material deposited is different from the one volatilized. This process is regularly used to make nanopowders of oxides and carbides of metals if carbon or oxygen are present with the metal. The method can also be used to generate nanopowders of pure metals, although not so easy to do. CVD is often used to deposit a material on a flat surface. When a surface is exposed to a chemical vapor, the first layer of atoms or molecules that deposit on the surface can act as a template on which material can grow. The structures of these materials are often aligned. During deposition, a site for crystallization may form in the depositional axis (the axis perpendicular to the surface to be coated). As a result, aligned structures start to grow vertically. This is therefore an example of self-assembly bottom-up. Several materials have been prepared utilizing this method.
1.3.3 Pulsed laser deposition process (PLD)

Pulsed laser deposition (PLD) is a process that can be used in preparation of thin films by the ablation of one or more targets illuminated by a focused pulsed-laser beam. The first PLD experiment was carried out shortly after the invention of the pulsed ruby laser [10], in favor of the need of Dijkkamp and coworkers for the preparation of semiconductors and dielectric thin films [11] on high-temperature superconductors in 1987. Their work already showed main characteristics of PLD, namely the stoichiometry transfer between target and deposited film, high deposition rates of about 0.1 nm per pulse and the occurrence of droplets on the substrate surface.

Pulsed laser deposition (PLD) is a unique physical vapor deposition (PVD) process that uses a pulsed laser such as KrF to ablate the target material, forming a highly energetic plume that deposits the film onto the substrate. Material is then vaporized and deposited as a thin film on a substrate facing the target. This process can occur in ultra high vacuum or in the presence of a background gas, such as oxygen when depositing films of oxides. Compared to Molecular Beam Epitaxy PLD could be used to produce films with high quality [12]. Another very important advantage of PLD is the simplicity of the technique. The laser is completely separated from the actual deposition chamber. During an experiment, the laser beam is pointed onto a target inside the chamber through a viewport in alignment with the target. Under these unique conditions the deposition chamber can contain any working atmosphere.

A variety of materials were produced using PLD, such as the growth of higher temperature superconductor, ferroelectric and semiconductor materials like YBaCuO [13], BaTiO [14] and YiBa$_2$Cu$_3$O$_{7-x}$ [15-20] and La$_{1.85}$Sr$_{0.15}$CuO$_{4-x}$, in addition to HTS also a variety of metal oxides fabricated using the PLD technique such as zinc oxide thin films and nanostructured materials [21-23].
1.3.4 Sputtering Process

Sputter deposition is a widely used technique to deposit thin films on substrates. The technique is based upon ion bombardment of a source material, the target. Ion bombardment results in a vapor due to a purely physical process, i.e. the sputtering of the target material. Therefore, this technique is one of the classes of PVD techniques. The most common approach for growing thin films by sputter deposition is the use of a magnetron source in which positive ions present in the plasma of a magnetically enhanced glow discharge bombard the target. The target can be powered in different ways, ranging from dc for conductive targets, to RF for nonconductive targets, to a variety of different ways of applying current and/or voltage pulses to the target. Since sputtering is a purely physical process, adding chemistry to, for example, deposit a compound layer must be done ad hoc through the addition of a reactive gas to the plasma, i.e. reactive sputter. Sputtering is the ejection of atoms by the bombardment of a solid or liquid target by energetic particles, mostly ions. It results from collisions between the incident energetic particles, and/or resultant recoil atoms, with surface atoms. A measure of the removal rate of surface atoms is the sputter yield Y, defined as the ratio between the numbers of sputter ejected atoms and the number of incident projectiles. Excellent review articles on sputtering are available in the literature [24-26]. Many materials have been prepared by sputtering Al$_2$O$_3$ films have also been prepared by reactive sputtering and their formation process has been studied [27, 28].

1.3.5 Metal-organic Chemical Vapor deposition (MOCVD)

Metal organic chemical vapor deposition is a CVD materials preparation type. It's widely used in semiconductor thin film growth. Since a wide variety of materials which could not be deposited by the conventional halide CVD process, because halide reactive do not exist or are not volatile, can now be grown by MOCVD. This includes metals and different multi-component materials such as semiconductor and intermetallic compounds as well as carbides, nitrides, oxides, borides, silicides and chalcogenides. The success of this technique is mainly due to its versatility and to the increasing interest for the low temperature deposition processes. MOCVD have been utilized in the growth of large number of materials like ZnO nanowires [29] and Ga-
doped ZnO single-crystal nanotips [30]. Commercially MOCVD used in manufacturing light-emitting diodes (LEDs), lasers, transistors, solar cells and other electronic and opto-electronic devices, and is the key enabling technology for future markets with high growth potential. The LED lighting applications that will become the widespread standard in the private, commercial and public lighting market in the coming years are a prime example of this tendency.

1.3.6 Sol-gel method

In the sol-gel process, the aqueous or organic solvents, precursors hydrolyzed and condensed to form inorganic polymers composed of M-O-M bonds. The most commonly used organic precursors are metal alkoxides \([\text{M(OR)}_x]\), where \(R\) is an alkyl group \((\text{C}_x\text{H}_{2x+1})\) [31]. The term sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid. Whereas the gel consists of a three dimensional continuous network, which encloses a liquid phase, in a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel, the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved. The idea behind sol-gel synthesis is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner. The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction. It can be used to produce materials with various shapes such as porous structures, thin fibers, dense powders and thin films. A large range of nanostructures has been prepared using this method like CdO, TiO$_2$–CeO$_2$, ZnO, CuO, V$_2$O$_5$ etc. [32-35].
1.3.7 Sonochemical Methods

This technique employs the Ultrasound in the synthesis of nanostructured materials. Applying high frequency ultrasonic waves during the reaction without combination of the ultrasound with the chemical species driven by the formation, growth, and collapse of bubbles in a liquid. Sonication acoustic cavitations phenomenon generates cavities in the liquid solution of the reactants. The cavitations processes consist of the creation, growth and implosive collapse of gas vacuoles in the solution. According to the “hot-spot” theory, extreme temperatures (> 5000 K) and high pressures (> 1000 atm) occur within the bubbles during cavitational collapse [36-41]. Under such extreme conditions the solvent molecules undergo hemolytic bond breakage to generate radicals, H\(^+\) and OH\(^-\) when H\(_2\)O is sonicated for example. The liberated radicals therefore, may lead to various chemical and physical effects in reaction pathways and mechanisms. Sonochemical method have been used for the synthesis of TiO\(_2\) nanoparticles [42].

1.3.8 Electrochemical deposition process

The electrochemical deposition technique is one of the widely utilized techniques for the preparation of nanomaterials. In this type of synthesis, the reactions have well-defined cathodic and anodic reactions. In the case of electrochemical deposition, an external power supply (direct current or pulsed current) is required to drive the reaction, while in electroless deposition the electrons for metal ion reduction come from a reducing agent added to the base metal electrolyte (e.g., hypophosphite in the case of electroless Ni—P) [43]. Several materials have been synthesized by electrochemical deposition such as ZnO [44], CuInSe\(_2\) [45] and copper oxide [46]. However, a variety of applications implemented the electrodeposition e.g. semiconductor chips are the heart and brain of the Information Age and the Internet Revolution. Everything from supercomputers to personal computers, personal digital assistants, cellular phones, modern cars, airplanes, household appliances and medical devices need sophisticated chips to run. The ubiquitous semiconductor chips have altered the way people communicate, do business, gain education and entertainment. Key technological breakthroughs and innovations include the flip-chip and copper interconnects.
1.3.9 Chemical precipitation method

Chemical precipitation is an effective treatment process for the removal of many contaminants. The removability of substances from water by precipitation depends primarily on the solubility of the various complexes formed in water. Solids have low solubility limits in water. Thus, because of the formation of insoluble hydroxides and carbonates, the metals will be precipitated out of solution. Chemical precipitation is one of the most commonly used processes in water treatment. The experience with this process has produced a wide range of treatment efficiencies. Precipitation formation is both a physical and chemical process. The physical part of the process composed in two phases: nucleation and crystal growth. Nucleation begins with a supersaturated solution (i.e., a solution that contains a greater concentration of dissolved ions than can exist under equilibrium conditions). Under such conditions, a condensation of ions will occur, forming very small (invisible) particles. The degree of supersaturation required for nucleation to occur varies. However, the process enhanced by the presence of preformed nuclei that introduced, for example, through the return of settled precipitate sludge, back to the process. Crystal growth follows nucleation as ions diffuse from the surrounding solution to the surfaces of the solid particles. This process continues until the condition of supersaturation has been relieved and equilibrium is established. Variety of nanostructured materials produced by chemical precipitation process, to name a few, copper oxide, zinc oxide, gallium oxide and so on [47].

1.3.10 Hydrothermal process

Hydrothermal processing defined as any heterogeneous reaction in an aqueous solvent (or non-aqueous solvent for solvothermal process) under high pressure and temperature conditions, which induces the dissolution and recrystallisation of materials that are relatively insoluble under ordinary conditions. Hydrothermal method in the 21st century not just confined to the crystal growth or leaching of metals, but it is going to take a very broad shape covering several interdisciplinary branches of science. The usual medium for this process is water. Water is one of the most important solvent present in nature in abundant amount and has remarkable properties as a reaction medium under hydrothermal conditions. Water shows
different characteristics under hydrothermal conditions than that of standard conditions.

Hydrothermal synthesis offers many advantages over conventional and non-conventional synthesis methods. Unlike many advanced methods that can prepare a large variety of forms, the respective costs for instrumentation, energy and precursors are far less for hydrothermal methods. From the environmental perspective, hydrothermal methods are more environmentally benign than many other methods.

1.4 Importance of semiconductor Nanostructures

Since their breakthrough, semiconductor nanostructures field becomes the subject interest in a number of disciplines, due to their remarkable and versatile properties. However, the benefit of size reduction helps in obtaining functional materials with novel electrical, mechanical and chemical properties. Furthermore, the size effect was the main phenomena that have been widely used in the synthesis of relevant materials, and device fabrication. However, nanomaterials and nanostructures play a very important supporting role in the application in nanoscience and nanotechnology. Accordingly, they can be employed in a wide range of life needs from basic science to technological applications and medicine. Nonetheless, incorporation of nanotechnology and biomedical sciences led the improvement of current diagnostic and therapeutic techniques in clinical medicine [48]. Aside from diagnostic platforms, nanomaterials-based technologies being developed to improve current therapeutic strategies and to create novel treatment methods to combat various diseases and pathological conditions. From small-scale drug delivery systems with controllable release to non-invasive tumor targeting vehicles, [49, 50] the implementation of nanotechnology in clinical medicine has rapidly gained interest from both academic and industrial audiences. Information and technology been strongly affected by the size effect of nanostructure like cell phones, computers, and so forth.

The development of these new materials has also contributed in the IT industry for the fabrication of suitable devices that will have a guide role in the size reduction of device under consideration such as transistor CPUs, high-density storage
field emission displays and logical devices. Several semiconductor nanostructures utilized in a variety of applications, among these, zinc oxide (ZnO), copper oxide (CuO), hematite (α-Fe₂O₃), tin sulfide (SnS), etc. In the study we concentrated on CuO, α-Fe₂O₃ and SnS. Copper Oxide is p-type semiconductor with band gap of 1.2 eV. Due to various important chemical and physical properties of CuO, it is used in variety of applications such as catalysis,[51,53] sensors (chemical and biosensors) [54-57], electrode materials,[58] field emission (FE) emitters,[59] photovoltaic devices,[60] magnetic storage media,[61] electrode materials for lithium ion battery applications[62-64], and so on.

This thesis reports the detailed structural characterizations of the hexagonal CuO disks and fabrication of highly sensitive, robust, reliable and reproducible 4-nitrophenol (4-NP) chemical sensor based on CuO nanocubes. The second material that we have studied is the α-Fe₂O₃, it is one of the n-type semiconductor materials with superior properties and functionalities and hence used extensively in various high-technological applications such as catalysis, pigments, sensors, bio-medical (diagnosis and therapy) applications and so on [65,66]. As for hematite (α-Fe₂O₃) is concerned, it is one of the most stable iron oxide under ambient conditions. In this regard, the synthesized α-Fe₂O₃ nanoparticles characterized and utilized as photocatalysts for photocatalytic application and used as efficient electron mediator for the fabrication of highly sensitive aqueous ammonia chemical sensor. The last class of materials investigated in this thesis is IV–VI group semiconductors, tin sulfides (SnS, SnS₂). Among large number of binary tin sulfides (SnS, SnS₂, Sn₂S₃, Sn₃S₄, Sn₄S₅ SnS and SnS₂), the SnS and SnS₂ possesses special place due to its own properties and wide applications in solar cells, lithium-ion batteries, optoelectronics, photoluminescence and so on [67,68]. In this thesis, SnS nanosheets and SnS₂ nanoflakes synthesized and characterized in detail.

Moreover, the prepared SnS₂ nanoflakes used as efficient photocatalysts for photocatalytic degradation of Rhodamine B under visible light [69]. As an efficient electron mediators for the fabrication of nitroaniline chemical sensor characterized by simple I-V technique. Furthermore, the prepared SnS nanosheets utilized to fabricate p-SnS/ n-TiO₂ heterojunction assembly [70, 73].
1.5 Investigated semiconductor nanomaterials

1.5.1 Copper Oxide (CuO): Properties and applications

Semiconductor nanostructure based on CuO have attracted considerable attention especially such as nanotubes [74.], nanoribbons [75], nanorods [76], nanowires [77] and nanobelts [78], due to their unique physical and chemical properties because of its high surface-to-volume ratio compared with micro or bulk-sized [79]. Copper forms two well-known oxides: tenorite (CuO) and cuprite (Cu₂O). Copper oxide (CuO) is a p-type semiconductor material with a band gap energy ranging from 1.21 to 1.5 eV [80] have been studied for applications in photothermal [81], photoconductive [82], magnetic [83] and superconductors' devices. As a p-type semiconductor, conduction arises from the presence of holes in the valence band (VB) due to doping/annealing [84]. CuO is attractive as a selective solar absorber since it has high solar absorbency and a low thermal emittance [85]. Various efforts directed toward the fabrication of nanostructured CuO to enhance its performance in currently existing applications. In particular, a variety of CuO nanostructures prepared by high-temperature approaches.

Hydrothermal method has gained space as a versatile method for preparation of copper oxide in temperatures ranging from 100 to 200 °C for different times [86]. CuO nanoparticles dispersed in semiconductor tin oxide (SnO₂) improve the sensitivity of SnO₂ sensors for H₂S gas detection [87]. Moreover, this oxide also is an important material for the fabrication of lithium ion battery [88]. Due to these applications, morphology-controlled synthesis and well-defined shapes for the formation of CuO are technologically interesting due to the chemical and physical properties of this material depend on its composition, structure, phase, shape, size, and size distribution [88-92]. Thus, different morphologies obtained for the CuO. The abundance of its source material (Cu) together with other features such as low-cost production, good thermal stability, and electrochemical properties make CuO a promising material for various applications. Furthermore, the ionicity of the Cu-O bonds increases when the size of the material approached the nanodomain. This property combined with the relatively large aspect ratio of CuO nanomaterials is very
attractive for applications such as gas sensing and as a catalyst for degradation of hazardous chemicals.

1.5.1.1 Properties of Copper oxide (CuO):

a Crystal structure of CuO:

Transition metal oxides have attracted much attention in recent years because of their size dependent optical properties and electronic structure [93]. Copper oxide is a transition-metal oxide with a monoclinic structure [94, 95], with a crystallographic point group of 2/m or $C_{2h}$. The space group of its unit cell is C2/c, and its lattice parameters are $a = 4.6837(5)$, $b = 3.4226(5)$, $c = 5.1288(6)$, $\alpha = 90^\circ$, $\beta = 99.54(1)^\circ$, $\gamma = 90^\circ$. [96]. The copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration as shown in the Figure (1.4). The coordination of atoms in CuO is that each atom has four nearest neighbors of the other kind. In the (110) plane, each Cu atom is linked to four nearly coplanar O atoms at the corner of an almost rectangular parallelogram. The O atom is coordinated to four Cu atoms in the form of a distorted tetrahedron.
b **Optical properties:**

Materials with length scales in the nanometer regime demonstrate properties that are remarkably different from analogous bulk counterparts. One potential application for nanomaterials is the use in optical applications. Semiconductor nanostructures based on CuO demonstrate a variety of optical properties, because of their band gap which ranges from 1.21-1.85 eV. The narrow band gap of this material (1.2 eV) favors its use in photoconductive and photothermal applications [74, 98, and 99]. As an important heterogeneous catalyst for many important chemical processes, CuO nanostructures are used for degradation of nitrous oxide, selective catalytic reduction of nitric oxide with ammonia, oxidation of CO at low temperature,[100] hydrocarbon and other organic moieties in supercritical water,[101,102]. Due to the photoconductive and photochemical properties, CuO nanostructures are also promising materials for the fabrication of optical switches [103] and solar cells. [104]
Cupric oxide (CuO) is an important p-type transition-metal semiconductor with a narrow band gap. It has received much attention for its numerous applications in the fields of innovative science and technology. This material has been used in a wide range of applications because of its remarkable structures such as nanoparticles, nanoribbons, nanosheets, nanoneedles, nanorings, nanowhiskers, nanorod, nanotubes, nanoleaves, and nanoflower. It has been used in applications such as gas sensors, solar photovoltaics, heterogeneous catalysis, lithium ion electrode, dye-sensitized solar cells, and field emission emitters, in addition to its use in environmental safety since it is one of the serious concerns for the scientific community because of rapid increase in the use of organic pollutants in agriculture and various industries.

Table 1.1 Properties of CuO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>CuO</td>
</tr>
<tr>
<td>Molar mass</td>
<td>79.545 g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>black to brown powder</td>
</tr>
<tr>
<td>Odour</td>
<td>odourless powder</td>
</tr>
<tr>
<td>Density</td>
<td>6.315 g/cm$^3$</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2,000 °C; 3,630 °F; 2,270 K</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Melting point</td>
<td>1326 °C (2418 deg F @ 760 mm Hg)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.63</td>
</tr>
<tr>
<td>Lattice Constants</td>
<td>$a = 4.6837(5), b = 3.4226(5), c = 5.1288(6), \alpha = 90^\circ, \beta = 99.54(1)^\circ, \gamma = 90^\circ.$</td>
</tr>
<tr>
<td>Relative Dielectric Constant</td>
<td>18.1</td>
</tr>
<tr>
<td>Energy Gap</td>
<td>1.21-1.85 eV, direct</td>
</tr>
<tr>
<td>Hole Effective mass</td>
<td>0.24 $m_o$</td>
</tr>
<tr>
<td>Hole mobility (at 300K)</td>
<td>0.1-10 cm$^2$/Vs</td>
</tr>
</tbody>
</table>
1.5.2 Iron Oxide: Properties and applications

Developments in nanotechnology are dependent on the availability of new materials, and the ability to design and synthesize new nanostructured materials. However, Iron oxide is one of the versatile materials considered for a variety of applications. It can appear in many phases such as ferromagnetic $\alpha$-Fe$_2$O$_3$ (hematite), $\beta$-FeOOH (akaganeite), magnetite (Fe$_3$O$_4$) and maghemite ($\gamma$-Fe$_2$O$_3$). Among various metal oxide nanostructures, iron oxide presents itself as one of the promising metal oxide materials with superior properties and functionalities and hence used extensively in various high-technological applications such as catalysis, pigments, sensors, bio-medical (diagnosis and therapy) applications and so on [65, 66]. As far as hematite ($\alpha$-Fe$_2$O$_3$) is concerned, it is one of the most stable iron oxide under ambient conditions. Owing to its various interesting properties such as n-type semiconducting behavior, band gap ($E_g$= 2.1 eV), low-cost synthesis, non-toxic nature, high resistant to corrosion, the $\alpha$-Fe$_2$O$_3$ is widely used in variety of high-technological applications such as sensors, photocatalysis, pigments, magnetic recording media, etc. [105-111]. Because of the high electrical conductivity and high-sensitivity to gaseous environment, $\alpha$-Fe$_2$O$_3$ also used as an efficient material for the fabrication of effective gas sensors [112,113].

Maghemite is of particular interest because of its application in magnetic recording media pigments, catalysts and gas sensitive materials. It has a cubic spinel structure and known to be a ferrimagnetic with a saturation magnetization of 390 kAm$^{-1}$. Maghemite is a metastable phase at ambient conditions, and tends to transform to a stable phase of antiferromagnetic haematite ($\alpha$-Fe$_2$O$_3$) when heated above 400°C [114]. It is therefore of great interest to deposit ferrimagnetic maghemite and suppress its transformation to the equilibrium antiferromagnetic haematite structure.

Akaganéite, $\beta$-FeOOH, is named after the Akagane mine in Iwate, Japan, where the mineral was first discovered [115]. $\beta$-FeOOH is a typical product of the hydrolysis of dilute or concentrated ferric chloride solution at low pH value, and the subject of numerous studies due to its sorption, ion exchange, and catalytic
properties.\[116,117\] β-FeOOH exists in the environment as a fine-grained material with a large specific surface area, which increases significantly with decreasing particle size. β-FeOOH was first recognised by Weiser and Milligan, who distinguished it from other members of the Fe–O–H–Cl system by means of powder diffraction.

1.5.2.1 Properties of Iron Oxide:

a Structural properties:

Due to the diversity of the atomic structure of iron oxide from its stable hematite to the other unstable phases, it possesses a variety of crystal structure. Figure (1.3) clearly displays the crystal structure of \( \alpha\text{-Fe}_2\text{O}_3 \). Hematite mined as the main ore for producing iron. The structure of \( \alpha\text{-Fe}_2\text{O}_3 \) (Figure (1.5) a is similar to that of corundum \( \alpha\text{-Al}_2\text{O}_3 \) which crystallizes in the rhombohedral system, as determined by Pauling and Hendricks in 1925\[111\] and the lattice parameters given in the hexagonal cell, shown in Figure (1.5) b, are \( a = b = 5.0346 \, \text{Å} \) and \( c = 13.752 \, \text{Å} \).

Figure 1.5(a) The rhombohedral unit cell of \( \alpha\text{-Fe}_2\text{O}_3 \) (b) ball and stick model unit cell outline of the hematite [118].
b  Magnetic properties of α-Fe₂O₃:

There are a number of magnetic properties used to characterize the different iron oxides. These properties mainly developed in the frame of paleomagnetic studies in the geosciences and materials sciences. The most important properties are the type, strength and direction of the remanent magnetization. These can be used to identify the remanence carrier and the (magnetic) domain type of the particle that is multidomain, single domain, pseudo single domain and superparamagnetic; usually the particle size decreases in this order. The magnetic properties of materials can usually be measured by means of the so called the vibrating sample magnetometer (VSM) and the superconducting quantum interference device (SQUID) magnetometer. Experimentally and theoretically, the relationship between the size and the magnetic properties of nanoparticles has attracted much attention [119-121]. It has been found nanoparticles smaller than a critical size (~40 nm) present a variety of size-dependent behaviors [119]; e.g., the cooperative phenomenon in ferromagnetism no longer observed, and the particles behave like single domains, showing magnetic susceptibilities higher that of the bulk, and the superparamagnetic behavior appears.

c  Optical properties:

The optical properties of iron oxides are very important for designing electrochromic devices, photoelectrochemical generation of hydrogen, solar radiation filters, etc. [122- 125]. Magnetite and Wustite show thermally induced electronic transitions assigned to intervalence charge transference; and for this reason, they exhibit absorption in the visible and near-IR region [126]. Maghemite and hematite are insulators and do not present any absorption in the near-IR region. The oxidation process of magnetite nanoparticles to maghemite monitored by the loss of optical absorption in the near-IR region [126]. For hematite films, the direct optical band gap determined through Tauc plots ranges from 2.0 to 2.7 eV [127,128], while the indirect transition energy is around 1.9 eV [127]. Direct band gaps of 1.73 and 1.97 eV reported for amorphous and b-Fe₂O₃ films, respectively [129]. The band gap of bulk maghemite is 2.0 eV [130], while maghemite nanoparticles exhibit an energy gap of 2.47 eV due to the quantum confinement effects [131].
1.5.3 Tin Sulphide (SnS and SnS$_2$): Properties and applications

Semiconductor nanostructures have been attracting worldwide attention due to their exceptional electrical, optical, and magnetic properties, and their potential applications in nanoscale electronics, photonics, and functional materials as well [132-134]. Among them, tin sulfide (SnS) has sparked intensive interest for its semiconducting and optical properties. The SnS$_2$ is n-type semiconductor receiving much attention owing to its layered hexagonal CdI$_2$-type crystal structure with two layers of close-packed sulfur anions and tin cations sandwiched between them in an octahedral coordination manner. Due to its absorption tunable band gap of 2.2 eV, the crystalline SnS$_2$ could be a promising photocatalytic material for the photocatalytic degradation of organic dyes in the presence of visible-light [69]. Moreover, SnS$_2$ nanomaterials possess good oxidative and thermal stability in acid and neutral environment [70, 72].

1.6 Investigated applications of semiconductor nanomaterials (CuO, α-Fe$_2$O$_3$ and SnS and SnS$_2$) presented in this thesis

1.6.1 Sensor applications of targeted semiconductor nanostructures

A sensor is a technological device that converts one form of energy to another, so it detects and conveys information about some physical, chemical or biological phenomena. The basic idea of any kind of sensor based on energy conversion. No matter what one is going to measure but usually deals with some sort of energy transfer from the object of measurement to the sensor. This explains that sensing is particular case of information transferring as in the case of our natural sensors where communication occurs between the specified sensor and the brain. Sensors are effective tools for the detecting and navigating a variety of dangerous materials in the environment. However, a rapid development in the fabrication of efficient materials and selective and reliable sensors is now the one of the most interesting topics.

Industrial developments have extended rapidly and widely in a broad range of disciplines, which result in the environmental pollution. One of the major environmental issues is the release of harmful gases, liquids and chemicals in the
environment through industrial effluents, agricultural chemicals, fertilizers and so on. Ammonia is one of the toxic gases and liquids and widely used in chemical industries, fertilizer factories, refrigeration systems, environmental monitoring food decomposition and so on [135-137,237]. This leads to the fabrication of different types of sensors direct and complex. A direct sensor converts a stimulus into an electrical signal or modifies an electrical signal by using an appropriate physical effect, whereas a complex sensor in addition needs one or more transducers of energy before a direct sensor employed to generate an electrical output. There are two kinds of sensors, passive and active. A passive sensor does not need any additional energy source and directly generates an electric signal in response to an external stimulus; that is, the input stimulus energy converted by the sensor into the output signal. The active sensors require external power for their operation, which called an excitation signal. In this thesis, we focus on chemical sensors based on metal oxide nanostructure. Chemical sensors are of great interests that invoke the development of scientific fundamentals and technologies of preparation of high sensitivity sensor structure. Highly sensitive chemical sensors were fabricated using CuO nanocubes and $\alpha$-Fe$_2$O$_3$ nanoparticles for the detection of ammonia, nitro-aniline and 4-nitrophenol. The fabrication details and sensor performances of the fabricated sensors demonstrated in detail in chapter 3.

1.6.2 Photocatalyst applications of the investigated semiconductor nanostructures

Due to the rapid increase in the usage of chemicals in a wide range of industrial applications and products, huge environmental pollution has been produced which directly affect the human beings and animals and severely pollute the environment. Moreover, pollution considered as the sufferings of soil and water on earth surface from contamination of organic pollutants widely at different levels. These organic chemicals found as pollutants in wastewater effluents from industrial or domestic sources. It has become important for a better understanding of some abiotic transformations of these organic pollutants naturally occurring in the environment, such as some catalytic processes at mineral surfaces. In fact, these processes may play a fundamental role in decontamination and mineralization of organic pollutants under a natural condition [138-140]. In order to overcome the organic pollutants, several
noble methods were developed [141] with photocatalysis gaining a lot of attention in the field of pollutant degradation.

In the degradation process the size of the energy band gap plays a central role in determining the color of the semiconductor, because they absorb light having energy equal to or higher than $E_G$ energy. Such light absorption causes electron transfer from a valence band to a conduction band. The energy of visible light lies in the region of 1.5 (red) - 3.0 eV (violet). Thus, the semiconductors having a narrow band gap of about 1.5 eV are black, those having a band gap of about 3.0 eV - white. WO$_3$ and CdS, which absorb part of the wavelength from the visible region, are yellow [142]. In this thesis, we have synthesized $\alpha$-Fe$_2$O$_3$ hexagonal nanoparticles and utilized them as efficient photocatalysts for the degradation of hazardous Rhodamine B (RhB) dye. The details of photocatalytic degradation of $\alpha$-Fe$_2$O$_3$ hexagonal nanoparticles and of SnS$_2$ nanoflakes towards Rhodamine B (RhB) dye already presented in chapter 3.

1.6.3 p-n Heterojunction diode application of SnS nanosheets

A p-n heterojunction diode can be formed by using two semiconductors of different band gaps and with opposite doping impurities. Examples of p-n heterojunction diodes are Ge/GaAs, Si/SiGe, AlGaAs/GaAs, InGaAs/InAlAs, InGaP/GaAs, InGaAs/InP, and GaN/InGaN heterostructures. The p-n heterojunction diode is in principle very similar to a homojunction. The main problem that want tackled is the effect of the band gap discontinuities and the different material parameters, which make the actual calculations more complex even though the p-n diode concepts need almost no changing. Single crystals and polycrystalline thin films of SnS have shown indirect optical transitions with an optical band gap of about 1.3 eV, and p-type electrical conductivity whose dark value can be increased by doping with Ag, Al, N and Cl [143-145]. Since its optical band gap lies in the optimum range in which absorber materials used in solar cell applications [146], the SnS compound, with an optimized thickness, could be use in photovoltaic structures. Single crystal and polycrystalline thin films of SnS$_2$ have shown optical band gaps in the range of 2.12–2.44 eV [147–150], and n-type electrical conductivity with magnitude
depending on the preparation technique. Both characteristics make this compound suitable for a window material in a heterojunction structure. For heterojunction devices, p-type SnS materials being the absorber material necessitates an n-type semiconductor material with wide band gap as heterojunction partner [151,152]. Various n-type semiconductors such as SnO$_2$, ZnO, CdS and ZnS could be expected as suitable heterojunction materials for p-type SnS.[327] Previously, M. Ichimura studied the theoretical estimation of band offsets in CdS/SnS heterojunction using the first principle, density functional and pseudo-potential method.[330] A. Tiburcio-Silver et. al., have fabricated SnS$_2$/SnS heterojunction thin film diodes by plasma-enhanced chemical vapor deposition [153]. In this work, a heterojunction device fabricated with solution processed SnS nanosheets (p-type)/TiO$_2$ nanoparticles (n-type) and a top Pt thin layer to form Pt/SnS/TiO$_2$/FTO diode assembly.

1.7 Objectives and Importance of the thesis

This thesis contains four chapters. The first chapter briefly presents an introduction on semiconductors, semiconductor nanosturctures, and their various synthesis techniques. Chapter 2 describes the synthesis, characterization and fabrication techniques of semiconductor nanostructures studied in this thesis. Chapter 3 demonstrates the detailed characterizations and applications of the investigated semiconductor nanomaterials in this work. This chapter contains three main sections and each section is composed of two subsections. With a brief introduction, and concise experimental details, the results and discussions of each sections are presented in detail. For applications view point, most of the investigated semiconductor nanomaterials were used as effective electron mediators for the fabrication of efficient chemical sensors and effective photocatalysts for the photocatalytic degradation of toxic chemicals and dyes. Moreover, the prepared SnS nanoflakes were successfully used to fabricate heterojunction diodes. Finally, chapter 4 provides an overall conclusions of the thesis.
CHAPTER-2

Chapter 2 deals with the details of the synthesis and characterization techniques used for the prepared semiconductor nanomaterials targeted in this thesis. All the presented semiconductor nanomaterials synthesized by simple and facile hydrothermal process. The synthesized nanomaterials examined by variety of techniques in terms of their morphological, structural, optical, compositional and electrical properties. Moreover, the prepared nanomaterials used for various applications such as sensing, photocatalytic and heterojunction diodes. In brief, this chapter provides all the detailed experimental procedures for the synthesis, and characterizations of the investigated semiconductor nanomaterials in this thesis.
2 EXPERIMENTAL PROCEDURES

Various semiconductor nanomaterials such as Copper oxide (CuO), iron oxide (Fe$_2$O$_3$) and tin sulphides (SnS and SnS$_2$) investigated in this thesis. All the nanomaterials synthesized by simple and facile hydrothermal process at low-temperature. Moreover, the as-synthesized nanostructures extensively characterized in terms of their morphological, structural, optical, compositional and electrical properties. The general morphologies of the prepared nanomaterials examined by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). To examine the structural properties, the prepared nanomaterials have been characterized with high-resolution TEM (HRTEM) and x-ray diffraction (XRD) pattern. The elemental and chemical compositions of prepared nanomaterials investigated by energy dispersive x-ray spectroscopy (EDS) and Fourier transform infrared (FTIR) spectroscopy, respectively. The optical properties examined by UV-visible spectroscopy at room temperature. Finally, the synthesized semiconductor nanomaterials used for sensing, photocatalytic and p-n heterojunction diode applications.

2.1 Details of hydrothermal synthetic technique

The term hydrothermal has its geological origin, though geologists have used it for decades in synthesizing ceramics. Sir Roderick Murchison (1792-1871), used it for the first time to describe the action of water at elevated temperature and pressure, leading to the formation of various rocks and minerals in the earth’s crust [154]. Definition for the word hydrothermal has undergone several changes from the original Greek meaning of the words ‘hydros’ meaning water and ‘thermos’ meaning heat. Hydrothermal processing defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under elevated temperature and high-pressure conditions to dissolve materials that are relatively insoluble under ordinary conditions in order to crystallize them. In hydrothermal method, highly corrosive salt used to synthesize inorganic materials for longer reaction time. In the 20th century, hydrothermal synthesis clearly identified as an important technology for material synthesis mainly for single crystal. [155].
In fact, hydrothermal synthesis offers the chance to control the size and shape of the nanostructure at relatively low temperature and short reaction times, leading to a well-crystallized product and with high purity and definite homogenized composition. Hydrothermal process is indeed promising for controllable synthesis of low dimensional nanostructures. Among a rich family of solution-based chemical processes, the hydrothermal process has been widely used for the synthesis of a vast range of solid-state compounds such as oxides, sulfides halides, zeolites and other microporous phases.

Hydrothermal is a simple chemical process that utilizes water as reaction medium. Accordingly water have the remarkable properties in addition to the amount abundant compared to the other solvents. There are several advantages for the use of water as reaction medium for the hydrothermal process that water shows diverse characters under hydrothermal conditions than that of standard condition. It is also cheap and environmental friendly. By tuning the temperature and pressure, it can work as a good catalyst for the formation of desired materials. Moreover, water is nonflammable, nontoxic, and has stable thermodynamic properties.

The device that usually been used for this type of process is called auto clave, reactor, pressure vessel or high-pressure bomb; it is generally a vessel with a suitable volume containing a Teflon beaker. The vessel is typically a stainless steel container, which can keep to some extent the pressure stable during the reaction procedure. The autoclave must be capable of sustaining highly corrosive solvent at high temperature and pressure for a longer duration of time. Due to the larger coefficient of thermal expansion of Teflon (the liner) versus metal (the material in which the liner is enclosed), the Teflon will expand and contract much more upon heating and cooling cycles than its enclosure material. The autoclave that we utilized for growth of semiconductor nanomaterials presented in this thesis shown in Figure 2.1 and Figure 2.2. In order to synthesize semiconductor nanomaterials, several steps should be followed. Starting with preparation of the solution then transfer it to the Teflon beaker and then sealed in the autoclave. Finally, the sealed autoclave heated up above 100°C at ambient pressure for the desired time.
For the hydrothermal growth of semiconductor nanomaterials studied in this thesis, in a typical reaction process, appropriate metal salt was dissolved in de-ionized
(DI) water and stirred for 20 min. After stirring, normally ammonium hydroxide (NH$_4$OH) or sodium hydroxide (NaOH) was added in the solution to maintain the pH= 9-12 of the prepared solution.

The final solution was vigorously stirred for 20-30 min and consequently transferred to teflon lined autoclave which was then sealed and heated up to an appropriate temperature for certain time. After terminating the reaction, the autoclave was allowed to cool at room-temperature and the obtained products washed several times with DI water and ethanol, sequentially and dried at appropriate temperature. The as-synthesized products investigated in terms of their morphological, structural, and optical properties. Finally, the prepared nanomaterials used for sensing, photocatalytic and p-n heterojunction diode applications.

2.2 Characterization of prepared semiconductor nanomaterials

The prepared semiconductor nanomaterials presented in this thesis characterized in detail in terms of their morphological, structural, compositional and optical properties. The morphological properties of the synthesized semiconductor nanomaterials characterized by field emission scanning electron microscopy (FESEM; JEOL-JSM-7600F) and transmission electron microscopy (TEM; JEM-2100F) equipped with high-resolution TEM (HRTEM). The structural properties were examined by X-ray diffraction (XRD; PANalytical Xpert Pro.) with Cu-K$_\alpha$ radiation ($\lambda$=1.54178 Å) in the range of 10-80°. The elemental and chemical compositions were examined by using energy dispersive spectroscopy (EDS), attached with FESEM and Fourier transform infrared (FTIR; Perkin Elmer-FTIR Spectrum-100) spectroscopy, respectively. The optical properties examined by using UV-visible spectroscopy (Perkin Elmer-UV/VIS-Lambda 950) at room temperature.

2.2.1 Field emission scanning electron microscopy (FESEM)
Electron microscopy is a technique, which makes use of highly energetic electrons that interact with materials under investigation on a very fine scale. Electron microscopy provides the information about material such as crystallography, morphology, elemental composition and so on. When an electron impinges the sample, they may be scattered by nuclei or by other electrons. During this process, the electron beam can eject some of the inner shell electrons from the attractive field of the nucleus in an atom. Therefore, a variety of characteristic electrons produced as depicted in Figure 2.3. Every type of electrons utilized in imaging e.g. secondary electrons and backscattered electrons in SEM or elastically scattered electrons in TEM; or chemical analysis, e.g. characteristic X-rays in EDX analysis. Elastic electron-electron interactions usually result in a relatively low scattering angle, while electron-nucleus interactions cause higher-angle scattering. For TEM investigation, elastically scattered electrons are essential for the construction of diffraction patterns and diffraction contrast images.
Field emission electron microscope (FESEM) is an instrument that scans a sample surface with a finely converged electrons in a high vacuum, detects the information (signals) produced at that time from the sample and presents an enlarged image of the sample surface on the monitor screen. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nanometers in size. Due to the way these images formed, SEM micrographs have a very large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

Studying of nanomaterials has strongly driven the development of recent electron microscopy, with demands not only for increasing resolution but also for more information from the sample. Electron microscopes use a beam of highly energetic electrons to probe objects on a very fine scale [156]. In standard electron microscopes, electrons mostly generated by “heating” a tungsten filament (electron gun). They also produced by a crystal of LaB$_6$. The use of LaB$_6$ results in a higher...
electron density in the beam and a better resolution than that with the conventional device. In a field emission (FE) electron microscope, on the other hand, no heating but a so-called "cold" source employed. Field emission is the emission of electrons from the surface of a conductor caused by a strong electric field. An extremely thin and sharp tungsten needle (tip diameter 10–100 nm) works as a cathode. The FE source reasonably combines with scanning electron microscopes (SEMs) whose development supported by advances in secondary electron detector technology. The acceleration voltage between cathode and anode is commonly in the order of magnitude of 0.5 to 30 kV, and the apparatus requires an extreme vacuum (~10^{-6} Pa) in the column of the microscope. Figure 2.4 illustrates the schematic diagram and typical photo of the FESEM that utilized in the characterization of samples used in this thesis. The FESEM is composed of a column that assembles the following parts:

**Electron Gun:** produces a source of electrons and accelerates these electrons to energy in the range of 0.5-30 keV. The beam diameter produced directly by the conventional electron gun is too large to generate a sharp image at high magnification.

**Electron lenses:** used to reduce the diameter of this source of electrons and place a small, focused electron beam on the specimen. Most SEMs can generate an electron beam at the specimen surface with a spot size of less than 10 nm while still carrying sufficient current to form an acceptable image.

**Sample Stage:** At sample stage, the specimens placed for investigation.

**Display:** Imaging and microanalysis can be performed.

**Detectors:**

**Energy Dispersive X-Ray Spectroscopy:** Maps of element distributions over areas of interest and quantitative composition tables provided as necessary.

**(EDS) and Electron Backscatter Diffraction (EBSD):** crystallographic information obtained from samples.
Figure 2.4 Schematic block diagram (from JEOL) and real picture of field emission scanning electron microscope (FESEM; JEOL JSM 7600 F).
2.2.2 Transmission electron microscopy (TEM)

In this type of electron microscopes, the electrons pass through a thin specimen. Transmission electron microscopes (TEM) are operates on thin samples (≤150 nm) and at much higher voltages (≥100 kV). Sample in the form of a thin foil is irradiated by electrons having energy of the order of hundreds of keV. In the interior of the crystal the electrons are either undeviated or they are scattered (elastically or inelastically), or reflected. Electron scattering may be elastic or inelastic. In the first process, the electrons interact with the electrostatic potential of nuclei of atoms. This potential deviate the trajectory of incident electrons without any appreciable energy loss; only the direction is changed. In fact, a small loss occurs because of the change of the momentum. However, because of the disparity of the mass of the scattered electron and the atom the loss is too small ($\Delta E/E^0 \sim 10^{-9}$ at aperture angles used in TEM) to affect the coherency of the beam.

A conventional TEM consists of a number of electron-optical components, as illustrated in Figure 3.7. Electrons produced by thermionic emission from a W or LaB6 filament, or by field emission from a single crystal W filament gun. A conventional TEM consists of a number of electron-optical components, and the used microscope in characterization illustrated in Figure 2.5. Electrons produced by thermionic emission from a W or LaB$_6$ filament, or by field emission from a single crystal W filament gun. A series of condenser lenses focus the electrons into a probe and are responsible for varying the spot size. The condenser aperture filters out electrons far from the optic axis and controls the number of electrons incident on the specimen. The electron beam transmitted through the specimen, generally inserted on a plane normal to the optic axis and situated close to the focal plane of the objective lens. The objective aperture, located in the back focal plane of the objective lens, blocks any transmitted electrons with a large scattering angle, thereby enhancing the contrast of the projected image. The image projected onto an electron sensitive fluorescent screen or a charged couple device (CCD) camera by the projector lens. Images recorded on photographic film or digitized to be stored on computer.
Images in TEM can be formed either using directly transmitted or scattered electrons. The electrons selected by inserting an aperture into the back focal plane of the objective lens, thus blocking out most of the diffraction pattern. If the central spot was chosen, a bright field image is formed using directly transmitted electrons. There are three modes of contrast formation in TEM images. In amorphous samples, thicker regions of the sample and areas with a higher atomic number appear dark, due to mass-thickness contrast. Low index crystalline orientations of crystalline samples that satisfy Bragg diffraction also appear dark, termed diffraction contrast. Further, if the objective aperture is removed, images with contrast arising from constructive and destructive interference of the electron waves, termed phase contrast, can reveal lattice with atomic resolution, known as HRTEM. In all cases, regions imaged with the transmitted beam are termed bright field (BF).
Figure 2.5 Schematic diagram, and the image of the transmission electron microscope (TEM; JEOL 2010F).
2.2.3 Selected area electron diffraction (SAED)

Selected area electron diffraction (SAED) gives information about the structure and morphology of a crystal from an area of about half a micron in diameter. The method therefore, has the promise of elucidating the crystal structure of fine-grained layer silicates like clay minerals. The angle of diffraction ($\theta$) in SAED is very small because of the very small wavelength of high energy electrons (as compared with the wavelength of X-rays) resulting in small distances between the transmitted electron beam and diffracted spots, $d_{hkl}$, as shown in Figure 2.6.

![Figure 2.6 Schematic diagram illustrating the concept of the camera constant in TEM.](image)

Form Figure 2.6

Here:

$$\frac{x}{L} = \tan 2\theta$$

$$\tan 2\theta \approx \sin 2\theta \approx 2\theta$$
Then

\[ \frac{X}{L} = 2\theta = \frac{2\lambda}{2d_{hkl}} \]

Hence:

\[ d_{hkl} = \frac{L\lambda}{X} \]

Where:

L: is the camera length, the effective distance between the specimen and the recording plane.

\( \lambda \): electrons wavelength which fixed by the accelerating voltage,

X: is the distance measured between the transmitted beam and the diffracted beam.

\( L\lambda \): is termed the camera constant and can be obtained using a reference sample of known lattice parameter under the same electron-optic conditions. By using this equation, crystal plane spacing, \( d_{hkl} \), of an unknown material can be calculated and associated diffraction spots indexed.

### 2.2.4 X-ray diffraction (XRD)

X-ray are electromagnetic waves that lie between ultra violet and high energy gamma rays, with wavelength in the range 0.01 – 10 nm the order of magnitude of the distance between molecules and crystal lattice spacing. They are produced when rapidly moving electrons strike a solid target and their kinetic energy is converted into radiation. The wavelength of the emitted radiation depends on the energy of the. It was first discovered by Wilhelm Konrad Röntgen in 1895, for which he was awarded the first Nobel Prize in Physics in 1901.

X-rays are commonly, utilized in the characterization of materials structure. For that there exist two types of characteristic x-rays namely \( K\alpha \) and \( K\beta \), the first one can be generated when a transition from the energy level L to K occurs, and those which produced by the transition from M to K are the \( K\beta \) x-rays. Figure 2.7 represents the characteristic x-rays when an atom bombarded by an electron and the
characteristic peaks for molybdenum and the Bremsstrahlung x-rays. The characteristic wavelength for common target used in X-ray diffraction instruments.

![Figure 2.7(a) Generation of x-ray rays and (b) the characteristic x-rays [157].](image)

<table>
<thead>
<tr>
<th>Anode</th>
<th>$K\alpha_1$ (100)</th>
<th>$K\alpha_2$ (50)</th>
<th>$K\beta$ (15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.54060</td>
<td>1.54439</td>
<td>1.39222</td>
</tr>
<tr>
<td>Cr</td>
<td>2.28970</td>
<td>2.29361</td>
<td>2.08487</td>
</tr>
<tr>
<td>Fe</td>
<td>1.93604</td>
<td>1.93998</td>
<td>1.75661</td>
</tr>
<tr>
<td>Co</td>
<td>1.78897</td>
<td>1.79285</td>
<td>1.62079</td>
</tr>
<tr>
<td>Mo</td>
<td>0.70930</td>
<td>0.71359</td>
<td>0.63229</td>
</tr>
</tbody>
</table>

### 2.2.4.1 X-ray crystallography

X-ray crystallography, also called X-ray diffraction, used to determine crystal structures by interpreting the diffraction patterns formed when X-rays are scattered by the electrons of atoms in crystalline solids. X-rays are sent through a crystal to reveal
the pattern in which the molecules and atoms contained within the crystal are arranged. Thus x-ray crystallography was developed by physicists William Lawrence Bragg and his father William Henry Bragg. In 1912-1913, the younger Bragg developed Bragg’s law, which connects the observed scattering with reflections from evenly spaced planes within the crystal. However, an incident x-ray beam by an angle $\theta$ on a crystal lattice, will be reflected by the lattice planes with same angle. Bragg's law of diffraction governs the relation between the x-rays beam and the angle of reflection given by the following formula:

$$ n\lambda = 2dsin\theta \ldots \ldots (2.1) $$

Where, $d$ is the lattice spacing, $\lambda$ is the X-ray wavelength and $\theta$ is the angle of diffraction. XRD investigations were performed using PANalytical X' Pert Pro X-ray diffractometer operating at 45 kV and 40 mA, using a CuK$\alpha$ radiation source ($\lambda = 0.154$ nm). Analysis were carried out at a 20 step rotation of 0.01° with a dwell time of 1.5 sec at room temperature (~25 °C). Crystalline phase features were identified using X' Pert Data Collector computer software. However, verification of Bragg's law requires a source of x-rays, crystal under investigation and a detector as schematically and photographically shown in Figure 2.8.
Figure 2.8 a) schematic diagram for an x-ray Bragg Diffractometer [159] and (b) PANalytical X’ Pert Pro. Image.
2.2.4.2 Particle size

For crystals with size less than about $10^{-5}$ cm (1000Å), the term "particle size" is usually used and the crystals in this size range cause broadening of the Debye rings. The particle size of nanostructures were determined by measuring peak breadth in an X-ray diffraction pattern that is given by:[158]

$$\beta(2\theta) = \frac{KL}{\cos \theta} \quad \ldots \quad (2.2)$$

where $\beta$ is the peak width at half maximum (FWHM) intensity in radians. The constant of proportionality, $K$ (the Scherer constant) depends on how the width is determined, the shape of the crystal, and the size distribution, where the most common values for $K$ are 0.94 for FWHM of spherical crystals with cubic symmetry, 0.89 for integral breadth of spherical crystals. The Scherer const. $K$ actually varies from 0.62 to 2.08 and $\theta$ is the peak position and $L$ is the crystallite size. The value of $\beta$ can increase through instrumental broadening, which depends on the geometry of the diffractometer and spectral characteristics of the incident beam. Instrumental broadening can be corrected by subtracting the $\beta$ value of a standard reference sample, assumed to comprise infinitely thick particles, from the measured $\beta$ value.

2.2.5 Energy dispersive X-ray spectroscopy (EDS)

Most Scanning electron microscopy (SEM), today are equipped with Energy Dispersive X-ray Spectrometer (EDX), to complete the information on the specimen morphology in terms of its elemental composition, shape, structure and size that cannot be obtained by any bulk analytical approach. EDS usually uses backscattered electron images in the SEM display compositional contrast that results from different atomic number elements and their distribution. It allows one to identify what those particular elements are and their relative proportions (Atomic % for example). Initial EDS analysis usually involves the generation of an X-ray spectrum from the entire scan area of the SEM section 2.2.1. However, an electron from an outer shell L3 fills the hole in the K shell. The extra energy is emitted as a characteristic X-ray quantum as shown in Figure 2.9. The energy of the X-ray is a characteristic of the specimen atomic number from which it can be derived.
The detection of the characteristic X-ray requires a specific type of detectors the EDX that consists of six parts such as collimator, Electron trap, Window, Crystal, Field Effect Transistor and Cryostat. The typical description of the detector shown in Figure 2.10 and its image appears in Figure 2.4 of our FESEM image.
The EDS detector converts the energy of each individual X-ray into a voltage signal of proportional size. This can be achieved through a three-stage process. Firstly, the X-ray is converted into a charge by the ionization of atoms in the semiconductor crystal. Secondly, this charge is converted into the voltage signal by the field effect transistor (FET) preamplifier. Finally, the voltage signal is input into the pulse processor for measurement. The output from the preamplifier is a voltage ramp where each X-ray appears as a voltage step on the ramp. When an incident X-ray strikes the detector crystal, its energy is absorbed by a series of ionizations within the semiconductor to create a number of electron-hole pairs. The electrons are raised into the conduction band of the semiconductor and are free to move within the crystal lattice. When an electron is raised into the conduction band, it leaves behind a hole, which behaves like a free positive charge within the crystal. A high bias voltage, applied between electrical contacts on the front face and back of the crystal, then sweeps the electrons and holes to these opposite electrodes, producing a charge signal, the size of which is directly proportional to the energy of the incident X-ray.

2.2.6 Fourier Transform Infrared (FTIR) Spectroscopy
The vibrational spectrum of a molecule considered as a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an “unknown” with previously recorded reference spectra. Many different types of available spectrometers and spectroscopic techniques exist, which provide spectral measurements over a range of frequencies covering the infrared (IR) to ultraviolet (UV). Two of the more popular instruments are Fourier transform infrared (FTIR) spectrometers and grating monochromators. FTIR offers advantages in multiplexing and throughput, particularly important at long wavelengths. Among FTIR spectrometers, several instrument designs are available.

2.2.6.1 Principles of FTIR Spectroscopy

In the most basic terms, the infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule. First, it is important to reflect on the distribution of energy possessed by a molecule at any given moment, defined as the sum of the contributing energy terms.[162]. FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments, grating monochromator or spectrograph, FTIR spectrometer collect all wavelengths simultaneously. This feature is called the Multiplex or Felgett Advantage. FT-IR Spectrometers are often simply called FTIRs. But for the purists, an FT-IR is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FT-IR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. An FT-IR is a typically based on the Michelson Interferometer Experimental Setup and the utilized FTIR Perkin Elmer spectrometer image shown in Figure. 2.11. The interferometer consists of a Beam splitter, a fixed mirror, and a mirror that translates back and forth, very precisely.
2.2.7 Raman-Scattering Spectroscopy

Raman spectroscopy is a nondestructive tool used in measurements of vibrational motion of a molecule like the infrared spectroscopy. The difference
between Raman spectroscopy and IR spectroscopy, Raman spectroscopy is due to the scattering of light by the vibrating molecule while IR based on the absorption of light by a vibrating molecule. Raman spectra can be obtained from most molecular samples, i.e. solids, liquids, gels, slurries, powders, films, etc. Raman spectra can even be obtained from some metals. In 1928, C.V. Raman discovered another type of light scattering in which the frequency changes when the light is scattered. The frequency shift occurs when a molecule, which is excited into vibrational motion, takes some of the energy of the scattered photon up. The scattering process can be thought of as the incoming photon raising the molecule to a virtual (i.e., non-existent) excited state.

The atoms of a molecule can vibrate in many ways- these are called the normal modes of vibration. The normal modes have different excitation energies so the Raman spectrum will consist of more than one line [Harris, D.C., Bertolucci, M.D., Symmetry and spectroscopy: an introduction to vibrational and electronic spectroscopy, Oxford University Press (1978)]. The Raman Effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. In quantum mechanics, the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in $10^{-14}$ seconds or less. The virtual state description of the scattering shown in Figure 2.12.
The arrows of different lengths in Figure 2.12 represent the energy difference between the incident and scattered photons. Numerically, the Raman shift in wave numbers (cm$^{-1}$), is calculated through Eqn. 2.3.

\[
\bar{\nu} = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}} \quad \text{..................} (2.3)
\]

In which the $\lambda$’s are the wavelengths (in cm) of the incident and Raman scattered photons, respectively. A small fraction of the molecules is in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state. The scattered photon appears at higher energy, as shown in Figure 2.3(b). This anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, but at room temperature, it is strong enough to be useful for vibrational frequencies less than about 1500 cm$^{-1}$. The Stokes and anti-Stokes spectra contain the same frequency information. The anti-Stokes spectrum can be used when the Stokes spectrum is not directly observable, for example, because of poor detector response at lower frequencies [164]. An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained from aqueous solutions. In addition, glass or quartz cells can be
employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials. The mechanism of Raman spectrometer is that, the laser beam falls on the filter and then it passes to the objective and collides with the Sample. The light will be scattered in all directions and will be reflected to the objective again. After the reflected light reaches the objective it falls down on the spectrometer system and finally to the CCD or PMT detectors. Typical diagram describing the mechanism and image of Perkin Elmer Raman spectrometer are presented in Figure 2.13.
2.2.8 UV-Visible (UV-vis.) Spectroscopy

Ultraviolet (UV) and visible radiation comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic, and X-rays. The energy associated with electromagnetic radiation is defined by the following equation:

\[ E = h \nu \]  \hspace{2cm} (2.4)
Where $E$ is energy (in joules), $h$ is Planck’s constant ($6.626 \times 10^{-34}$ Js), and $\nu$ is the frequency (in Hz). It follows from the above equations that radiation with shorter wavelength has higher energy. In UV-visible spectroscopy, the low-wavelength UV light has the highest energy. In some cases, this energy is sufficient to cause unwanted photochemical reactions when measuring sample spectra (remember, it is the UV component of light that causes sunburn). When radiation interacts with matter, a number of processes can occur, including reflection, scattering, absorbance, fluorescence/phosphorescence (absorption and reemission), and photochemical reaction (absorbance and bond breaking). In general, when measuring UV-visible spectra, we want only absorbance to occur. Because light is a form of energy, absorption of light by matter causes the energy content of the molecules (or atoms) to increase. The total potential energy of a molecule generally represented as the sum of its electronic, vibrational, and rotational energies.

UV-Visible spectroscopy (radiations with wavelengths between 10 and 1000 nm) offers information about the transition of the most external electrons of the atoms. Since atoms or molecules absorb UV-visible radiation at different wavelength, spectroscopy/spectrometry is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them. This technique is also used to assess the concentration or amount of a given species using the Beer-Lambert – law. This law relates the absorption of a radiation to the properties of the material through which is passing through. Eqn. 2.5 gives Beer-Lambert-law.

$$A = \epsilon l c \quad \text{(2.5)}$$

Where $A$ is the absorbance $\epsilon$ is the molar absorptivity constant. At each wavelength, $l$ is the path length, and the distance of solution that the light has to travel through $c$ is the concentration of the solution. The absorbance based primarily on those three factors. Figure 2.14 displays a schematic diagram of a diode array spectrophotometer, and the photo of the used spectrophotometer in this thesis.
2.3 Applications of the investigated semiconductor nanomaterials

The synthesized semiconductor nanomaterials used for the fabrication of sensing, photocatalytic, and p-n heterojunction diode applications.

2.3.1 Sensing applications of metal oxide nanomaterials

To fabricate the sensor, slurry of as grown semiconductor nanomaterials is prepared by addition of conducting binders and coated on silver (AgE, Surface area 0.0214 cm$^2$) or gold (AuE, surface area 0.0214 cm$^2$) or on glassy carbon electrode
Prior to the modification of electrodes, the surface of given electrodes is polished with alumina-water slurry on a polishing cloth, followed by washing them with water thoroughly.

In order to modify the electrode surface, the optimized amounts of as synthesized nanomaterials powder (~ 85-90%) and conducting agent (Butyl carbital acetate) were mixed well to make slurry. Finally, a certain amount of the slurry was casted on the electrode. The modified electrode is then dried and aged at 60 ± 5 °C for 5-6 hrs to get a uniform and dry layer over active electrode surface. To evaluate the sensing performance, a simple two-electrode system (current-voltage, \( I-V \) technique) was used in which the modified electrode is used as a working electrode and Pd wire as a counter electrode. An electrometer (Keithley, 6517A, USA) is used as a voltage source for \( I-V \) measurement. The current response is measured over a small potential ranging from almost 0 to 2.0 volts while the time delaying and response times can be fixed to 1.0 and 10.0 sec, respectively. Various analytes concentrations were prepared in a phosphate buffer solution (PBS, pH-7.0, 0.1M). The sensitivity considered as the vital indicator of the sensing performance of any chemical sensor. Therefore, the sensitivity of the proposed chemical material was calculated from the slope of the current-concentration calibration profile. The sensitivity was obtained when the slope of the current-concentration calibration profile was divided by the active surface area of the working electrode according to the following equation:

\[
\text{Sensitivity} = \frac{\text{Slope of calibration profile}}{\text{Surface area of electrode}}
\]

Figure 2.15(a) presents the schematic representation of nitro aniline chemical sensor fabricated based on \( I-V \) technique using \( \text{SnS}_2 \) nanoflakes modified GC electrode as a working electrode; (b) chemical reaction describing the sensing mechanism.
Figure 2.15(a) Schematic representation of nitro aniline chemical sensor fabricated based on I-V technique using SnS$_2$ nanoflakes modified GC electrode as working electrode; (b) chemical reaction describing the sensing mechanism.

2.3.1.1 Photocatalytic degradation of semiconductor nanomaterials

The photocatalytic degradation of toxic dye was carried out in a three-neck pyrex flask reactor using semiconductor nanomaterials as photocatalyst under UV illumination of xenon arc lamp (300W, Hamamatus: L 2479). For the photocatalytic degradation, a certain concentration of dye solution was prepared in 100 ml DI water in which certain amounts of photocatalysts (semiconductor nanomaterials) were added and the resultant mixtures were purged with Ar gas under continuous stirring. Consequently, the obtained suspensions were equilibrated for 30 min to stabilize the absorption of dyes over semiconductor nanomaterials prior to the light exposure. The photocatalytic degradation of the dyes was estimated by measuring the absorbance of dye solution in the presence of photocatalyst exposed at different time intervals (10min). The absorbance was measured by UV-vis. spectrophotometer (Perkin Elmer-UV/VIS-Lambda 950). The degradation rates of the dyes were estimated according to the following equation [166,167]:

\[
\text{Degradation rate(\%) } = (C_o - C/C_o) \times 100 = (A_o - A/A_o) \times 100 \ldots (2.6)
\]

Where: $C_o$ represents the initial concentration, $C$ the variable concentration, $A_o$ the initial absorbance, and $A$ the variable absorbance.
2.3.1.2  p-n Heterojunction diode application of p-SnS nanosheets

For heterojunction device fabrication, the nanocrystalline TiO$_2$ (P-25, Degussa) thin film electrode was obtained by the deposition of the TiO$_2$ (0.5 g of TiO$_2$ nanoparticles powder with 2 ml of aqueous polyethylene glycol solution) onto the clean fluorine doped tin oxide (FTO) glass through simple doctor blade technique. The active area of TiO$_2$ electrode is estimated to be $\sim$0.15 cm$^2$. Afterwards, the TiO$_2$ deposited FTO substrates were calcined at 450$^\circ$C for 20 min in a static air furnace. The suspension of synthesized SnS nanosheets was obtained by the sonication in ethanol and the prepared TiO$_2$/FTO electrodes were dipped into the suspension to create a thin layer of SnS nanosheets and then annealed at 200$^\circ$C for 15 min. Finally, a thin layer of Pt deposited on SnS/TiO$_2$/FTO substrates by ion sputtering technique to achieve the p–n heterostructure of Pt/SnS/TiO$_2$/FTO. The current (I) - voltage (V) measurements were carried out at room temperature with an applied voltage ranging from $-1$ V to $+1$ V to evaluate the electrical properties of Pt/SnS/TiO$_2$/FTO.

3  CHAPTER-3  RESULTS AND DISCUSSION
This chapter will demonstrate the detailed characterizations and applications of various semiconductor nanomaterials. With an introduction, and a brief experimental details, the results and discussions of each section will be presented in detail. Most of the investigated semiconductor nanomaterials presented in this thesis were synthesized by facile hydrothermal process and characterized in detail in terms of their morphological, structural, compositional and optical properties. For applications view point, most of the investigated semiconductor nanomaterials were used as an effective electron mediators for the fabrication of efficient chemical sensors and effective photocatalysts for the photocatalytic degradation of toxic chemicals and dyes. Moreover, the prepared SnS nanoflakes were successfully used to fabricate heterojunction diodes.

This chapter is divided into various sections. Each section will consist of systematic synthesis and growth of the investigated semiconductor nanomaterials, their detailed characterization, details of explored application and the necessary conclusion.

3.1 Structural and optical properties of CuO layered hexagonal disks synthesized by low-temperature hydrothermal process
3.1.1 Introduction

Among various metal oxide, the copper oxide (CuO) present itself as one of the promising materials possessing various properties suitable for the fabrication of various efficient devices and system. CuO is an important p-type transition metal oxide and possessing the narrow band gap of 1.2 eV. Due to various important chemical and physical properties of CuO, it is used in variety of applications such as catalysis [51-53] sensors (chemical and biosensors), [54-57] electrode materials, [58] field emission (FE) emitters, [59] photovoltaic devices, [60] magnetic storage media [61] electrode materials for lithium ion battery applications [62-64] and so on. As an important heterogeneous catalyst for many important chemical processes, CuO nanostructures are used for degradation of nitrous oxide, selective catalytic reduction of nitric oxide with ammonia, oxidation of CO at low temperature, [52] hydrocarbon and other organic moieties in supercritical water. [101,102]. Due to the Teng G photoconductive ad photochemical properties, CuO nanostructures are also promising materials for the fabrication of optical switch [103] and solar cells [104]. In addition, to this, CuO nanomaterials are possessing magnetic phases as demonstrated by Punnoose et al., who observed that CuO nanoparticles exhibited antiferromagnetic behavior with TN≈230K and TN decreases with decrease in particle size [168]. Due to aforementioned properties, of CuO nanostructures, it is used in variety of high-technological applications such as catalysis, electrode materials for Li⁺ batteries, field emission (FE) emitters, photovoltaic devices, magnetic storage media, and so on [51,88,219-225]. Till yet, various methods such as simple solution process, hydrothermal growth process, thermal evaporation process, thermal decomposition, etc., have been used for the synthesis of CuO nanostructures with various morphologies, reported in the literature [51,166-184]. Various 1D morphologies of CuO nanostructures such as nanorods, [173,174] nanowires, [175,176] nanoneedles, [51] nanobelts/nanoribbons, [177] nanotubes, [51] nanofibres, [51] and etc were synthesized by using numerous synthetic techniques. In addition to 1D CuO nanostructures, various complex morphologies of CuO were also synthesized, to name a few, flower-shaped, [58,169] nanoellipsoidal-shaped, [170] oval nanosheets, [171] nanosheets, [172] nanowhiskers, [179] 3D peanut-like patterns, urchin-like structures, [187] nanodendrites, [188] nanoellipsoids, [189] dandelion-shaped hollow
structures,[182] nanospheres [172,183] etc. Among various synthetic techniques, the hydrothermal technique presents itself as one of the effective techniques for the preparation of nanomaterials, due to its easy, reliable, low-cost, environmental friendly, and low-temperature growth process. Previously, Z. Jiang et al., demonstrated the growth of CuO nanostructures possessing various shapes by using copper nitrate, \((\text{NH}_4)_2 \text{CO}_3\) and polyethylene glycol via hydrothermal process, at various temperatures, i.e. 150 °C, 160 °C, and 180 °C[184]. By utilizing the hydrothermal process, recently S. Wang et al., reported the growth of CuO hollow microspheres at 180 °C by using copper nitrate, \(\text{CO(NH}_2)_2\) and CTAB[185]. Flower-like CuO nanoarchitectures were synthesized via hydrothermal process, using highly pure copper threads, \(\text{HCl}, \text{K}_2\text{Cr}_2\text{O}_7\) and \(\text{H}_2\text{SO}_4\) at 140 °C and reported in the literature [186]. In all above mentioned reports, the obtained products were synthesized at higher temperature with the assistance of additives and/or complex chemicals. Hence, it is important to develop a low-temperature synthesis method by using easily and low-cost chemicals for the synthesis of high surface to volume ratio CuO structures for future device applications.

In this work, we demonstrate a very simple hydrothermal process for the efficient growth of layered hexagonal disks of CuO at comparatively low-temperature of 130 °C. To the best of our knowledge, it is the first report in which layered hexagonal disks of CuO was prepared and characterized in detail. The synthesized structures were characterized in detail in terms of their structural and optical properties. In addition to this, based on the observed properties, a plausible growth mechanism has also been proposed for the successful formation of CuO layered hexagonal disks based on the chemical reaction involved and the crystallographic habits of CuO. The as-synthesized CuO layered hexagonal disks exhibited high surface to volume ratio, hence it is predicted that the as-synthesized CuO structures could present themselves as promising material for catalysis and sensor applications.

3.1.2 Experimental Details
Layered hexagonal disks of CuO were synthesized via a simple hydrothermal process by using copper nitrate, hexamethylenediamine and NH$_4$OH at low-temperature of 130 °C. For the synthesis, all the chemicals were purchased from Aldrich and used as received, without any further purification. In a typical synthesis process, 0.1 M copper nitrate solution, made in 50 ml deionized water was mixed slowly with the 0.5 M hexamethylenediamine solution and stirred for 1h. The pH of the resultant solution was then maintained at pH=10 using NH$_4$OH and stirred for 2 hours at ~80 °C. The resultant solutions were then transferred into a Teflon-lines autoclave and heated up to 130 °C for 3-10 h. After terminating the reaction, the autoclave was allowed to cool at room-temperature and finally black colored precipitates were obtained which were washed with methanol and ethanol several times and dried at room-temperature for further structural and optical characterizations.

To check the morphologies of as-synthesized layered hexagonal disks of CuO, field emission scanning electron microscopy (FESEM; JEOL-JSM-7600F) and transmission electron microscopy (TEM; JEOL-JEM-2100F) were used. The crystallinity and crystal phases of the synthesized structures were analyzed by the X-ray diffraction (XRD; PAN analytical X' pert Pro.) pattern measured with Cu-Kα Radiation (λ=1.54178Å) in the range of 10-70°. The typical composition of the synthesized structures were analyzed by using energy dispersive spectroscopy (EDS), elemental mapping attached with FESEM and Infrared (FTIR; Perkin Elmer-FTIR Spectrum-100) spectroscopy. The FTIR measurement was carried out at room temperature in the range of 400-4000 cm$^{-1}$. To check the optical properties of as-synthesized products, UV-visible spectroscopy (Perkin Elmer-UV/VIS-Lambda 950) measurement was done at room-temperature.

### 3.1.3 Results and Discussion

#### 3.1.3.1 Structural properties of as-grown layered hexagonal disks of CuO
To check the general morphologies of as-grown CuO structures, FESEM performed and results shown in Figure 3.1, which represents the low-magnification image of as-grown CuO structures and confirmed that the products are synthesized in a large scale. It is important to note that no other shape was obtained and only uniform growths of layered hexagonal disks were attained from the whole sample. The synthesized products are layered hexagonal disks of CuO as revealed by the high-magnification FESEM images presented in Figure 3.1 (b) and (c). It is seen that the hexagonal disks are made by the accumulation of many small nanosheets of CuO. These nanosheets arranged themselves in such a special manner that they made almost perfect hexagonal shape of the final products. The larger sheets are at the base of the structure while the smaller sheets arranged above the larger sheets properly. The average length and width of the synthesized CuO layered hexagonal disks are in the range of 3-4 μm and 1.5 -2.0 μm, respectively as shown in (Figure3.1-c). Interestingly, it is seen that some of the nanosheets are perpendicularly aligned on the surfaces of the hexagonal disks. It has been predicted that these nanosheets were deposited on the upper surfaces of the disks once the formation of disks was completed. For the deposition of these small nanosheets at the upper side of disks, the initially formed disks provide themselves as substrates and due to proper lattice match between substrate (CuO disks) and the deposited nanostructures (CuO nanosheets), these small nanosheets were perpendicularly deposited on the upper surface of the disks. To know exactly the thickness of the synthesized disks, tilted FESEM images of the samples were taken and shown in Figure 3.1 (d). As can be seen from Figure 3.1 (d) and inset (d), the disks are made in many layers. The number of layers for the synthesized disks is 3 or more. The total thicknesses of these disks are in the range of 150-180 nm.
Figure 3.1 Typical (a and b) low-resolution and (c) high-magnification FESEM images of as-synthesized layered hexagonal disks of CuO by hydrothermal process. (d) Typical FESEM image of side view of the as-synthesized layered hexagonal disks. Inset of (d) shows the side view of a single layered hexagonal disk.

To check the crystallinity and crystal phases of the as-synthesized layered hexagonal disks of CuO, X-ray diffraction pattern have been performed and the results are shown in Figure 3.2 (a). All the obtained peaks in the pattern are well matched with the base centered monoclinic phase of CuO bulk crystals and well consistent with the JCPDS card (card no. 048-1548). According to the PDF card, the lattice constants for the CuO layered hexagonal disks are estimated to be $a = 4.6883$ Å, $b = 3.4229$ Å and $c = 5.1319$ Å. Two dominating peaks appeared at $2\theta = 35.6^\circ$ and $38.8^\circ$ indexed as (111) - (002) and (111)-(200) planes, are seen in the observed XRD pattern which are characteristic peaks for the pure monoclinic CuO crystalline phase.
However, no peak related with any by-product such as Cu(OH)$_2$, Cu$_2$O or Cu are seen in the observed pattern which confirms that the as-synthesized products are pure and well-crystalline CuO without any impurity. The obtained results are well consistent with the previously reported literature [187]. To check the composition and purity of the synthesized products, EDS analysis was performed and results are shown in Figure 3.2 (b). The EDS spectrum demonstrates clear peaks related to cupper and oxygen, which confirms that the synthesized products are made by cupper, and oxygen only, up to the detection limit of EDS.
Figure 3.2 Typical (a) XRD pattern and (b) EDS spectrum of as-synthesized layered hexagonal disks of CuO by hydrothermal process.
To further examine the composition and elemental distribution in the as-synthesized layered hexagonal CuO disks, FESEM-elemental mapping was performed and represented in Figure 3.3. As can be seen from the figures, the distributions of cupper and oxygen contents in the lattices of as-synthesized CuO hexagonal disks are clearly visible. By this observation, it is confirmed that the as-synthesized CuO layered hexagonal disks are almost made with cupper and oxygen.

Figure 3.3 Typical images for elemental mapping of as-synthesized layered hexagonal disks of CuO by hydrothermal process.

The as-synthesized CuO structures were further investigated for detailed structural characterizations by TEM and high-resolution TEM (HRTEM) and demonstrated in Figure 3.4. For TEM measurements, as-synthesized structures were ultrasonically dispersed from the substrate in acetone and a drop of acetone which contains the layered hexagonal disks of CuO was placed on the TEM grid and
examined. Figure 3.4 (a) exhibits the low-resolution TEM image of a single layered hexagonal disk of CuO which is totally consistent with the FESEM observations shown in Figure 3.1 in terms of its morphology and dimensionality. It can be seen clearly that the small nanosheets are assembled in such a special manner that they made hexagonal shaped morphology. Interestingly, accumulations of the nanosheets are in such a way that smallest nanosheet is on the top while the largest nanosheet is at the bottom.
From the TEM image, it is also clear that the hexagonal disk is made of layers. The typical lengths and width of the synthesized layered hexagonal disks of CuO are
in the range of 3-4 μm and 1.5 -2.0 μm, respectively. Figure 3.4 (b) shows the HRTEM image of the corresponding layered hexagonal disk of CuO shown in figure 3.4 (a). The straight and parallel lattice fringes of the grown structures revealed that the synthesized products are well crystalline. The measured spacing of the crystallographic planes is ~0.27 nm, corresponding to the [110] lattice fringes of the monoclinic CuO.

The quality and composition of as-synthesized layered hexagonal disks of CuO was further characterized by Fourier transform infrared (FTIR) spectroscopy and the result is depicted in Figure 3.5. Various clear absorption bands have been observed from the FTIR spectrum of layered hexagonal disks of CuO. The presence of absorption bands at 505 and 608 cm\(^{-1}\) are due to \(\nu\) (Cu-O) modes which confirm the formation of monoclinic CuO crystals [180]. Absorption band appeared at 1385 cm\(^{-1}\) was originated due to the presence of \(\text{CO}_3^{2-}\). This band generally appear in the FTIR spectrum, if the samples are prepared in the air.[189,190] A very small absorption peak appeared at 1628 cm\(^{-1}\) was observed for bending vibration of absorbed water and surface hydroxyl, and a broad peak in the range of ~3000-3500 cm\(^{-1}\) was due to the O-H stretching mode.[188-190] As, no absorption peak for \(\text{CH}_2\), \(\text{CH}_3\) and others impurities were obtained in the spectrum confirmed that the synthesized products are purely CuO without any impurity.
3.1.3.2 Optical properties of the as-grown layered hexagonal disks of CuO

To examine the optical properties of the synthesized layered CuO hexagonal disks, UV-visible study has been performed at room temperature (inset (a) of Figure 3.6). Utilizing the Tauc’s formula the optical band gap $E_g$ can be experimentally obtained from absorption coefficient according to the following equation:

$$ (\alpha h\nu) = A(h\nu - E_g)^n $$ \hspace{1cm} 3.1

Where $\alpha$ is the absorption coefficient, $A$ is constant, and $n$ is equal to $\frac{1}{2}$ for a direct transition semiconductor and 2 for indirect transition semiconductor. Furthermore, in order to have a precise determination of the energy position of the absorption edge, one can take the edge position to be determined by the maximum of the first derivative of the optical absorption with respect to the energy and it corresponds to the optical band gap [191,192].

Figure 3.5 Typical Fourier transform infrared (FTIR) spectrum of as-synthesized CuO layered hexagonal disks by hydrothermal process.
Figure 3.6 Indirect band gap estimation of as-synthesized layered CuO hexagonal disks. Inset (a) shows the UV-Vis absorption spectrum and inset (b) shows the first derivative of this in a specific energy range.

The corresponding graphs for indirect and direct transitions as well as the first derivatives of the absorption spectrum are shown in Figures 3.6 and 3.7, respectively. As we can see the indirect band gap is 1.27 eV (1.24 eV from the diagram of the first derivative inset (b)) and the direct band gap is 3.45 eV (3.73 eV from the diagram of the first derivative inset). The indirect and direct band gap values are slightly blue shifted in comparison with the bulk values [193,194] (1.2 eV and 3.25 eV, respectively). The blue shift in the indirect and direct band edges is due to the quantum confinement effect [193,195,196].
Figure 3.7 Direct band gap estimation of as-synthesized layered CuO hexagonal disks. Inset shows the first derivative of the UV-Vis absorption spectrum in a specific energy range.

3.1.3.3 Plausible growth mechanism for the formation of layered hexagonal disks of CuO:

From the obtained results, one can predict a plausible growth process for the formation of CuO structures. For the growth of CuO structures, copper nitrate, hexamethylenediamine (HMDA) and NH$_3$.H$_2$O were used. In the reaction process, the NH$_3$.H$_2$O was used as a basic media to adjust the pH of the solution. In addition to this, during reaction, the NH$_3$.H$_2$O coordinated with copper nitrate and forms the copper-ammonium Cu(NH$_3$)$_4^{2+}$ complex. This formed complex may act as molecular transporters which transport the Cu$^{2+}$ to the growing nanosheet tips with OH$^{-}$ legends attached. [177,198] the formation of Cu(NH$_3$)$_4^{2+}$ complex in the reaction can be well understood according to the equation given below: [199,200]

\[
Cu(NO_3)_2 \cdot 2H_2O + 4NH_3 \cdot H_2O \rightarrow
\]
\[ \text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2 + 4\text{H}_2\text{O} \rightarrow \text{Cu}(\text{NH}_3)_4^{2+} + 2\text{NO}_3^- \quad \ldots \ldots \quad 3.2 \]

As the synthesis was performed at higher pH=10, and at higher pH of the reactant solution, the concentration of \( \text{Cu}(\text{NH}_3)_4^{2+} \) complex is higher. Therefore, with relatively high \( \text{Cu}(\text{NH}_3)_4^{2+} \) concentrations, the nucleation of \( \text{Cu(OH)}_2 \) could start from localized regions. [200] the formation of \( \text{Cu(OH)}_2 \) can be well understood with the equation given below:

\[ \text{Cu}(\text{NH}_3)_4^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 + 2\text{NH}_3 \quad \ldots \ldots \quad 3.3 \]

Once the nuclei of \( \text{Cu(OH)}_2 \) formed, the growth of the crystal starts. For the synthesis of \( \text{CuO} \); the formation of \( \text{Cu(OH)}_2 \) is very important as it serve as building blocks for the formation of the final product. In addition to this, it is mentioned in the literature that the crystallographic structure of \( \text{Cu(OH)}_2 \) has tendency and ability to form plate like structures.[201] Accordingly, plate-like \( \text{CuO} \) structures were obtained by the thermal dehydration of \( \text{Cu(OH)}_2 \) moieties without any significant changes in the morphologies. The formation of \( \text{CuO} \) from \( \text{Cu(OH)}_2 \) can be well understood with the reaction shown below:

\[ \text{Cu(OH)}_2 \xrightarrow{\Delta} \text{CuO} + \text{H}_2\text{O} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 3.4 \]

For the growth of \( \text{CuO} \), hexamethylenediamine (HMDA) was also used which plays important roles in maintaining the pH of the solution by providing the \( \text{OH}^- \) ions and acts as structural directing agent and additives for controlling the morphologies and shapes of the synthesized products. At proper reaction conditions, the HMDA can be hydrolyzed in the presence of distilled water and generates the \( \text{OH}^- \) ions. This reaction can be expressed by the equation mentioned below:

\[ \text{H}_2\text{N(CH}_2)_6\text{H}_2\text{N} + 2\text{H}_2\text{O} \rightarrow \text{H}_3\text{N}^+(\text{CH}_2)_6\text{H}_3\text{N}^+ + 2\text{OH}^- \quad \ldots \ldots \quad 3.5 \]

The generated \( \text{OH}^- \) ions from the HMDA also help much in the growth of \( \text{Cu(OH)}_2 \) and hence continuous generation of \( \text{Cu(OH)}_2 \) which finally converts into \( \text{CuO} \) by thermal hydration process and forms the sheet-shaped \( \text{CuO} \) structures.
It is apparently observed from the FESEM (Figure 3.1 (d)) and TEM images (Figure 3.4) that the formed sheets are arranged in layer-by-layer manner. According to the crystallographic habits of CuO nanosheets, three main directions are involved in the self-organization and self assembly of the nanosheets, i.e., [001], [100] and [010] directions which follows the assembling order as [010] > [100] > [001] [173]. In addition to this, among various planes of CuO nanocrystals, the (001) surface plan in the most stable while (010) plane is the least stable because of different copper atom densities on these planes.[201] In our synthesized CuO nanosheets, the upper surface is (100) while the side and front surfaces are (001) and (010), respectively. It is believed that the growth of basic unit i.e. CuO nanosheet, for the formation of layered hexagonal disks of CuO, was achieved by the preferential growth along the {010} and {100} crystal planes. Regarding the growth of layered sheets, we believe that several nanosheets were formed in the solution and attached with their adjacent nanosheets through their identical crystallographic surfaces as confirmed by FESEM images shown in Figure 3.1 (d). It is reported, in case of oxide crystals based on crystal growth kinetics, that the oxide nanocrystals are very favorable for the oriental attachment [201]. In this regard, it is believed that the attachment of two nanosheets of CuO through their identical crystallographic surfaces follows the “oriental attachment” mechanism. In addition to this, several small nanosheets are perpendicularly grown over the upper side of the hexagonal disks. It is believed that these nanosheets were grown over the disks at the end of the reaction, once the formation of layered hexagonal disk was complete. As these small nanosheets are grown over the disks in almost perpendicular fashion, hence it is predicted that the layered hexagonal disks provide themselves as substrates and due to proper lattice match between substrate (layered hexagonal disk of CuO) and the deposited nanostructures (CuO nanosheets), these small nanosheets were perpendicularly deposited on the upper surface of the disks.
3.1.4  Conclusion

In summary, CuO layered hexagonal disks were synthesized on a large scale via simple hydrothermal growth at low-temperature of 130 °C. The as-synthesized structures were characterized in detail in terms of their detailed morphological, structural and optical properties. The detailed morphological examinations by FESEM and TEM show that the synthesized structures are made by the layer-by-layer accumulation of several small sheets which finally arranged themselves in hexagonal shape. The detailed structural investigations revealed that the synthesized CuO structures possess well crystalline and monoclinic structure and the UV-Vis absorption spectrum indicates the existence of slightly blue shifted indirect and direct band gaps. A plausible growth mechanism has also been proposed for the successful formation of layered hexagonal disks of CuO.
3.2 CuO nanocubes based highly-sensitive 4-nitrophenol chemical sensor

3.2.1 Introduction

The nitro-phenols are considered as one of the most important aromatic nitro-compounds which are used extensively in the production of dyes, pharmaceuticals, pesticides and insecticides, etc. Out of various nitro-phenolic compounds, 4-nitrophenol (4-NP), a derivative of parathion, is used to produce insecticides at mass scale. The 4-NP has been listed at top in the priority list of pollutants of the U.S.A. Environmental Protection Agency (EPA) due to its carcinogenetic behavior, low degradability and persistence in the soil and water [202]. Due to its utilization in various industries and agriculture sector in particular, 4-NP is inevitably released into environment and thus has become a common pollutant which is usually detected in groundwater, fresh water and marine water. Moreover, the low degradation and high stability of 4-NP make it highly toxic chemical. In addition to these threats, the acute ingestion of 4-NP in human beings causes drowsiness, headaches and cyanosis.[203]

The above mentioned facts compel human beings to control and supervise the application of 4-NP strictly. Therefore, the development of simple and efficient techniques for the trace determination of 4-NP is having a considerable importance.

Several analytical methods such as fluorescence [204], capillary electrophoresis [205], gas chromatography [206,207], high performance liquid chromatography [208], and liquid chromatography combined with mass spectrometry [209], are routinely used techniques for the determination of 4-NP. However, these methods are multi-step, time consuming, need high-end instrumental facilities, thus they are not considered economical.

Among various techniques applied for the determination of 4-NP, electrochemical method has attracted great attention due to its various salient features such as rapid, simple, cost effective, selectivity and high sensitivity [210-214]. There have been reports on the detection of 4-NP using nanoporous gold [215], graphene oxide [216], and Ag nanoparticles polyaniline nanofibres [217]. Nowadays, electrochemical sensors based on nanostructure materials particularly metal oxides have been widely used in the fields of environmental analysis because of their rapid
analytical performance time, high sensitivity, inherent simplicity, cost effectiveness and reliability in a straightforward and simple 2-electrodes system (Current-Voltage, I-V technique)[106,218].

Copper oxide nanostructures are used for variety of applications, but to the best of our knowledge, there is no literature available for the application of CuO nanomaterial as an efficient electron mediators for the sensing of 4-NP. Hence, in the research presented herein, we have successfully synthesized the CuO nanocubes using a very simple low-temperature hydrothermal procedure and utilized the as-synthesized CuO nanocubes as an efficient electron mediators for the fabrication of reproducible and highly-sensitive (~132.84 ± 0.02 mA.cm⁻².( mol L⁻¹)⁻¹) chemical sensor for the effective detection of 4-NP. A very low-detection limit of ~5×10⁻⁹ mol L⁻¹ was observed for the fabricated chemical sensor. Moreover, the synthesized CuO nanocubes were characterized for their morphological, structural, compositional and optical properties.

3.2.2 Experimental Details:

3.2.2.1 Synthesis of CuO nanocubes

Well-crystalline CuO nanocubes were synthesized by facile low-temperature hydrothermal process using copper nitrate (Cu(NO₃)₂·2H₂O), urea (CO(NH₂)₂) and ammonium hydroxide (NH₄OH). In a typical reaction process, 0.1 molL⁻¹ Cu(NO₃)₂·2H₂O was mixed well with 0.1 molL⁻¹ CO(NH₂)₂ solution, both dissolved in 50 mL Distilled water (DW), under continuous stirring for 2h. After stirring, few drops of (NH₄OH) were added in the resultant solution to maintain the pH=6. Again, the final solution was vigorously stirred for 30 min and consequently transferred to teflon lined autoclave, sealed and heated upto 140 °C for 3h. After desired reaction time, the autoclave was allowed to cool at room-temperature and finally a black precipitate was obtained which was extensively washed several times with DW, ethanol and acetone, sequentially and dried at 55 °C for 3h. The dried powder was then characterized. Finally, the synthesized material was used as efficient electron mediators for the fabrication of reproducible and highly sensitive 4-NP chemical sensor.
3.2.2.2 *Characterizations of as-synthesized CuO nanocubes:*

The as-synthesized CuO nanocubes were characterized in detail by various techniques. The general and detailed morphologies of as-synthesized nanocubes were done by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) equipped with high-resolution TEM (HR-TEM). The crystallinity and crystal phases were examined by the X-ray diffraction (XRD). The elemental composition and elemental distribution into the lattices of CuO nanocubes were investigated by energy dispersive spectroscopy (EDS) and elemental mapping, both attached with FE-SEM, respectively. The chemical composition of as-synthesized CuO nanocubes were examined by Fourier transform infrared (FT-IR) spectroscopy, measured at room temperature, in the range of 400-4000 cm\(^{-1}\). To check the optical properties of as-synthesized products, UV-visible spectroscopy (Perkin Elmer-UV/VIS-Lambda 950) measurement was performed at room-temperature.

3.2.2.3 *Fabrication and characterization of 4-nitrophenol chemical sensor by I-V technique*

To modify the electrode surface, firstly, the surface of glassy carbon electrode (GCE) was polished with commercially available alumina, followed by rinsing with DW thoroughly. For the GCE surface modification for 4-nitrophenol chemical sensor, slurry of CuO nanocubes was made by mixing an appropriate composition of CuO nanocubes and conducting agent (butyl carbital acetate). Finally, a small amount of the slurry was casted on GCE (surface area 0.0316 cm\(^2\)) surface, and then the modified electrode was dried in electric oven at 60 ± 5 °C for 4h. The sensor analytical performance was investigated using I-V technique [226]. For I-V measurements; an Electrometer (Keithley, 6517A, USA) was used as a voltage source and the CuO modified GCE was used as a working electrode while Pd wire was employed as a counter electrode. The current response was measured from 0.0 to 1.6 volts while the time delaying and response time were 1.0 s and 10.0 s, respectively. The amount of 0.1 mol L\(^{-1}\) phosphate buffer solution (PBS; 10.0 mL) was kept constant for all the measurements. For the concentration studies, a wide range of 4-nitrophenol concentrations (10\(^{-5}\) molL\(^{-1}\) to 0.1 molL\(^{-1}\)) was used. The sensitivity of the fabricated 4-nitrophenol chemical sensor was estimated from the slope of the current *versus* concentration from the calibration plot divided by the value of active surface.
area of sensor/electrode. All the sensing experiments were carried out at room-
temperature.

3.2.3 Results and discussion:

3.2.3.1 Morphological, structural and optical properties of as-synthesized CuO nanocubes:

Figure 3.8 exhibits the typical FESEM images of as-synthesized CuO products which reveals that the synthesized material possess cube-shape particles. Figure 3.8 (a) and (b) exhibits the low-resolution FESEM images and confirm that the nanocubes are synthesized in large quantity. Due to large quantity growth, the nanocubes are connected with each other through one or two of their surfaces (Figure 3.8 (c)). The typical sizes of the nanocubes are in the range of 175 ± 25 nm. Few smaller/ bigger nanocubes were also seen in the micrograph (Figure 3.8 (c) and (d)).
Figure 3.8 Typical (a and b) low-resolution and (c and d) high-magnification FESEM images of as-synthesized CuO nanocubes.

The crystallinity, crystal phases and elemental composition of as-synthesized CuO nanocubes were examined by X-ray diffraction and EDS spectroscopy, respectively. Figure 3.9 (a) demonstrates the typical XRD pattern of as-synthesized CuO nanocubes and exhibits full consistency with the base centered monoclinic phase of CuO bulk crystals [227]. All the observed diffraction reflections in the pattern are well matched with the JCPDS card 048-1548 and the calculated lattice constants were \( a = 4.6883 \, \text{Å}, \ b = 3.4229 \, \text{Å} \) and \( c = 5.1319 \, \text{Å} \). The appearance of two dominated diffraction reflection in the pattern at \( 2\theta = 35.6^\circ \) and \( 38.8^\circ \) indexed as (111) - (002) and (111)-(200) planes are the characteristic reflections of pure monoclinic CuO crystalline phase.
This affirms that the synthesized CuO nanocubes possess well-crystallinity, pure and monoclinic nature. No reflection related with any impurity or by products such as Cu (OH)$_2$, Cu$_2$O or Cu were observed in the pattern which further confirms the purity of as-synthesized CuO nanocubes [228].

The elemental composition of as-synthesized CuO nanocubes was examined by using EDS spectroscopy attached with FESEM. Figure 3.9 (b) reports the typical
EDS spectrum of CuO nanocubes which clearly exhibits well defined peaks related with Cu and O and corroborate that the synthesized product is made of Cu and O. There was no impurity peak detected in the spectrum, up to the detection limit of EDS, further emphasizes that the synthesized material is pure CuO.

For further and detailed structural characterizations, the as-synthesized CuO nanocubes were characterized by TEM combined with high-resolution TEM (HR-TEM). Figure 3.10 (a) and (b) exhibit the typical low-resolution TEM images of as-synthesized nanocubes. The general morphologies and dimensions of nanocubes observed by TEM are well consistent with the FESEM results mentioned in Figure 3.8. As for the TEM measurements, the nanocubes sample was ultrasonically dispersed in acetone and a drop of acetone which contains the CuO nanocubes was placed on the TEM grid for examination, hence, some broken nanocubes were also seen in the TEM micrograph (Figure 3.10 (a)). Figure 3.10 (c) and (d) demonstrate the high-resolution TEM (HRTEM) images of as-synthesized nanocubes.
Figure 3.10 Typical (a and b) Low-magnification and (c and d) high-resolution TEM (HRTEM) images of as-synthesized CuO nanocubes.

The observed lattice fringes are very clear and well-defined that verifies the well-crystallinity of as-synthesized nanocubes. Moreover, the distance between two parallel lattice fringes was measured and found to be ~0.27 nm corresponding to the [110] crystallographic plane of monoclinic CuO. In addition to this, the lattice fringes are nicely arranged without any dislocation. This fact strengthens that the synthesized nanocubes are almost pure with no or very less structural defects.

To examine the chemical composition, the as-synthesized CuO nanocubes were examined by Fourier transform infrared (FT-IR) spectroscopy. Figure 3.11 reveals the typical FT-IR spectrum of as-synthesized nanocubes showing various well-defined absorption bands at 451, 530, 601, 1381, 1632 and 3450 cm\(^{-1}\). The peaks
appeared at 451, 530 and 601 are related to $\nu$(Cu-O) modes and confirms the formation of monoclinic CuO nanocrystals [188,229-231].

![Fourier transform infrared (FTIR) spectrum of as-synthesized CuO nanocubes.](image)

The appearance of a small absorption band at 1381 cm$^{-1}$ is most probably due to the nitrate (NO$_3^-$) group [230-232]. Two very small or almost negligible absorption bands are also seen in the spectrum at 1632 and 3450 cm$^{-1}$ related to the bending vibration of absorbed water and surface hydroxyl, and O-H stretching mode, respectively [188,229-231].

To investigate the optical properties, the CuO nanocubes were characterized by UV-Vis. spectroscopy at room-temperature and results are demonstrated in Figure 3.12. The typical room-temperature UV-Vis spectrum depicted in Figure 3.12 (a) of as-synthesized CuO nanocubes while (b) and (c) show the derived spectra for the relationship of $(ahv)^{1/2}$ vs. $hv$. By using equation 3.1, the optical band gap ($E_g$) can
be obtained experimentally from absorption coefficient. Figure 3.12 (b) and (c) demonstrate the corresponding graphs for indirect and direct transitions as well as the first derivatives of the absorption spectrum. The obtained indirect band gap was 1.21 eV while the direct band gap was calculated to be ~3.64 eV. The indirect and direct band gap values are blue shifted in comparison to the bulk values (1.2 eV and 3.25 eV, respectively) [232,233]. It is believed that the blue shift in the indirect and direct band edges could be due to the quantum confinement effect [234].

![Graphs](image)

Figure 3.12(a) Room-temperature UV-Vis absorption spectrum (b) The indirect band gap estimation (c) The direct band gap estimation of as-synthesized CuO nanocubes

**3.2.3.2 Nitrophenol chemical sensor application of as-synthesized CuO nanocubes:**

The analytical performance of the CuO nanocubes modified GCE sensor chemical sensor was investigated to detect 4-NP in a simple I-V system. In this I-V system, the modified electrode was employed as working electrode while the Pd wire was applied as a counter electrode. The fabrication and sensing steps of the proposed sensor have been elaborated in schematic design shown in Figure 3.13.
Figure 3.14 (a) demonstrates the current responses of GCE in 10.0 ml, 0.1 mol L\(^{-1}\) PBS solution without (red) and with (black) of 4-NP. The marked increase in the current response was obtained in the presence of 4-NP in PBS solution as compared to the solution without 4-NP. This observation indicates that CuO nanocubes are responsible for a significant change in the current response towards 4-NP sensing. However, the mechanism of 4-NP sensing is very complicated phenomenon which has been discussed in the following paragraph. It has been stated in the literature that the adsorption of oxygen at the nanomaterial surface (CuO nanocubes) from the surrounding environment or bulk solution containing the analyte of interest (4-NP) plays a vital role in the sensing mechanism. Firstly, according to reaction (a), the gaseous form of oxygen is chemisorbed in the bulk solution of PBS buffer. When this adsorbed oxygen comes in contact of CuO nanocubes surface, it captures the electrons from the conduction band of CuO nanocubes and subsequently converted into highly dynamic oxygen species as depicted in reaction (b).
The emission of the electrons leads to decrease in the conductive behavior (increase in resistance) of the CuO nanocubes. However, when the target analytes (4-NP) is used in the sensor system, 4-NP is first reduced to hydroxylamine species but utterly oxidized into 4-nitrosophenol in the presence of previously obtained dynamic oxygen species (i.e. $O^-$) by discharging 2 electrons ($e^-$) and 2 protons ($H^+$) into the conduction band of CuO nanocubes material and hence conductivity of material increased and consequently, the response of current is enhanced as illustrated in Figure 3.14 (a). The possible reaction of 4-NP is demonstrated in the reaction (c) mentioned above [235,236].

In further experiments, the effect of change in concentrations of 4-NP was investigated over currents responses. A wide range of 4-NP concentrations ($10\times10^{-6}$ mol L$^{-1}$ to 0.1 mol L$^{-1}$) prepared in 0.1M PBS solution (pH =7.2), was used for these experiments. The acquired typical I-V responses were shown in Figure 3.14 (b) for the fabricated 4-NP chemical sensor at different 4-NP concentrations. It is evident from the concentration measurements that by increasing the concentration of 4-NP, the current increases gradually which is due to production of the more number of ions. Thus, the conductivity of modified electrode was enhanced due to supply of the excess electrons to the conduction band of as-synthesized CuO nanocubes. The calibration curve was plotted from the wide concentration range of 4-NP (Figure 3.14 (c)). The calibration curve shows that the value of the current is increased with the increase in the concentration of 4-NP in the 0.1mol L$^{-1}$ PBS solution. The sensitivity of the CuO nanocubes modified chemical sensor was calculated from the slope of the lower concentration region of calibration and found to be $(132.84 \pm 0.02)$ mA.cm$^{-2}$ (mol L$^{-1}$)$^{-1}$. The fabricated sensor demonstrated a linear dynamic range (LDR) from $10^{-8}$ mol L$^{-1}$ to $10^{-3}$ mol L$^{-1}$ whereas the estimated detection limit for the fabricated sensor was found to be $\sim5\times10^{-9}$ mol L$^{-1}$. 
Figure 3.14(a) Typical I-V responses of CuO nanocubes in (GCE) in 10 ml, 0.1 mol L⁻¹ PBS solution (pH=7.2): (●) with 10×10⁻⁹ mol L⁻¹ 4-nitrophenol and (■) without 4-nitrophenol; (b) I-V response for various concentrations (from 10×10⁻⁹ mol L⁻¹ ~ 0.1 mol

Furthermore, the mechanism of 4-NP can also be explained according to grain boundary model. The 4-NP reacts with O⁻ ads and releases the trapped electron to the conduction band of CuO nanocubes as indicated by the decrease of potential barrier at grain boundary as shown in Figure3.15. Moreover, when reducing molecules comes in contact with negatively charged oxygen adsorbates, the trapped electrons are given back to conduction band of the material. In this phenomenon, sufficient energy is released required for the electrons jumping up into the conduction band so as to increase conductivity of the proposed chemical sensor.
Figure 3.15 Sensing mechanism for 4-nitrophenol and changes in potential barrier at the grain boundaries (a) adsorbed oxygen on the surface of CuO grains and (b) on exposure to 4-nitrophenol.

For comparison, the performance of the fabricated 4-NP chemical sensor based CuO nanocubes was evaluated with the previously reported 4-NP chemical sensors fabricated based on the utilization of various electron mediators and the results have been assembled in table 3.1. It is apparent from the table 3.1 that the fabricated 4-NP chemical sensor based on CuO nanocubes exhibits highest sensitivity and lowest detection limit which confirmed that the fabricated sensor is promising candidate for the effective detection of 4-NP [216, 237]. The CuO nanocubes modified electrodes offered distinct advantages such as a short response time of ~10 s and extremely high sensitivity. The rapid electron exchange behavior, high electrocatalytic activity, and excellent adsorption ability of CuO nanocubes were responsible for the high sensitivity for 4-NP.

The CuO modified electrode for 4-NP modified sensor showed high stability for over 6 weeks. To investigate the stability of the chemical sensor under study, measurements were repeated for different time. From the several experiments, it was observed that there was no significant change in current response for approximately 5
weeks; however, the current response was decreased gradually from the 6th week. The stability of the proposed chemical sensor evaluated for the determination of 4-NP is found to be better than 4% (RSD). Therefore, these results indicate the excellent stability and reliability of the CuO modified sensor for 4-NP. The above mentioned results clearly reflect that CuO materials can be used as efficient electron mediators for the fabrication of effective chemical sensors.

Table 3.1 Comparison summary of the performances of 4-NP chemical sensors fabricated based on the utilization of various nanomaterials as electron mediators.

<table>
<thead>
<tr>
<th>Electrode Materials</th>
<th>Sensitivity</th>
<th>Detection Limit</th>
<th>LDR</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO nanocubes</td>
<td>~132.84±0.02mA.cm^2,(mol L^-1)^1</td>
<td>~ 5x10^-9 mol L^-1</td>
<td>10^-8 to 10^-3 mol L^-1</td>
<td>This work</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>-</td>
<td>2x10^-6 mol L^-1</td>
<td>10^-8 to 1.2x10^-4 mol L^-1</td>
<td>[216]</td>
</tr>
<tr>
<td>Poly(safranine) Film</td>
<td>-</td>
<td>3x10^-6 mol L^-1</td>
<td>8x10^-6 to 4x10^-5 mol L^-1</td>
<td>[237]</td>
</tr>
<tr>
<td>MWNT-Nafion/GCE</td>
<td>-</td>
<td>4x10^-6 mol L^-1</td>
<td>10^-7–10^-5 mol L^-1</td>
<td>[238]</td>
</tr>
<tr>
<td>p-NiTiSPc/p-PPD Coated Carbon Fiber</td>
<td>80 nA.L.mg^-1</td>
<td>40 µg/L</td>
<td>0.01 to 10 mg/L</td>
<td>[239]</td>
</tr>
<tr>
<td>Hydroxyapatite nanopowder/GCE</td>
<td>-</td>
<td>6x10^-7 mol L^-1</td>
<td>10^-6 to 3x10^-4 mol L^-1</td>
<td>[240]</td>
</tr>
<tr>
<td>Nano-Cu_2O/Pt electrode</td>
<td>-</td>
<td>10^-2 mol L^-1</td>
<td>10^-4 to 10^-3 mol L^-1</td>
<td>[241]</td>
</tr>
</tbody>
</table>
3.2.4 Conclusion

In summary, well-crystalline CuO nanocubes were synthesized by facile hydrothermal process and used as an efficient electron mediators for the fabrication of highly-sensitive, robust, reproducible and reliable chemical sensor for the effective detection of 4-nitrophenol. The as-synthesized CuO nanocubes were analyzed in detail using various morphological, structural and optical characterization techniques. The detailed characterizations confirmed the well-crystallinity and monoclinic structure for as-synthesized CuO nanocubes. Direct and indirect band gap values for as-synthesized CuO nanocubes were also determined. The fabricated 4-nitrophenol chemical sensor exhibits a reproducible and reliable high-sensitivity of \(~132.84 \pm 0.02\) mA.cm\(^{-2}\).(mol L\(^{-1}\))\(^{-1}\) and detection limit of \(~5\times10^{-9}\) mol L\(^{-1}\). The obtained LDR for the fabricated sensor was from \(10\times10^{-9}\) mol L\(^{-1}\) to \(1\times10^{-3}\) mol L\(^{-1}\)[216, 237, 238]. The promising merits of the CuO nanocubes modified 4-nitrophenol chemical sensor opens a broad way to apply simply synthesized CuO nanostructures for the fabrication of efficient, reliable and reproducible chemical sensors.
3.3 High-yield synthesis of well-crystalline $\alpha$-Fe$_2$O$_3$ nanoparticles: structural, optical and photocatalytic properties:

3.3.1 Introduction

Due to various exotic and versatile properties and wide-range applications, recently, the metal oxide nanostructures have received a considerable attention and are increasingly being studied [65]. Among various metal oxide nanostructures, iron oxide presents itself as one of the promising metal oxide materials with superior properties and functionalities and hence used extensively in various high-technological applications such as catalysis, pigments, sensors, bio-medical (diagnosis and therapy) applications and so on [65,66]. As for hematite ($\alpha$-Fe$_2$O$_3$) is concerned, it is one of the most stable iron oxide under ambient conditions. Owing to its various interesting properties such as n-type semiconducting behavior, band gap ($E_g= 2.1$ eV), low-cost synthesis, non-toxic nature, high resistant to corrosion, the $\alpha$-Fe$_2$O$_3$ is widely used in variety of high-technological applications such as sensors, photocatalysis, pigments, magnetic recording media, etc; [106-112]. Because of the high electrical conductivity and high-sensitivity to gaseous environment, $\alpha$-Fe$_2$O$_3$ is also used as an efficient material for the fabrication of effective gas sensors [113,114]. Recently, it is observed that $\alpha$-Fe$_2$O$_3$ is one of the competent candidates as electrode materials for low-voltage rechargeable lithium ion batteries from both cost and environmental standpoints [65,242, 244]. As a result of various important properties and wide applications, considerable efforts have been made for the synthesis and characterizations of variety of $\alpha$-Fe$_2$O$_3$ nanostructures and reported in the literature [245-250]. The nanostructures of $\alpha$-Fe$_2$O$_3$ include, nanoparticles,[245-246] nanorods [247-248], nanowires [249], nano-tubes [250], nanoovals [251], hollow core/shell hierarchical nanostructures [252], dendritic pine like nanostructures [253] etc. Among various nanostructures, the nanoparticles possess high-surface-to-volume ratio which enhance the functionality of nanoparticles and hence widen the applications of this class of nanostructure.
In this work, we demonstrate a high-yield facile synthesis, detailed characterization and photocatalytic application of \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles synthesized via very simple hydrothermal process by using aqueous mixtures of iron chloride, hexamethylenediamine and sodium hydroxide at low temperature of 110 °C. The synthesized nanoparticles were characterized in detail in terms of their structural and optical properties. Photocatalytic degradation of methylene blue was also examined and found that the as-synthesized \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles exhibit good photocatalytic properties.

### 3.3.2 Experimental Details:

For the synthesis of \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles, a facile hydrothermal process was used. In a typical reaction process for the synthesis of \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles, 0.73 g FeCl\(_3\).6H\(_2\)O and 0.52 g hexamethylenediamine (HMDA) was added in 50 ml DI water under vigorous stirring for 30 min. The pH of the resultant solution was then maintained at pH=7 using NH\(_3\).H\(_2\)O and stirred for 2 h. After vigorous stirring for 2 h, the resultant solution was loaded into a Teflon-lined stainless steel autoclave, sealed it and heated up to 110 °C for 3-5 h. After completing the reaction in desired time, the autoclave was naturally allowed to cool at room-temperature and finally dark brown product was obtained which was washed with DI water, ethanol and acetone sequentially and dried at room-temperature. The as-synthesized products were investigated in terms of their morphological, structural and optical properties. Photocatalytic decomposition of methylene blue was also investigated by using the as-synthesized nanoparticles.

The general morphologies of the as-synthesized nanoparticles were investigated by using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The detailed structural characterizations and composition of the as-synthesized nanoparticles were examined by using X-ray diffraction (XRD), high-resolution TEM (HRTEM), energy dispersive spectroscopy (EDS) attached with FESEM and Fourier transform infrared spectroscopy (FTIR). UV-Visible spectrophotometer was used to evaluate the optical properties of the as-synthesized nanoparticles. To examine the photocatalytic properties of the as-
synthesized nanoparticles, photocatalytic degradation of methylene blue (MB) was performed under irradiation of UV light for various time intervals. The MB degradation was monitored by measuring the absorbance at regular time intervals by using UV, Vis. Spectrophotometer.

3.3.3 Results and Discussion:

3.3.3.1 Structural properties of as-synthesized well-crystalline \( \alpha-\text{Fe}_2\text{O}_3 \) nanoparticles:

Figure 3.16 (a-c) demonstrates the typical FESEM images of as-synthesized iron oxide products which reveals that the synthesized products are nanoparticle. From the low-magnification image, it is clear that the nanoparticles are synthesized in very high yield (Figure 3.16 (a)). The as-synthesized nanoparticles possess almost spherical shape with average diameter in the range of \( \sim 35 \pm 5 \) nm (Figure 3.16(b) and (c)). Some other shapes of nanoparticles, such as elongated, rectangular and ellipsoidal-shaped, were also seen in the micrographs. Interestingly, it was also observed from the micrographs that some nanoparticles are jointed with their adjacent nanoparticles and enhance the particle size. To check the crystallinity and crystal phase purity of the as-synthesized nanoparticles, X-ray diffraction measurement was performed and result is displayed in Figure 3.16 (d). The XRD pattern was measured with Cu-K\( \alpha \) Radiation (\( \lambda=1.54178\text{Å} \)) in the range of 10-70\(^\circ\). All the obtained diffraction peaks in the pattern are well matched to the rhombohedral \( \alpha-\text{Fe}_2\text{O}_3 \) structures (JCPDS 84-0311). The obtained diffraction peaks are sharp and strong which reveals that the synthesized products are well-crystalline without any impurities. Except rhombohedral \( \alpha-\text{Fe}_2\text{O}_3 \), no other peak from any impurity was obtained in the pattern which confirms that the as-synthesized products are highly pure and crystalline.
Figure 3.16 Typical (a) and (b) low-magnification and (c) high-resolution FESEM images and (d) XRD pattern of as-synthesized well-crystalline \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles synthesized by hydrothermal process.

To examine in detail the composition of as-synthesized \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles, EDS analysis attached with FESEM was done and demonstrated in Figure 3.17. The typical EDS spectrum of the as-synthesized \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticle illustrated in Figure 3.17 (a). It is clear from the EDS spectrum that the synthesized nanoparticles are only composed of Fe and oxygen. No other peak related with any impurity has been detected in the FESEM-EDS, until the detection limit of the EDS, which confirms that the synthesized nanoparticles are highly pure and made by iron and oxygen. The detailed structural characterization of as-synthesized nanoparticles was performed by (TEM) and high-resolution TEM.
Figure 3.17 Typical (a) SEM image and (b) corresponding EDS spectrum of as-synthesized well-crystalline \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles synthesized by hydrothermal process.

The low-magnification TEM images of the as-synthesized \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles; shown in Figure 3.18 (a). The observed TEM images of the nanoparticles are fully consistent with the obtained FESEM images in terms of their morphologies and dimensions. The as-synthesized nanoparticles possess various shapes, i.e. spherical, rectangular and some are in ellipsoidal shape as can be seen in Figure 3.18 (a). The typical dimensions of the synthesized nanoparticles are in the range of \( \sim 35 \pm 5 \) nm. Figure 3.18 (b) exhibits the typical HRTEM image of the white
circled portion of $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticle shown in Figure 3.18 (a). Due to highly crystalline nature of the as-synthesized nanoparticles, the lattice fringes are clearly seen in the HRTEM image. The lattices fringes are separated by 0.266 nm which can be indexed to the (104) plane of the rhombohedral $\alpha$-$\text{Fe}_2\text{O}_3$ structure. The obtained HRTEM results are well matched with other reported literature [206,207]. In addition to this, the HRTEM is fully consistent with the observed X-ray diffraction results and confirms that the synthesized nanoparticles are well-crystalline.

![Figure 3.18](image)

Figure 3.18 Low-magnification (a) and high-resolution TEM images (b) of as-synthesized well-crystalline $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles synthesized by hydrothermal process.

To examine exactly the purity and composition of the as-synthesized $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles, FTIR measurement was carried out at room temperature in the range of 400-4000 cm$^{-1}$. Figure 3.19 exhibits the typical FTIR spectrum of as-synthesized $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles. Several absorption bands have been observed from the obtained FTIR spectrum, i.e. 465, 551, 1628 and 3450 cm$^{-1}$. The origination of two sharp absorption bands at 465 cm$^{-1}$ and 551 cm$^{-1}$ are due to the formation of Fe-O bonds which clearly confirmed the formation of iron oxide crystals [110,111]. The appearance of a very short band at 1628 cm$^{-1}$ and a broad band at 3450 cm$^{-1}$ are due to the bending vibration of absorbed water and surface hydroxyl, and O-H stretching mode, respectively [188]. As the FTIR spectrum exhibits only Fe-O and hydroxyl
absorption bands, hence one can confirm that the synthesized products are highly pure iron oxide without any impurity.

Figure 3.19 FTIR spectrum of as-synthesized well-crystalline $\alpha$-Fe$_2$O$_3$ nanoparticles synthesized by hydrothermal process.

The synthesis of $\alpha$-Fe$_2$O$_3$ nanoparticles can be understood based the chemical reactions involved in the growth process. For the synthesis of $\alpha$-Fe$_2$O$_3$ nanoparticles, iron chloride hexahydrate, hexamethylenediamine (HMDA) and NH$_3$.H$_2$O were used. During the reaction, the NH$_3$.H$_2$O was used as a basic media to adjust the pH of the solution while HMDA was used for two different purposes. i.e. (i) maintain the pH of the solution by providing the OH$^-$ ions and (ii) works as an additive for controlling the shapes of the synthesized products. Firstly, iron chloride hexahydrate (FeCl$_3$.6H$_2$O) reacts with NH$_3$.H$_2$O and forms Fe (OH)$_3$ according to the simple chemical reaction mentioned below:

$$FeCl_3.H_2O \ (aq) + 3NH_3.H_2O \ (aq) \rightarrow Fe(OH)_3 \ (s) + 3NH_4Cl \ (aq) \ \ \ \text{3.6}$$
In addition to this, at proper reaction conditions, the HMDA can be hydrolyzed in the presence of distilled water and generates the OH\(^-\) ions. This reaction can be expressed by the equation mentioned below:

\[
H_2N(CH_2)_6H_2N + 2H_2O \rightarrow H_3N^+(CH_2)_6H_3N^+ + 2OH^- \tag{3.7}
\]

The generated OH\(^-\) ions from the HMDA react with iron chloride hexahydrate and form Fe (OH)\(_3\). Finally, Fe (OH)\(_3\) was decompose to form the stable \(\alpha\)-Fe\(_2\)O\(_3\) phase. The Fe(OH)\(_3\) was decomposed in Fe\(_2\)O\(_3\) according to the following chemical reaction:

\[
2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \tag{3.8}
\]

The continuous formation of Fe\(_2\)O\(_3\) nuclei finally leads the formation of stable \(\alpha\)-Fe\(_2\)O\(_3\) phase nanoparticles via simple hydrothermal process.

### 3.3.3.2 Optical Properties of as-synthesized well-crystalline \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles

The optical properties of as-synthesized well-crystalline \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles was examined using UV-visible spectrum measured at room-temperature and demonstrated in Figure 3.20 (a). In order to have a precise determination of the energy position of the absorption edge, one can take the edge position to be determined by the maximum of the first derivative of the optical absorption with respect to the energy and it corresponds to the optical band gap [191,192]. The first derivative of the spectrum as is shown in Figure 3.20 (b) indicates two peaks at 1.79 eV and 2.14 eV, which are similar to optical band gap values that have been reported in the literature [254]. As it is also well known by utilizing the Tauc’s formula 3.1, the relationship between absorption coefficient and the incident photon energy of semiconductors can be obtained. Hence, the optical band gap \(E_g\) can be experimentally obtained from absorption coefficient according to the Tauc’s equation 3.1. The corresponding graphs for indirect and direct transitions are shown in Figure 3.20 (c) and (d). As is seen from Figure 3.20 (c) and (d) the optical band gaps which have been obtained with extrapolation [255] (1.8 eV and 2.02 eV) are similar with the energy values that have been obtained in Figure 3.20 (b). Therefore, this is attributing the energy values of Figure 3.20 (b) to indirect and direct transition, respectively.
Figure 3.20(a) UV spectrum of as-synthesized well-crystalline $\alpha$-Fe$_2$O$_3$ nanoparticles synthesized by hydrothermal process (b) First derivative of it. (c) Tauc plot for indirect transitions (d) Tauc plot for direct transitions.

3.3.3.3 Photocatalytic degradation of methylene blue by using $\alpha$-Fe$_2$O$_3$ nanoparticles:

From environmental research viewpoint, the studies on photocatalytic degradation of organic pollutants have received a great attention recently and hence various photocatalysts were synthesized, utilized for degradation of organic pollutants and reported in the literature [65, 106-114]. Recently, nanostructures of $\alpha$-Fe$_2$O$_3$ have also been used as photocatalysts for the degradation of organic pollutants and reported in the literature [243, 256-258]. Most of the published articles report the photocatalytic degradation of salicylic acid or phenol by utilizing various kinds of $\alpha$-Fe$_2$O$_3$ nanostructures as photocatalyst [243, 256-258]. In this work, experiments were performed to evaluate the photocatalytic properties of well-crystalline $\alpha$-Fe$_2$O$_3$ nanoparticles by photocatalytic degradation of methylene blue (MB).
The photocatalytic decomposition was monitored by measuring the absorbance at regular time intervals by using UV-Vis. Spectrophotometer at a wavelength of 663 nm. The catalytic reaction was carried out in a 250 ml beaker, which contain 150 ml of methylene blue solution (0.025 mM) and 150 mg of as-synthesized α-Fe$_2$O$_3$ nanoparticles (catalyst). Prior to UV irradiation to the prepared solution suspension, the solution was stirred and bubbled with oxygen for at least 15 min in the dark to allow equilibrium of the system so that loss of compound due to the adsorption can be taken into account. In addition to this, the suspension was continuously purged with oxygen bubbling throughout the experiment. Irradiation was carried out using 250 W Mercury lamps.

Typical plot for the change in % degradation as a function of irradiation time of oxygen saturated aqueous suspension of α-Fe$_2$O$_3$ nanoparticles containing methylene blue. To monitor the degradation, the samples (5 ml in each case) were collected from the prepared suspension and MB concentrations were analyzed using UV-Vis. spectrophotometer (at a wavelength of 663 nm) at different time intervals. Figure 3.21 exhibits the change in absorption spectra for the photocatalytic degradation of MB as a function of time. From the absorption spectra, one can see that the absorption intensity of MB was decreased with increasing the irradiation time which confirms that the degradation of MB was increased with increasing the visible light exposure time. It is also concluded from the absorption spectra that the degradation of MB begins once the irradiation started.
The typical plot for the change in the absorption intensity as a function of irradiation time of oxygen saturated aqueous suspension of \( \alpha\)-Fe\(_2\)O\(_3\) nanoparticles containing MB illustrated in Figure 3.22. It is clearly seen from the plot that no considerable decomposition of MB was observed from the solution suspension when the MB degradation reaction was carried out without \( \alpha\)-Fe\(_2\)O\(_3\) nanoparticles (dotted line). In contrast, when the \( \alpha\)-Fe\(_2\)O\(_3\) nanoparticles were used as a catalyst for the photocatalytic degradation of MB, a significant decomposition was observed (solid line) which clearly reflects that \( \alpha\)-Fe\(_2\)O\(_3\) nanoparticles can be used as an efficient photocatalysts for the degradation of organic pollutants. Figure 3.22 (b) shows the typical plot for the \% degradation as a function of irradiation time of oxygen saturated aqueous suspension of \( \alpha\)-Fe\(_2\)O\(_3\) nanoparticles containing MB. From the \% degradation plot one can see that without adding the photocatalyst (\( \alpha\)-Fe\(_2\)O\(_3\) nanoparticles), there was almost no degradation of MB whereas the degradation percentage of MB increased with increasing the irradiation time and reached up to 40\% in a period of 230 min when the \( \alpha\)-Fe\(_2\)O\(_3\) nanoparticles was used a catalyst.
Figure 3.22(a). Typical plot for the change in the absorption intensity as a function of irradiation time of oxygen saturated aqueous suspension of α-Fe₂O₃ nanoparticles containing methylene blue and (b). Typical plot for the change in % degradation as a function of irradiation time of oxygen saturated aqueous suspension of α-Fe₂O₃ nanoparticles containing methylene blue.

3.3.4 Conclusion

In conclusion, well-crystalline α-Fe₂O₃ nanoparticles were synthesized in high-yield through a facile hydrothermal process at low temperature of 110 °C. The synthesized nanoparticles were characterized in detail in terms of their structural, optical and photocatalytic properties. The detailed structural characterizations reveal that as-synthesized nanoparticles are almost spherical shaped with the average diameters of ~ 35 ± 5 nm and are well crystalline and possessing pure α-Fe₂O₃ phase. The UV-Vis absorption spectrum of the synthesized nanoparticles demonstrated the existence of two optical band gaps, which correspond to direct and indirect transitions, respectively. The as-synthesized α-Fe₂O₃ nanoparticles were used as photocatalyst for the photocatalytic degradation of methylene blue and by detailed experiments, it was confirmed that the as-synthesized α-Fe₂O₃ nanoparticles exhibit good photocatalytic properties on the photocatalytic decomposition of methylene blue.
3.4 Highly Sensitive Ammonia Chemical Sensor based on $\alpha$-Fe$_2$O$_3$ nanoellipsoids

3.4.1 Introduction

Due to rapid increase of the environmental pollutions, many attentions have been paid by the environmental scientists to investigate various environmental safety issues. One of the major environmental issues is the release of harmful gases, liquids and chemicals in the environment through industrial effluents, agricultural chemicals, fertilizers and so on. Ammonia is one of the toxic gases and liquids and widely used in chemical industries, fertilizer factories, refrigeration systems, environmental monitoring food decomposition and so on [136-138,259]. As the liquid ammonia and aqua ammonia, also called as ammonium hydroxide, is widely used in chemical industries and excess release of it in the environment may cause life-threatening situations and small dose of ammonia inhalation may cause acute poisoning [237, 260-263]. In addition to this, ammonium hydroxide may cause corrosion to materials and various diseases to human being such as lung disease, permanent blindness, burning of skin and so on. In this regard, there is a common motto for both scientific and industrial communities to develop a cheap, reliable and low-temperature efficient ammonia chemical sensor. In this regard, variety of sensor techniques have been explored and used for the early detection of ammonia (in gaseous and liquid phase) in the environment. Among various sensor techniques, the electrochemical method provide itself as one of the best technique which offers several benefits such as easy use, low operational temperature, cost effective process, etc. To fabricate the electrochemical sensors, various electron mediators were used and reported in the literature [51,264,265]. Among various electron mediators, metal oxide semiconductor nanostructures have been special place due to easy and cost effective fabrication process [51,264,265]. Out of several various metal oxide nanostructures, the hematite ($\alpha$-Fe$_2$O$_3$), one of the most stable iron oxide under ambient conditions, has been studied as one of the unique and attractive materials due to its both fundamental investigations and practical applications. It possess various interesting properties which include its n-type semiconducting behavior, low-cost synthesis, non-toxic nature, high resistant to corrosion, etc. Due to variety of exotic properties,
α-Fe₂O₃ is widely used in various high-technological applications such as sensors, photocatalysis, pigments, magnetic recording media, etc [51]. Different pure phases of Fe₂O₃ have been utilized for the fabrication of sensor and their application in gases (CO and hydrocarbon gases), liquid (alcohol), sensing [266-269], etc. Furthermore, various Fe₂O₃ doped nanostructures have been synthesized and applied for the detection of biological molecules such as glucose [270] and dopamine [271], an important neurotransmitter. A detailed comprehensive review regarding synthesis and applications of Fe₂O₃ is recommended to the readers [272]. Even though, it exhibit various interesting properties and wide applications, but yet the aqueous ammonia sensor of this material is rare.

This work, reports the facile hydrothermal synthesis of α-Fe₂O₃ nanoellipsoids and their effective utilization for the fabrication of efficient and highly sensitive aqueous ammonia chemical sensor. The synthesized nanoellipsoids are characterized in detail in terms of their structural and optical properties. The fabricated aqueous ammonia sensor based on nanoellipsoids demonstrates very high and reproducible sensitivity of ~4.678 µA.cm⁻².mM⁻¹ and detection limit ~0.04 nM [239].

3.4.2 Experimental Details

3.4.2.1 Synthesis of α-Fe₂O₃ nanoellipsoids by low-temperature hydrothermal process:

For the synthesis of α-Fe₂O₃ nanoellipsoids, aqueous solutions of 0.05 M iron chloride hexahydrate (FeCl₃.6H₂O) and 0.05M hexamethylenetetramine (HMTA) (each 50.0 ml) were mixed under continuous stirring and subsequently few drops of sodium hydroxide (NaOH) was slowly added until the solution pH become 9. After vigorous stirring for 30 min, the resultant solution was loaded into a Teflon-lined stainless steel autoclave, sealed it and heated up to 120 °C for 5 h. After completing the reaction, the autoclave was naturally allowed to cool at room-temperature. Dark brown products were obtained which were filtered off, washed thoroughly with DI water, ethanol and acetone sequentially and dried at room-temperature. The as-synthesized products were examined in terms of their morphological, structural, optical and sensing properties.
3.4.2.2 Characterizations of α-Fe₂O₃ nanoellipsoids by low-temperature hydrothermal process

The general morphologies of synthesized α-Fe₂O₃ nanoellipsoids were examined by FESEM (JEOL-JSM-7600F) attached with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM; JEOL-JEM-2100F) equipped with high-resolution TEM (HRTEM). The crystallinity and crystal phases were characterized by X-ray diffraction (XRD; PANanalytical Xpert Pro.) pattern measured with Cu-Kα Radiation (λ=1.54178Å) in the range of 20-70º. The composition of as-prepared α-Fe₂O₃ nanoellipsoids was examined by Fourier transform infrared (FTIR; Perkin Elmer-FTIR Spectrum-100) spectroscopy in the range of 450-4000 cm⁻¹. To check the optical properties of as-synthesized products, UV-visible spectroscopy (Perkin Elmer-UV/VIS-Lambda 950) measurement was done at room-temperature.

3.4.2.3 Fabrication and characterization of aqueous ammonia chemical sensor by using α-Fe₂O₃ nanoellipsoids modified GC electrode:

For the fabrication of aqueous ammonia chemical sensor, as-synthesized α-Fe₂O₃ nanoellipsoids were mixed with conducting binders and coated on glassy carbon electrode (GCE, surface area 0.0316 cm²) surface, and then the modified electrode was dried in an electric oven at 60 °C for 3-5 hrs. The sensor performance was evaluated with a simple two electrode system in which α-Fe₂O₃ nanoellipsoids modified GCE was used as a working electrode while Pd wire was employed as a counter electrode. Electrometer (Keithley, 6517A, USA) was used as a voltage source for I-V measurement in simple two electrode system. The current response was measured from 0 to + 1.6 volts while the time delaying and response time were 1.0 sec and 10.0 sec, respectively. Fixed amount of 0.1M phosphate buffer solution (PBS; 10.0 ml) was kept constant for all the measurements. Wide concentrations range of ammonium hydroxide (0.05 nM ~ 0.05 mM) was used for all the experiments. The sensitivity of the fabricated aqueous ammonia chemical sensor was estimated from the slope of the current Vs concentration from the calibration plot divided by the value of active surface area of sensor/electrode.
3.4.3 Results and Discussion:

3.4.3.1 Morphological and Structural properties of as-synthesized \( \alpha-\text{Fe}_2\text{O}_3 \) nanoellipsoids:

The general morphologies of as-synthesized \( \alpha-\text{Fe}_2\text{O}_3 \) products was examined by field emission scanning electron microscopy (FESEM) and shown in Figure 3.23 (a) and (b) which exhibit that the synthesized structures are clearly ellipsoidal shape and are grown in large-quantity. As can be seen by the micrograph images that the density of synthesized nanoellipsoids are too high and the outer surfaces of each ellipsoid is totally touched with another one. The as-synthesized nanoellipsoids possess almost uniform sizes with the typical central diameters of \( \sim 40 \pm 10 \) nm and lengths of \( \sim 100 \pm 10 \) nm. In addition to nanoellipsoids, few spherical nanoparticles were also seen in the micrographs.

To check the composition of as-synthesized \( \alpha-\text{Fe}_2\text{O}_3 \) nanoellipsoids, energy dispersive spectroscopy (EDS) attached with FESEM was done and results are demonstrated in the inset of Figure 3.23 (b). It is clear from the obtained EDS spectrum that the synthesized nanoellipsoids are made from iron and oxygen. Except Fe and O, no other peak related with any impurity element was detected in the spectrum, up to the detection limit of EDS, which clearly reflects that the synthesized \( \alpha-\text{Fe}_2\text{O}_3 \) nanoellipsoids are formed by iron and oxygen. The crystallinity and crystal phases of as-synthesized products was examined by X-ray diffraction and shown in Figure 3.23 (c). As can be seen, all the reflections in the observed pattern are well matched with the rhombohedral \( \alpha-\text{Fe}_2\text{O}_3 \) structures with calculated lattice constants of \( a = 5.0356 \) Å and \( c = 13.7489 \) Å. The obtained results are well matched with the reported data (JCPDS 33-0664). The appearance of sharp and strong diffraction reflections in the pattern confirms the good crystallinity and purity of the synthesized nanoellipsoids. Except rhombohedral \( \alpha-\text{Fe}_2\text{O}_3 \), no reflection for other impurities such as FeOOH, Fe\text{3}O\text{4}, etc were found in the pattern which further confirms that the as-synthesized products are pure and well-crystalline.
The chemical composition of as-synthesized $\alpha$-Fe$_2$O$_3$ nanoellipsoids was examined by Fourier transform infrared (FTIR) spectroscopy at room-temperature in the range of 400-4000 cm$^{-1}$. To measure FTIR of as-prepared sample, a certain amount of as-synthesized material was mixed well with potassium bromide (KBr) and then compressed in the form of pellet under high-pressure of $\sim$4 tons. The prepared pellet was then used for the FTIR measurement. Figure 3.23 (d) exhibits the typical FTIR spectrum of as-synthesized $\alpha$-Fe$_2$O$_3$ nanoellipsoids. Various distinct absorption bands were seen in the obtained FTIR spectrum. The appearance of two well-defined absorption bands at $\sim$473 cm$^{-1}$ and $\sim$561 cm$^{-1}$ are due to: iron-oxygen (Fe-O) bonds which confirmed the formation of iron oxide [273-275]. Including two distinct absorption bands, two small peaks are also seen in the spectrum. The origination of the two small absorption bands at 1632 cm$^{-1}$ and 3420 cm$^{-1}$ are due to the bending
vibration of absorbed water and surface hydroxyl, and O-H stretching mode, respectively [222].

For the detailed morphological and structural characterizations of as-synthesized \(\alpha\)-Fe\(_2\)O\(_3\) nanoellipsoids, transmission electron microscopy (TEM) equipped with high-resolution TEM (HRTEM) was done and shown in Figure 3.24. Figure 3.24 (a) and (b) exhibit the low-magnification TEM images of the as-synthesized \(\alpha\)-Fe\(_2\)O\(_3\) nanoellipsoids which exhibit the full consistency with the FESEM observations in terms of morphologies and dimensions of synthesized products. The grown structures exhibit ellipsoidal shape with the typical central diameters of \(~40\) nm and lengths of \(~100\) nm. In addition to the nanoellipsoidal structures, some spherical nanoparticles were also seen in the micrograph. Figure 3.24 (c) and (d) show the typical HRTEM images of as-synthesized \(\alpha\)-Fe\(_2\)O\(_3\) nanoellipsoids. Well-defined lattice fringes, separated by 0.266 nm were observed which can be indexed to the (014) plane of the rhombohedral \(\alpha\)-Fe\(_2\)O\(_3\) structure. The well-defined and clear lattice fringes of as-synthesized \(\alpha\)-Fe\(_2\)O\(_3\) nanoellipsoids clearly confirm the excellent crystallinity of the synthesized nanoellipsoids.
3.4.3.2 Optical properties of as-synthesized α-Fe₂O₃ nanoellipsoids:

The optical property of as-synthesized nanoellipsoids was examined by room temperature UV-vis. spectroscopy and results are demonstrated in Figure 3.25. In order to have a precise determination of the energy position of the absorption edge, one can take the edge position to be determined by the maximum of the first derivative of the optical absorption with respect to the energy and it corresponds to the optical band gap [191,192]. The first derivative of the spectrum as is shown in Figure 3.25 (b) indicates two peaks at 1.796 eV and 2.19 eV. By applying the Tauc’s equation 3.1, the optical band gap energy (E_g) of the as-synthesized nanoellipsoids can be calculated. By utilizing equation 3.1, the relationship between absorption coefficient and the incident photon energy of semiconductors can be obtained. Figures 3.25 (c) and (d) exhibit the optical band gaps, obtained with extrapolation, for indirect and direct transitions and found to be ~1.87 eV for indirect transitions and 2.15 eV for
direct transitions, which are very close to optical band gap values that have been reported in the literature [254].

Figure 3.25 Typical (a) UV-Vis. spectrum, (b) First derivative, (c) Tauc plot for indirect transitions and (d) Tauc plot for direct transitions of as-synthesized α-Fe₂O₃ nanoellipsoids.

3.4.3.3 Detection of aqueous ammonia chemical sensor by using α-Fe₂O₃ nanoellipsoids modified GC electrode:

The as-synthesized α-Fe₂O₃ nanoellipsoids based aqueous ammonia chemical sensor performance was evaluated by I-V technique using two electrode systems in which the modified GCE was used as a working electrode while Pd wire was employed as a counter electrode. The aqueous ammonia (ammonium hydroxide, 25%) was used as a sensing target liquid. Figure 3.26(a) demonstrates a typical I-V response of GCE in 10.0 ml, 0.1M PBS solution: without (black) and with nanoellipsoids coating (red) on GCE. A visible decrease in the current was observed, which was may be due to high resistance generated to the GCE surface by nanoellipsoids coating in the presence of conducting binders. Figure 3.26 (b) exhibits the I-V response of nanoellipsoids modified GCE electrode, without (red) and with (black) of NH₄OH.
Interestingly, a significant enhancement in the current was observed when small amount (100.0 µL) of 0.05 nM NH₄OH was added in 10.0 mL phosphate buffer solution (0.1M PBS, pH = 7.0). In the other hand, in the absence of NH₄OH, no significant increase in the current was observed. This clearly exhibits the sensitive nature of utilized α-Fe₂O₃ nanoellipsoids towards liquid ammonia sensing [276]. In case of metal oxide based sensors, the adsorption of O⁻ is the most interesting and important process as metal oxides can easily adsorb O₂⁻ and O⁻ species from the atmosphere by extracting an electron from the conduction band of the material [277-279]. The adsorbed O⁻ react with target chemical and discharge the trapped electron to the conduction band of the material and hence conductivity of the material increased [280,281].
In our case, when applying the current, the NH₃OH catalytically dissociates into ammonium (NH₄⁺) and hydroxide (OH⁻) ions and due to increase in the carrier ions, the conductivity of α-Fe₂O₃ nanoellipsoids increases as by this reaction, excess electrons were delivered to the conduction band of the material which significantly enhance the conductivity of the utilized α-Fe₂O₃ nanoellipsoids [280,281]. The
following reactions scheme demonstrated the liquid ammonia sensing on \( \alpha \text{-Fe}_2\text{O}_3 \) nanoellipsoids modified sensor.

\[
O_2(g)\{air/liquid\ \text{interface}\} \rightarrow O_{2\ ads} \ (\alpha - \text{Fe}_2\text{O}_3)
\]

\[
O_{2\ ads} \ (\alpha - \text{Fe}_2\text{O}_3) + ne \rightarrow (\alpha - \text{Fe}_2\text{O}_3)
\rightarrow 2O - ads \ (O^-/O_2^-) \ \text{[dynamic species]}
\]

\[
NH_4OH + O^- \rightarrow NH_4 + OH^- + ne \ \ \ \ \ \ \ \ \ \text{…………………(3.9)}
\]

To check in detail, the aqueous ammonia sensing behavior of \( \alpha \text{-Fe}_2\text{O}_3 \) nanoellipsoids, the electrical responses of nanoellipsoids modified GCE was examined at various \( NH_4OH \) concentrations and demonstrated in Figure 3.27 (a). A wide range of \( NH_4OH \) concentrations (0.05 nM ~ 0.05 mM) was added into 0.1 M PBS solution (pH =7.0), at room-temperature for these experiments.

![Figure 3.27(a)](image)

Figure 3.27(a) Typical I-V response of \( \alpha \text{-Fe}_2\text{O}_3 \) nanoellipsoids modified GCE towards various concentrations of \( NH_4OH \) (from 0.05 nM ~ 0.05 mM) into 0.1 M PBS solution (pH=7) and (b) Extended view of figure 5 (a) and (c) calibration curve.

Figure 3.27 (a) exhibits the typical I-V characteristic of the fabricated sensor at different \( NH_4OH \) concentrations. In all the cases, it is clear that with increasing the
concentration of NH$_4$OH, the current increases gradually which reflects that the conductivity of modified electrode was enhanced due to supply of the excess electrons to the conduction band of as-synthesized nanoellipsoids. To clearly see the electrical responses towards various concentrations of liquid ammonia for the fabricated sensor, an enlarge view of Figure 3.27 (a) is presented and shown in Figure 3.27 (b). It is clearly shown in Figure 3.27(b) that with increasing the concentration of ammonia the current also increases significantly which confirms that the fabricated sensor is quite sensitive with the ammonia concentration. Figure 3.27 (c) exhibits the typical calibration curve, plotted from the wide range of NH$_4$OH concentrations. It is clear from the calibration curve that the response current increases with increasing the concentration of NH$_4$OH and finally at high NH$_4$OH concentration, the current reaches almost at a saturated value which may be due to the unavailability of free sites in nanoellipsoids for NH$_4$OH adsorption. The fabricated chemical sensor demonstrated a correlation coefficient R=0.995. The calculated sensitivity, from the slope of the lower concentration region of calibration curve, was found to be 4.678 µA cm$^{-2}$ m M$^{-1}$.

The estimated detection limit for the fabricated sensor was ~0.04 nM [239]. The saturated steady state current was achieved in ~ 10 sec from the α-Fe$_2$O$_3$ modified electrode which confirms a good and fast electron exchange behavior of synthesized α-Fe$_2$O$_3$ nanoellipsoids modified electrode. The obtained very high sensitivity of the fabricated sensor was due to the excellent adsorption ability and high electrocatalytic activity of the as-synthesized α-Fe$_2$O$_3$ nanoellipsoids. The estimated sensitivity of the fabricated sensor is relatively higher than previously reported ammonium hydroxide sensor fabricated based on the utilization of nanomaterials, composite and/or materials modified electrodes [282-284]. In addition to this, the calculated detection limit of the fabricated ammonium hydroxide sensor was less than recently reported literature [283]. The observed high-sensitivity and low-detection limit of the fabricated liquid ammonia sensor based on α-Fe$_2$O$_3$ nanoellipsoids modified electrode was mainly due to the good adsorption ability and catalytic activity and biocompatible nature of as-prepared α-Fe$_2$O$_3$ nanoellipsoids. The proposed α-Fe$_2$O$_3$ nanoellipsoids sensor showed high stability for over 11 days. It was observed that there were not significant changes
in current response for approximately 11 days. Therefore, it can be concluded that the present liquid ammonia sensor was stable and offered good stability too. The above mentioned results clearly reflect that α-Fe₂O₃ nanomaterials can be used as efficient electron mediators for the fabrication of effective chemical sensors.

3.4.4 Conclusions

In summary, α-Fe₂O₃ nanoellipsoids were synthesized by facile hydrothermal process and characterized in detail in terms of morphological, structural and optical properties. The detailed structural and optical characterization confirms the rhombohedral α-Fe₂O₃ structures and good optical properties. The fabricated aqueous ammonia sensor based on α-Fe₂O₃ nanoellipsoids exhibits reproducible sensitivity of 4.678 µA.cm⁻².mM⁻¹ and detection limit ~0.04 nM with correlation coefficient (R) of 0.995. Due to the easy synthesis and electrode fabrication process, high sensitivity and low-detection limit, this work demonstrates that simply synthesized α-Fe₂O₃ nanostructures can be effectively use for the fabrication of efficient chemical sensors.
3.5 Visible-light-driven photocatalytic and chemical sensing properties of SnS$_2$ nanoflakes:

3.5.1 Introduction

The aquatic environmental imbalance mainly occurs by the contamination of water with the harmful non-biodegradable materials [66,285]. Various textile and chemical industries release many harmful organic macromolecules and dyes [286-288]. Particularly the disposable of colored organic waste water from the textile dyeing industries causes a serious problem to aquatic ecosystem and hence contaminate the environment which cause a serious threat to the living organisms [289,290]. Among various water soluble dyes, Rhodamine B (RhB) with non-volatile nature and bright reddish violet in color are extensively used in various prospect applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy and ELISA [291,292] and also applied for dying cottons, bamboo, weed, stamp pad inks etc. The waste of RhB dye hazardously affects natural environments especially aquatic life and leads the mutagenic effects to humans and other living organisms [293-298]. Conventionally, a biological treatment or degradation process utilizes to decolorize the dyes, but it is ineffective for the complete removal and degradation of dye. Last few years, the catalytic process derived by solar energy or other radiation energy has been studied for the successful degradation of harmful organic dyes into environmental friendly materials [71,299,300]. In this regard, because of the unique band gap and various other physical and chemical properties, the nanoscale inorganic semiconductors such as metal oxides, metal sulfides etc were used as active catalysts for the degradation/oxidation of organic dyes and reported in the literature [301,302]. The photocatalytic degradation occurs due to the effective separation of excited electron in conduction band (CB) and hole in valance band (VB) under the light illumination, which could capture by some surface species in the surroundings such as hydroxyl or O$_2$ groups [303]. These catalysts are usually active under the UV- light. Among various semiconducting materials, the metal sulfides have received a great deal of interest as promising photocatalysts under the visible light illumination [304].
K. Domen et al. demonstrated a high photo-activity for hydrogen evolution over the surface of synthesized nanostructured CdS under visible light [305].

Recently, the IV–VI group semiconductors such as tin sulfides (SnS, SnS$_2$) have received much attention owing to their strong anisotropy of optical properties and potential applications in solar cells as well as electrical switching [150,306-310]. Among large number of binary tin sulfides (SnS, SnS$_2$, Sn$_2$S$_3$, Sn$_3$S$_4$, Sn$_4$S SnS and SnS$_2$), the SnS$_2$ possesses special place due to its own properties and wide applications in solar cells, lithium-ion batteries, optoelectronics, photoluminescence and so on [67,68]. The SnS$_2$ is a n-type semiconductor and is receiving much attention owing to its layered hexagonal CdI$_2$-type crystal structure with two layers of close-packed sulfur anions and tin cations sandwiched between them in an octahedral coordination manner. Due to its absorption tunable band gap of 2.2 eV, the crystalline SnS$_2$ could be a promising photocatalytic material for the photocatalytic degradation of organic dyes in the presence of visible-light [69]. Moreover, SnS$_2$ nanomaterials possess good oxidative and thermal stability in acid and neutral environment [70-73].

In this work, we demonstrate the facile and large-scale synthesis of well-crystalline SnS$_2$ nanoflakes by simple hydrothermal process. The synthesized nanoflakes were characterized in detail in terms of their morphological, structural and compositional properties. The as-synthesized nanoflakes were used as efficient photocatalysts for photocatalytic degradation of Rhodamine B under visible light. Moreover, the prepared nanoflakes were used as efficient electron mediators for the fabrication of nitroaniline chemical sensor by simple I-V technique.

3.5.2 Experimental details:

3.5.2.1 Synthesis of SnS$_2$ nanoflakes:

All the chemicals utilized for the synthesis of SnS$_2$ nanoflakes were purchased from Sigma-Aldrich and used without further purification. Distilled water (DW) was used for all the synthesis process. Well-crystalline SnS$_2$ nanoflakes were synthesized by facile low-temperature hydrothermal process. In a typical reaction process, aqueous solutions of 0.02M SnCl$_4$·5H$_2$O and 0.05 mol/L of thiourea, both prepared in 50 mL DI water, were mixed well under constant stirring. After constant and vigorous
stirring for 30 min, the resultant solution was transferred to teflon lined autoclave, sealed and heated upto 140 °C for 3h. After desired reaction time, the autoclave was allowed to cool at room-temperature and finally yellowish precipitate was obtained which was extensively washed several times with DW, ethanol and acetone, sequentially and dried at 55 °C for 3h. During the reaction, the thiourea reacts with water and produce H\textsubscript{2}S which further reacted with Sn\textsuperscript{4+} ions obtained from SnCl\textsubscript{4}. The chemical reactions involved in the synthesis process can be written as:

\[
\text{NH}_2\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{H}_2\text{S} + \text{CO}_2 \ldots \ldots \ldots (3.10)
\]

\[
\text{Sn}^{4+} + \text{H}_2\text{S} \rightarrow \text{SnS}_2 \downarrow + 4\text{H}^+ \ldots \ldots \ldots (3.11)
\]

The dried powder was then characterized in detail in terms of their morphological, structural and compositional properties and utilized as efficient photocatalyst for photocatalytic degradation of Rhodamine B and as an electron mediator for the fabrication of reproducible and highly sensitive nitro-aniline chemical sensor.

3.5.2.2 Characterizations of as-synthesized SnS\textsubscript{2} nanoflakes:

The as-synthesized SnS\textsubscript{2} nanoflakes were characterized in detail by various analytical tools. The general and detailed morphologies of as-synthesized nanoflakes were done by field emission scanning electron microscopy (FESEM; JEOL-JSM-7600F) and transmission electron microscopy (TEM) equipped with high-resolution TEM (HR-TEM). For HRTEM analysis, the synthesized products were ultrasonically dispersed in acetone and a drop of acetone solution, which contains the SnS\textsubscript{2} nanostructures, was placed on a copper grid and examined. The crystallinity and crystal phases were examined by the X-ray diffraction (XRD; PANanalytical Xpert Pro.) pattern measured with Cu-K\textsubscript{α} Radiation (\(\lambda=1.54178\text{Å}\)) in the range of 10-65°. The chemical composition of as-synthesized SnS\textsubscript{2} nanoflakes were examined by Fourier transform infrared (FT-IR) spectroscopy, measured at room-temperature, in the range of 400-4000 cm\textsuperscript{-1}. To prepare the sample for FTIR measurements, small amount of the as-synthesized SnS\textsubscript{2} nanoflakes was mixed well with the potassium bromide (KBr) and subsequently compressed under high-pressure (~4 tons) for pellet preparation. The obtained pellet, composed of SnS\textsubscript{2} nanoflakes and KBr, was used for the FTIR measurements.
3.5.2.3 Photocatalytic decomposition of Rhodamine B using as-synthesized SnS$_2$ nanoflakes:

The photocatalytic performance of the synthesized SnS$_2$ nanoflakes was examined by studying the photocatalytic decomposition of RhB. The photocatalytic degradation of RhB dye was performed under the illumination of Xenon arc lamp (300 W, Hamamatus: L 2479), attached with UV cut-off filter of wavelength 400 nm (FSQGG-400) which limited the illumination in a range of 400–800 nm, i.e. visible light. The degradation of RhB was calculated by measuring the UV-Vis absorbance at 552 nm wavelength at certain time intervals. The photo-catalytic degradation was established in a 250 ml beaker using 150 ml of RhB dye solution (10 ppm). Prior to the light illumination, the prepared RhB dye solution was bubbled with oxygen for 30 min to allow the equilibrium of the system. For the photocatalytic experiments, 150 mg of the as-prepared SnS$_2$ nanoflakes were added to the prepared RhB dye solution, as photocatalyst, and stirred for 10 min for the initial physical adsorption of dye over SnS$_2$ nanoflakes surfaces. The decomposed dye solution was measured by using (UV-Vis spectrophotometer Perkin Elmer-UV/VIS-Lambda 950) after regular time intervals.

3.5.2.4 Fabrication and characterization of nitro-aniline chemical sensor by I-V technique:

To modify the electrode surface, firstly, the surface of glassy carbon electrode (GCE) was polished with commercially available alumina, followed by rinsing with DW thoroughly. For the GCE surface modification for nitro-aniline chemical sensor, slurry of SnS$_2$ nanoflakes was made by mixing an appropriate composition of SnS$_2$ nanoflakes and conducting agent (butyl carbital acetate). Finally, a small amount of the slurry was casted on GCE (surface area 0.0316 cm$^2$) surface, and then the modified electrode was dried in electric oven at 60 ± 5 ºC for 4h. The sensor analytical performance was investigated using I-V technique as discussed in our previous reports [106]. For I-V measurements; an Electrometer (Keithley, 6517A, USA) was used as a voltage source and the SnS$_2$ nanoflakes/GCE was used as a working electrode while Pt wire was employed as a counter electrode. The current response was measured from 0.0 to 2.0 V while the time delaying and response time were 1.0 sec and 10.0 sec, respectively. The amount of 10.0 mL phosphate buffer
solution was kept constant for all the measurements. For the concentration studies, a wide range of nitroaniline concentrations (1.56×10^{-6} \text{ mol/L} \text{ to } 1×10^{-3} \text{ mol/L}) were used. The sensitivity of the fabricated nitro-aniline chemical sensor was estimated from the slope of the current \textit{versus} concentration from the calibration plot divided by the value of active surface area of sensor/electrode. All the sensing experiments were carried out at room-temperature.

3.5.3 Results and discussion:

3.5.3.1 Structural, morphological and compositional properties of SnS₂ nanoflakes:

Prior to any applications, the as-synthesized SnS₂ nanoflakes were characterized in terms of their structural, morphological and compositional properties. To examine the crystallinity and crystal phase, the as-synthesized SnS₂ nanoflakes were examined by X-ray diffraction (XRD). Figure 3.28 exhibits the typical XRD pattern for as-synthesized nanoflakes. All the reflections in the diffraction pattern are well matched with the typical SnS₂ crystals and can be indexed to the hexagonal SnS₂ phase with a lattice constant \(a = 3.649 \text{ Å}\) and \(c = 5.899 \text{ Å}\). The observed XRD results are well matched with already reported literature (JCPDPS card no. 22–0951). Moreover, no other reflection, except SnS₂ reflections are seen in the pattern which confirms the formation of pure SnS₂ nanomaterials.
The general morphologies of as-prepared SnS$_2$ nanomaterials were examined by FESEM and shown in Figures 3.29 (a) and (b). Figure 3.29 (a) exhibits the typical low-magnification image and revealed that the prepared SnS$_2$ nanomaterials possess flake-shaped morphology and are synthesized in large quantity. It is clear from the high-resolution images that the flakes are thin nanosheets which are curly in shape and randomly arranged (Figure 3.29 (b)). Moreover, due to larger size, the nanosheets are interconnected with each other in such a manner that they made some porous architecture structures and hence possess larger surface area. Therefore, these materials are promising candidates for photocatalysts and sensors applications. The typical thicknesses of the nanosheets are in the range of 60 ± 20 nm with several micro meters in width. The detailed morphological investigations of as-synthesized SnS$_2$ nanoflakes were examined by TEM equipped with high-resolution TEM (HRTEM). For the TEM analysis, the prepared SnS$_2$ nanoflakes were ultrasonically dispersed in acetone and a drop of acetone which contains the nanoflakes was placed on the TEM grid and examined.
Figure 3.29 (a) Low and (b) high-magnification FESEM, (c) low- and (d) high-resolution TEM images of the as-synthesized SnS$_2$ nanoflakes prepared by facile hydrothermal process at low-temperature.

Figure 3.29 (c) exhibits the typical low-resolution TEM image of as-synthesized SnS$_2$ nanoflakes. It is clear from the TEM image that the nanoflakes were made by the thin SnS$_2$ nanosheets. Moreover, due to large in size, the nanosheets are interconnected with each other which lead the formation of some porous architecture. The typical thicknesses of the nanosheets are in the range of 60 ± 20 nm. It is also clear from the observed TEM image that the nanoflakes are synthesized in large quantity. All the TEM observations regarding shape, size and thickness are well matched with the obtained FESEM results. For further structural properties, the nanoflakes were investigated by HRTEM and results are shown in Figure 3.29 (d). The observed HRTEM exhibit a very clear and well-defined lattice fringes with the lattice spacing of ~0.32 nm, which is fully consistent with the distance of (100) crystalline plane of the hexagonal SnS$_2$. The obtained HRTEM results are well matched with the XRD observations.
The chemical composition of as-synthesized SnS$_2$ nanoflakes was examined by using FTIR spectroscopy, as shown in Figure 3.30. Several well-defined absorption bands were observed in the spectrum at 631, 1411 and 1641 cm$^{-1}$. The peak appeared at 631 cm$^{-1}$ in the spectrum is due to the formation of Sn-S bond [227,311]. The origination of two very weak peaks at 1411 and 1641 cm$^{-1}$ are due to the formation of C-H and C-O bands, respectively [304]. Finally, due to presence of Sn-S bond, it is confirmed that the synthesized nanomaterial is SnS$_2$.

![Figure 3.30 FTIR spectrum of the as-synthesized SnS$_2$ nanoflakes prepared by facile hydrothermal process at low-temperature](image)

3.5.3.2 Visible-light driven photocatalytic properties of SnS$_2$ nanoflakes:

To define the photocatalytic activity of synthesized SnS$_2$ nanoflakes, the degradation of RhB dye was performed under the visible light irradiation. The degradation rate of RhB dye was estimated by following relation [185]:

\[
\text{Degradation rate(\%) = \left( C_o - C/C_o \right) \times 100 = \left( A_o - A/A_o \right) \times 100 \ldots \ldots (3.12) }
\]
Where, $C_0$ represents the initial concentration, $C$ the variable concentration, $A_0$ the initial absorbance, and $A$ the variable absorbance. Figure 3.31 depicts the UV-Vis absorption spectra (a), (b) % degradation rate versus time; (c) a plot for $A_0/A$ versus time and (d) pie degradation chart of decomposed RhB dye solution by synthesized SnS$_2$ nanoflakes under the visible light irradiation. The photocatalytic decomposition was monitored by measuring the absorbance at regular time intervals (10 min) under visible light at the wavelength of 552 nm. Interestingly, it was observed that the relative absorption intensity continuously decreases as increasing the visible light exposure time which indicates that the RhB dye decomposes gradually over the surface of the photocatalyst, i.e. SnS$_2$ nanoflakes (Figure 3.31 (a)). Under visible light irradiation, the synthesized SnS$_2$ nanoflakes significantly degraded the RhB dye by ~61% within 120 min. However, the degradation rate of RhB dye was almost negligible when photocatalytic reaction is performed under visible light irradiation without SnS$_2$ nanoflakes which clearly suggested that the degradation rate increases in presence of the photocatalyst, i.e. SnS$_2$ nanoflakes. Figure 3.31 (c) shows the plot of the variation in the relative concentration ($A/A_0$) versus time interval for the photo-degradation of RhB dye over the surface of SnS$_2$ nanoflakes under visible light irradiation. Interestingly, the obtained results clearly display the gradual degradation of RhB dye over the surface of synthesized catalyst. The relative concentration of RhB dye decreases with increasing the visible light irradiation exposure time while in the absence of synthesized SnS$_2$ nanoflakes catalyst, negligible degradation is detected under visible light irradiation. The pie degradation chart of RhB dye (Figure 3.31 (d)) reveals that most of dye molecules are degraded in 80 min and afterward the degradation rate slows down. Conclusively, the synthesized SnS$_2$ nanoflakes as photocatalyst are able to degrade harmful RhB dye into the environment friendly residues under visible light irradiation.
Figure 3.31 (a) UV–Vis absorbance spectra of decomposed RhB dye solution by visible light over as-synthesized SnS$_2$ nanoflakes, (b) degradation rate (%) and (c) extent of decomposition ($A/A_0$) of RhB dye with respect to time intervals, (d) pie degradation chart of RhB dye.

The mass spectroscopy of RhB dye before and after photocatalytic reaction has been examined to investigate the possible degradation products/intermediates of photocatalytic degradation of RhB dye, as shown in Figure 3.32 (a). At 0 min, RhB dye solution shows a strong mass signal at m/z = 451.1, which is close to the mass of RhB dye. It is seen that a number of mass signals are detected in the RhB dye solution after 120 min, indicating the degradation of RhB dye over the surface of SnS$_2$ nanoflakes under visible light. The main mass signal at m/z = 451.1 becomes weak after 120 min and splits into various mass signals.
Figure 3.32(a) Mass spectra of RB dye solutions over as synthesized SnS$_2$ nanoflakes after 0 min and 120 min with the scan 100–500 m/z and (b) the possible reaction intermediates after the photocatalytic reaction.

In Figure 3.32 (b) we demonstrated the possible degradation intermediates during the photocatalytic reactions which are illustrated on the observed mass signals. These possible reaction intermediates from fragmentations of the RhB dye contain the oxy groups in their rings. Thus, the formations of these intermediates might be helpful for the complete mineralization of organic dye [312]. The schematic illustration to understand the degradation mechanism of RhB dye over the surface of SnS$_2$ nanoflakes was presented in Figure 3.33.
In general, the generation of oxyraicals such as hydroxyl (OH•) and superoxide (O$_2^-$, HO$_2^-$) are responsible for the degradation of organic dyes under light irradiation and these radicals are formed over the surface of semiconductors by the separation of electron-hole pairs [313,314]. Importantly, the presence of carbon species on surface of SnS$_2$ catalyst is responsible for creating active sites which is helpful for the degradation of dye under light illumination [315,316]. From the mechanism, upon light illumination SnS$_2$ nanoflakes absorbs the visible light and the electron (e$^-$) from VB excites to CB which effectively causes a separation between e$^-$ and hole (h$^+$) pairs [317].

The RhB dye molecules firstly adsorb on the surface of the SnS$_2$ nanoflakes photocatalyst which reacts with water on the surface of SnS$_2$ nanoflakes photocatalyst to generate RhB$^{+\cdot}$ and OH$^-$ radicals. The flakes morphology of synthesized SnS$_2$ nanomaterial sufficiently produces the large number of RhB$^{+\cdot}$ under visible light irradiation and credit to the easy transformation or oxidation of harmful organic dye into less harmful chemicals. Moreover, the unique band gap and large surface area (34.6 m$^2$/g) of synthesized SnS$_2$ nanoflakes photocatalyst could able to provide...
efficient ē and h+ separation, resulting in the formation of large number of RhB⁺⁺ and OH’ radicals [318]. In this work, the high degradation of RhB dye is due to morphologies of nanoflakes and generation of RhB⁺⁺ and OH’ radicals on the surface of SnS₂ nanoflakes.

### 3.5.3.3 Nitroaniline chemical sensor application of as-synthesized SnS₂ nanoflakes:

The detailed methodology to modify the GC electrode with SnS₂ nanoflakes is described in experimental details section. Figure 3.34 (a) exhibits the schematic representation of nitro-aniline chemical sensor fabricated based on SnS₂ nanoflakes coated GCE electrode and its sensing mechanism by IV technique. Briefly, slurry of SnS₂ nanoflakes was made by mixing it with appropriate amount of binder and casted on GC electrode. In two electrode system, the SnS₂ modified electrode was used as working electrode while the Pt wire was employed as counter electrode. The current (I)-voltage (V) measurements have been carried out to evaluate the sensing properties such as sensitivity, detection limit, correlation coefficient, etc of SnS₂ nanoflakes electrode towards nitroaniline chemical. Figure 3.34 (b) shows the proposed mechanism of nitroaniline sensing over the SnS₂ nanoflakes electrode. The detection of nitroaniline chemical over the surface of SnS₂ nanoflakes electrode might explain by the push-pull system which depends on the existing functional groups in conjugated π-π backbone [319]. In case of nitroaniline, the amino group acts as electron donor or pushing group and nitro group acts as electron acceptor or pulling group. In electrochemical system or sensor, the active sites on the surface of SnS₂ nanoflakes electrode are easily attracted amino group [320]. On the other hand, nitro group recombines with ē and simultaneously reacts with H₂O to form non harmful nitrous compound which responses in the I-V measurements in the form of increment of current.
Figure 3.34 (a) Schematic representation of nitro aniline chemical sensor fabricated based on I-V technique using SnS$_2$ nanoflakes modified GC electrode as working electrode; (b) chemical reaction describing the sensing mechanism.

Figure 3.35 (a) depicts the I-V measurements of the fabricated chemical sensor based on SnS$_2$ nanoflakes modified GC electrode without and with nitro-aniline. A sharp increase in the current of ~20.3 µA is observed after the addition of nitro-aniline (15.6×10$^{-6}$ mole/L) as compared to chemical sensor without nitro-aniline, suggesting the electrocatalytic activity of SnS$_2$ electrode towards the nitro-aniline chemical. The sensing parameters of fabricated nitro aniline chemical sensor with SnS$_2$ nanoflakes electrode are evaluated by performing a series of the I-V measurements with different concentration of nitro-aniline in PBS.
Figure 3.35 (a) Typical I-V responses of SnS$_2$ nanoflakes in (GCE) in 10 ml, 0.1 mole/L PBS solution, (■) with nitro-aniline (15.6×10^{-6} mole/L) and (●) without nitro-aniline; (b) I-V response for various concentrations of nitro-aniline (from 15.6×10^{-6} mole/L to 1×10^{-3} mole/L) and (c) calibration curve.

To the best of our knowledge, it is the first report on the sensing behavior of SnS$_2$ nanoflakes electrode towards the detection of nitro-aniline. To investigate the detailed sensing performance of the SnS$_2$ nanoflakes modified electrode, systematic I-V measurement experiments have been done by varying the concentration of nitro-aniline in 10 ml of PBS (0.1 M). Figure3.35 (b) exhibits the I-V responses of SnS$_2$ nanoflakes modified GCE towards various concentrations of nitro-aniline (from 15.6×10^{-6} mole/L to 1×10^{-3} mole/L). It is clear from the observed graph that the current gradually increases as increasing the nitro-aniline concentrations ranging from 15.6×10^{-6} mole/L to 1×10^{-3} mole/L which reveals that the modified SnS$_2$ nanoflakes electrode based chemical sensor presents the good sensing response to the nitro-aniline. It is reported that incremental enhancement in current is related to the generation of ions and enlargement in ionic strength of PBS solution. In our case, the incremental addition of nitro-aniline might generate the large number of ions and hence increase the ionic strength of the solution.
For the evaluation of the sensitivity of the fabricated sensor, a calibration curve of current versus nitro-aniline concentrations has been plotted and shown in Figure 3.35 (c). Importantly, the calibrated current linearly increases up to the nitro-aniline concentrations of $\sim 0.5 \times 10^{-3}$ mole/L. This phenomenon suggests the good linearity of fabricated chemical sensor based on SnS$_2$ nanoflakes electrode in the range of $15.6 \times 10^{-6}$ mole/L – $0.5 \times 10^{-3}$ mole/L. In other words, the unique nanoflakes morphology of SnS$_2$ might provide the enough active sites over the surface of modified electrode, which results the high adsorption of nitro-aniline through SnS$_2$ nanoflakes electrode. The sensitivity of fabricated nitro-aniline sensor, was estimated by the slope of the calibrated current curve. A high and a reproducible sensitivity of a $\sim 505.82 \pm 0.02$ mA cm$^{-2}$ (mole/L)$^{-1}$ with the experimental detection limit of $\sim 15 \times 10^{-6}$ mole/L in a short response time of $\sim 10.0$ s is achieved by the fabricated nitro-aniline chemical sensor based on SnS$_2$ nanoflakes electrode.

To examine the stability of the fabricated chemical sensor based on SnS$_2$ nanoflakes electrode, the sensing responses of the fabricated sensor was measured for three consecutive weeks. After each experiment, the fabricated sensor was stored in phosphate buffer solution ($\text{pH}=7.0$). Interestingly, no significant decrease was observed in the sensing parameters for three weeks which conclude that the fabricated sensor possess good performance and stability. Finally, due to very specific morphology and various interesting physical and chemical properties, it is proposed that of SnS$_2$ nanoflakes is very potential, promising and effective electrocatalytic material for the detection of hazardous chemicals like nitro-aniline.

### 3.5.4 Conclusion

In summary, well-crystalline SnS$_2$ nanoflakes have synthesized by facile hydrothermal process at low-temperature. The detailed studies reveal that the synthesized products are well-crystalline nanoflakes and are grown in large quantity. The synthesized SnS$_2$ nanoflakes are used as efficient photocatalyst for photocatalytic degradation of Rhodamine B and as an electron mediator for the fabrication of reproducible and highly sensitive nitro-aniline chemical sensor. The photocatalytic degradation based on SnS$_2$ nanoflakes of Rhodamine B under visible light irradiation
exhibit about 61% degradation. The fabricated chemical sensor exhibits a very high sensitivity of \(~505.82 \pm 0.02 \text{ mA cm}^{-2} \text{ (mole/L)}^{-1}\) and experimental detection limit of \(~15 \times 10^{-6} \text{ mole/L}\) in a short response time of \(~10.0\) s. This research exhibits that the synthesized SnS\(_2\) nanoflakes can effectively be used as visible-light-driven photocatalysts and chemical sensors applications.
3.6 Electrical properties of solution processed p-SnS nanosheets/n-TiO$_2$ heterojunction assembly

3.6.1 Introduction

The IV–VI group semiconductors with orthorhombic crystal structure are recently recognized as most promising materials for various high-technological applications, to name a few, electronics, solar cells, and electrical switching devices, owing to their strong anisotropy of optical properties[321-324]. Among various tin sulphides (SnS, SnS$_2$, Sn$_2$S$_3$, Sn$_3$S$_4$, Sn$_4$S), SnS semiconductors are highly explored materials in numerous optoelectronics applications such as heterojunction and solar devices due to its unique optical band gap of 1.3 eV[323]. Typically, SnS semiconductor possesses layered orthorhombic structure and each Sn atom is surrounded by six S atoms via the coordination bond with weak Van der Waals forces.[325] Moreover, SnS is a p-type semiconductor and considered as promising materials for the fabrication of low-cost photovoltaic devices[326]. It is also a suitable material for the development of heterojunction devices.

Generally, for heterojunction devices, p-type SnS materials being the absorber material necessitates an n-type semiconductor material with wide band gap as heterojunction partner [151,152]. Various n-type semiconductors such as SnO$_2$, ZnO, CdS and ZnS could be expected the suitable heterojunction materials for p-type SnS [327]. Previously, M. Ichimura studied the theoretical estimation of band offsets in CdS/SnS heterojunction using the first principle, density functional and pseudo-potential method [328]. Noguchi et al., have fabricated CdS/SnS heterojunction by successive deposition of n-type CdS, p-type SnS and Ag on ITO coated glass substrate and utilized the fabricated assembly for solar cell applications.[329] Recently, some works are reported in the literature regarding the fabrication and photo-electrochemical/photovoltaic characterizations of SnS/TiO$_2$ heterostructure devices[283-285]. Wang et al., have prepared nanocrystalline SnS by chemical bath deposition process and studied the photovoltaic behaviour or SnS/TiO$_2$ assembly [330]. Recently, Jia et al., have demonstrated the synthesis of SnS/TiO$_2$ heterostructure nanotube arrays (NTAs) by successive ionic layer adsorption and
reaction process and examined the photo-electrochemical properties of SnS/TiO$_2$ heterostructure NTAs in liquid junction PEC solar cells [331]. In another report, Guo et al., have also exhibited the highly efficient inorganic–organic heterojunction solar cells based on SnS-sensitized spherical TiO$_2$ electrodes and reported in the literature [332]. Recently, Li et al., synthesized SnS nanoparticles with the diameter of 5.0–6.5 nm and prepared SnS/Carbon composite thin-film electrode for lithium ion batteries after carbonization at 650 °C.[333] SnS nanomaterials exhibit a variety of morphologies such as nanoparticles [334], nanowires [335], fullerene-like nanoparticles[336], and nanobelts[337].

In this thesis, we present a facile and low-temperature synthesis of SnS nanosheets by simple hydrothermal method and utilizes in the fabrication of p-SnS/n-TiO$_2$ heterojunction assembly. The synthesized SnS nanosheets were extensively characterized in terms of their morphological, structural and composition properties and the fabricated p-SnS/n-TiO$_2$ heterojunction device presents very good electrical properties.

3.6.2 Experimental details

Well-crystalline SnS nanosheets were synthesized by facile hydrothermal process using stannous chloride (SnCl$_2$.2H$_2$O) and thiourea (NH$_2$CSNH$_2$) as precursors and DI water as solvent. All the chemicals used for the synthesis of SnS nanosheets were purchased from Aldrich; and used as received without further purification. In a typical reaction process, appropriate amount of SnCl$_2$.2H$_2$O and NH$_2$CSNH$_2$ (weight ratio = 1:3), dissolved in DI water, were mixed well under constant stirring for 20 min. Consequently, the resultant solution was then transferred to Teflon-lined autoclave, which was sealed and heated up to 180°C for 3h and then cooled to room temperature naturally. Finally, black precipitates were collected, washed with ethanol and DI water and then dried at 80°C for 2h.

For heterojunction device fabrication, the nanocrystalline TiO$_2$ (P-25, Degussa) thin film electrode was obtained by the deposition of the TiO$_2$ (0.5 g of TiO$_2$ nanoparticles powder with 2ml of aqueous polyethylene glycol solution) onto the clean fluorine doped tin oxide (FTO) glass through simple doctor blade technique.
The active area of TiO₂ electrode is estimated to \( \sim 0.15 \text{ cm}^2 \). Afterward, the TiO₂ deposited FTO substrates were calcined at 450°C for 20 min in a static air furnace. The suspension of synthesized SnS nanosheets was obtained by the sonication in ethanol and the prepared TiO₂/FTO electrodes were dipped into the suspension to create a thin layer of SnS nanosheets and then annealed at 200°C for 15 min.

Finally, a thin layer of Pt deposited on SnS/TiO₂/FTO substrates by ion sputtering technique to achieve the p–n heterostructure of Pt/SnS/TiO₂/FTO. The current (I) - voltage (V) measurements were carried out at room temperature with an applied voltage ranges from −1 V to +1 V to evaluate the electrical properties of Pt/SnS/TiO₂/FTO.

### 3.6.3 Results and discussion

The general morphologies of synthesized products was examined by FESEM and demonstrated in Figure 3.36. Figure 3.36 (a) and (b) demonstrate the typical FESEM images of the synthesized SnS products, which reveal that the prepared materials possessing sheet-like morphologies and grown in very large quantity. The nanosheets are flat and irregular in shape and due to high-density growth; several instances the nanosheets are stacked and connected each other and forms nano-networks (inset b). The typical thicknesses of the synthesized nanosheets are in the range of 30±10 nm with the average dimensions of 500 ± 100 nm. For detailed morphological investigations, the as-synthesized SnS nanosheets were examined by transmission electron microscopy (TEM) equipped with high-resolution TEM (HRTEM) and shown in Figure 3.36 (c) and (d).
Figure 3.36(a, b) FESEM images, (c, d) TEM images, and (e) HRTEM image of as-synthesized SnS nanosheets.

The observed TEM result is fully consistent with the obtained FESEM images in terms of the morphologies and dimensionality. The nanosheets are grown in very high density and hence adjacent nanosheets are stacked and connected each other to form nanosheets interconnects. The typical thicknesses of the nanosheets are ~ 30 ±10 nm while the dimensions are in the range of 500 ± 100 nm. Figure 3.36 (e) exhibits the HRTEM image of as-synthesized SnS nanosheets and exhibits clear and well-defined lattices fringes, which confirm the highly crystalline nature of the prepared material. In addition to this, the distance between two lattice fringes are ~0.40 nm which corresponds to the (110) lattice plane of orthorhombic SnS.

To examine the crystallinity and crystal phases, the as-prepared SnS nanosheets were characterized by X-ray diffraction pattern measured with Cu-Kα Radiation (λ=1.54178Å) in the range of 20-80° and shown in Figure3.37 (a). Several well-defined diffraction reflections are seen in the observed pattern which can be indexed to the pure orthorhombic structure of SnS and well matched with the reported JCPDS card no. 39-0354.
The chemical composition and purity of as-synthesized SnS nanosheets were examined by Fourier transform infrared (FTIR) spectroscopy (Figure 3.37(b)), measured at room temperature, in the range of 400-3000 cm\(^{-1}\). Several well-defined absorption bands were observed in the spectrum at 632, 1399 and 1651 cm\(^{-1}\). The origination of a strong and well-defined absorption band at 632 cm\(^{-1}\) in the spectrum is due to the formation of Sn-S bond [227]. Moreover, the presence of two weak peaks at 1399 and 1651 cm\(^{-1}\) are due to the formation of C-H and C-O bands, respectively [227]. Therefore, due to the presence of a strong Sn-S bond, it is confirmed that the synthesized nanomaterial is SnS without any significant impurity.

Figure 3.37(a) Typical XRD pattern (b) FTIR spectrum and (c) Raman-scattering spectrum of as-synthesized SnS nanosheets.
To examine the detailed structure and bonding states, the as-synthesized orthorhombic structured SnS nanosheets were characterized by Raman spectroscopy. Well-defined peaks at 101, 166, 192, and 206 cm\(^{-1}\) are observed in the Raman-scattering spectrum, which confirmed that the synthesized nanosheets are pure SnS. The Raman peaks at 101 and 166 cm\(^{-1}\) are assigned to A\(_g\) and B\(_{3g}\) modes, respectively. The appearance of well-defined peak at 192 cm\(^{-1}\) can be assigned as A\(_g\) mode, however, a peak shown at 206 cm\(^{-1}\) is related with B\(_{1g}\) mode. The observed Raman-scattering results of SnS nanosheets are well matched with the reported literature [68,338].

For the fabrication of heterojunction diode, TiO\(_2\) nanoparticles were coated on FTO glass substrate by using doctor blade technique and later the prepared SnS nanosheets were deposited on the FTO/TiO\(_2\) assemblies via dip coating. Figure 3.38 (a) exhibits the typical cross-section FESEM image of TiO\(_2\) nanoparticles coated on the FTO glass substrate which reveal that the TiO\(_2\) nanoparticles are finely coated on the FTO substrate surface. Figure 3.38 (b) demonstrate the cross-section FESEM image of the p-SnS /n-TiO\(_2\)/FTO heterostructure assembly. From this figure, it is clear that the SnS nanosheets are uniformly coated on the TiO\(_2\) nanoparticles.
I-V characteristics of the fabricated p-SnS/n-TiO$_2$ heterostructure assembly is studied at room temperature in the forward and reverse bias conditions shown in Figure 3.38 (c) - (d). The obtained results illustrate a rectifying behavior for the fabricated junction, which is clearly indicated by the exponential increase in the
forward current with increase in voltage, as shown in Figure 3.38 (c). It can be shown that the junction exhibits a diode-like behavior with an on-set threshold voltage in the range of 0.4-0.75V with a corresponding current between 0.0112 and 0.2366 mA. At a forward bias of voltage ~ 1V the current reaches a value of 0.78 mA. In the reverse-bias, however, an on-set threshold voltage between 0.65 and 0.8 V gives leakage currents 0.004 and 0.051 mA, respectively. Moreover, a reverse leakage current of 0.335 mA is obtained at reverse breakdown voltage of ~ 1V.

Additionally, Figure 3.38 (d) displays the I-V characteristics of fabricated p-SnS/n-TiO$_2$ heterostructure assembly under light illumination, which carries the light-generated current. The nature of I-V curve is different from the I–V characteristics under dark condition, suggesting the absorption of photons by the fabricated device for the generation of current under light illumination. Fabricated p-SnS/n-TiO$_2$ heterostructure assembly shows the reasonable short circuit current ($J_{SC}$) of ~24.2 $\mu$A and open circuit voltage ($V_{OC}$) of ~0.455 V. Thus, the fabricated p-SnS/n-TiO$_2$ heterostructure assembly poses a photovoltaic behavior itself without using any liquid junction. Moreover, the junction exhibits the optimal rectifying ratio of 7.65 at V= 0.5 V. The barrier height is obtained using the relation

$$I_0(T) = A A^* T^2 e^{-\left(\frac{eV_{eff}}{kT}\right)} \quad \text{.......... (3.13)}$$

Here $I_0 (T)$, $e$, $k$, $A$ and $A^*$ are temperature-dependent saturation current, electronic charge, Boltzmann constant, the contact area and Richardson constant, respectively.

The barrier height is calculated and found $V_{eff}$ ~ 0.634 V when Richardson constant of $A^* = 24 A \, cm^{-2} \, K^{-2}$ for p-SnS and contact area $A = 4.55 \, mm^2$ are used. The quality factor $n$ is calculated using the well-known formula that relates junction current to applied voltage, i.e.

$$I = I_0(T) e^{\left(\frac{eV}{nkT}\right)} \quad \text{.......... (3.14)}$$

The series resistance of the device of ~ 270 $\Omega$ is evaluated from the slope of I-V plot at higher voltages of Figure 3.38 (c). This high value of series resistance may be due to surface structure resulted from metal contacts formed on the semiconductor.
material or/and from the top Pt thin layer, shown in Figure 3.38 (e), which was deposited by ion sputtering to form Pt/SnS/TiO$_2$ diode. This high value of resistance may act as a shunt resistance that leads to a partial drop in the output current of the whole structure. The saturation current $I_s (T)$ (used in equation 3.13) is obtained from the intercept of straight line fit in region I of Figure 3.39 (a).

![Figure 3.39(a) ln (I) versus V plot and (b) ln (I) versus ln (V) plot of Pt/SnS/TiO$_2$/FTO heterojunction diode.](image)

The value of $n$ is obtained from the slope of the graph of $ln (I)$ versus $V$, in Figure 3.39 (a). A higher value of 31 in region I, $V < 0.3$ V, than that of 4.74 in region II, $V > 0.3$ V is resulted. The high value of $n$ may be attributed to several factors like high lattice mismatch, thermionic emission, and minority carrier injection and recombination.

The higher value of $n$ which measures the conformity of the diode to pure thermionic emission is the one that is extracted from the slope of region I. Figure 3.39 (b) shows $ln (I)$ versus $ln (V)$ plot. Two different regions are distinctly seen. At region I, $V < 0.3$ V, the current is linearly dependent on the voltage, which indicates transport mechanism obeying Ohm's law. However, at region II, $V > 0.3$ V, the transport mechanism of the heterojunction device dominated by recombination tunneling which manifests itself by the exponential dependence of the current on the voltage.
3.6.4 Conclusion

In summary, well crystalline SnS nanosheets were synthesized by facile hydrothermal process at low-temperature and utilizes for the fabrication of heterojunction assembly in which SnS nanosheets were used as p-layer and nanocrystalline TiO$_2$ as n-layer. The detailed morphological, structural and compositional characterizations revealed that the synthesized SnS nanosheets are pure, uniformly grown in high density with well crystallinity. The fabricated Pt/SnS/TiO$_2$/FTO heterojunction diode exhibits the non-linear nature with the rectifying ratio of 7.65 at 0.5V, which indicates the weak rectifying behavior of diode. Pt/SnS/TiO$_2$/FTO heterojunction diode presents significantly improved electrical properties with high current of 0.78 mA at 1V. These improvements might be attributed to the formation of Schottky junction at the interface of Pt and SnS/TiO$_2$ layer, and the good charge carrier transportation at junction through high crystallinity of SnS nanosheets. Although the barrier height of 0.634 eV is relatively high, the carriers can flow through the interface states via the tunneling process.
Conclusion and Future work
4.1 OVERALL CONCLUSION

Developments in nanotechnology are dependent on the availability of new materials, and the ability to design and synthesis new nanostructured materials. Semiconductor nanostructures are of great interest partially due to their flexibility of allowing control of their electronic and optical properties. By studying these properties, we can better understand the materials and tailor them for advanced applications. These materials have attracting worldwide attention due to their exceptional electrical, optical, and magnetic properties, and their potential applications in nanoscale electronics, photonics, and functional materials as well. The main aspects of this thesis were the synthesizing, characterizing and device application of the semiconductor nanostructures.

This thesis divided into four chapters; the first chapter gives a brief overview on semiconductors, semiconductor nanostructures, and some of the semiconductor nanostructures synthesis techniques. The investigated materials investigated in this work also have been introduced in terms their techniques of synthesis, their properties and applications. Short descriptions of the investigated semiconductor nanomaterials and aimed applications, such as sensing, photocatalytic and heterojunction diodes, are also demonstrated in this chapter.

In chapter 2 we generally introduce the synthesis techniques of the investigated materials. All the materials were prepared by the facile hydrothermal method. The as synthesized materials were characterized in terms of their structural, morphological, optical, compositional and electrical properties, and their sensing properties. The prepared nanomaterials were used for various applications such as sensing, photocatalytic and heterojunction diodes.

Chapter 3 provides detailed information about the materials under investigation including a literature review, synthesis characterization, and application. detailed characterizations and applications of various semiconductor nanomaterials. With a brief introduction, and concise experimental details, the results and discussions of each section will be presented in detail. Most of the investigated semiconductor nanomaterials presented in this thesis were synthesized by facile hydrothermal
process and characterized in detail in terms of their morphological, structural, compositional and optical properties. In section 3.1 a feasibility study layered hexagonal disks of CuO were synthesized on a large scale via low-temperature hydrothermal growth process at 130 °C by using copper nitrate, hexamethylenediamine (HMDA) and NH₄OH. The detailed morphological examinations by FESEM and TEM show that the synthesized structures made by the layer-by-layer accumulation of several small sheets, which finally arranged themselves in hexagonal shape. The detailed structural investigations revealed that the synthesized CuO structures possess well crystalline and monoclinic structure and the UV-Vis absorption spectrum indicates the existence of slightly blue shifted indirect and direct band gaps. A plausible growth mechanism has also been proposed for the successful formation of layered hexagonal disks of CuO. The indirect band gap was found to be 1.27 eV (1.24 eV from the diagram of the first derivative inset (b) of Figures 3.6) and the direct band gap is 3.45 eV (3.73 eV from the diagram of the first derivative inset). The indirect and direct band gap values are slightly blue shifted in compared to the literature (1.2 eV and 3.25 eV, respectively). The blue shift in the indirect and direct band edges is due to the quantum confinement effect.

Section 3.2 Presents detailed information on the fabrication of highly sensitive, robust, reliable and reproducible 4-nitrophenol (4-NP) chemical sensor based on CuO nanocubes. The CuO nanocubes were characterized in detail for their morphological, structural and optical properties. The observed lattice fringes are very clear and well defined that verifies the well crystallinity of as-synthesized nanocubes. Moreover, the distance between two parallel lattice fringes was measured and found to be ~0.27 nm corresponding to the [110] crystallographic plane of monoclinic CuO. FT-IR spectrum of as-synthesized nanocubes showing various well-defined absorption bands at 451, 530, 601, 1381, 1632 and 3450 cm⁻¹. The peaks appeared at 451, 530 and 601 are related to ν(Cu-O) modes and confirms the formation of monoclinic CuO nanocrystals. The obtained indirect band gap was 1.21 eV while the direct band gap was calculated to be ~3.64 eV. The indirect and direct band gap values are blue shifted in comparison to the bulk values (1.2 eV and 3.25 eV, respectively). It is believed that the blue shift in the indirect and direct band edges could be due to the
quantum confinement effect. The as-synthesized CuO nanocubes were used as efficient electron mediators for the fabrication of 4-nitrophenol chemical sensor by simple I-V technique. High-sensitivity of ~132.84 ± 0.02 mA.cm².(mol L⁻¹)⁻¹ and detection limit of ~5×10⁻⁹ mol L⁻¹ in a short response time of ~10.0 s were observed for the fabricated 4-nitrophenol sensor. This work shows that simply synthesized CuO nanostructures have great potential for the fabrication of efficient and reliable chemical sensors.

**Section 3.3**, reports the high-yield facile synthesis, detailed characterization and photocatalytic application of α-Fe₂O₃ nanoparticles. The synthesis was done via simple hydrothermal process by using aqueous mixtures of iron chloride, hexamethylenediamine and NH₃·H₂O at low temperature of 110 ºC. The detailed structural characterizations and composition of the as-synthesized nanoparticles were investigated by using X-ray diffraction (XRD), high-resolution TEM (HRTEM), energy dispersive spectroscopy (EDS) attached with FESEM and Fourier transform infrared spectroscopy (FTIR) which substantiated that the as-synthesized nanoparticles are well crystalline and pure α-Fe₂O₃. The UV-Vis absorption spectrum of the synthesized nanoparticles demonstrated the existence of two optical band gaps that correspond to direct and indirect transitions, respectively. From the absorption spectra, one can see that the absorption intensity of MB was decreased with increasing the irradiation time, which confirms that the degradation of MB was increased with increasing the visible light exposure time. It is also concluded from the absorption spectra that the degradation of MB begins once the irradiation started. The as-synthesized α-Fe₂O₃ nanoparticles exhibit good photocatalytic properties on photocatalytic degradation of methylene blue.

Section 3.4 deals with the effective utilization of Fe₂O₃ nanoellipsoids for the fabrication of highly sensitive aqueous ammonia chemical sensor by I-V technique. The as-synthesized α-Fe₂O₃ nanoellipsoids were characterized in terms of their morphological, structural and optical properties. The detailed structural and optical properties confirmed the rhombohedral α-Fe₂O₃ structure and indirect (1.87 eV) and direct (2.15 eV) band gap, respectively, for synthesized nanoellipsoids. The fabricated aqueous ammonia sensor based on nanoellipsoids exhibits very high and reproducible
sensitivity of $\sim 4.678 \, \mu A.cm^{-2}.mM^{-1}$ and detection limit $\sim 0.04 \, nM$ with correlation coefficient ($R$) of 0.995 in short response time (10.0 sec). The presented work demonstrates that simply synthesized iron oxide nanostructures can efficiently be used for the fabrication of reliable and reproducible chemical sensors. The estimated sensitivity of the fabricated sensor is relatively higher than previously reported ammonium hydroxide sensor fabricated based on the utilization of nanomaterials, composite and/or materials modified electrodes.

Section 3.5 demonstrates that the detailed morphological studies of the prepared SnS$_2$ revealed that the synthesized products were nanoflakes and were grown in large quantity. The XRD pattern and detailed compositional studies confirmed that the synthesized SnS$_2$ nanoflakes were well-crystalline and possessing hexagonal SnS$_2$ phase. The prepared SnS$_2$ nanoflakes were used as efficient photocatalysts for photocatalytic degradation and effective electron mediators for the fabrication of chemical sensor. The photocatalytic properties of SnS$_2$ nanoflakes towards the photocatalytic degradation of Rhodamine B under visible light irradiation showed reasonably good degradation of $\sim 61\%$. Moreover, the as-synthesized SnS$_2$ nanoflakes were used as efficient electron mediators for the fabrication of nitroaniline chemical sensor by simple $I$-$V$ technique. Very high-sensitivity of $\sim (505.82 \pm 0.02) \, mA.cm^{-2}(mole/L)^{-1}$ and experimental detection limit of $\sim 15\times10^{-6}$ (mole/L) in a short response time of $\sim 10.0 \, sec$ with LDR in the range of $15.6\times10^{-6}$ (mole/ L) to $0.5\times10^{-3}$ mole/ L were observed for the fabricated nitroaniline chemical sensor [216, 237, 238]. The observed results indicated that the SnS$_2$ nanoflakes can efficiently be used as visible-light-driven photocatalysts and the fabrication of ultra-high sensitive chemical sensors.

Section 3.6 introduces the synthesis of well crystalline SnS nanosheets via facile hydrothermal process at low-temperature and utilizes for the fabrication of heterojunction assembly in which SnS nanosheets were used as p-layer and nanocrystalline TiO$_2$ as n-layer. The detailed morphological, structural and compositional characterizations revealed that the synthesized SnS nanosheets are pure, uniformly grown in high density with well-crystallinity. The fabricated Pt/SnS/TiO$_2$/FTO heterojunction diode exhibits the non-linear nature with the
rectifying ratio of 7.65 at 0.5V, which indicates the weak rectifying behavior of diode. Pt/SnS/TiO$_2$/FTO heterojunction diode presents significantly improved electrical properties with high current of 0.78 mA at 1V. These improvements might be attributed to the formation of Schottky junction at the interface of Pt and SnS/TiO$_2$ layer, and the good charge carrier transportation at junction through high crystallinity of SnS nanosheets. Although the barrier height of 0.634 eV is relatively high, the carriers can flow through the interface states via the tunnelling process.

Finally, it is concluded that the presented work in this thesis has explored the successful synthesis, characterization and applications of various semiconductor nanomaterials prepared by facile and simple hydrothermal process. The synthesized semiconductor nanomaterials were used in various applications such as photocatalytic, sensor and heterojunction diodes. The detailed studies presented in this thesis, it is obvious that the simply synthesized semiconductor nanomaterials can efficiently be used for variety of applications. Finally, I hope that the work presented in this thesis has contributed in some or other way in the synthesis, characterization and potential applications of some potentially important semiconductor nanomaterials.
4.2 FUTURE WORK

Some of the suggestions and future work
Detailed investigation on growth mechanism of the studied materials is required for understanding their role in chemical sensor, photocatalitic degradation application to improve their properties.

Structural, optical properties and electrical properties should be addressed in detail by introducing these materials with different morphology.

Comparisons between N-type, and P-type semiconductor nanostructure chemical sensor application in terms of their morphology such α-Fe₂O₃ nanoellipsoids, SnS₂ nanoflakes and CuO nanocubes.

- Pt/SnS/TiO₂/FTO heterojunction diode of SnS nanosheets exhibits non-linear nature leads to a weak rectifying behavior of diode, detailed characterization of the electrical properties in this regard should be introduced.

- Studying doped metal oxide semiconductor nanostructure in terms of their structural, chemical, gas sensing application and their field emission applications.

- Supercapacitors fabrication utilizing metal oxides nanostructures such as ZnO or α-Fe₂O₃.
5 References


[65] Ed. Ahmad Umar, Y. B. Hahn, “Metal Oxide Nanostructures and Their Applications”, 5 Vol. Set, American Scientific Publishers, Los Angeles, USA

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