

METAL OXIDE-CARBON NANOCOMPOSITES PREPARATION IN HYDROTHERMAL METHOD FOR PHOTOCATALYST APPLICATION

Submitted in partial fulfilment of the requirements for the award of

Master of Science in CHEMISTRY

by

KONDEPOGU DEVAIAH

(REGISTER NO: 40910015)



DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

ACCREDITED WITH GRADE "A" BY NAAC

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI-600119

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Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600 119

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **Mr. K. DEVAIAH (40910015)** who carried out the project entitled **METAL OXIDE-CARBON NANOCOMPOSITES PREPARARION IN HYDROTHERMAL METHOD FOR PHOTOCATALYST APPLICATION**” under my / our supervision from **Nov 2021-May 2022**

Internal Guide
(Dr. S. SUNITHA)

External Guide
(Dr. G. MURUGADOSS)

Head of the Department
(Name in Capital letters with Seal & Signature)

Submitted for Viva voce Examination held on _____

Internal examiner

External Examiner

DECLARATION

I **Mr. K.DEVAIAH** student of **SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY** hereby declare that the Project Report entitled **“METAL OXIDE-CARBON NANOCOMPOSITES PREPARARION IN HYDROTHERMAL METHOD FOR PHOTOCATALYST APPLICATION”** done by me under the guidance of **Dr. S.SUNITHA, M.Sc., M.Phil., Ph.D. Assistant Professor, Sathyabama Institute of Science and Technology Department of Chemistry** and **Dr. G.MURUGADOSS, M.Sc., Ph.D. Scientist-E at International Research Centre, Sathyabama Institute of Science and Technology, Chennai** is submitted in partial fulfillment of the requirements for the award of **Master of Science degree in CHEMISTRY.**

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K DEVAIAH

METAL OXIDE-CARBON NANOCOMPOSITES PREPARATION IN HYDROTHERMAL METHOD FOR PHOTOCATALYST APPLICATION

VISION

**“TO EXPLORE NEW FRONTIERS IN CHEMICAL SCIENCE THROUGH
INNOVATION AND COLLABORATION”**

ABSTRACT

Carbon-magnetite/zinc oxide (C-Fe₃O₄-ZnO) nanocomposites were synthesized by the hydrothermal method using different ratios of zinc oxide and iron oxide. The structural, morphological, and optical properties of nanocomposites were analysed by X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), Scanning electron microscope (SEM), UV-Vis spectra. (C-Fe₃O₄-ZnO) has a strongly quenching in UV intensity indicating stability between electrons and holes (e⁻/h⁺). The photocatalytic activities of C-Fe₃O₄-ZnO nanocomposites were investigated by the degradation of methylene blue in aqueous solution under visible light in different condition of pH, initial concentration and different trapping agents for free radicals (Tert-butyl alcohol (TBA), p-benzoquinone (BQ) and disodium ethylenediaminetetraacetic acid (Na₂-EDTA)). The results shows that the photodegradation efficiency of ZnO compound with presence of magnetite improved. The optical results show enhancement of nanocomposite absorption under the visible region with a high life time between e⁻/h⁺ at the optimum ratio between (C-Fe₃O₄-ZnO), which can applied to obtain high photocatalytic degradation of methylene blue under visible light. Finally, the catalytic activity has been stabled when such photocatalyst was utilized again for several cycles.

Key words : zinc oxide, Iron oxide, photocatalyst, photoluminescence.

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CHAPTER-1

INTRODUCTION

Metal oxides/ Mixed metal oxides have wide applications as catalyst, Adsorbents, Superconductors, semiconductors, ceramics, antifungal agents and also have spacious applications in medicines

Metal oxides play a very important role in many areas of chemistry, physical and materials science.

Metal oxides are formed as a consequence of co-ordination tendency of metal ions so that oxide ions form co-ordination sphere around metal ions and give rise to close packed structure.

The different physical, magnetic, optical and chemical properties of metal oxides are of great interest to chemists because these are extremely sensitive to change in composition and structure.

Extensive studies of this relationship leads to a better understanding of the chemical bond in crystal. The metal oxides are attracting special attention of scientists due to their easy mode of formation and multifunctional behavior.

The transition metals and their compounds are used as catalysts in chemical industry and in battery industries.

Besides, these compounds can be used in formation of interstitial compounds and alloy formation. The transition metals have the special properties of formation of coloured compounds and show magnetic properties.

Metals of d-block elements are used for many industrial applications. They behave as catalysts, super conducting materials, sensors, ceramics, phosphors, crystalline lasers etc.

Besides these they are excellent photoactive materials and work as photosensitizer. Mixed metal oxide (MMO) electrodes are devices with useful properties for chemical electrolysis.

Metal/Mixed metal oxides have wide applications as catalyst because of their high surface area and reactive sites. Number of scientists and academicians are using metal/mixed metal oxides as catalyst in various organic reactions.

Metal Oxide Nanoparticles are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts.

1.1 NANO PARTICLES

These days, we live in an escalated advancement of science known as nanotechnology. The normal size of particles framing a sample in the range of 1–1000 nm ($1\text{ nm} = 10^{-9}\text{ m}$). There are so meanings of nanoparticles. One of them says that, whose at any rate one measurement is more than 100 nm, then such material can be called as “nanomaterial”.

Another definition “nanomaterial” as a material which after “miniaturization” to nanoscale uncovers changed physicochemical properties in contrast with the mass item (naturally visible). The nanoparticles displays a novel physical, chemical and biological properties at nanoscale contrasted with their specific particles at higher scales.

This happens because of a larger surface area to the volume, increase in reactivity or stability in a chemical reaction, improved mechanical strength, and so on. These properties of nanoparticles have prompted its utilization in different applications.

The nanoparticles differ from shapes, sizes and structure. It can vary from 1 nm to 100nm in size.

The surface can be uniform or unpredictable with surface varieties. Some nanoparticles are translucent or shapeless with single or multi gem solids either free or agglomerated. Various synthesis techniques are either being created or improved to upgrade the properties and lessen the production costs.

A few techniques are adjusted to accomplish measure explicit nanoparticles to increment their physical, chemical, optical and mechanical properties. A huge advancement in the instrumentation has prompted an improvement in nanoparticle characterization and application [1].

Based on the application like imaging, diagnosis or treatment various kinds of nanoparticles have been proposed, some of them are utilized for multiple purposes.

Nanoparticles come under two main categories: organic and inorganic nanoparticles. The primary group includes micelles, dendrimers, liposomes, hybrid and minimized polymeric nanoparticles. The second group includes fullerenes, quantum dots, silica and gold nanoparticles.

1.2 TYPES OF NANOPARTICLES

1.2.1 ONE DIMENSIONAL NANOPARTICLE:

Atoms are arranged in one dimension in nano scale range. one dimension is outside the nanoscale. This class includes nanotubes, nanorods, and nanowires. coatings and thin films.

1.2.2 TWO-DIMENSIONAL NANOPARTICLES:

Atoms are arranged in two-dimensional nano scale range. Examples are nanotubes, biopolymers, nanowires.

1.2.3 THREE DIMENSIONAL NANOPARTICLES:

Atoms are arranged in three-dimensional nano scale range. Examples are fullerenes.

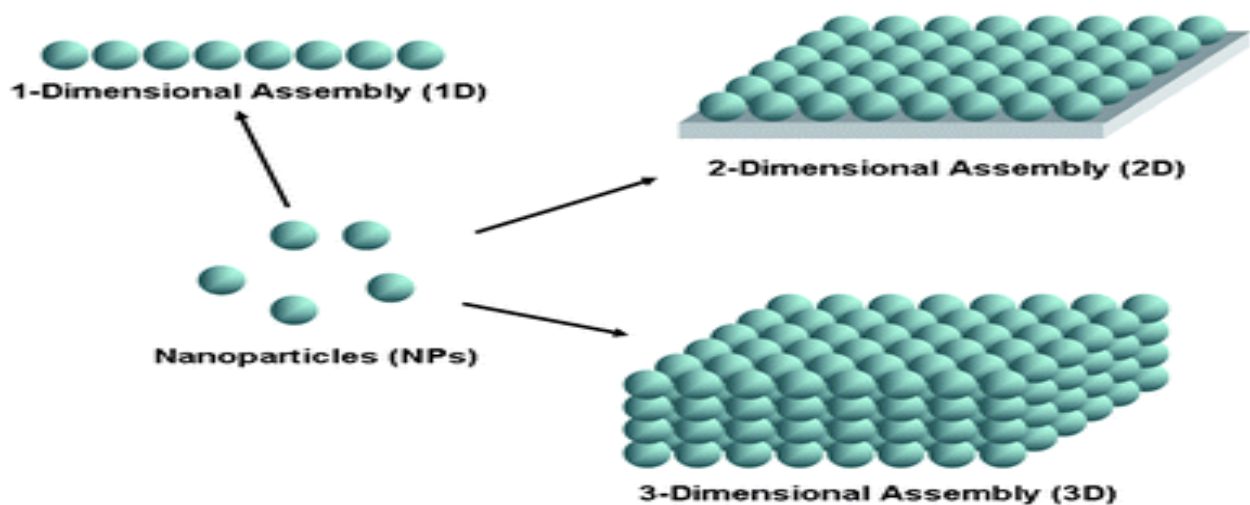


Figure 1.2 : Types of nano particles

1.3 CLASSIFICATION OF NANOPARTICLES

Nanoparticles can be classified into different types according to the size, morphology, physical and chemical properties. Some of them are carbon-based nanoparticles, ceramic nanoparticles, metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles and lipid-based nanoparticles.

1.3.1 CARBON BASED NANOPARTICLES

Carbon-based nanoparticles are of two main materials: carbon nanotubes (CNTs) and fullerenes. CNTs are nothing but graphene sheets rolled into a tube. These materials are mainly used for the structural reinforcement as they are 100 times stronger than steel.

Fullerenes contain nanomaterial that are made of globular empty enclosure like allotropic structures of carbon because of their electrical conductivity, high strength, structure, electron affinity, and flexibility. These materials possess pentagonal and hexagonal carbon units, while every carbon is sp^2 hybridized. CNTs are tubular, elongated, 1–2 nm in measurement. These can be anticipated as metallic or semiconducting dependent on their measurement helicity. These resemble graphite sheet rolling upon itself.

The sheets can be single, double or numerous walls and in this way, they are named as single-walled (SWNTs), double walled (DWNTs) or multi-walled carbon nanotubes (MWNTs). Individually, they are synthesized by carbon precursors, by electric arc on metal nanoparticles. They are synthesized by Chemical Vapour Deposition (CVD).

Because of their unique physical, chemical and mechanical properties, these materials are utilized in various applications like filler and as in organic and inorganic catalyst.

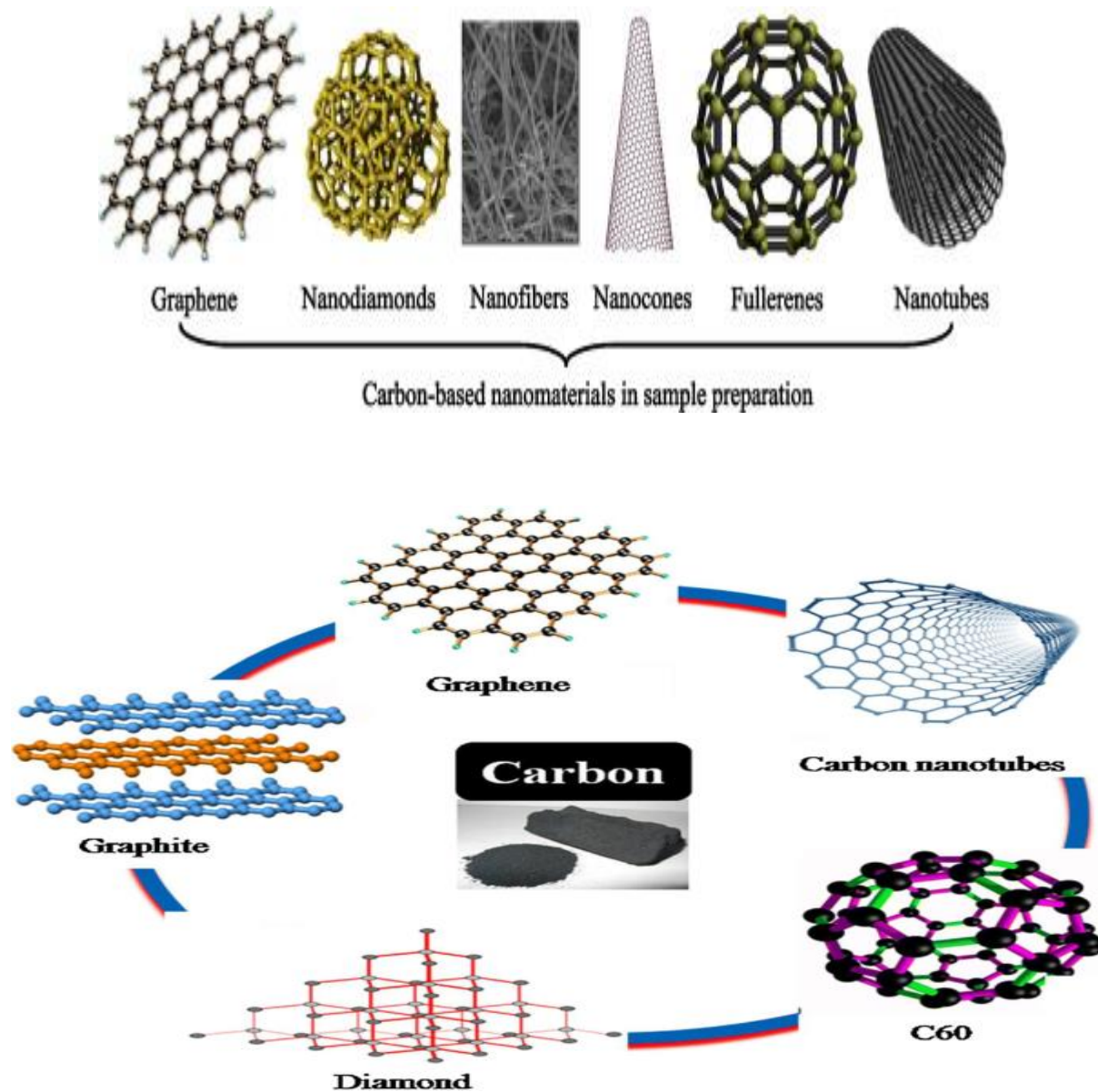


Figure 1.3.1: carbon-based nanoparticles

1.3.2 APPLICATIONS OF CARBON-BASED NANOPARTICLES

Carbon-based nanomaterials are “fullerenes, carbon nanotubes, graphene and its derivatives, graphene oxide, nanodiamonds, and carbon-based quantum dots”.

There are several important applications of nanomaterials such as aviation and space, chemical industry, optics, solar hydrogen, fuel cell, batteries, sensors, power

generation, aeronautic industry, building/construction industry, automotive engineering, consumer electronics, thermoelectric devices, pharmaceuticals.

Due to their unique structural dimensions and excellent mechanical, electrical, thermal, optical and chemical properties, these materials have attracted interest in diverse areas, including biomedical applications.

In particular, the intrinsic two-photon fluorescence property of carbon based-nanomaterials in the long wavelength region (near-infrared II) allows deep-tissue optical imaging.

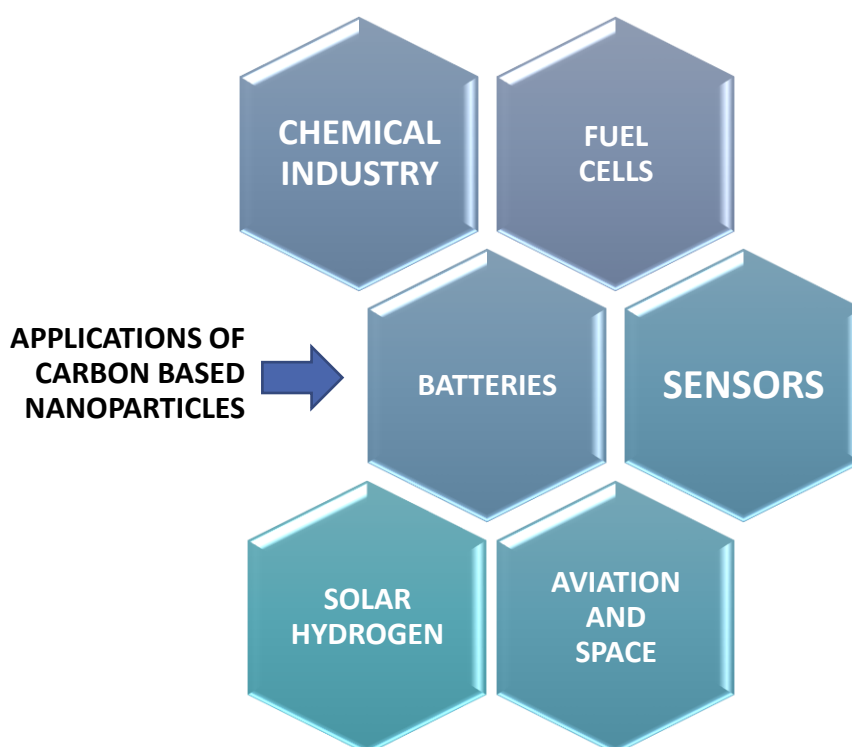


Figure 1.3.2: Applications of carbon based nanoparticles

1.3.3 INORGANIC BASED NANOPARTICLES

Inorganic nanoparticles are non-toxic, hydrophilic, biocompatible and highly stable compared to organic materials. Drug delivery systems designed for enhanced drug efficacy and reduced adverse effects have evolved accompanied by the development of novel materials.

These nanomaterials incorporate metal furthermore, metal oxide nanoparticles and nanostructured materials. These nanomaterials can be combined into metals like Au

or Ag nanoparticles, metal oxides, for example, Fe_3O_4 , CeO_2 , TiO_2 and ZnO nanoparticles, and semiconductors like silicon and ceramics.

Inorganic nanoparticles, such as quantum dots, polystyrene, magnetic, ceramic and metallic nanoparticles, have a central core composed of inorganic materials that define their fluorescent, magnetic, electronic and optical properties.

1.3.4 ORGANIC BASED NANOPARTICLES

These incorporate nanomaterials made for the most part from organic matter, barring carbon-based or inorganic-based nanomaterials.

The use of non-covalent weak interactions for the self-assembly and designs of atoms assists with changing the organic nanomaterials into specific structures, for example, dendrimers, micelles, liposomes and polymer nanoparticles.

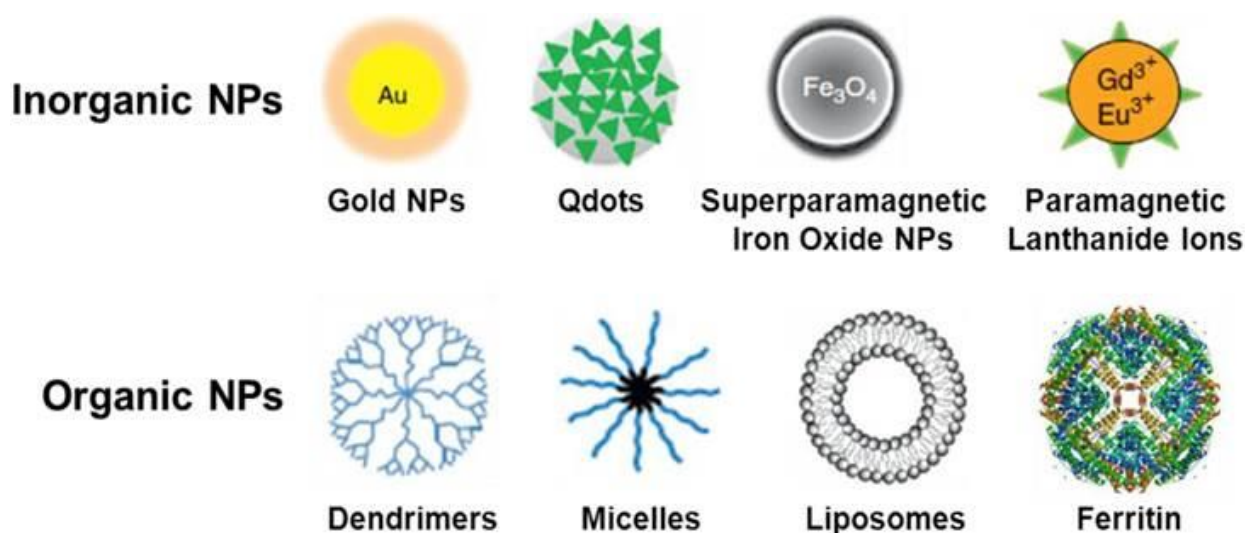


Figure 1.3.4 : inorganic and organic nanoparticles(NPs)

1.3.5 COMPOSITE BASED NANOPARTICLES

Composite nanomaterials are multiphase nanoparticles and nanostructured materials with one stage on the nanoscale measurement that can either consolidate nanoparticles with different nanoparticles or nanoparticles joined with bigger or with bulk materials or more complicated structures, for example, metal organic systems.

Nanocomposites are a class of nanomaterials wherein one or more phases at nano-sized dimension (zero dimension, one dimension, and two dimensions) are embedded in a ceramic, metal, or polymer material.

These composites might be a mixture of carbon-based, metal-based, or natural based nanomaterials with any type of metal, polymer, or ceramic based materials. Nanomaterials are synthesised in various morphologies relying upon the necessary properties for the required application [2].

1.4 PROPERTIES OF NANOPARTICLES

Various physicochemical properties namely large surface area, chemically reactive, optically active and mechanically strong makes the nanoparticles incredibly unique and makes them suitable for numerous applications. Some of their properties are mentioned below

1.4.1 PHYSICAL PROPERTIES

The physical properties of nanoparticles are dependent on the size, shape, composition, crystal structure, surface ligand or capping agents and the medium in which they are dispersed.

1.4.2 OPTICAL PROPERTIES

Due to the quantum confinement effect, nanomaterials with small particle sizes exhibit better optical emission as well as nonlinear optical properties. The effect of size on nanoparticle optical properties is caused by two distinct phenomena: surface phenomena and an increase in energy level spacing due to the confinement of energy states, which is most notable in semiconductors [3].

1.4.3 MAGNETIC PROPERTIES

After surface cooling, magnetic nanoparticles exhibit extraordinary new phenomena including strong field irreversibility, high saturation field, super para magnetism, extra anisotropy effects, or shifted loops. The magnetic nature of individual nanoparticles is because of narrow and finite-size effects, as well as surface effects [4].

1.4.4 MECHANICAL PROPERTIES

Magnetic nanoparticles can be superparamagnetic and responds to external magnetic fields very fast with almost zero remanence. These properties provide bases for applications like biomedical imaging and information storage technology. The mechanical properties of nanoparticles such as hardness and elastic modulus, interfacial adhesion and friction, movement law, as well as its size-dependent effect

1.5 SYNTHETIC METHODS

Approaches come under two main categories namely: top-down approach and bottom-up approach and they differ in their cost, speed and degree of quality. The Approaches have been summerised in below

NANOTECHNOLOGY OF METAL OXIDES

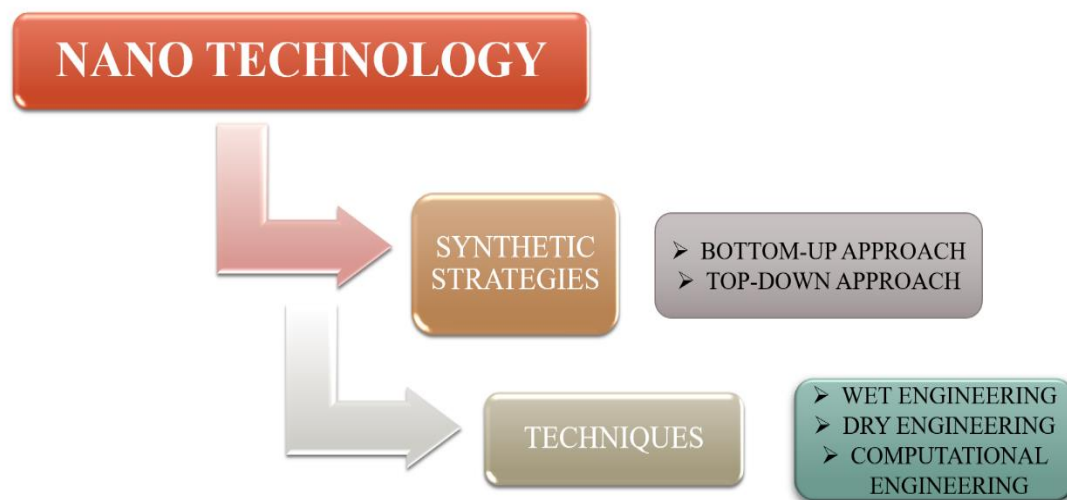


Figure 1.5 (a): Nanotechnology of metal oxides

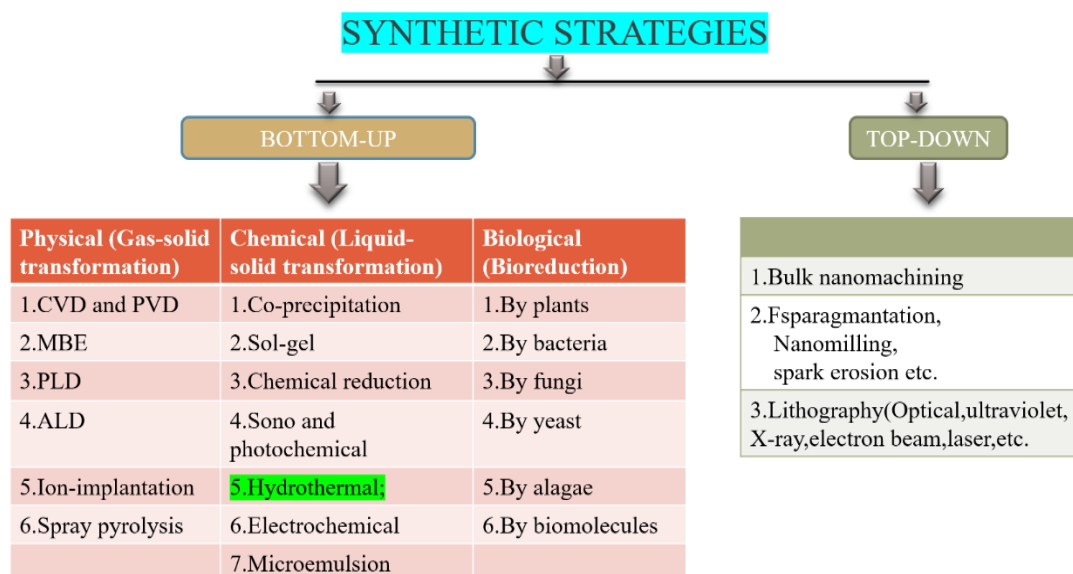


Figure 1.5 (b): BOTTOM-UP and TOP-DOWN approaches

1.5.1 BOTTOM-UP APPROACH

This method is the reverse of top-down approach. These nanoparticles are formed from simple substances and hence it is called as building up approach. Examples are hydrothermal, spinning, pyrolysis, sol-gel, CVD, etc.

1.5.1.1 PHYSICAL VAPOR DEPOSITION

The particle size is determined by the rate of evaporation and the pressure of the gases in the chamber. Gases such as H₂, O₂, NH₃, and N₂ are used, and the material interacts with them, forming nitrides, hydrides, and oxide particles. The gas pressure in the deposition chamber defines the size and form of the evaporated substance. Both the processes were carried out in a vacuum chamber to produce a high-purity nanomaterial [5].

1.5.1.2 SOL-GEL METHOD

Two materials are involved in this method they are sol and gel. It is a low temperature process and consumes less energy. Synthesis of nanoparticles like nanotubes, nanorods can be obtained by this method. Sol-gel synthesis involves hydrolysis, condensation, gelation and drying process by various routes [5].

1.5.1.3 CHEMICAL VAPOUR DEPOSITION (CVD)

The deposition of a thin film of gaseous reactants onto a substrate is Chemical Vapour Deposition. At ambient temperature gas molecules are combined and the deposition is carried out in a reaction chamber. Chemical reaction occurs when a heated substrate comes in contact with the combined gas.

A thin film of product on the substrate surface is produced and that is recovered and used. The influencing factor in CVD is the substrate temperature. CVD produces nanoparticles that are strong, uniform and hard. CVD requires special equipment and the gaseous by products are toxic.

1.5.1.4 HYDROTHERMAL METHOD

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water.

This method is very effective for getting nanosized particles in single shape at low temperature, however without this method we need to maintain high temperatures to get the same sample in nano size.

A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

Advantages of the hydrothermal method is used to tuning the shape of the crystals over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition.

Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows if a steel tube is used. There are

autoclaves made out of thick-walled glass, which can be used up to 300 °C and 10 bar.



Figure 1.5.1.4: Hydrothermal method using autoclaves

1.6 APPLICATIONS OF NANOPARTICLES

- Nanoparticles are now being used in the manufacture of scratchproof eyeglasses, crack-resistant paints, anti-graffiti coatings for walls, transparent sunscreens, stain-repellent fabrics, self-cleaning windows and ceramic coatings for solar cells.
- Nanoparticles are widely used in drug delivery system. Certain drugs are not metabolised in the first pass. To resolve this, nanoparticles can be modified, and they also allow for regulated, long-term drug release from the matrix.
- When they're adhered to short DNA segments, they can also be used to detect genetic sequences. Nanotechnology allows damaged tissue to be repaired or replicated. The use of nanotechnology can revolutionise organ transplantation or artificial implantation [6].

- The need for new antimicrobial agents has risen. Because of their inbuilt antimicrobial properties, nanoparticles (NPs) are now being considered as an effective nanotechnology for regulating harmful micro-organisms.

1.7 METAL OXIDES

Metal oxides are crystalline solids that contain a metal cation and an oxide anion. They typically react with water to form bases or with acids to form salts.

Metal oxides plays a important role in numerous zones like chemistry, physics, and materials science. Metal oxides exhibits semiconductor, metallic or insulator properties and can adopt a number of structural geometries and it also possess an electronic structure.

Metal oxide nanoparticles have been used in different fields due to its excellent functional properties. When metal oxides are coupled with other structures, they enhance the unique properties of the materials.

The main Metal oxides/ Mixed metal oxides have wide applications as catalyst, Adsorbents, Superconductors, semiconductors, ceramics, antifungal agents and also have spacious applications in medicines. This review article is focused on their applications as photocatalyst in various organic reactions nanoparticles are shown in the figure.

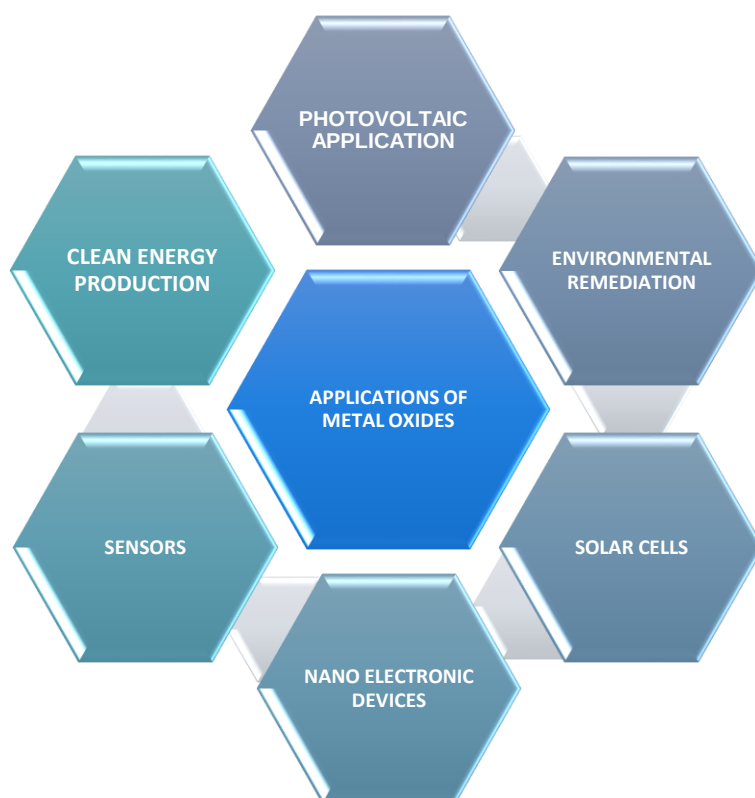


Figure 1.7(a): Applications of metal oxides

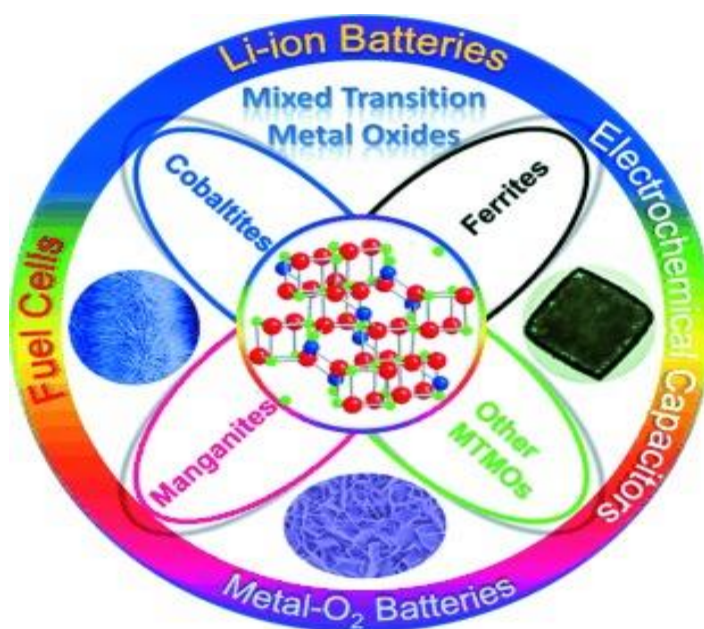


Figure 1.7(b): Applications of mixed metal oxides

1.8 TRANSITION METAL OXIDES

1.8.1 IRON OXIDE (Fe_3O_4) NANOPARTICLE

Iron oxide is the chemical compound with formula Fe_3O_4 . It occurs in nature as the mineral magnetite. It is one of a members of iron oxides

Iron oxide nanoparticles are iron oxide particles with diameters between about 1 and 100 nano meters. The two main forms are magnetite (Fe_3O_4) and its oxidized form maghemite ($\gamma\text{-Fe}_2\text{O}_3$).

They have attracted extensive interest due to their superparamagnetic properties and their potential applications in many fields (although cobalt and nickel are also highly magnetic materials, they are toxic and easily oxidized).

Applications of iron oxide nanoparticles are magnetic storage devices, catalysis, sensors, superparamagnetic relaxometry, high-sensitivity biomolecular magnetic resonance imaging, separation of biomolecules, and targeted drug and gene delivery for medical diagnosis and therapeutics.

These applications require coating of the nanoparticles by agents such as long-chain fatty acids, alkyl-substituted amines, and diols. They have been used in formulations for supplementation.

Magnetite has an inverse spinel ($\text{Fe}_3\text{O}_4 \rightarrow \text{FeFe}_2\text{O}_4$) system with oxygen forming a face-centered cubic crystal system. In magnetite, all tetrahedral sites are occupied by Fe^{3+} and octahedral sites are occupied by Fe^{3+} and Fe^{2+} .

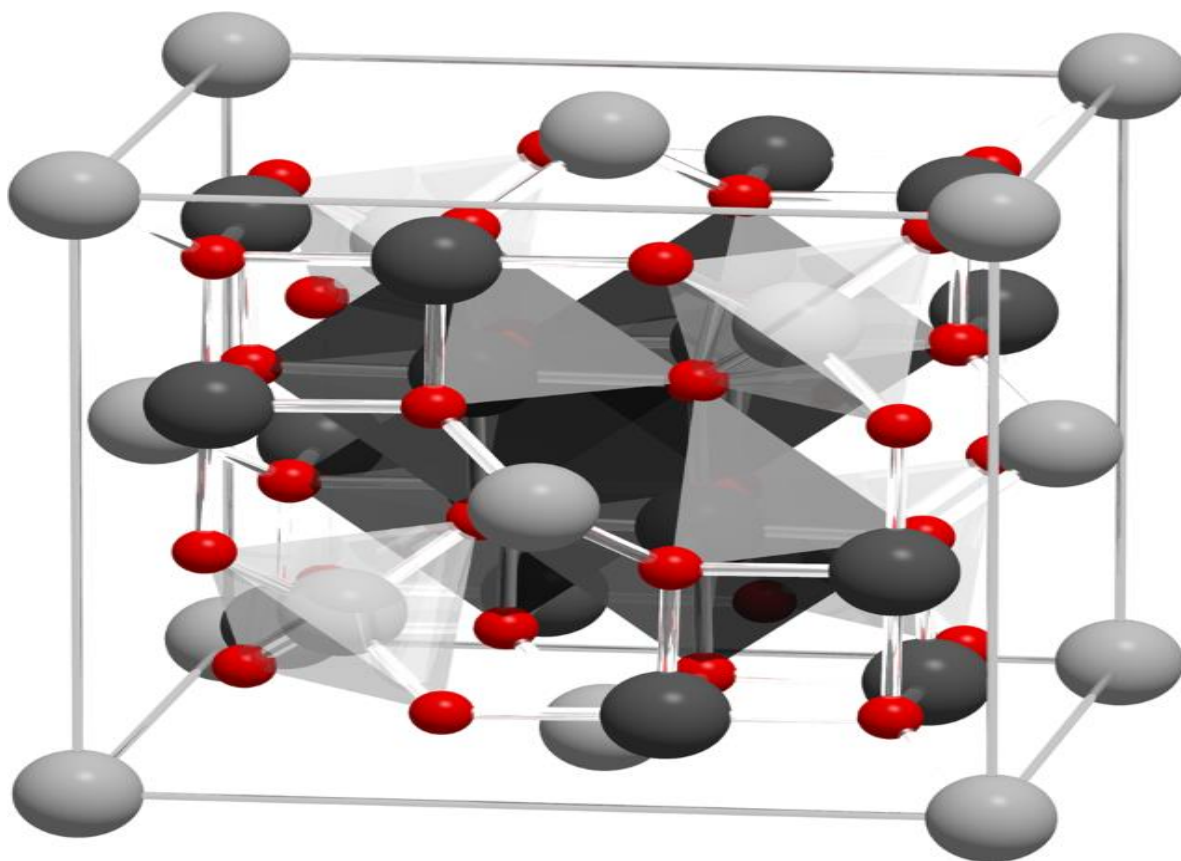


Figure 1.8.1: Crystal structure of iron oxide (Fe_3O_4)-Magnetite

1.8.2 ZINC OXIDE NANOPARTICLE

Zinc oxide nanoparticles are nanoparticles of zinc oxide (ZnO) that have diameters less than 100 nano meters. They have a large surface area relative to their size and high catalytic activity. The exact physical and chemical properties of zinc oxide nanoparticles depend on they are synthesized.

Some possible ways to produce ZnO nano-particles are laser ablation, hydrothermal methods, electrochemical depositions, sol-gel method, chemical vapour deposition, thermal decomposition, two-step mechano chemical- thermal synthesis anodization, co-precipitation, electrophoretic deposition and precipitation processes using solution concentration, pH and washing medium. ZnO is a wide- bandgap semiconductor with an energy gap of 3.37 eV at room temperature.

ZnO nanoparticles are one of the most produced nanomaterials, along with titanium dioxide nanoparticles and silicon dioxide nano particles. The most common use of ZnO nanoparticles is in sunscreen. They are used because they effectively

absorb ultraviolet light, but possess a large enough bandgap to be completely transparent to visible light.

They are also being investigated to kill harmful microorganisms in packaging, and in UV-protective materials such as textiles. Many companies do not label products that contain nanoparticles, making it difficult to make statements about production and pervasiveness in consumer products.

ZnO nanoparticles are a relatively new material, there is concern over the potential hazards they can cause. Because they are very tiny, nanoparticles generally can travel throughout the body, and have been shown in animal studies to penetrate the placenta, blood–brain barrier, individual cells, and their nuclei.

Tissues can absorb them easily due to their size which makes it difficult to detect them. However, human skin is an effective barrier to ZnO nanoparticles, for example when used as a sunscreen, unless abrasions occur. ZnO nanoparticles may enter the system from accidental ingestion of small quantities when putting on sunscreen. When sunscreen is washed off, the ZnO nanoparticles can leach into runoff water and travel up the food chain.

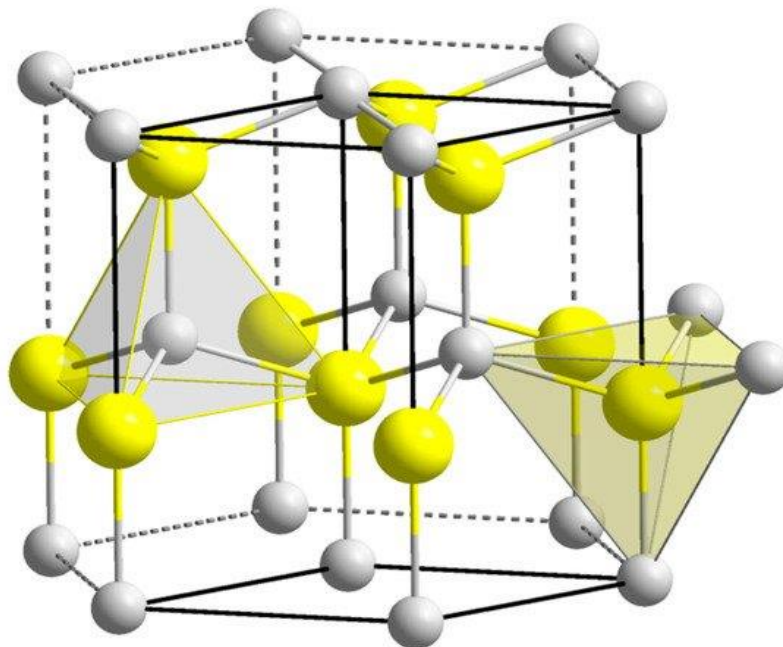


Figure 1.8.2: Crystalline structure of zinc oxide

1.9 PHOTOCATALYST

Materials that cause photocatalytic reactions when exposed to light is called as photocatalyst. A chemical reaction caused by photo absorption of a solid substance, or "photocatalyst," which stays unchanged throughout the reaction is a general description of photocatalysis. As a result, a "photocatalyst" must act catalytically, that is, without modification, when exposed to light [7].

1.9.1 PHOTOCATALYSIS

Photocatalysis is a combination of the Greek words photo (light) and catalysis (to break apart or decompose). In general, photocatalysis is used to describe a mechanism in which light is used in the excitation of photocatalyst. Photocatalyst is not involved in accelerating the rate of chemical reaction.

It is the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals: $\bullet\text{OH}$) able to undergo secondary reactions. Its practical application was made possible by the discovery of water electrolysis by means of titanium dioxide (TiO_2).

In other words, photocatalysis is a photoinduced reaction that is stimulated in the presence of a catalyst. Photocatalysis is broadly classified into two categories: homogeneous and heterogeneous [8].

- Homogeneous catalysis:

When both the photocatalyst and the reactant are in the same phase then the reaction is called as homogeneous catalysis. Most common examples of homogeneous catalysis are dyes, coordination compounds, natural pigments and so on.

- Heterogeneous catalysis:

In this type of reaction, the photocatalyst and the reactant exist in different phase. Example of heterogeneous catalysis are transition metal chalcogenides which exhibits unique characteristics.

1.9.2 MECHANISM OF PHOTOCATALYSIS

When the photocatalyst is irradiated with light of a specific wavelength, a electron is excited to the conduction band (CB), leaving a positive hole in the valence band (VB). The hole in the VB can be utilized for oxidizing some compounds whereas the electron in the CB is used to reduce any substrate. This is shown in the figure given below [8].

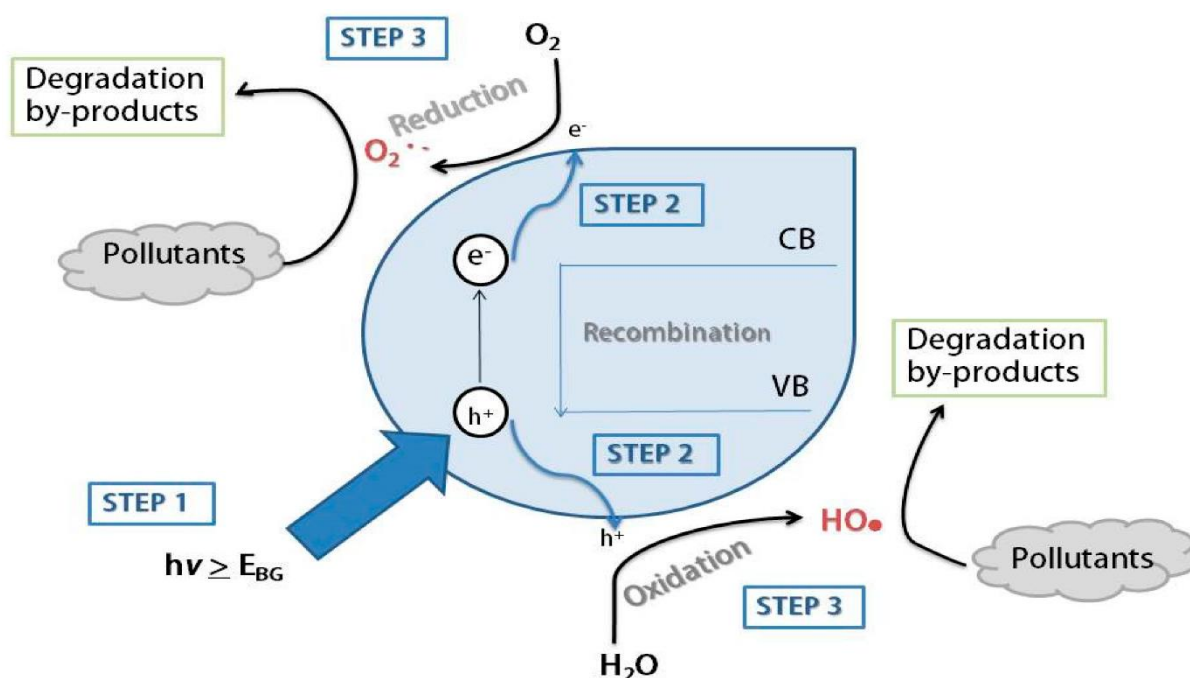


Figure 1.9.2: Mechanism of photocatalysis

1.9.3 APPLICATIONS OF PHOTOCATALYST

Photocatalytic technique has been proven to be one of the most “green” and successful environmental remediation techniques. Some semi-conducting materials, such as 'photocatalysts,' cause or accelerate chemical reactions when exposed to light, resulting in the decomposition of organic molecules, for example, Nanosized catalyst particles have a slightly higher reactivity than larger particles or bulk content owing to their large surface area. Charge separation happens when a photocatalyst is exposed to light with an energy greater than the photocatalyst's band gap energy.

The photocatalyst then initiates an oxidation-reduction reaction using the electrons and holes produced by charge separation[9]. Visible absorption spectroscopy is

generally used for the photocatalytic degradation of dyes [10]. The major role of the photocatalyst is shown in the figure.

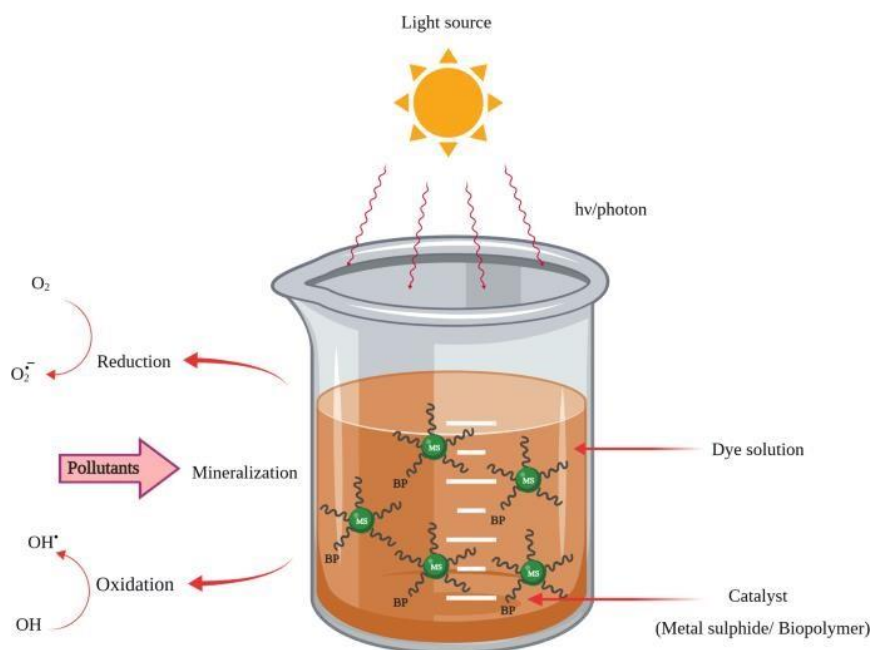


Figure 1.9.3: Role of photocatalyst

Photocatalytic degradation has gained popularity as and is used as a tool for treating dye-contaminated water among a number of treatment methods. Nanoparticles, nanowires, 2D compounds, planar films, 3D porous films, and complex hierarchical nanostructures are just some of the structures and morphologies found in photocatalysts. A variety of implementations have been developed to get the most out of these photocatalysts.

CHAPTER-2

LITERATURE SURVEY

1.Title: ZnO–ZnFe₂O₄/Fe₃O₄/Carbon Nanocomposites for Ultrasensitive and Selective Dopamine Detection

Authors: Richard Appiah-Ntiamoah, Anteneh Fufa, Baye and Hern Kim

Journal and year: April 7, 2022 (<https://doi.org/10.1021/acsanm.1c04222>)

Inference: This method a ZnO- ZnFe₂O₄/Fe₃O₄/carbon nanocomposite, which possesses the aforementioned synergy and therefore displays impressive sensing capabilities. ZnO-ZnFe₂O₄/Fe₃O₄/carbon is synthesized in situ via the carbothermal reduction of Congo red (CR)- decored ZnO-ZnFe₃O₄ nanofibers.

2.Title: Elaboration of Fe₃O₄/ZnO nanocomposite with highly performance photocatalytic activity for degradation methylene blue under visible light irradiation.

Authors: Rania Elshypany, Hanaa Selim, K. Zakaria, Ahmed H. Moustafa, Sadeek A. Sadeek, S.I. Sharaa, Patrice Raynaud, Amr A. Nada.

Journal and year : June 2021 Environmental Technology & Innovation 23(2):101710 (DOI:10.1016/j.eti.2021.101710)

Inference: Fabricating Fe₃O₄/ZnO in order to enhance its photocatalytic activity through different preparation methods to obtain different structure and morphology. Karunakaran et al. (2014) reported that the core–shell of Fe₃O₄/ZnO nanosheets by hydrothermal synthesis allows the band gap of Fe₃O₄ to be conjugated inside the band gap of ZnO for 98.5%, 25% photodegradation of 25 ppm methylene blue under UV and visible light.

3.Title: Synthesis of Rectorite/Fe₃O₄/ZnO Composites and Their Application for the Removal of Methylene Blue Dye.

Authors: Huanhuan Wang, Peijiang Zhou, Rui Guo, Yifei Wang, Hongju Zhan and Yunfei Yuan.

Journal and year: 9 March 2018

Inference: The fabricated REC/Fe₃O₄/ZnO composite possessed a high specific surface area and high capacity of adsorption and photocatalysis toward methylene blue (MB) dye. The adsorption isotherm of the dye on the composite fitted well to the Langmuir model, with a maximum adsorption of 35.1 mg/g [14].

4.Title: Multifunctional Fe₃O₄-ZnO nanocomposites for environmental remediation applications.

Authors: Prateek Goyal, Swaroop Chakraborty, Superb K. Misra.

Journal and year: Materials Science and 5-3-2018.

Inference: In this developed a one-pot synthesis route for multifunctional (ZnO-Fe₃O₄) nanocomposites. The Fe₃O₄ nanoparticles were decorated on the surface of ZnO. The formation of ZnO- Fe₃O₄ (ZF) nanocomposite was confirmed using XRD, FE-SEM and ICP-OES. This work comprises of adsorption, photocatalysis and antibacterial studies. Photocatalytic property of ZF nanocomposite was tested using degradation of methylene blue (MB) dye under UV irradiation[15].

5.Title: Three-dimensional (Fe₃O₄/ZnO)@C Double-core@shell porous nanocomposites with enhanced broadband microwave absorption

Authors: Xun Meng, Yequn Liu, Guanghui Han, Weiwei Yang, Yongsheng Yu

Journal and year: CARBON 15085 and 14 February 2020

Inference: The synergistic effect of magnetic and dielectric materials makes this kind of composite as an ideal microwave absorber. So far, composite absorbing materials of Fe₃O₄ and carbon have been extensively studied and achieved excellent absorption properties. However, this type of absorber has always the problem at narrow effective absorption band ($RL \leq -10$ dB). In this article, we have prepared 3D (Fe₃O₄/ZnO) @C double-core@shell nanocomposites by a clever method [16].

CHAPTER- 3

AIM AND SCOPE OF PRESENT INVESTIGATION

This project work is mainly focused on the following objectives:

- To synthesis novel C-Fe₃O₄-ZnO nanocomposite by a hydrothermal method
- Characterization of the nanocomposite using XRD, UV, FT-IR, SEM
- Determine morphology and size of the nanocomposites
- Photocatalytic degradation of the *crystal violet* dye using C-Fe₃O₄-ZnO nanocomposite
- Summarize the obtained results

CHAPTER-4

EXPERIMENTAL AND CHARACTERISATION TECHNIQUES

4.1 EXPERIMENTAL SYNTHESIS OF (CARBON-Fe₃O₄-ZnO)

Carbon based mixed metal oxides have been synthesized in the hydrothermal method as we discussed below

4.2 MATERIALS

In the process of synthesizing carbon based metal oxides urea is used as main source of carbon and Iron (II) chloride, zinc acetate, polyvinyl pyrrolidone (PVP), sodium hydroxide chemical materials have been used in this synthesis.

4.3 SYNTHESIS OF CARBON-Fe₃O₄-ZnO NANOPARTICLE

The carbon-based metal oxide nanoparticle has been synthesized in the hydrothermal method, initially taken 20g urea, 0.2M Iron (II) chloride, 0.2 M Zinc acetate, 1g Polyvinyl pyrrolidone (PVP) in a 200 ml deionised water at 120 degrees temperature.

Stirred this mixed solution for 1 hour in magnetic stirrer and then take 5g sodium hydroxide in 50 ml water in another beaker stir the hydroxide pellets completely it gets dissolved.

After completely dissolving the sodium hydroxide pellets, add this 50 ml sodium hydroxide solution into the solution were stirred in magnetic stirrer by using dropper by drop by drop until the solution completes

After adding the sodium hydroxide solution cover the whole solution with aluminium foil. Allow this solution is stirred for 1 hour after adding the sodium hydroxide with temperature.

After completing the 1 hour stirring, take it out the solution before we are going to drop the solution in autoclave clean those autoclaves with deionised water first and then

clean with acetone, after cleaning the autoclaves allow to dry for 5 minutes, after drying the autoclaves, drop the prepared solution in autoclaves.

After dropping the solution in autoclaves, close the caps of autoclaves by using bolts tightly, one more time cross check the autoclaves whether u packed tightly or not, if we are not packed tightly due to over pressure inside the autoclave the solution come with huge pressure it will make holes of ceiling that much pressure inside the autoclaves have been generated.

This hydrothermal is very useful because we can get nanosized particles at low temperature, without this method we need high temperature ex: 1000 ° that we did not get proper shape, but in this we will get almost exact shape as we expect. this is one more advantage of this method is it tuning the shape.

After tightly packing the autoclaves keep it them hot air oven at 170° temperature for 24hours, after completing the 24 hours heating take it out autoclaves from hot oven and keep it for cooling.

After cooling the autoclaves open them carefully and drop the solution into a clean beaker and then add few ml of deionised water in that. allow it that solution for settling. after settling the solution drop the water and one more time add water and allow it to settle down.

After sometime drop the water where it comes from the sample, finally clean the sample with acetone. after washing with acetone remaining will be kept at hot air at 170 ° for 12 hours, after drying the solution take it out from the oven and collect the sample by grinding by using mortar. After grinding the sample collect it and store it in cleaned packing beaker.

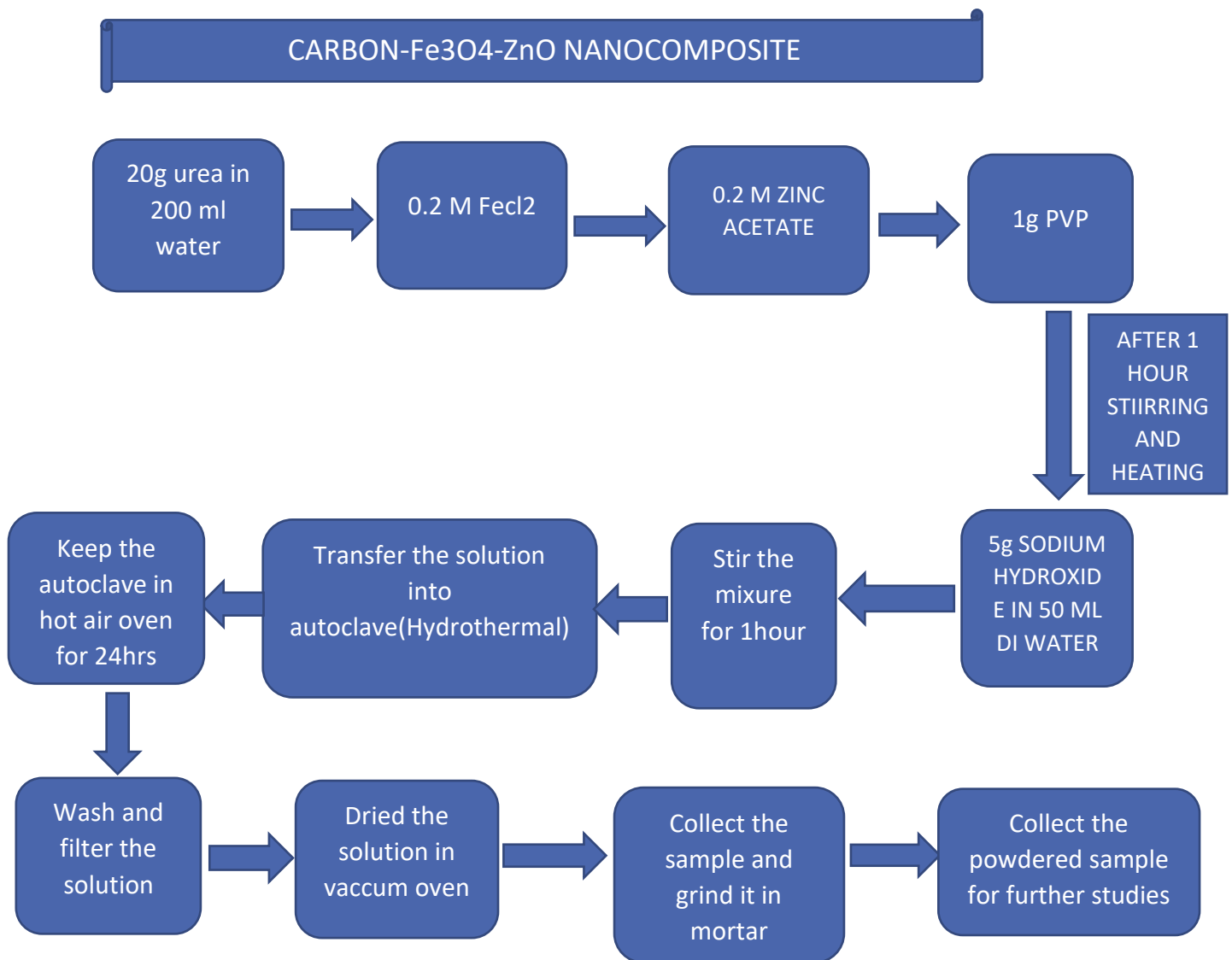


Figure 4.3: synthesis of CARBON-Fe₃O₄-ZnO nanocomposite

Finally Carbon-Fe₂O₃-ZnO Nanoparticles will be confirmed by characterisation techniques (UV, FTIR, SEM, XRD).

4.4 CHARACTERISATION TECHNIQUES

Crystal structure, morphology, compositional information, and photocatalytic application of the synthesized nanoparticles were characterized using the following instruments. These include X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infra-red spectroscopy (FTIR), UV-Vis spectroscopy [17].

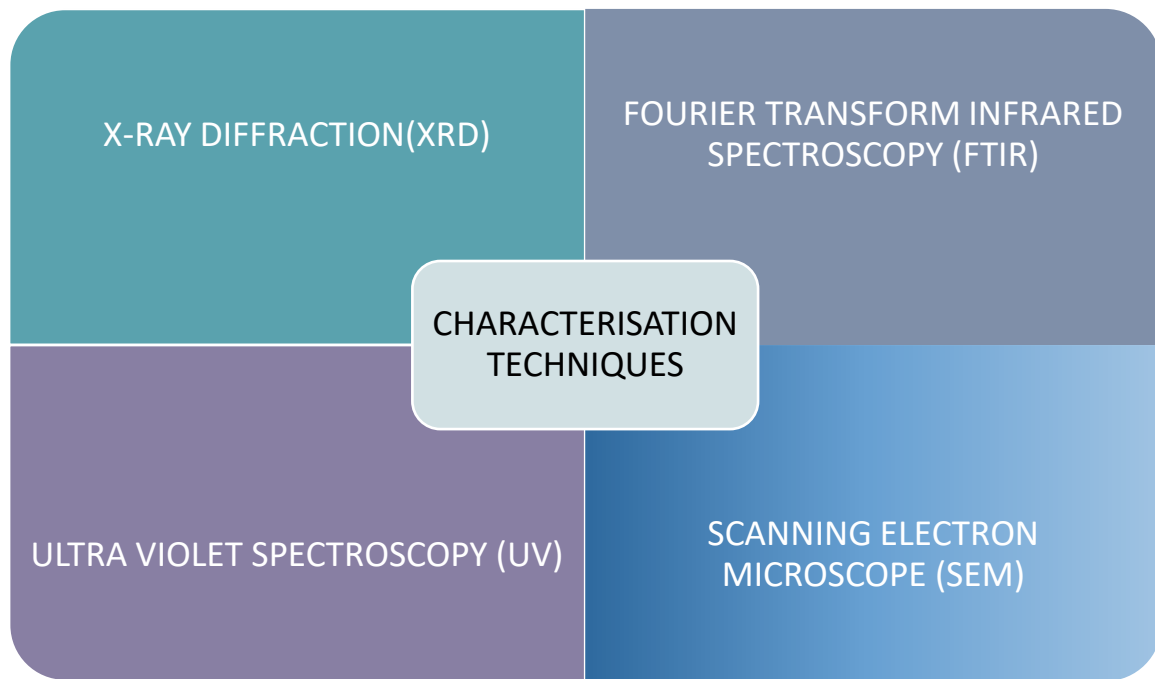


Figure 4.4: characterisation techniques of nanocomposite

4.4.1 X-RAY DIFFRACTION (XRD)

XRD is one the characterisation technique that reveals the structural properties of nanoparticles. It provides information on the phase, chemical composition, symmetry of unit cells, crystallinity, lattice constant and properties of the nanoparticles. This technique is employed for the identification of both single and multiphase nanoparticles [18].

XRD is considered as one of the oldest non-destructive methods for the analysis of nanoparticles. The XRD pattern is influenced by the size and shape of the unit cell of the crystal. Consequently, properties of a material are dependent on their structure of about 90% solid materials are crystalline in nature and each crystalline has a significant X-ray diffraction pattern which can be used as fingerprint to detect the material [19].

Diffraction pattern is obtained only when the X-rays are interacted with the crystal. Information like symmetry of the unit cell, stress, strain, size of crystallite and growth orientation etc. are obtained from the diffraction patterns.

BRAGG'S LAW

When a material is irradiated with a monochromatic light of wavelength around the inter atomic distance of the material, light gets dispersed by the atoms and interfere to give rise to diffracted light with a higher intensity [20]. The arrangement of atoms in the material is related to the intensity of the scattered light. If wavelength of light is λ and the incident angle is θ and the constructive interference is obtained at an angle 2θ from the incident beam of light if Bragg's equation is satisfied. Bragg's equation is given by,

$$n\lambda = 2d \sin \theta$$

where,

n is the diffraction order,

d is the distance between the diffracting planes and

θ is the Bragg's angle.

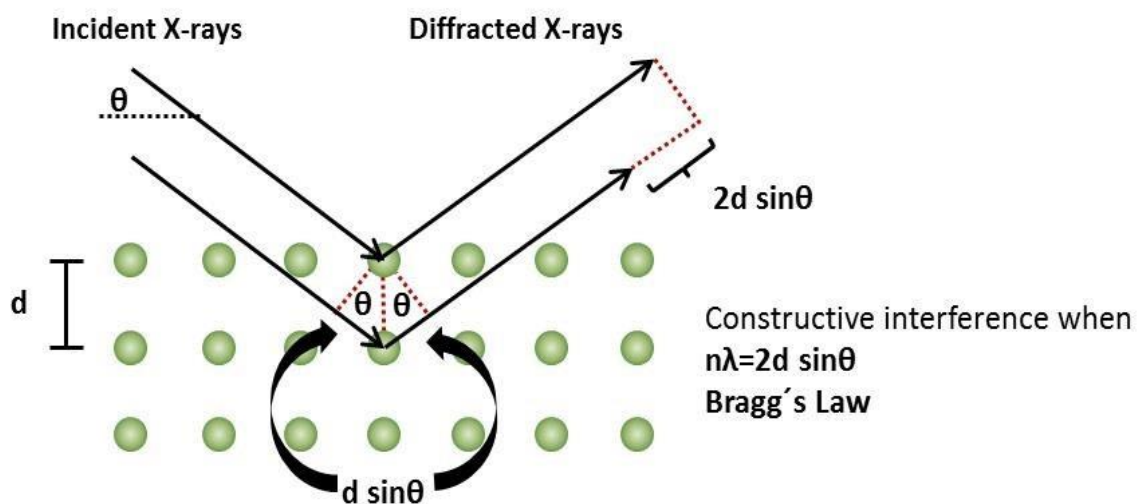


Figure 4.4.1: schematic representation of Bragg's law

4.4.2 SCANNING ELECTRON MICROSCOPE (SEM)

High resolution scanning electron microscope (SEM) is a very useful for the characterization of size and shape of the nanoparticle. The sample preparation and acquisition of images are relatively easy and convenient. Since the SEM image is a two-dimensional (2D) representation of three-dimensional (3D) structures from a certain viewing angle, it does provide a certain amount of 3D detail that can be used to recreate the shape of a basic structure with sub-nm precision using model-based measurement [21].

Secondary electrons (SEs) and/or backscatter electrons (BSE) produced when the sample is bombarded by the primary electron (PE) beam provide the signal that causes a SEM image to be created. A SEM's overall accelerating voltage is usually 30 kV. The SE has a limited escape depth in the region of a few nm owing to their low energy below 50 eV, while the BSE has a slightly higher escape depth in the range of a few nm.

The demand for SEM in laboratories to characterise nanoparticulate materials is increasing because of the application of nanoparticles in the commercial products.

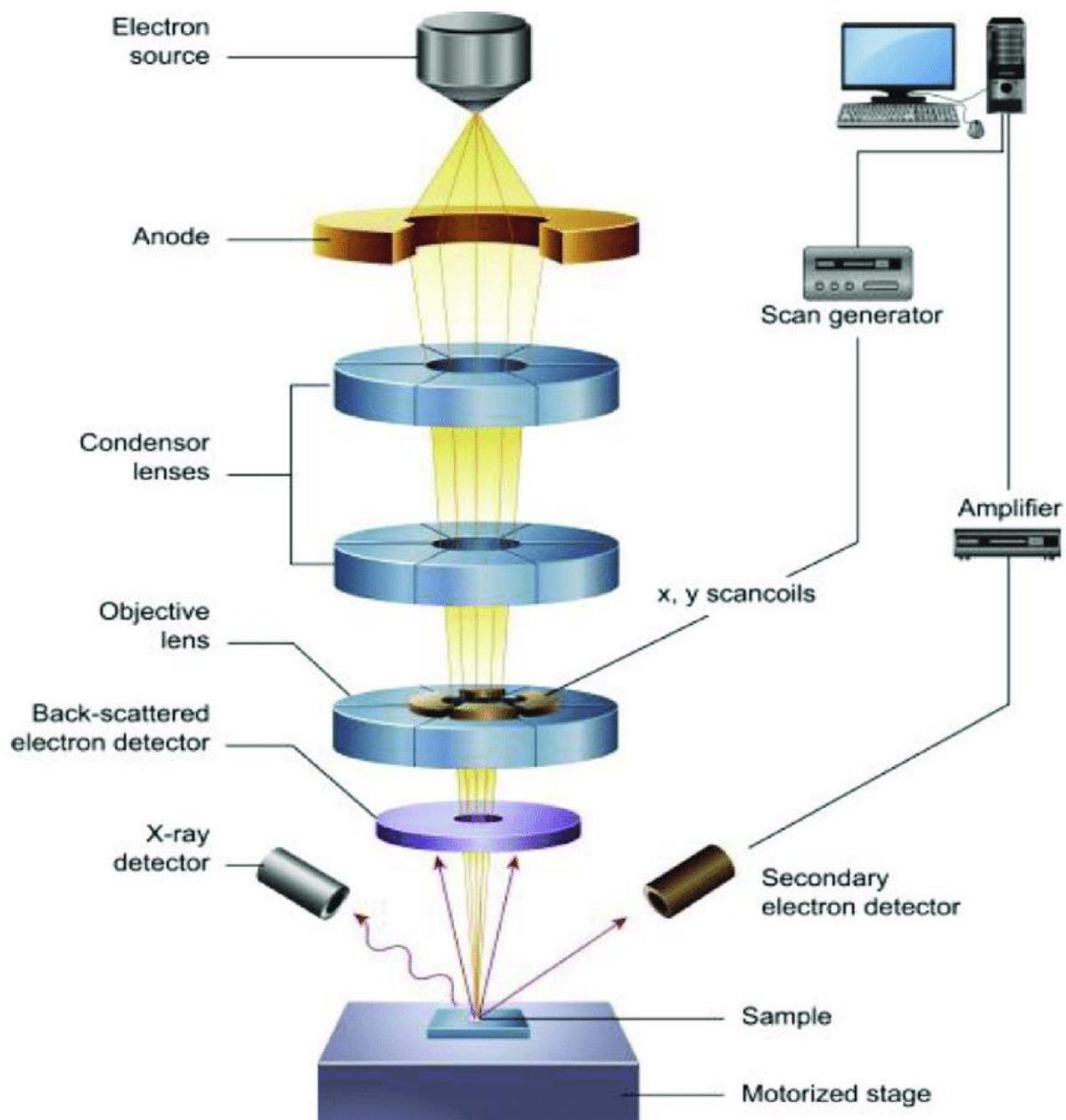


Figure 4.4.2: Schematic representation of SEM

4.4.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared (FTIR) spectroscopy is a very efficient non-destructive characterization technique for surface characterization of nanoparticles' surfaces, providing a specific setup is connected to the spectrometer [22].

it is used to determine the functional groups. The chemical structure of the nanoparticles' surface and the surface reactive sites responsible for surface reactivity can be determined under particular conditions.

The structure and bands of the synthesised nanoparticles, FTIR may be used to test a variety of components, including bulk or thin films, liquids, solids, pastes, powders, fibres, and other materials. FTIR analysis may be used for quantitative (amount) analysis as well as qualitative (identification) analysis of materials where appropriate criteria are used. FTIR can test samples up to 11 mm in diameter and weigh in bulk or the top 1 mm of the sample [23].

The difficulty in FTIR characterization is mainly because of high degree of overlapping of the IR absorption bands which makes difficult for the attribution of certain functional groups, despite the fact that up to date computer-searchable databases are available.

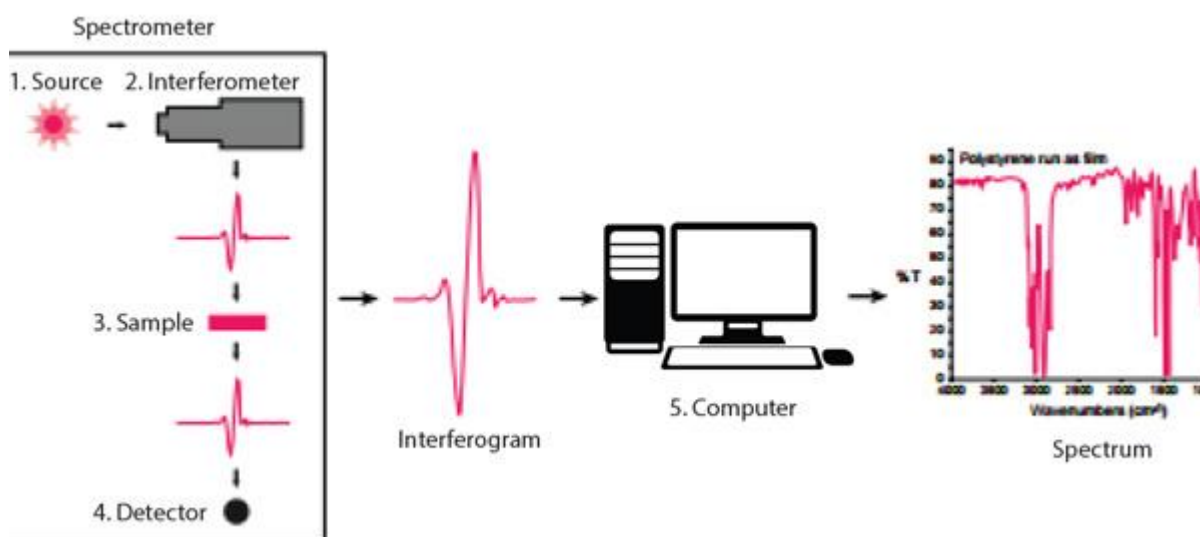


Figure 4.4.3 : Schematic representation of FTIR

4.4.4 UV-VISIBLE SPECTROSCOPY

UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample.

Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions of electrons from the excited state to

the ground state, while absorption measures transitions from the ground state to the excited state [25].

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals.

The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. There are four possible types of transitions ($\pi-\pi^*$, $n-\pi^*$, $\sigma-\sigma^*$, and $n-\sigma^*$), and they can be ordered as follows: $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes or sample, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied [26].

All diluted inorganic solutions are UV active

Solutions of transition metal ions can be coloured (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another.

The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption ($\lambda_{\max}$).

While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

The Beer–Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the

absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve [27].

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward–Fieser rules, for instance, are a set of empirical observations used to predict $\lambda_{\max}$, the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample.

The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer–Lambert law:

where A = absorbance

I = intensity of the incident is the transmitted intensity,

L = the path length

c = concentration of absorbing species

ϵ = molar absorptivity coefficient.

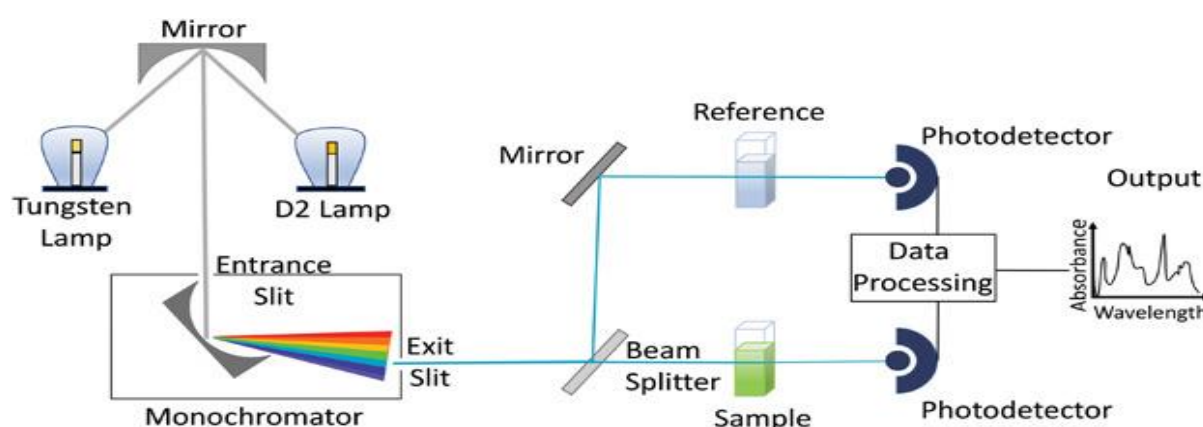


Figure 4.4.4: schematic representation of uv-visible spectroscopy

CHAPTER - 5

RESULTS AND DISCUSSION

Crystal structure, morphology, structural composition and functional group analysis of the given nanocomposite have been confirmed by characteristic techniques like XRD, SEM, UV-Vis spectroscopy, FTIR.

5.1 X-RAY DIFFRACTION (XRD)

Carbon-Magnetite and zinc oxide were elaborated with different ratios to form a homogeneous nanocomposite. X-ray diffraction (XRD) was used for detecting the crystalline phases represented in below figure.

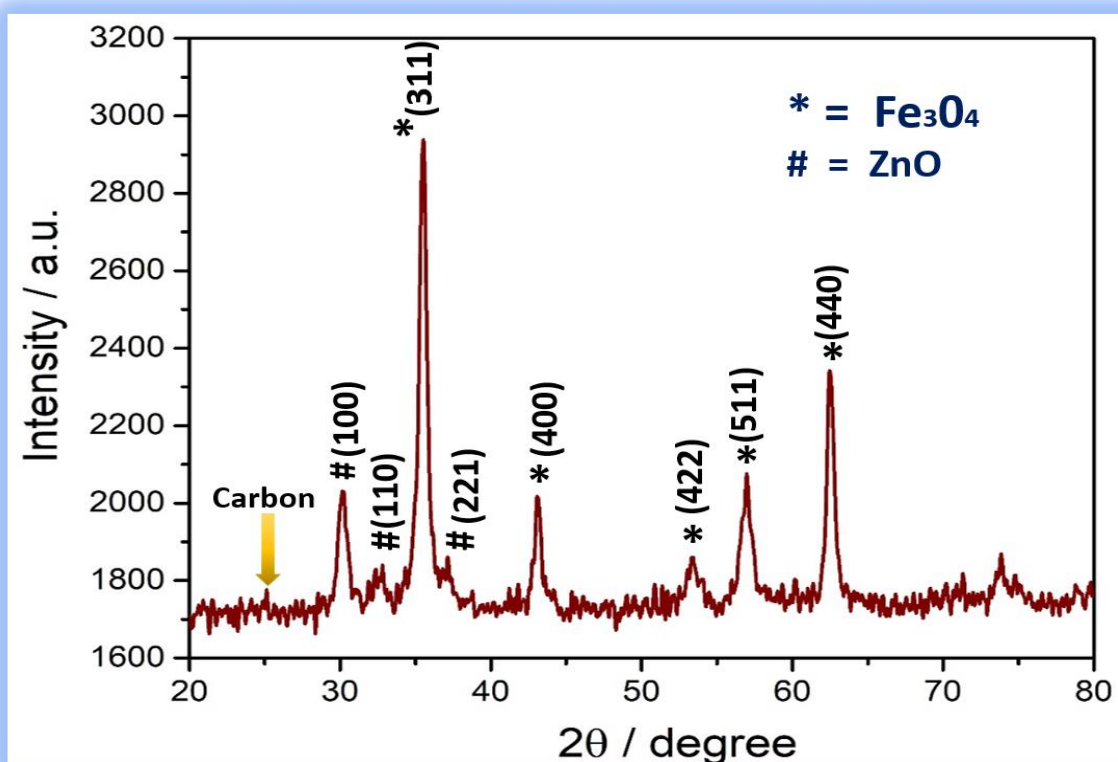


Figure 5.1: XRD of C- Fe_3O_4 -ZnO

S.NO	PLANE	2 THETA(DEGREE)
1	Fe ₃ O ₄ (311)	35.50
	Fe ₃ O ₄ (400)	43.14
	Fe ₃ O ₄ (422)	53.44
	Fe ₃ O ₄ (511)	57.40
	Fe ₃ O ₄ (440)	62.58
2	ZnO (100)	31.7
	ZnO (110)	34.4
	ZnO (221)	36.2

The first set magnetite Fe₃O₄ phase with diffraction peaks at 35.50, 43.14, 53.44, 57.40, and 62.58 corresponding to Miller indices (311), (400), (422), (511), and (440), respectively and for ZnO is well indexed to hexagonal wurtzite structure with the planes (100), (110), and (221) corresponding to $2\theta = 31.7, 34.4$ and 36.2 .

These peaks are attributed to the cubic spinal structured magnetite. No significant peaks corresponding to impurities were detected in the XRD pattern. After mixing CARBON -Fe₃O₄-ZnO, peaks of carbon- magnetite and zinc oxide are detected. In the nanocomposite, some intensities of the peaks changed due to peak interference.

5.2 SCANNING ELECTRON MICROSCOPE (SEM)

Scanning electron microscope is especially used for size and shape characterization, because the required sample preparation and image analysis is relatively quick and simple [28]. The scanning Electron Microscopy (SEM) images allowed a detailed study on the morphological structure of the nanoparticles [29].

The scanning electron microscope operates in the same manner as an optical microscope, but instead of detecting photon, it detects electrons scattered from the sample. The wavelength of electrons can be made shorter than that of photons because electrons can be accelerated by an electric potential. As a result, the SEM will magnify pictures up to 200.000 times.

The morphological variations in the synthesised sample nanoparticles were detected and analysed. Nickel oxide analysed by SEM is shown in figure. Carbon-Fe₃O₄-ZnO nanoparticles thus synthesised at low temperature was analysed and the images are displayed in the below figure.

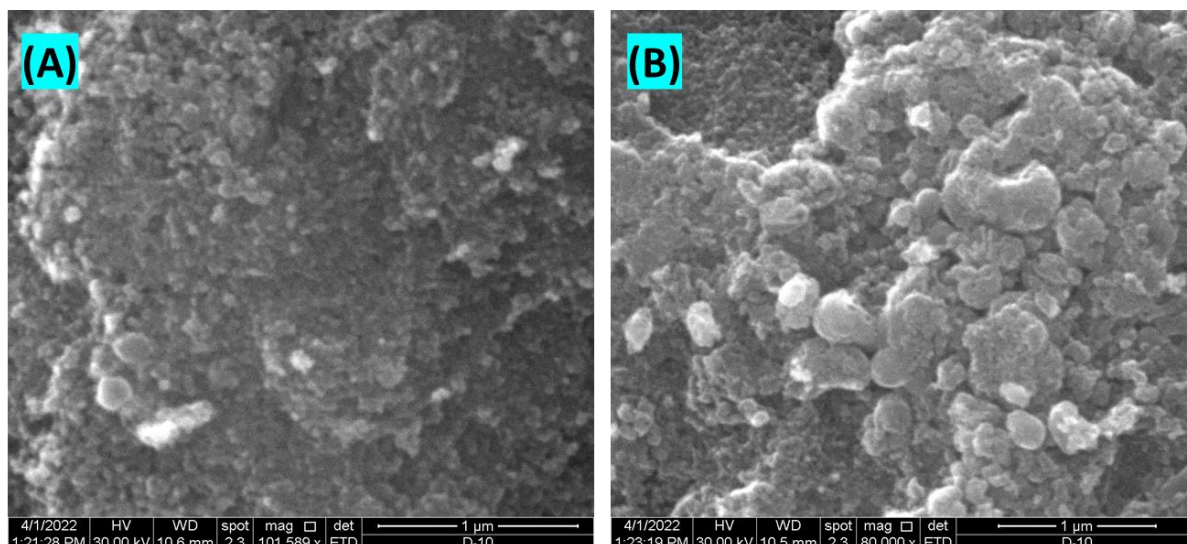


Figure 5.2: (A-B) Different magnifications of SEM images of the C-Fe₃O₄-ZnO nanocomposite.

C-Fe₃O₄-ZnO composites show the cubic and spherical morphology with average diameter 10.5 to 10.6 nm for Carbon-Fe₃O₄-ZnO, respectively as the nanocomposites structure

5.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

This technique is used to determine the functional groups present in the given nanocomposite.

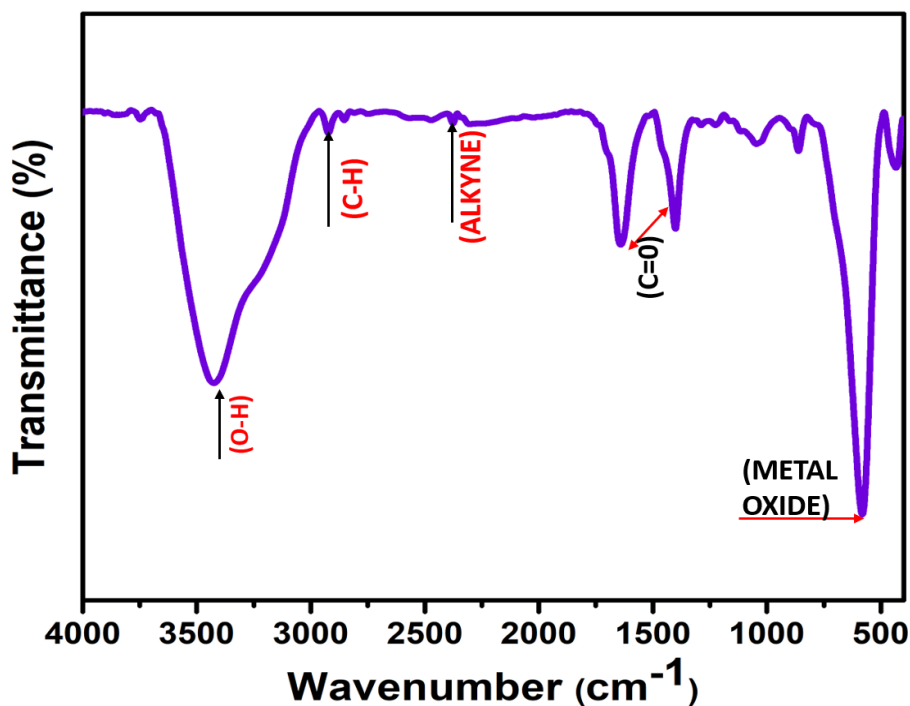


Figure 5.3: FTIR OF C-Fe₃O₄-ZnO NANOCOMPOSITE

S.NO	FUNCTIONAL GROUP	WAVENUMBER (CM ⁻¹)
1	O-H	3450
2	C-H	2950
3	ALKYNE	2480
4	C=O	1750
5		1350
6	METAL OXIDE	700

The above table shows that the various functional groups present at different wavenumbers, in this O-H group observed at 3450 cm⁻¹ then C-H group was observed at 2950 cm⁻¹ then after this alkyne group was observed at 2480 and then C=O group was observed at 1750 cm⁻¹ and 1350 cm⁻¹ and finally metal oxide peak was observed at 700 cm⁻¹.

5.4 UV-Visible SPECTROSCOPY

Ultraviolet-visible (UV-Vis) spectroscopy is a widely used technique in many areas of science ranging from bacterial culturing, drug identification and nucleic acid purity checks and quantitation, to quality control in the beverage industry and chemical research.

It is a quantitative technique used to measure how much a chemical substance absorbs light. This is done by measuring the intensity of light that passes through a sample with respect to the intensity of light through a reference sample or blank.

This spectroscopy technique is also used to determine the absorption of the given polymer under neutral condition.

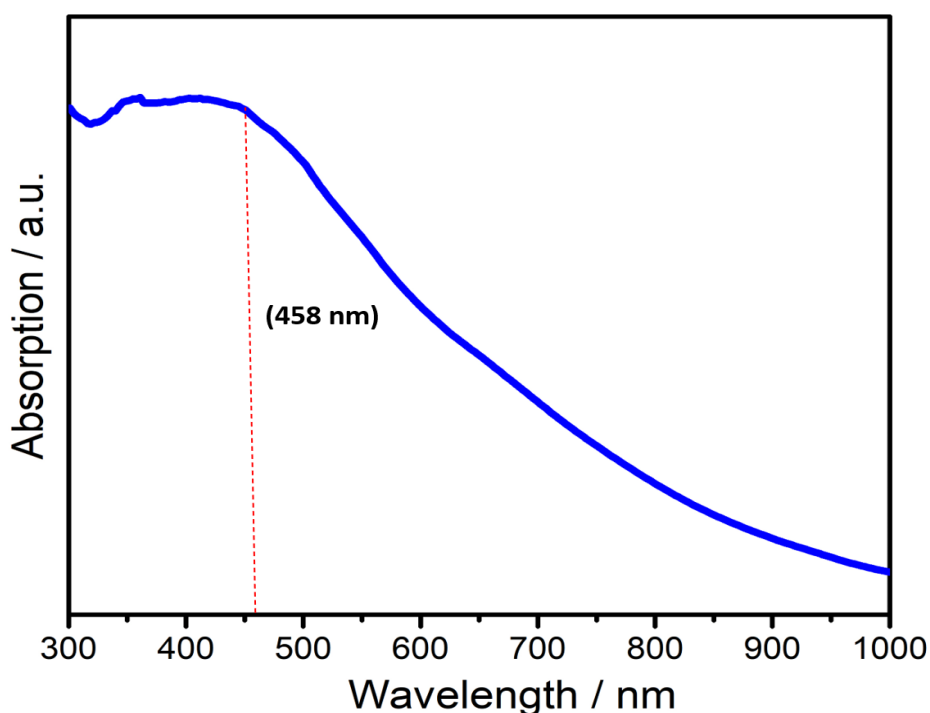


Figure 5.4: UV-VISIBLE SPECTRA OF C-Fe₃O₄-ZnO

From the graph, we come to know that the absorption peak was obtained at 458 nm.

5.4.1 BAND GAP

The band gap (E_G) is the gap in energy between the bound state and the free state, between the valence band and conduction band. Therefore, the band gap is the

minimum change in energy required to excite the electron so that it can participate in conduction. Schematic of the energy bands for electrons in a solid.

As the electronegativity difference $\Delta\chi$ increases, so does the energy difference between bonding and antibonding orbitals. The band gap is a very important property of a semiconductor because it determines its colour and conductivity.

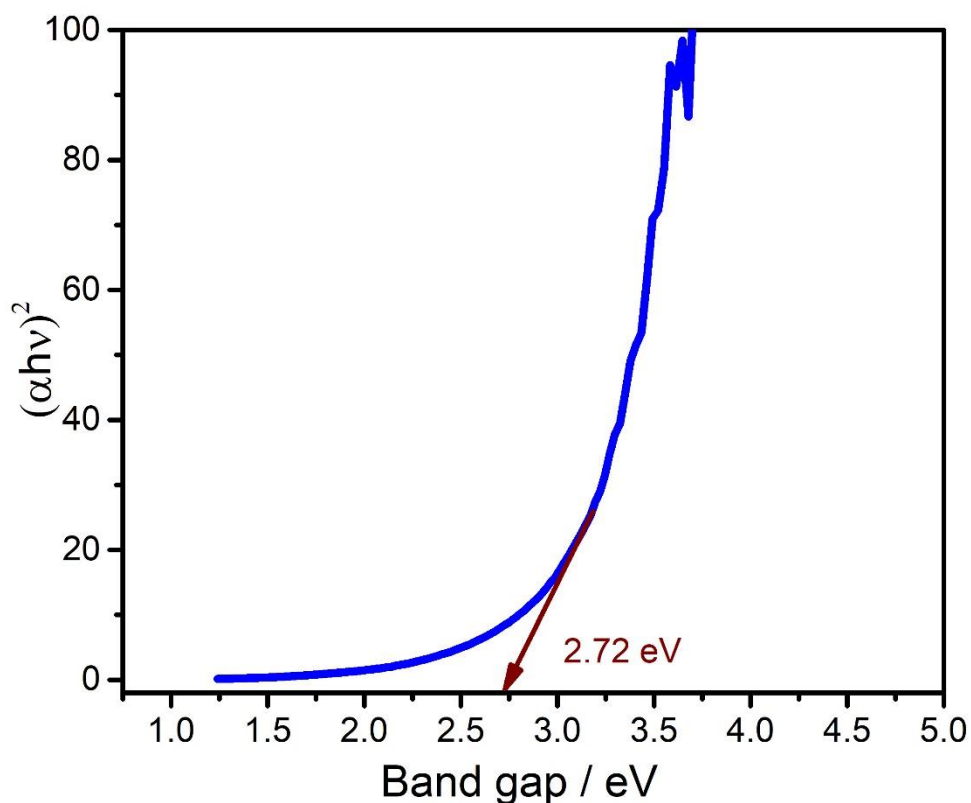


Figure 5.4.1: BAND GAP OF NANOCOMPOSITE

The above figure shows the band gap of nanocomposite band gap and this nanocomposite shows the band gap at 2.72 eV. This means our compound shows that the good conductivity and good electron absorber.

5.5. Photodegradation study

5.5.1. Photocatalytic activity test

Crystal violet (CV) was chosen as the model organic pollutants to test the photocatalytic dye degradation analysis for the catalyst. Typically, a catalyst (20 mg) was added into the 50 ml of aqueous dye solution (20 mg L^{-1}) then, the dye solution was kept in dark room to attain the adsorption and desorption equilibrium of dyes on surface of catalyst. Then, the dye solution was irradiated on sunlight for overall time period of 120 minutes. 2 ml of solution was taken at appropriate interval of time. The collected solution was centrifuged and filtered using a $0.2 \text{ }\mu\text{m}$ syringe filter. The degradation efficiency is determined by the degradation of organic dyes on UV-Vis spectrophotometer. The degradation efficiency is calculated by the formula,

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C and C_0 are initial and final concentration of dye molecules. After 1st completed the photocatalytic reaction, the catalyst was collected by centrifuge and washed with water and dried at 70°C . The regenerated catalyst was used to evaluate the stability and reusability of catalyst by degradation the dye solution.

The first order kinetic reaction value were used to determine the correct degradation rate of MB as follows;

$$-\ln(C/C_0) = kt \quad (2)$$

Where, k = rate of reaction constant and t is time. The Photocatalytic dye degradation activity were performed during the well sun shining between 11:00 AM to 2:00 PM in clear sky. The average solar light intensity was measured about 1.00×10^5 lux

5.5.2. Photocatalytic activity

The photocatalytic degradation efficiency of as prepared catalysts of C- Fe_3O_4 -ZnO nanocomposite was resolute by the deprivation of CV dye under irradiation of Sun light. When irradiating the CV dye solution, the concentration of the dye was noticeably reduced and it was confirmed by the significant color variation. For C- Fe_2O_3 -ZnO catalyst, the catalyst influences the organic molecule to achieve the efficiency of about 94.5 % within 120 mins. The rate of electron-hole pair

recombination was delayed and higher absorption by incorporation of metal oxide nanocomposite structure results increased the degradation efficiency.

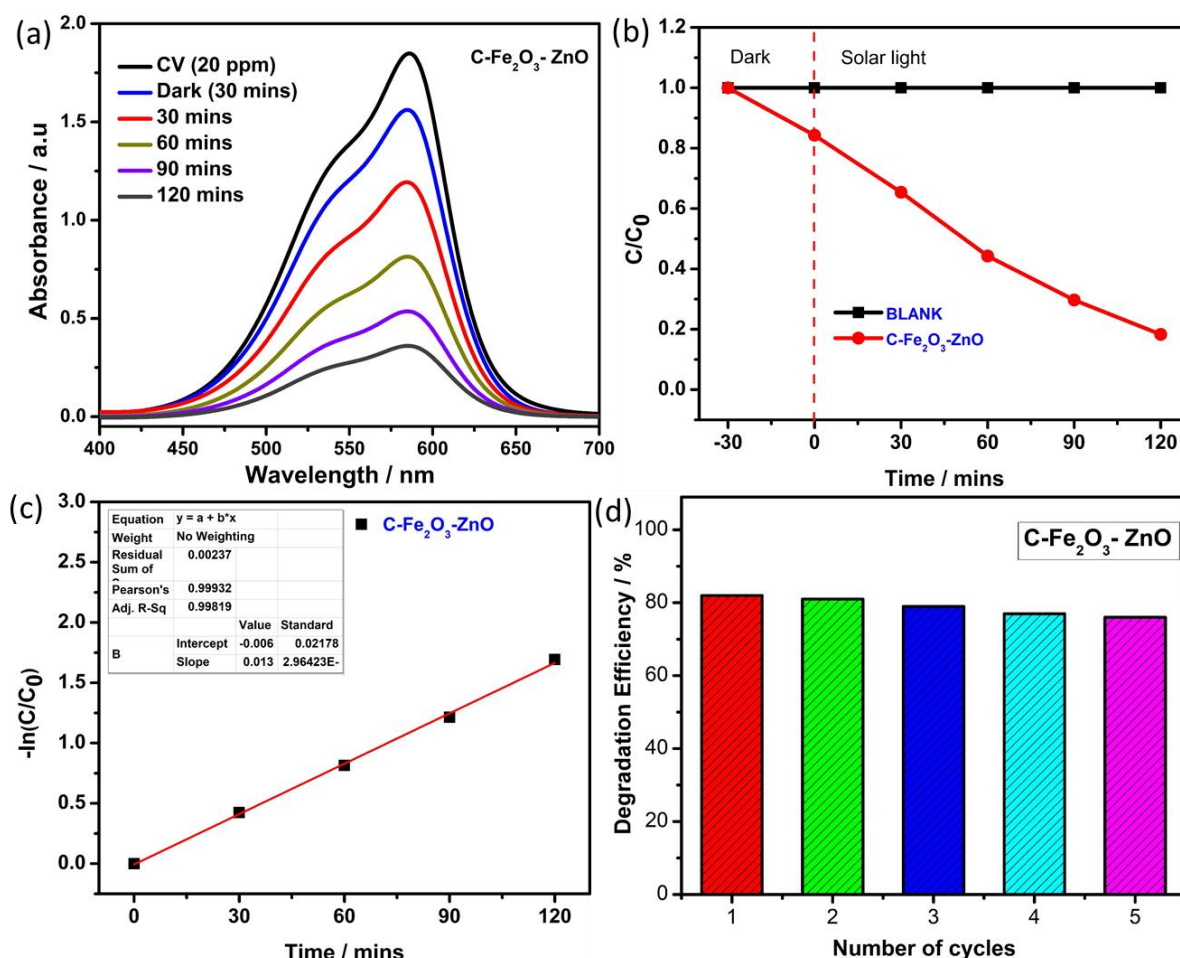


Figure.5.5 (a) represents the UV-visible spectra for the CV with occurrence of catalysts C-Fe₂O₃-ZnO was irradiated by sun light for 120 minutes. (c) C/C_0 versus time interval plot of CV dye (d) $-\ln(C/C_0)$ versus time interval plot of CV dye (d) reusability test of CV dye solution

The significant improvement of the degradation efficiency is due to the presence of different metal and effective incorporation and energy level matching. Hence reduce the recombination of excited charge carriers (electron-hole pair) and higher energy absorption to produce large number of reactive oxygen species (ROS radicals).

Figure.5.5 b depicts the changes in initial and final concentration of dye in the presence and absence of photocatalyst against the light irradiation with respect to time (t) for the CV dye solution. Addition investigation of pseudo-first order kinetics studies shown in Figure.5.5 c the degradation rates was 0.052 min^{-1} for C-Fe₃O₄-ZnO

nanocomposites against CV dye, respectively. From the studies rate constant value and R^2 values are listed in the Table.3. The Figure 5.6 showed schematic diagram illustrating the mechanism of charge separation, generation of reactive oxygen species (ROS) and photocatalytic activity of photocatalyst under the sunlight irradiation [30].

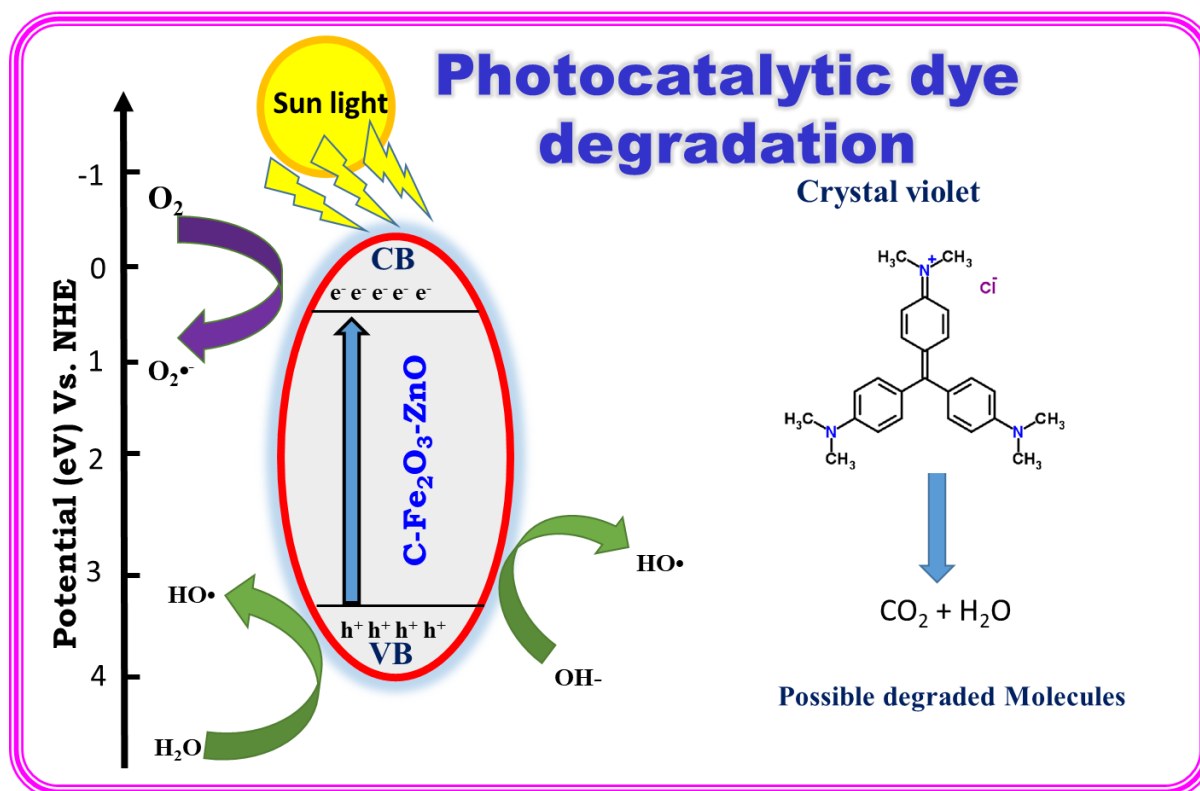


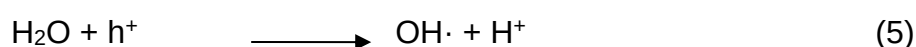
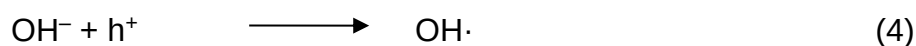
Figure 5.6: Schematic diagram illustrating the mechanism of charge separation and photocatalytic activity of photocatalyst under the sunlight irradiation

The mechanism of CV dye degradation for the C-Fe₃O₄-ZnO catalyst is described as follows,

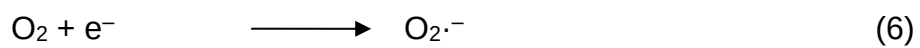
(i) Formation of electron hole pair



(ii) Formation of hydroxyl radicals



(iii) Formation of superoxide radicals



(iv) Photo degradation of CV dye



Table 3 photocatalytic activity result of NiO, and Ag/ Ni(OH)₂ nanocomposites.

S.No	Catalyst	Band gap (eV)	Degradation efficiency (%) (120 minutes)	K (min ⁻¹)	R ²
Acid yellow-36 (20 ppm)					
1	C-Fe ₃ O ₄ -ZnO	3.21	81.7	0.029	0.99

SUMMARY AND CONCLUSION

- Mixed Metal oxide nanocomposite have attracted much attention due to its applications in catalysis, dye degradation, electrode materials in battery and optoelectronic devices.
- Polyvinylpyrrolidone was used as surfactant to reduce particle size.
- Herein, low temperature based C-Fe₃O₄-ZnO nanocomposite was
- Synthesized by a “one-pot” hydrothermal method.
- Equal concentration of precursors were used.
- Crystallite structure and size were confirmed by XRD. The size of the crystallite was calculated using Debye Scherrer formula, the size was found to be 21.3 nm
- The SEM microscopy demonstrated the synthesized nanoparticles were in nanoscale region with asymmetric surface morphology structure. Organic functional groups presence on the surface of the nanoparticles were identified using FT-IR spectroscopy.
- The investigated photocatalytic result demonstrated that C-Fe₃O₄- ZnO nanocomposite showed excellent dye degradation of CRYSTAL VIOLET which is due to its effective charge carriers creation and followed by the free radical formation during the light irradiation.
- Thus, the prepared cost effective and low temperature C-Fe₃O₄-ZnO could be the suitable candidate for water purification, through the photocatalysis process.

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