Development of Titanium Dioxide Nanoparticles for Catalytic and Waste Water Treatment Applications

A thesis submitted toward partial
fulfilment of the requirements for
the degree of

Master of Technology in Nanoscience and Technology

Submitted by

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CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled "**Development of Titanium Dioxide Nanoparticles for Catalytic and Waste Water Treatment Applications**" is a legitimate work done by **Aaishiki Saha** under our supervision and guidance to fulfill the requirement for the degree of Master of Technology in Nanoscience and Technology in the School of Materials Science and Nanotechnology from the academic session 2021-2023.

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Dedicated to

my

PARENTS

for their support and

encouragement...

My Sincere gratitude to

All my teachers…

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Abstract

Water is a fundamental and vital resource for all life on Earth. Its importance cannot be overstated, as it plays numerous critical roles in the environment and human society. Water is essential for the survival of all living organisms. It is required for hydration, metabolic processes, and the growth of plants and animals. Water sustains aquatic ecosystems, providing habitats for a wide variety of species. It also contributes to the overall health of terrestrial ecosystems through processes like precipitation, runoff, and groundwater recharge. Water is a fundamental resource in agriculture, used for irrigation to grow crops and raise livestock. Adequate water supply is crucial for food production. Many industries rely on water for manufacturing processes, cooling, and cleaning. Clean water is essential to maintain the efficiency and sustainability of these processes. Access to safe and clean drinking water is a fundamental human right. It is crucial for public health and helps prevent waterborne diseases. Clean water bodies, such as rivers, lakes, and oceans, are essential for recreational activities like swimming, boating, and fishing. They also attract tourists and contribute to local economies. Water is a source of renewable energy through hydropower generation. Dams and hydroelectric power plants harness the kinetic energy of flowing water to produce electricity.

Photocatalysis in water treatment: Photocatalysis is a promising technology that can be used to treat and purify water, addressing various water-related challenges:

1. Pollutant removal: Photocatalysis involves the use of photocatalysts (usually semiconductors like titanium dioxide) that, when exposed to light (typically UV or visible light), can catalyze chemical reactions. These reactions can break down and degrade various water pollutants, including organic compounds, dyes, pesticides, and even certain pathogens.

2. Demineralization: Photocatalysis can be effective in removing heavy metals and other inorganic contaminants from water, making it suitable for consumption and industrial use.

3. Disinfection: Photocatalysis can also disinfect water by inactivating harmful microorganisms, such as bacteria and viruses, through the production of reactive oxygen species.

4. Environmental remediation: Photocatalysis can be employed for environmental remediation, such as cleaning up contaminated groundwater or surface water bodies by degrading persistent pollutants.

5. Green and sustainable: Photocatalysis is considered an environmentally friendly and sustainable technology since it relies on renewable energy sources like sunlight. It doesn't produce harmful by products and can be integrated into wastewater treatment processes.

Photocatalysis can also contribute to energy storage through processes like photoelectrochemical water splitting. It converts excess energy (e.g., from solar panels) into chemical energy stored in the form of hydrogen, which can be used later for electricity generation or fuel production. Photocatalytic degradation, a promising technique for eliminating organic contaminants from water systems, has gained recognition.

In this study, here investigated the photocatalytic degradation of Rhodamine B (RhB) dye using various catalysts, including TiO_2 solvothermal, TiO_2 hydrothermal, TiO_2 annealed, and the corresponding composite of annealed TiO_2 with gC_3N_4 and exfoliated $g\text{-}C_3N_4$ (Exf gC_3N_4). The aim was to evaluate the effectiveness of these photocatalysts in breaking down hazardous RhB dye and to explore the collaborative interactions between titanium dioxide (TiO_2) nanoparticles and graphitic carbon nitride (gC_3N_4), as well as exfoliated graphitic carbon nitride (Exf gC_3N_4). The synthesis of titanium dioxide and the nanocomposites involved a hydrothermal method followed by annealing. To assess the structural, morphological, compositional, and optical, electro-chemical characteristics of the photocatalysts, the synthesized samples are employed some sophisticated techniques such as Powder X-ray diffraction (PXRD), Field emission scanning electron microscopy (FESEM), High resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), UV–Vis diffuse reflectance spectroscopy (DRS), Photoluminescence spectroscopy (PL), Mott- Schottky, etc. The results revealed that the most significant improvement in photocatalytic activity was observed in the annealed TiO_2/Exf gC_3N_4 photocatalyst, achieving a degradation rate of 99.84% within 90 minutes irradiation under UV light. The breakdown of RhB dye occurred under UV light radiation, with its concentration monitored at regular intervals using UV-Vis spectroscopy. Both pristine tungsten trioxide and its nanocomposites exhibited substantial photocatalytic activity in RhB dye degradation. The nanocomposite containing exfoliated graphitic carbon nitride displayed enhanced degradation efficiency, indicating potential synergistic effects with titanium dioxide. The photocatalytic process followed pseudo-first-order kinetics, and the degradation rate constants were determined. Incorporating exfoliated gC_3N_4 with TiO_2 enhanced photocatalytic performance, showcasing the potential of this nanocomposite for organic pollutant treatment in wastewater remediation. These findings contribute to the development of efficient and durable photocatalytic materials for environmental remediation applications.

In summary, photocatalysis offers a versatile and sustainable approach to addressing various energy and environmental challenges. By harnessing the power of sunlight or artificial light sources, it can contribute to clean energy production, efficient resource utilization, and the remediation of polluted environments. Its applications span from solar energy conversion to wastewater treatment and air purification, making it a valuable technology in the quest for a more sustainable and environmentally friendly energy future.

Keywords: Transition metal oxide, Titanium Dioxide (TiO_2), Graphitic Carbon Nitride (gC_3N_4), Nanocomposite, Photocatalysis, Water Remediation.

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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION PAGE NO.

CHAPTER 2: REVIEW OF PAST WORK

CHAPTER 3: INSTRUMENTS AND APPARATUS

CHAPTER 4: KINETICS RATE CONSTANT EVALUATION OF DYE DEGRADATION UNDER UV LIGHT ASSISTED WATER REMEDIATION IN A CATALYTIC REACTOR USING TiO_2 NANOPARTICLES

CHAPTER 5: ENHANCED DEGRADATION PERFORMANCE OF RHODAMINE B DYE WITH TiO_2/gC_3N_4 NANOCOMPOSITE UNDER UV LIGHT IRRADIATION

CHAPTER 6: CONCLUSION & SCOPE FOR FUTURE WORK

CHAPTER 1

INTRODUCTION

1.1 Nanoscience and Nanotechnology

The growing fascination with nanoscience, which explores low-dimensional systems, reflects the embodiment of Feynman's renowned assertion that "There's Plenty of Room at the Bottom". The prefix ‘nano’ is a Greek prefix meaning ‘dwarf’ or something very small and depicts one thousand millionth of a meter (10^{-9} m). We should distinguish between nanoscience and nanotechnology. Nanoscience is the study of structures and molecules on the scales of nanometers ranging between 1 and 100 nm, and the technology that utilizes it in practical applications such as devices etc. is called nanotechnology [1,2].

The properties of a material can undergo significant changes when transitioning from the bulk scale to the nanoscale. These changes are primarily attributed to the altered physical and chemical characteristics that emerge at the nanoscale due to quantum and surface effects. Some of the key property changes include:

- Mechanical Properties: At the nanoscale, materials can become stronger, harder, and more ductile compared to their bulk counterparts. The smaller grain sizes and high-density dislocations can enhance mechanical properties, making nanomaterials attractive for reinforcing composite materials.
- Optical Properties: Nanomaterials often exhibit unique optical properties, such as quantum confinement, plasmonic effects, and enhanced light absorption or emission. These properties find applications in sensors, optoelectronics, and advanced imaging techniques.
- Electrical Properties: The electronic behaviour of nanomaterials can differ significantly from bulk materials due to quantum confinement and increased surface area. Nanomaterials can display higher electrical conductivity or insulating behaviour depending on their composition and structure.

- Chemical Reactivity: The increased surface area-to-volume ratio of nanomaterials leads to a higher density of surface atoms, making them more chemically reactive. This enhanced reactivity is utilized in catalysis, where nanomaterials act as efficient catalysts for various chemical reactions.
- Thermal Properties: Nanomaterials can exhibit unique thermal conductivity and heat transfer properties. Carbon-based nanomaterials, such as carbon nanotubes and graphene, have exceptional thermal conductivity, making them suitable for applications in thermal management.
- Magnetic Properties: Nanoscale manipulation of magnetic materials can result in new magnetic behaviors, such as super-paramagnetism. These properties are essential in data storage and medical imaging (MRI) applications.
- Quantum Effects: As materials reach the nanoscale, quantum mechanical effects start to dominate, leading to changes in electronic energy levels and band structures. Quantum dots are a notable example of nanomaterials that exhibit quantum confinement effects.
- Surface Properties: The increased significance of surface atoms in nanomaterials affects various surface-related properties, including adsorption, wetting behavior, and catalytic activity.

It is crucial to note that not all properties change in the same way or direction when transitioning to the nanoscale. The specific property changes depending on the material's composition, size, shape, and fabrication techniques used to produce the nanomaterials. These unique property changes at the nanoscale have enabled the development of new materials and technologies with exciting applications in various industries. However, they also require careful consideration of potential risks and ethical implications.

1.2 Nanomaterials

Nanomaterials are materials with at least one external dimension that measures 100 nanometers (nm) or less or with internal structures measuring 100 nm or less. The nanomaterials that have the same composition as known materials in bulk form may have different physicochemical properties. Nanomaterials can be engineered or naturally occurring and they find applications in various fields due to their exceptional properties [1,2].

1.2.1 Classification of Nanomaterials

1.2.1.1 Based on Dimensions

- In zero-dimensional (0D) nanomaterials all the dimensions are measured within the nanoscale (no dimensions are larger than 100 nm). Most commonly, 0D nanomaterials are nanoparticles. These particles have sizes in the nanometer range and can be made from various materials like metals, metal oxides, and quantum dots. Due to their small size and unique properties, nanoparticles have a wide range of applications in catalysis, electronics, medicine, and more (Figure 1.1).

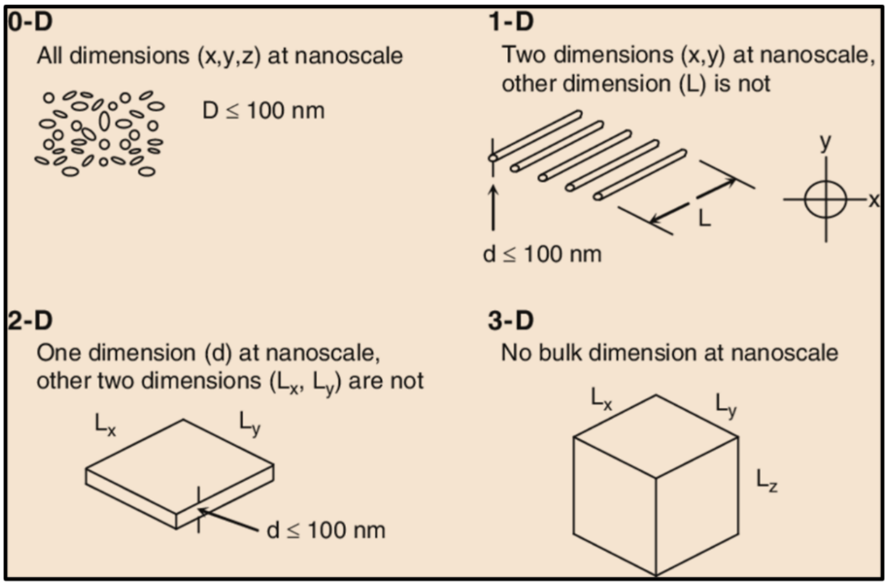

Figure 1.1 Classification of nanomaterials based on dimension

In one-dimensional nanomaterials (1D), one dimension is outside the nanoscale. This class includes nanotubes, nanorods, and nanowires. These materials often exhibit excellent mechanical, electrical, and thermal properties and are used in nanoelectronics, sensors, and as reinforcements in composites.

- In two-dimensional nanomaterials (2D), two dimensions are outside the nanoscale. This class exhibits plate-like shapes and includes graphene, nanofilms, nanolayers, and nanocoatings. Graphene, for example, is a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice and has remarkable electronic and mechanical properties, making it an essential material for various applications.
- Three-dimensional nanomaterials (3D) are materials that are not confined to the nanoscale in any dimension. This class can contain bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers.

1.2.1.2 Based on Materials

According to their structural makeup, nanoparticles can be broadly divided into four groups: organic/dendrimers, inorganic, carbon-based, and composite.

- Organic nanomaterials: Some examples of organic nanoparticles or polymers are liposomes, dendrimers, micelles, and ferritin.
- Inorganic nanomaterials: Nanoparticles that lack carbon atoms and are known as inorganic nanoparticles. Typically classified as those composed of metal-based or metal oxide-based nanomaterials.

a. Metal Nanomaterials: Gold, silver, and iron oxide nanoparticles are widely used in catalysis, electronics, and medical applications.

b. Metal Oxide Nanomaterials: Titanium dioxide, zinc oxide, and iron oxide nanoparticles find applications in photocatalysis, sunscreen formulations, and antimicrobial agents.

c. Semiconductor Nanomaterials: Quantum dots have unique optical properties used in imaging, displays, and solar cells.

d. Ceramic Nanomaterials: Alumina, silica, and hydroxyapatite nanoparticles find applications in catalysis, biomedical devices, and coatings.

- Lipid-based Nanomaterials: Generally spherical, with diameters ranging between 10 and 100 nm. It consists of a solid core made of lipids and a matrix containing soluble lipophilic molecules. They have applications in the biomedical field as a drug carrier and RNA release therapy in cancer therapy.

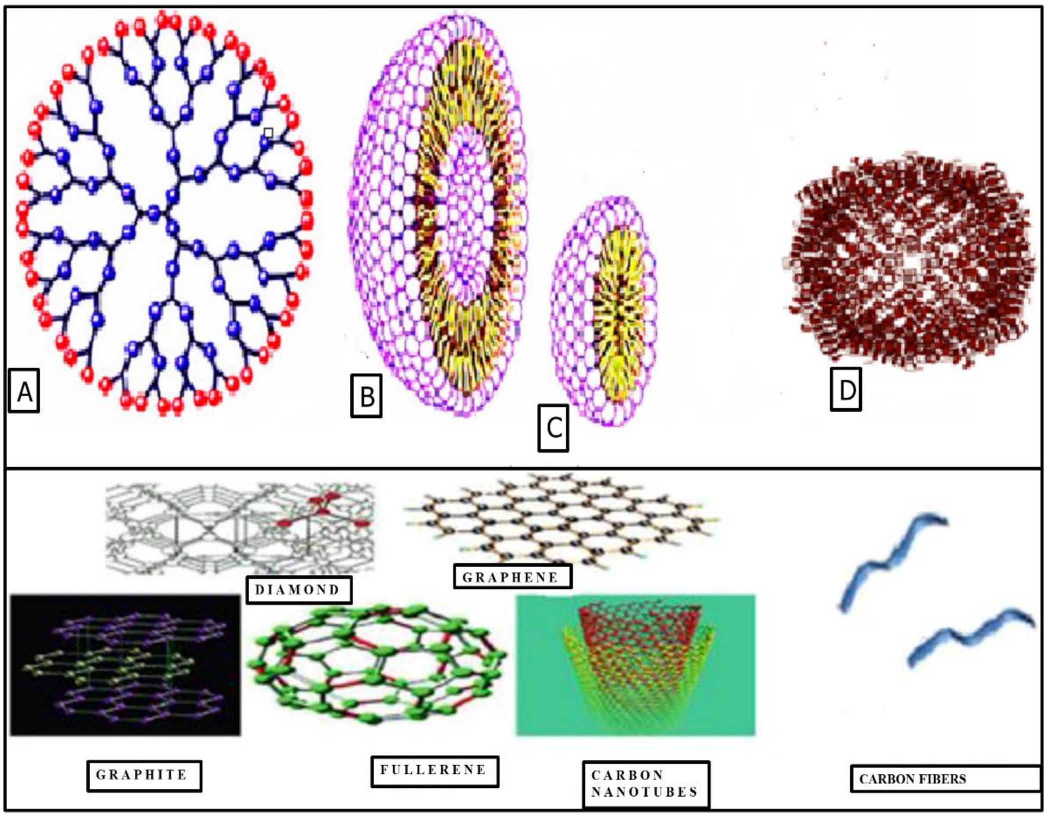

Figure 1.2 Organic Nanomaterials: A) Dendrimer B) Liposomes C) Micelles D) Ferritin and different types of Carbon-based Nanomaterials

- Carbon-based Nanomaterials: Carbon nanotubes, graphene, and fullerenes possess outstanding mechanical, electrical, and thermal properties for electronics, composites, and energy storage (Figure 1.2).

- Composite Nanomaterials: Combinations like polymer-based nanocomposites and metal-polymer nanocomposites exhibit synergistic properties for various applications.

1.2.2 Benefits of Nanomaterials over Bulk Materials

Nanomaterials offer several advantages over their bulk counterparts due to their unique properties and behaviors at the nanoscale. Some of the key benefits of nanomaterials include:

- Enhanced Mechanical Properties: Nanomaterials can have significantly improved mechanical properties, such as increased strength, hardness, and toughness. Their small grain sizes and high surface area-to-volume ratio contribute to enhanced mechanical performance, making them ideal for reinforcing composites and creating stronger materials.
- Improved Electrical Properties: Some nanomaterials exhibit exceptional electrical conductivity or insulating behavior. These properties are advantageous for applications in electronics, sensors, and energy storage devices.
- Superior Optical Properties: Nanomaterials can exhibit novel optical phenomena, such as quantum confinement and plasmonic effects. These properties are utilized in advanced imaging, photonics, and optoelectronics.
- High Surface Area: Nanomaterials possess a significantly higher surface area compared to their bulk counterparts. This large surface area increases their reactivity, making them suitable for applications like catalysis and gas sensing.
- Controlled Drug Delivery: Nanomaterials are employed in targeted drug delivery systems, where drugs can be encapsulated in nanoparticles and released at specific sites in the body, leading to improved treatment efficacy and reduced side effects.

- Environmental Applications: Nanomaterials are used in environmental remediation to remove pollutants from air and water due to their high surface area and catalytic activity.
- Lightweight and Space-Efficient: Nanomaterials often have reduced weight and volume compared to bulk materials while maintaining or improving their performance. This benefit is crucial in applications where space and weight constraints are significant factors.
- Flexibility in Design: Nanomaterials can be engineered with precision to achieve specific properties and functionalities, allowing for tailored materials to suit particular applications.
- Energy Efficiency: The unique properties of nanomaterials enable the development of more energy-efficient devices and technologies, contributing to sustainability efforts.
- Miniaturization: Nanomaterials play a vital role in miniaturizing electronic components and devices, leading to smaller and more powerful electronics.

1.2.3 Limitations of Nanomaterials

Despite their many advantages, nanomaterials also come with several disadvantages and challenges that need to be carefully considered. Some of the key disadvantages of nanomaterials include:

- Safety Concerns: Nanoparticles can pose health and environmental risks due to their small size and unique properties. Some nanomaterials can accumulate in the body or environment and their long-term effects are not fully understood. Therefore, there is a need for careful study and regulation of nanomaterials to ensure their safe use. In certain cases, they may exhibit higher toxicity compared to their bulk counterparts, raising concerns about potential adverse effects on human health and the environment.

- Lack of Comprehensive Understanding: The behaviour of nanomaterials can be complex and not entirely predictable due to quantum effects and surface phenomena. Our understanding of their interactions with biological systems and the environment is still evolving, which requires further research to ensure their safe use.
- Manufacturing Challenges: The synthesis and production of nanomaterials can be complex and require specialized equipment and processes. The scalability and reproducibility of nanomaterials can be challenging, impacting their commercial viability.
- Environmental Impact: The potential release of nanomaterials into the environment during their production, use, and disposal can raise concerns about their impact on ecosystems and long-term environmental sustainability.
- Lack of Standardization: Nanomaterials exhibit diverse properties depending on their composition, size, and shape. The lack of standardized testing methods and characterization techniques can hinder their comparison and regulation.
- Cost: Some nanomaterials can be costly to produce due to the need for precise control over their size and structure. This can limit their widespread adoption in various applications, particularly in economically constrained sectors.
- Surface Reactivity: Nanomaterials' high surface area-to-volume ratio can lead to increased reactivity, affecting their stability and behavior in various applications.
- Risk of Nanoparticle Release: During the use of nanomaterials, there is a risk of nanoparticles being released into the air or other media, potentially causing unintended exposure to humans or the environment.
- Impact on Waste Management: The disposal and recycling of products containing nanomaterials may present challenges due to the potential release of nanoparticles during waste processing.

- Ethical and Societal Concerns: The rapid development and integration of nanotechnology can raise ethical questions about potential privacy issues, unequal access to benefits, and societal impact.

To address these disadvantages, it is essential to conduct thorough risk assessments, implement safety measures, establish proper regulations, and conduct continued research on the behavior and impacts of nanomaterials. A responsible and sustainable approach to nanotechnology can help maximize the benefits of nanomaterials while minimizing potential risks and disadvantages.

1.2.4 Synthesis of Nanomaterials

There are various methods and techniques employed to synthesize nanomaterials depending on the desired material and its applications. Two main approaches are used for nanomaterial synthesis (Figure 1.3) [1,2,10]:

a. Top-down approach: The top-down method, also known as a destructive method, decomposes bulk materials into smaller materials, which then transform into nanomaterials. Lithography, mechanical milling or ball milling, laser ablation, sputtering, electron explosion, arc discharge, and thermal decomposition are examples of the top-down method.
b. Bottom-up approach: The bottom-up method, also known as the constructive method, involves the building of material from atoms to clusters to nanoparticles. CVD, sol-gel, spinning, pyrolysis, and biological synthesis are all examples of bottom-up methods

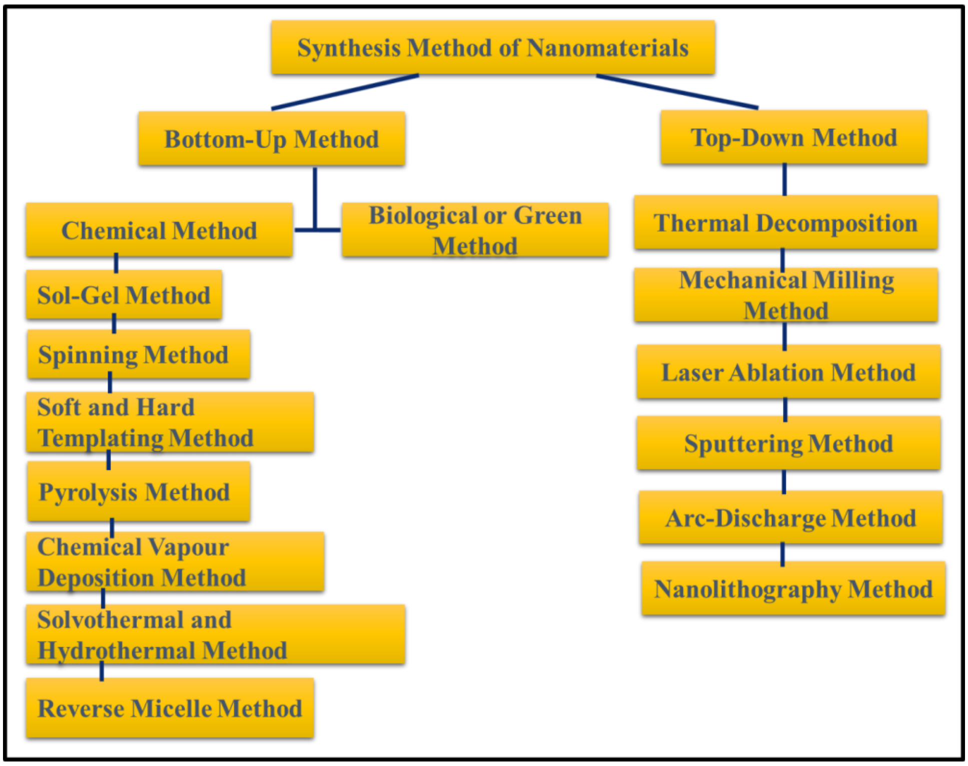

Figure 1.3 Different Synthesis Methods of Nanomaterials

a.1 Thermal Decomposition: Nanomaterials undergo thermal decomposition, breaking down into smaller constituents or converting to other substances under elevated temperatures. Their thermal stability may differ from bulk materials due to distinct surface area and energy effects. Some nanomaterials decompose at lower temperatures than their bulk counterparts. This process induces phase shifts, like altering crystal structures or changing states (solid to liquid or gas), determined by temperature. Additionally, nanomaterials display catalytic behavior during thermal decomposition, enabling unconventional chemical reactions.

a.2 Mechanical Milling: Mechanical milling creates nanomaterials by grinding or milling, reducing bulk substances to nanoparticles using mechanical energy. Material is placed with milling media (balls/rods) in a container, exposed to forces for particle size reduction. This can cause structural modifications like lattice distortions, defects, and changed properties.

- **Advantages:** Mechanical milling is a versatile and scalable method that does not require high temperatures or complex reaction conditions. It enables the production of a variety of nanomaterials from different starting materials.
- **Limitations:** Can introduce impurities from the milling media or container and may lead to particle agglomeration. Controlling milling parameters is crucial for achieving desired particle sizes and material properties.

a.3 Laser Ablation Method: The laser ablation method uses a focused laser to create nanoparticles from a target material. The laser vaporizes the material's surface, forming plasma of atoms, ions, and clusters. This plasma cools, leading to nucleation and growth, eventually resulting in nanoparticles. Factors like laser parameters (pulse duration, energy, and wavelength), target properties and surrounding gas environment affect nanoparticle size.

- Advantages: Ability to produce nanomaterials with precise control over size, composition, and crystallinity. Laser ablation is versatile and can be used to synthesize a wide range of nanomaterials, including metals, metal oxides, semiconductors, and more. It has applications in fields such as nanoelectronics, catalysis, photonics, and biomedical engineering.
- Limitations: It requires sophisticated equipment and careful optimization of laser parameters to achieve desired nanoparticle properties.

a.4 Sputtering Method: Sputtering is a versatile technique used for the synthesis and deposition of nanomaterials, primarily thin films and coatings, through the interaction of energetic ions or particles with a target material. This process involves the physical ejection of atoms or molecules from the target's surface, followed by their deposition onto a substrate. Sputtering offers several distinct processes, each with its variations and applications:

- DC Sputtering: In DC sputtering, a direct current (DC) voltage is applied between the target material (cathode) and the substrate (anode) within a low-pressure gas environment. The energetic ions in the plasma collide with the target, causing atom ejection. These ejected atoms then condense on the substrate, forming a thin film. DC sputtering is relatively simple and widely used for various materials.
- RF Sputtering: Radiofrequency (RF) sputtering employs an alternating electric field to generate plasma from the process gas. This plasma consists of positively charged ions and electrons that bombard the target. The target's surface atoms are dislodged and deposited onto the substrate. RF sputtering offers better control over the energy of the impacting particles and is suitable for materials with poor electrical conductivity.
- Magnetron Sputtering: Magnetron sputtering involves the use of a magnetic field near the target surface. This magnetic field traps electrons, creating a high-density plasma near the target. The increased ionization efficiency enhances the sputtering process, resulting in higher deposition rates and improved film quality.
- Pulsed Laser Deposition (PLD): While not a conventional sputtering method, PLD involves using a pulsed laser to ablate the target material, creating a plasma plume. The ejected material is then deposited onto the substrate. PLD allows for precise control over film composition and is often used for complex oxides and thin film growth.
- Ion Beam Sputtering (IBS): In IBS, an ion beam is directed at the target material to sputter it. This technique offers excellent control over energy and angle of incidence, allowing for precise thin film deposition and surface modification.
- **Advantages:** control over composition, uniformity, and the ability to deposit a wide range of materials, including metals, alloys, semiconductors, and insulators. It finds

applications in semiconductor manufacturing, optics, electronics, and various research areas.

- **Limitations:** Challenges such as target erosion, gas contamination, and film stress must be managed for successful nanomaterial synthesis using sputtering techniques.

a.5 The Arc-Discharge Method: The setup as requires a water-cooled vacuum chamber and electrodes to strike an arc between them. Usually, the gap between the electrodes is 1 mm and a high current of 50–100 A is passed from a low voltage power supply (12–15 V). Inert gas pressure is maintained in the vacuum system. Arc-discharge entails applying a high voltage between two electrodes in an inert gas atmosphere, leading to the formation of a high-temperature plasma. The intense heat causes vaporization and ionization of the target material, and subsequent cooling results in the condensation of vaporized atoms or clusters into nanoscale structures. In the case of carbon-based materials, such as carbon nanotubes, the vaporized carbon atoms reassemble into tubular or spherical nanostructures.

- **Advantages:** This method offers control over nanomaterial characteristics like diameter, length, and chirality.
- **Limitations:** This method is mostly found to be suitable for the deposition of fullerenes or carbon nanotubes.

a.6 Nanolithography Method: Nanolithography is a precise fabrication method used to create nanoscale patterns, structures, or devices on a substrate. These include techniques like optical lithography, electron beam lithography, and scanning probe lithography. Patterns are created using masks, electron beams, or sharp tips. Nanolithography is pivotal in semiconductor manufacturing, nanoelectronics, and photonics, enabling the production of intricate and miniaturized devices.

b.1 Sol-Gel Method: This is a wet chemistry method used for the fabrication of nanostructured ceramic materials and thin films. The process involves the conversion of salts or metal alkoxides (organometallic compounds) into nanostructured inorganic solids through inorganic polymerization. The process consists of two steps:

- Hydrolysis: Metal alkoxides undergo hydrolysis forming metal hydroxide - **'SOL'** (a colloidal solution).

  M-OR + H-OH$\rightarrow$ M-OH (sol) + ROH M = Si/Al/Ti etc.

- Polycondensation: Condensation has two types:
  i) Water Condensation:

     M-OH + H-O-M $\rightarrow$ M-O-M + H_2O

  ii) Alcohol Condensation:

     M-OH + R-O-M $\rightarrow$M-O-M + ROH

The sol is kept at RT for 7-10 days and water/alcohol molecules are evaporated. The sol undergoes condensation and polymerizes. A point is reached when the sol will not flow down on inverting the beaker and this is the get point.

A gel is a semisolid mass of oxide formed by the condensation of sol by forming a 3D network of particles. This method finds applications in optics, electronics, catalysis, sensors, biomaterials, and more. Its ability to produce nanomaterials with tailored properties makes it a valuable technique in the field of nanotechnology and materials science.

- **Advantages:** Includes controls over composition, purity and homogeneity, versatility, coating and film formation.
- **Limitations:** Slow and complex process, the gel can undergo shrinkage while drying leading to cracking and distortion of the final material, sensitive to impurities, transitioning from lab-scale to large-scale production may need modification.

b.2 Spinning Method: Electrospinning is a nanomaterial synthesis technique where an electric field is applied to a polymer solution or melt, resulting in the formation elongated jet that stretches and solidifies into nanofibers as it moves towards a collector. Electrospinning yields nanofibers with high surface area and tunable properties, suitable for applications like tissue engineering, filtration, and sensors.

b.3 Soft and Hard Templating Method: Soft templating involves using a pre-existing template, often a soft material like a surfactant micelle or a polymer, to guide the formation of nanomaterials with desired structures. This method is used in catalysts, sensors, and drug delivery systems.

Hard templating involves using a rigid, pre-existing template, often made of a different material, to shape the nanomaterial during synthesis. This method is used for creating nanowires, nanotubes, and other structured nanomaterials.

- **Advantages:** Both methods offer ways to control the structure and properties of nanomaterials for various applications.
- **Limitations:** Complete removal of the template material can be challenging, leading to potential contamination or residual effects in the final nanomaterial.

b.4 Pyrolysis Method: Pyrolysis involves subjecting precursor materials, often organic compounds or polymers, to high temperatures in an inert or controlled atmosphere. The heat causes the precursor to decompose into volatile gases, leaving behind solid residues or nanoparticles. The solid residues undergo further reactions, leading to the formation of nanoscale particles with controlled sizes and properties. It is used to produce a variety of nanomaterials, including carbon nanotubes, metal nanoparticles, and ceramic materials. Pyrolysis is a valuable method for creating nanomaterials with specific properties, finding applications in electronics, catalysis, energy storage.

- Advantages: Offers versatility, scalability, and the ability to tailor material properties through parameter adjustments.

- Limitations: Precise control of heating conditions and precursor chemistry is essential to achieve desired nanomaterial characteristics.

b.5 Chemical-Vapour Deposition Method: There are many variants of CVD like Metallo Organic CVD (MOCVD), Atomic Layer Epitaxy (ALE), Vapour Phase Epitaxy (VPE), Plasma Enhanced CVD (PECVD). They differ in source gas pressure, geometrical layout and temperature used. The basic CVD process, however, can be considered as a transport of reactant vapour or reactant gas towards the substrate. In CVD, precursor gases are introduced into a reaction chamber, where they decompose or react at elevated temperatures. This leads to the formation of volatile compounds that transport to the substrate. On the substrate's surface, these volatile species **undergo chemical reactions**, resulting in the deposition of atoms or molecules that form a thin film or coating. Parameters like temperature, pressure, and precursor flow rates are controlled to manipulate the composition, thickness, and morphology of the deposited nanomaterial. Widely used to synthesized nanomaterials like carbon nanotubes, graphene, metal films, semiconductors, and ceramic coatings.

- **Advantages:** Offers precise control, scalability, and the ability to coat complex structures. It allows for uniform and conformal deposition on various substrates.
- **Limitations:** Optimization of parameters can be intricate, and unwanted reactions or impurities may occur. High temperatures might limit certain applications.

****Physical-Vapour Deposition:** Vapor Deposition (PVD) is a nanomaterial synthesis technique that involves the deposition of thin films or coatings onto a substrate through physical processes such as evaporation or sputtering.

In summary, PVD relies on physical processes to deposit material, while CVD involves chemical reactions to form thin films or coatings. Both methods have their advantages and applications, and the choice between them depends on the desired material, properties, and specific application requirements.

b.6 Solvothermal and Hydrothermal Method: The Solvothermal Method is a nanomaterial synthesis technique that involves the use of a solvent at elevated temperatures and pressures to promote chemical reactions and the formation of nanoscale materials. Here's a concise explanation of the solvothermal method in nanomaterial synthesis:

- Process: Solvothermal synthesis takes place in a closed vessel where precursor compounds are dissolved in a solvent. The vessel is heated to a high temperature and pressure, promoting chemical reactions.
- Nucleation and Growth: The high temperature and pressure conditions within the solvent facilitate nucleation and controlled growth of nanoscale particles.
- Precursor Decomposition: Precursor compounds decompose in the solvent, and the resulting ions or molecules react to form nanomaterials.
- Control: Solvothermal conditions can be adjusted to control particle size, shape, and crystallinity by modifying factors like temperature, pressure, and reaction time.
- Applications: Solvothermal synthesis is used for a variety of nanomaterials, including nanoparticles, nanocrystals, and nanowires, and finds applications in catalysis, materials science, and nanoelectronics.
- Advantages: Solvothermal synthesis allows precise control over particle properties and offers scalability for industrial production.
- Limitations: Reaction conditions can be demanding, and the use of high temperatures and pressures may limit the types of solvents and precursors that can be employed.

Solvothermal synthesis is a valuable technique for tailoring nanomaterial properties and has led to advancements in various fields due to its ability to produce well-defined nanoscale structures.

The Hydrothermal Method of synthesis belongs to a group of synthesis techniques in which substances in high-temperature and high-pressure aqueous solutions are crystallized. Hydrothermal method is based on this premise wherein the materials are dissolved in water under high temperature and pressure conditions. These dissolved substances are then crystallized to obtain the desired end products. Hydrothermal processing is usually performed in a steel pressure vessel also defined as an autoclave wherein the processing conditions are controlled by adjusting the temperatures and/or pressures. The autoclave may or may not be coated with protective Teflon coatings. The processing is carried out in aqueous solution.

- **Instrumentation in Hydrothermal Approach**

Since hydrothermal processing frequently involves high temperatures and pressures, the reaction container must be able to sustain such conditions without undergoing any structural or compositional damage. Experimental facilities must be available for routine and reliable operation under extreme environments. Designing an ideal hydrothermal reaction container, often termed as ‘autoclave’, should consider the following (Figure 1.4) [8,9]:

- The vessel/container should not react with acid, base, or any other oxidizing agents.
- It must be easy to assemble and dissemble when required.
- Its dimensions must allow achievement of high temperatures.
- It must be leakage proof and should be able to sustain the highest possible temperature and pressure values likely to be encountered during its operating life.
- The material of the vessel as well as the vessel itself must be able to endure repeated elevated temperatures and pressures for long durations. Additionally, it should be

stable and there should not be any requirement of any type of treatment or machining after each experiment.

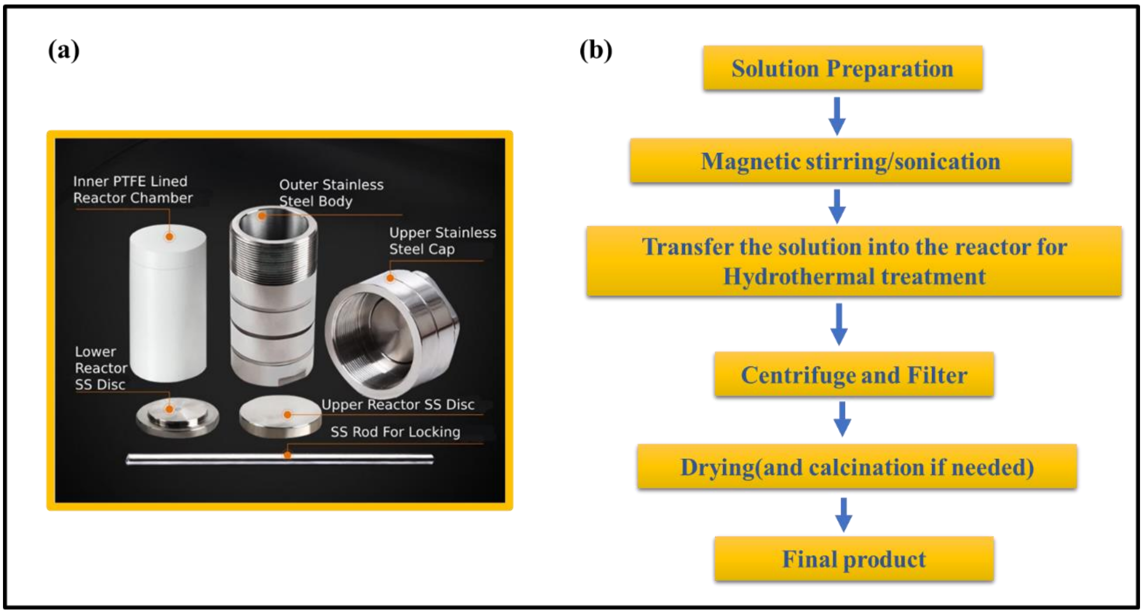

Figure 1.4 (a) Hydrothermal Synthesis Autoclave Reactor with PTFE Lined Vessel (b) Process Flow of Hydrothermal Treatment

- **Mechanism of Crystal Growth by Hydrothermal Synthesis**

➢ The hydrothermal method for synthesizing nanomaterials involves a direct crystallization process from solutions, encompassing two main stages: crystal nucleation and subsequent crystal growth.

➢ Nucleation occurs when solutes surpass the solubility limit within the solution, resulting in a state of supersaturation.

➢ This irreversible reaction triggers the precipitation of solutes into clusters of crystals, initiating the enlargement of crystals into a macroscopic scale.

➢ After nucleation, crystals experience sequential growth through a series of steps. This progression involves the integration of growth units, which share the same composition as crystal entities but exhibit either identical or distinct structures from the bulk solution.

- ➢ This integration process leads to the augmentation of existing crystal entities, resulting in increased size.
- ➢ The overall process can be categorized into distinct phases: the transportation of units through the solution, the attachment of units to the surface, the movement of units across the surface, and the bonding of units to growth sites.

- **Advantages:** Hydrothermal technique is environmentally benign. It gives good control over the particle shape and size. It can often be a one-step synthesis, reducing the need for additional post-processing steps. It applies to a wide range of materials, including metals, semiconductors, ceramics, and composites. It also uses cost-effective precursor materials, making it economically viable.
- **Limitations:** Uncontrolled conditions can lead to the formation of particle aggregates or irregular shapes, affecting product quality. High-temperature and high-pressure conditions pose safety risks, requiring careful handling and equipment. Certain materials might not dissolve well in water, limiting the choice of solvent. Transitioning from laboratory-scale to large-scale production might face challenges in maintaining reproducibility.

b.7 Reverse Micelle Method: Reverse micelles are formed in the case of a water-in-oil emulsion, with the hydrophilic heads pointing towards a water-containing core. A surfactant is dissolved in a solvent, forming aggregates known as micelles. In the reverse micelle method, the hydrophilic (water-attracting) parts of the surfactant molecules face outward, surrounding the hydrophobic (water-repellent) core. The micelles act as nanoreactors, providing confined spaces where chemical reactions can occur in a controlled manner. Precursor compounds are introduced into the micelle's hydrophobic core. Depending on the type of reaction, these precursors can react to form nanoparticles, nanocrystals, or other nanomaterials. As the reaction progresses, nanoparticles or nanocrystals form within the micelles, leading to the growth of nanomaterials. The nanomaterials are typically isolated from the micellar solution after the reaction is complete.

- **Advantages:** offers advantages such as controlled reaction environments, tunable particle size, and the ability to synthesize various nanomaterials. It is used in fields like nanotechnology, catalysis, and materials science for producing nanoparticles with specific properties.
- **Limitations:** Isolating the nanomaterials from the surfactant can be difficult and may require additional purification steps. The need for specialized surfactants and potential purification steps can increase the overall cost of the synthesis process.

b.8 Biological or Green Method of Nanomaterial Synthesis: Biosynthesis is an environmentally friendly and green approach to the synthesis of non-toxic and biological nanoparticles. Green synthesis nanoparticles have distinct and enhanced properties that make them suitable for biomedical applications. Microorganisms (like bacteria or fungi), enzymes, or plant extracts are employed as natural agents to facilitate nanomaterial synthesis. These biological agents can interact with precursor compounds to promote the reduction, nucleation, and growth of nanoscale materials. The biological method can be applied to various materials, including metals, metal oxides, and carbon-based nanomaterials. Achieving precise control over nanomaterial properties can be challenging due to the complex and variable nature of biological systems.

1.3 Application of Nanotechnology [12]

- **Everyday material and Processes:**

- ➢ Using nanotechnology, materials can effectively be made stronger, lighter, more durable, more reactive, more sieve-like, or better electrical conductors, among many other traits.

- Nanoscale materials are beginning to enable washable, durable “smart fabrics” equipped with flexible nanoscale sensors and electronics with capabilities for health monitoring, solar energy capture, and energy harvesting through movement. Lightweighting of cars, trucks, airplanes, boats, and spacecraft could lead to significant fuel savings.
- Nanoscale additives in polymer composite materials are being used in baseball bats, tennis rackets, bicycles, motorcycle helmets, automobile parts, luggage, and power tool housings, making them lightweight, stiff, durable, and resilient. Clear nanoscale films on eyeglasses, computer and camera displays, windows, and other surfaces can make them water- and residue-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive.
- Nanoscale materials are also being incorporated into a variety of personal care products to improve performance. Nanoscale titanium dioxide and zinc oxide have been used for years in sunscreen to protect from the sun while appearing invisible on the skin.

- **Electronics and IT:**

- Ultra-high-definition displays and televisions are now being sold that use quantum dots to produce more vibrant colors while being more energy efficient. Flexible electronics have been developed using, for example, semiconductor nanomembranes for applications in smartphone and e-reader displays.
- Other nanomaterials like graphene and cellulosic nanomaterials are being used for various types of flexible electronics to enable wearable and “tattoo” sensors, photovoltaics that can be sewn onto clothing, and electronic paper that can be rolled

up. Making flat, flexible, lightweight, non-brittle, highly efficient electronics opens the door to countless smart products.

- Using magnetic random-access memory (MRAM), computers will be able to “boot” almost instantly. MRAM is enabled by nanometer-scale magnetic tunnel junctions and can quickly and effectively save data during a system shutdown or enable resume-play features.
- Other computing and electronic products include Flash memory chips for smartphones and thumb drives; ultra-responsive hearing aids; antimicrobial/antibacterial coatings on keyboards and cell phone casings; conductive inks for printed electronics for RFID/smart cards/smart packaging; and flexible displays for e-book readers.

- **Medical and Healthcare:**

- Commercial applications have adapted gold nanoparticles as probes for the detection of targeted sequences of nucleic acids, and gold nanoparticles are also being clinically investigated as potential treatments for cancer and other diseases.
- Better imaging and diagnostic tools enabled by nanotechnology are paving the way for earlier diagnosis, more individualized treatment options, and better therapeutic success rates.
- Nanotechnology researchers are working on several different therapeutic, where a nanoparticle can encapsulate or any other way help to deliver medication directly to cancer cells and minimized the risk of damage to healthy tissue. This has the potential to change the way doctors treat cancer and dramatically reduce the toxic effects of chemotherapy.

- **Energy Applications:**
  - Nanotechnology is improving the efficiency of fuel production from raw petroleum materials through better catalysis. It also enables reduced fuel consumption in vehicles and power plants through higher-efficiency combustion and decreased friction. Nanotechnology can be incorporated into solar panels to convert sunlight to electricity more efficiently, promising inexpensive solar power in the future.
  - An epoxy containing carbon nanotubes is being used to make windmill blades that are longer, stronger, and lighter-weight than other blades to increase the amount of electricity that windmills can generate.
  - In the area of energy harvesting, researchers are developing thin-film solar electric panels that can be fitted onto computer cases and flexible piezoelectric nanowires woven into clothing to generate usable energy on the go from light, friction, and/or body heat to power mobile electronic devices. Similarly, various nanoscience-based options are being pursued to convert waste heat in computers, automobiles, homes, power plants, etc., to usable electrical power.
  - Nanotechnology is improving the efficiency of fuel production from raw petroleum materials through better catalysis. It is also enabling reduced fuel consumption in vehicles and power plants through higher-efficiency combustion and decreased friction.

- **Environmental Remediation:**
  - Nanotechnology could help meet the need for affordable, clean drinking water through rapid, low-cost detection and treatment of impurities in water.
  - Engineers have developed a thin film membrane with nanopores for energy-efficient desalination. This molybdenum disulfide (MoS_2) membrane filtered two to five times more water than current conventional filters.

- Nanotechnology-enabled sensors and solutions are now able to detect and identify chemical or biological agents in the air and soil with much higher sensitivity than ever before.
- Researchers have developed a nano fabric "paper towel" woven from tiny wires of potassium manganese oxide that can absorb 20 times its weight in oil for cleanup applications. Researchers have also placed magnetic water-repellent nanoparticles in oil spills and used magnets to mechanically remove the oil from the water.
- Many airplane cabins and other types of air filters are nanotechnology-based filters that allow “mechanical filtration,” in which the fiber material creates nanoscale pores that trap particles larger than the size of the pores. The filters also may contain charcoal layers that remove odors.

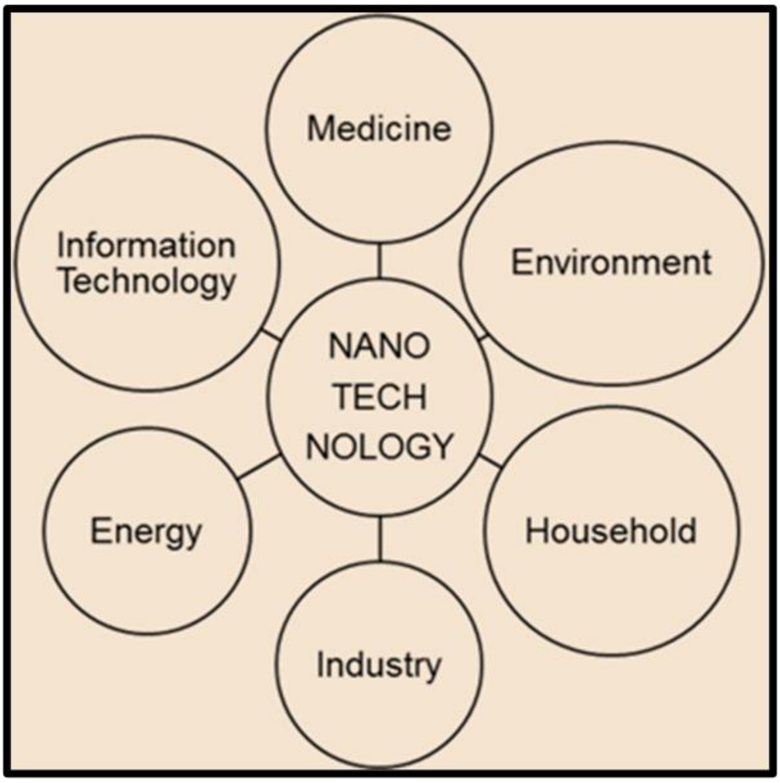

Figure 1.5 Applications of Nanotechnology

1.4 Nanomaterials used for this Work

1.4.1 Titanium Dioxide (TiO_2)

- Titanium dioxide (also known as titania, chemical formula TiO_2) is a semiconducting substance that is unreactive chemically. However, it displays photocatalytic properties when exposed to light energy that matches or exceeds its band gap energy. These attributes open up a diverse array of potential uses. Consequently, due to its reasonable cost in terms of both raw materials and production, Titania has garnered considerable interest in recent years.
- In all of its primary dioxide compounds, titanium displays octahedral geometry, forming bonds with six oxide anions. These oxides, in turn, connect to three titanium centers. The overall crystal structures of rutile and anatase exhibit tetragonal symmetry, while brookite displays orthorhombic symmetry. The arrangements of oxygen atoms within these substructures deviate slightly from close packing: rutile features oxide anions in a distorted hexagonal close-packing arrangement, anatase approaches cubic close-packing and brookite adopts a "double hexagonal close-packing" configuration. The rutile structure is also prevalent in other metal dioxides and difluorides like RuO_2 and ZnF_2 (Figure 1.6).

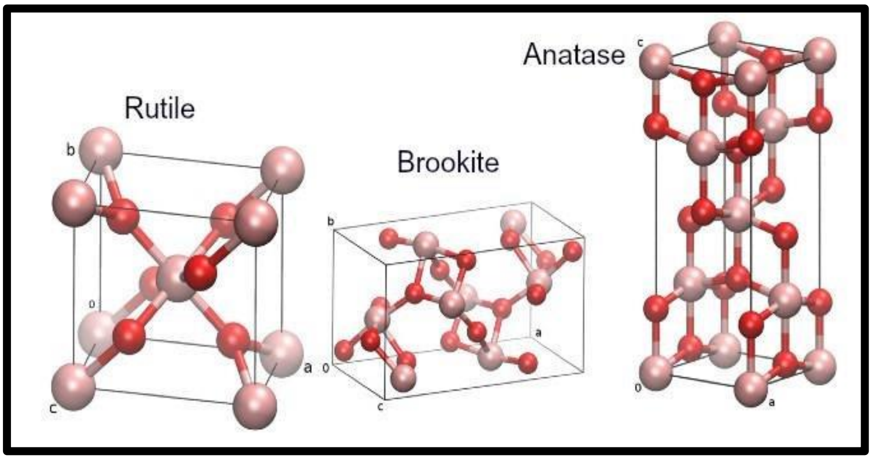

Figure 1.6 Crystal structure of titanium dioxide of rutile, brookite and anatase phase

- When titanium dioxide is in a molten state, its local structure involves each titanium atom being coordinated with approximately five oxygen atoms on average. This differs from its crystalline forms, where titanium typically coordinates with six oxygen atoms.
- Titanium dioxide is a chemical compound composed of titanium and oxygen, with the chemical formula TiO_2. It exists in various crystalline forms, with the most common being rutile and anatase.
- Titanium dioxide is a white, opaque solid with a high refractive index, meaning it has strong light-scattering properties. This property is what makes it useful in applications like sunscreens and paints.
- Industrial Preparation: Titanium dioxide (TiO_2) is industrially prepared through the sulfate process or chloride process. In the sulfate process, ilmenite ore is reacted with sulfuric acid, hydrolyzed, and calcined. In the chloride process, rutile or ilmenite is chlorinated, oxidized, hydrolyzed, and calcined. Both methods yield TiO_2 for diverse applications.
- Laboratory Preparation: In the laboratory, titanium dioxide (TiO_2) can be prepared through various synthetic routes, with the sol-gel method and hydrothermal synthesis being commonly used.

  Sol-Gel Method:

  - Precursor Solution: Titanium alkoxides (such as titanium isopropoxide) are hydrolyzed and polymerized to form a precursor solution containing titanium oxide species.
  - Gel Formation: The precursor solution is allowed to undergo a controlled hydrolysis and condensation process, leading to the formation of a gel.

- Drying and Calcination: The gel is dried and then calcined at elevated temperatures to remove organic components and form the desired TiO_2 crystalline structure.

Hydrothermal Synthesis:

- Precursor Mixture: Titanium-containing precursors (such as titanium salts) are mixed with a hydrothermal solvent (usually water) under controlled conditions.
- Reaction and Crystallization: The mixture is heated in a sealed container at elevated temperatures and pressures. TiO_2 crystallization occurs over time.
- Cooling and Collection: After the hydrothermal reaction, the system is cooled, and the resulting TiO_2 product is collected and purified.

Both methods allow for the controlled preparation of TiO_2 nanoparticles or other forms with specific properties for various applications, such as catalysis, sensing, and photovoltaics, among others. The laboratory approach offers flexibility and control over the synthesis parameters to tailor the material's characteristics as needed.

- The band gap of titanium dioxide (TiO_2) varies depending on its crystalline form. The two most common forms are rutile and anatase. Rutile TiO_2 has a band gap of around 3.0 eV, indicating it is a wide-bandgap semiconductor requiring relatively high energy to move electrons between its valence and conduction bands. Anatase TiO_2, on the other hand, has a band gap of about 3.2 eV, also categorizing it as a wide-band gap semiconductor. These band gap values influence how these materials interact with light energy and contribute to their applications in areas like photocatalysis, solar cells, and sensors.
- Titanium dioxide has photocatalytic properties, which means it can accelerate certain chemical reactions when exposed to light. This property has applications in self-

cleaning surfaces (e.g., self-cleaning windows), air and water purification, and even as a potential component in renewable energy technologies.

- Application: Titanium dioxide nanoparticles have been explored for various medical and dental applications, including drug delivery systems, imaging agents, and dental materials. Other applications include pigments, coatings, sunscreen, cosmetics, ceramics, photovoltaics, self-cleaning surfaces, antimicrobial coatings, air/water purification, catalysis, textiles, and electronics.

1.4.2 Graphitic Carbon Nitride (gC_3N_4)

- Graphitic carbon nitride (gC_3N_4) has gained immense attention as a promising visible light photocatalyst. However, the photocatalytic efficiency of bulk gC_3N_4 is limited. This can be attributed to its fast charge recombination process, low surface-to-volume ratio, and weak redox ability. Currently, gC_3N_4 is produced on a large scale by the pyrolysis of urea under ambient pressure without additive assistance. This method involves four steps. First, urea ($CO(NH_2)_2$) is pyrolyzed to isocyanic acid (HNCO) at a low temperature (<200 °C) equation (i). Subsequently, isocyanic acid is converted into cyanuric acid, which is further converted into melamine by self-supported NH_3(g) equation (ii). Melamine is then condensed at about 350 – 450°C to form melam, which then evolves to form melem ($C6H_6N_{10}$) via a self-condensation equation (iii). At approximately 500 °C, melem is further pyrolyzed and is then condensed to form melon ($-[C_6H_3N_9]_n$) with a low degree of polymerization. Finally, at 450 - 650 °C, these polymers are further condensed to form gC_3N_4 with a high degree of polymerization (equation (iv)).

  - $CO(NH_2)_2\ (\xrightarrow{-NH_3})$ HNCO $(\xrightarrow{\text{Nucleophilic Addition}})$ ….(i)
  - $C_3H_3N_3O_3\ (\xrightarrow{\text{Self – supported } NH_3})\ C_3H_6N_6\ (\xrightarrow{-NH_3})$ ….(ii)
  - $C6H9N11\ (\xrightarrow{-NH_3})\ C6H6N10\ (\xrightarrow{\text{Polycondensation } -NH_3})$ ….(iii)

- ➢ $[C_6H_3N_9]$ ($\xrightarrow{\text{Polymerization}}$) gC_3N_4 ….(iv)

- Band gap energy of graphitic carbon nitride is 2.7 eV, thus it can act as a visible light-driven photocatalyst. The energy location of the conduction band and valence band via hydrogen electrode is at -1.1 and 1.6 eV respectively. Graphitic carbon nitride is resistant to attack from heat, strong alkaline and acid solutions.
- gC_3N_4 can be easily made by thermally polycondensing inexpensive N-rich precursors such urea, melamine, melamine cyanurate, dicyanamide, and cyanamide, as opposed to other metal-containing photocatalysts that need to be made with expensive metal salts.

- Structure of Graphitic Carbon Nitride: Graphitic carbon nitride (gC_3N_4)-based materials exhibit an organized layered porous structure and a band position optimum for the development of various optoelectronic devices and photocatalysts (Figure 1.7).

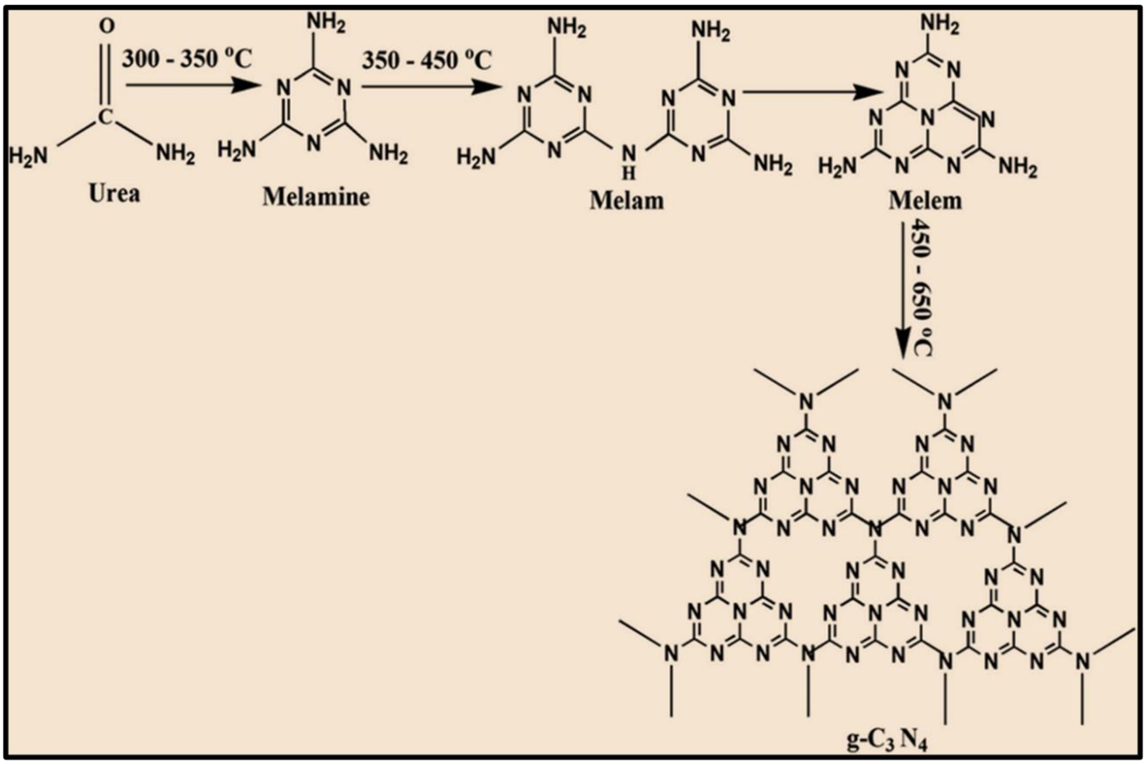

Figure 1.7 Schematic for Synthesis of gC_3N_4

- Synthesis of Graphitic Carbon Nitride: The gC_3N_4 synthesis began in 1834 with Berzelius creating a polymeric derivative, melon. The material's detailed structure emerged in 1922, revealing variable polymer sizes and shapes. The research followed synthesis methods and structure-property relations. Starting compounds rich in carbon and nitrogen are used, synthesized around 400-600 ºC. The building block's planar structure leads to 2D sheet-like gC_3N_4, with diverse morphologies like tubes or rods reported. Kouvetakis et al. made amorphous gC_3N_4 from melamine at 450-600ºC. Extreme conditions (800 ºC, 2.5 GPa, hydrogen) yielded near-perfect graphite stacking in gC_3N_4. Yet, high temp led to low nitrogen and imperfect C: N ratio. Crystalline gC_3N_4 structures form via HCl elimination at high pressure and temperature using 2-amino-4, 6-dichloro triazine precursors. In situ, HCl plays a key role in structure development. Komatsu introduced ordered 2D gC_3N_4 synthesis. Schnick isolated stable intermediate melem, revealing a 500-600 ºC ideal. Solvothermal reactions at 200°C with cyanurchloride-sodium amide/azide form gC_3N_4, are less graphitic due to lower temperature.
- Application: Graphitic carbon nitride (gC_3N_4) has applications in photocatalysis (pollutant removal), solar energy conversion, hydrogen production, gas sensing, batteries, field emission, catalysis, antibacterial coatings, carbon capture, chemical synthesis, superhydrophobic surfaces, and more. Its versatile properties find use in energy, environment, electronics, and materials science.

1.5 Semiconductor

Semiconductors are materials that have a conductivity between conductors (generally metals) and non-conductors or insulators (such as ceramics). This conductivity arises from factors like impurity doping or temperature changes (Figure 1.8) [17,20].

1.5.1 p-type Semiconductor

A p-type semiconductor is an intrinsic semiconductor doped with boron or indium. The majority of carriers in p-type semiconductors are holes. Electrons are minority carriers in a p-type semiconductor. In a p-type semiconductor, the hole density is much greater than the electron density. The acceptor energy level of the p-type is close to the valency bond and away from the conduction band.

1.5.2 n-type Semiconductor

The majority of charge carriers in n-type semiconductors are electrons. Holes are minority carriers in a n-type semiconductor. In the n-type of semiconductor, the electron density is much greater than the hole density. The donor energy level of the n-type is close to the conduction band and away from the valency band. In an n-type semiconductor, an intrinsic semiconductor is doped with phosphorus or antimony as an impurity.

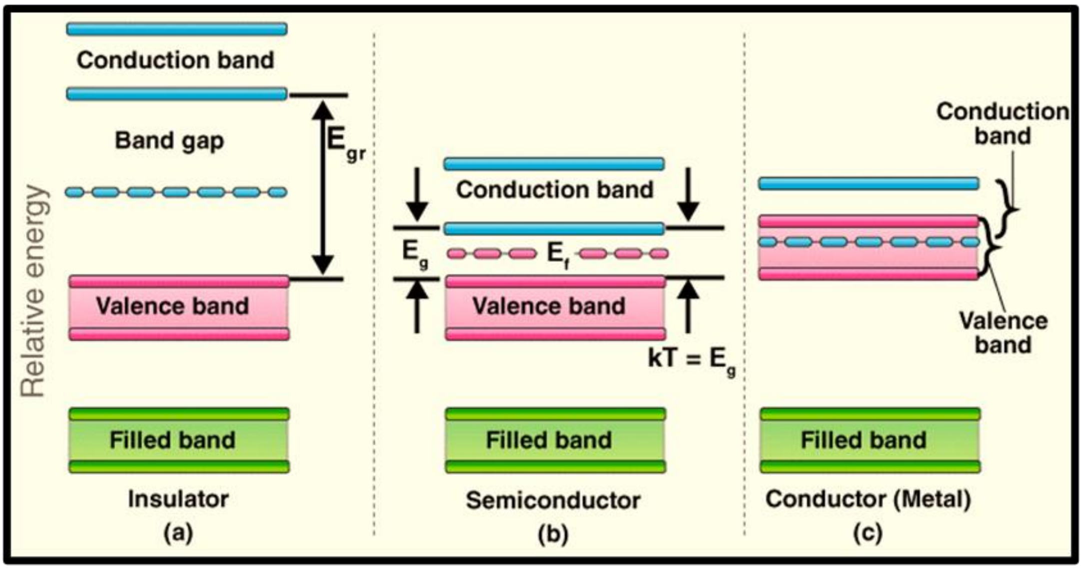

Figure 1.8 Band diagram of (a) Insulator, (b) Metal and (c) Semiconductor

1.6 Catalysis

Catalysis is the process of change in the rate of a chemical reaction by adding a substance known as a catalyst. Catalysts are not consumed by the reaction and do not undergo permanent change after it. The presence of the catalyst leads to higher reaction rates and reduced energy usage, enabling the reaction to occur more rapidly.

1.6.1 Activation Energy

A catalyst is not destroyed, consumed, or permanently changed in the reaction. A catalyst does this by lowering the activation energy. Activation energy is the energy needed to start a reaction between two or more elements or compounds. A reaction with high activation energy may proceed slowly, or not at all[14].

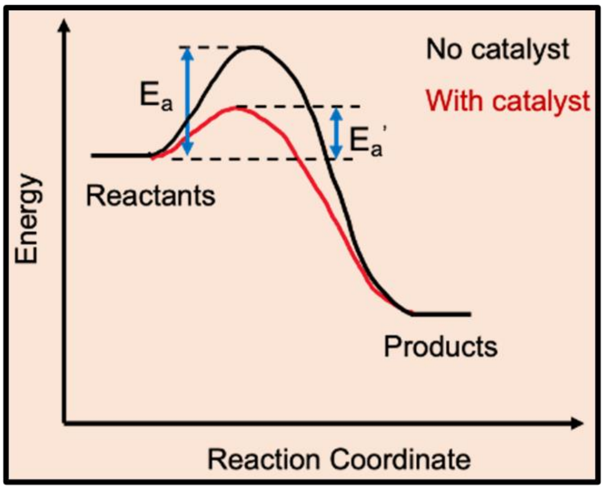

Figure 1.9 Activation Energy Barrier

The graph (Figure 1.9) shows the energy of a reaction both with and without a catalyst present. The x-axis is the reaction coordinate or progression of the reaction from reactant (leftside) to product (right side). The y-axis is the energy. With the catalyst present, the activation energy (E_a) is smaller. A catalyst lowers the activation energy by changing the transition state of the reaction. The reaction then goes through a different pathway/mechanism than the uncatalyzed reaction. The catalyst does not change the net energy difference between reactant and product. The reaction's net equation will be the same in a catalyzed and uncatalyzed reaction even though the transition state changes.

Overall reaction: A + B + catalyst –> AB + catalyst

Net Reaction: A + B –> AB

1.6.2 Catalytic Promoter

A catalytic promoter is a substance that increases the catalytic efficiency of any reaction. They are also known as activators. Activators are added in small amounts to increase the catalytic activity.

1.6.3 Catalytic Inhibitor

A catalytic inhibitor is a chemical substance that affects the activity of the catalyst added in a chemical reaction and decreases the reaction rate.

1.6.4 Types of Catalysis

- **Homogenous Catalysis:** Refer to the reaction where reactants and catalyst, are in the same phase may it be the solid, liquid, or gaseous physical state.
- **Heterogenous Catalysis:** Here catalyst and reactants are in different phases. In most cases, the catalyst is in the solid face while reactants are either in liquid or gas face.
- **Auto-Catalysis:** This includes the reaction where one of the products formed acts as a catalyst. In the starting, the rate of the reaction is low and increases very slowly but as soon as the products are formed after certain intervals of time the rate increases rapidly.

1.6.5 Different Catalytic Processes

- **Photocatalysis:** Photocatalysis is a catalytic process in which light energy is used to initiate and accelerate a chemical reaction. A photocatalyst, typically a semiconducting material, absorbs photons from a light source and generates electron-hole pairs. These energetic charge carriers then participate in chemical reactions on the catalyst's surface or with adsorbed reactants (Figure 1.10) [15].

- Light Activation: Photocatalysis relies on the absorption of photons, usually from ultraviolet or visible light, to create electron-hole pairs.
- Semiconducting Catalysts: Photocatalysts are often semiconducting materials like titanium dioxide (TiO_2), zinc oxide (ZnO), or other metal oxides. They have a bandgap that matches the energy of the absorbed photons.
- Electron-Transfer Reactions: Generated electron-hole pairs can participate in redox reactions, enabling the conversion of reactants into products.

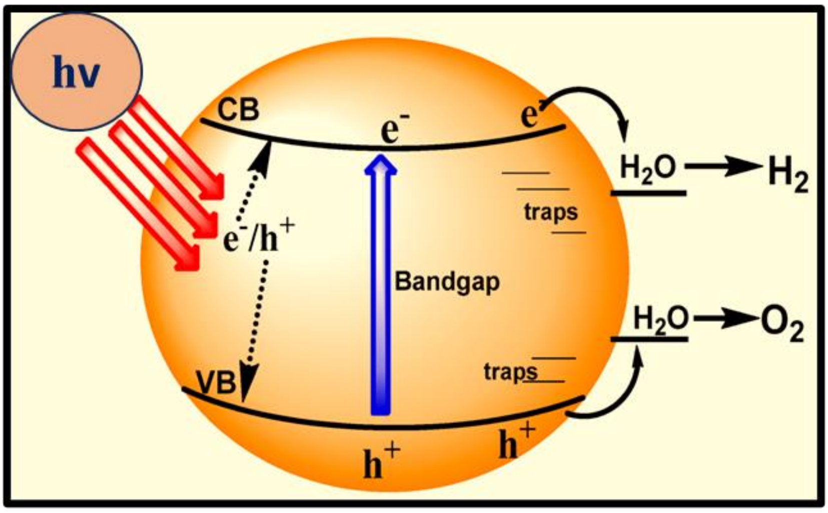

Figure 1.10 Mechanisms of Photocatalysis

- Environmental Applications: Photocatalysis is used for air and water purification, breaking down pollutants and toxins into harmless substances using sunlight.
- Hydrogen Production: Photocatalysts can generate hydrogen gas from water by splitting water molecules under light irradiation, offering a renewable and clean energy source.

- Organic Synthesis: Photocatalysis is employed in synthetic chemistry to facilitate organic transformations, enabling the creation of complex molecules under mild conditions.
- Photodegradation: Photocatalysts can degrade organic compounds through photocatalytic reactions, playing a role in waste treatment and environmental remediation.
- Surface Modifications: Photocatalysis can modify material surfaces, creating self-cleaning or antifouling properties.
- Limitations: Catalyst stability, selectivity, and reaction efficiency are challenges in developing effective photocatalytic processes.
- Photocatalysis harnesses renewable light energy to drive chemical reactions and has promising implications for sustainable technologies and environmental protection.

- **Sono-catalysis:** Sono-catalysis is a catalytic process in which sound waves, typically ultrasonic waves, are used to enhance a chemical reaction. The mechanical energy generated by the sound waves induces cavitation, creating tiny bubbles that rapidly collapse and generate localized high temperatures and pressures. These extreme conditions facilitate chemical reactions on the surfaces of catalysts or substrates, leading to increased reaction rates and efficiency.
- **Electro-catalysis:** Electrocatalysis can be defined as the heterogeneous catalysis of electrochemical reactions, which occur at the electrode–electrolyte interface and where the electrode plays both the role of electron donor/acceptor and catalyst.
- **Piezo-catalysis:** Piezo-catalysis is a catalytic process that takes advantage of mechanical forces generated by piezoelectric materials to enhance or drive chemical reactions. Piezoelectric materials generate an electric charge when subjected to

mechanical stress, such as pressure or vibration. This electric charge can influence the reaction pathway or provide additional energy to facilitate chemical transformations.

1.7 Reason for using Semiconductors in Photocatalysis instead of Metal or Insulators

Semiconductors are preferred over metals or insulators for photocatalysis due to their unique electronic properties that enable efficient light-driven chemical reactions [7].

- Bandgap: Semiconductors have a bandgap energy that allows them to absorb photons and generate electron-hole pairs when exposed to light. This energy conversion process initiates catalytic reactions.
- Electron Transfer: The generated electron-hole pairs in semiconductors can participate in redox reactions, driving the conversion of reactants into products on the catalyst's surface.
- Efficient Charge Separation: The inherent properties of semiconductors facilitate the separation of photo-generated charges, preventing recombination and increasing the likelihood of productive reactions.
- Tunable Properties: The bandgap of semiconductors can be tuned by adjusting their composition, enabling optimization for specific photocatalytic reactions.
- Catalytic Surfaces: The surface of a semiconductor can serve as a platform for adsorbing reactants and facilitating their interaction, leading to efficient reaction pathways.
- Non-corrosive: Unlike metals, semiconductors are less prone to corrosion in aqueous environments, making them suitable for long-term photocatalytic applications.
- Wide Applicability: Semiconductors can be tailored for various photocatalytic processes, such as water splitting, pollutant degradation, and organic synthesis.
- Sustainability: Many semiconductors used in photocatalysis are environmentally friendly and non-toxic, aligning with the principles of sustainable and green chemistry.

In contrast, metals often lack the appropriate bandgap for efficient photon absorption, and insulators typically do not promote charge separation and redox reactions necessary for photocatalysis.

1.8 Photocatalytic Activity of Titanium Dioxide (TiO_2)

- The primary contaminants in wastewater originate from dye discharges by textile and leather sectors. It's recognized that the textile industry consumes substantial water volumes, with approximately 90% of this utilized water being discharged as wastewater. Industries release carcinogenic dyes in wastewater, endangering humans and the environment. Effective methods are employed to remove pollutants and provide clean water.
- Photocatalysis is widely regarded as a highly effective method for treating wastewater due to its capability to break down hazardous substances into safer, simpler forms.
- Titanium dioxide acts as an efficient photocatalyst due to its nontoxicity, degradation efficiency and thermal stability. The wide band gap value of TiO_2 results in the activation of this material under UV light irradiation.
- To improve the photocatalytic effectiveness of titanium dioxide, it is combined with graphitic carbon nitride possessing band gap energy of 2.7 eV. Consequently, the resulting titanium dioxide/graphitic carbon nitride nanocomposite serves as a proficient photocatalyst, effectively degrading Rhodamine B dye under visible light.
- Heterogeneous Photocatalysis is a promising advanced oxidation process for water purification, given its potential to fully oxidize organic pollutants and to inactivate microorganisms.
- The enhanced photocatalytic efficacy of the nanocomposite arises from the reduction in electron-hole pair recombination rate and the heightened separation efficiency within the conduction and valence bands. Different morphologies of graphitic carbon

nitride are manipulated to assess its degradation performance relative to tungsten trioxide and titanium dioxide/graphitic carbon nitride.

- The photocatalytic activity of degrading Rhodamine B (RhB) using TiO_2-doped GCN (Graphitic Carbon Nitride) nanoparticles involves utilizing the composite's unique properties. When exposed to UV or visible light, TiO_2-doped GCN nanoparticles generate electron-hole pairs due to their semiconductor nature. These charge carriers initiate redox reactions, leading to the degradation of RhB molecules into simpler, harmless byproducts. The TiO_2 component enhances light absorption and promotes efficient charge separation, while GCN acts as a support matrix. This synergistic effect accelerates the degradation process, making the composite a powerful photocatalyst for wastewater treatment, particularly in the removal of carcinogenic dyes like RhB.

1.9 Types of Dyes

Dyes can be broadly categorized into two main groups: inorganic dyes and organic dyes. These categories are based on the chemical composition of the dyes and their source [19,20].

- **Inorganic Dyes:** Inorganic dyes are derived from inorganic compounds and elements. They are often minerals or metal complexes and tend to have limited color options compared to organic dyes they find applications in areas like ceramics, glass, and pigments. Examples of inorganic dyes include:

- Prussian Blue: A deep blue pigment made from a complex of iron and cyanide ions.
- Chrome Yellow: A bright yellow pigment derived from lead chromate.
- Ultramarine: A blue pigment derived from the mineral lapis lazuli, often used in art.
- Cadmium Red: A red pigment containing cadmium, used in art and some industrial applications.

- **Organic Dyes:** Organic dyes are derived from carbon-based compounds and are the most common type of dyes used in textile and fabric dyeing. They offer a wide range of colors and shades, better color stability, and various application methods. Examples of organic dyes include:
  - Azo Dyes: These are among the most widely used synthetic organic dyes, known for their bright and varied colors.
  - Anthraquinone Dyes: These dyes produce colors ranging from red to violet and are often used for cellulose fibers.
  - Phthalocyanine Dyes: These dyes are known for their vibrant blue and green colors and are used in a variety of applications, including textiles and printing inks.
  - Reactive Dyes: These dyes form covalent bonds with fibers and are commonly used for cotton, wool, and silk.
  - Cationic Dye: Cationic dyes are composed of elements that cause them to break down into positively charged ions when in contact with water. They have an alkaline or basic nature. For example, Methylene Blue (MB) and Rhodamine B (RhB).
  - Anionic Dye: Anionic dyes consist of components that lead to the formation of negatively charged ions when they interact with water. They possess an acidic nature. For example, Methyl orange (MO) and Orange G (OG).
  - Non-Ionic Dye: Non-Ionic dyes comprise elements that result in the creation of neutrally charged ions when exposed to water. They are neutral in character. For example, Green 97 (G97) and Disperse Red 60 (DR60).

1.10 Arrangement of Thesis

In this study, an extensive examination was conducted by reviewing prior research on transition metal oxides, specifically titanium dioxide (TiO_2). The review encompassed various aspects, including different types of TiO_2, synthesis methods, morphological characteristics, surface modifications, mechanical properties, electrical properties, chemical properties, and its applications as a photocatalyst. Following the literature review, the study delves into the instrumentation and apparatus employed for characterizing all the synthesized samples. Subsequently, the study is divided into two main chapters. The first chapter focuses on the evaluation of kinetic rate constants for dye degradation under UV light in a catalytic reactor using TiO_2 nanoparticles. The second chapter explores the enhanced degradation performance of Rhodamine B when using TiO_2/gC_3N_4 under UV light. These chapters provide an in-depth analysis of the photocatalytic behaviour of these materials. Finally, the study concludes by presenting the results obtained and outlining the potential future directions for research in the field of photocatalysis.

1.11 Aims and Objectives

The primary objective of using TiO_2 as a photocatalyst is to harness its unique properties to initiate and facilitate photochemical reactions under light exposure. TiO_2's photocatalytic activity arises from its ability to generate electron-hole pairs when exposed to light, which can participate in redox reactions. By utilizing TiO_2 as a photocatalyst the aim is to:

- Efficiently degrade harmful pollutants, disinfect water, and promote various chemical transformations, all driven by the energy from light sources. This environmentally friendly approach has applications in wastewater treatment, air purification, self-cleaning surfaces, and more, contributing to sustainable and cleaner technologies.
- Evaluate and enhance the photocatalytic activity of TiO_2, which involves the efficient generation of electron-hole pairs when exposed to UV light.
- Improve the efficiency of TiO_2 photocatalysis by modifying TiO_2 nanoparticles, such as doping with other elements (Graphitic Carbon Nitride) or optimizing particle size and morphology.

- Assess the environmental impact of TiO_2 photocatalysis by studying its byproducts and ensuring they are non-toxic.
- Investigate the long-term stability of TiO_2 photocatalysts to ensure they maintain their activity over extended periods.
- Explore cost-effective methods for synthesizing and using TiO_2 photocatalysts to make the technology practical and accessible.
- Integrate TiO_2 photocatalysis with other technologies, such as solar panels or water treatment systems, to maximize energy conversion or pollutant removal.

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CHAPTER 2

REVIEW OF PAST WORK

2.1 General Idea

The chapter review centers on existing research concerning the photocatalytic capabilities of transition metal oxides. These oxides have garnered significant attention due to their potential in applications like environmental remediation, energy conversion, and water splitting. The introductory section provides a comprehensive overview of transition metal oxides, highlighting their distinctive electronic and structural features and their viability as photocatalytic options. It explores various transition metal oxides, examining their crystal structures, band gaps, and relevant attributes, including titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten trioxide (WO_3), perovskite oxides ($SrTiO_3$), magnetite (Fe_3O_4) niobium pentaoxide (Nb_2O_5), etc. The review delves into the mechanisms underpinning the photocatalytic actions of transition metal oxides, elucidating the processes of light absorption, charge separation, and reactive species generation. It investigates how modifications to surfaces, incorporation of co-catalysts, and introduction of dopants can enhance the photocatalytic efficacy of these oxides. Essential factors such as crystallinity, particle size, and surface area that influence photocatalytic performance are addressed. Moreover, the review thoroughly investigates the existing literature on how transition metal oxides are used in photocatalysis and how their semiconducting properties are applied in specific electronic domains. It underscores the efficacy of these materials in degrading organic pollutants, producing hydrogen via water splitting, wastewater treatment, harnessing solar energy for electricity generation. Challenges faced during practical implementation are scrutinized, along with proposed alternative solutions. In conclusion, the chapter review offers a comprehensive critique of earlier research on transition metal oxides as photocatalysts. It not only lays the foundation for future advancements in this field but also furnishes valuable insights into their intrinsic characteristics, photocatalytic mechanisms, methods of characterization, and potential applications.

2.2 Transition Metal Oxide

Transition metal oxides are compounds formed by combining transition metals with oxygen. These oxides exhibit a wide range of properties and applications due to the unique characteristics of transition metals and their interactions with oxygen. They are of great interest in various scientific and technological fields, including catalysis, electronics, energy storage, optics, and more. Some examples of transition metal oxides include titanium dioxide (TiO_2), iron oxide (Fe_2O_3), and copper oxide (CuO) [13,23].

2.2.1. Different types of Transition Metal Oxides

Transition metal oxides encompass a broad range of compounds with varying chemical and structural characteristics. Some of the different types of transition metal oxides include:

i. Binary Oxides: These are composed of one transition metal and oxygen. Examples include titanium dioxide (TiO_2), iron oxide (Fe_2O_3), and zinc oxide (ZnO).

ii. Perovskite Oxides: These have a perovskite crystal structure (ABO_3) and often exhibit complex electronic properties. Examples include strontium titanate ($SrTiO_3$) and lanthanum strontium manganite ($La1\text{-}xSrxMnO_3$).

iii. Spinels: These oxides have a spinel crystal structure (AB_2O_4) and show diverse magnetic and electrical properties. Examples include magnetite (Fe_3O_4) and cobalt aluminate ($CoAl_2O_4$).

iv. Rutile-Type Oxides: These oxides have a rutile crystal structure and often display interesting electrical and optical properties. An example is niobium pentoxide (Nb_2O_5).

v. Delafossite Oxides: These oxides have a layered structure with triangular coordination of metal atoms. Examples include copper aluminum oxide ($CuAlO_2$) and silver gallium oxide ($AgGaO_2$).

vi. Spinel Ferrites: These are magnetic oxides with the spinel structure, often used in electronic devices and data storage. Examples include iron ferrite (Fe_3O_4) and cobalt ferrite ($CoFe_2O_4$).

vii. Complex Oxides: These are oxides with intricate crystal structures and multifunctional properties. Examples include perovskite-based complex oxides like strontium titanate cobaltite ($SrTi_{0.5}Co_{0.5}O_{3-\delta}$).

viii. Layered Double Hydroxides (LDHs): These materials have a layered structure and can intercalate various anions between their layers. Examples include hydrotalcite-like compounds.

ix. Mixed Metal Oxides: These are oxides composed of multiple transition metals. Examples include ternary oxides like bismuth vanadate ($BiVO_4$) and ternary spinel oxides.

x. Vanadium Oxides: Vanadium oxides have varying oxidation states of vanadium and exhibit interesting electronic properties. Examples include vanadium pentoxide (V_2O_5) and lithium vanadium oxide (LiV_3O_8).

These are just a few examples of the diverse types of transition metal oxides, each with their unique properties and potential applications in fields like catalysis, energy storage, electronics, and more.

2.2.2 Applications of Transition Metal Oxides

Transition metal oxides find applications across various fields due to their versatile properties. Some notable applications include [13]:

i. Catalysis: Transition metal oxides like titanium dioxide (TiO_2) are used in photocatalysis for environmental cleanup and water purification.

ii. Electronics and Optoelectronics: Metal oxides serve as semiconductors in electronic devices and sensors. Indium tin oxide (ITO) is used in transparent conductive coatings for displays and solar cells.

iii. Energy Storage: Lithium cobalt oxide ($LiCoO_2$) is a cathode material in lithium-ion batteries. Vanadium oxide materials are explored for energy storage and smart windows.

iv. Photovoltaics: Transition metal oxides enhance solar cell efficiency by improving electron transport and light absorption.

v. Gas Sensing: Metal oxide semiconductors are used in gas sensors to detect harmful gases and pollutants.

vi. Ceramics and Coatings: Transition metal oxides like zirconium oxide (ZrO_2) are used in ceramic materials and high-temperature coatings.

vii. Magnetic Material: Transition metal oxides exhibit magnetic properties, used in data storage and medical imaging.

viii. Environmental Remediation: Transition metal oxides are employed for removing pollutants and heavy metals from water and soil.

ix. Biomedical Applications: Metal oxides play a role in drug delivery, bioimaging, and therapeutic applications.

x. Catalytic Converters: Cerium oxide (CeO_2) is used in catalytic converters to reduce harmful emissions from vehicles.

xi. Superconductors: Some transition metal oxides exhibit superconducting properties at low temperatures.

xii. Water Splitting: Certain oxides are used as photocatalysts in water splitting to generate hydrogen fuel.

xiii. Corrosion Protection: Metal oxide coatings provide corrosion resistance to metals in harsh environments.

xiv. Memory Devices: Transition metal oxides are used in non-volatile memory devices.

These applications demonstrate the broad impact of transition metal oxides on various industries, technologies, and scientific advancements.

xv. Photodetectors: Transition metal oxides (TMOs) serve as effective photodetectors due to their exceptional optoelectronic properties. Notably, titanium dioxide (TiO_2) and zinc oxide (ZnO) are employed for ultraviolet (UV) photodetection, while tungsten oxide (WO_3) finds use across UV, visible, and even near-infrared ranges. These TMOs exhibit high sensitivity and rapid response times, making them valuable for various light detection applications. Their tunable properties, including bandgap engineering and surface modifications, enable tailored photodetector designs for diverse wavelength ranges, fostering advancements in sensors, imaging, and communication systems.

2.2.3 Report on Morphological Changes of Transition Metal Oxide

Earlier research closely investigated the changes in shape and structure of transition metal oxides, exploring their impact on various industries like catalysis, energy storage, electronics, and sensing. These studies provide valuable insights into how altering their form can enhance their performance. In catalysis, the morphology of transition metal oxides significantly affects surface area, active sites, and diffusion paths, influencing their catalytic activity. For instance, controlled modifications in the morphology of titanium dioxide (TiO_2) nanoparticles, such as increasing surface area and light absorption, have been found to enhance photocatalytic efficiency. Similarly, adjusting the morphology of tungsten oxide catalysts can improve their performance in oxidation and ammonia production processes. This emphasizes the importance of morphological control in enhancing the functionality of transition metal oxides. The shape of transition metal oxide electrodes plays a vital role in their electrochemical performance for energy storage. Research indicates that altering the morphology of transition metal oxide nanomaterials, like creating hierarchical structures, nanowires, and nanosheets, can enhance energy storage capacity. These changes increase the specific surface area and decrease ion diffusion pathways. This has proven effective in enhancing the performance of energy storage technologies like lithium-ion batteries and supercapacitors, where controlled morphologies of transition metal oxides have been successfully implemented. In electronics, transition metal oxide morphology significantly influences charge transport and device performance. For instance, the controlled growth of zinc oxide nanowires enhances charge carrier mobility, making them promising for electronic devices like field-effect transistors. Morphological changes have also been explored to enhance electrical conductivity and interface properties of transition metal oxide thin films in optoelectronic devices such as solar cells and LEDs. Moreover, morphological adjustments impact sensing applications in these materials. The surface shape and structure of metal oxide-based gas sensors influence gas adsorption and reaction, impacting sensing performance. Controlled morphological alterations like porous structures, nanoparticles, or nanowires have been shown to enhance gas sensing sensitivity and response times [9,12].

2.2.4 Report on Surface Modification of Transition Metal Oxide

Surface modification of transition metal oxides involves altering the outermost layer of these materials to achieve specific properties or functionalities. For instance, introducing functional groups or coatings onto the surface of transition metal oxide nanoparticles can improve their stability, reactivity, and interaction with other substances. The modification of transition metal oxides in catalysis enhances stability, selectivity, and catalytic activity. A common approach is to introduce doping or heteroatoms to the surface. For example, doping titanium dioxide (TiO_2) with metals like silver (Ag) or platinum (Pt) boosts photocatalytic activity by promoting charge separation and reducing recombination. Another method involves modifying surfaces with metal nanoparticles or clusters to create active sites, enhancing catalytic performance in processes like hydrogenation and oxidation. In sensors, it can optimize sensitivity and selectivity to target analytes. Studying past research on modifying the surfaces of transition metal oxides highlights the importance of this approach in improving their properties and capabilities. Enhancing catalysis, energy storage, charge transport, and sensing can be achieved through surface modifications like doping, coating, and functionalization. Ongoing exploration of these techniques will further advance the use of transition metal oxides in catalysis, energy storage, electronics, and sensing [14].

2.2.5 Report of the Mechanical Properties of Transition Metal Oxide

Transition metal oxides display varying mechanical properties, including hardness, stiffness, and brittleness, influenced by factors, like crystal structure and bonding. Titanium dioxide and zirconium oxide, known for high hardness, find use in wear-resistant applications. Understanding these properties is vital for designing durable and functional materials. Focusing on the elastic properties of transition metal oxides, studies employ techniques like atomic force microscopy and nanoindentation to measure characteristics such as Young's modulus and hardness. For instance, research on titanium dioxide (TiO_2) demonstrates its elastic modulus can vary based on factors like crystal structure, phase, and doping. Mechanical properties of other oxides, like zinc oxide (ZnO) and tungsten oxide (WO_3), are also investigated. Additionally, researchers analyze the strength and fracture toughness of these materials. Tantalum oxide (Ta_2O_5) and zirconium oxide (ZrO_2), with high fracture toughness, are studied for applications needing mechanical stress resistance. Research into the mechanical properties of transition metal oxides has provided crucial insights into their elasticity, and strength, and how size, shape, and environmental conditions impact them. This knowledge is vital for their effective application in structural materials, sensors, and microelectromechanical systems (MEMS). Further exploration of their mechanical behavior is essential to tailor transition metal oxide materials for specific uses, enabling customized properties through continued investigation [2].

2.2.6 Report of the Electrical Properties of Transition Metal Oxide

The electrical properties of transition metal oxides refer to their behavior in conducting or insulating electric current. These properties are essential for various applications in electronics, energy conversion, and sensing. Transition metal oxides can exhibit a wide range of electrical behaviors, including metallic conductivity, semiconducting behavior, and insulating characteristics. These properties depend on factors like crystal structure, doping, and defects. For instance, some transition metal oxides, such as indium tin oxide (ITO), exhibit transparent conductive behavior, making them suitable for applications like touch screens and solar cells. Understanding the electrical properties of transition metal oxides is crucial for designing efficient electronic devices and optimizing their performance in various technologies. Titanium dioxide (TiO_2) exhibits semiconductor characteristics due to its wide bandgap, limiting its electrical conductivity. However, by doping or altering its structure, its electrical properties can be enhanced. TiO_2 is employed in photocatalysis and solar cells, where it generates and transports charge carriers upon light exposure. Managing TiO_2's electrical properties is vital for optimizing its performance in electronics and energy applications. They also exhibit unique redox properties, making them promise for energy storage. In lithium-ion batteries, TMOs like lithium cobalt oxide ($LiCoO_2$) serve as cathode materials, facilitating reversible redox reactions for efficient energy storage. Innovatively, a manganese oxide-derived material was synthesized, enhancing capacity and stability in sodium-ion batteries, and offering prospects for advanced energy storage technologies.

2.2.7 Report of the Chemical Properties of Transition Metal Oxide

Transition metal oxides display chemical properties through their reactions with other substances, including oxidation, reduction, and complex formation. These properties are influenced by composition, crystal structure, and oxidation state. Some oxides exhibit catalytic activity in redox reactions by exchanging oxygen with reactants. Recognizing these properties is vital for developing catalysts, sensors, and materials for catalysis, electronics, and energy conversion applications. The chemical properties of titanium dioxide (TiO_2) pertain to its reactions and behavior in various chemical processes. TiO_2 is well-known for its photochemical and catalytic properties. In photocatalysis, under light illumination, TiO_2 can generate electron-hole pairs that lead to redox reactions with surrounding molecules, promoting the degradation of pollutants. As a catalyst, TiO_2's surface can facilitate various reactions, including oxidation and reduction. TiO_2 also exhibits acid-base behavior due to its amphoteric nature, being able to act as both an acid and a base. These chemical properties make TiO_2 valuable in applications such as environmental remediation, solar energy conversion, and heterogeneous catalysis. Different transition metal oxides exhibit varied chemical properties based on factors like composition, crystal structure, and oxidation state of the metal. For instance, manganese oxide (MnO_2) is known for its redox behavior, often used as an oxidizing agent. Copper oxide (CuO) has semiconducting properties and participates in catalytic reactions, while iron oxide (Fe_2O_3) is involved in oxidation-reduction processes. Zinc oxide (ZnO) displays both amphoteric behavior and semiconducting characteristics. These properties are integral to applications such as catalysis, electronics, and energy storage, showcasing the diverse roles of transition metal oxides in various chemical contexts. The chemical stability of transition metal oxides is pivotal in assessing their utility. These oxides exhibit varying reactivity, oxidation resistance, and corrosion resistance levels, influenced by factors like crystal structure and environmental conditions. To ensure their efficacy in applications such as coatings and corrosion protection, understanding their stability is vital. Further research is needed to enhance the stability and durability of transition metal oxide-based materials. Their redox activity, catalytic potential, ion exchange properties, and chemical stability make them highly sought-after for diverse applications. The studies highlighted in this review underscore the importance of understanding and manipulating these properties to develop enhanced materials. Ongoing research in this realm holds the promise of unlocking novel applications and advancing the materials science field [3].

2.3 Different Phases of Titanium Dioxide (TiO_2)

Titanium dioxide (TiO_2) exists in multiple phases, each with distinct structural and chemical properties. The three main phases are rutile, anatase, and brookite. Rutile is the most thermodynamically stable phase and exhibits good optical and electrical properties. Anatase possesses high photoactivity and is commonly used in photocatalysis. Brookite is less common and has unique crystallographic features. The phase of TiO_2 can significantly impact its properties and applications, making phase control crucial in various fields such as catalysis, electronics, and energy conversion [16].

i. Rutile: Rutile is the most thermodynamically stable phase of TiO_2. It has a tetragonal crystal structure and is known for its excellent optical and electrical properties. Due to its good refractive index and conductivity, Rutile TiO_2 is often used in optical coatings, high-quality pigments, and electronic devices. Some notable XRD peaks include (110), (101), (211) found at around 27.4°, 36.1° and 54.3° respectively (JCPDS Card no. 21-1276).

ii. Anatase: Anatase is another common phase of TiO_2. It has a different crystal structure, which results in higher photoactivity compared to rutile. This phase is extensively used in photocatalysis, where it can generate electron-hole pairs under light illumination and catalyze various chemical reactions. The increased surface area and reactivity of anatase make it suitable for applications like air and water purification. Some notable XRD peaks include (101), (004) and (200) found at around 25.3, 37.8 and 48.1° respectively (JCPDS Card no. 21-1272).

iii. Brookite: Brookite is the least common phase of TiO_2. It has an orthorhombic crystal structure and possesses unique properties compared to rutile and anatase. Brookite is often found as a minor phase in naturally occurring TiO_2 minerals. While it is less studied and less prevalent, it still plays a role in understanding the overall behavior of TiO_2. Some notable XRD peaks include (121), (131) and (230) found at around 27.6, 33.5 and 53.0° respectively (JCPDS Card no. 29-1360).

The choice of TiO_2 phase depends on the desired application. Rutile is favored for its stability and electrical properties, anatase excels in photocatalysis due to its high photoactivity, and brookite, while less explored, contributes to a comprehensive understanding of TiO_2's properties. Researchers often study methods to control the phase transformation of TiO_2 to tailor its properties for specific applications, further enhancing its versatility and utility in various fields.

2.3.1 Review of Different Synthesis Methods of TiO_2

TiO_2 itself was officially first named and created in a laboratory in the late 1800s. It wasn’t mass manufactured until the early 20th century, when it started to take over as a safer alternative to other white pigments. The element titanium and the compound TiO_2 are found around the world, linked to other elements such as iron, in several kinds of rock and mineral sands (including a component of some beach sands). Titanium most commonly occurs as the mineral ilmenite (a titanium-iron oxide mineral) and sometimes as the mineral rutile, a form of TiO_2. These inert molecular compounds must be separated through a chemical process to create pure TiO_2.

There are various synthesis methods to produce titanium dioxide (TiO_2) with different properties and applications. Some common synthesis methods include:

i. Sol-Gel Method: This involves the hydrolysis and condensation of precursor solutions to form a gel, which is then calcined to obtain TiO_2. The sol-gel process produces fine, spherical powders of uniform size and has been widely used to synthesize TiO_2 materials and normally proceeds via an acid-catalyzed step of titanium (IV) alkoxides.

ii. Hydrothermal Synthesis: TiO_2 is synthesized under high-pressure and high-temperature conditions using a hydrothermal reactor. This method can lead to the formation of specific crystal phases and controlled nanostructures. The first report of the hydrothermal growth of crystals was by a German geologist Karl Emil in 1845. The advantages of the hydrothermal method are that it is an easy method to obtain nanotube morphology, variation in the synthesis method can be implemented to enhance the properties of TiO_2 nanotubes, and it is a feasible method for different applications.

iii. Precipitation Method: It involves the precipitation of TiO_2 from a solution by adding a precipitating agent. The obtained precipitate is then washed, dried, and calcined.

iv. Solvothermal Method: Similar to hydrothermal synthesis, but performed at lower temperatures using organic solvents. It can yield unique morphologies and properties due to the different solvent properties.

v. Flame Synthesis: TiO_2 nanoparticles are produced by injecting precursor materials into a flame, where they react and form particles through rapid combustion.

vi. Spray Pyrolysis: Precursor solutions are sprayed into a high-temperature furnace, where they undergo pyrolysis and form TiO_2 particles. This method allows for large-scale production.

vii. Vapor Phase Synthesis: Involves chemical vapor deposition (CVD) or physical vapor deposition (PVD) methods to deposit TiO_2 thin films onto substrates.

viii. Template-Assisted Synthesis: Templates like polymers or micelles are used to guide the formation of TiO_2 nanoparticles with specific sizes and shapes.

ix. Electrochemical Synthesis: TiO_2 can be electrodeposited or electro-synthesized from precursor solutions using electrochemical methods.

x. Sono-chemical Method: The sono-chemical method has been applied to produce highly photoactive TiO_2 nanoparticles by the hydrolysis of titanium tetra-isopropoxide (TTIP) in pure water or an ethanol/water mixture under ultrasonic radiation.

xi. Microwave-assisted Method: Microwave radiations can also be applied to produce various TiO_2 nanomaterials. In industrial processing, this method has the advantage of rapid heat transfer and selective heating. This technique provides uniform distribution of energy within the sample, better reproducibility and excellent control of experimental parameters. The colloidal TiO_2 nanoparticles can be prepared in a short period (within 5–60 minutes) compared to several hours needed for the conventional methods of forced hydrolysis at high temperatures (~195 °C). TiO_2 nanotubes which are open-ended and multi-walled with diameters of 8–12 nm and lengths between 200 and 1000 nm were also prepared using this method. TiO_2 nanoparticles in the anatase phase were prepared by Baldassari et al. using microwave-assisted hydrolysis of titanium tetrachloride ($TiCl_4$) in a dilute acidic aqueous medium. They found out that the product almost completely crystallized in a short reaction time of 30 minute under microwave-hydrothermal conditions. The acid that they used was to obtain a pure anatase phase was H_2SO_4 since the sulfate prevented the crystallization of brookite.

Each synthesis method offers advantages and disadvantages in terms of control over particle size, morphology, and crystal phase, making them suitable for different applications such as photocatalysis, sensors, and electronics. The choice of method depends on the desired properties and applications of the TiO_2 material.

2.3.2 Properties of Titanium Dioxide (TiO_2)

i. Electrical Properties: The band gap of titanium dioxide (TiO_2) is approximately 3.2 to 3.4 eV The exact value can vary depending on the specific crystal structure and phase of TiO_2. The band gap is an important parameter that determines the energy required to promote an electron from the valence band to the conduction band, enabling it to conduct electricity or participate in optical transitions. This property makes TiO_2 a widely used material in applications such as photocatalysis, solar cells, and optoelectronic devices.

ii. Mechanical and Thermal Properties: Titanium dioxide (TiO_2) possesses a hardness of 6-7 on the Mohs scale and Young's modulus of 100-230 GPa, reflecting its mechanical durability and stiffness. Its thermal conductivity ranges from 6-10 W/(m·K), and its coefficient of thermal expansion is $7\text{-}9 \times 10^{-6}$ /°C. With a high melting point of 1,843 °C, TiO_2 finds applications in abrasives, ceramics, coatings, and environments with varying temperatures.

iii. Catalysis: The large surface area and diverse surface sites of TiO_2 nanoparticles offer active sites for catalysis, promoting interactions with reactants and facilitating reaction pathways. It is renowned for its photocatalytic activity, wherein it can initiate chemical reactions in the presence of light. When exposed to UV or visible light, TiO_2 generates electron-hole pairs that participate in redox reactions, breaking down organic pollutants, disinfecting water, and promoting self-cleaning surfaces. Furthermore, it is an effective oxidation and reduction catalyst. It can facilitate reactions that involve the transfer of electrons, making it useful in processes such as water oxidation, hydrogen generation, and organic compound oxidation.

iv. Semiconducting: The band gap allows TiO_2 to absorb photons in the ultraviolet (UV) and visible light spectrum, making it sensitive to a broad range of light wavelengths. When TiO_2 absorbs photons with energy greater than its band gap, electron-hole pairs are generated. These charge carriers contribute to the material's conductivity, leading to changes in electrical properties that can be detected and measured.

2.3.3 Application of Titanium Dioxide (TiO_2)

2.3.3.1 Energy storage

TiO_2 may not offer the highest energy density compared to some other materials; its safety, stability, and sustainable energy storage advantages make it a valuable contender for next-generation energy storage technologies [27,28].

i. Supercapacitors: TiO_2-based materials are investigated for supercapacitor electrodes due to their high surface area and capacitance. Nanoporous TiO_2 structures can store and release energy quickly, making them suitable for applications requiring rapid energy storage and release.

ii. Lithium-Ion Batteries: TiO_2 can be used as an anode material in lithium-ion batteries. While it has a lower energy density compared to traditional graphite anodes, TiO_2 offers improved safety, longer cycle life, and reduced risk of lithium dendrite formation.

iii. Sodium-Ion Batteries: TiO_2 has shown promise as an anode material for sodium-ion batteries. Its ability to intercalate sodium ions during charging and discharging cycles contributes to energy storage in these batteries.

iv. Photocatalytic Hydrogen Generation: In combination with solar energy, TiO_2 can facilitate the photocatalytic splitting of water molecules to produce hydrogen gas, which can be used as a clean and renewable energy source.

v. Flexible and Wearable Energy Storage: The unique properties of TiO_2 can be harnessed to develop flexible and wearable energy storage devices, enhancing the integration of energy storage into various applications.

vi. Hybrid Energy Storage Systems: TiO_2 can be combined with other materials, such as carbon nanotubes or conductive polymers, to create hybrid systems that enhance energy storage capacity and performance.

vii. Fast Charging and Discharging: TiO_2's ability to quickly adsorb and release ions contributes to its potential in energy storage systems that require rapid charging and discharging, such as portable electronics.

2.3.3.2. Photodetectors

Titanium dioxide (TiO_2) is utilized as a photodetector due to its unique electronic properties that enable it to sense light and convert it into measurable signals. TiO_2's photocurrent generation, wide bandgap, and photoconductivity make it a suitable material for photodetectors, especially in the UV region. Its integration into various devices and technologies contributes to light detection and measurement in a range of applications [29,30].

i. Photocurrent Generation: TiO_2's semiconductor nature allows it to absorb photons and generate electron-hole pairs when exposed to light. This leads to the generation of a photocurrent, which is an electrical current produced in response to light.

ii. Wide Bandgap: TiO_2 has a relatively wide bandgap, making it sensitive to ultraviolet (UV) light. When UV light is absorbed by TiO_2, it can create electron-hole pairs that contribute to the photocurrent.

iii. Photoconductivity: The generation of electron-hole pairs increases the conductivity of TiO_2, which can be measured as a change in electrical resistance or current flow. This change is used to detect the presence and intensity of light.

iv. Quantum Efficiency: TiO_2's ability to efficiently convert absorbed photons into electron-hole pairs contributes to its high quantum efficiency, making it an effective photodetector material.

v. Applications: TiO_2-based photodetectors find applications in UV sensing, flame detection, environmental monitoring, and light detection in scientific instruments and optical communication systems.

vi. Thin Film Photodetectors: TiO_2 can be fabricated as thin films using techniques like sputtering or chemical vapor deposition. These thin films can be integrated into devices for light detection.

vii. Hybrid Structures: Hybrid structures combining TiO_2 with other materials can enhance photodetectors' sensitivity and spectral range. For instance, coupling TiO_2 with graphene or other nanoparticles can improve performance.

viii. Responsive to Environmental Changes: The photocurrent in TiO_2 photodetectors are influenced by factors like incident light intensity and wavelength, allowing for the detection of various light sources and variations in illumination.

ix. Photodetector Arrays: Arrays of TiO_2-based photodetectors can be organized to capture light from different directions or wavelengths, enabling applications in imaging and sensing.

2.3.3.3 Photovoltaics

TiO_2 is a fundamental component in dye-sensitized solar cells (DSSCs). It acts as an electron transport material, facilitating the movement of electrons between the dye molecules and the electrode. This interaction helps convert sunlight into electricity.

2.3.3.4 Thermoelectric Devices

TiO_2-based thermoelectric materials can convert heat into electricity or vice versa. Its semiconducting properties contribute to the Seebeck effect, generating a voltage difference in response to a temperature gradient.

2.3.3.5 Nanoelectronics

TiO_2's electrical and optical properties at the nanoscale, its potential in nanoelectronics applications grows, paving the way for advancements in computing, communication, sensing, and energy-efficient technologies. TiO_2 can be used as a semiconductor material in FETs. By controlling the gate voltage, the conductivity of TiO_2 can be modulated, allowing for the creation of transistors and logic circuits on a nanoscale. TiO_2-based resistive switching devices, also known as memristors, are explored for non-volatile memory applications. These devices store information by altering their resistance state, offering the potential for high-density and energy-efficient memory storage. TiO_2 quantum dots, which are nanometer-sized semiconductor particles, can be incorporated into nanoelectronic devices for various applications, including quantum dot lasers and single-electron transistors. TiO_2 nanoparticles can be utilized in light-emitting diodes (LEDs) to enhance their efficiency and performance. By optimizing the properties of TiO_2 nanoparticles, LEDs with improved color purity and luminous efficiency can be achieved [13,17,28].

2.3.3.6 Medical Industry

Traditional chemotherapy cancer treatment can have catastrophic effects on cells due to their toxic nature. As a result, the focus has been placed on how nanotechnology can be used to diagnose and treat cancer. Currently, the most significant challenge to overcome is reducing the side effects of nanotechnology-enabled drug systems.

TiO_2 has inhibitory activity due to photocatalytic action, which is mainly due to excessive production of highly reactive oxygen products (ROS) such as O_2, OH, and H_2O_2. Because of its chemical and mechanical qualities, titanium is commonly used in dental implants. Long-term dental implant success hinges on infection control and the acquisition of new technology for implant placement in bone.

2.3.3.7 Photocatalysis

TiO_2 photocatalysis involves the generation of electron-hole pairs upon absorbing photons from light, primarily in the ultraviolet (UV) range. These charge carriers can react with water and oxygen to produce hydroxyl radicals (OH•), which are highly reactive species capable of breaking down organic pollutants into harmless byproducts [8].

2.3.3.8 Other applications

i. TiO_2 is used as an opacifying agent in ceramics, providing white color and opacity to ceramic products.

ii. Adding TiO_2 to glass can enhance its UV-blocking capabilities, protecting interiors from harmful UV radiation.

iii. In cosmetics and sunscreens, TiO_2 acts as a physical sunblock by absorbing and scattering UV radiation, protecting against skin damage from sun exposure. TiO_2's UV-blocking properties make it a common ingredient in sunscreens, helping to prevent skin damage and sunburn.

iv. Coatings and Paints: TiO_2 is added to coatings and paints for its ability to absorb and scatter UV radiation, protecting underlying surfaces from damage caused by sun exposure. The high refractive index makes it useful in creating reflective coatings for glass and metals. They also exhibit anti-microbial properties, which are advantageous in environments requiring reduced microbial growth.

2.3.4 Application of Titanium Dioxide (TiO_2) in Photocatalysis

Titanium dioxide (TiO_2) is widely used in photocatalysis due to its remarkable ability to harness light energy and initiate chemical reactions. Some notable applications of TiO_2 in photocatalysis include:

i. Environmental Remediation: TiO_2 photocatalysts can break down organic pollutants, such as volatile organic compounds (VOCs) and dyes, in air and water under UV or visible light. This property is harnessed for cleaning polluted air and wastewater.

ii. Self-Cleaning Surfaces: TiO_2-coated surfaces, when exposed to sunlight, can decompose organic materials that settle on them, leading to "self-cleaning" effects. This is utilized in applications like self-cleaning glass and building materials.

iii. Water Treatment: TiO_2 photocatalysis helps in the disinfection and degradation of pathogens, bacteria, and organic contaminants in water, making it valuable for water purification systems.

iv. Hydrogen Production: By utilizing solar energy to split water molecules, TiO_2 photocatalysts can facilitate the production of hydrogen, which is a clean and renewable energy source.

v. Air Purification: TiO_2 photocatalysts can effectively remove harmful pollutants, odors, and even pathogens from indoor and outdoor air, contributing to improved air quality.

vi. Anti-Microbial Coatings: TiO_2-coated surfaces can exhibit anti-microbial properties by destroying bacteria, viruses, and fungi upon exposure to light.

vii. Textile Industry: Photocatalytic coatings can be applied to textiles to enhance their ability to break down organic stains and odors when exposed to sunlight.

viii. Photodegradation of Contaminants: TiO_2 photocatalysis can be used for the degradation of persistent organic pollutants and hazardous chemicals.

ix. Solar Energy Conversion: In dye-sensitized solar cells and other photovoltaic devices, TiO_2 nanoparticles help in converting sunlight into electrical energy.

TiO_2's photocatalytic properties stem from its ability to generate electron-hole pairs upon light absorption, which initiates redox reactions on its surface. The versatility of TiO_2 photocatalysis makes it an essential tool for addressing environmental, energy, and health-related challenges.

2.4 Conclusion

The analysis of existing literature has highlighted the various uses of TiO_2, underscoring its significance in fields such as photocatalysis, optoelectronics, gas sensing, and energy storage. Furthermore, the review investigates diverse methodologies for producing TiO_2, including solid-state synthesis, sol-gel techniques, hydrothermal synthesis, and chemical vapor deposition. These methods enable the creation of tailored TiO_2 structures with enhanced attributes tailored to specific purposes.

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CHAPTER 3

INSTRUMENTS
&
APPARATUS

3.1 General Description of Synthesis Methods of Nanomaterials

Nanomaterials have emerged as an exciting class of materials that are in high demand for a range of practical applications. Nanomaterials' physical and chemical properties depend upon their precise composition, shape, and size. The effects of nanomaterials on health and the environment also depend upon their size, shape, etc. The synthesis of nanomaterials is a multidisciplinary field that combines principles from chemistry, physics, materials science and engineering. The choice of synthesis method depends on the desired properties, scalability and applications of nanomaterials. Proper characterization and understanding of the synthesized materials are required to harness their potential and ensure their safe and effective use. The process of synthesis of nanomaterials can be broadly divided into Top-Down Approach and Bottom-Up Approach. The top-down process of synthesis mainly includes laser ablation, mechanical milling, thermal decomposition, sputtering, arc discharge which offer benefits like precise control over shape and size, integration into existing technologies, large-scale production, rapid prototyping etc. On the other hand, the bottom-up approach mainly involves chemical processes like sol-gel method, spinning method, chemical vapour deposition, physical vapour deposition, solvothermal and hydrothermal methods. They contribute to the construction of nanomaterials characterized by atomic precision and novel attributes, including self-assembly, controlled arrangement, customized functionalities within composite structures. This results in distinctive materials with the potential for application in diverse fields. To implement these techniques, we require the aid of various instrumental devices, outlined as follows:

3.1.1 Hydrothermal Synthesis Set-up

A hydrothermal setup is a laboratory apparatus used for performing hydrothermal synthesis, a technique in which materials are synthesized under high temperature and pressure conditions in an aqueous environment. This setup typically consists of several components designed to create the necessary conditions for controlled material formation (Figure 3.1).

Figure 3.1: Hydrothermal Setup

i. Autoclave Reactor: The core component of the setup is an autoclave reactor, often made of stainless steel or other high-strength materials. This reactor is designed to withstand high pressure and temperature. It contains precursor materials, which can be solid powders or solutions.

ii. Teflon Lining: Inside the autoclave, a Teflon lining is used to prevent the reagents from reacting with the metal walls of the autoclave. This lining ensures the purity of the synthesized material.

iii. Heating System: The autoclave is equipped with a heating system, which can be electric or gas-powered. This system raises the temperature inside the reactor to the desired level for the synthesis process.

iv. Pressure Control: The autoclave setup includes a pressure control mechanism to achieve the required pressure. This can involve using inert gases like nitrogen to pressurize the reactor.

v. Stirring Mechanism: Many hydrothermal reactions require consistent mixing to ensure uniform temperature distribution and even reagent interaction. A magnetic stirrer or mechanical stirrer is commonly used for this purpose.

vi. Cooling System: Once the hydrothermal synthesis is completed, a cooling system is employed to gradually bring down the temperature of the autoclave and its contents. This prevents abrupt changes that could affect the synthesized material.

vii. Pressure Release Valve: Safety is crucial in a hydrothermal setup. A pressure release valve is incorporated to safely release excess pressure in case it builds up beyond the set limits.

viii. Monitoring and Control Instruments: Various instruments such as temperature and pressure sensors are integrated into the setup to accurately monitor and control the reaction conditions.

The hydrothermal setup allows researchers to create a wide range of nanomaterials, particularly metal oxides, nanoparticles, nanowires, and other complex structures. By carefully controlling the temperature, pressure, and reaction time, researchers can precisely control the synthesized nanomaterials' properties and morphology. This method is widely used in materials science, chemistry, and nanotechnology for its ability to produce unique materials with tailored properties.

3.2 General Description of Major Synthetic Apparatus for Synthesis of Nanomaterials

3.2.1 Weighing balance

A device utilized to measure an object's weight or mass is a weighing machine. This tool is crucial in environments such as laboratories, commercial kitchens, and pharmacies, and it is offered in a range of sizes, each capable of handling varying weights Figure 3.2(a).

3.2.2 Magnetic Stirring

To agitate a liquid without magnetic properties inside a vessel, a magnetic stirrer employs a rotating magnetic field. This is achieved by positioning a magnet beneath the container, which generates the rotational field. As the magnet rotates, it generates a circular magnetic field that extends into the liquid Figure 3.2(b).

3.2.3 Sonicator

Sonication uses sound waves to agitate particles in a given solution. In addition, it converts an electrical signal into physical vibration that can break substances apart. Therefore, these disruptions can mix solutions, accelerating a solid's dissolution into a liquid Figure 3.2(c).

3.2.4 Hot Air Oven

A hot air oven is a lab device for drying, sterilizing, and heating materials. It circulates hot air within the chamber to evenly distribute heat. It's used in research, industry, and education, with a temp range of ambient to 250 °C or higher. Some have fans for even heating. The principle involves dry air sterilization through convection, conduction, and radiation. Heating elements produce heat transferred to chamber air, circulated by fans. Items in the oven contact with hot air, heat moves via conduction, reaching their core gradually Figure 3.2 (d).

Figure 3.2: (a) Weighing Machine (b) Magnetic Stirrer (c) Sonicator (d) Hot Air Oven (e) Centrifuge Machine (f) Placement of Centrifuge tubes inside the machine

3.2.5 Centrifuge

A laboratory centrifuge is a piece of laboratory equipment, driven by a motor, which spins liquid samples at high speed. There are various types of centrifuges, depending on the size and the sample capacity. Like all other centrifuges, laboratory centrifuges work by the sedimentation principle, where centripetal acceleration is used to separate substances of greater and lesser density. This is accomplished by rapidly spinning the fluid inside a container to separate liquids from solids or fluids with varying densities (such as cream from milk). Denser materials and particles travel outward in a radial direction as a result of their action. Less dense objects are also transported to the centre and dispersed at the same time. Due to the radial acceleration, denser particles sink to the bottom of sample tubes used in laboratory centrifuges while low-density materials ascend to the top. Using a centrifuge as a filter to remove pollutants can be highly successful Figure 3.2(e & f).

3.3 Characterization Tools

3.3.1 X-ray diffractometer (XRD)

X-ray diffraction (XRD) is a technique that utilizes X-rays to study the atomic and molecular structure of materials. By measuring the angles and intensities of diffracted X-rays, XRD provides information about the crystallography, composition, and lattice parameters of crystalline materials. This technique is widely used in materials science, geology, chemistry, and various fields to analyze the arrangement of atoms in solids. The theory behind XRD is a result of pioneering works of Bragg. The discovery showed the wave nature of X-rays and a new direction for investigation of structure of matter was explored. Solid matter can be classified as follows: Amorphous and Crystalline. Bragg's law (Figure 3.3) suggests that the crystal structure can be considered as an array of atom forming planes. The X-ray on striking an atom will scatter in the same direction. The scattered X-ray can interfere constructively if they are in phase or destructively if they are out of phase. The path difference between the two X-rays scattering from the two planes can be easily seen to be $2d\sin\theta$, where d = interplanar spacing, θ = incident angle. For the two waves to interfere constructively, they should satisfy, the following relation $2d\sin\theta = n\lambda$ (λ = wavelength of X-ray). Now, if we consider the XRD graph for a crystalline material, we will get same intensity peaks in some material and for an amorphous material, no peaks will throw but we get a bump. Using the JCPDS card, we can identify the material and by using Scherrer formula we can get size of the material from the XRD graph.

$$\mathbf{D = k\lambda/\beta\cos\theta}$$

where D = size of the particle

k = dimensionless shape factor

λ = wavelength of X-ray

β = line broadening at half of maximum intensity (FWHM)

θ = Bragg’s Angle

- Advantages: X-ray diffraction (XRD) is valuable for studying materials due to its non-destructive nature, precise crystal structure determination, phase identification, microstructural insights, quantitative analysis, and versatility across fields. It offers rapid results, requires minimal sample preparation, and complements other techniques effectively.
- Limitations: X-ray diffraction (XRD) has limitations, including its need for crystalline samples, surface sensitivity, single crystal requirements, potential sample damage, peak overlap in complex samples, and low sensitivity to certain elements like hydrogen. It also demands well-prepared samples, expert interpretation, and can be time-consuming. Instrument quality and cost are considerations, but despite these limitations, XRD remains a valuable technique for studying crystalline materials.

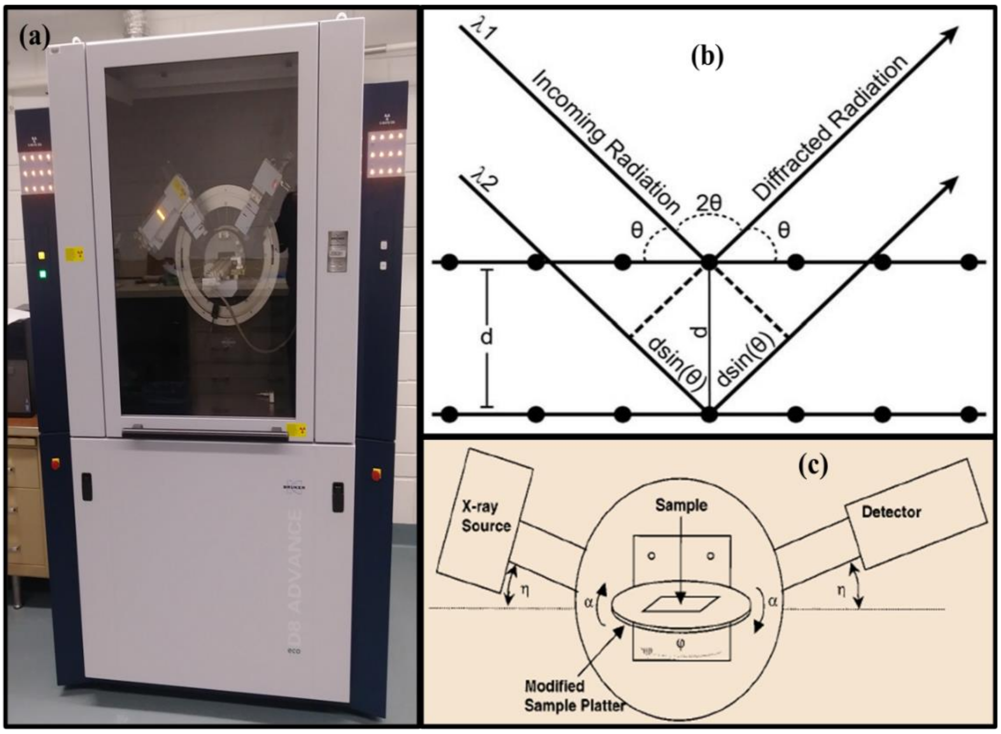

Figure 3.3: (a) Digital image of XRD machine, (b) Schematic of path difference between X-rays, (c) Schematic diagram for the scintag X11 X-ray diffractometer with an azimuthal (‘) spinner and the system can rotate the sample about the (‘) directions

3.3.2 Field Emission Scanning Electron Microscope (FESEM)

It is an advanced microscopy technique that provides high-resolution images of the surfaces of materials at nanoscale levels. It employs a focused beam of electrons to scan the surface of a specimen, producing detailed images with exceptional magnification and clarity. FESEM is widely used in various scientific fields, including materials science, nanotechnology, biology, and geology, to visualize and analyze the topography, morphology, and composition of a wide range of samples.

- Advantages: FESEM offers high-resolution imaging of nanoscale surfaces, versatile magnification, and clear three-dimensional visualization. It excels in surface morphology, provides compositional insights, and allows elemental analysis through EDS. FESEM is non-destructive, compatible with various samples, and suitable for real-time observations. It's multi-modal capability and broad applications in different fields enhance its analytical prowess.

- Limitations: FESEM has limitations, including the need for conductive samples, vacuum operation affecting volatile samples, potential sample damage, artifacts, and complexity. It may require specialized preparation for non-conductive or biological samples and involves expert training. Additionally, cost, resolution optimization, and challenges in observing certain dynamic processes are considerations.

3.3.3 High-resolution Transmission Electron Microscopy (HRTEM)

HRTEM is an advanced microscopy technique that uses a focused beam of electrons to create high-resolution images of the internal structures of thin specimens. It transmits electrons through the sample, producing detailed images that reveal the ultrafine details of materials at the nanometer scale. TEM is widely used in various scientific fields, including materials science, biology, and nanotechnology, to study samples' morphology, composition, crystallography, and defects.

- Advantages: HRTEM advantages include ultra-high resolution for nanoscale imaging, visualization of internal structures, crystallography insights, composition analysis, and direct imaging without staining. It offers dynamic process observation, 3D imaging, and quantitative measurements. TEM is versatile across materials, providing atomic-level insights and educational value for nanoscale research.

- Limitation: HRTEM limitations include challenging sample preparation, potential sample damage, vacuum operation restricting volatile samples, small sample size requirement, sensitivity-related, complexity, and potential image artifacts. Interpretation demands expertise, while cost and limited in-situ capabilities are considerations. Despite these limitations, TEM is a valuable nanoscale imaging and analysis tool.

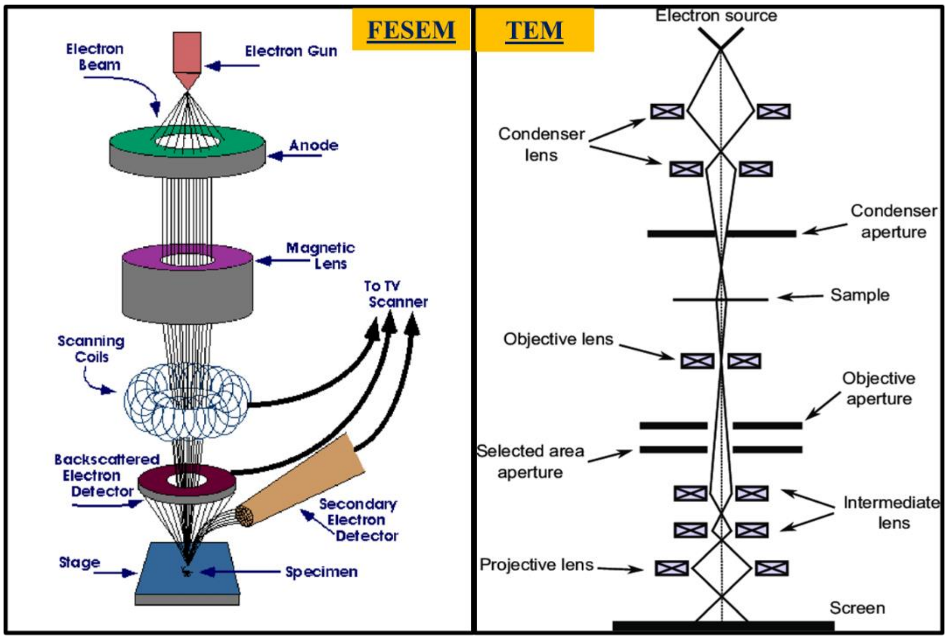

Figure 3.4: Schematic diagram of FESEM and TEM

**** Difference Between FESEM and TEM**

The major difference between Field-Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) lies in their imaging techniques and sample interactions (Figure 3.4).

i. Imaging Technique:

FESEM: Provides surface images by detecting secondary electrons emitted from the sample's surface. It offers detailed surface morphology and compositional information.

TEM: Provides internal structural images by transmitting electrons through the sample. It reveals ultrafine details of internal structures, such as cell organelles, crystal defects, and nanoparticles.

ii. Sample Interaction:

FESEM: It interacts with the sample's surface, making it suitable for imaging surface morphology and features.

TEM: It interacts with the entire thickness of the sample, allowing visualization of internal structures and providing information about materials' depth.

iii. Resolution:

FESEM: Offers high-resolution surface imaging in the range of nanometers.

TEM: Provides extremely high-resolution imaging at the atomic and nanometer scales, surpassing FESEM in terms of resolution.

iv. Sample Preparation:

FESEM: Sample preparation for FESEM involves coating non-conductive samples and optimizing surface flatness.

TEM: Requires ultra-thin sample sections, often involving complex procedures for creating thin electron-transparent sections.

v. Sample Types:

FESEM: FESEM is suitable for a wide range of samples, including conductive and non-conductive materials.

TEM: TEM applies to various materials, including biological specimens, nanoparticles, and crystalline materials.

vi. Depth Information:

FESEM: Primarily provides surface information, limiting depth perception.

TEM: Offers insight into three-dimensional structures, making it suitable for determining material thickness and layering.

vii. Sample Size:

FESEM: Can accommodate larger sample sizes than TEM.

TEM: Requires small, thin samples due to the electron transparency requirement.

viii. In-situ Capabilities:

FESEM: Offers limited in-situ observation capabilities compared to TEM.

TEM: Provides advanced in-situ observation of dynamic processes, enabling real-time studies.In summary, FESEM specializes in high-resolution surface imaging and composition analysis, while TEM excels in providing ultra-high-resolution internal structural insights. The choice between FESEM and TEM depends on the research goals, the type of information needed, and the sample characteristics.

3.3.4 Photoluminescence (PL)

Photoluminescence spectroscopy, often referred to as PL, is when light energy, or photons, stimulates the emission of a photon from any matter. It is a non-contact, non-destructive method of probing materials. In essence, light is directed onto a sample, where it is absorbed and where a process called photo-excitation can occur. The photo-excitation causes the material to jump to a higher electronic state, and will then release energy, (photons) as it relaxes and returns to back to a lower energy level. The emission of light or luminescence through this process is photoluminescence, PL (Figure 3.5).

Figure 3.5: Photoluminescence analysis carried out by Horiba Jobin Yvon Fluromax

- Advantages: Photoluminescence (PL) spectroscopy advantages include non-destructiveness, sensitivity to electronic transitions, quantitative analysis, broad material applicability, defect characterization, temperature dependence insights, and real-time monitoring capabilities. It offers spatial resolution, surface and interface analysis, and versatile measurement modes, making it valuable for semiconductor research, optoelectronics, photovoltaics, and nanomaterial studies.

- Limitations: Photoluminescence (PL) spectroscopy limitations include surface sensitivity, sample dependence, excitation energy influence, quantitative challenges.

3.3.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is a technique used to analyze the vibrational modes of molecules by measuring the absorption or emission of infrared light. It provides insights into the chemical composition and molecular structure of materials. By analyzing the characteristic absorption bands in the infrared spectrum, researchers can identify functional groups, determine molecular bonding, and gather information about sample properties. FTIR spectroscopy is widely used in fields such as chemistry, materials science, pharmaceuticals, and environmental analysis for qualitative and quantitative analysis of a variety of samples. Analysis using an FTIR proceeds as follows (Figure 3.6).

1. The source: IR energy is emitted from a glowing black-body source and the beam passes through an aperture, which controls the amount of energy.

2. The interferometer: The IR beam enters the interferometer where “spectral encoding” takes place as already described. The interferometer uses a reference laser for precise wavelength calibration.
3. The sample: The IR beam enters the sample compartment where it is transmitted through or reflected off the surface of the sample; specific frequencies of energy that are uniquely characteristic of the sample are absorbed by the sample.
4. The detector: The beam finally passes to the detector for final measurement.
5. The computer: The signal is digitized, the FFT calculation takes place and the final infrared spectrum is presented to the user.

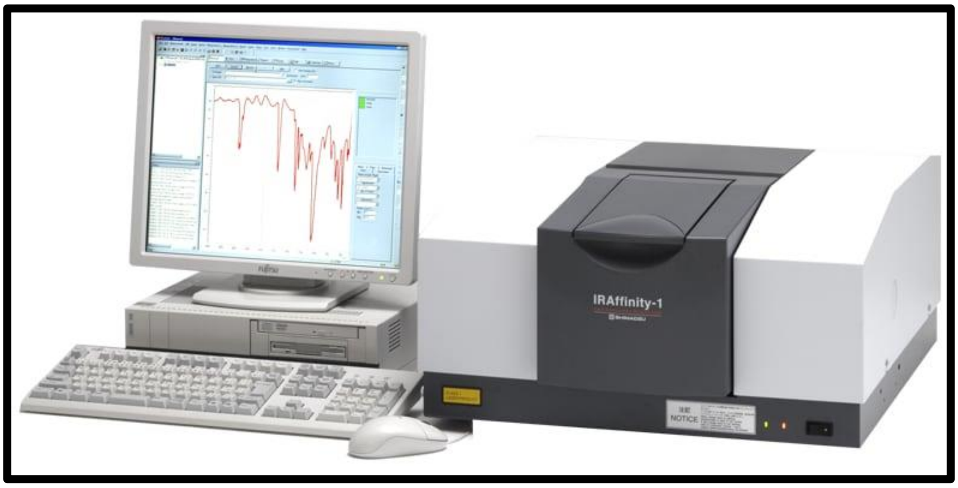

Figure 3.6: Digital image of FTIR Spectrometer

- Advantages: Advantages include chemical identification, compatibility with diverse sample types, non-destructiveness, quantitative analysis, rapid measurements, sensitivity to structural changes, and functional group information. It requires small sample sizes, provides information-rich spectra, and is suitable for in-situ and real-time analysis. FTIR is widely applicable across industries, requires no specialized training, and can be used in combination with other techniques for comprehensive analysis.

- Limitations: The sample must be transparent to infrared radiation, which limits the analysis of opaque or thick samples. FTIR may have limited sensitivity for detecting trace amounts of certain compounds. Hygroscopic samples can absorb moisture from environment leading to spectral changes. The low-frequency (far-IR) region can be challenging to analyze due to frequency limitations.

3.3.6 Ultraviolet-visible spectroscopy

Spectroscopy is the study of electromagnetic radiation's interaction with matter. In UV-VIS spectroscopy, the spectrum range is from UV to visible light range. The wavelength of electromagnetic radiation within this range is incident upon sample and the desired concentration of certain compounds present in the sample is calculated by this method. Working Principle: When light hits a molecule/compound/element, it excites the electrons which jump to a higher energy level indicating a certain amount of energy transfer. The light after passing through the sample a certain fraction is absorbed and a certain fraction is transmitted. From Beer-Lambert's Law, we get the relation between absorbance and concentration. Beer-Lambert law is a combination of two different laws: Beer's law and Lamber's law. The concentration can be calculated with this method with an unknown sample (Figure 3.7).

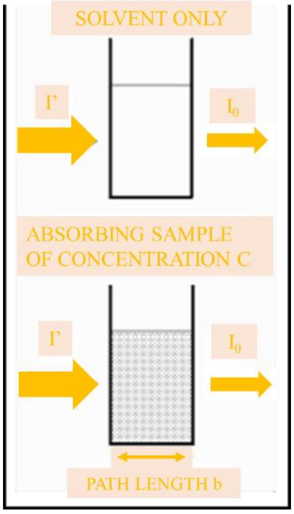

Figure 3.7: Diagram for calculation of concentration

i. I’ = Incident Light intensity,
ii. I_0 = Intensity of light after passing through control (i.e. reference say water),
iii. I = Intensity of light after passing through test sample,
iv. Transmittance = I/I_0,
v. Percentage Transmittance = T*100 (T%),
vi. Absorbance (A) = -log T,
vii. Transmittance (T) = $- 10^A$,

From Beer Lambert’s Law we get, $A = \in Cl$ where,

A = amount of light absorbed for a particular wavelength by the sample

$\in$ = molar extinction coefficient

C = concentration of the absorbing species

l = distance covered by the light through the solution

Absorption spectrum:

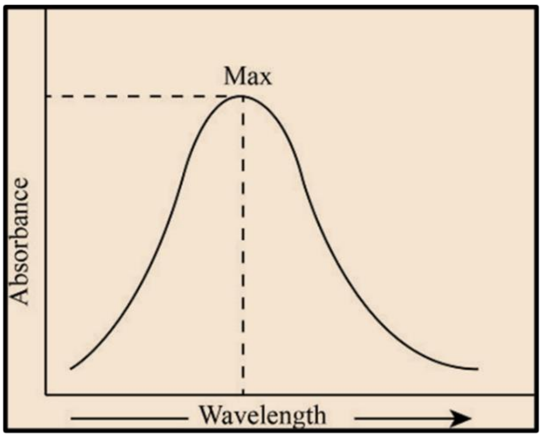

Figure 3.8: Plot of absorbance vs. wavelength

It is the plot of absorbance vs. wavelength of incident light (Figure 3.8). From this, we can get the wavelength at which we can have maximum absorbance. And concentration value for maximum absorbance can be calculated. Using this UV-VIS method, we can easily calculate the concentration of unknown samples and measure how much a chemical substance can absorb light.

3.3.6.1 Configuration of the Instrument

The transmittance or absorbance of a sample as a function of the wavelength of electromagnetic radiation is measured by a spectrophotometer. A spectrophotometer's essential elements are (Figure 3.9):

i. Source: The ideal light source would have low noise, long-term stability, and a constant intensity across all wavelengths. However, there isn't a source like that. UV-visible spectrophotometers frequently use two sources. A continuous UV spectrum is produced when deuterium or hydrogen is electrically excited under low pressure. The mechanism entails the production of an excited molecular species, which disintegrates to produce two atomic species, an ultraviolet photon, and other by-products. You can represent this as follows:

$D_2 + \text{electrical energy} \rightarrow D_2^* \rightarrow D' + D'' + hv$

Radiation from deuterium lamps is visible in the 160–375 nm range. These lamps must have quartz cuvettes and windows since glass absorbs light with wavelengths shorter than 350 nm. As a Visible source of light tungsten filament lamp is commonly used. This type of lamp is employed in the wavelength range of 350-2500 nm.

ii. Monochromator: All monochromators have specific parts, including an exit slit, collimating mirrors, focusing mirrors, a dispersing device (often a prism or grating), and an input slit. Through the entrance slit, multi-wavelength polychromatic light enters the monochromator. After collimating, the beam strikes the dispersing component at an angle. The grating or prism divides the beam's wavelengths into their components. Only radiation of a specific wavelength exits the monochromator through the exit slit when the dispersing element or the exit slit is moved.

iii. Sample Container: The cuvettes used to hold the reference solution and sample solution must be transparent to the radiation that will flow through them. For UV spectroscopy, quartz or fused silicacuvettes are necessary.

iv. Detector: A detector creates an electrical signal from a light signal. Commonly employed in UV-VIS spectroscopy as a detector is the photomultiplier tube. The device comprises a photo-emissive cathode, numerous dynodes, and an anode. A photo-emissive cathode produces electrons when photons of radiation strike it. A multichannel photon detector is a linear photodiode array, which is another type of detector. These detectors can concurrently measure every component of a scattered radiation beam. Photodiode arrays are intricate gadgets with exceptional durability due to their solid-state construction.

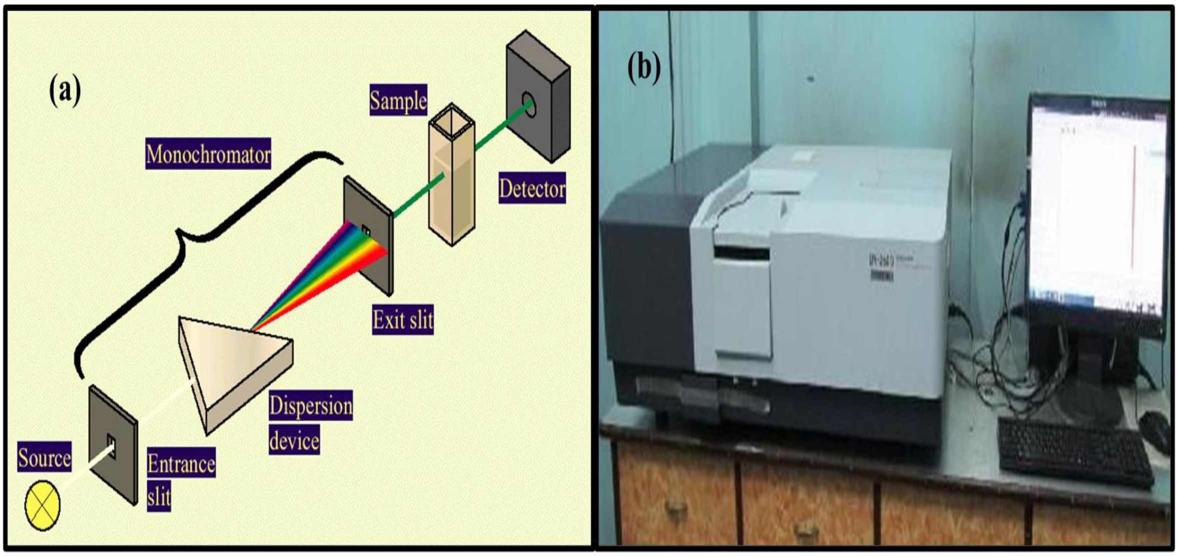

Figure 3.9: (a) Experimental setup and (b) digital image of UV-Vis Spectrometer

3.3.7 Electrochemical Analysis

The Mott-Schottky process, named after Sir Nevill Mott and Walter Schottky, is a phenomenon related to the behavior of semiconductor-electrolyte interfaces. It describes the relationship between the capacitance of the semiconductor-electrolyte system and the applied voltage. In this process, when a voltage is applied to a semiconductor-electrolyte interface, it results in the formation of a space charge region within the semiconductor. This space charge region can act as a capacitor and its capacitance changes with the applied voltage. The Mott-

Schottky equation is a mathematical expression that describes this relationship and is often used to analyze semiconductor-electrolyte interfaces. It is particularly useful in characterizing the doping levels and flat band potentials of semiconductors and can provide insights into the electrical properties of these interfaces.

3.4 Photocatalytic Measurements

The photocatalytic performance of the synthesized materials was assessed under ambient conditions at a pH of 7. To maintain a consistent temperature in the catalytic reactor, a double-walled glass beaker was employed, with cold water flowing between the two walls. To evaluate the photocatalytic efficiency, 30 mg of the catalyst was mixed with a 10^{-5} M RhB dye solution (40 mL). The catalyst-dye mixture was vigorously stirred in the dark for 1 hour to ensure proper adsorption-desorption equilibrium. Subsequently, the system was exposed to a 400 W high-pressure mercury lamp (Phillips-HPL-N G/74/2, MBF-400W, 200-250V), covering the range from 365 to 679 nm as the visible light source. A UV cut-off filter ($\lambda >$ 400 nm) was used to eliminate UV emission. At specific time intervals, 3 mL of the reaction solution was withdrawn, centrifuged to remove the catalyst, and the RhB dye concentration was analyzed using a UV-Vis absorption spectrophotometer. The degradation efficiency (η) of the prepared samples can be calculated from the plot of C_t/C_0 versus time (t) using the equation:

$$\boldsymbol{\eta = (C_0 - C_t)/C_0 \times 100\%}$$

where C_0 represents the initial concentration of RhB dye and C_t represents the concentration at time t.

CHAPTER 4

Kinetic Rate Constant Evaluation of Dye Degradation under UV Light Assisted Water Remediation in a Catalytic Reactor Using TiO_2 Nanoparticles

Abstract

In this study, we successfully created highly crystalline Titanium Dioxide (TiO_2) samples prepared by three distinct synthesis methods. We thoroughly examined these TiO_2 samples using advanced techniques to gain insights into phase formation, chemical bonds, composition, morphology, and various properties. We also conducted experiments by altering synthesis conditions, such as temperature and duration, to observe how they influenced phase formation, morphology, and the material's catalytic activity. These samples demonstrated effective degradation of the toxic Rhodamine B dye when exposed to both visible and UV light. Additionally, we proposed a detailed mechanism for this photocatalytic activity through extensive first-principles calculations.

4.1 Introduction

Modern water purification is essential due to the pollution from textile and chemical industries, releasing around one thousand tons of toxic, non-degradable dyes yearly. These dyes, especially Rhodamine B (RhB) and Methyl Orange (MO) are challenging to remove. Developing cost-effective photocatalytic materials is crucial to break down these dyes and conserve the environment. Titanium oxide (TiO_2) is a favoured choice for its photochemical reactivity and low environmental impact. Photocatalysis represents an environmentally friendly approach to address pollution issues using solar energy. This method has primarily been applied to break down volatile organic compounds (VOCs) and clean up wastewater. Over the last thirty years, titanium dioxide (TiO_2) has emerged as a highly researched metal oxide due to its exceptional photocatalytic capabilities and its ability to induce hydrophilicity through photoactivation. When the inner surface of transparent containers, such as glass or plastic bottles, is coated with a layer of extremely fine titanium dioxide particles, the effectiveness of light is increased. This leads to faster destruction of organic molecules and microorganisms because the presence of water generates highly reactive hydroxyl free radicals (•OH). These hydroxyl free radicals are extremely potent oxidizing agents, targeting the structure of cell membranes and breaking down organic compounds. Consequently, microorganisms are eliminated. Titanium dioxide is the most frequently used photocatalyst for water and air purification. It is relatively cheap and abundant. Titanium dioxide possesses several notable characteristics, such as it is not harmful, does not dissolve in water, and demonstrates resistance to a wide range of chemicals, including acids, bases, and solvents. Its primary advantage as a photocatalyst stems from its semiconductor properties. In specific conditions, semiconductors can enable the movement of electrons. To facilitate this, the semiconductor must receive the appropriate amount of energy. In the case of titanium dioxide, the required energy has a wavelength of approximately 400 nm, falling within the electromagnetic radiation spectrum at the intersection of visible and ultraviolet light. In semiconductors with band gaps equal to or less than 3 electron volts (eV), they can absorb visible light, elevating an electron from the valence band to the conduction band, a process referred to as excitation (Figure 4.1). As a result, the conduction band carries a negative charge due to the additional electron, while the valence band loses an electron, creating an electron-hole and consequently acquiring a positive charge. When this semiconductor is immersed in water, it can facilitate redox reactions. Regions with surplus electrons can promote reduction reactions, while electron holes can initiate oxidation processes.

4.2 Experimental Details

4.2.1 Materials

97% purity, Titanium Isopropoxide [Ti{$OCH(CH_3)_4$], Titanium (IV) Oxide, anatase [TiO_2] were purchased from Sigma Aldrich. 99% purity, 2-propanol or Isopropanol [C_3H_8O] was obtained from Merck Emplura. Deionized Water (18.3MΩ) was used for all synthesis purposes.

4.2.2 Preparation of TiO_2 Nanoparticles

The precursor, the reagents molar concentration, and the synthesis period are varied significantly in the current work. All of the reagents were of analytical quality and employed without further purification (Figure 4.1) [5].

- **Synthesis of TiO_2 Nanoparticles by Solvothermal Process (TiO_2 Solvothermal)**

Titanium Isopropoxide was used as the starting material to prepare TiO_2 Nanoparticles. In this technique, 5mL TTIP solution was slowly added dropwise into 10mL deionized water while it was being stirred magnetically. 60 minutes were spent stirring the solution at 40 degrees C. A white precipitate of TiO_2 nanoparticles could be observed at the bottom of the beaker after the solution had been thoroughly mixed. This precipitate was then separated by centrifugation at 4500 rpm and washed many a time alternatively with DI and Ethanol. Finally, the sample was kept at 80 degrees C in an oven for overnight drying and collected the next day after cooling down [5].

- **Synthesis of TiO_2 Nanoparticles by Hydrothermal Process (TiO_2 Hydrothermal)**

For the preparation of TiO_2 Nanoparticles hydrothermally, again TTIP solution was used as the precursor material. Keeping the ratios constant as in the previous process, 5mL TTIP was slowly added dropwise into 10mL deionized water while it was being stirred magnetically. The above solution was placed on the magnetic stirrer for 60 mins. The solution was transferred into a stainless-steel PTFE-lined autoclave of 25 mL and subsequently heated for 4h at 180 degrees C. After completion of the reaction, the whole system was naturally kept at ambient temperature for cooling down. The precipitate was collected and then separated by centrifugation at 4500 rpm and washed several times alternatively with DI and Ethanol. The final powdered products were obtained after overnight drying of the washed samples in an oven at 80 °C.

- **Synthesis of TiO_2 Nanoparticles by Hydrothermal Process followed by Annealing (TiO_2 Annealed:**In this procedure, TTIP and Isopropanol are applied as the precursor materials 10 mL Isopropanol was taken in a beaker and placed on a magnetic stirred. 5 mL TTIP was slowly dropwise added and the solution was kept under stirring conditions for 60 minutes until a homogenous mixture was formed. The resulting solution was transferred into a stainless-steel PTFE-lined autoclave of 25 mL and subsequently heated for 4 hours at 180 degrees C. After completion of the reaction, the whole system was naturally kept at ambient temperature for cooling down. The precipitate was collected and then separated by centrifugation at 4500 rpm and washed several times alternatively with DI and Ethanol. The final powdered product was obtained after overnight drying of the washed samples in an oven at 80 °C. The synthesized TiO_2 was annealed at 350 degrees C for 2 hours to obtain crystalline TiO_2 nanoparticles.

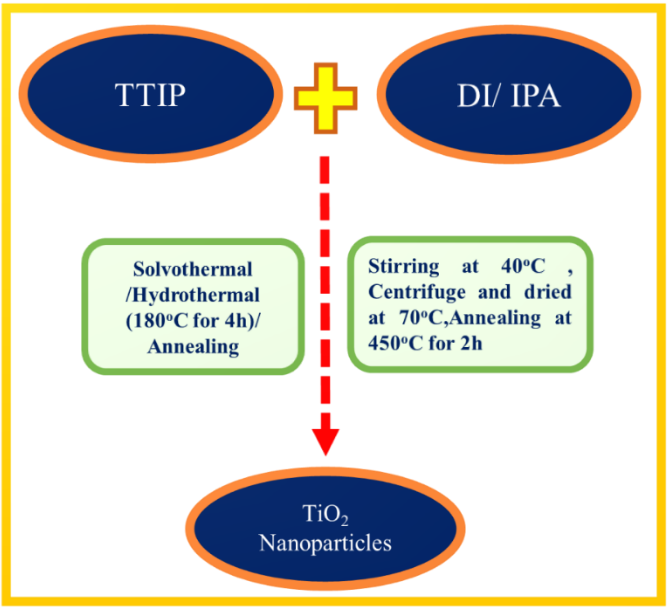

Figure 4.1: Block Diagram of all Synthesized Samples

4.2.3 Characterization of Sample

The as-prepared samples were subjected to several sophisticated techniques. The PXRD (powder X-ray diffraction) was recorded from D8 Bruker advanced X-ray diffractometer with a radiation source of Cu Kα (λ = 1.54 Å) and at a scanning rate of 2θ of 5 ○/min for proper identification of phases, crystallite size, and dimension of samples. The different chemical structures of the pure and composite samples were analyzed by XPS (X-ray photoelectron spectroscopy) using an Al Kα source (WF = 4.39 eV) of Thermo Fisher (ESCALAB Xi+). The morphology of the samples was perceived from FESEM (Field emission scanning electron microscopic) images operated at 10 kV accelerating voltage using Bruker Nano GmbH Berlin, Germany (Esprit 1.9), and the EDX (Energy dispersive X-ray spectra) measurements were used by FESEM instrument (Hitachi S-4800) with accelerating voltage at 15 kV. The HRTEM (High-resolution transmission electron microscopic) analysis was performed by JEOL-JEM 2100 PLUS. UV-Vis DRS (Diffuse reflectance spectra) measurements of the samples were carried out by UV–vis spectrophotometer (Shimadzu 3600 UV–Vis–NIR) using barium sulfate ($BaSO_4$) as standard reflective material. Knowledge about the nature of bonds and their formation was obtained from FTIR (Fourier transform infrared spectroscopy) analysis of the samples (Shimadzu FTIR-8400S). For the electrochemical impedance measurement, the working electrodes were prepared by mixing a 40 mg sample with 5 mg acetylene black and 5 mg PVDF along with a certain amount of NMP to form black slurry which was stirred continuously for 3 hours. It was then applied uniformly on previously cleaned Ni foam having an area of 1 cm^2. In the three-electrode electrochemical system, the Pt electrode served as a counter electrode and Ag/AgCl electrode served as the reference electrode. 0.2 M Na_2SO_4 solution was used as the electrolyte.

4.2.4 Activity of Photocatalysis

The photocatalytic dye degradation property of the fabricated TiO_2 sample was recorded by studying the degradation activity of 10^{-5} M concentration of aqueous solution of organic textile dye Rhodamine B (RhB) under ambient conditions in the presence of UV light irradiation and at a neutral pH value (pH 7). The photocatalytic experimental procedure of the as-synthesized sample was carried out in a customized quartz beaker. In this system, 30 mg of as-prepared catalyst was dispersed in 40 mL of aqueous dye (RhB) solution.Then the respective dye solution was continuously stirred for 1 hour to procure the adsorption-desorption equilibrium condition. Thereafter, the entire system was transferred under a UV light source. At certain periods of time duration, 4 mL of the aqueous solution was taken and immediately centrifuged to separate the catalyst material from the dye solution and the absorbance spectra of this dye solution were then evaluated from UV–vis spectrophotometer.

4.3 Results and Discussion

4.3.1 Structural Analysis

Powder X-ray Diffraction (PXRD)

As they were initially prepared, the samples underwent PXRD (Powder X-ray Diffraction) analysis. Powder X-ray diffraction patterns were obtained using a D8 Bruker advanced X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.54 angstrom). The data was collected at a scanning rate of 5 degrees per minute to accurately identify the sample. The peaks of pure TiO_2 at 25.3, 37.8, 48.0, 53.9 and 62.7 ° correspond to the (101), (004), (200), (105), (204) crystal planes of anatase TiO_2 (JCPDS 21-1272). The 2theta at peak 25.3° confirms the TiO_2 anatase structure. Strong diffraction peaks at 25° and 48° indicate TiO_2 in the anatase phase. The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite (Figure 4.2).

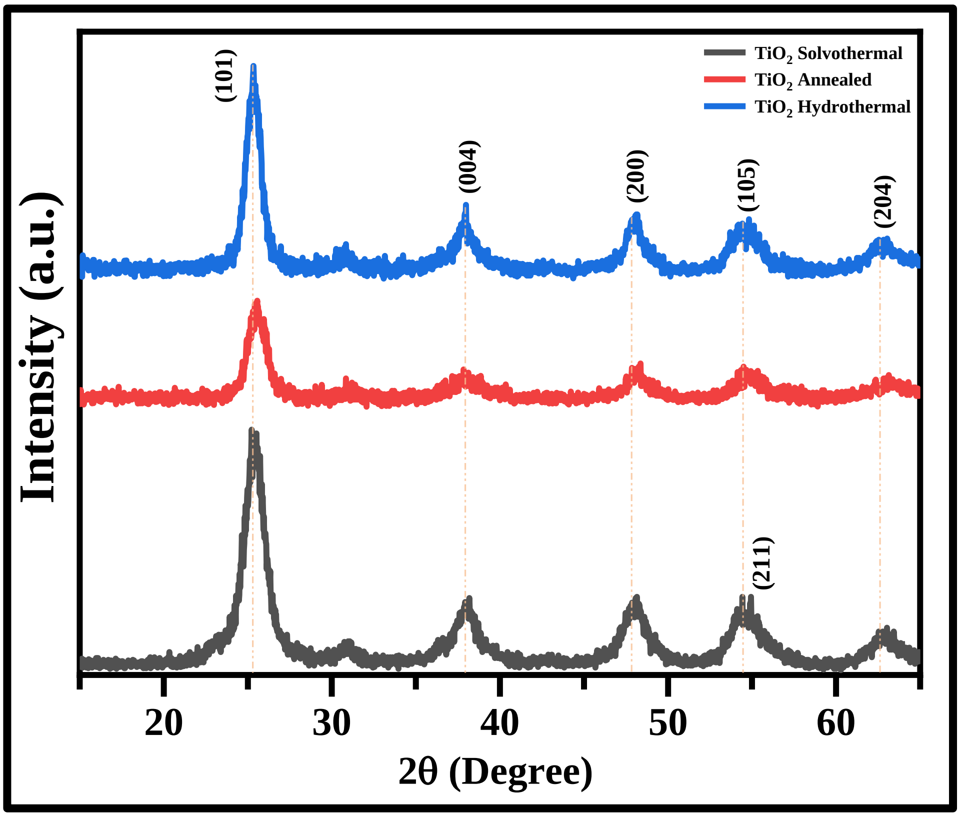

Figure 4.2: The XRD spectra of all synthesized samples

4.3.2 Morphological Analysis

(a) Field Emission Scanning Electron Microscopy (FESEM)

SEM has been employed for the characterization of the morphology of TiO_2 powder. Most of the TiO_2 powders are uniform with clear grain boundaries. The almost spherical-looking nanoparticles revealed agglomeration shown in Figure 4.3. The annealed TiO_2 sample has large grain size then other synthesized materials. The average lengths of the materials are 2-3 μm.

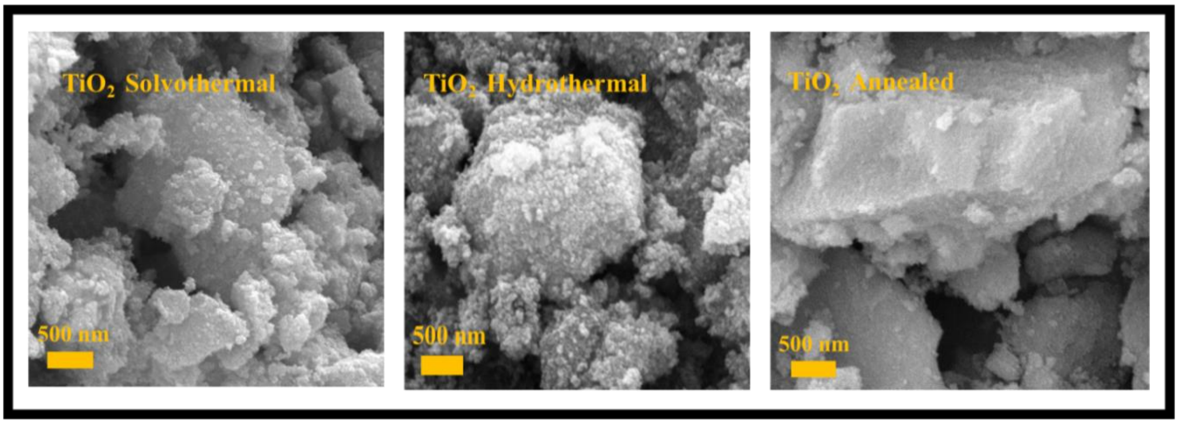

Figure 4.3: The FESEM of all synthesized samples

(b)Transmission Electron Microscopy (TEM)

Figure 4.4 shows that the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the as-prepared TiO$_2$ annealed sample. Figure 4.4 reveals the arrangement of various nanosheets in a solid cluster. This agrees with the respective FESEM image shown in Figure 4.3. The SAED pattern of the as-synthesized nanomaterial is shown, and which reveals the polycrystalline nature of the sample.

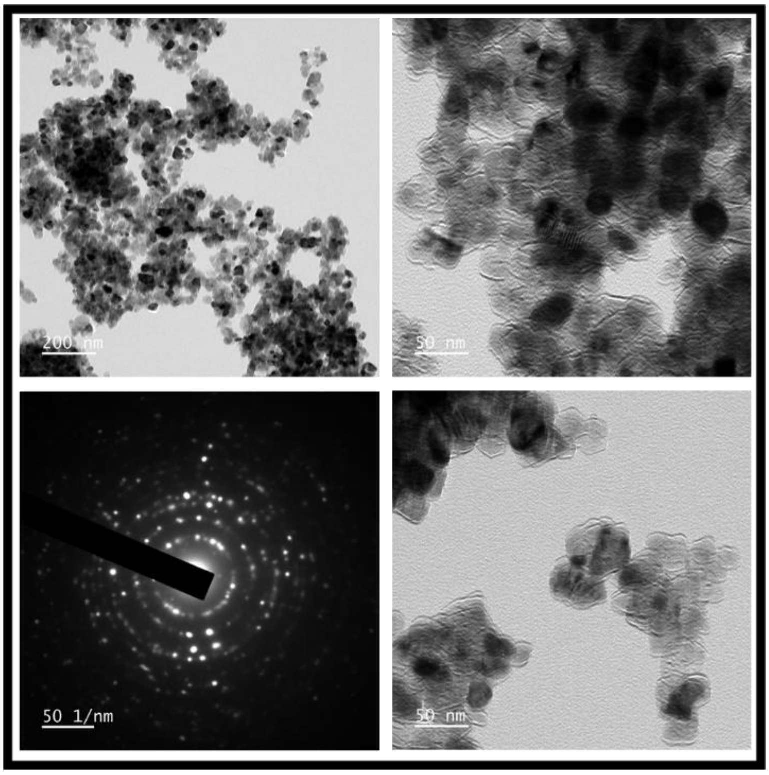

Figure 4.4: The TEM image of TiO$_2$ Synthesized by annealing method with their corresponding SAED image

4.3.3 Compositional Analysis

Fourier transforms infrared spectroscopy (FTIR) analysis

To gain a better understanding of how bonds are formed, FTIR spectroscopy of synthesized samples was conducted. FTIR spectra of TiO_2 solvothermal, TiO_2 hydrothermal and TiO_2 annealed are presented in Figure 4.5. FTIR is an effective method to analyze the composition of compounds or products. TiO_2 demonstrates bands in the region of 400–700 cm^{-1} due to Ti–O–Ti stretching vibrations while O–H stretching vibration occurs around 3400 cm^{-1}. Ti-O bending mode and deformative vibration of Ti-OH stretching mode may be observed at 447 and 1623.50 cm^{-1} respectively. Asymmetrical and symmetrical stretching vibrations of hydroxyl group (-OH) may be observed at 3402.98 cm^{-1}. The 1623.58 cm^{-1} band may be attributed to water adsorbed on the TiO_2 surface.

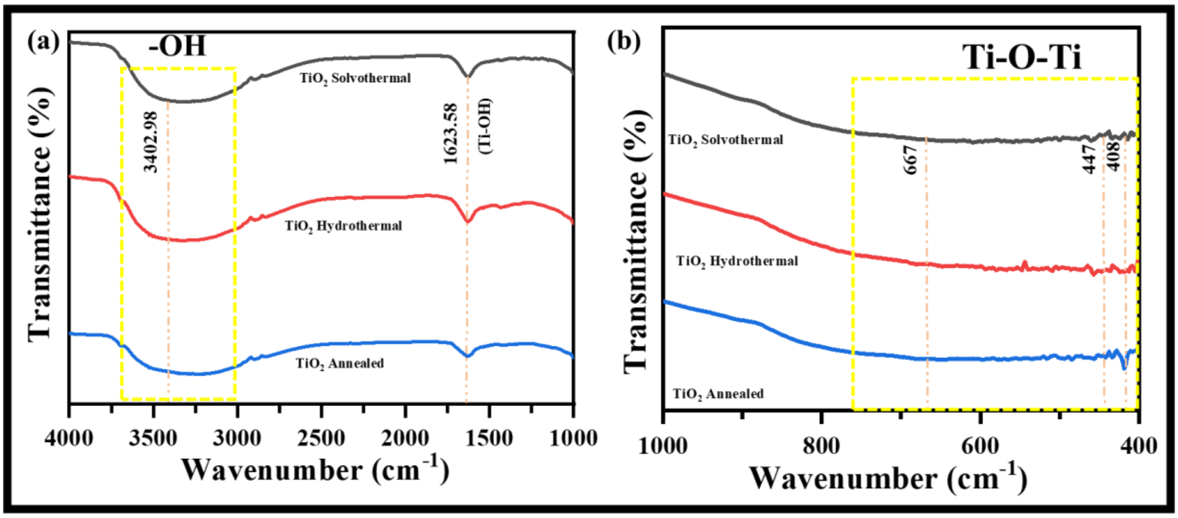

Figure 4.5: The FTIR spectra of all synthesized samples

4.3.4 Optical Analysis

(a) UV-Vis DRS

In diffuse reflectance spectroscopy (DRS) the plot between Reflectance (%) and wavelength (nm) is in Figure 4.6(a). The DRS analysis of TiO_2 solvothermal, TiO_2 hydrothermal and TiO_2 annealed is shown from which can infer that there is a fall in reflectance spectra at 397, 407 and 428 nm respectively. The indirect band gap of the as-synthesized samples has been calculated from DRS by employing the Kubelka-Munk method. The indirect band gaps of the three synthesized samples were calculated about at 3.12, 3.04 and 2.89 eV respectively demonstrated in Figure 4.6(b).

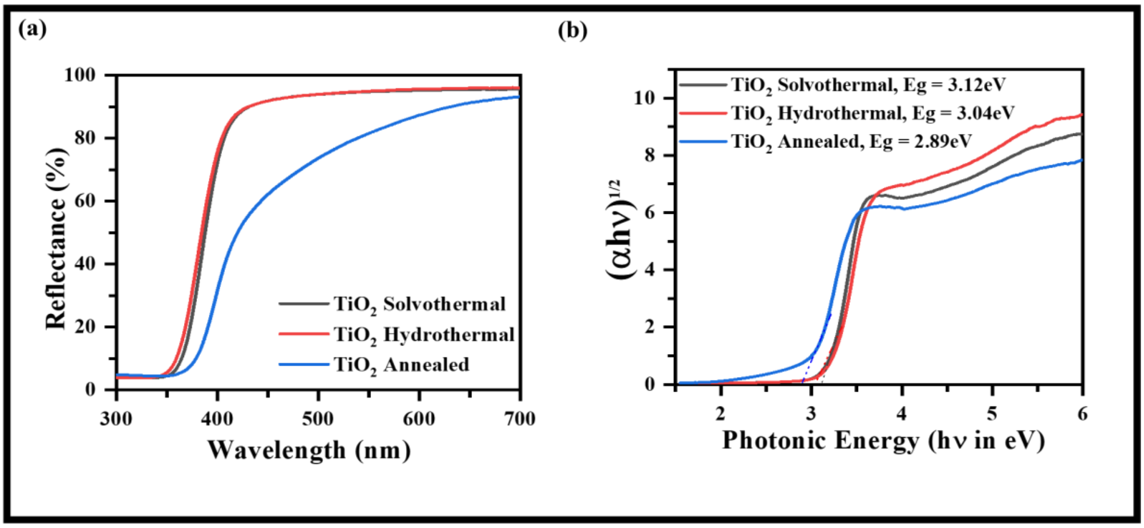

Figure 4.6: (a)The diffuse reflectance spectra of all synthesized samples and (b) the Kubelka-Munk plots for calculation of indirect band gaps

(b) Photoluminescence Analysis (PL)

The PL analysis spectra were employed to further investigate the transport and separation of the photogenerated carriers. Figure 4.7 shows PL spectra of TiO_2 solvothermal, TiO_2 hydrothermal and TiO_2 annealed.

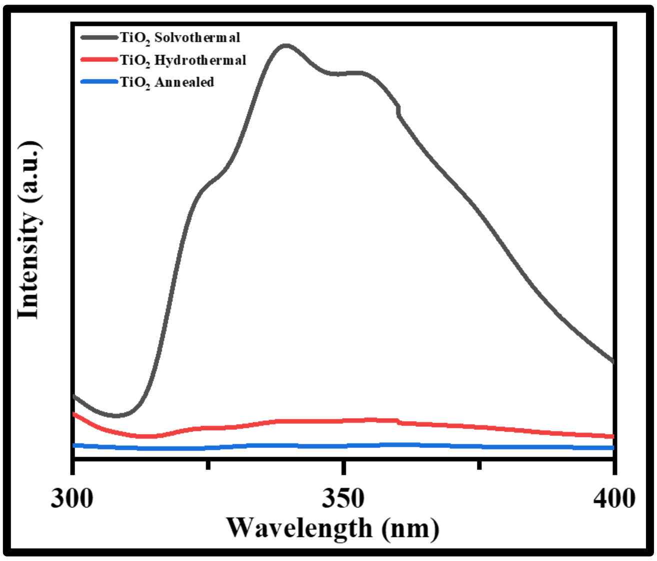

Figure 4.7: The PL Spectrum of all synthesized samples

From Figure 4.7 it can be noticed that the intensity emission peaks of these three synthesized TiO_2 samples are in decreasing order signifying the recombination rate of the photogenerated electron-hole pair is faster in the case of TiO_2 solvothermal than annealed TiO_2 which effectively blocks the recombination rate leading to the enhancement of its photocatalytic activity.

4.3.5 Photocatalytic Performance Analysis

The photodegradation of the active photocatalytic performances of all materials were studied by efficiently degrading RhB dye under UV light irradiation. RhB dye absorbance pattern is shown in Figure 4.8 after catalytic reactions in the synthesized samples. The catalytic performances of the materials completely degrade after about 120 minutes of UV light irradiation. Figure 4.9(a) shows the C/C_0 vs. irradiation time plot, and $\ln(C_0/C)$ vs. irradiation time plot shown in Figure 4.9(b) [8,9,10].

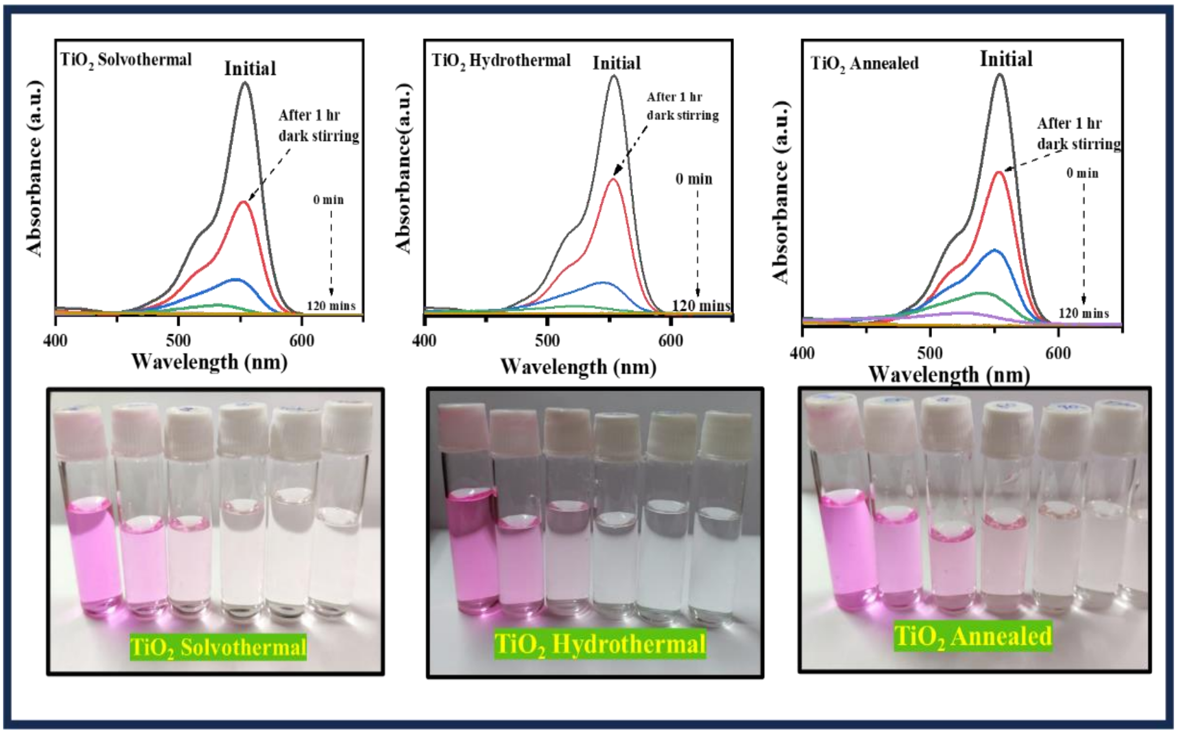

Figure 4.8: Absorbance Spectrum of all synthesized samples

This plots also known as the 1st order rate kinetics of the materials. The linear fitting of the plot of $\ln(C_0/C)$ vs. time (t) gave the rate constant values from the slope. The corresponding bar graph showing the rate constant values for the samples is presented in Figure 4.9(c).

$$\ln(C_0/C) = k_{app}*t$$

where,

C_0 = initial concentration of aqueous Rhodamine B dye,

C = final concentration of aqueous RhB dye and catalyst solution at time ‘t’,

k_{app} = apparent first-order kinetics rate constant, and

t = irritation time.

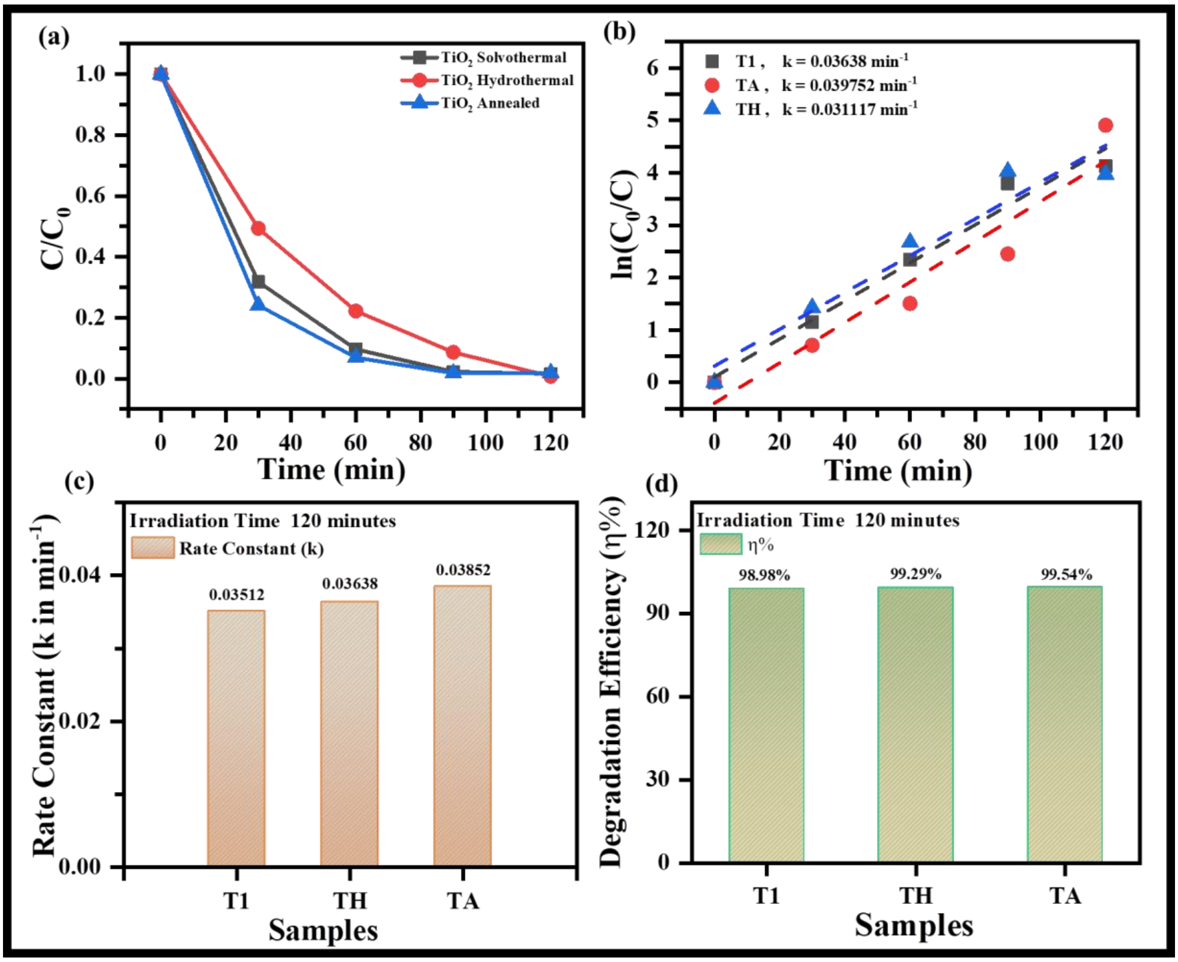

Figure 4.9: (a) C/C_0 vs. irradiation time plot and (b) $\ln(C_0/C)$ vs. irradiation time plot (c) the bar plots of 1st order rate constant and (d) the photodegradation efficiency for the materials

The photodegradation efficiency can be seen from the bar plot Figure 4.9(d), that annealed TiO_2 degrades the RhB dye at an efficiency of 99.54% which is higher than the photodegradation efficiency of TiO_2 solvothermal (98.98%) and TiO_2 hydrothermal (99.29%). The photodegradation efficiency was calculated by the equation:

$$\eta\% = (\eta_0 - \eta_t / \eta_0) * 100$$

where,

$\eta\%$ = photodegradation efficiency of the photocatalyst,

η_0 = initial absorbance of aqueous Rhodamine B dye solution, and

η_t = final absorbance of aqueous RhB dye and catalyst solution at the time 't.

4.3.5.1 Scavenger Test

In the photocatalytic dye degradation, the primary active radicals are hydroxyl radical, electrons, holes, and superoxide anions, whose active involvement in the redox reactions can very efficiently degrade the RhB dye under UV light irradiation. The TiO_2 Annealed catalyst was subjected to different scavengers of active radicals like p-benzoquinone ((BQ) 0.01 mol/L), Silver Nitrate (0.01mol/L), ethylene diamine tetra acetate disodium ((EDTA-2Na) 0.01 mol/L) and isopropyl alcohol ((IPA) 0.01 mol/L), to analyze the effect of these scavengers on the degradation efficiency of the catalyst. The corresponding degradation efficiency bar graphs are shown in Figure 4.10(a & b).

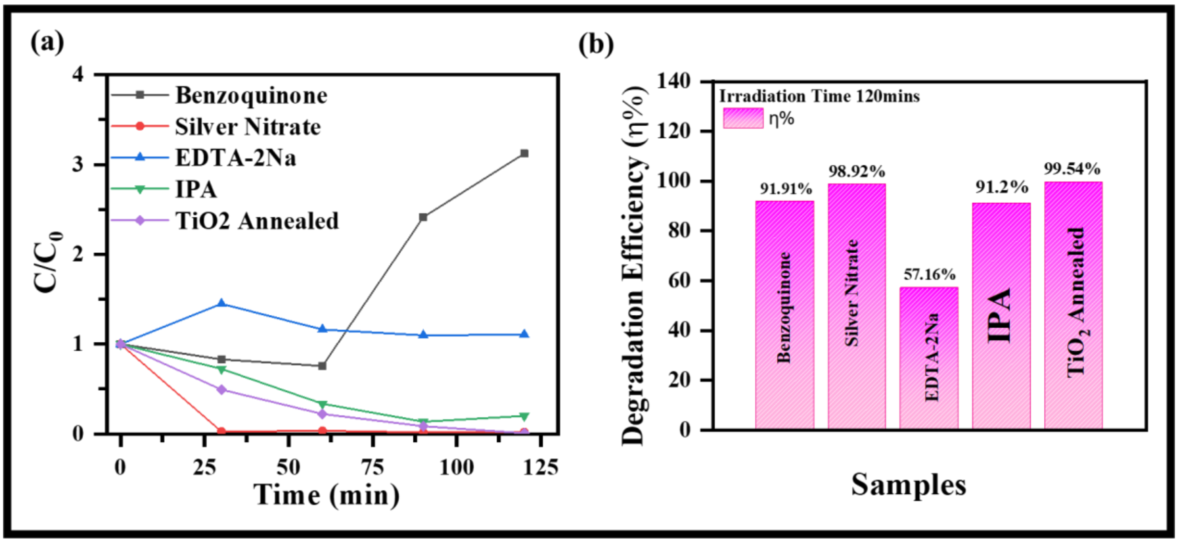

Figure 4.10: Scavenger Test for Active Radicals(a) C/C_0 vs Irradiation Time Plot (b) Bar Plot of Degradation Efficiency

It clearly shows that the degradation efficiency significantly changed with the addition of BQ which acted as the superoxide anion quencher, and also on the addition of EDTA-2Na which acted as hole scavenger; whereas on adding IPA, the scavenger for hydroxyl radicals and on adding Silver Nitrate which acted as electron scavenger the reaction rate did not change considerably. Thus, from these results, it can be concluded that the superoxide radical and the photogenerated holes are necessary radicals required for photocatalytic degradation.

4.3.5.2 Proposed Mechanism

From Figure 4.11 it can be observed that the irradiation of titanium dioxide with photons having energy equal to or greater than 3.06 eV results in the excitation of an electron from the valence band to the conduction band. This excitation results in the formation of an electron–hole pair. These photo-induced charges move to the surface of titanium dioxide and promote a series of redox reactions. The positive holes lead to the formation of vacancies in titanium dioxide as well as excite the reduced species. The photoinduced electrons produce $\bullet O_2^-$ free radicals. These free radicals are highly reactive and unstable species, so they react further. This whole process can be summarized as follows [19].

Production of positive hole and electron by excitation of TiO_2

$TiO_2 + h\nu \rightarrow h^+ (TiO_2) + e^- (TiO_2)$

Recombination of positive hole and electron

$h^+(TiO_2) + e^-(TiO_2) \rightarrow$ Heat

Production of OH radical by oxidation of water by reaction with positive hole

$h^+(TiO_2) + H_2O \rightarrow OH^\bullet$

Reduction of oxygen by reaction with electron

$e^- (TiO_2) + O_2 \rightarrow O_2^-$

Production of OH radical by reaction of superoxide anion with water

$O_2^- + H_2O \rightarrow OH^\bullet$

Reaction of OH radicals with reactants

Reactants + $OH^{\bullet} \rightarrow$ Products

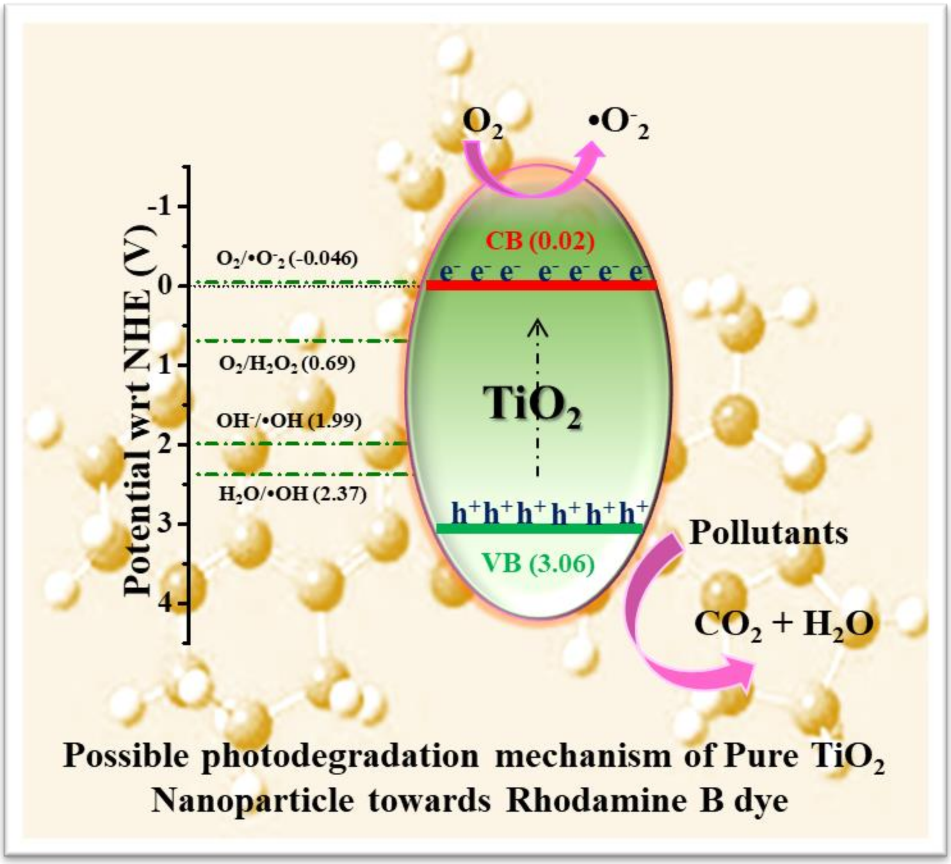

Figure 4.11: A Schematic Illustration of the photocatalysis mechanism of TiO_2 Annealed upon UV light exposure

4.4 Conclusion

In conclusion, we were able to successfully synthesize three different types of TiO_2 material by Solvothermal, Hydrothermal and Annealing Methods, and the various properties like identification of phases and chemical structures were efficiently confirmed by sophisticated techniques like XRD, FTIR, UV–Vis DRS, PL, FESEM, HRTEM, EDX. Amongst these TiO_2 Annealed was effectively accomplished in the photodegradation of harmful, organic pollutant Rhodamine B (RhB) dye within a short time period assisted by visible light irradiation, and the photodegradation efficiency of the material was found to be around 99.54% which supported the composite's highly active photocatalytic nature. A feasible mechanism was also suggested to comprehend the reaction events occurring during the catalytic degradation procedure by TiO_2. In this way, the catalyst is efficiently performed in wastewater treatment for the removal of toxic pollutants present in aqueous ecosystems.

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CHAPTER 5

Enhanced Degradation Performance of Rhodamine B Dye with TiO_2/gC_3N_4 Nanocomposite under UV Light Irradiation

Abstract

Photocatalytic degradation, a prominent technology holds immense promise. In this research, innovative nanocomposites comprising graphitic carbon nitride and titanium dioxide (g-C_3N_4/TiO_2) were synthesized through a straightforward hydrothermal approach followed by annealing. The assessment of photocatalytic performance was carried out through the degradation of Rhodamine B (RhB). The physicochemical attributes of the photocatalyst, specifically the interaction between g-C_3N_4 and TiO_2, were thoroughly explored using techniques such as XRD, SEM, TEM, FT-IR, PL, and UV-vis DRS. The observed enhancement in photocatalytic activity was attributed to the efficient interfacial charge transfer occurring between g-C_3N_4 and TiO_2. This study underscores the potential of hybridization in creating promising solar-driven materials for environmental remediation purposes.

5.1 Introduction

In recent decades, semiconductor-based photocatalysis has emerged as an eco-friendly technology for wastewater treatment due to its ability to efficiently degrade a wide spectrum of inorganic and organic contaminants. The effectiveness of photocatalysis hinges significantly on the generation and separation of photoinduced electron-hole pairs, which predominantly rely on the intrinsic properties of the photocatalytic materials. Extensive research has been conducted to advance photocatalyst materials, including metal oxides, sulfides, and nitrides. Among these, titanium dioxide (TiO_2) has risen to prominence as a promising photocatalyst with the potential for commercialization. TiO_2, categorized as an n-type semiconductor, has gained widespread adoption due to its notable attributes, including high efficiency, cost-effectiveness, non-toxicity, and long-term stability. However, the widespread application of TiO_2 (particularly the anatase form) has been hindered by its relatively large band gap energy of 3.2 eV and its propensity for rapid electron-hole pair recombination. Notably, these limitations have constrained its versatility. More recently, a novel metal-free photocatalyst, graphitic carbon nitride (g-C_3N_4), has emerged as a viable alternative. It boasts exceptional thermal and chemical stability and possesses a moderate band gap energy ranging from 2.7 to 2.8 eV, rendering it effective for harnessing solar energy. The delocalized conjugated structure of g-C_3N_4 results in a comparatively slower charge recombination rate and facilitates rapid separation of photoinduced charges during the electron transfer process. This makes g-C_3N_4 a compelling candidate as a sensitizer for the design of efficient visible-light-driven photocatalysts. However, the inherent limitations of pure g-C_3N_4 include low quantum efficiency and a high rate of recombination of photogenerated electron-hole pairs, which contribute to its relatively low photocatalytic efficiency. Furthermore, g-C_3N_4's photoreduction capability is significantly influenced by its high redox potential (-1.3 V vs. the normal hydrogen electrode at pH 7), in contrast to TiO_2's lower potential of -0.5 V. Additionally, g-C_3N_4's valence band (VB) energy level is situated at 1.4 V (vs. the normal hydrogen electrode at pH 7), compared to TiO_2's higher level of 2.7 V. Consequently, g-C_3N_4 lacks the necessary thermodynamic driving force (oxidative capability) for water oxidation and fails to produce sufficient hydroxyl radicals. Consequently, pristine g-C_3N_4 has found limited utility in the photodegradation of organic contaminants in water. To address these limitations, it is crucial to explore the integration of g-C_3N_4 with other materials. Such hybridization is expected to significantly enhance the photocatalyst's overall performance by improving electron-hole pair separation, thereby expanding its applicability in environmental remediation and wastewater treatment. It is expected that coupling TiO_2 with g-C_3N_4 would be able to significantly improve absorption, carriers' separation, and capability for photooxidation by the created interfaces. Liu *et al.* prepared g-C_3N_4/ZnO hybrid photocatalyst with a higher activity in Rhodamine B (RhB) degradation than either a single phase of ZnO or g-C_3N_4. Ge *et al.* synthesized PANI:g-C_3N_4 by ‘‘in situ’’ deposition of oxidative polymerization of aniline monomer in the presence of g-C_3N_4 powder. The PANI-g-C_3N_4 composites showed significantly enhanced photocatalytic activities in MB degradation. Ge *et al.* also prepared MoS_2-g-C_3N_4 via a facile impregnation method, and MoS_2-g-C_3N_4 samples demonstrated improved photocatalytic H_2 evolution under visible light irradiations. The 0.5% (by mass) MoS_2-g-C_3N_4 exhibited the highest H_2 evolution rate of 23.10 $umol \cdot h^{-1}$, which was about 11.3 times higher than that of pure g-C_3N_4. In this research, we combined hydrothermal-annealed TiO_2 with g-C_3N_4 and synthesized Exf g-C_3N_4. We then assessed these photocatalysts for their ability to degrade Rhodamine B (RhB) under UV light exposure. Notably, the photocatalytic activity observed in the degradation of Rhodamine B (RhB) was the most pronounced when TiO_2 was hybridized with Exf g-C_3N_4, outperforming all other photocatalysts when subjected to UV light irradiation. The study delves into the synergistic effects of these nanocomposites and the enhancements they bring to the photocatalytic efficiency during the RhB degradation process.

5.2 Experimental Details

5.2.1 Materials

97% purity, Titanium Isopropoxide [Ti{$OCH(CH_3)_4$], Titanium (IV) Oxide, anatase [TiO_2] were purchased from Sigma Aldrich. 99% purity, 2-propanol or Isopropanol [C_3H_8O], Urea [H_2NCONH_2] and Acetone obtained from Merck and Deionized Water (18.3 MΩ) were used for all synthesis purposes.

5.2.2 Preparation of Composite Nanoparticles

5.2.2.1 Synthesis of g-C_3N_4

The bulk g-C_3N_4 was synthesized by thermal treatment of urea in a muffle furnace at 600 ^oC in the air for 4 hours at 5 ^oC/min heating rate. The light-yellow colored sample was obtained. After that for exfoliation following steps were followed [10]:

- Acetone was poured in a round bottom flask and synthesized g-C_3N_4 was added in theround bottom flask.
- The above solution was sonicated for 16 hours for proper exfoliation of graphiticcarbon nitride.
- Then the above product was filtered with deionized water several times.
- Whitish-yellow precipitate was collected.
- Then it was dried at 60 °C overnight to obtain the product.

5.2.2.2 Synthesis of Exfoliated gC_3N_4

The above-prepared gC_3N_4 powder was dispersed in Isopropanol and then the mixture was ultrasonicated for approximately 12 – 16 hours until a desired level of exfoliation was observed. The mixture of gC_3N_4 and the solvent was prepared in a round-flask beaker. Ultrasonication generates high-frequency sound waves creating bubbles in the liquid, leading to the exfoliation of gC_3N_4. Finally, the mixture was centrifuged followed by overnight drying.

5.2.2.3 Synthesis of TiO_2/ gC_3N_4

In this procedure, TiO_2 prepared by Annealing Process is doped with gC_3N_4 in DI solution. The mixture was thoroughly sonicated and then transferred into a stainless-steel PTFE-lined autoclave and subsequently heated for 4 hours at 180 degrees C. After completion of the reaction, the whole system was naturally kept at ambient temperature for cooling down. The precipitate was collected and then separated by centrifugation at 4500 rpm and washed several times alternatively with DI water and Ethanol. The final powdered product was obtained after overnight drying of the washed samples in an oven at 80 °C. The synthesized TiO_2 was annealed at 450 degrees C for 2 hours to obtain crystalline composite nanoparticles.

5.2.2.4 Synthesis of TiO_2/ ExfgC_3N_4

The procedure used to create the composite containing Exfoliated gC_3N_4 was identical to the one employed for the composite comprising Annealed TiO_2 doped with gC_3N_4.

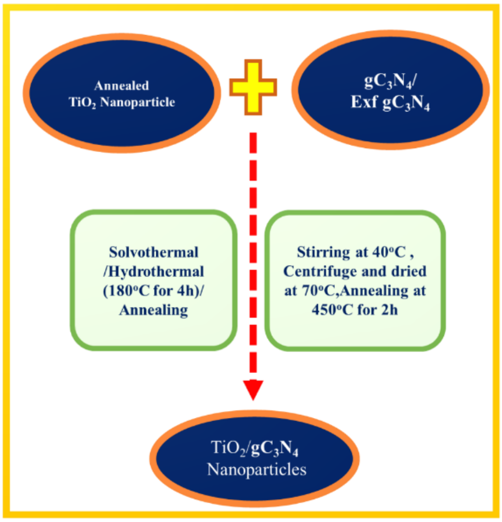

Figure 5.1: Block Diagram of Synthesis Process

5.2.3 Characterization of Sample

The as-prepared samples were subjected to several sophisticated techniques. The PXRD (powder X-ray diffraction) was recorded from D8 Bruker advanced X-ray diffractometer with a radiation source of Cu Kα (λ = 1.54 Å) and at a scanning rate of 2θ of 5 °/min for proper identification of phases, crystallite size, and dimension of samples. The different chemical structures of the pure and composite samples were analyzed by XPS (X-ray photoelectron spectroscopy) using an Al Kα source (WF = 4.39 eV) of Thermo Fisher (ESCALAB Xi+). The morphology of the samples was perceived from FESEM (Field emission scanning electron microscopic) images operated at 10 kV accelerating voltage using Bruker Nano GmbH Berlin, Germany (Esprit 1.9), and the EDX (Energy dispersive X-ray spectra) measurements were used by FESEM instrument (Hitachi S-4800) with accelerating voltage at 15 kV. The HRTEM (High-resolution transmission electron microscopic) analysis was performed by JEOL-JEM 2100 PLUS. DRS (Diffuse reflectance spectra) measurements of the samples were carried out by UV–vis spectrophotometer (Shimadzu 3600 UV–Vis–NIR) using barium sulfate ($BaSO_4$) as standard reflective material. Knowledge about the nature of bonds and their formation was obtained from FTIR (Fourier transform infrared spectroscopy) analysis of the samples (Shimadzu FTIR-8400S).

5.2.4 Activity of Photocatalysis

The photocatalytic dye degradation property of the fabricated TiO_2 sample was recorded by studying the degradation activity of 10^{-5} M concentration of aqueous solution of organic textile dye Rhodamine B under ambient conditions in the presence of UV light irradiation and at a neutral pH value (pH 7). The photocatalytic experimental procedure of the as-synthesized sample was carried out in a customized quartz beaker. In this system, 30 mg of as-prepared catalyst was dispersed in 40 mL of aqueous dye (RhB) solution. Then the respective dye solution was continuously stirred for 1 hour to procure the adsorption-desorption equilibrium condition. Thereafter, the entire system was transferred under a UV light source. At certain periods of time duration, 4 mL of the aqueous solution was taken and immediately centrifuged to separate the catalyst material from the dye solution and the absorbance spectra of this dye solution were then evaluated from UV–vis spectrophotometer.

5.3 Results and Discussion

5.3.1 Structural Analysis

Powder X-ray Diffraction (PXRD)

The samples, as they were initially prepared, underwent Powder X-ray Diffraction (PXRD) analysis. PXRD data was collected using a D8 Bruker advanced X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.54 angstrom), and the scan was conducted at a rate of 5 degrees per minute to accurately identify the sample [2].

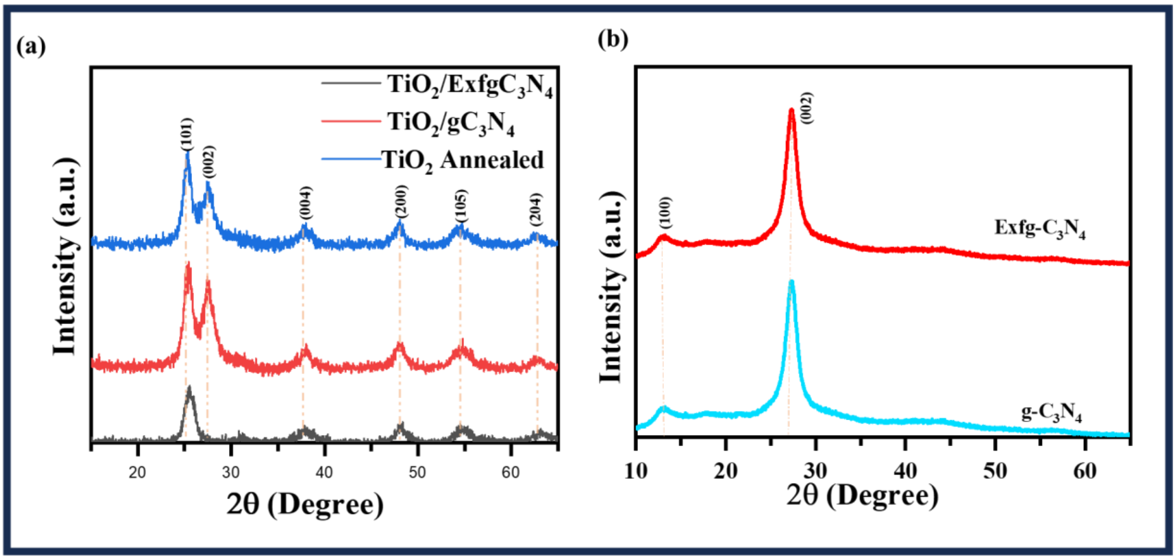

Figure 5.2: The XRD spectra of all synthesized samples

The XRD patterns of TiO_2 Annealed, g-C_3N_4, Exf g-C_3N_4, TiO_2/ g-C_3N_4 and TiO_2/Exf g-C_3N_4 composites are shown in Figure. Two peaks were found from the diffraction pattern of the pristine g-C_3N_4, indicating a typical graphitic structure without any impurity phase. The strong peak at 27.5º represents the stacking of the conjugated aromatic system, which is indexed to graphitic materials as the (002) crystal plane. The weak peak at 12.9º is indexed as

(100) associated with the interlayer. They also could be attributed to the in-plane ordering of the tri-s-triazine units and the interplanar stacking. The peaks of pure TiO_2 at 25.3, 37.8, 48.0, 53.9 and 62.7 ° correspond to the (101), (004), (200), (105) and (204) crystal planes of anatase TiO_2 (JCPDS 21-1272). The g-C_3N_4 characteristic peaks were found in all g-C_3N_4/TiO_2 photocatalysts. The positions and shapes of characteristic TiO_2 peaks of g-C_3N_4/TiO_2did not significantly change compared with pure TiO_2, indicating that coupling with g-C_3N_4 did not influence the lattice structure of TiO_2, which might be beneficial for the photocatalytic activity of hybrid photocatalyst.

5.3.2 Morphological Analysis

(a) Field Emission Scanning Electron Microscopy (FESEM)

The morphologies of pure TiO_2, pristine g-C_3N_4, exfoliated g-C_3N_4 and their composites were investigated by FESEM [4].

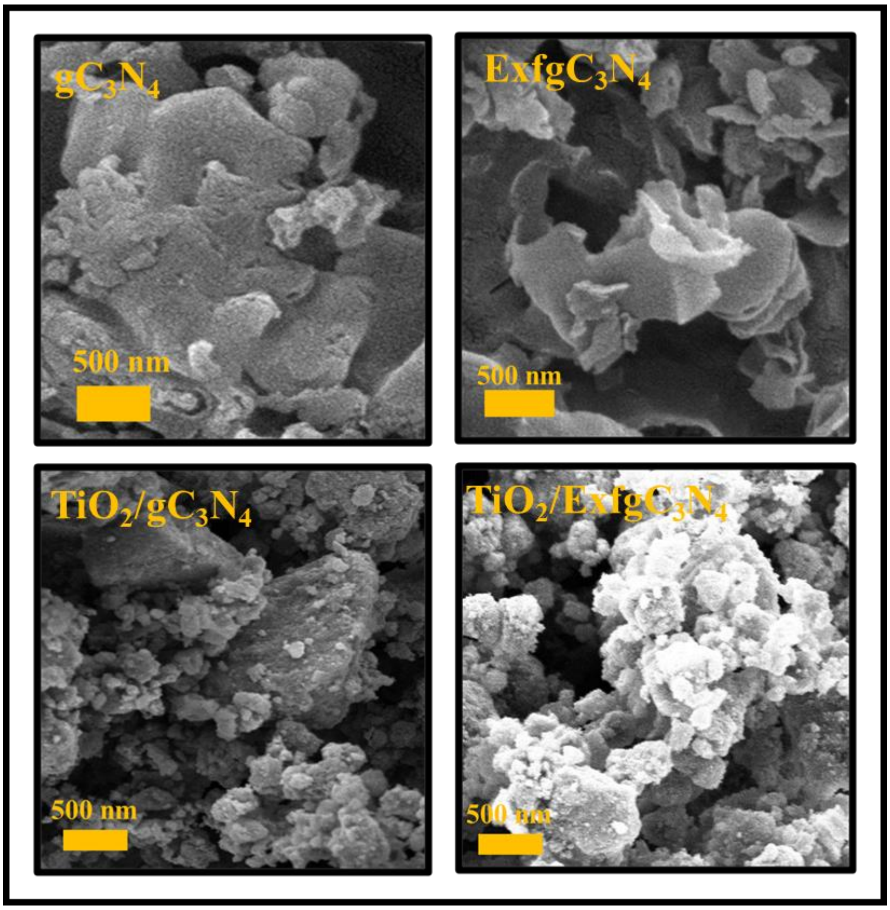

Figure 5.3: The FESEM of all synthesized samples

Pristine g-C_3N_4 presents a bulk structure with sheet-like sub-blocks. Pure TiO_2 presents spherical-like particles that agglomerate. It can be seen that the g-C_3N_4 Sheet dispersed on the surface of TiO_2. The still firm connection between TiO_2 and g-C_3N_4 displayed in the g-C_3N_4/TiO_2 composites indicated that there would be an intense interaction between g-C_3N_4 and TiO_2 rather than a simple physical adsorption. It also deduced that g-C_3N_4 could inhibit the aggregation of TiO_2 nanoparticles. The good dispersion can close interfacial connections between g-C_3N_4 and TiO_2 nanoparticles and improve the electron–hole separation efficiency.

(b) Transmission Electron Microscopy (TEM)

TEM images suggest TiO_2 nanoparticles embedded in the lamellar structure. TEM images demonstrated that there are close interfacial connections between g-C_3N_4 and TiO_2, which are beneficial for carrier transfer between g-C_3N_4 and TiO_2.

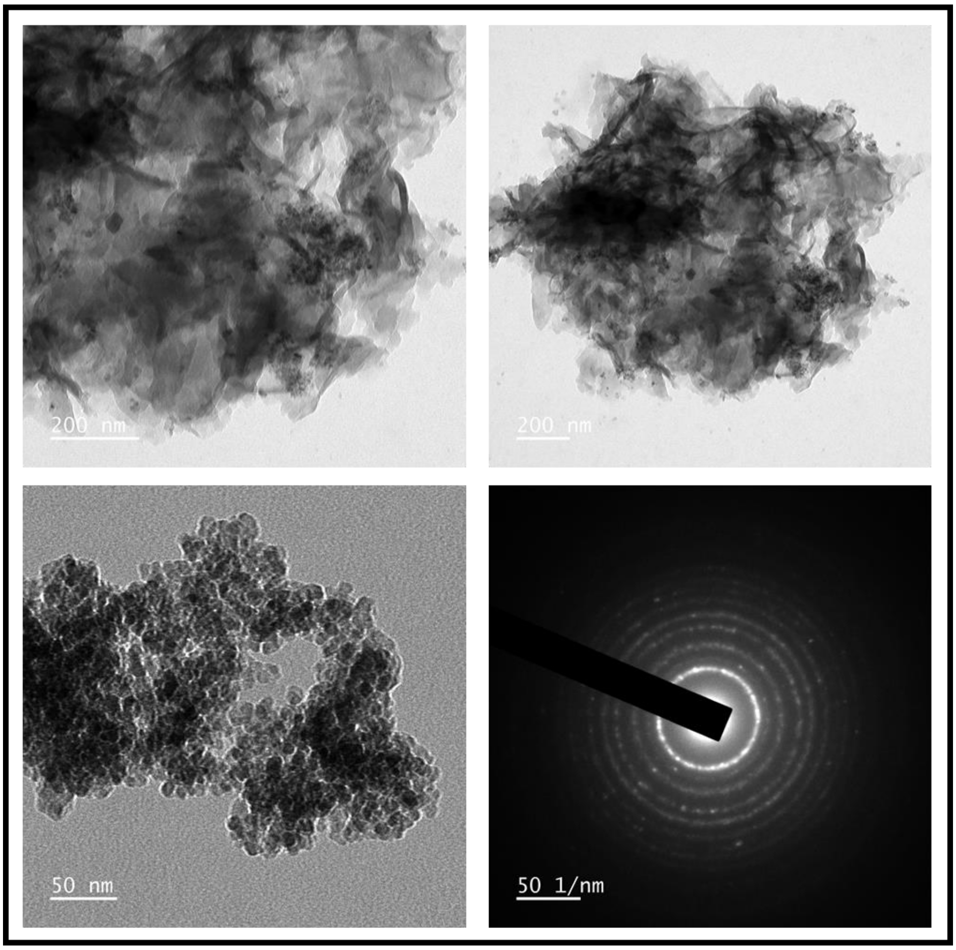

Figure 5.4: The TEM of TiO_2/ExfgC_3N_4 synthesized samples and corresponding SAED Image

The EDX spectrum of TiO_2/Exfg-C_3N_4 is provided in Figure 5.5. The spectrum shows the element species and contents, confirming the formation of heterojunction between g-C_3N_4 and TiO_2. The EDX study reveals the presence of carbon and nitrogen for g-C_3N_4 and titanium and oxygen for TiO_2 observed in the doped sample.

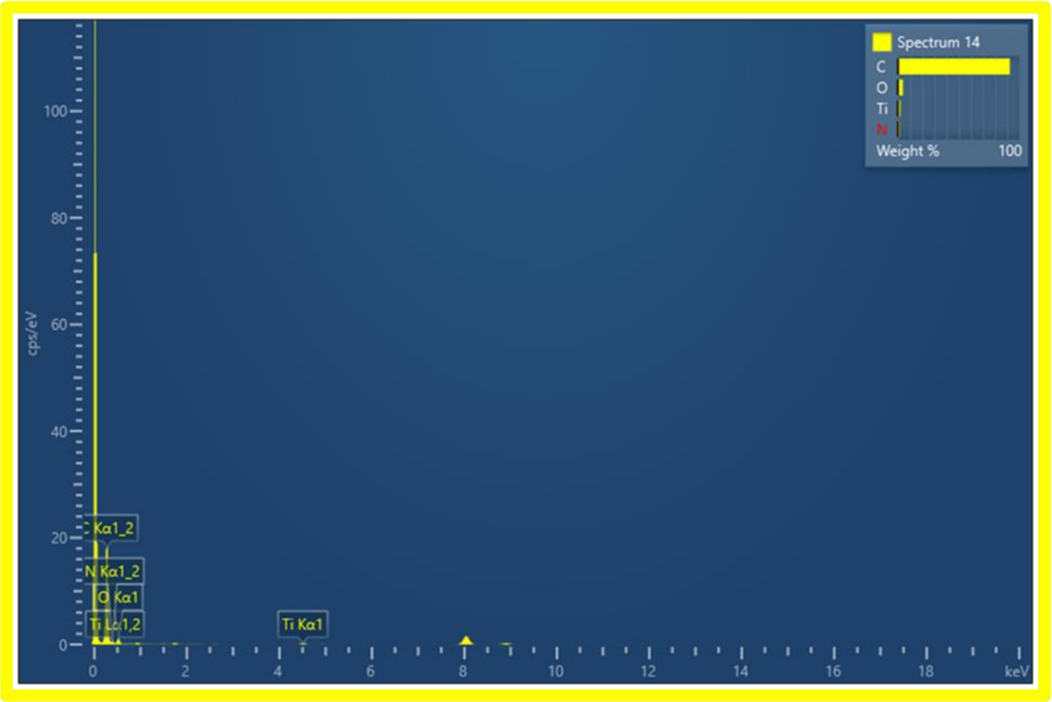

Figure 5.5: EDX Spectrum of TiO_2/Exfg-C_3N_4

5.3.3 Compositional Analysis

Fourier transform infrared spectroscopy (FTIR) analysis

Figure 5.6. shows the FT-IR spectra of g-C_3N_4, Exfg-C_3N_4, TiO_2/ g-C_3N_4 and TiO_2 / Exfg-C_3N_4 composites. FT-IR spectrum of pure and exfoliated g-C_3N_4 shows several strong bands in 1200-1650 cm^{-1}, corresponding to typical stretching modes of CN heterocycles. The peak at 1638 cm-1 is assigned to C-N stretching vibration mode, while those at 1247, 1332, 1417 and 1461 cm^{-1} are associated with C-N heterocycle stretching of g-C_3N_4. Among that the peaks at 1332 and 1247 cm-1 were assigned to stretching vibration of connected trigonal units of C–N(–C)–C or bridging C–NH–C (partial condensation). The band at 812 cm−1 corresponds to the breathing mode of the heptazine arrangement. A broad band in the range

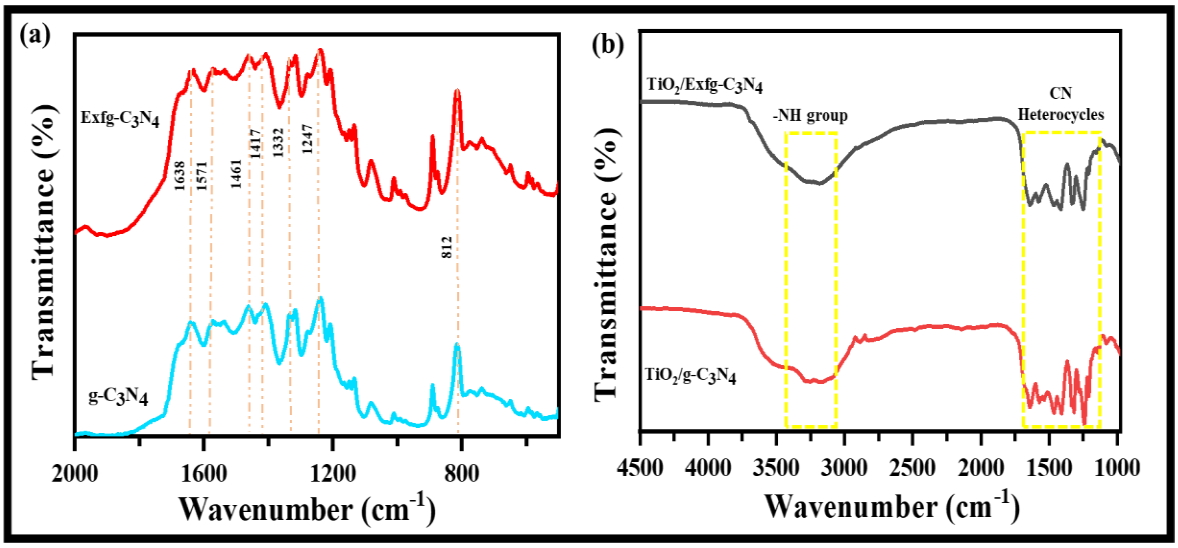

Figure 5.6: The FTIR spectra of all synthesized samples

of 3150-3300 cm-1 is attributed to the stretching vibration modes of terminal NH groups. The spectra display that the main characteristic peaks of both g-C_3N_4 and Exf g-C_3N_4 appeared in both TiO_2 /g-C_3N_4 and TiO_2 /Exfg-C_3N_4 samples, suggesting the formation of a composite between g-C_3N_4, Exfg-C_3N_4 and TiO_2.

5.3.4 Optical Analysis

5.3.4.1 UV-Vis DRS

In DRS the Plot is between Reflectance (%) and Wavelength (nm) in Figure 5.7(a) is shown from which we can infer that there is a fall in reflectance spectra occurring at 440, 444, 442 and 447 nm for gC_3N_4, ExfgC_3N_4, TiO_2/ gC_3N_4 and TiO_2/ExfgC_3N_4 respectively. The indirect band gap of the as-synthesized samples has been calculated from DRS by employing the Kulbelka-Munk Method in Figure 5.7(b). The indirect band gap of these synthesized samples is calculated about at 2.8, 2.7, 2.8 and 2.77 eV respectively. Upon loading gC_3N_4 and Exf gC_3N_4 with TiO_2 the light absorption region was further extended to a longer wavelength and suggested the nanocomposites could provide an efficient utilization of visible light as well which would be beneficial to the photocatalytic process [10,11].

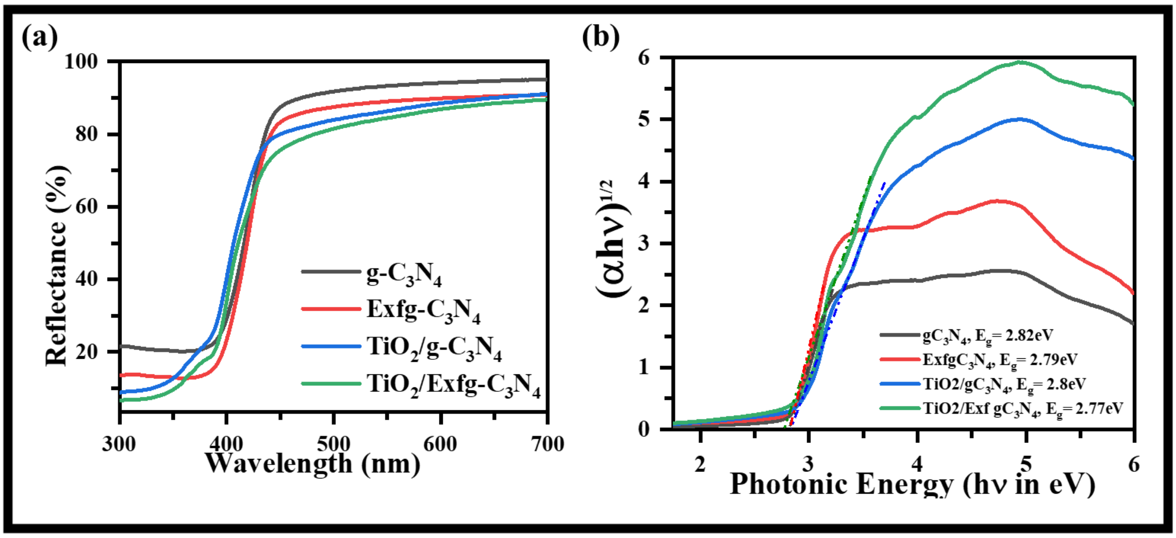

Figure 5.7: (a) Diffuse Reflectance Spectra of all synthesized samples and (b) Kubelka-Munk plots for calculation of indirect band gaps

5.3.4.2 Photoluminescence Analysis (PL)

The PL analysis spectra were employed to further investigate the transport and separation of the photogenerated carriers. Figure 5.8 shows the PL Spectra of annealed TiO_2 and its nanocomposites formed with bulk and exfoliated gC_3N_4.

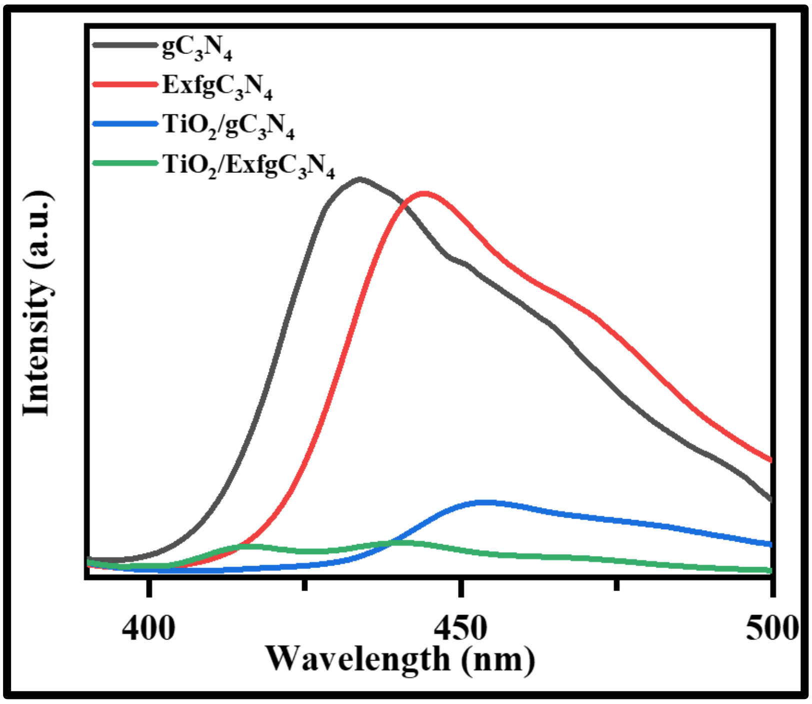

Figure 5.8: The PL Spectra of all synthesized samples

From the Figure, it can notice the intensity emission peaks of gC_3N_4, Exf gC_3N_4, TiO_2/gC_3N_4 and TiO_2/Exf gC_3N_4 in decreasing order which signifies that the recombination rate of photogenerated electron-hole pair is faster in case of gC_3N_4 than TiO_2/Exf gC_3N_4 which effectively blocks the recombination rate leading to the enhancement of its photocatalytic activity.

5.3.5 Electrochemical Analysis

Mott-Schottky

The nature of the as-prepared semiconductor materials and their respective flat band potentials (V_{fb}) are obtained from their electrochemical impedance measurement in dark conditions without any light illumination by using the following Mott-Schottky equation:

$$1/C^2 = (2/\ \varepsilon_r \varepsilon 0 N_d\, e) * (V - V_{fb} - (k_B T/e))$$

Here, C = depletion layer capacitance,

ε_r = dielectric constant of semiconductor (10 approximately),

ε_0 = vacuum permittivity ($8.85\times10{-}12\ N^{-1}\ C^2 m^{-2}$),

N_d = carrier donor density, and

$k_B T/e$ = temperature dependent correction term

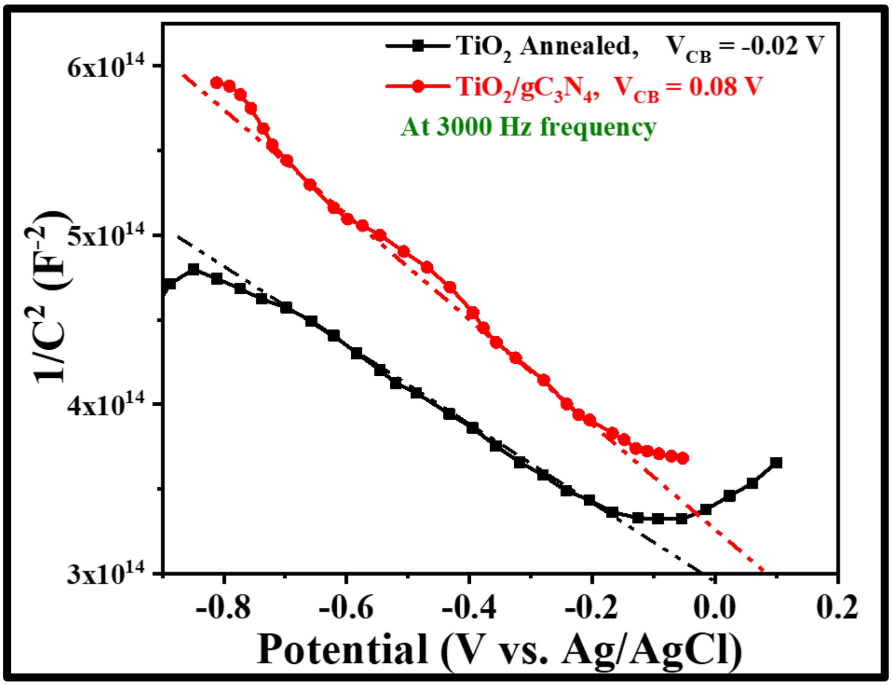

Figure 5.9: Mott-Schottky Plot of TiO_2 annealed and TiO_2/gC_3N_4

It is a known fact that for an n-type semiconductor electrode at an open circuit, the semiconductor has a Fermi level higher than the redox potential of the electrolyte; as a result of electrons get transferred from the semiconductor into the solution. This results in a positive charge associated with the space charge region which is evident from the upward bending of the band edges. The positive slopes in the Mott-Schottky plots ($1/C^2$ vs. V) of all the pure and doped samples reveal the ‘n-type characteristics of the as prepared semiconductors. Also, it is known that the flat band potential V_{fb} corresponds to the conduction band edge potential (V_{cb}) in the case of an “n” type semiconductor whereas it corresponds to the valence band edge potential (V_{vb}) for a “p” type semiconductor. Hence the values of V_{cb} of all the samples can be calculated from the x-intercept of the Mott-Schottky plots ($1/C^2=0$) as a function of the applied potential which has been shown in Figure 5.9. The synthesized annealed TiO_2 and sample TiO_2/gC_3N_4 have minimum V_{cb} values of −0.02 V and 0.08 V (vs. Ag/AgCl) respectively. The positive shift in comparison to the pure sample suggests a decrease in the bending of band edges which in turn is attributed to the increased material/electrolyte interface that can significantly improve the charge carrier transfer efficiency.

5.3.6 Photocatalytic Performance Analysis

By observing the degradation, the active photocatalytic performances of both pristine and composite materials were studied by efficiently degrading Rhodamine B (RhB) dye under UV light irradiation. RhB dye absorbance pattern is shown in Figure 5.10 after catalytic reactions in the synthesized samples: catalyst materials degrade after about 90 minutes of UV light irradiation. In the Figure 5.11(a) shows the C/C_0 vs. irradiation time plot, and $\ln(C_0/C)$ vs. irradiation time plot shown in Figure 5.11(b), it also known as the 1st order rate kinetics of the materials. The linear fitting of the plot of $\ln(C_0/C)$ vs. time (t) gave the rate constant values from the slope. The corresponding bar graph showing the rate constant values for the samples is presented in Figure 5.11(c) [5].

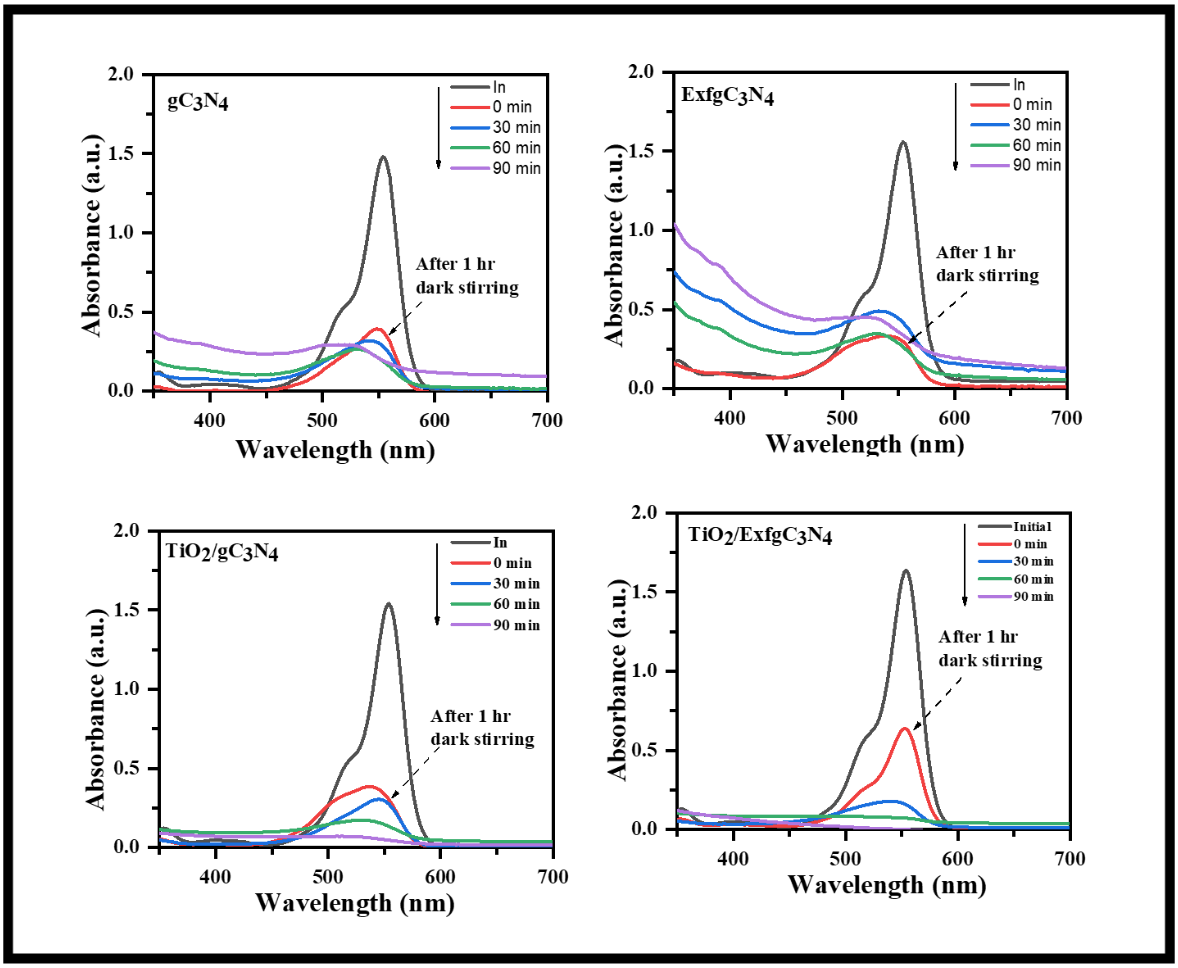

Figure 5.10: Absorbance Spectra of all Synthesized Samples

$\ln(C_0/C) = \mathrm{kapp} * t$

where,

C_0 = initial concentration of aqueous Rhodamine B dye,

C = final concentration of aqueous RhB dye and catalyst solution at time ‘t’,

kapp = apparent first-order kinetics rate constant, and t = irritation time

The photodegradation efficiency can be seen from the bar plot Figure 5.11(d), that TiO_2/Exf gC_3N_4 degrades the RhB dye at an efficiency of 99.84 % which is higher than the photodegradation efficiency of other materials. The photodegradation efficiency was calculated by the equation:

$\eta\% = (\eta_0 - \eta_t / \eta_0) * 100$

where,

η % = photodegradation efficiency of the photocatalyst,

η_0 = initial absorbance of aqueous Rhodamine B dye solution, and

η_t = final absorbance of aqueous RhB dye and catalyst solution at the time 't'.

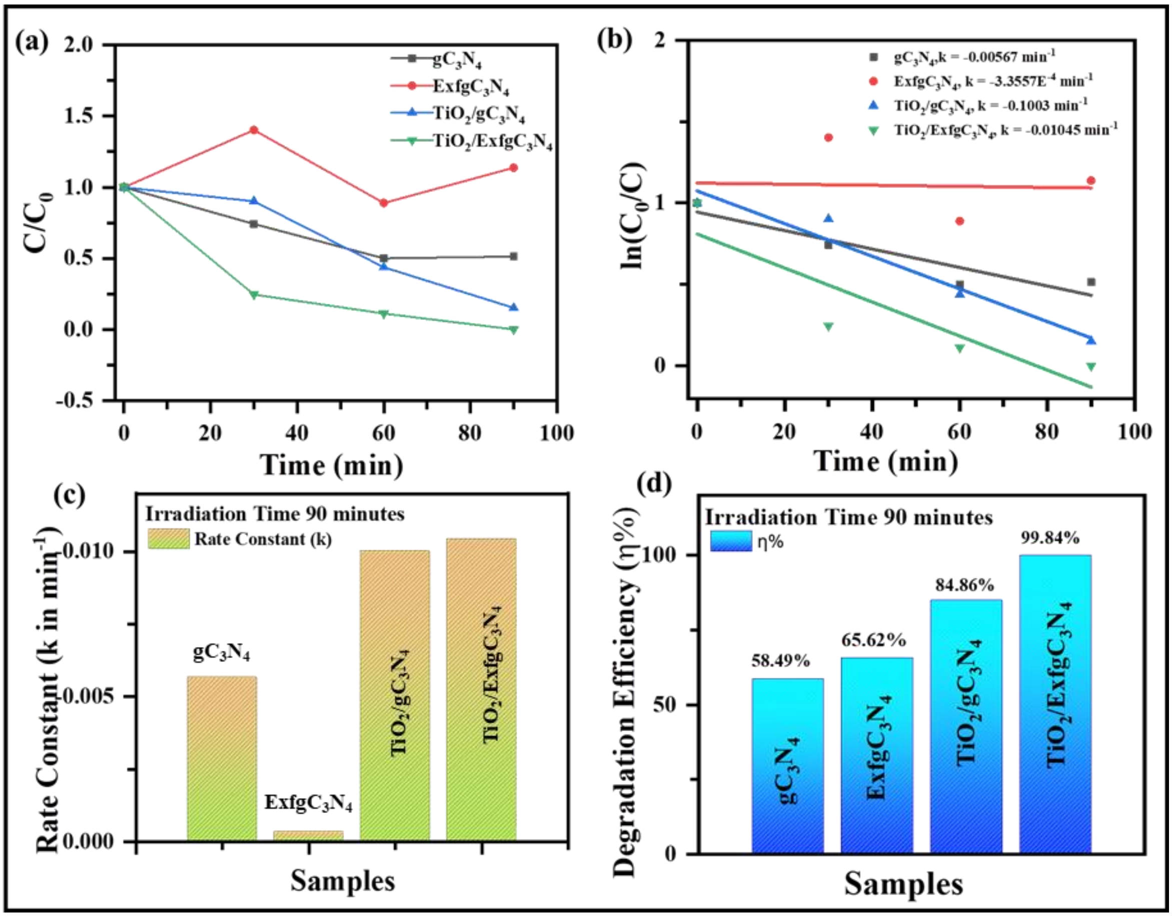

Figure 5.11: (a) C/C_0 vs. irradiation time (t) plots and (b) $\ln(C_0/C)$ vs. irradiation time, (c) the bar plots of 1st order rate constant and (d) photodegradation efficiency of all synthesized samples

5.3.7 Proposed Mechanism

The probable proposed photocatalytic performance enhancement mechanism for RhB dye degradation using g-C_3N_4/TiO_2 (Figure 5.12). The photo-induced holes are prone to stay at the valence band (VB) of TiO_2, whereas the electrons are transferred from the conducting band (CB) of TiO_2 to VB of g-C_3N_4. Thus, O_2 dissolved in the water will trap the electrons that remain in the CB of gC_3N_4, O_2 will be formed as a result, and the O_2 radical plays an important role in breaking RhB up into colourless products. In addition, the photoinduced holes make the degradation reaction occur on the VB of TiO_2. Therefore, the heterojunction structure enhances the separation efficiency of photo-induced carriers, which indeed contributes to enhancing the photocatalytic activity [8,10].

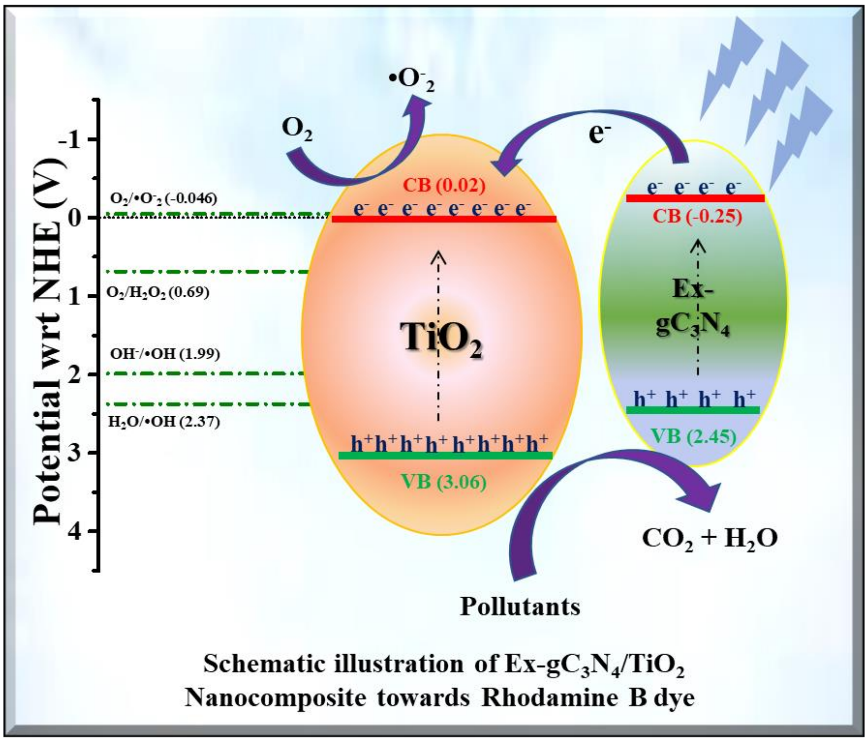

Figure 5.12: Possible UV light photodegradation mechanism of TiO_2/Exf gC_3N_4 towards RhB

5.4 Conclusion

In conclusion, we were able to successfully synthesize TiO_2/Exf gC_3N_4 nanocomposite material by hydrothermal method, and the various properties like identification of phases and chemical structures were efficiently confirmed by sophisticated techniques like XRD, FTIR, UV–Vis DRS, PL, FESEM, HRTEM, EDX, MOTT-SCHOTTKY. The nanocomposite was effectively accomplished in the photodegradation of harmful, organic pollutant Rhodamine B (RhB) dye within a short time period assisted by visible light irradiation, and the photodegradation efficiency of the material was found to be around 99.84% which supported the composite's highly active photocatalytic nature. A feasible mechanism was also suggested to comprehend the reaction events occurring during the catalytic degradation procedure by TiO_2/ExfgC_3N_4. In this way, the catalyst is efficiently performed in wastewater treatment for the removal of toxic pollutants present in aqueous ecosystems.

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CHAPTER 6

CONCLUSION
&
SCOPE FOR FUTURE WORK

6.1 Conclusion

In this study, pure TiO_2 was effectively synthesized through three distinct methods, and nanocomposites of TiO_2 and g-C_3N_4 were additionally generated via hydrothermal processes. The employment of advanced analytical techniques such as PXRD, FTIR, UV-VIS DRS, PL, FESEM, HRTEM, Mott-Schottky, etc. for comprehensive structural and optical analysis. The nanocomposite exhibited significantly enhanced degradation efficiency compared to pristine titanium dioxide. Moreover, the photodegradation efficiency of titanium dioxide/exfoliated graphitic carbon nitride (99.84%) surpassed that of titanium dioxide/graphitic carbon nitride (84.86 %). Furthermore, the annealed nanocomposites outperformed their non-annealed counterparts in terms of photodegradation efficiency. Within a short period, the nanocomposites effectively photodegraded Rhodamine B dye, a hazardous organic pollutant, under ultraviolet irradiation. The improved degradation efficiency of the nanocomposite in comparison to pure titanium dioxide can be attributed to a feasible mechanism. Consequently, the catalyst proves highly effective in eliminating harmful contaminants from aquatic ecosystems during wastewater treatment.

6.2 Scope for Future Work

Future research into nanocomposites comprising titanium dioxide (TiO_2) and exfoliated graphitic carbon nitride (ExfgC_3N_4) holds tremendous potential across various scientific and technological domains. These hybrid materials leverage the distinctive attributes of both constituents, paving the way for enhanced performance and multifaceted applications. One area ripe for exploration is the utilization of TiO_2/g-C_3N_4 nanocomposites as efficient catalysts in electrochemical reactions, specifically in the realms of oxygen reduction and evolution reactions pertinent to fuel cells and metal-air batteries within the energy storage and conversion domain. The synergy between TiO_2 and g-C_3N_4 can significantly bolster reaction stability and kinetics, thereby elevating the overall efficacy of energy devices. Moreover, photocatalysis and environmental remediation represent additional promising avenues. The shared characteristics of TiO_2 and g-C_3N_4, encompassing high surface area, tunable bandgaps, and potent light absorption capabilities, position them as compelling candidates for proficiently addressing challenges in contaminant degradation, water splitting, and the production of solar fuels. To further enhance catalytic efficiency and durability, future investigations should concentrate on the meticulous tailoring of the nanocomposite's composition, structure, and fabrication methodologies. This meticulous approach holds the key to unlocking the full potential of TiO_2/g-C_3N_4 nanocomposites. Beyond energy-related applications, TiO_2/g-C_3N_4 nanocomposites exhibit great promise in optoelectronics, electronics, and sensor technologies. Gas sensors, photodetectors, and solar cells can reap substantial benefits from the inclusion of exfoliated g-C_3N_4 within TiO_2 matrices. This addition augments electrical conductivity, charge carrier mobility, and light absorption characteristics, opening doors to advanced electronic functionalities and heightened device performance. In the future, research on TiO_2/exfoliated g-C_3N_4

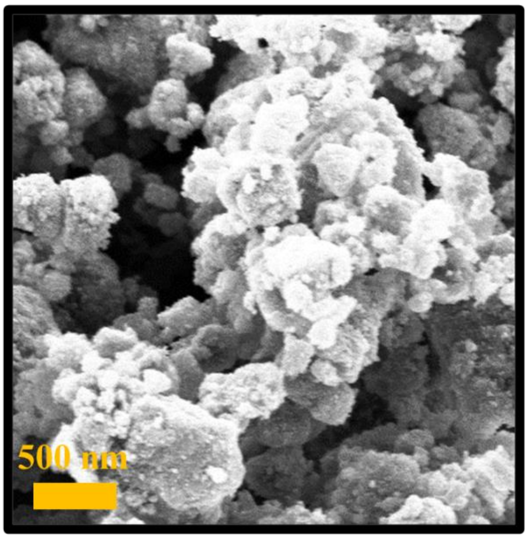

Figure 6.1: FESEM image of as-synthesized TiO_2/ExfgC$_3$N$_4$ Nanocomposite

nanocomposites should prioritize sophisticated synthesis methods, comprehensive characterization techniques, and systematic investigations into their performance across diverse applications. By harnessing the synergistic properties of these materials, researchers can usher in an era of innovative functional nanocomposites, elevating the efficiency and capabilities of energy, environmental, and electronic technologies to unprecedented heights.