

**g-C₃N₄ DECORATED ZINC OXIDE NANOCOMPOSITES PREPARED BY CHEMICAL
PRECIPITATION METHOD FOR PHOTOCATALYST APPLICATIONS**

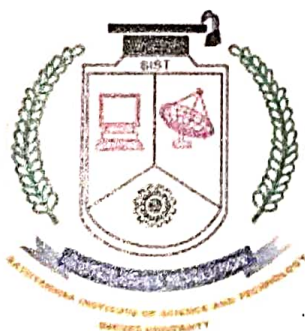
Submitted in partial fulfilment of the requirements for the award of

Master of Science in CHEMISTRY

by

B.DHAKSHNAMOORTHY

(REGISTER NO : 41910005)



DEPARTMENT OF CHEMISTRY

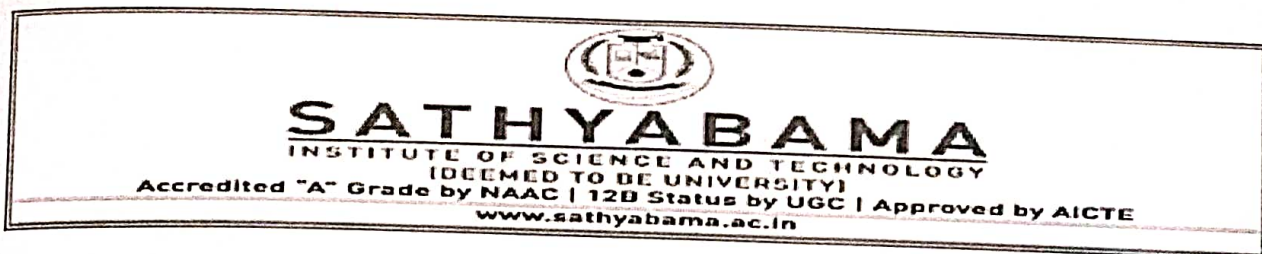
SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY (DEEMED TO BE UNIVERSITY)

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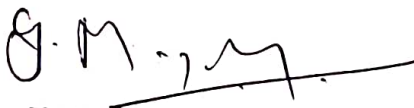
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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of Mr. B. DHAKSHNAMOORTHY (41910005) who carried out the project entitled **g-C₃N₄ DECORATED ZINC OXIDE NANOCOMPOSITES PREPARED BY CHEMICAL PRECIPITATION METHOD FOR PHOTOCATALYST APPLICATIONS** under our supervision.


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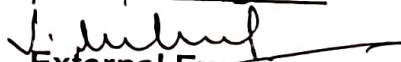

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I Mr. B. DHAKSHNAMOORTHY student of SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY hereby declare that the Project Report entitled g-C₃N₄ DECORATED ZINC OXIDE NANOCOMPOSITES PREPARED BY CHEMICAL PRECIPITATION METHOD FOR PHOTOCATALYST APPLICATIONS" done by me under the guidance of Dr. Y. SASIKUMAR, M.Sc., Ph.D. 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.

DATE: 8/05/23

PLACE: Chennai



SIGNATURE OF THE CANDIDATE

WISDOM

TO EXPLORE NEW FRONTIERS IN SCIENCE THROUGH
INNOVATION AND COLLABORATION

ACKNOWLEDGEMENT

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I wish to express my thanks to all Teaching and Non-teaching staff members of the Department of Chemistry who were helpful in many ways for the completion of the project.

**B DHAKSHNAMOORTHY g-C₃N₄ DECORATED BY ZINC OXIDE
NANOCOMPOSITES PREPARATION IN CHEMICAL PRECIPITATION
METHOD FOR PHOTOCATALYST APPLICATION**

VISION

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

ABSTRACT

Graphitic carbon nitride (g-C₃N₄) has, since 2009, attracted great attention for its activity as a visible light-active photocatalyst for hydrogen evolution. Since it was synthesized in 1834, g-C₃N₄ has been extensively studied both catalytically and structurally. While its 2D structure seems to have been solved, its 3D crystal structure has not yet been confirmed.

Graphitic carbon nitride with Cadmium Sulphide (g-C₃N₄ -ZnO) nanocomposites were synthesized by the fractional thermal polymerization method (or) powder preparation method using melamine different ratios of Graphitic carbon nitride with Zinc 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.

Photocatalytic process is based on the generation of e⁻/h⁺ hole pair in the semiconductor on the absorption of light.

The generated electron – hole reacts with O₂ from the surroundings of the aqueous solution to give highly reactive O₂ species such as superoxide + peroxide radicals these are responsible for the photocatalytic degradation of the organic contaminants.

Graphene (G) based nanomaterials received a lot of attention in the field of photocatalytic waste water treatment. It has been extensively explored and utilized for the alteration of semiconductor photocatalysts due to its exceptional properties i.e. high specific surface area, high electron conductivity and high thermal stability. On the other hand, zinc oxide (ZnO) as a photocatalyst possesses excellent qualities as strong oxidation ability, good photocatalytic property, chemical stability, biocompatibility, non-toxicity, high photosensitivity, piezoelectric and pyroelectric properties. But inherited with some limitations such as absorption in Ultraviolet (UV) region, photocorrosion etc. as a consequence of modification due to demand of visible light active photocatalysis. Hybrid of ZnO with graphene based nanocomposites is an alternative for the degradation of organic and inorganic contaminants present in water. This

chapter presents an overview of the numerous methods used for synthesis and applications of graphene based nanomaterials (graphene oxide (GO), reduced graphene oxide (rGO)), ZnO and their coupling with highly porous ZnO nanoparticles (NPs). Accordingly, graphene supported ZnO nanocomposites are better electron collectors that strongly obstruct electron-hole pair recombination and enhance the visible light adsorption for productive usage of solar energy.

Key words: ZnO Graphene Photocatalysis Supported photocatalytic system
Wastewater treatment

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CHAPTER-1

INTRODUCTION

Graphitic carbon nitride, g-C₃N₄, is a polymeric material consisting of C, N, and some impurity H, connected via tris-triazine-based patterns. Compared with the majority of carbon materials, it has electron-rich properties, basic surface functionalities and H-bonding motifs due to the presence of N and H atoms. It is thus regarded as a potential candidate to complement carbon in material applications.

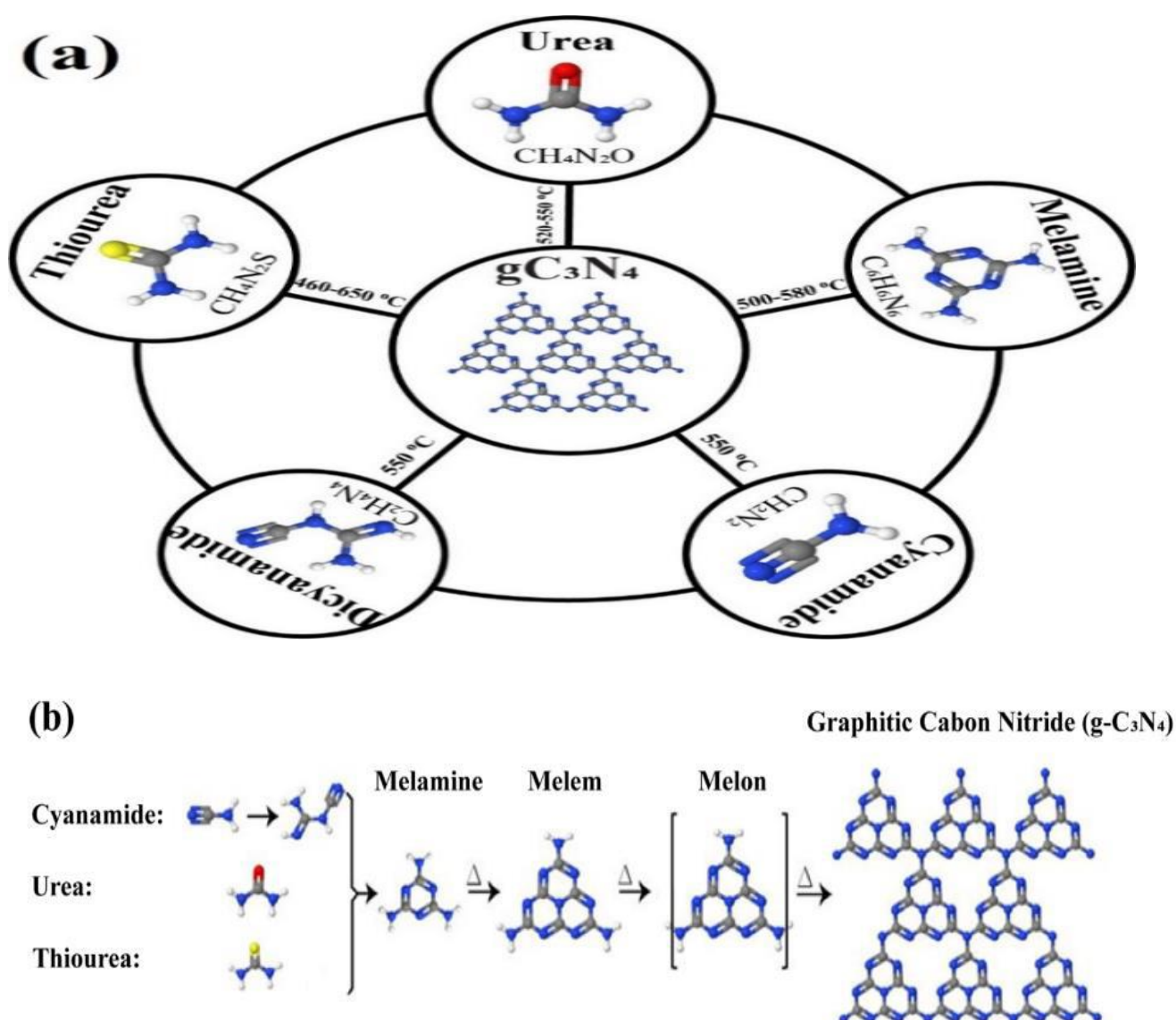
Graphitic carbon nitrides were synthesized starting from melamine.

reacts with melamine by condensation at temperatures in the range of 400–600 °C.

Introduction to g-C₃N₄ is given, the methods used for synthesizing this material with different textural structures and surface morphologies are described, and its physicochemical properties are referred. In addition, four aspects of the applications of g-C₃N₄ in catalysis are discussed:

- (1) as a base metal-free catalyst for NO decomposition,
- (2) as a reference material in differentiating oxygen activation sites for oxidation reactions over supported catalysts,
- (3) as a functional material to synthesize nanosized metal particles,
- (4) as a metal-free catalyst for photocatalysis.

The reasons for the use of g-C₃N₄ for such applications are also given, and we expect that this paper will inspire readers to search for further new applications for this material in catalysis and in other fields



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.

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.

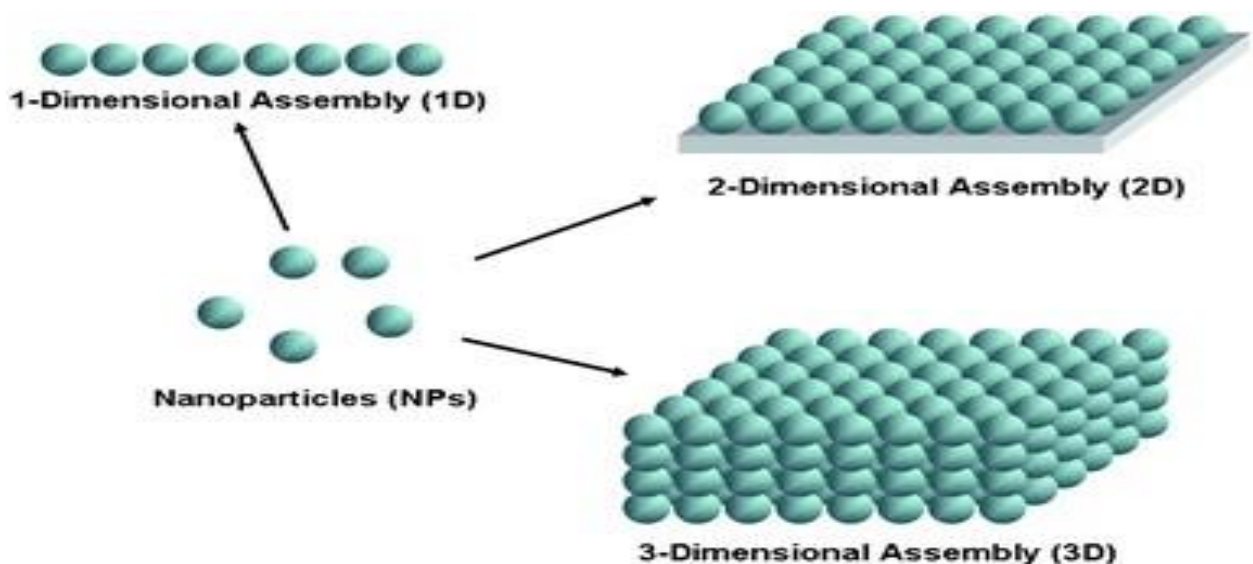


Figure 1.2 : Types of nano particles

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 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, Fe₃O₄, CeO₂, TiO₂ 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.

1.3.2 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.

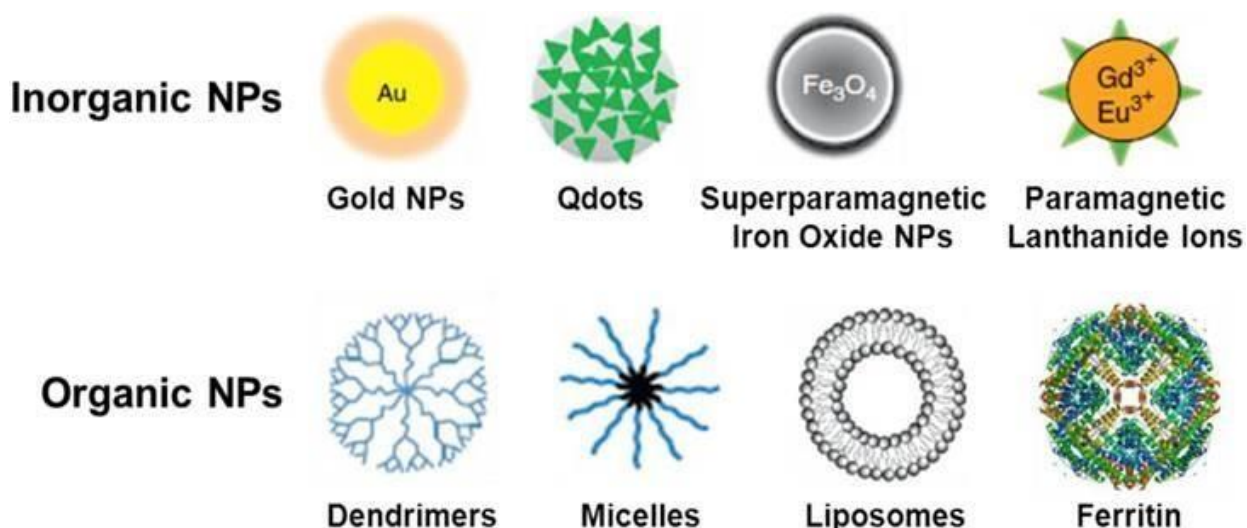


Figure 1.3.1AND 1.3.2 : inorganic and organic nanoparticles(NPs)

1.3.3 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 nanosized 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.

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.

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 .

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

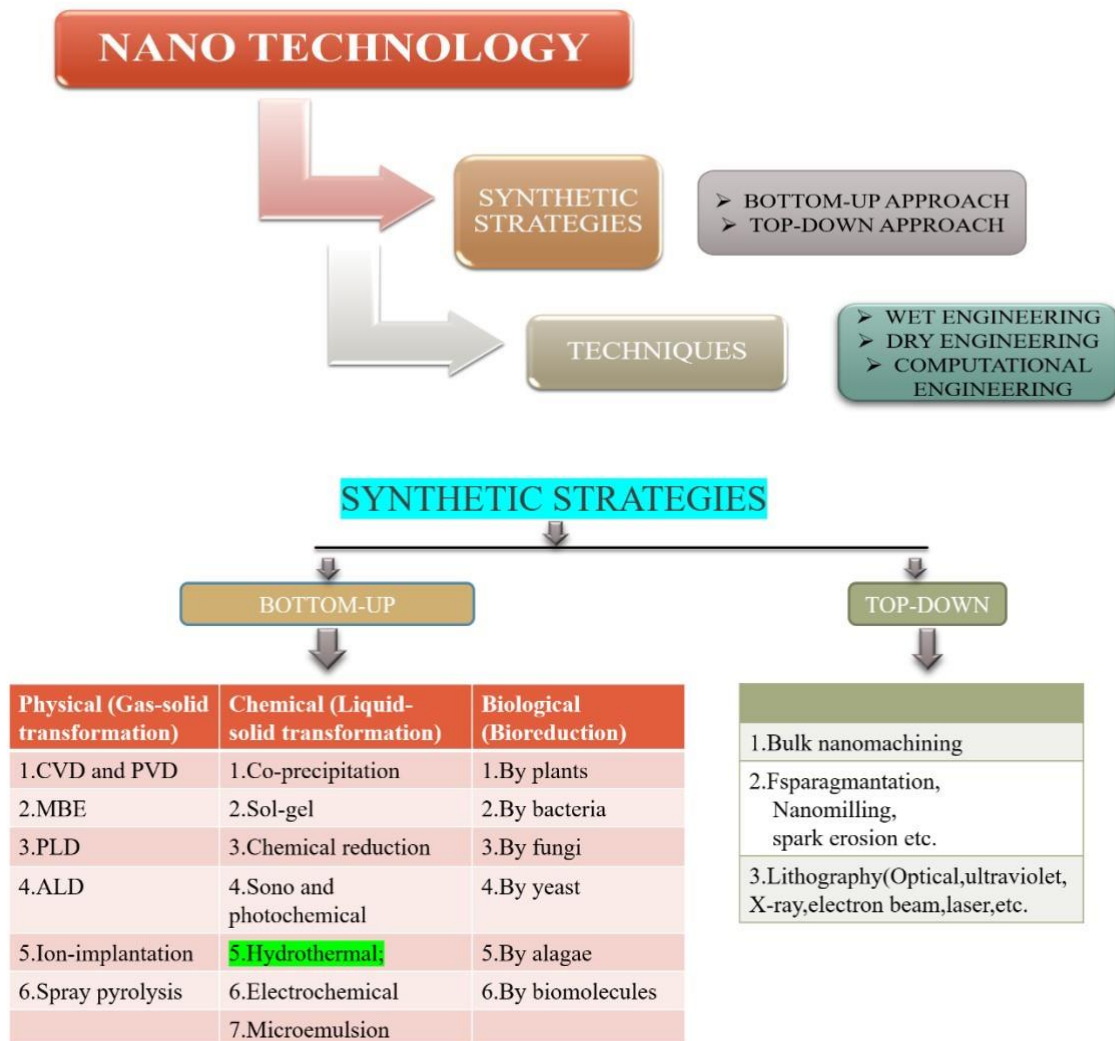


Figure 1.5 : BOTTOM-UP and TOP-DOWN approaches

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.

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.

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.

1.6 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.
- 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 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 vapor deposition, thermal decomposition, ,two-step mechanochemical–thermal synthesis, anodization, co-precipitation, electrophoretic deposition, and precipitation processes using solution concentration, pH, and washing medium. ZnO is a widebandgap 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.

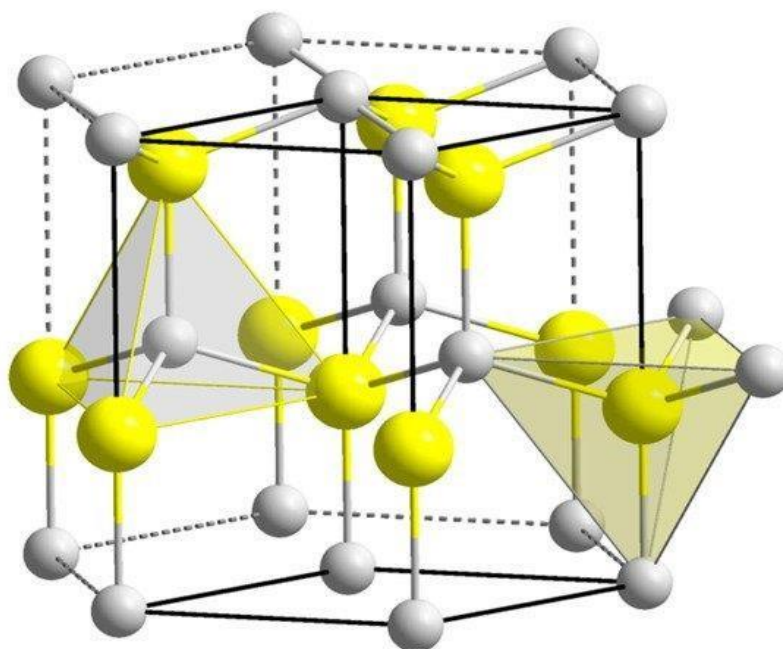


Figure 1.7: Crystalline structure of zinc oxide

1.8 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.

1.8.1 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.

- 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.

1.8.2 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

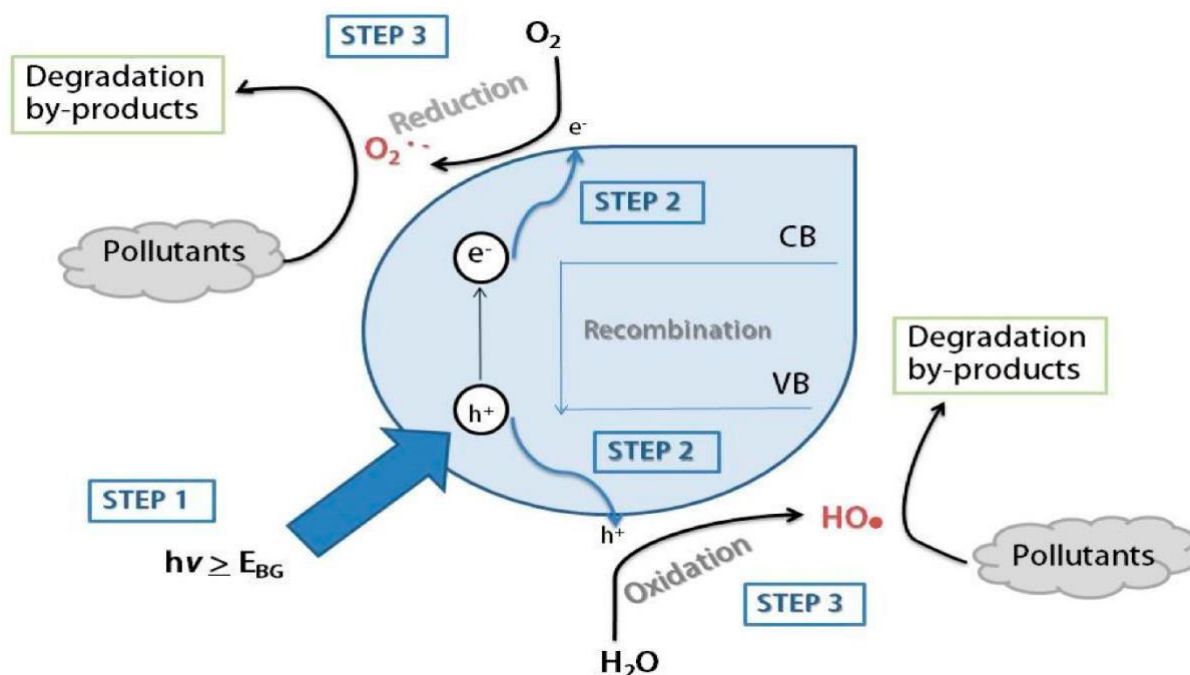


Figure 1.8.2 : Mechanism of photocatalysis

1.8.3 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. The major role of the photocatalyst is shown in the figure.

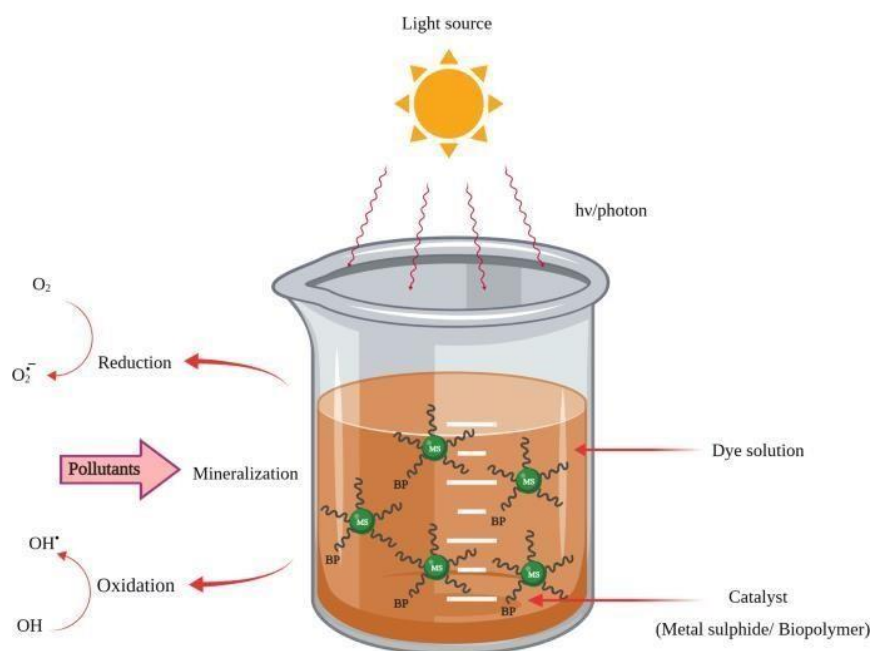


Figure 1.8.3 : Role of photocatalyst

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: *g*-C₃N₄ decorated ZnO nanorod arrays for enhanced photoelectrocatalytic performance

Authors: Pan-Yong Kuang , Yu-Zhi Su , Gao-Feng Chen ^a, Zhuo Luo , Shu-Yang Xing , , Zhao-Qing Liu

Journal and year : 15 December 2015

2.Title : Hydrophilic polypyrrole and g-C₃N₄ co-decorated ZnO nanorod arrays for stable and efficient photoelectrochemical water splitting†

Authors : Xiaoyu Xie, Ru Wang, Jinping Chen, Yi Ma, Zhiyong Li, Qiannan Cui, Zengliang Shi and Chunxiang Xu .

Journal and year: 09 Nov 2022

3.Title: *In-situ* synthesis of ZnO modified g-C₃N₄ composite: a potential photocatalyst and adsorbent for waste water remediation

Authors : Deepti Sharma, Ajay Saini, Divyansh Choudhary, Meena Kumari, Archana Chaudhary, Veena Dhayal

Journal and year : 17 Mar 2021

4.Title : The controlled synthesis of g-C₃N₄/Cd-doped ZnO nanocomposites as potential photocatalysts for the disinfection and degradation of organic pollutants under visible light irradiation

Authors : Mudassar Sher, Mohsin Javed, Sammia Shahid, Shahid Iqbal, Muhammad Azam Qamar, Ali Bahadur and Muhammad Abdul Qayyum

Journal and year: 07 Jan 2022

CHAPTER- 3

AIM AND SCOPE OF PRESENT INVESTIGATION

This project work is mainly focused on the following objectives:

- To synthesis novel g-C₃N₄ -ZnO nanocomposite by a chemical perception method
- Characterization of the nanocomposite using XRD, UV, FT-IR, SEM
- Determine morphology and size of the nanocomposites
- Application of photocatalysis
- Summarize the obtained results

CHAPTER-4

EXPERIMENTAL AND CHARACTERISATION TECHNIQUES

4.1 EXPERIMENTAL SYNTHESIS OF g-C₃N₄ DECORATED BY ZINC OXIDE

g-C₃N₄ decorated by Zinc oxide have been synthesized in the chemical perception method as we discussed below

Melamine is heated at 600 degrees in air atmosphere or muffle furnace .and yellow powder is obtained .This yellow powder is named as g-C₃N₄.Then g-C₃N₄ is added to 100ml distilled water along with 0.2M Zinc acetate and kept for stirring in a stirrer. 50ml distilled water with 2M NaOH is added in a separate beaker .And these two are

Added together and kept for stirring for 4hours and precipitate is settled down and the remaining residue is dried in oven and then it is powdered in mortar .

4.2 CHEMICAL PRECIPITATION METHOD :

Chemical precipitation is the process of conversion of a solution into solid by Converting the substance into insoluble form or by making the solution a super saturated one

Among various strategies in the development of nanoparticles,chemical precipitation serves as one of the promising methods to develop the nanocatalysts ,since it allows the complete precipitation of the metal ions also,nanoparticles of higher surface areas are commonly prepared by using this method .

Finally ZnO with g-C₃N₄ Nanoparticles will be confirmed by characterisation techniques (UV,FTIR,SEM,XRD).

4.3 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.

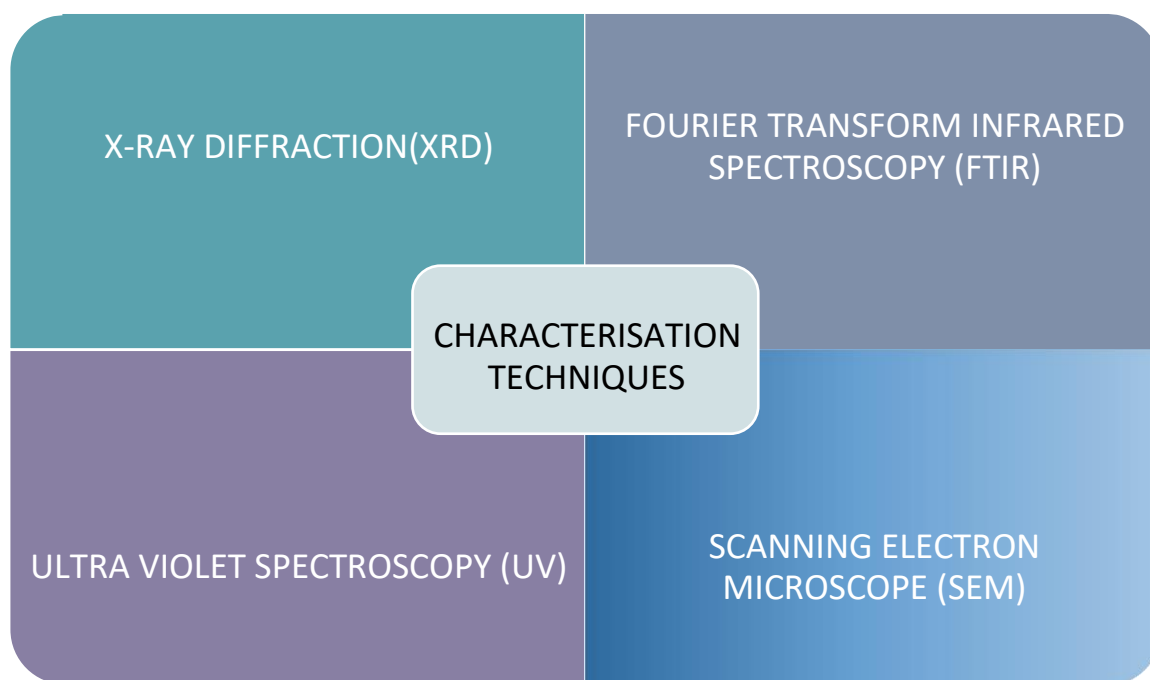


Figure 4.4 : Characterisation Techniques of Nanocomposite

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.

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.

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. 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.

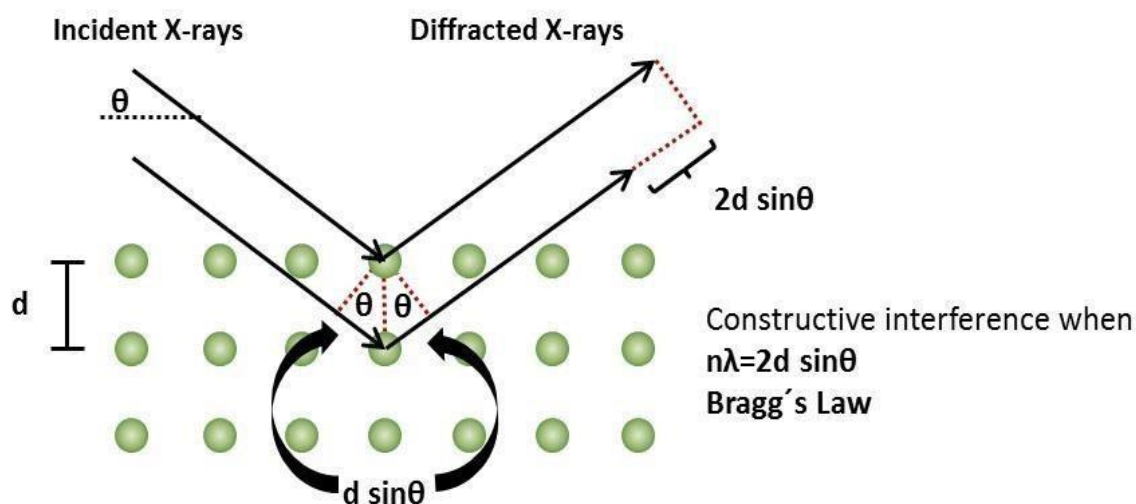


Figure 4.4.1: schematic representation of Bragg's law

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.

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.

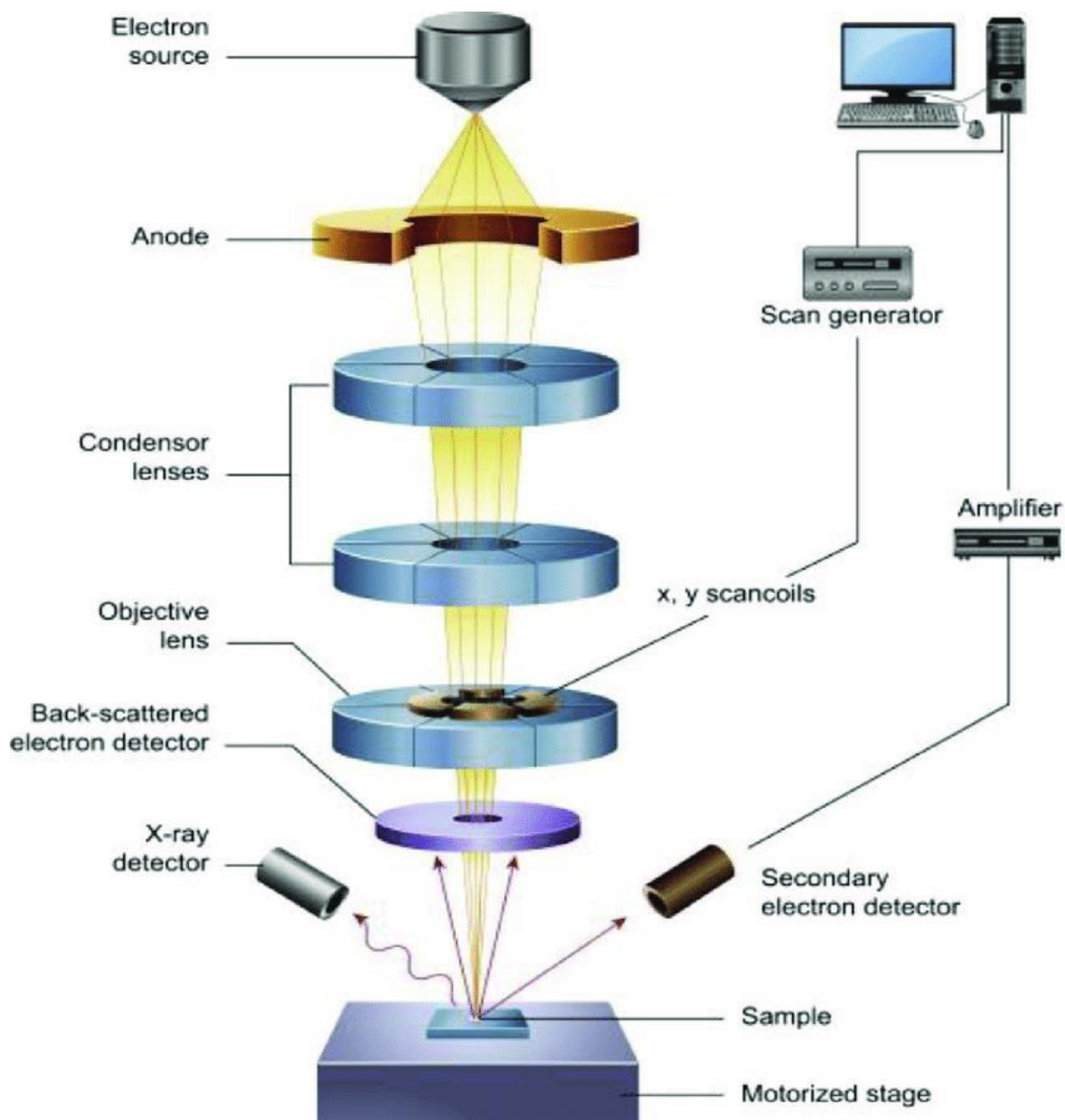


Figure 4.4.2 : Schematic representation of SEM

4.4.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

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

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.

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 computersearchable databases are available.

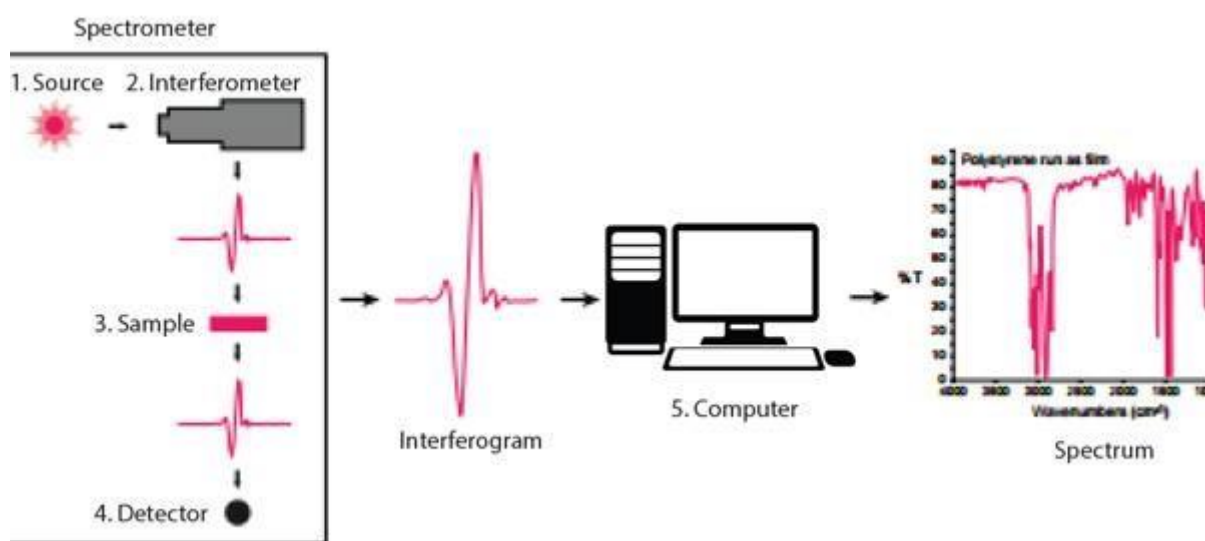


Figure 4.4.3 : Schematic representation of FTIR

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.

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.

- All diluted inorganic solutions are uv active
- Solutions of transition metal ions can be colored (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 (λ_{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.

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 λ_{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.

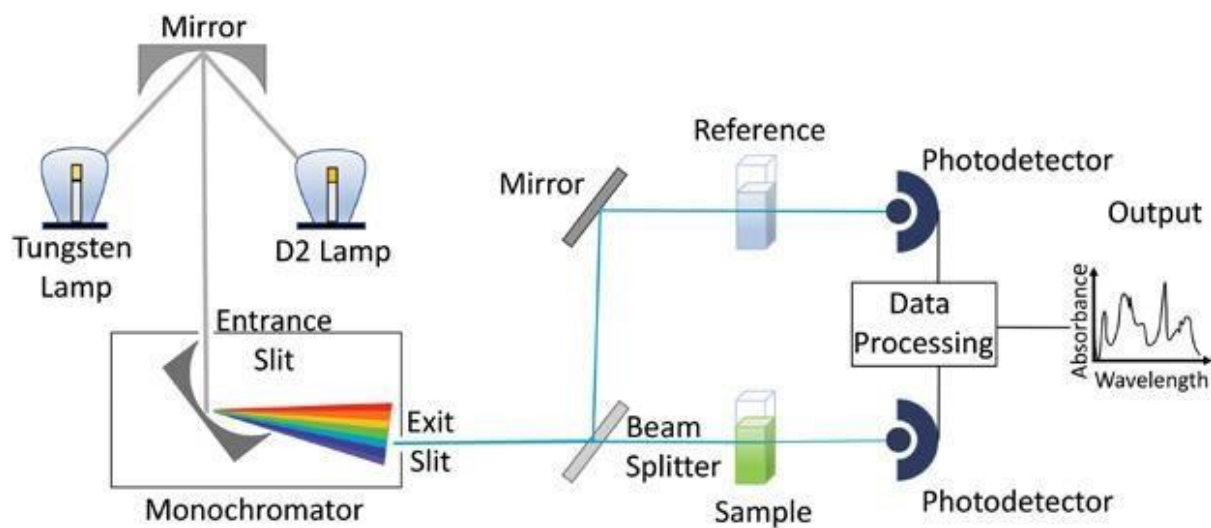


Figure 4.4.4 : Schematic Representation of UV-Visible Spectroscopy

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)

g-[C₃N₄] 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.

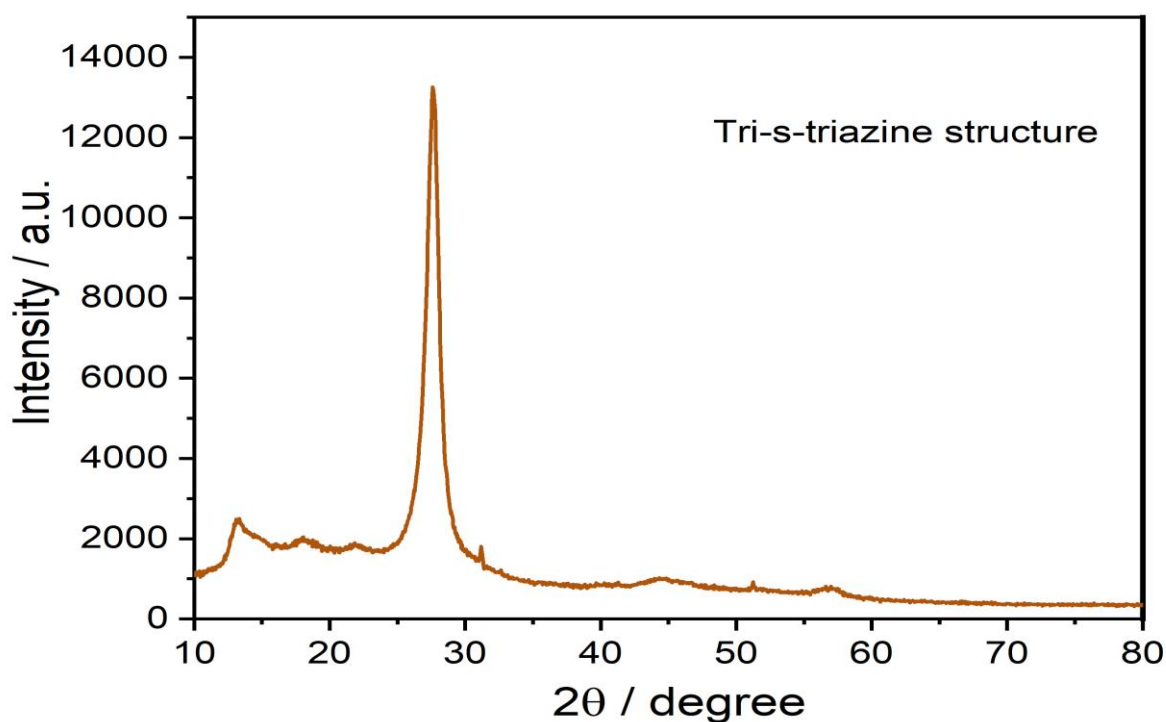
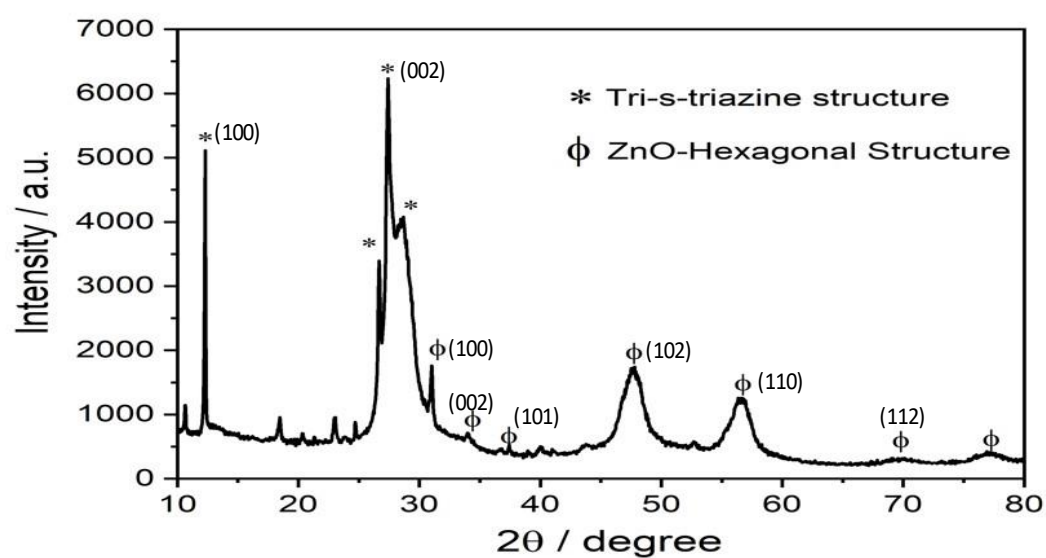


Figure 5.1 SPECTRUM OF XRD FOR g-C₃N₄

S.NO	PLANE	2THETA(DEGREE)
1	g-C ₃ N ₄ (100)	14
	g-C ₃ N ₄ (002)	27
	g-C ₃ N ₄ (201)	47
2	g-C ₃ N ₄ -ZnO(100)	32
	g-C ₃ N ₄ -ZnO(102)	47
	g-C ₃ N ₄ -ZnO(120)	57

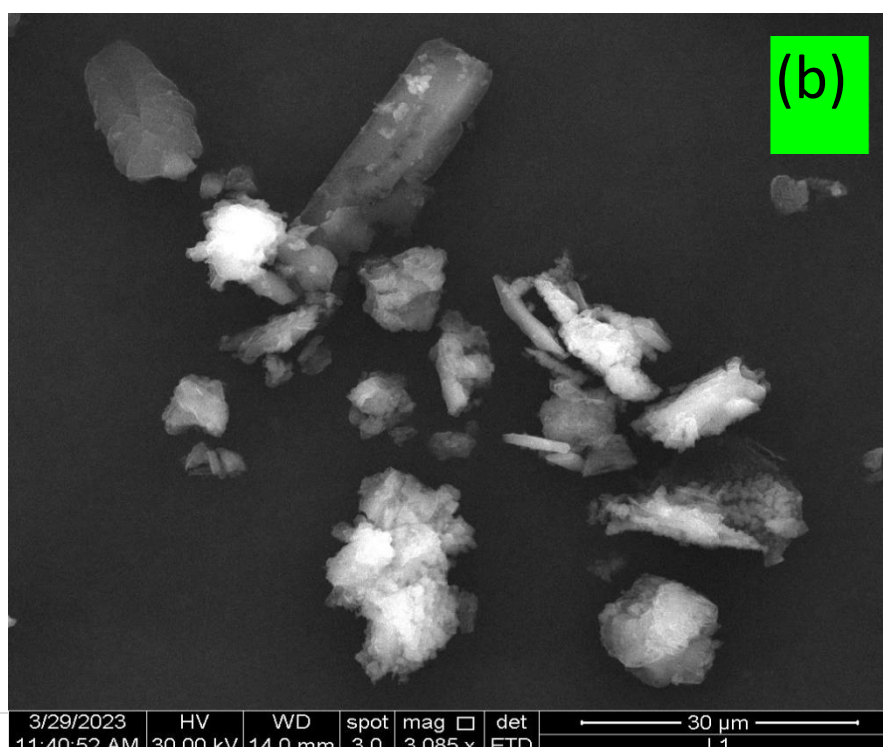
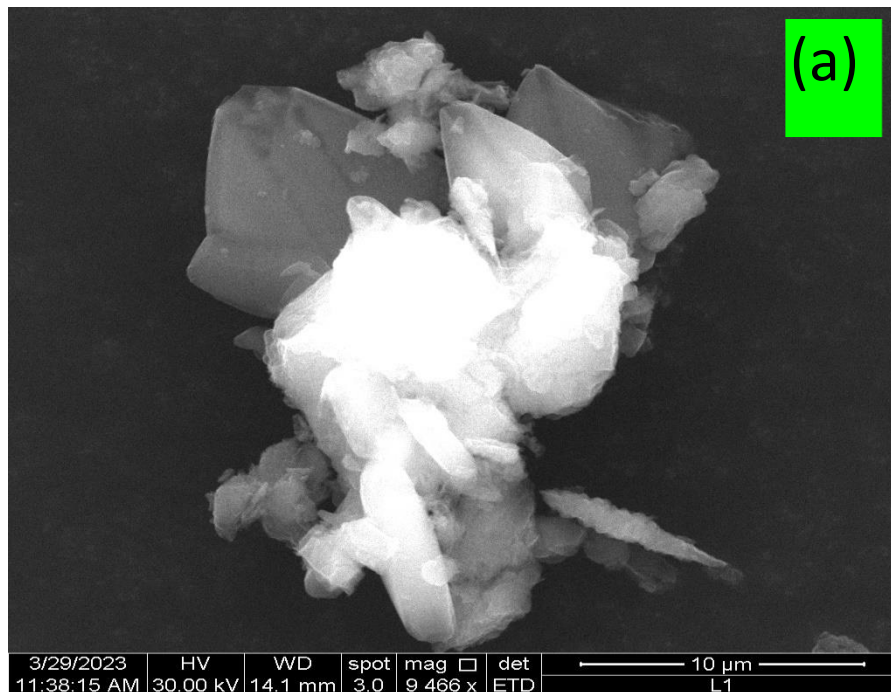


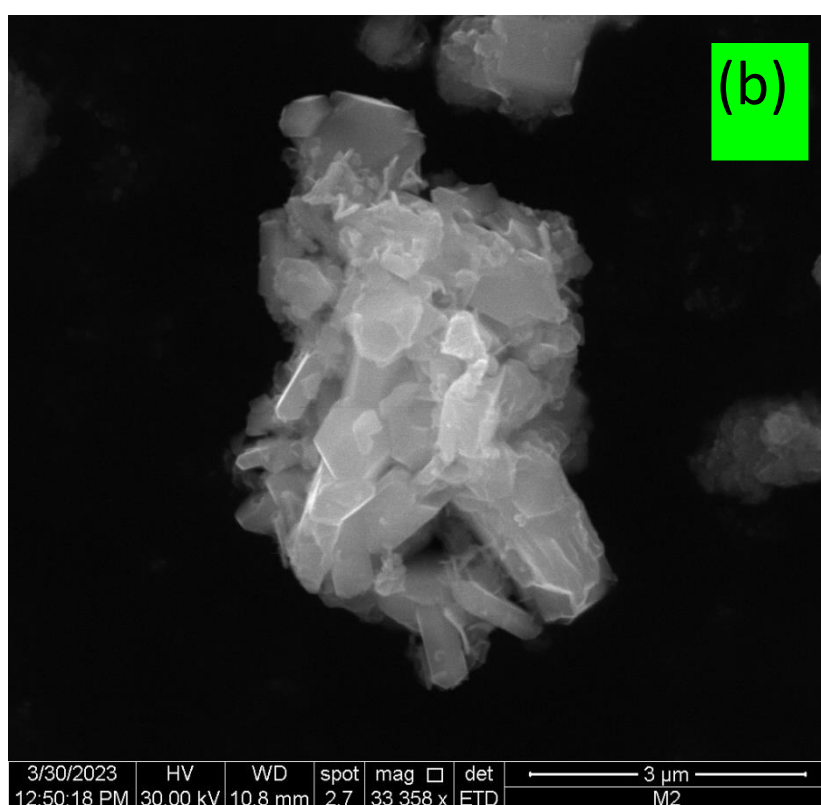
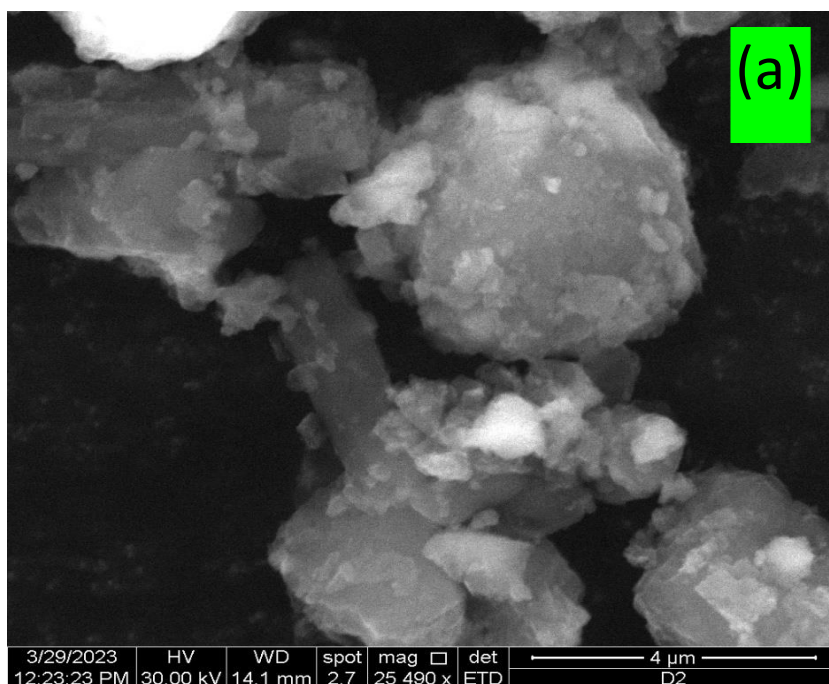
SPECTRUM OF XRD FOR g-C₃N₄ DECORATED BY ZnO

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. The scanning Electron Microscopy (SEM) images allowed a detailed study on the morphological structure of the nanoparticles. 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.





SEM PICTURES FOR $g\text{-C}_3\text{N}_4$ DECORATED BY ZnO

5.3 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.

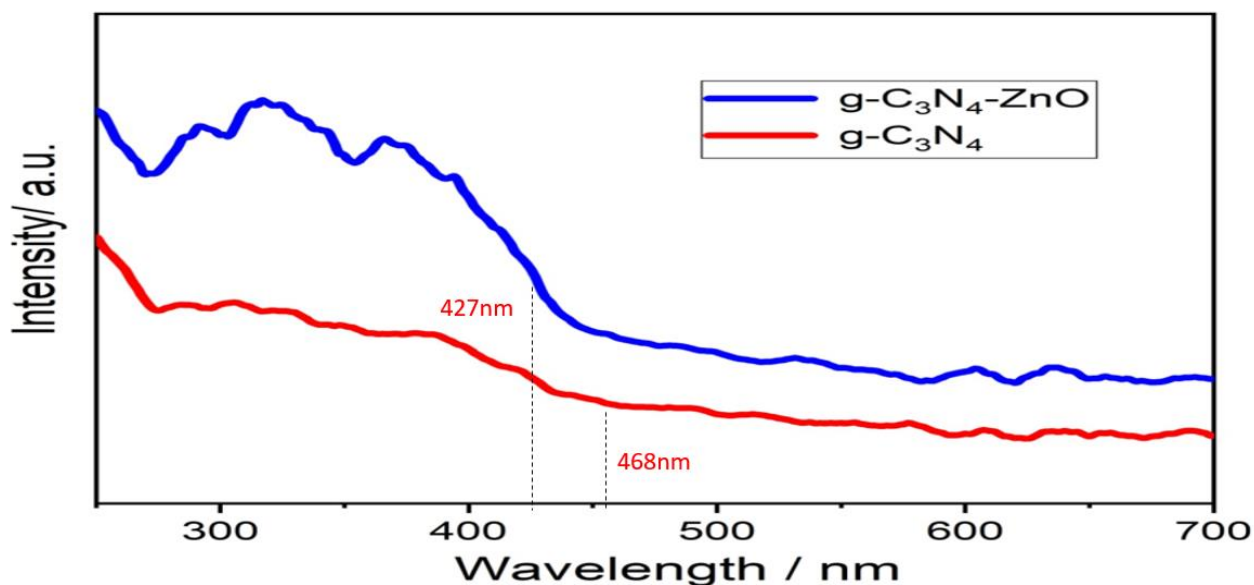


Figure 5.3 : UV-VISIBLE SPECTRA OF g-C₃N₄ WITH ZnO

From the graph, we come to know that the absorption peak was obtained at 468 nm.

5.3.1 BAND GAP

The band gap (EG) 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.

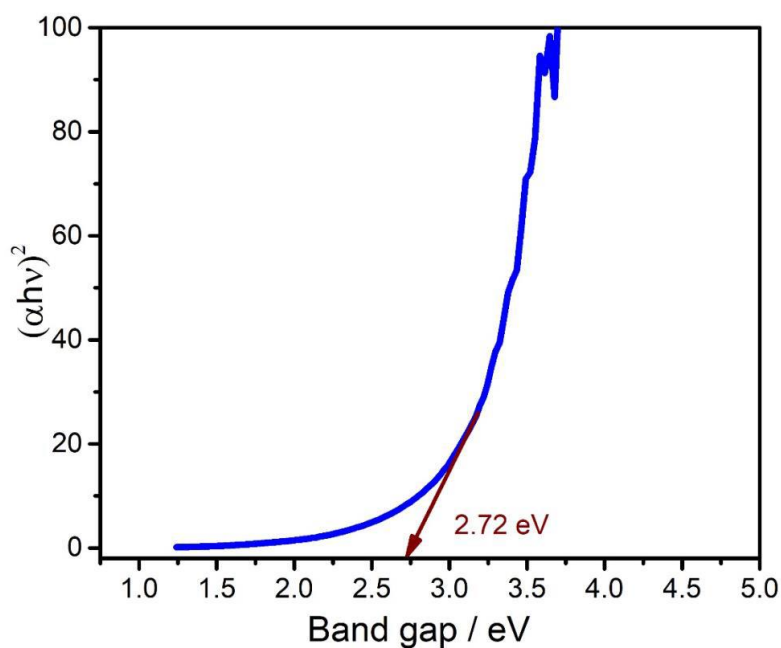


Figure 5.3.1 BAND GAP OF NANOCOMPOSITE

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.

5.4: FOURIER-TRANSFORM INFRARED SPECTROSCOPY

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

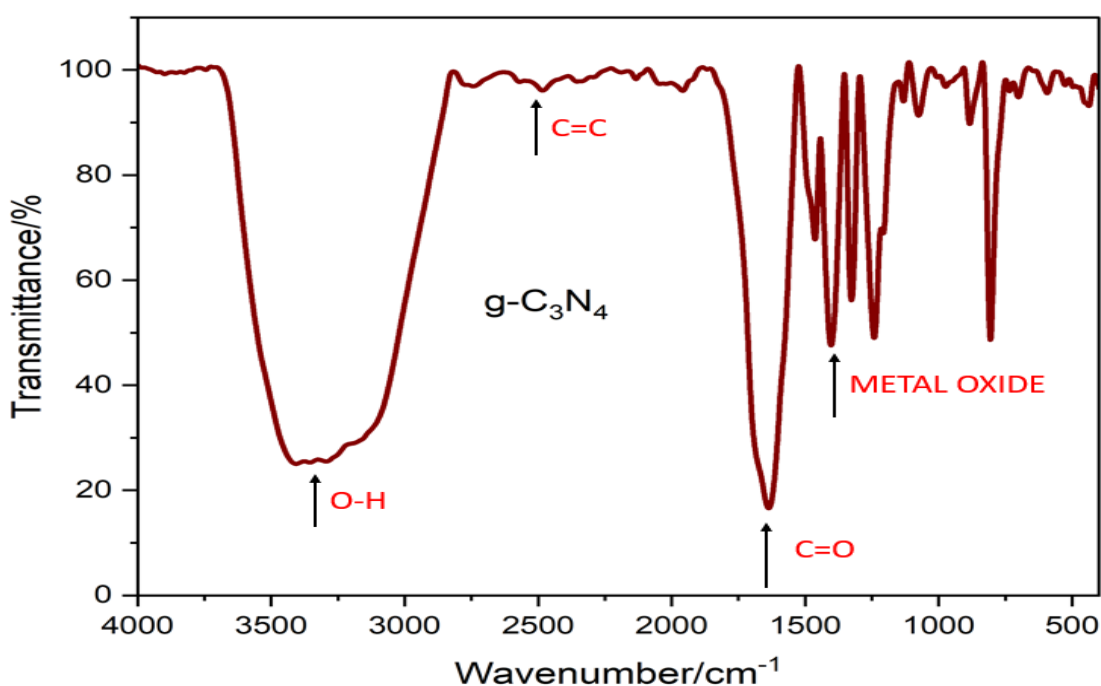
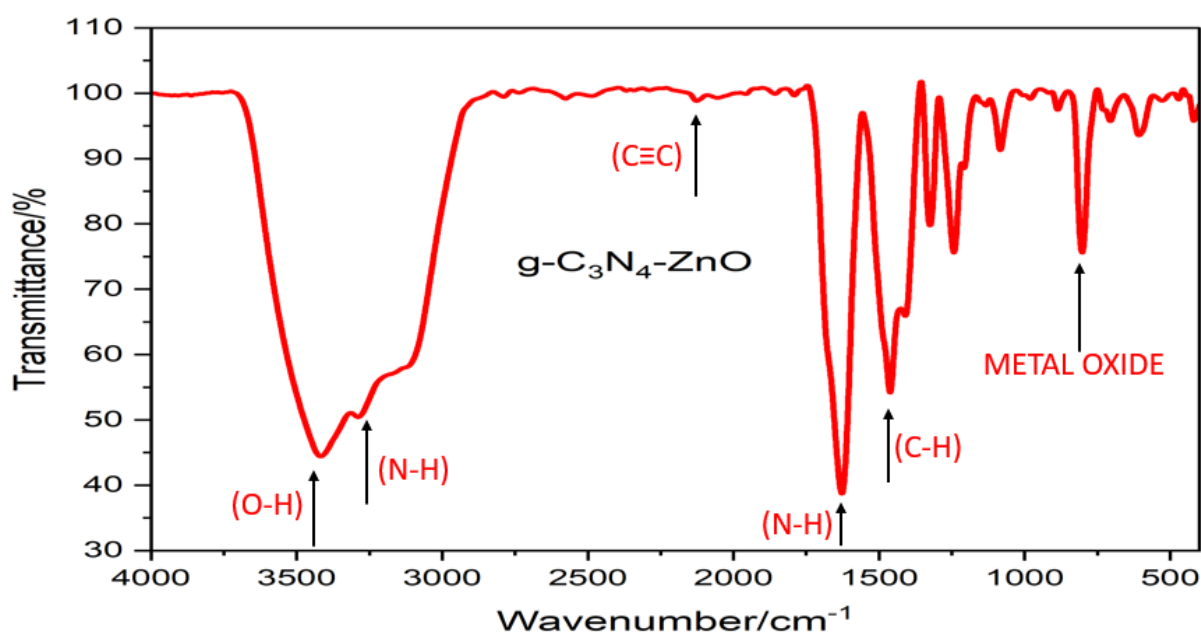


Figure 5.4: FTIR OF g-C₃N₄ NANOCOMPOSITE



FTIR OF g[-C₃N₄] & g-C₃N₄ -ZnO NANOCOMPOSITE

S.No.	FUNCTIONAL GROUP	WAVE NUMBER
1	O-H	3470
2	N-H	3280
3	C≡C	2170
4	N-H	1650
5	C-H	1460
6	METAL OXIDE	1300

The above table shows that the various functional groups present at different wavenumbers, in this O-H group observed at 3470 cm⁻¹ then N-H group was observed at 3280 cm⁻¹ then after C≡C group was observed at 2170 cm⁻¹ Then N-H group was observed 1650 cm⁻¹ and C-H group was observed 1460 cm⁻¹ and finally metal oxide peak was observed at 1300 cm⁻¹.

CHAPTER 6

APPLICATION OF PHOTOCATALYSIS

6.1. Photocatalytic activity test

Methyl orange (MO) was chosen as the model organic pollutants to test the photocatalytic dye degradation analysis for the catalyst. Typically, a catalysts (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 $0.2 \mu\text{m}$ 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 was used to determine the correct degradation rate of MO 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.

6.2 Photocatalytic activity

The photocatalytic degradation efficiency of as prepared catalysts of ZnO, and g-C₃N₄/ZnO nanocomposites were resolved by the deprivation of MO dye under irradiation of Sun light. When irradiating the MO dye solution, the concentration of the dye was noticeably reduced, and it was confirmed by the significant color variation.

For ZnO catalyst, the catalyst influences the organic molecule to achieve the efficiency of about 57.7% within 120 minutes. The photocatalyst experiment was further extended to nanocomposite sample. The degradation reaction of g-C₃N₄/ZnO sample was performed by the same process. The rate of electron-hole pair recombination was delayed by doping the metal ions into the ZnO structure results increased the degradation efficiency. Compared to ZnO catalyst, g-C₃N₄/ZnO catalysts reached high efficiency of degradation of 77.5%, respectively[1,2].

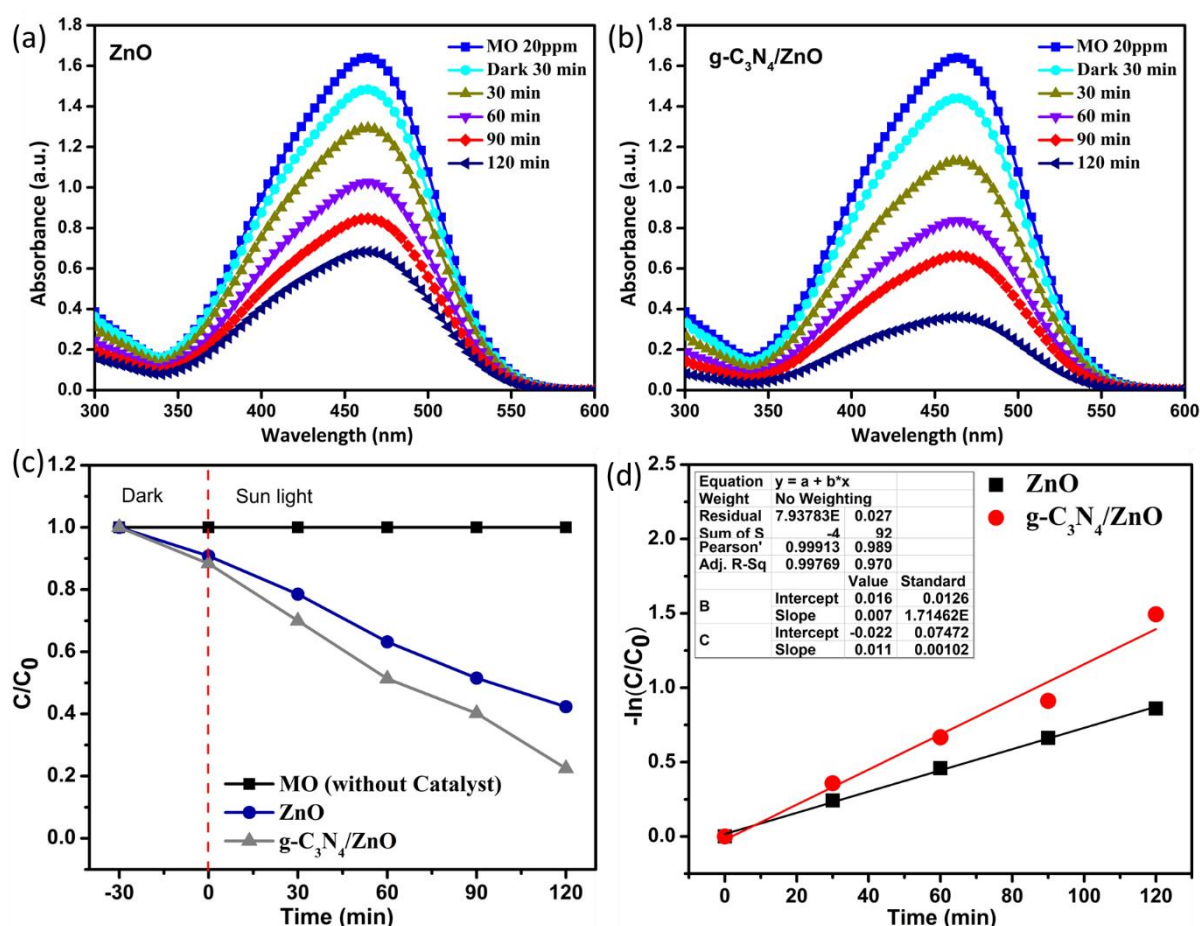


Figure.1 (a-b) represents the UV-visible spectra for the MO with occurrence of catalysts ZnO, and g-C₃N₄/ZnO were irradiated by sun light for 120 minutes. (c) C/C₀ versus time interval plot of MO dye (d) -ln(C/C₀) versus time interval plot of MO dye

The significant improvement of the degradation efficiency is due to the doping effect of highly porous and adsorptive 2D nanomaterial of g-C₃N₄/ZnO lattice sites, it reduces recombination of excited charge carriers (electron-hole pair). Fig.1 c 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 MO dye solution. The g-C₃N₄/ZnO catalyst shows highest degradation ability due to the fact that sub energy-level acts as traps for recombination. Based on the sub energy level of the conduction band helps to produce the large number of reactive oxygen species (ROS).

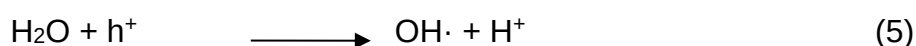
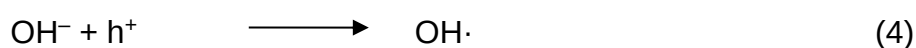
Additional investigation of pseudo-first order kinetics studies shown in Figure.1d the degradation rates were 0.016 min⁻¹ and 0.025 min⁻¹ for ZnO, and g-C₃N₄/ZnO nanocomposites against MO dye, respectively. From the studies rate constant value and R² values are listed in the Table.1.

The mechanism of MO dye degradation for the g-C₃N₄/ZnO catalyst is described as follows,

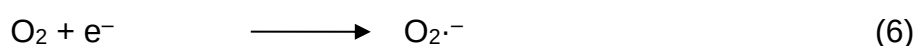
(i) Formation of electron hole pair



(ii) Formation of hydroxyl radicals



(iii) Formation of superoxide radicals



(iv) Photo degradation of methyl orange dye



Basically, a heterogeneous photocatalytic dye degradation reaction is composed of two consecutive steps, i) Dye molecules interact with the catalyst (adsorption occurs on the surface) ii) Photodegradation of the dye begins. So, the photocatalytic system is majorly depending on adsorption and photodegradation capability of the catalyst. Subsequently, as the highest degradation efficiency achieved for the g-C₃N₄/ZnO nanocomposites amongst all catalyst, it was only selected for the scavenger study for further understanding the degradation mechanism. In general, the photo active catalyst produce the reactive oxygen species (h⁺, OH[•], and O₂^{• -}) and it is important to categorise which reactive species impacts a major role during photo

degradation. Hence, the h^+ , $OH^\bullet$, and $O_2^{\bullet-}$ are eliminated by accumulation of related scavengers such as EDTA (h^+ scavenger), Methanol ($OH^\bullet$ scavenger), and p-BQ ($O_2^{\bullet-}$ scavenger) into reaction solution, respectively. Fig. 2(a) illustrates the efficiency of with and without scavengers. Since scavenger studies, the p-BQ only shows the prominent deviations in efficiency of dyes. Therefore, the superoxide radicals play significant role the overall photodegradation efficiency[3].

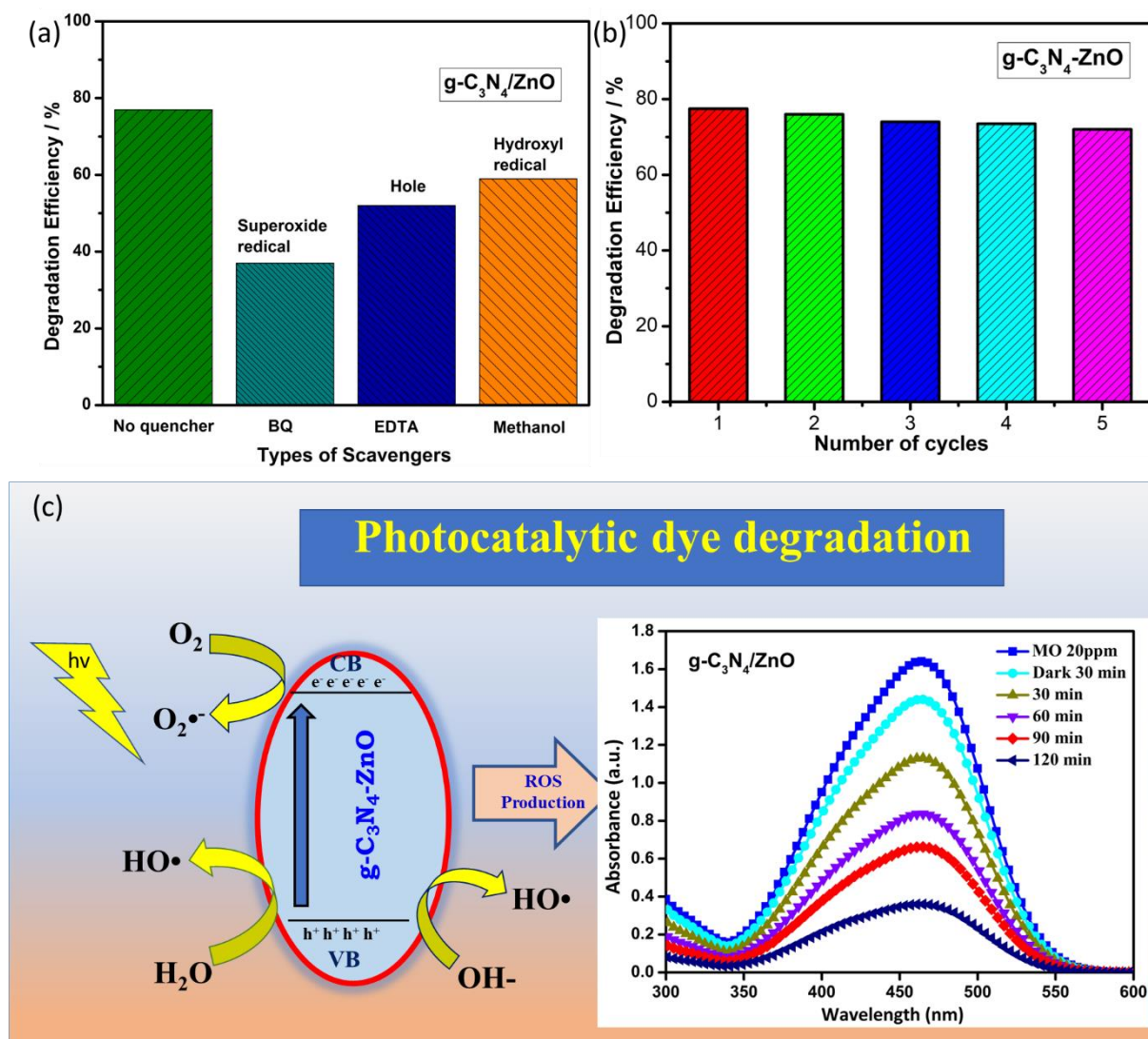


Figure. 2 (a) Scavengers study (b) reusability test graph of photocatalytic activity (c) Schematic diagram illustrating the mechanism of charge separation and photocatalytic activity of photocatalyst under the sunlight irradiation

Table 1 photocatalytic activity result of ZnO and g-C₃N₄/ZnO nanoparticles.

S.N	Catalys	Ban	Degradati	K	R ²
o	t	d	on	(mi	
		gap	efficiency	n ⁻¹)	
		(eV)	(%) (120		
			minutes)		
Methylene blue (20 ppm)					
1	ZnO	-	57.7	0.01	0.9
				6	9
2	g-	-	77.5	0.02	0.9
	C ₃ N ₄ /Zn			5	7
	O				

Additionally, a very essential study is stability and reusability of photocatalysts (g-C₃N₄/ZnO nanocomposites). For reusability test, the results reveal the stability of the catalyst and there is no significant loss in degradation efficiency even after five cycles of the photocatalytic process shown in Fig. 2(b). After 5 cycles, the efficiency of catalyst is decreased due to the loss of sample while washing process.

The Fig.2(c) showed schematic diagram illustrating the mechanism of charge separation, generation of reactive oxygen species (ROS) and photocatalytic activity of photocatalyst under the sunlight irradiation [2].

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CONCLUSION

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 g-C₃N₄ - ZnO nanocomposite showed excellent dye degradation of METHYL ORANGE 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 g-C₃N₄ - ZnO could be the suitable candidate for water purification, through the photocatalysis process.

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Year: Received: 15 March 2023 / Revised: 31 March 2023 / Accepted: 2 April 2023 / Published: 4 April 2023

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Authors: E. Jackcina Stobel Christy, Anitha Pius

Year: 2021

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Authors: Pan-Yong Kuang, Yu-Zhi Su, Gao-Feng Chen^a, Zhuo Luo, Shu-Yang Xing, Zhao-Qing Liu

year : 15 December 2015

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year: 09 Nov 2022

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year : 17 Mar 2021

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Authors : Mudassar Sher, Mohsin Javed, Sammia Shahid, Shahid Iqbal, Muhammad Azam Qamar, Ali Bahadur and Muhammad Abdul Qayyum

year: 07 Jan 2022