Photocatalytic Applications of Graphene Oxide Decorated Zinc Oxide Nanoparticles

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INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD IIUI

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FINAL APPROVAL

It is certified that the work presented in this thesis entitled

“Photocatalytic Applications of Graphene Oxide Decorated Zinc Oxide Nanoparticles”
by

Ms. Salma Danish bearing **Registration No. 334-FBAS/MS PHY/S15** is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad.

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A thesis submitted to

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MS in Physics (Nanotechnology)

Declaration

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Salma Danish

SALMA DANISH

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DEDICATED

To

My Parents

&

Husband

Acknowledgement

Firstly, all praises are to **Allah Almighty**, the Most Merciful and Beneficent, who enabled me to complete this thesis work, and His Holy Prophet Muhammad (SAW), the most Perfect among all ever born on earth, and forever being the light of guidance and knowledge for humanity.

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List of Abbreviations:

Abbreviation	**Meaning**
ZnO	Zinc Oxide
GO	Graphene Oxide
XRD	X-ray diffraction
SEM	Scanning electron microscopy
FTIR	Fourier Transform Infrared Spectroscopy
EHPs	Electron hole pairs
e^-	Electron
cb	Conduction Band
h	Hole

Abstract

This work reports on synthesis of graphene oxide decorated zinc oxide nanoparticles for photo catalysis using wet chemical method. Graphene Oxide sheets are successfully coated on Zinc Oxide Nano rods. Different samples are prepared with different ratio of Graphene oxide while keeping the amount of ZnO constant to study the effect of coating of carbon based material on semiconductor. The catalyst samples are then characterized by using different techniques like X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy(FTIR). XRD results confirm hexagonal wurtzite structure of the composites. The nanocomposite shows high photo activity under the visible light because of small crystal structure, reduced recombination rate of electrons and holes and band gap value.

Chapter No. 1

INTRODUCTION

1. Photocatalysis:

With the passage of time rapid economic growth, development of industries, transportation, ecological problems and along with the environmental contamination, including contamination in air, water and soil becoming the severe confronts to the human beings [1]. These problems cause disturbance in environment and leads towards the disappearance of biological species. There must be a potential strategy which must be adopted to overcome the problems relating to energy crisis and environmental pollution to produce less toxic products like carbon dioxide and H_2O in case of degradation of organic pollutants [2]. Photocatalysis is a technique which has been used to remove organic compounds from waste water and convert the harmful compounds into simplest elements by mineralizing them. Photocatalysts with good photocatalytic activity and high stability are indispensable for exploiting the semiconductor-based photocatalysis technology into practical applications. On the horizon of material science, semiconductor photocatalysis has fascinated huge consideration from the past few decades because its prospective utilization to conversion of solar energy into electricity, water splitting and environmental purification [3]. Due to photo-stability, nontoxicity, chemical and biological inertness, light absorption, good charge transport property and low cost semiconductor based photocatalysis have been broadly used in heterogeneous (photo) catalysis, including hydrogen creation, water purification and air detoxification [4-5]. These characteristics mould them significance in practical applications as well as in research. Semiconductor photo catalysis is revolutionary technique for the eradication of toxic and organic pollutants from environment. In Heterogeneous photocatalysis exploitation of many semiconductors such as, TiO_2, ZnO, ZnS and CdS is involved. These catalysts are exposed to light of a suitable wavelength to produce highly reactive transitory oxidative species (i.e. $\cdot OH$, $\cdot O^{-2}$, and HO_2) for the mineralization of organic compounds and impurities. After TiO_2, ZnO is known as an excellent photo catalyst because it is cheap and nontoxic nature and strong oxidizing ability [1-4].

Photocatalysis was first introduced in 1839. The word photocatalysis is combination of two parts photo and catalysis where the prefix photo means "light", and catalysis is such a procedure in which a material is involved in changing the rate of a chemical conversion of the reactants into reactants without changing itself. Such a substance is known as the catalyst which

increases the rate of a reaction by reducing the activation energy. So, we can say that a reaction in which light is used to make a substance active and that substance changes the rate of chemical reaction without being involved itself is called photocatalysis. We can easily differentiate between conventional thermal catalyst and photocatalyst. Conventional thermal catalyst is activated by heat while photons of appropriate energy are used to activate photocatalysts.

There are two types of photocatalytic reactions:

- Homogeneous photocatalysis
- Heterogeneous photocatalysis

Researchers are focusing on heterogeneous photocatalysis because that type of catalytic reactions have many potential applications in many fields. This type of catalysis involves the formation of interface between a solid catalyst and a fluid containing reactants and products.

1.1. Photocatalytic oxidation:

A photocatalytic oxidation process is a process in which when a semiconductor absorbs a photon produces highly reactive radicals and these radicals are very good in oxidizing organic compounds [5]. In Catalysis, all the reactions or photo-induced molecular transformations occur on the surface of the catalyst. Main advantage of photocatalytic oxidation is that it provides free radicals in a very high amount. If we introduce low levels of photocatalytic oxidations into a room, this removes the odour of organic compounds, smoke, bacteria and fungi etc.

Photocatalytic oxidation replaces several methods like ozonation, chlorination and UV-C irradiation. These methods are dangerous and produce many by-products which are harmful for human health. These photo catalysts can be made either in powder form or in the form of film. These can be prepared very easily.

1.2. Mechanism of Photocatalysis:

In photocatalysis, all organic compounds are mineralized into carbon dioxide, mineral acids and water. Complete mechanism of reaction involved in photo catalysis as shown in figure 1.1. When a photocatalyst is illuminated by a very strong light which is much energetic then its band gap energy it excites electrons from valance to conduction band this result the formation of holes in valance band. These holes can produce highly oxidizing hydroxyl radicals. Holes also react with dye molecules or organic pollutants and degradation occurs.

Efficiency of a photocatalyst can be calculated the by measuring the number of reactions occur when one photon is absorbed. Number of reactions depends on following factors:

- Level of energy of photo excited electron hole pairs
- Rate of generation of electron hole pairs(EHPs)
- Fate of migration

Rate of generation of EHPs is dependent on many factors like energy and flux of irradiated photons and many optical absorption properties of our photocatalyst like surface area, size and band gap. Reaction that occur on surface of the particle and inside the particle regulates the fate of EHPs. e.g. Zinc oxide is considered as most efficient photocatalyst for the purification and detoxification of water because it can efficiently produce H_2O_2, its reaction and mineralization rate is very high and its surface is highly reactive as it has high number of active sites. [6,7] ZnO acts as substrate and H_2O and O_2 are considered as adsorbates. Chemical equations for the reaction are as followed:

$$\mathrm{ZnO + hv} \longrightarrow \mathrm{ZnO\ (e^{-}\ cb + h + vb)} \quad \dots\dots\dots\dots\dots\dots \ (1)$$

$$\mathrm{ZnO\ (e\text{-}cb + h + vb)} \longrightarrow \mathrm{ZnO + heat} \quad \dots\dots\dots\dots\dots\dots \ (2)$$

$$\mathrm{ZnO + H_2O(ads)} \longrightarrow \mathrm{ZnO + OH^{-} + H^{+}} \quad \dots\dots\dots\dots\dots\dots \ (3)$$

$$\mathrm{e\text{-}\ cb + O_2ads} \longrightarrow \mathrm{O_2\ e\text{-}\ \ cb + O_2ads\ O_2\text{-}} \quad \dots\dots\dots\dots\dots\dots \ (4)$$

$$\mathrm{h + vb + OH^{-}} \longrightarrow \mathrm{OH^{\cdot}} \quad \dots\dots\dots\dots\dots\dots \ (5)$$

$$\mathrm{OH^{\cdot} + Organics} \longrightarrow \mathrm{H_2O,\ CO_2} \quad \dots\dots\dots\dots\dots\dots \ (6)$$

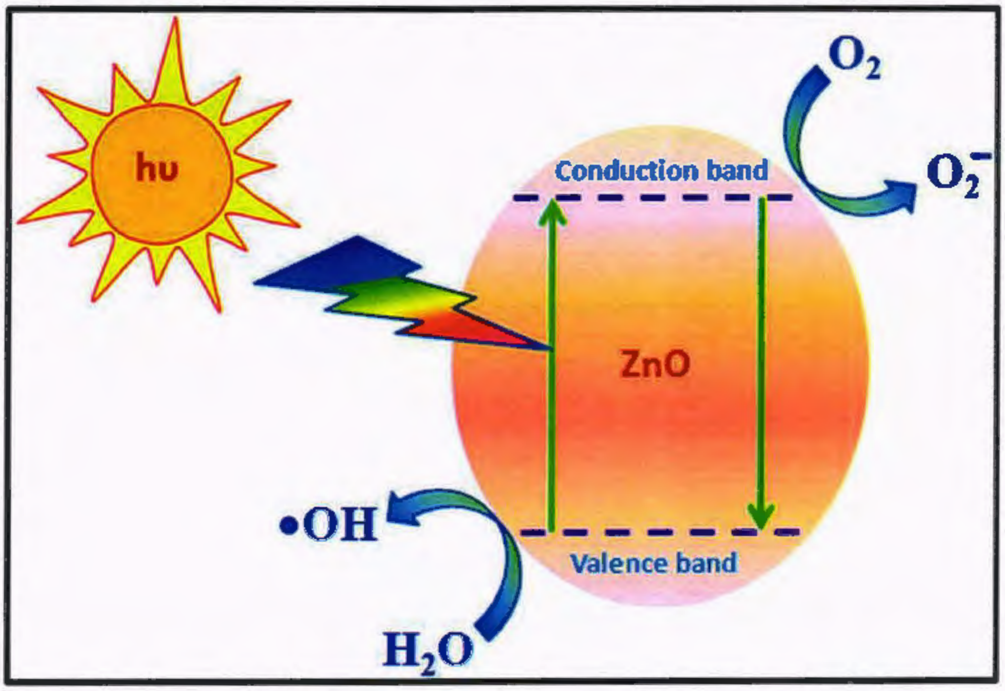


Figure 1.1: Photocatalytic mechanism of ZnO

Photocatalytic process utilizes in several applications e.g. to clean environment, water houses etc. pollution from air and water can be removed by developing this technology. Infections and diseases can also be decreased using this technology.

1.3. Metal Oxides as Photocatalysts:

Characteristic features of photocatalytic systems like desired band gap, suitable morphology, high surface area and stability which are essential for semiconductor photo- catalysts. Metal oxides for catalysis such as zinc oxide, tin oxide, cerium oxide, titanium oxide and chromium oxide are the best examples with significant features. These oxides follow primary photocatalytic oxidation process such as absorption of light. In this process metal is illuminated with UV or visible light. This causes photo oxidation of electrons from valance band to conduction band and generates electron hole pairs. In metal oxides, there are two sources of photocatalytic process:

- Generation of OH radicals by oxidation of OH^- anions
- Generation of O_2^- radicals by reduction of O_2

These anions and radicals are used to degrade organic compounds by reacting with these compounds. Among all metal oxides ZnO and TiO_2 are extensively used as photocatalysts because they have capability to produce charge carriers when illuminated with light. In addition, these oxides are biologically compatible and stable [8].

1.4. Introduction to ZnO:

Globally there is an extensive range of Nano sized semiconductors implicitly large applications as well as novel properties like optoelectronic, photoelectric energy conversion materials [9-13]. The combination of size as well as shape controlled metal oxide nanostructures are requisite to monitor their physical and chemical properties for their potential applications. In recent years, Optical properties of Nano-crystalline semiconductors have been studied. When there is the shrinkage of size of the material the band gap turns out to be bigger, that amends the optical as well as electrical properties of the material, which renders novel applications and devices with the various new techniques to alter the electrical as well as optical properties of a semiconductor by adding the impurities, or doping. An inorganic compound having formulation ZnO in white powder which is not soluble in water, and extensively utilize in various materials containing plastics, glass, rubbers, cement, ceramics and other lubricants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes.it is pertinent to mention here that its normally occurs as the mineral zincate, most ZnO has been fabricated synthetically [14].

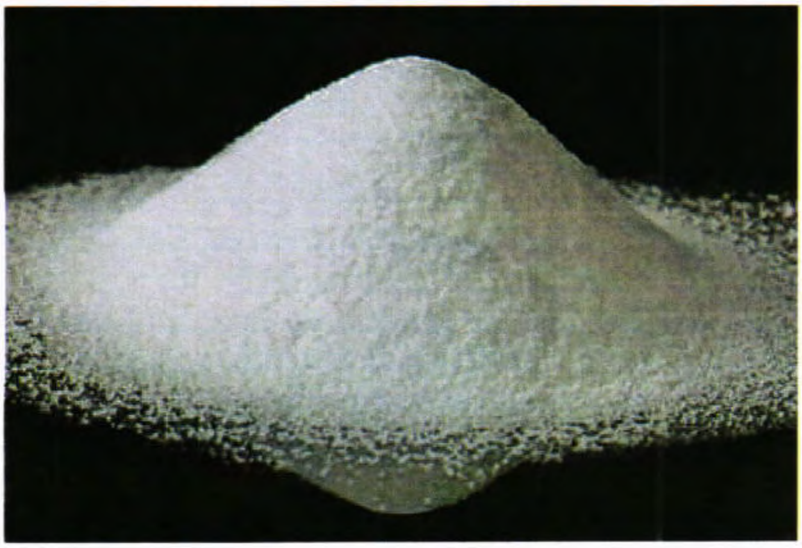


Figure 1.2: Powdered ZnO

Zinc oxide has a wide band gap which is 3.37 ev semiconductor of the periodic table II-VI Group. It is appropriate for short wavelength because of its band-gap (3.37ev) Due to the high exciton (B. E = 60 Mev) the Lattice of ZnO guaranteed systematic exciton emission at ambient temperature. It is indeed a requisite material having diverse applications and characteristics in near ultraviolet region as well as visible. Lattice structure of zinc oxide is Wurtzite, zinc blende, as well as rock salt however most stable lattice structure of ZnO is wurtzite also standard and common at room temperature.

1.4.1. Structure of Zinc Oxide:

The crystal lattice structure of ZnO has two foremost forms, hexagonal and cubic zinc blende. When at the standard room temperature condition, it is stable and the structure of zinc oxide is the most common. If the ZnO has been raised on substrates the zinc blende form has been formed with stable cubic lattice structure Because of both ways, Zn and O_2 centres are purely tetrahedral, maximum characteristic geometry of zinc is Hexagonal as well as zinc blende polymorphs does not possess inversion symmetry. These properties lead towards piezoelectricity of zinc blende and hexagonal zinc oxide as well as pyro electricity of hexagonal zinc oxide.

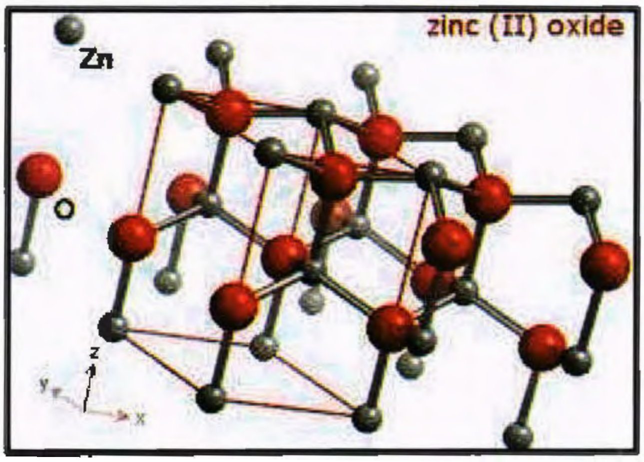


Figure 1.3: Structure of ZnO

Lattice constants are measured as a = 3.25Å and c=5.2Å and their c/a ratio is nearly equal to 1.60, this vale is very close to c/a ratio of hexagonal cell which is 1.633. Zinc oxide possess ionic bonding (Zn^{2+}_ O^{2-}). The corresponding radii of Zn^{2+} is 0.074nm and radii of O^{2-} is 0.140nm. These properties confirm the piezoelectricity of zinc oxide as well as development of wurtzite structure instead of zinc blende. Polar Zn-O bonds makes zinc and oxygen planes electrically charged [15].

1.4.2. Properties of Zinc Oxide:

Some of the properties of ZnO are tabulated below:

Table 1.1: Properties of ZnO

<table>
<tr><th colspan="5">Chemical Properties</th></tr>
<tr><th>Chemical symbol</th><th colspan="2">Group</th><th colspan="2">Electronic configuration</th></tr>
<tr><td rowspan="2">ZnO</td><td>Zinc</td><td>12</td><td>Zinc</td><td>[Ar] $3d^{10} 4s^2$</td></tr>
<tr><td>Oxygen</td><td>16</td><td>Oxygen</td><td>[He] $2s^2 2p^4$</td></tr>
<tr><th colspan="5">Chemical Composition</th></tr>
<tr><th colspan="3">Zinc</th><th colspan="2">Oxygen</th></tr>
<tr><td colspan="3">80.34%</td><td colspan="2">19.5%</td></tr>
<tr><th colspan="5">Thermal Properties</th></tr>
<tr><th colspan="3">Melting Point</th><th colspan="2">Boiling Point</th></tr>
<tr><td colspan="3">1975°C</td><td colspan="2">2360°C</td></tr>
<tr><th colspan="5">Physical Properties</th></tr>
<tr><th colspan="3">Density</th><th colspan="2">Molar Mass</th></tr>
<tr><td colspan="3">5600 kg/m^3</td><td colspan="2">81.40 g/mol</td></tr>
</table>

The various requisite properties of Zinc oxide semiconductor are as under:

- High electron Mobility
- Crystalline in nature
- Wide band Gap
- High Ambient Temperature Luminescence

Properties of zinc oxide was strongly relying on the lattice structure of the ZnO and the morphology, aspect ratio, size, orientation, and density of crystal. The zinc oxide properties were efficiently used in prototype applications Such as: saving energy and the protecting heat on windows, the crystals liquid displays made by zinc oxide used in transparent electrodes, as well as thin-film transistors electronics and (LED, s) light-emitting diodes. Zinc oxide guaranteed the efficient exciton emission at ambient temperature Due to the high exciton Binding energy (B. E= 60Mev) the Lattice of ZnO guaranteed systematic exciton emission at ambient temperature. Which is greater than GaN whose Binding energy (B. E=25Mev) consequently it is prominent photonic material in the Blue-UV region. [16] The zinc oxide Nano structures having electronic as well as optical properties are mostly relying on their composition as well as crystal lattice structure.

Zinc oxide when Synthesized with the aqueous solution has many benefits like, it is of low-cost, reaction temperature is very low and it can be used commercially. Crystal structure of initial crystal seed and the interaction of different crystal seed facets with capping agents determines the crystal morphology of the nanomaterials [17].

1.4. 3. Application of ZnO:

Globally there is a huge range of applications of metal oxides materials ascended in human civilization and the utilization of nano-sized particles are even more requisite. The ZnO nanoparticles are dependably in the focal point of consideration because of their intriguing properties and broad application.

It owns the extensive wide range applications potentials in

- Photocatalysis
- Environment
- Antibacterial activity
- Solar cells
- Optoelectronics
- Sensors
- Light emitting diodes(LED) [18]

A portion of alternate uses of zinc oxide nanoparticles are given underneath:

- Zinc oxide is utilized as a part of the produce of elastic rubber as well as cigarettes (utilized as a filter).
- Famously known calamine cream is made from zinc oxide powder. It is additionally utilized as a part of a large group of different creams and ointments that are utilized to treat skin diseases.

- As an additive in the manufacture of concrete.
- Ceramic industry has several uses for zinc oxide powder.
- It is also used as an additive in food products such as breakfast cereals.
- Various paints use zinc oxide as a coating agent [19].

1.5. Strategies to improve photodegradation efficiency of Znic Oxide:

In semiconductor photocatalysis main disadvantage is the recombination of photo generated holes and electrons. During recombination process quantum yield decreases and a large amount of energy is wasted. To ensure enhanced and efficient photocatalytic activity electron hole pair recombination should be stopped or lowered. This problem could be solved by doping a metal as doping enhances the charge separation between electrons and holes. In addition, generation of hydroxyl radicals and active oxygen species will increase, this result from enhancement in charge separation efficiency [20].

1.5.1. Coating of Graphene Oxide on Zinc Oxide:

If a covering is applied on the surface of substrate this is called coating. In recent years, the technique of connecting of graphene oxide and graphene with semiconductors is gaining great attention and this increases charge transport, photocatalytic activity and thermal conductivity. GO/ZnO hetrostructure is very useful for the inverted structure of hybrid solar cells, transparent electrode in optoelectronic devices, photocatalytic active devices and sensors [21-24]. ZnO is combined with metals, nonmetals and semiconductors to improve its photocatalytic activity. Graphene has very astonishing electronic properties and its specific surface area is very large. Its mechanical performance stabilizes the process of catalysis meanwhile it provides a two-dimensional plane to deposit catalyst. These characteristics enhances the chance of combination of GO with ZnO [25]. Most of researchers conducted studies to increase the photocatalytic activity in visible region which covers 46% of sunlight. Many factors involve in increasing the catalytic activity which includes extension of excitation wavelength by doping with anions or cations, reduction of charge carrier recombination by surface coupling with metals or semiconductors and increasing the number of photoactive regions by modifying the complete structure of catalyst [26-30].

When we mix graphene with metal or semiconductor then recombination of photo or electro chemically produced electron hole pair decreases and the process of photo-oxidation of impurities increases. This process occurs via active transfer of charge from semiconductor to graphene with electrical junction and from graphene to semiconductor using π-π exchange. When we coat a photocatalyst like ZnO It induces visible light activity by increasing the excitation wavelength to longer wavelength. GO/ZnO nanocomposite shows 10-fold enrich photo degradation activity as compared to GO or ZnO when visible light is used [31-33].

1.6. Graphene oxide (GO):

Graphene is the thinnest known material in the universe and the strongest ever measured. Its electrical conductivity is very high and strong mechanical properties. Because these characteristics GO is considered as best electron transport substance in catalysis when compared with C_{60} and graphite. When graphene sheet is modified with oxygen functional groups it is called graphene oxide [34]. It is also called graphitic oxide or graphitic acid. It is composed of carbon, oxygen and hydrogen which is gained by reacting graphite with strong oxidizers. When graphite is oxidized with strong oxidizing agents, oxygenated functionalities appear in the graphite layer which increases the separation of layer as well as makes material hydrophilic. By using this property one can exfoliate graphite oxide in water by using sonication which leads towards the generation of graphene oxide. Number of layers are the core difference between graphene oxide and graphite oxide. Graphite oxide contains on multilayers while graphene oxide consists of few layers. Graphene has very low chemical reactivity therefore graphene oxide is excellent material for chemical functionalization because it consists of many reactive oxygen functional groups [35].

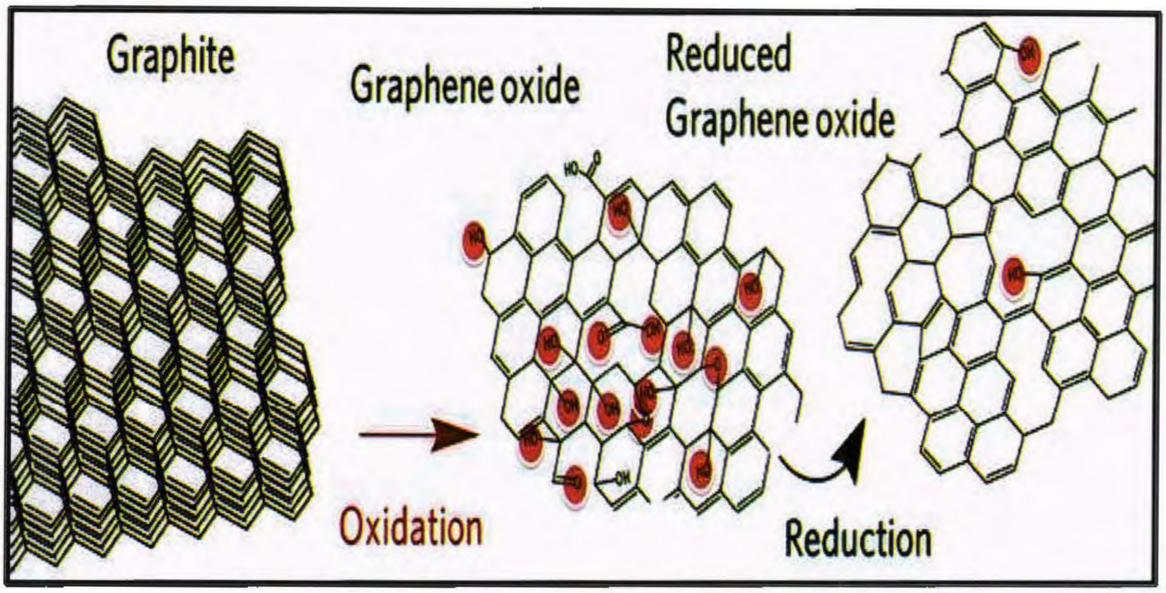


Figure 1.4: Oxidation and reduction of Graphite

1.6.1. Applications:

Graphene oxide has a wide range of applications in many fields. some are listed below:

- Graphene research
- Biomedical field
- Solar cells
- Batteries
- Supercapacitors
- Support for metallic catalysts
- Low permeability materials
- Biosensors

1.7 Specific Objectives of Work:

This research work has specific objectives which are described as follows:

- The purpose of this work is to enhance the photocatalytic activity of graphene oxide decorated zinc oxide under the UV irradiation. Firstly, the prepared catalysts were characterized thoroughly by Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy.
- Secondly the degradation of methyl orange is elevated under UV light illumination

Chapter No. 2

LITERATURE REVIEW

2.1. Zinc oxide:

In the past, few decades ZnO gained much attention because of its extensive usage in photocatalysis, solar cells, coatings, cosmetics, optics and electronics.

In 2016 Bishal Bhuyan *et. al* [36] synthesized ZnO nanomaterials using hydrothermal heating method. This is very effective and cheap method to synthesize zinc oxide nanoparticles. By using powder XRD pattern it is studied that the structure of ZnO NPs is hexagonal close pack and the average crystallite size is 21.93 nm. XRD pattern shows that these nanoparticles are pure and highly crystalline in nature. The shape of these nanoparticles is cylindrical having size of 20-50nm. These nanoparticles are very efficient for catalysis

Zhang *et al* [37] in 2002 worked on synthesis of flower shape zinc oxide nanoparticles by decomposing $Zn(OH)_2^{-\ 4}$ and $Zn(NH_3)_2^{+\ 4}$ in water and ethanol respectively. Solution based method is used. This method is helpful to control the morphology of zinc oxide. It is concluded that the morphology of zinc oxide is effected by changing solvent, precursor, reaction temperature and time, and solution basicity.

In 2012 P. M. Narayanan *et. al* [38] reported the fabrication of zinc oxide nanomaterials using NaOH and zinc nitrate. They used chemical (precipitation) method. They used these nanoparticles for antimicrobial activity. zinc oxide nanoparticles exhibit strong antimicrobial activity against all tested pathogens. With the decrease in particle size and concentration of zinc oxide nanoparticles the antibacterial activity increases.

Abdulaziz Bagabas *et. al* [39] in 2013 worked on synthesizing zinc oxide in different media and then used these particles for cyanide photodegradation. When zinc oxide is prepared in ethanol, the morphology of nanoparticles is polyhedral. When water is used, chunky particles are observed. Cyclohexylamine (CHA) is used to make precipitates, and zinc nitrate hexahydrate is used to extract zinc, in both water and ethanol. Calcined and uncalcined samples are obtained for both media. SEM investigation of uncalcined zinc oxide in ethanolic media shows that particles are homogeneously defined while uncalcined nanoparticles in water are irregular and overlapped.

Calcination of these two samples makes them regular and enhances nanoparticles 'features. Furthermore, results show that there is a great impact of medium on the photocatalytic activity. High efficiency of zinc oxide(ethanol) is noticed than that of zinc oxide in water to degrade cyanide.

In 2013 Donya Ramimoghadam *et. al* [40] reported green technique to synthesize ZnO flakes by using rice as bio template. By using different concentrations of rice different morphologies are obtained. Pore size and other features are template dependent. The main advantage of rice using as bio template is that it enhances the specific surface area of resulting nanoparticles. Zinc acetate and NaOH are used with rice powder.

P.N. Mbuyisa *et. al* [41] in 2015 reported hydrothermal method to synthesize zinc oxide nanorods. Direct current magnetron sputtering is used to deposit zinc oxide films. These films are used as template for the synthesis of zinc oxide nanorods. The density of nanorods is very high due to film and the dimension is non-uniform. ZnCl2 is used as precursor. Results shows that pressure of deposited film greatly influence the morphology of zinc oxide nanorods.

Peiyan Ma *et. al* [42] in 2011 published an article on the shape control synthesis of three-dimensional zinc oxide nanoparticles. They mainly focused on porous zinc oxide nanoparticles. These nanoparticles are synthesizing in aqueous solution. Sodium citrate, zinc acetate and hexamine are used. Amount of Sodium citrate and reaction time plays an important role in synthesizing different morphologies. XRD results shows that all structures show excellent crystalline nature. UV-vis absorption shows that zinc oxide exhibits excellent optical properties. These nanoparticles are used for photocatalytic applications

In 2014 Kai Loong Foo *et. al* [43] synthesized zinc oxide nanorods by using sol gel method and investigated their optical and structural properties. They used these nanorods for optoelectronic applications. They used 4 solvents which are ethanol, methanol, isopropanol and 2-methoxyethanol and studied the impact of these on structural properties of ZnO nanorods. Si substrate is used to grow zinc oxide nanorods. $[Zn(CH3COO)_2 \cdot 2H_2O]$ is used as precursor and monoethanolamine is used as stabilizer. SEM analysis shows that ZnO NRs have hexagonal-faceted morphology. The average diameter is approximately 20 to 50nm. XRD analysis shows that all samples are of hexagonal structure and have high orientation of c axis. Results shows that ZnO NRs prepared using 2-methoxyethanol exhibit best optical and structural properties. These NRs shows smallest grain size, highest band gap value and smallest crystallite size.

In 2014 Musarrat Jabeen *et. al* [44] synthesized ZnO NRs using hydrothermal technique. HMTA hexamethylenetetramine and zinc nitrate hexahydrate are used as reagents.

Hexamethylenetetramine works as a nonpolar chelating agent. XRD analysis shows zinc oxide possess wurtzite morphology with lattice a= 0.3288nm, b= 0.3288 c= 5.2054nm and the density of the nanorods is 5.68g/cm3. UV-vis analysis shows abrupt increase in absorption spectrum which indicates that nanorods are pure and crystalline. Then they used these nanorods for enhanced gas sensing applications.

Y. Dai et. al [45] in 2002 worked on synthesis of tetrapod like ZnO NRs and studied their optical properties. They formed these nanorods by the oxidation of Zn powder. Vapor solid mechanism is used to control the growth of nanorods. FE-SEM analysis confirms the tetrapod morphology of particles having four legs. The length of the legs is measured to be 2-3μm. XRD pattern shows that the sample is highly pure and crystalline in nature. TEM examination confirms the low density of structural defects. These tetrapod NRs can be successfully used as light emitting devices in nanoscale optoelectronic devices.

In 2002 Lin Guo *et. al* [46] reported a novel method to synthesize highly pure and crystalline zinc oxide NRs. They used dodecyl benzene sulfonic acid sodium salt sodium as modifying agent. NRs prepared by this method show high regularity and the crystals are well ordered. The diameter of the NRs is 150±10nm and the length is measured to be 2.17±0.13μm. SEM results shows that the shape of one end of the nanorod is well-faceted and the shape of another end is like hemispherical. Results show that increase in concentration of dodecyl benzene sulfonic acid sodium salt leads to rodlike structure. By using this method perfect single crystal can be achieved.

Gyu-Chul Yi *et. al* [47] in 2005 reported many physical and chemical methods for the synthesis of ZnO NRs like vapor phase synthesis, metal-organic chemical vapour deposition and hydrothermal synthesis. They then discussed wide range of properties and applications of these rods.

2.2 Graphene oxide:

In 2015 Paulchamy B *et. al* [48] reported Hummer's method to synthesize graphene oxide. They used graphite as starting material and modified it to expanded graphite using H2SO4 and NaNO3. Potassium permanganate plays significant role in synthesizing graphene oxide. Modified Hummer's method involves oxidation and exfoliation. XRD analysis shows a diffraction peak at

26° which confirms the presence of graphite and interlayer distance is found to b 0.34nm. XRD confirms the presence of oxygen functional groups. FTIR results indicate a broader peak at 2885cm-1 which is due to O-H stretching of water molecules. This proves that graphene oxide is highly absorptive material.

2.3 Graphene Oxide Coated Zinc Oxide:

To enhance the photocatalytic activity of zinc oxide it is coated with other materials like noble metals and carbon based materials. This reduces the rate of recombination of electron-hole pair. Shaohua Xu *et. al* [49] in 2015 prepared flower zinc oxide coated with GO composite having excellent photocatalytic activity. They used simple one pot hydrothermal method. $Zn(NO_3)_2.6H_2O)$ and Hydrazine are used to prepare ZnO flowers. Reaction is carried out at 140°C. SEM results shows that ZnO flowers contain rods bonding at one junction having length of 1μm. As they increase the amount of GO dispersion the size of the ZnO flower decreases. XRD analysis of pure GO shows a peak at 11.2° but this peak vanishes in all ZnO/RGO composites which indicates that GO is successfully reduced during hydrothermal treatment. A broader peak at 26° is observed when the amount of GO is increased. Red shift in UV confirms the reduction of GO. Photocatalytic activity is observed by measuring the degradation of MB. When GO is used as photocatalyst no degradation occurs which shows that GO is not a good catalyst. But when they introduced GO on ZnO flowers the composite shows enhanced photocatalytic activity. These composites can be used for practical applications in pollutant management.

Da Chen *et. al* [50] in 2015 used a simple facile lyophilization method to prepare graphene-wrapped ZnO nanospheres. Zinc acetate is used as precursor. Reaction is carried out at very low temperature. Results shows that the diameter of ZnO Nano spheres ranges from 100 to 400nm. Methylene blue is used as dye for photodegradation. ZnO-Graphene nanosperes shows good photocatalytic activity as compared to ZnO nanospheres. These Nano spheres are successfully used in photocatalysis, solar energy conversion and gas sensing applications.

In 2014 Fatin Saiha Omar *et. al* [51] worked on synthesis of ZnO/rGO nanocomposites using diethylene-triamine. They used facile microwave method. The main advantage of using diethylene-triamine is that it controls final morphology of the sample. Photocatalytic activity purely depends on the amount of GO added in the sample. Raman spectra confirms the presence of zinc oxide and carbon.

Xinjuan Liu *et. al* [52] in 2012 successfully synthesized ZnO/rGO composites with excellent photocatalytic activity and used these composites for the reduction of Cr(VI). Results shows that when RGO in the composite is 1% removal rate of Cr(VI) is 96%. Zinc sulphate is used as precursor to synthesize ZnO. XRD results shows the peaks of ZnO and no significant peak of RGO is observed this is since RGO is in very low amount. FTIR results shows that with the increase in amount of RGO in the sample, absorbance of the of the composite increases. Removal rate of Cr(VI) for Pure ZnO is 67%. This rate increases with increasing amount of RGO. Results shows that when RGO in the composite is 1% removal rate of Cr(VI) is 96%.

In 2015 Xiaofeng Wu *et. al* [53] reported hydrolysis-deposition method to synthesize ZnO-graphene flake like photocatalyst. Graphene oxide and zinc acetate are used as starting material while ammonia is used as reductant. XRD analysis shows that the particle size and crystallization of sample increases when we add GO in it. Good crystallization results in the reduction of number of defects. They used Brilliant Red as dye. Addition of GO increases the photocatalytic activity of the composite but too much amount of GO plays a negative role also. It decreases the photocatalytic activity.

S.V. Nipane *et. al* [54] in 2015 reported precipitation method to synthesize GO/ZnO nanorod nanocomposite to use as photo catalyst under UV light. GO is fabricated using modified Hummer's method. Zinc acetate, polyvinyl alcohol and GO is added in water and stirred for an hour. Then solution of NaOH is mixed in the mixture dropwise hydroxide is added dropwise, stirred, sonicated and heated on oil bath. Final solid product is washed, centrifuged and dried in an oven at 200°C to obtain GO/ZnO nanorod nanocomposite. By XRD analysis the average crystallite size of GO/ZnO nanorod nanocomposite is calculated which is 21.7nm. TEM analysis reveals that the size of ZnO NR on GO is 10-20nm. Methyl Orange and Methylene blue are used as dyes to observe photocatalytic activity. Results shows that degradation rate of Methylene blue is greater than that of Methyl Orange.

In 2016 Xiaoju Men *et. al* [55] developed an efficient method to synthesize three dimensional free-standing ZnO/GO foam like composite and used these composites for photocatalysis and photocurrent generation. Zinc acetate and sodium hydroxide are used for preparation of zinc oxide Nano rods. Ni foam is used as template to form Nanorods arrays. SEM images show that RGO has a porous structure and the size of the pores is about hundreds of micrometers. When ZnO/RGO foam grows ZnO adopts the porous structure. Furthermore, these results also show that ZnO NR's are perpendicular to the surface of substrate. XRD analysis confirms the hexagonal wurtzite structure of the sample. It also shows that sample is highly pure and crystalline in nature. Electrochemical method is used to study the photoelectric properties of the sample. At 1.0 V the current density of ZnO/RGO is measured to be 0.27mAcm^{-2} and sample shows a photo response.

Chapter No. 3

EXPERIMENTS

3.1. Synthesis techniques:

There are several methods reported for the synthesis of Graphene Oxide Decorated Zinc Oxide nanoparticles. In my work, I used wet chemical method to synthesize graphene oxide coated zinc oxide nanoparticles.

Some are wet chemical methods are listed below:

- Co precipitation method
- Sol Gel process
- Polyol process
- Hydrothermal deposition

I synthesized graphene oxide coated zinc oxide nanoparticles using co-precipitation technique.

3.1.1. Co-precipitation method:

It is a synthesis method in which a solute that we dissolve in a solution precipitates out. There are some chemical similarities between a carrier and solute. These similarities tend to bind both carrier and solute. In Co-precipitation, the metal cations form a common medium are precipitated in different forms like hydroxides, oxalates, carbonates, formats or citrates.

The next step includes calcination at suitable temperature to obtain final product in powder form. In this process, the mixing is on atomic scale, so low calcining temperature is required to form the final product hence it leads to lower particle size. Like all synthesis processes co-precipitation also required some special conditions It is also compulsory to maintain pH, temperature and concentration to get required form. This process is very useful because when we mix the reactant precipitates it reduces the overall temperature of the reaction. In addition, it is a simple method to obtain fine and highly reactive metal oxide powders.

Following are four types of co-precipitation.

- Occlusion
- Mixed crystal formation surface adsorption

- crystal formation
- Mechanical entrapment

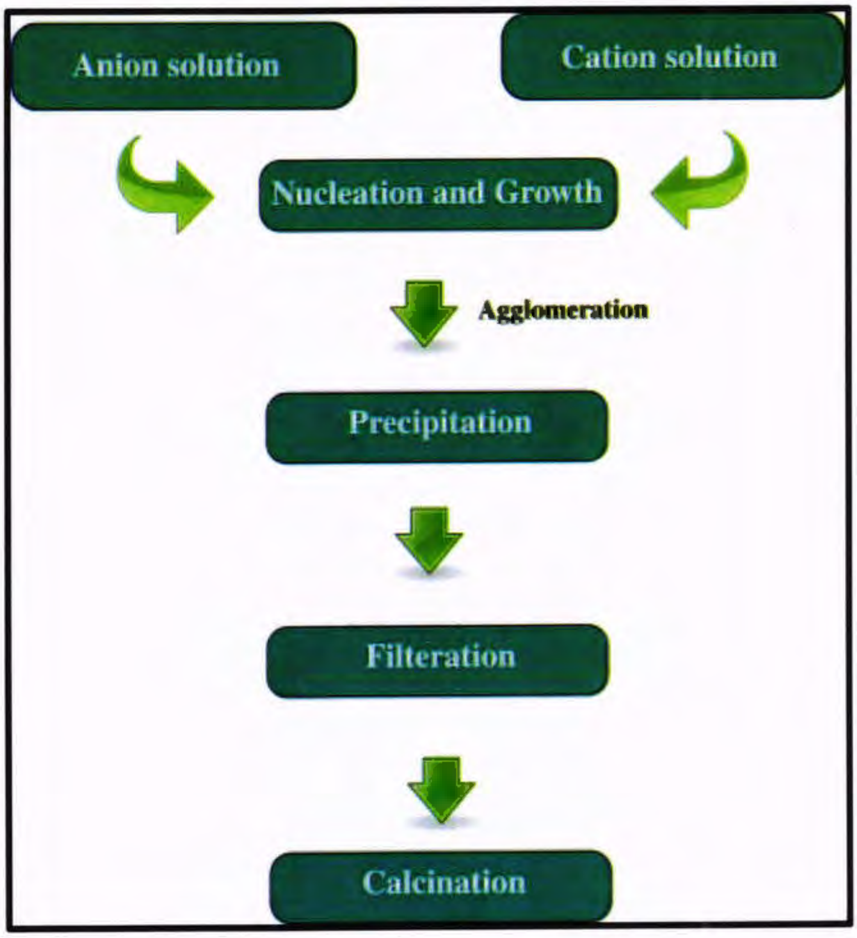


Figure 3.1: Co precipitation process

Table 3.1: Chemicals used

Reagents	Formula
Zinc Acetate Dihydrate	$Zn(O_2CCH_3)_2(H_2O)_2$
Sodium citrate	$Na_3C_6H_5O_7$
Hexamine	$C_6H_{12}N_4$
Ethanol	CH_3CH_2OH
Water	H_2O
Sulphuric Acid	H_2SO_4
Nitric Acid	HNO_3
Potassium bromide	KBr
Hydrochloric Acid	HCl
Hydrogen peroxide	H_2O_2

3.2. Synthesis of Graphene Oxide:

Graphene oxide is synthesized through Modified Hummer's Method. Expanded Graphite is used as precursor. To prepare expanded graphite 15ml of H_2SO_4 was added in 15 ml of HNO_3 dropwise to makbe a solution. In next step graphite powder was added to acid solution and kept it for 3 days. After 3 days soaked graphite powder was washed several times with distilled water and ethanol. After that mixture was centrifuged and dried at 60°C for 3 hours. Expanded graphite or graphite flake was obtained.

For Graphene Oxide, 40ml of H_2SO_4 is added in a beaker and stirred it for about 10 minutes at room temperature then 2.5g of expanded graphite is added in small intervals and stirred at room temperature. After stirring, beaker was placed in an ice bath and 7.5g of potassium permanganate ($KMNO_4$) was added in the beaker with intervals of 20 minutes and stirred slowly until a uniform liquid paste was formed. Ice bath was removed after the formation of this paste.

After the dark green paste achieved, stirring was stopped and deionized water was added to dilute this solution. Rapid stirring was carried out until a brown solution was formed. Then solution was placed in a water bath and subjected to uniform heating at 90^0C for 2 hours that gave dark green colour to solution again. After the removal of water bath, 2ml H_2O_2 was added in the solution. Yellowish bubbles started to appear.

Now the prepared solution was centrifuged to separate the particle. Then 1Molar solution of HCl was added and stirred slowly for about 3-4 hours. This solution was centrifuged again to obtain the particles. Deionized water was added to remove unwanted HCl and stirred for half an hour. Then solution was centrifuged again to obtain particles.

Final washing was carried out by adding ethanol and deionized water to wash out unwanted acid. Then above solution was Centrifuged to get separated particles. Final product was dried at 60^0C on heating plate and GO powder was obtained.

3.3. Preparation of graphene oxide decorated zinc oxide nanoparticles:

In a typical method 3.7g of Zinc acetate dihydrate was added to 350ml of distilled water and stirred for 10 minutes. After complete mixing 2.8g hexamine and 0.09g sodium citrate was added to above solution and stirred for 1 hour.

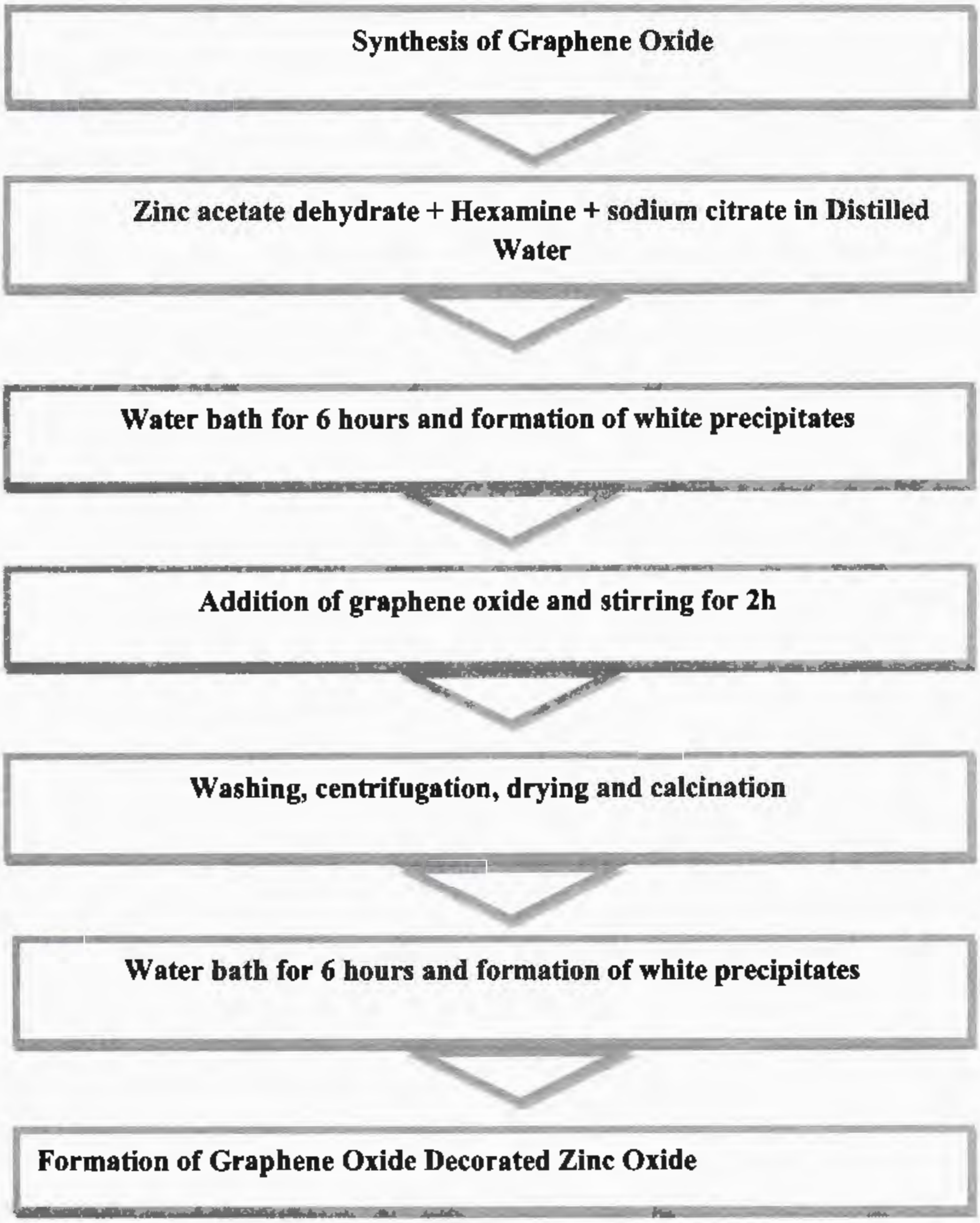
After that aqueous solution was transferred to 90°C water bath. After 6 hours of water bath, white precipitates were settled down in the beaker.

After white precipitates were formed, graphene oxide was added to the mixture and stirred for two hours. In the next step the solution was centrifuged and washed several times with distilled water and ethanol. Final product was dried at 90°C for 2 hours. A blackish powder was gained.

Obtained powder was calcined in a furnace at 200°C for 3 hours. Graphene Oxide decorated zinc oxide nanoparticles were formed.

In my work, I added 4 different concentrations of Graphene Oxide after the formation of white precipitates of ZnO to get 4 different samples. The different concentrations of GO are 1wt% GO, 2wt%GO, 5wt%GO and 10wt%GO.

Synthesis Flow Chart:



3.4. Characterization Techniques:

The most valuable aspect of materials research is the characterization of the fabricated materials that we use or study to acquire more knowledge about them. There are many important parameters of nanomaterials like texture and chemical surface that we use to check their properties. Characterization is a main point to study the properties of nanomaterials.

There are many parameters for the characterization of nanoparticles like surface area, porosity, solubility, particle size distribution, morphology, and aggregation.

To characterize nanostructures, we require some precautions. High sensitivity, atomic level resolution and accuracy is compulsory to obtain required accurate results. For this purpose, various microscopes are used. These microscopes are very good in measuring and characterizing nanostructured materials.

Various Spectroscopic methods are in use to visualize and magnify the structure of the sample. These techniques can be spectroscopic or can microscopic. Electrons and photons have dual nature. Hence by using these features of electrons and photons we can observe the materials in various techniques.

I used following techniques to examine nanomaterials:

- Scanning Electron Microscopy(SEM)
- Energy Dispersive Spectroscopy (EDS)
- X-Ray Diffraction Spectroscopy (XRD)
- Fourier Transform Infrared Spectroscopy (FT-IR)

3.4.1. Scanning Electron Microscopy (SEM):

Scanning electron microscopy is extensively used technique to study the structure of nanomaterials. In this microscope electrons are used instead of light. By using this technique morphology of nanostructured materials in nanometer to micrometer range can be studied and this gives magnified three-dimensional image of the surface of the nanomaterials. It has large depth of field as well as very high resolution so one can focus very large amount of sample at one time. Unlike traditional microscopes, electromagnets are used in SEM instead of lenses so that degree of magnification can be better controlled.

This technique has many advantages over optical microscopy as it provides topographical information and can analyze chemical composition near the surface. When electron beam interacts with the sample it provides different signals which contain thorough information about morphology, structure and surface characteristics.

SEM resolves morphology details less than of 50nm and it consist of a depth of focus 500nm times higher as compare with optical microscope with same magnification. This instrument is very fast and easily opera table.

3.4.1.1. Working of SEM:

In this technique, Sample is irradiated with a very fine beam of electrons. Thus, three types of electronic signals can be observed from the surface of the sample backscattered electrons, secondary electrons and auger electrons. In addition to electrons, a photon is also produced because of de-excitation of atoms in x-ray to visible range. These x-rays don't take any part in imaging rather these are used for chemical analysis of the sample. We can detect all electronic signals by using detectors. These signals establish image of the sample. We can obtain whole information of sample like surface morphology, structure, orientation and size.

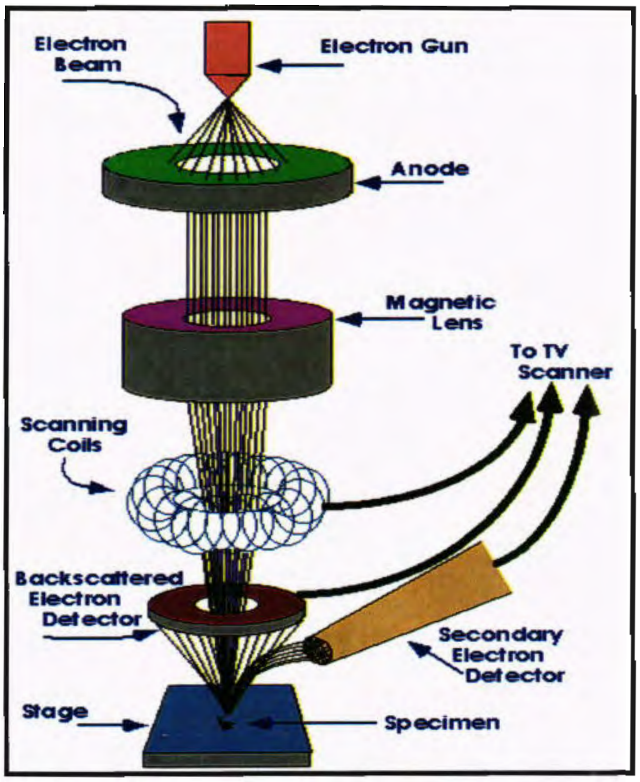


Figure 3.2: scanning electron microscope

3.4.2. Energy Dispersive Spectroscopy (EDS):

Energy Dispersive Spectroscopy (EDS) is a technique used for the investigation of chemical characterization and elemental composition of a specimen. When highly energized electrons are blassted on a sample in an electron microscope then this causes ejection of the electrons of surface atoms from inner shell. These ejected electrons create a vacancy. To occupy the hole, electrons from higher orbits moves towards lower orbits so characterisic X-rays are produced. X-ray mapping is used to analyse these X-rays. The top of the magnified image of the sample consists on the elemental composition of the specimen. This technique is used in SEM.

To classify the elemental composition of the specimen characteristic x-rays are used which are produced during transition process. To cllassify the elements, Xrays are used which generate during electronic transitions. Each element in the sample has itts own unique signal. So Energy Dispersive Spectroscopy is very useful in identifying a specific element along with its complete properties.

3.4.3. X-ray Diffraction Spectroscopy (XRD):

It is very important technique to characterize a sample in powder form. We can use it to determine the structure of the powder. Furthermore, it is used for phase analysis, detection of preferred orientation and determination of crystallite size. Phase and structure can be identified by the intensity and position of the peak. Different structural data like lattice parameters, lattice constant and porosity can be easily calculated. This tells us about that whether the material is crystalline, polycrystalline or amorphous. Phenomenon of constructive interference between x-rays and crystalline sample is observed. A cathode ray tube produces x-rays which are filtered, collimated and focused on sample.

3.4.3.1 Working of XRD:

Atoms, ions and molecules are regularly arranged in a crystal. A crystal consist of series of planes which are separated by distance ‘d’. ‘d’ is called inter planer distance. X-rays are electromagnetic waves with wavelength λ=0.5 to 2.5Å. This wavelength is approximately equal to inter atomic distance d of the solid material. Rays of longer wavelength cannot resolve the structure on an atomic scale and radiations of much smaller wavelength are diffracted through small angles. Crystal atoms are used to scatter X-rays. Theses scatter X-rays follow Interference phenomenon. When these rays are in phase, they produce constructive interference to form diffraction pattern in specific direction.

3.4.3.2. Bragg’s Law:

Bragg’s law is very useful to understand the diffraction pattern of the wavelength of the X-rays and the spacing between the atomic planes. When two monochromatic beams which are parallel fall on the crystal plane with an angle θ, they produce constructive interference. Bragg's condition can be applied on the path difference between two rays.

$2d\sin\theta = n\lambda$ (Bragg's law) 3.1

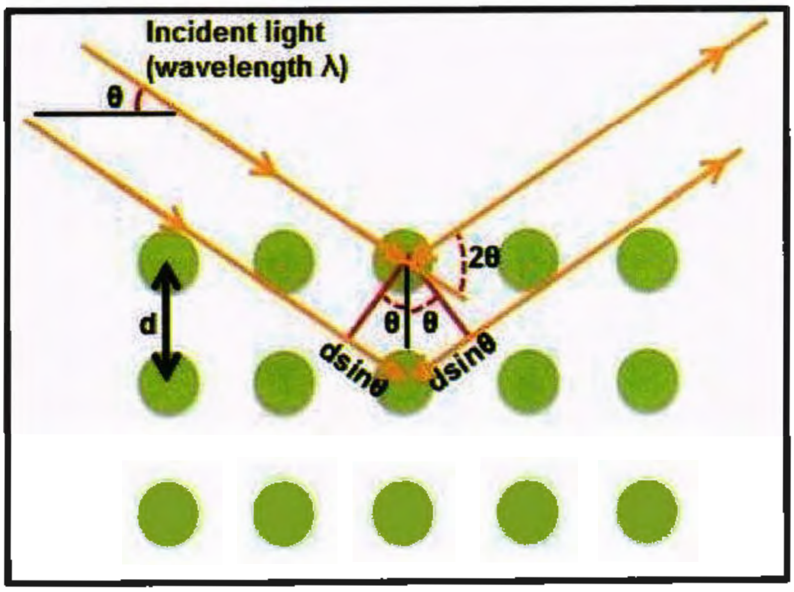


Figure 3.3: Schematic diagram of Bragg's Law

3.4.3.3. Calculation of crystallite size:

We can calculate particle's crystallite size by analyzing the expansion in X-ray line. Sometimes XRD pattern does not show sharp and broadened diffracted lines because of some defects in instrument. With the decrease in particle size the broadening of the lines increases. The broadening increases with decreasing crystallite size. We can use Debaye Scherrer's formula to calculate the crystallite size.

$d=0.9\lambda/(\beta\cos\theta)$..3.2

λ= wavelength of radiation

θ= Bragg's angle

β= Full width at half maxima

3.4.4. Fourier Transform Infrared Spectroscopy:

To attain infrared spectrum of emission or absorption of solids, liquids or gases we use a spectroscopic technique called Fourier transform infrared spectroscopy. It is used to identify the both organic and inorganic materials. It gives us high spectral resolution data.When the material is exposed to IR (infrared) rays passes through the material (sample), the characteristic FTIR spectrum is observed which gives the information of the relative molecular modes. Molecules have different characteristic vibrations in different modes thus they can only absorb the specific wavelengths of IR rays. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

3.4.4.1. Working of FTIR:

When we pass an infrared radiation through a specimen then molecules of the sample then molecules of the specimen absorb certain frequencies of radiation and due to this molecular vibration occur. Unique absorbed frequencies are associated with each molecule which gives information about a substance. An infrared source is used to fall the beam of IR light on a sample. The incident light ruptures into two components, one part is reflected towards fix mirror and other can transmit through moving mirror. Transmitted part of the light passes through the sample to provide information about sample.

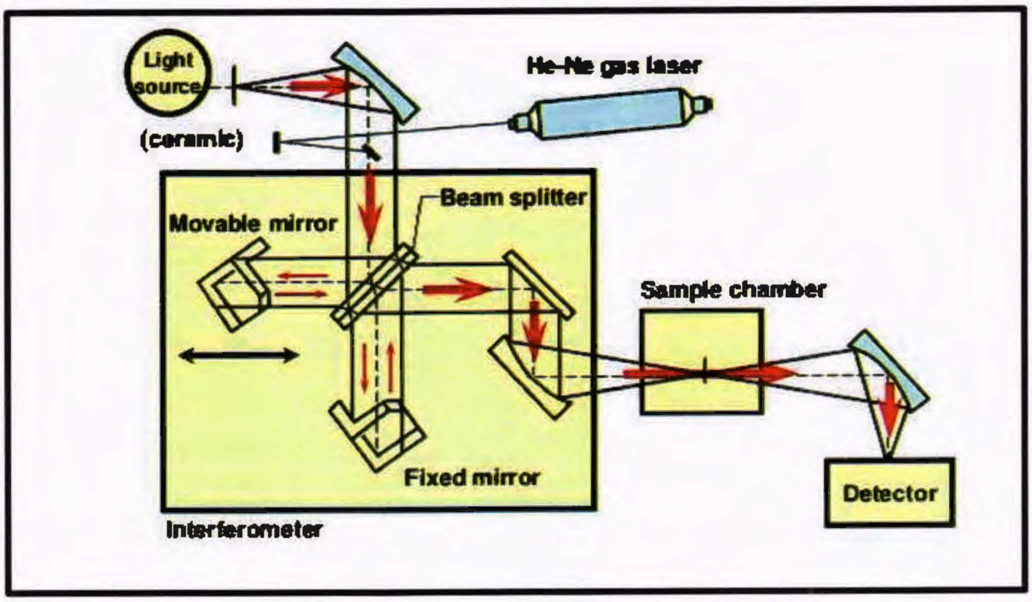


Figure 3.4: Working of FTIR

Chapter No.4

RESULTS AND DISCUSSION

The structural, chemical and morphological properties of the as prepared samples are examined by using SEM, EDS, XRD and FTIR. Morphology and particle size is checked by SEM. Detailed elemental composition is studied using EDS. Structural properties of the sample are analyzed using XRD. FTIR spectroscopy is performed to determine the chemical bonding.

Results and studies showed that as prepared samples are highly pure.

4.1. Scanning Electron Microscopy (SEM):

The morphologies and microstructures of different samples are revealed by SEM images. Figure4.1 depicts the SEM images of zinc oxide nanoparticles at different magnifications. In figure 4.1a and 4.1b, a dense network formation is exposed which confirms that ZnO nanoparticles possess agglomerated structure. Average particle size is measured to be 0.005nm.

4.1c and 4.1d represents zinc oxide nanorods coated with 1 wt% graphene oxide. Separate layers of graphene oxide are uniformly decorated on rods. The average diameter of zinc oxide nanorods is 44nm and length is approximately 1μm. The thickness of graphene oxide sheet is measured to be 19.95nm. Wrinkles and ripples were observed on the as-synthesized graphene sheets.

Fig 4.1e and 4.1f represents zinc oxide nanorods coated with 10 wt% graphene oxide. Average diameter of ZnO nanorods in this case is 39nm. Above two dimeters show that when concentration of graphene oxide is increased in sample the diameter of nanorods is decreased in the same ratio. The size of ZnO nanorods decreases when the GO dispersion was added during the preparation process. Well dispersed graphene oxide sheets are responsible for negatively charged sites, these negatively charged sites attract positively charged Zn^{2+} ions and these sites convert into nucleation sites for the formation of ZnO [49].

As we increase the amount of GO it provides more nucleation sites so the amount of Zn^{2+} ions per unit volume decreases and because of this size of zinc oxide nanorods reduces.

It is clearly to seen that from Fig. 4.1c and 4.1d that the ZnO/GO composite synthesized by a lower GO concentration solution (1 wt%) shows a partial coverage of GO sheets in the composite. After increasing the GO content from 1 to 10 wt%, the ZnO nanorods have been fully covered with GO sheets representing a network structure.

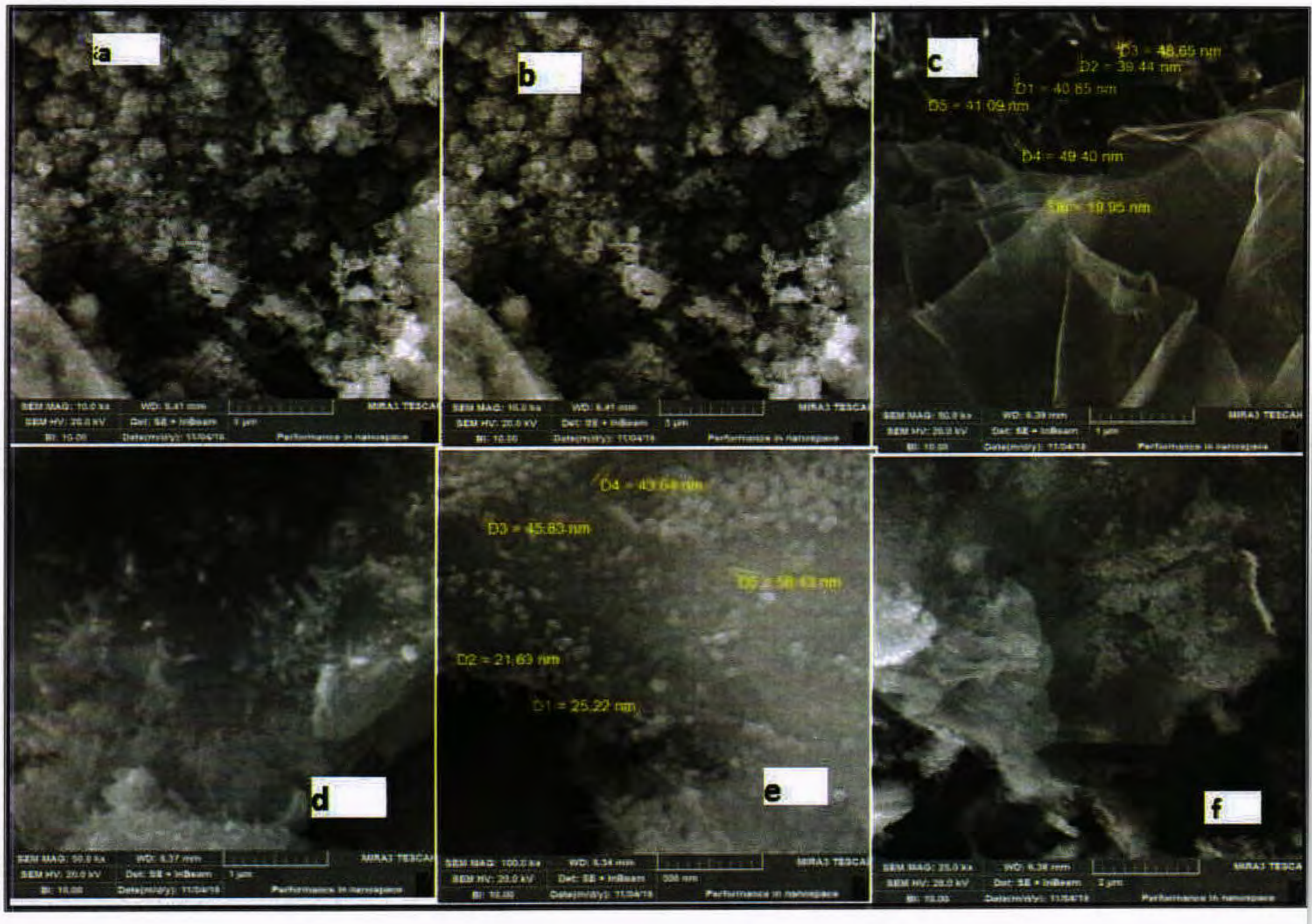


Fig4.1: SEM images **a&b)** of ZnO nanoparticles **c&d)** ZnO Coated with 10 wt% GO **e&f)** ZnO Coated with 1wt% GO

4.2. Energy Dispersive Spectroscopy (EDS):

Fig 4.2 represents energy dispersive spectrum of pure ZnO and ZnO decorated with GO. EDS spectrum of 4.2a, 4.2b and 4.2c clearly shows that as prepared composites are free from impurities. By comparing b and c when higher content of GO is introduced, the amount of carbon increases. EDS analysis confirms that all the samples are highly pure.

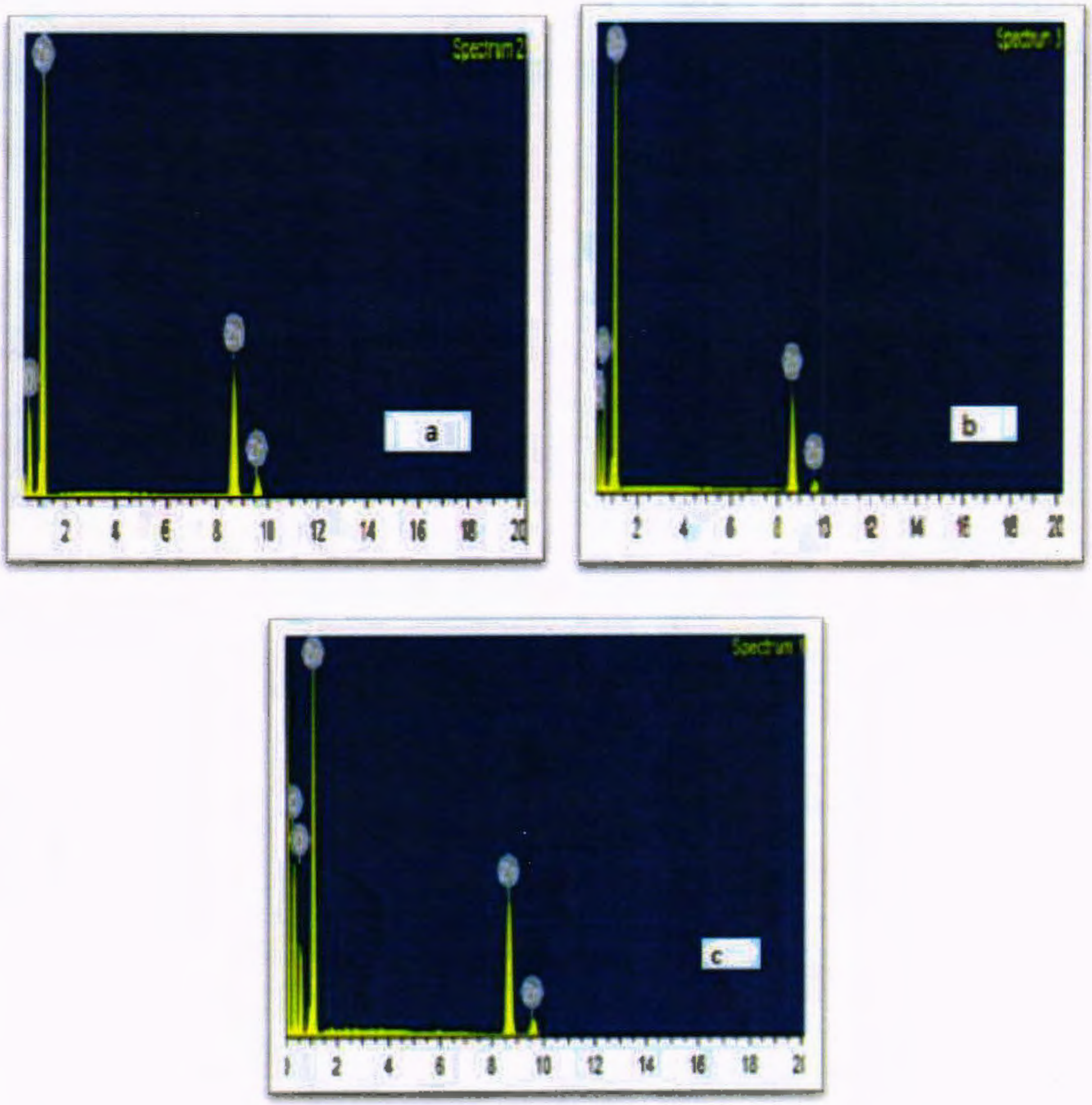


Fig4.2 : EDS of **a)** ZnO nanoparticles **b)** ZnO Coated with 1 wt% GO **c)** ZnO Coated with 10wt% GO

Table 4.1: EDS of **a)** ZnO nanoparticles **b)** ZnO Coated with 1 wt% GO **c)** ZnO Coated with 10wt% GO

(a) ZnO nanoparticles		
Element	**Weight %**	**Atomic %**
OK	16.52	44.71
ZnK	83.48	55.29
Total	100%	
(b) ZnO Coated with 1 wt% GO		
CK	29.93	54.69
OK	21.03	28.85
Znk	49.05	16.47
Total	100%	
(c) ZnO Coated with 10wt% GO		
CK	41.13	68.59
OK	14.14	17.70
ZnK	44.73	13.71
Total	100%	

4.3. X-Ray Diffraction Spectroscopy (XRD):

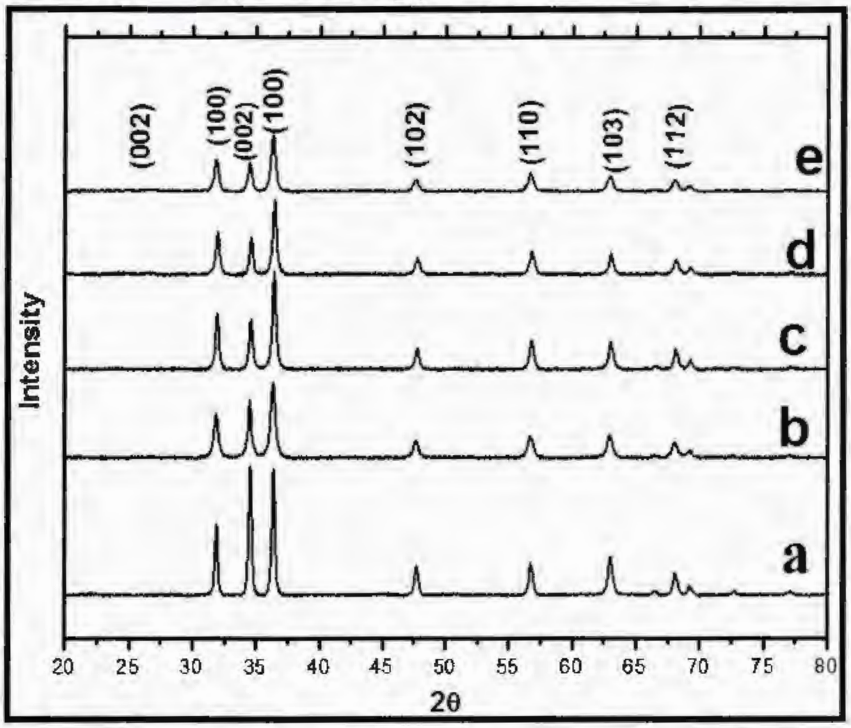


Fig4.3: XRD patterns of **a)** ZnO nanoparticles **b)** ZnO Coated with 1 wt% GO **c)** ZnO Coated with 2wt% GO **d)** ZnO Coated with 5wt% GO **e)** ZnO Coated with 10wt% GO.

The crystalline quality and crystal structure of all samples were examined by XRD as observed in figure 4.3. Figure 4.3 shows the XRD analysis of pure ZnO and composites of ZnO with GO. The diffraction peaks are observed at 31.8°, 34.6°,36.2°,47.5°,56.6°,62.9°,68°. The XRD pattern of GO decorated ZnO nanocomposites are identical to that of pure ZnO. The peaks of Pure ZnO and GO decorated ZnO nanocomposites are consistent having hexagonal phase wurtzite structure (JCPDS 36-1451) [49]. Sharp peaks of all samples indicate that specimen is highly pure and crystalline in nature. Peak position is same for all samples but the intensity is different for all. With the increase in amount of GO peaks are becoming broader. When we increased the amount of GO in the sample a hump is seen at 26.5°. Average particle Average Crystallite Size for ZnO nanoparticles d = 43nm measured by Debye Scherer formula.

4.4. Fourier Transform Infrared Spectroscopy:

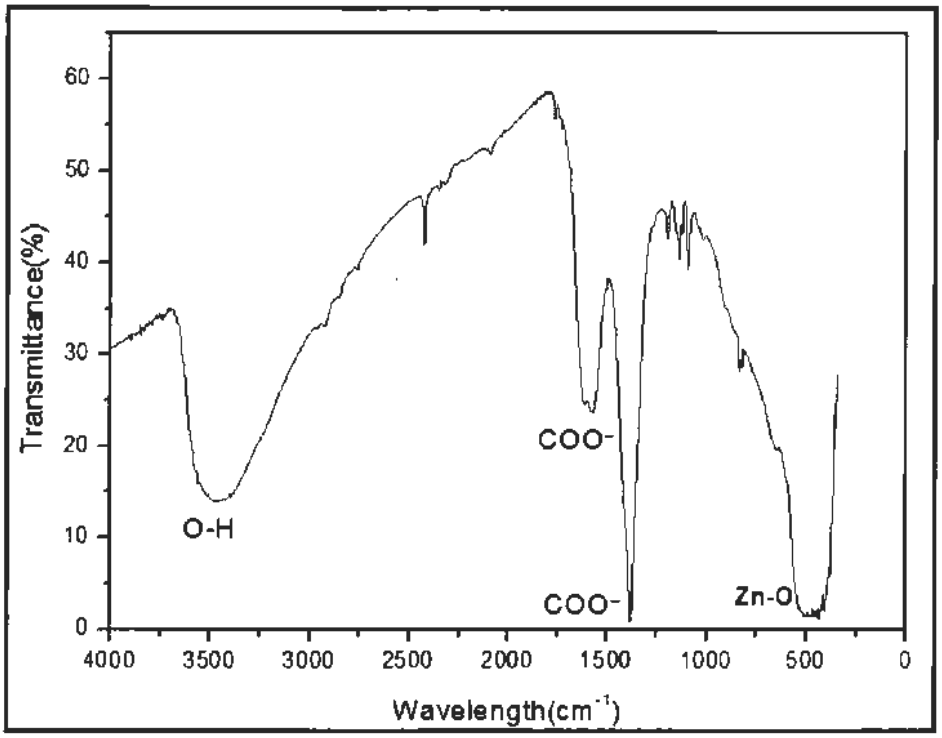


Fig4.4: FTIR spectra of pure ZnO

Fig 4.4 shows the FTIR spectra of pure zinc oxide nanoparticles. The peak at 3450cm^{-1} is due to O-H stretching vibration which is due to the absorbed water molecules and structural OH groups. At 1350cm^{-1} and 1550cm^{-1} stretching bands of COO^{-} are observed which is due to combination of citrate with ZnO. The characteristic absorption peak of ZnO is observed at 460cm^{-1}[42].

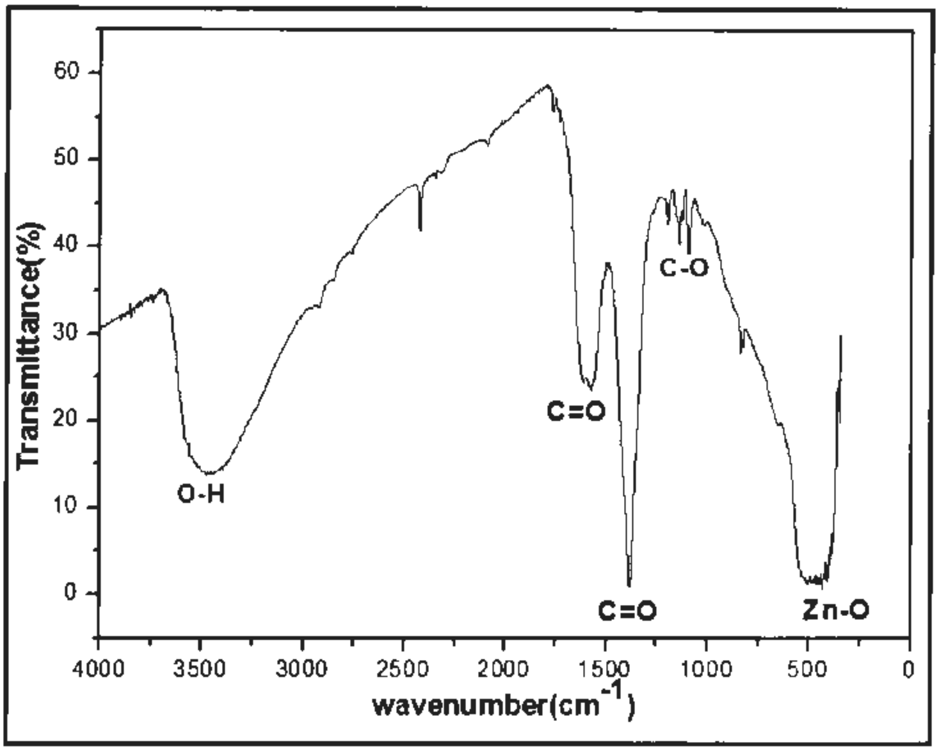


Fig4.5: FTIR spectra of ZnO Coated with 1 wt% GO.

Figure 4.5 represents FTIR spectra of ZnO Coated with 1 wt% GO. The peak at 3440cm^{-1} is stretching vibration of hydroxyl group which is due to water molecule absorption and structural OH groups. Peak at 1590 (C=O) is attributed to stretching vibration of alkenes. Peaks at 1060(C-O) and 1380(C=O) are characteristic peaks of stretching vibration. The absorption band of ZnO is observed at 460cm^{-1} which is due to the blue shift of ZnO[42].

4.5. Photocatalytic Activity Measurements:

Photocatalytic activity of graphene oxide coated zinc oxide nanocomposites was investigated using Methyl Orange. Visible light is used to study degradation process. 100mL quartz photochemical reactor is used for photocatalytic degradation process. The concentration of Methyl Orange is 50mgL^{-1} with catalyst loading of 1.0g L^{-1}. For visible light source purpose a 100-watt halogen lamp was used. Reaction continues for 5 h. A cut off glass filter was used to cut off short-wavelength parts of light. Water cooling system was used to cool the water jacketed photochemical reactor to maintain room temperature. Lamp was placed at 10cm from the center of quartz tube. The solution was sonicated for 20 minutes to mix completely and then stirred for 30 minutes in a dark room to maintain adsorption-desorption equilibrium. Stirring was continued during illumination of solution to keep the solution in suspension. After every 30 minutes' sample was taken for analysis.

4.6. Photocatalytic Degradation of Organic

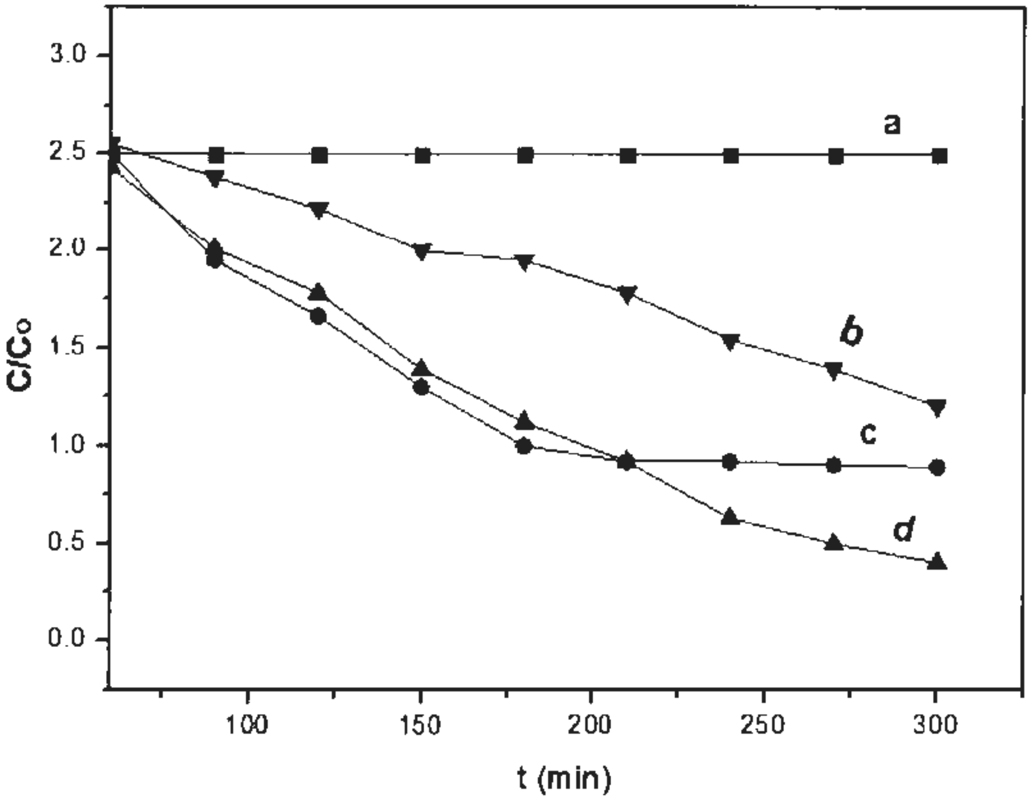


Figure 4.6: Photo degradation of Methyl Orange over **a)** GO sheets **b)** ZnO nanoparticles **c)** 5wt.% GO **d)** 10wt.% GO.

Fig 4.6 shows photo degradation of methyl orange. 4.6a shows that graphene oxide has no photocatalytic activity towards methyl orange. While, 4.6b represents that zinc oxide nanoparticles are good photo catalyst towards methyl orange. When we add graphene oxide in zinc oxide it enhances the photocatalytic activity. When we introduce GO in the sample this increase the absorption of composite because the surface area of GO is very high. The excessive amount of GO on ZnO can act as recombination centers. Transport through delocalized conjugated π structures allows charge carriers in graphene to achieve high mobility and relatively slow charge recombination. The thick layer of GO on ZnO impedes the contact between ZnO rods and MO molecules. When the sample is irradiated with UV light, the emitted electrons from conduction band of ZnO can be transferred to GO which is very effective to resist charge recombination [49].4.6c represents zinc oxide with 5 wt.% GO and 4.6d represents zinc oxide with 10wt.% GO. Above results indicate that when we increase the amount of graphene oxide, nanocomposite becomes excellent photo catalyst.

CONCLUSION:

- Graphene Oxide Decorated Zinc Oxide nano rods can be synthesized by simple, low cost and easy wet chemical method.
- Coating of graphene oxide can effectively reduce the band gap of zinc oxide.
- The characterization results indicate that prepared nanocomposites are pure and crystalline and graphene oxide sheets are uniformly coated on nanorods.
- We used these nanocomposites for photocatalytic applications.
- By fixing amount of ZnO and introducing higher contents of GO we developed a comparison and concluded that high ratio of GO is excellent for photocatalytic applications.

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