

**“ULTRAFAST DEGRADATION OF FAST GREEN DYE UNDER
VISIBLE LIGHT USING STRONTIUM DOPED NICKEL
 β –HYDROXIDE NANOPARTICLE”**

Submitted in partial fulfillment of the requirements for the award of
Master of Science in Chemistry

by

**R. DHEEPIKA
(39910004)**



DEPARTMENT OF CHEMISTRY

SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

Accredited with Grade “A” by NAAC

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119

MARCH – 2021



SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

Accredited with "A" grade by NAAC

Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600 119

www.sathyabama.ac.in

DEPARTMENT OF CHEMISTRY

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **Ms. R. DHEEPIKA (39910004)** who carried out the project entitled **"ULTRAFAST DEGRADATION OF FAST GREEN DYE UNDER VISIBLE LIGHT USING STRONTIUM DOPED NICKEL β -HYDROXIDE OXIDE NANOPARTICLE"** under my / our supervision from January 2021 to march 2021.

Internal Guide

Dr. S. SUNITHA, M.Sc., M.Phil., Ph.D.

External Guide

**Dr. G. MURUGADOSS, M.Sc., Ph.D.
(Scientist-E)**

Head of the Department

Dr. J. KARTHIKEYAN, M.Sc., Ph.D.

Submitted for Viva voce Examination held on _____

Internal examiner

External Examiner

DECLARATION

I **Ms. R.DHEEPIKA** student of **Sathyabama Institute of Science and Technology** hereby declare that the Project Report entitled **“ULTRAFAST DEGRADATION OF FAST GREEN DYE UNDER VISIBLE LIGHT USING STRONTIUM DOPED NICKEL β -HYDROXIDE NANOPARTICLE”** done by me under the guidance of Dr. S. SUNITHA, M.Sc., M.Phil., Ph.D. and Dr. G. MURUGADOSS, M.Sc., Ph.D. (Scientist-E) at International Research Centre, Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfillment of the requirements for the award of **Master of Science degree in Chemistry**.

DATE:

(R. Dheepika)

PLACE:

SIGNATURE OF THE CANDIDATE

ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to the board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

I convey my thanks to the **Dean**, School of Science and Humanities **Dr. J. KARTHIKEYAN**, Head of the Department, Dept. of Chemistry for providing me necessary support and details at the right time during the progressive reviews.

I would like to express my sincere and deep sense of gratitude to my Project Guide's **Dr. S. SUNITHA M.Sc., M.Phil., Ph.D.** (Internal Guide) and **Dr. G. MURUGADOSS M.Sc., Ph.D. (Scientist-E)** (External Guide) at International Research Centre, Sathyabama Institute of Science and Technology for their valuable guidance, suggestions, and constant encouragement paved way for the successful completion of my project work.

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

ABSTRACT

The Strontium doped Nickel hydroxide (Sr/Ni(OH)_2) nanoparticles and the pure NiO were synthesized by Coprecipitation method using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Sr(NO}_3)_2$ for Ni and Sr sources, respectively. Sodium hydroxide was used as a precipitator agent. Effect of Sr doping agent on the structural and their properties of nanostructures were characterized by XRD, SEM, FTIR techniques. Co-precipitation method was the most efficient and cost-effective way for the synthesis of nanoparticles. The Sr/Ni(OH)_2 was synthesised by a low temperature based method and is used in the application of photodegradation. The photocatalytic degradation of dyes has been studied all over the world, regardless of the country's scientific standard. The concentration of dye, the concentration of the oxidising species, the catalyst used, the strength and the source of photons used for degradation studies are all common variables to noted. The prepared NiO , Sr/Ni(OH)_2 were used as an efficient catalyst for the photodegradation of Fast green (FG) dye. Photocatalytic degradation of fast green dye followed first-order kinetics and dye degradation gave the best results. The photodegradation efficiency of fast green dye was about 50.64% for NiO and 95.2% for the prepared Sr/Ni(OH)_2 catalyst. The kinetic data obtained on the decolorization of the fast green dye have been analysed.

TABLE OF CONTENTS

1.INTRODUCTION	1
1.1 NANOPARTICLES	1
1.2HISTORY AND DEVELOPMENT OF NANOPARTICLES	2
1.3 TYPES OF NANOPARTICLES	2
1.3.1 One-dimensional nanoparticle.....	2
1.3.2 Two-dimensional nanoparticle.....	2
1.3.3 Three-dimensional nanoparticle.....	3
1.4 CLASSIFICATION OF NANOPARTICLE.....	3
1.4.1 Carbon based nanoparticle.....	3
1.4.2 Inorganic based nanoparticle.....	4
1.4.3 Organic based nanoparticle.....	4
1.4.4 Composite based nanoparticle.....	4
1.5 PROPERTIES OF NANOPARTICLES.....	5
1.5.1 Physical properties.....	5
1.5.2 Optical properties.....	5
1.5.3 Magnetic properties.....	5
1.5.4 Mechanical properties	5
1.6 SYNTHESIS METHODS	6
1.6.1 Top-down approach	6
1.6.1.1 Mechanical milling	6
1.6.1.2 Melt mixing	7
1.6.1.3 Laser ablation	7
1.6.2 BOTTOM-UP APPROACH	7
1.6.2.1 Physical Vapour Deposition	7
1.6.2.2 Sol-gel method	8

1.6.2.3 Chemical Vapour Deposition	8
1.7 PHOTOCATALYST	11
1.8 PHOTOCATALYSIS	11
1.9 MECHANISM OF PHOTOCATALYSIS	12
1.10 PHOTODYEDEGRADATION	12
1.11 APPLICATIONS OF PHOTOCATALYST	13
1.12 FAST GREEN DYE	14
2. LITERATURE SURVEY	15
3. AIM AND SCOPE OF THE PRESENT INVESTIGATION	17
4. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES.....	18
4.1 MATERIALS	18
4.2 SYNTHESIS OF NiO	18
4.3 SYNTHESIS OF Sr/Ni(OH) ₂	19
4.4 CHARACTERIZATION TECHNIQUES	20
4.4.1 X-ray Diffraction (XRD)	21
4.4.2 Scanning electron microscopy (SEM)	23
4.4.3 Fourier Transform Infra-red Spectroscopy (FT-IR)	24
5. RESULTS AND DISCUSSION	25
5.1 X-RAY DIFFRACTION (XRD)	25
5.2 SCANNING ELECTRON MICROSCOPE (SEM)	28
5.3 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FT-IR)	29
5.4 PHOTOCATALYTIC ACTIVITY TEST	31
5.5 PHOTOCATALYTIC ACTIVITY	32
6. SUMMARY AND CONCLUSION	35
7. REFERENCES	37

LIST OF ABBREVIATIONS

ABBREVIATIONS	EXPANSIONS
CNT	Carbon nanotubes
SWCNT	Single walled carbon nanotube
DWCNT	Double walled carbon nanotube
MWCNT	Multi walled carbon nanotube
PVD	Physical Vapour Deposition
CVD	Chemical Vapour Deposition
NPs	Nanoparticles
NiO	Nickel oxide
Ni(OH) ₂	Nickel hydroxide
CB	Conduction band
VB	Valence band
Sr/Ni(OH) ₂	Strontium doped Nickel hydroxide
XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
SE	Secondary electrons
BSE	Backscatter electrons
PE	Primary electron
FG	Fast green
ROS	Reactive organic species

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE NO.
1.1	Types of nanoparticles	3
1.2	Top-down and bottom-up approaches	6
1.3	Applications of metal oxide nanoparticles	9
1.4	Cubic structure of NiO	10
1.5	Mechanism of photocatalyst	12
1.6	Role of photocatalyst	13
1.7	Structure of fast green dye	14
4.1	Schematic diagram of NiO synthesis	19
4.2	Synthesis of Sr/Ni(OH) ₂	20
4.3	Characterization of nanoparticle	21
4.4	Schematic representation of Bragg's law	22
4.5	Working of SEM	23
4.6	Working of FT-IR	24
5.1	(a) NiO sample (b) Sr/Ni(OH) ₂	25
5.2	XRD peak of NiO and Sr/Ni(OH) ₂	27
5.3	(a) SEM image of pure NiO nanoparticle (b) SEM image of Sr/Ni(OH) ₂ nanoparticle	28
5.4	(a) FT-IR peak of NiO (b) FT-IR peak of Sr/Ni(OH) ₂	30
5.5	UV spectra of Fast green dye	32
5.6	Schematic diagram illustrating the mechanism of charge separation and photocatalytic activity of the photocatalyst	34

LIST OF TABLES

TABLE NO.	TITLE	PAGE NO.
1.	Photocatalytic activity result of NiO, and (Sr/Ni(OH) ₂) nanoparticles	34

CHAPTER-1

INTRODUCTION

1.1 NANOPARTICLES

These days, we live in an escalated advancement of science known as nanotechnology. The normal size of particles framing a given colloid is regularly in the range of 1–1000 nm ($1\text{ nm} = 10^{-9}\text{ m}$). There are numerous meanings of nanoparticles. One of them says that, at a point when a given material is made out of particles, whose at any rate one measurement is more modest than 100 nm, then such material can be called as “nanomaterial”. Another definition decides “nanomaterial” as a material which after “miniaturization” to nanoscale uncovers changed physicochemical properties in contrast with the mass item (naturally visible) [1].

The nanoparticles display novel physical, chemical and biological properties at nanoscale contrasted with their specific particles at higher scales. This happens because of a larger surface area to the volume, increase in reactivity or stability in a chemical reaction, improved mechanical strength, and so on. These properties of nanoparticles have prompted their utilization in different applications. The nanoparticles differ in shapes, sizes and structures. It can vary from 1 nm to 100 nm in size. The surface can be uniform or unpredictable with surface varieties. Some nanoparticles are translucent or shapeless with single or multi gem solids either free or agglomerated. Various synthesis techniques are either being created or improved to upgrade the properties and lessen the production costs. A few techniques are adjusted to accomplish measure explicit nanoparticles to increment their physical, chemical, optical and mechanical properties. A huge advancement in instrumentation has prompted an improvement in nanoparticle characterization and application [2].

Based on the application like imaging, diagnosis or treatment various kinds of nanoparticles have been proposed, some of them are utilized for multiple purposes. Nanoparticles come under two main categories: organic and inorganic nanoparticles. The primary group includes micelles, dendrimers, liposomes, hybrid and minimized polymeric nanoparticles. The second group includes fullerenes, quantum dots, silica and gold nanoparticles [3].

1.2 HISTORY AND DEVELOPMENT OF NANOMATERIALS

Nanoparticles and its structures have been utilized by people in the fourth century AD, by the Roman, which showed quite possibly the most fascinating instances of nanotechnology in the ancient world. The Lycurgus cup, from the British Museum collection, addresses quite possibly the most outstanding accomplishments in the ancient glass industry. It is the most established renowned illustration of dichroic glass. Dichroic glass portrays two unique kinds of glass, which change colour in certain lighting conditions. This implies that the cup has two unique colours. The glass seems green in direct light, and red-purple when light radiates through the glass. In 1990, the researchers dissected the cup utilizing transmission electron microscopy (TEM) to clarify the wonder of dichroism. The noticed dichroism (two colour) is because of the presence of nanoparticles with 50–100 nm in diameter.

X-ray study showed that these nanoparticles are silver-gold (Ag-Au) compound, with a proportion of Ag:Au of about 7:3, containing moreover about 10% copper (Cu) scattered in a glass grid. The Au nanoparticles produce a red colour as an effect of light absorption (~520 nm). The red-purple colour is because of the absorption by the larger particles while the green colour is credited to the light scattering by colloidal dispersions of Ag nanoparticles with a size > 40 nm. The Lycurgus cup is perceived as one of the most seasoned manufactured nanomaterials. A comparative impact is seen in late middle age church windows, sparkling a radiant red and yellow colour because of the combination of Au and Ag nanoparticles into the glass [4].

1.3. TYPES OF NANOPARTICLES

The types of nanoparticles have been discussed in detail and the diagrammatic representation is shown below in figure 1.1

1.3.1 ONE DIMENSIONAL NANOPARTICLE:

Atoms are arranged in one dimension in the nano scale range. Examples are surface coatings and thin films.

1.3.2 TWO-DIMENSIONAL NANOPARTICLES:

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

1.3.3 THREE DIMENSIONAL NANOPARTICLES:

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

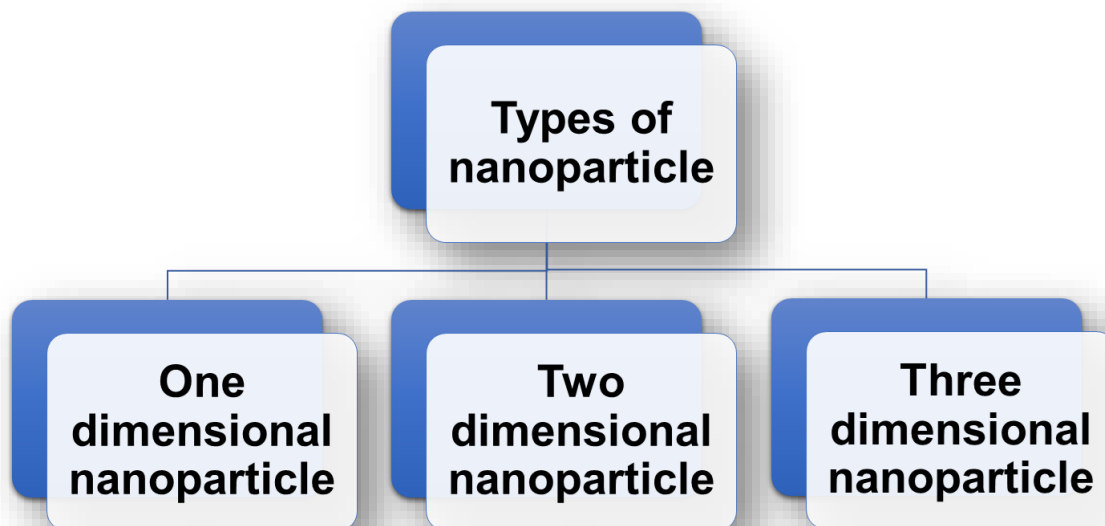


Figure 1.1 Types of nanoparticles

1.4 CLASSIFICATION OF NANOPARTICLES

Nanoparticles are extensively separated into different classifications relying upon their morphology, size and its chemical properties. Based on their characteristics nanoparticles are classified and given beneath.

1.4.1 CARBON BASED NANOPARTICLES

Fullerenes and carbon nanotubes (CNTs) address two significant classes of carbon-based nanoparticles. Fullerenes contain nanomaterial that is made of globular empty enclosure like allotropic structures of carbon because of their electrical conductivity, high strength, structure, electron affinity, and flexibility. These materials possess pentagonal and hexagonal carbon units, while every carbon is sp^2 hybridized. CNTs are tubular, elongated, 1–2 nm in measurement. These can be anticipated as metallic or semiconducting dependent on their measurement telicity. These resemble graphite sheets rolling upon themselves. The sheets can

be single, double or numerous walls and in this way, they are named single-walled (SWNTs), double walled (DWNTs) or multi-walled carbon nanotubes (MWNTs) individually, they are synthesized by carbon precursors, by electric arc on metal nanoparticles. Of late, they are synthesised by Chemical Vapour Deposition (CVD). Because of their unique physical, chemical and mechanical properties, these materials are utilized in various applications like filler and as in organic and inorganic catalyst.

1.4.2 INORGANIC BASED NANOPARTICLES

These nanomaterials incorporate metal furthermore, metal oxide nanoparticles and nanostructured materials. These nanomaterials can be combined into metals like Au or Ag nanoparticles, metal oxides, for example, TiO₂ and ZnO nanoparticles, and semiconductors like silicon and ceramics.

1.4.3 ORGANIC BASED NANOPARTICLES

These incorporate nanomaterials made for the most part from organic matter, barring carbon-based or inorganic-based nanomaterials. The use of non-covalent weak interactions for the self-assembly and designs of atoms assists with changing the organic nanomaterials into specific structures, for example, dendrimers, micelles, liposomes and polymer nanoparticles.

1.4.4 COMPOSITE BASED NANOPARTICLES

Composite nanomaterials are multiphase nanoparticles and nanostructured materials with one stage on the nanoscale measurement that can either consolidate nanoparticles with different nanoparticles or nanoparticles joined with bigger or with bulk materials or more complicated structures, for example, metal organic systems. These composites might be a mixture of carbon-based, metal-based, or natural based nanomaterials with any type of metal, polymer, or ceramic based materials. Nanomaterials are synthesised in various morphologies relying upon the necessary properties for the required application [5].

1.5 PROPERTIES OF NANOPARTICLES

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

1.5.1 PHYSICAL PROPERTIES:

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

1.5.2 OPTICAL PROPERTIES:

Due to the quantum confinement effect, nanomaterials with small particle sizes exhibit better optical emission as well as nonlinear optical properties. The effect of size on nanoparticle optical properties is caused by two distinct phenomena: surface phenomena and an increase in energy level spacing due to the confinement of energy states, which is most notable in semiconductors [6].

1.5.3 MAGNETIC PROPERTIES:

After surface cooling, magnetic nanoparticles exhibit extraordinary new phenomena including strong field irreversibility, high saturation field, superparamagnetism, extra anisotropy effects, or shifted loops. The magnetic nature of individual nanoparticles is because of narrow and finite-size effects, as well as surface effects [7].

1.5.4 MECHANICAL PROPERTIES:

Magnetic nanoparticles can be superparamagnetic and responds to external magnetic fields very fast with almost zero remanence. These properties provide bases for applications like biomedical imaging and information storage technology. The mechanical properties of nanoparticles such as hardness and elastic modulus, interfacial adhesion and friction, movement law, as well as its size-dependent effect [8].

1.6 SYNTHESIS METHODS

Approaches come under two main categories namely: top-down approach and bottom-up approach and they differ in their cost, speed and degree of quality. The approaches have been summarized in the figure 1.2 below.

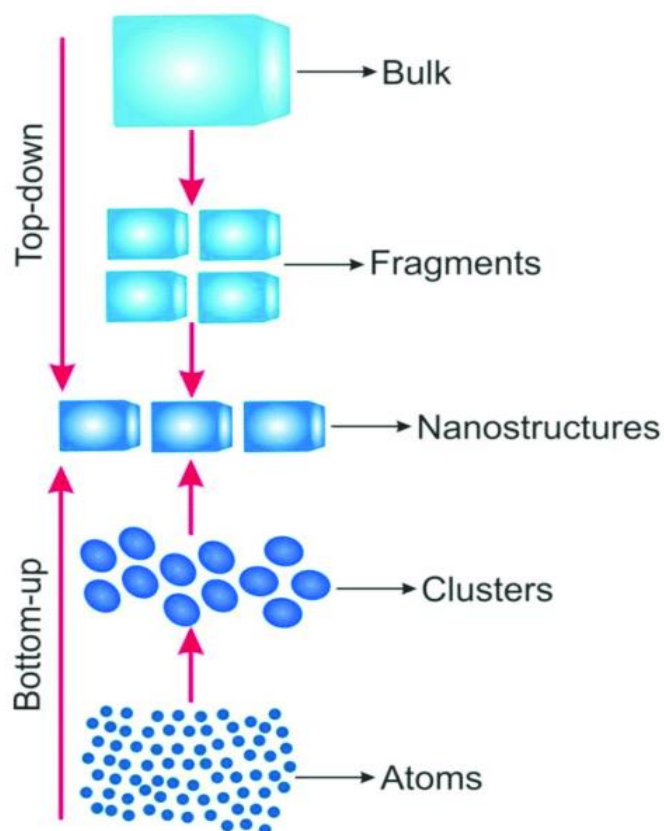


Figure 1.2 Top-down and bottom-up approaches [9]

1.6.1 TOP-DOWN APPROACH:

In this approach destructive method is employed. Starting from larger molecules which is disintegrated into smaller ones and afterwards these units are converted into its respective nanoparticles. Examples are mechanical milling, chemical etching, laser ablation, sputtering, etc [4].

1.6.1.1 MECHANICAL MILLING:

This is the simplest way of synthesising nanoparticles by using metals and alloys in powder form. Different types of mills can be employed in this process. Large quantities of finite particles can be synthesized by using one or two container. The size of the container completely depends upon the size of the nanoparticle taken. Hard steel balls are kept along with the powdered nanoparticle. Larger balls are used to obtain small grain size. High temperature is required for this process ranging from 100-1100°C and the containers are rotated at a high speed. Materials like Cr, Co, W, Al-Fe etc are converted to nanoparticles [4].

1.6.1.2 MELT MIXING:

Nanoparticles can be synthesised in glass by this method. Since glass is an amorphous solid and has symmetrical arrangement of atoms or molecules. Amorphous solid is formed when a liquid is cooled at a certain temperature. When they are cooled at a high cooling rate they are called metallic glasses. Elements like Si, B, P can be useful for the metallic glasses in amorphous state and it is possible to obtain nanocrystals by controlled heating within the metallic glasses. TiB₂ nanoparticles can be synthesised by this method [9].

1.6.1.3 LASER ABLATION:

Laser Ablation synthesis is most commonly used method for the synthesis of nanoparticle using various solvents. Metal is submerged in a liquid and is irradiated by a laser beam which condenses a plasma plume and that produces a nanoparticle. It is an alternative solution for the chemical reduction of metal nanoparticles. This method gives a stable synthesis of nanoparticles using organic solvents [2].

1.6.2 BOTTOM-UP APPROACH:

This method is the reverse of top-down approach. These nanoparticles are formed from simple substances and hence it is called as building up approach. Examples are spinning, pyrolysis, sol-gel, CVD, etc [4].

1.6.2.1 PHYSICAL VAPOR DEPOSITION:

The particle size is determined by the rate of evaporation and the pressure of the gases in the chamber. Gases such as H₂, O₂, NH₃, and N₂ are used, and the material interacts with them, forming nitrides, hydrides, and oxide particles. The gas pressure in the deposition chamber defines the size and form of the evaporated substance. Both the processes were carried out in a vacuum chamber to produce a high-purity nanomaterial [9].

1.6.2.2 SOL-GEL METHOD:

Two materials are involved in this method they are sol and gel. It is a low temperature process and consumes less energy. Synthesis of nanoparticles like nanotubes, nanorods can be obtained by this method. Sol-gel synthesis involves hydrolysis, condensation, gelation and drying process by various routes [9].

1.6.2.3 CHEMICAL VAPOUR DEPOSITION (CVD):

The deposition of a thin film of gaseous reactants onto a substrate is Chemical Vapour Deposition. At ambient temperature gas molecules are combined and the deposition is carried out in a reaction chamber. Chemical reaction occurs when a heated substrate comes in contact with the combined gas. A thin film of product on the substrate surface is produced and that is recovered and used. The influencing factor in CVD is the substrate temperature. CVD produces nanoparticles that are strong, uniform and hard. CVD requires special equipment and the gaseous by-products are toxic.

1.7 APPLICATIONS OF NANOPARTICLES

- Nanoparticles are widely used in drug delivery systems. Certain drugs are not metabolised in the first pass. To resolve this, nanoparticles can be modified, and they also allow for regulated, long-term drug release from the matrix.
- When they've adhered to short DNA segments, they can also be used to detect genetic sequences. Nanotechnology allows damaged tissue to be

repaired or replicated. The use of nanotechnology can revolutionise organ transplantation or artificial implantation [10].

- The need for new antimicrobial agents has risen. Because of their inbuilt antimicrobial properties, nanoparticles (NPs) are now being considered as an effective nanotechnology for regulating harmful micro-organisms [11].

1.8 METAL OXIDES

Metal oxides plays a vital role in numerous zones like chemistry, physics, and materials science. Metal oxides exhibits semiconductor, metallic or insulator properties and can adopt a number of structural geometries and it also possess an electronic structure [12]. Metal oxide nanoparticles have been used in different fields due to its excellent functional properties. When metal oxides are coupled with other structures, they enhance the unique properties of the materials [13]. The main applications of metal oxide nanoparticles are shown in figure 1.3.



Figure 1.3 Applications of metal oxide nanoparticles

1.9 TRANSITION METAL OXIDES

1.9.1 NICKEL OXIDE NANOPARTICLE:

Nickel oxide nanoparticle (NiO) is an important transition metal oxide nanoparticle that possesses a cubic lattice structure and that is shown in figure 1.4 given below. It has attracted attention due to its possible applications in a wide range of fields, including catalysis, battery cathodes, gas sensors, and magnetic materials. It is most commonly used in dye sensitised photocathodes. NiO is predicted to have a number of advantages over micrometre-sized NiO particles [14].

Due to its defect structure, non-stoichiometric nickel oxide is a strong P-type semiconductor, a possible gas sensor for H_2 , and highly active in the degradation of phenol and phenolic derivatives [15].

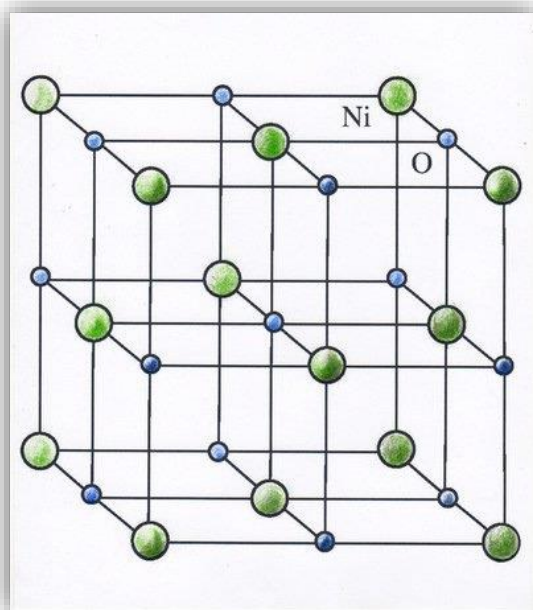


Figure 1.4 Cubic structure of NiO

1.10 NICKEL HYDROXIDE NANOPARTICLE

The nickel hydroxide nanoparticles exist in the form of white spherical metal particles with a high surface area. Their specific surface area is about 130-150 m^2/g . They are also obtained in high purity, carbon coated and in dispersed forms. Nickel

hydroxide nanoparticles exist in two phases α -Ni(OH)₂ and β -Ni(OH)₂. α -Ni(OH)₂ exist as cubic structure and β -Ni(OH)₂ exist as hexagonal.

1.11 PHOTOCATALYST

Materials that cause photocatalytic reactions when exposed to light is called as photocatalyst. A chemical reaction caused by photoabsorption of a solid substance, or "photocatalyst," which stays unchanged throughout the reaction is a general description of photocatalysis. As a result, a "photocatalyst" must act catalytically, that is, without modification, when exposed to light [16].

1.12 PHOTOCATALYSIS

Photocatalysis is a combination of the Greek words photo (light) and catalysis (to break apart or decompose). In general, photocatalysis is used to describe a mechanism in which light is used in the excitation of a photocatalyst. Photocatalyst is not involved in accelerating the rate of the chemical reaction. In other words, photocatalysis is a photoinduced reaction that is stimulated in the presence of a catalyst. Photocatalysis is broadly classified into two categories: homogeneous and heterogeneous [17].

- Homogeneous catalysis:

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

- Heterogeneous catalysis:

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

1.13 MECHANISM OF PHOTOCATALYSIS

When the photocatalyst is irradiated with light of a specific wavelength, a electron is excited to the conduction band (CB), leaving a positive hole in the valence band (VB). The hole in the VB can be utilized for oxidizing some compounds whereas the electron in the CB is used to reduce any substrate. This is shown in figure 1.5 given below. [17]

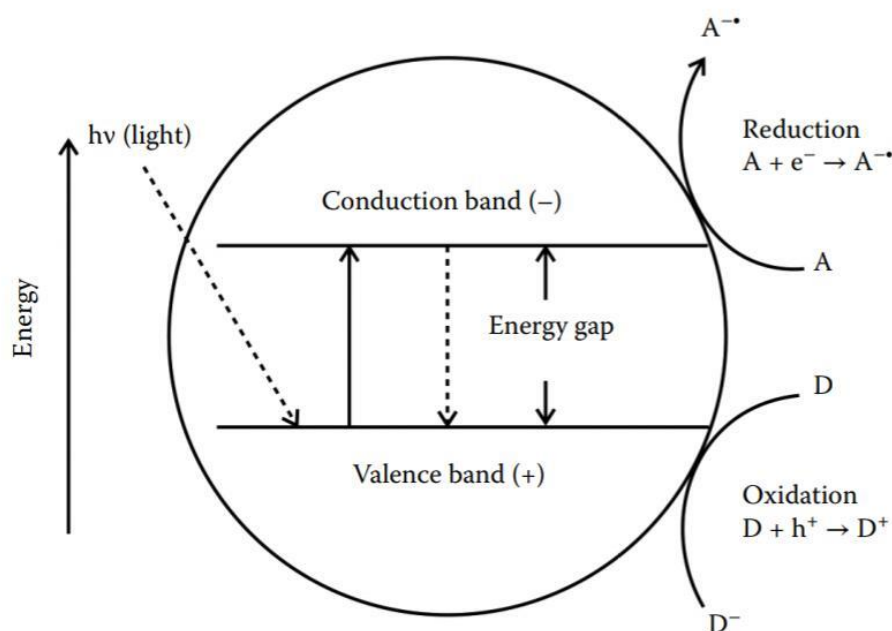


Figure 1.5 Mechanism of photocatalysis

1.14 PHOTODYEDEGRADATION

The presence of organic dyes in industrial wastewaters from the garment, clothing, and paper industry contaminates the environment massively. These dye-polluted effluents contain carcinogenic, non-biodegradable, and coloured pigments that can damage humans [18-20]. Dyes are easily visible in water even at extremely low concentrations (below 1 ppm). Dyes are easily detectable in water and have a substantial adverse effect on aquatic environment [19-21].

As a result, it is important to remove coloured organic dyes from waste streams. Adsorption [24] and coagulation [25] are typical strategies for removing organic dyes

from industrial wastewater. However, since dyes are only changed from a liquid to a solid form, these procedures result in secondary pollution. Hence, further treatments are needed to address the issue of secondary contamination [26-27].

Photocatalysis has been recognized as a successful alternative treatment for water purification in recent years [28].

1.15 APPLICATIONS OF PHOTOCATALYST

Photocatalytic technique has been proven to be one of the most “green” and successful environmental remediation techniques. Some semi-conducting materials, such as 'photocatalysts,' cause or accelerate chemical reactions when exposed to light, resulting in the decomposition of organic molecules, for example, Nanosized catalyst particles have slightly higher reactivity than larger particles or bulk content owing to their large surface area. Charge separation happens when a photocatalyst is exposed to light with an energy greater than the photocatalyst's band gap energy. The photocatalyst then initiates an oxidation-reduction reaction using the electrons and holes produced by charge separation [29]. Visible absorption spectroscopy is generally used for the photocatalytic degradation of dyes [30]. The major role of the photocatalyst is shown in figure 1.6.

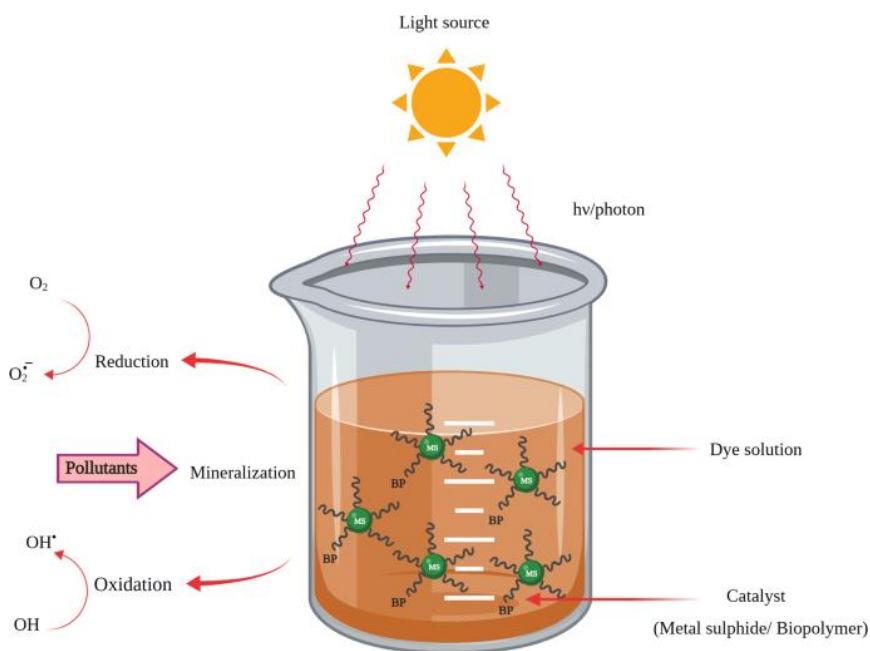


Figure 1.6 Role of photocatalyst [20]

Photocatalytic degradation has gained popularity and is used as a tool for treating dye-contaminated water among a number of treatment methods [31]. Nanoparticles, nanowires, 2D compounds, planar films, 3D porous films, and complex hierarchical nanostructures are just some of the structures and morphologies found in photocatalysts. A variety of implementations have been developed to get the most out of these photocatalysts [32].

1.16 FAST GREEN DYE

Fast green is also called as food green. The molecular formula of fast green is $C_{37}H_{34}N_2O_{10}S_3Na_2$, and its molar mass is 808.85 g/mol. The structure of fast green dye is given below in figure 1.7. In histology and cytology, fast green dye is commonly used. It has been shown to cause tumours in laboratory animals and to cause mutations in both experimental animals and humans. It also has the potential to irritate the pupils, scalp, digestive tract, and respiratory tract in its undiluted form [33].

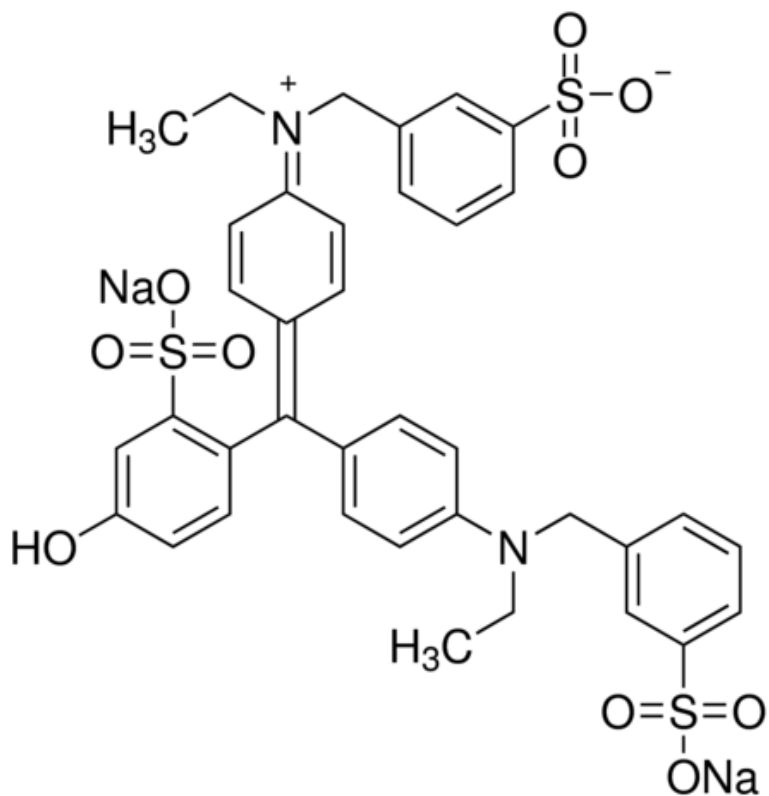


Figure 1.7 Structure of fast green dye

CHAPTER-2

LITERATURE SURVEY

Rishi Prasad, Pravin S Walke and Shekhar D Bhame have synthesised Strontium doped Zinc oxide nanoparticle using co-precipitation and hydrothermal method and studied the optical properties of the synthesised sample using characterization techniques like UV, SEM, FT-IR [34].

Teoh, Lay Gaik, and Kun-Dar Li. have used sol-gel method for the synthesis of NiO nanoparticles in the paper entitled "Synthesis and characterization of NiO nanoparticles by sol–gel method."The inorganic precursor was $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the surfactant was Poly(alkylene oxide) copolymer. The structure of NiO nanoparticles was studied. The microstructure and basic surface area of the samples were analyzed using TGA, XRD, and SEM [35].

Waghmare, Suraj S., Prashant B. Patil, Shiva K. Baruva, Madhuri S. Rajput, Ramesh J. Deokate, and Sarfraj H. Mujawar reported the synthesis of nickel hydroxide as an electrode material for supercapacitors using the hydrothermal method. Hexamethylenetetramine as a directing agent and nickel nitrate as a nickel source. The reaction was carried out for 18 hours at 160°C . The structural, morphological, and electrochemical properties of the samples were investigated [36].

Banerjee, Arghya Narayan, Sang Woo Joo, and Bong-Ki Min adopted sol-gel method for the synthesis of Ga doped anatase TiO_2 nanoparticles and the photocatalytic oxidation of the dye was carried out under UV irradiation. Photocatalytic activity of the nanoparticles came out with nearly 90% degradation efficiency within 3 hours of UV irradiation [37].

Wahab, A., M. Imran, M. Ikram, M. Naz, M. Aqeel, A. Rafiq, H. Majeed, and S. Ali confirmed that Co-precipitation was used to synthesis cobalt and manganese doped iron oxide nanoparticles. Mn and Co were added to Fe_3O_4 nanoparticles, which were then annealed. The cubic structure of Co and Mn-doped Fe_3O_4 was well matched to the JCPDS results. These results revealed that Co-doped magnetite exhibits superior properties than undoped magnetite, making it a promising

candidate for use as a nanocatalyst to replace existing waste water treatment techniques [38].

Rahimi, Rahmatollah, Mohammad Bozorgpour, and Mahboubeh Rabbani synthesized Fe doped NiO nanoparticles using a ball-mill method at room temperature. Under visible light irradiation, the photocatalytic degradation of the organic dye in water was investigated using prepared sample. Results shows that this semiconductor is a strong photocatalyst when exposed to visible light [39].

Rivera-Chaverra, María J., Elisabeth Restrepo-Parra, Carlos D. Acosta-Medina, Alexandre Mello, and Rogelio Ospina adopted laser ablation method was to synthesis the iron oxide nanoparticles by adjusting the laser's strength. DLS and STEM techniques were used to determine the morphology. This analysis revealed that there is an intense competition between the laser energy and the temperature, not only in terms of particle size but also in terms of standard deviation [40].

CHAPTER-3

AIM AND SCOPE OF THE PRESENT INVESTIGATION

3.1 AIM OF THE PRESENT WORK

- To synthesis Nickel oxide and a low temperature based Strontium doped Nickel hydroxide nanoparticle using Co-precipitation method.
- To characterize the synthesised compounds using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infra-red Spectroscopy (FT-IR).
- To study the crystallite structure and size using XRD.
- To study the surface morphology of the synthesised nanoparticle using SEM. and to identify the functional groups on the nanoparticles using FT-IR.
- To employ the synthesised nanoparticle in the application of photodyedegradation of fast green textile dye and to measure and compare their degradation efficiency in fast green dye.

3.2 SCOPE OF THE PRESENT WORK

- Nickel oxide and Strontium doped Nickel hydroxide nanoparticle were synthesised and detailed spectroscopic studies of the synthesised nanoparticles were carried out.
- Photocatalytic test were performed using the synthesised nanoparticles and measured their degradation efficiency in fast green textile dye.
- From the Spectroscopic studies and photocatalytic test, its evident that the synthesised Strontium doped Nickel hydroxide nanoparticle is a potential candidate for the photocatalytic dye degradation of fast green textile dye.

CHAPTER - 4

EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

Pure Nickel oxide and Strontium doped nickel hydroxide nanoparticles, preparation by Co-precipitation method and their material properties have been discussed.

4.1 MATERIALS

All the chemicals used in this experiment were of analytical grade and used without any further purification. Nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were purchased from Merck, Sodium hydroxide pellets (NaOH) was purchased from SRL, Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) was purchased from SRL, Polyvinyl Pyrrolidone (PVP) was purchased from SRL, Ethanol and Acetone were purchased from SRL. All of these solutions were prepared using deionized water.

4.2 EXPERIMENTAL METHODS

4.2.1 SYNTHESIS OF NIO:

Nickel oxide nanoparticles were synthesised by Co-precipitation method by the thermal decomposition of Nickel hydroxide ($\text{Ni}(\text{OH})_2$). About 0.5M of Nickel (II) chloride hexahydrate is taken in a 250ml beaker to which 50ml of deionized water is added. To that mixture 1g of PVP is added, the reason for adding PVP is to reduce the particle size and to prevent agglomeration.

The reaction mixture is stirred in a magnetic stirrer for almost 2 hours at room temperature. The product thus obtained is washed thoroughly with deionized water, to remove all the residues which is followed by washing with acetone. Finally, the sample is dried in air oven at 160°C and then calcinated to 450°C in muffle furnace. When calcinated, the colour of the sample changes from green to black. The resultant thus obtained is the Nickel oxide nanoparticle.

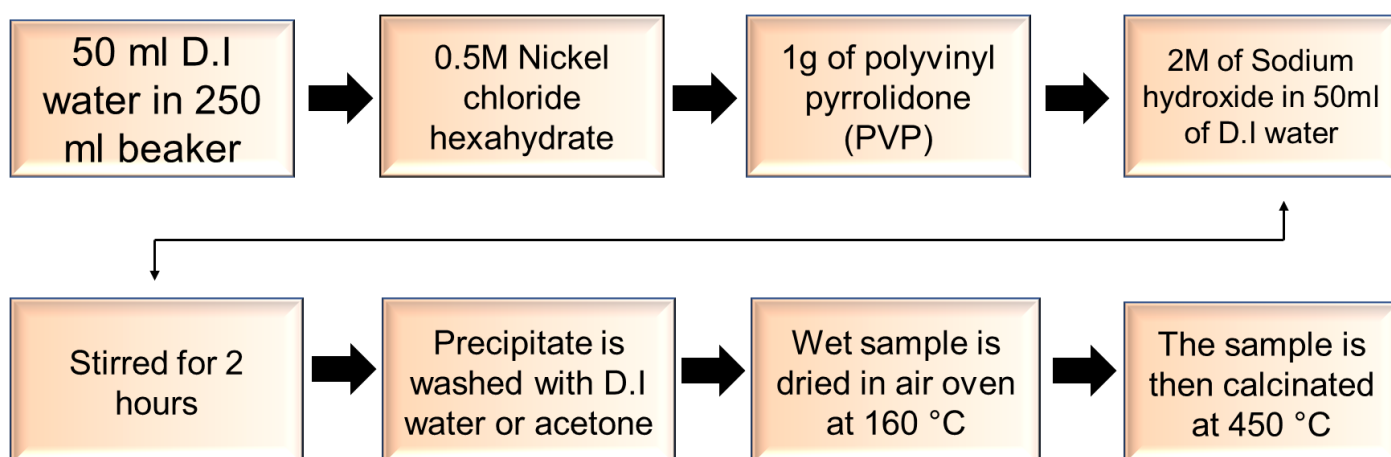


Figure 4.1 Schematic diagram of NiO synthesis

4.2.2 SYNTHESIS OF STRONTIUM DOPED NICKEL HYDROXIDE NANOPARTICLE ($\text{Sr}/\text{Ni}(\text{OH})_2$)

250ml beaker is taken with 50ml of deionized water and to that 0.5M of Nickel (II) chloride hexahydrate and 1g of polyvinyl pyrrolidone are added. To that mixture, 5% of strontium nitrate is added and stirred for 30 minutes in a magnetic stirrer. The temperature was maintained for about 80°C. Then 2M of sodium hydroxide pellets were weighed using a digital balance and was dissolved in 50ml deionized water and it is added drop by drop slowly into the mixture.

As the solution is continuously stirred, the colour of the solution changes from dark green colour to light green. Stirring is continued for almost 2 hours. Then a green coloured precipitate appears at the bottom of the beaker. The precipitate is then washed thoroughly with deionized water and acetone a number of times. Then the precipitate was dried at 160°C in hot air oven. The finally obtained sample is the Strontium doped Nickel hydroxide nanoparticle ($\text{Sr}/(\text{Ni}(\text{OH})_2)$) [32].

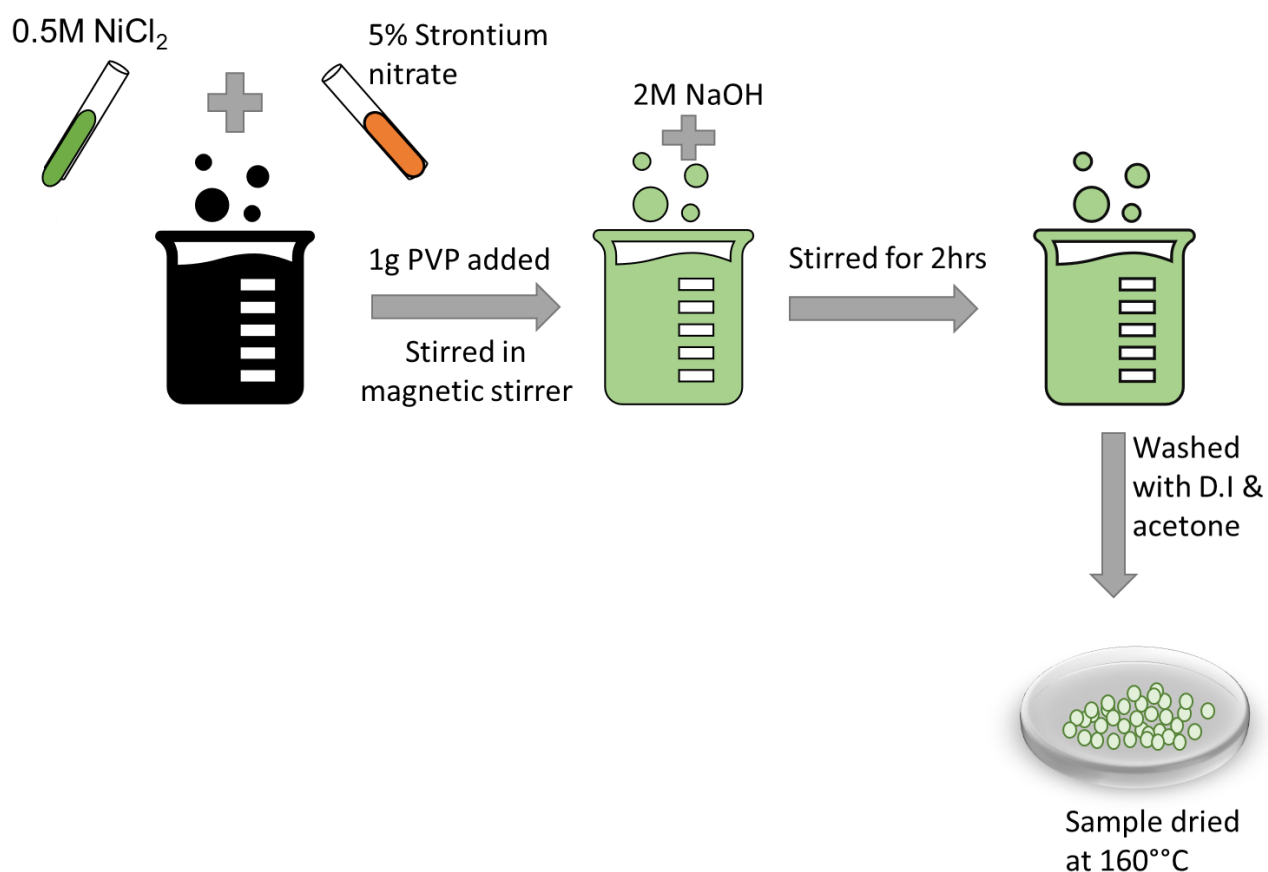


Figure 4.2 Synthesis of Sr/Ni(OH)₂

4.3 CHARACTERIZATION TECHNIQUES

Crystal structure, morphology, compositional information, organic functional groups on the surface and photocatalytic application of the synthesized nanoparticles were characterized using the following instruments. These include X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infra-red spectroscopy (FTIR). These highlighted techniques are presented in this project work. Brief information about the above techniques has been discussed in the following section [41].

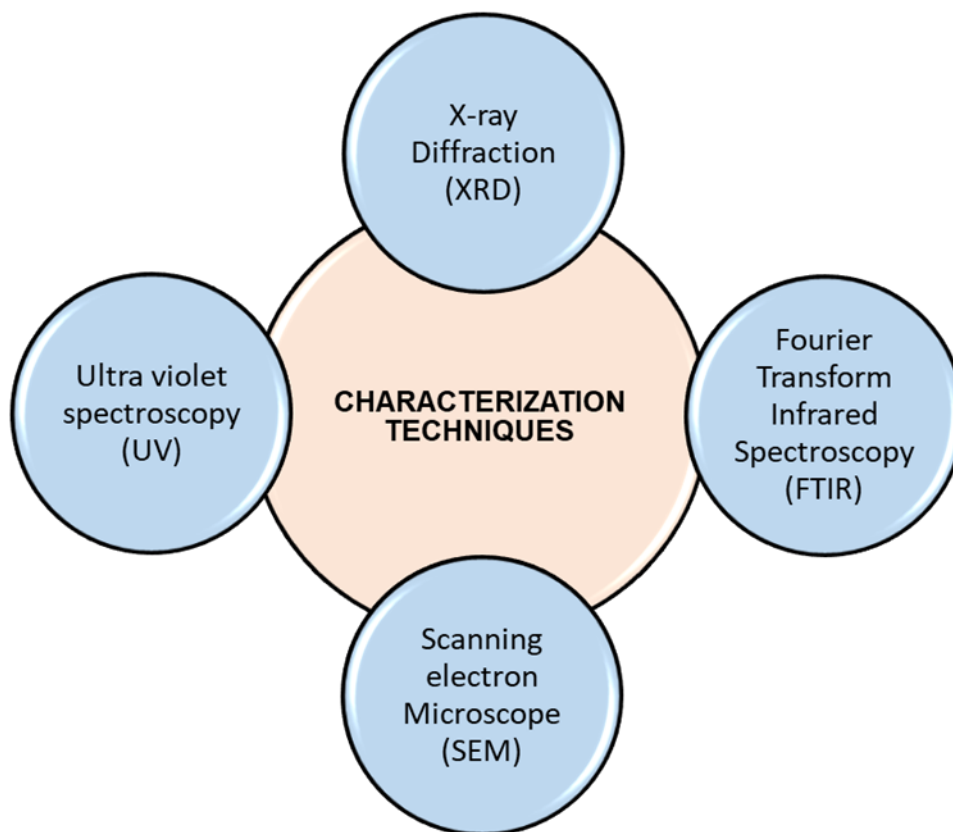


Figure 4.3 Characterization of nanoparticles

4.3.1 X-RAY DIFFRACTION (XRD):

XRD is one such unique technique that reveals the structural properties of nanoparticles. It provides information on the phase, chemical composition, symmetry of unit cells, crystallinity, lattice constant and properties of the nanoparticles. This technique can be used to identify single-phase and multiphase nanoparticles [2-3].

XRD is considered as one of the oldest non-destructive methods for the analysis of nanoparticles. The XRD pattern is influenced by the size and also the shape of the unit cell of the crystal. Consequently, the properties of a material are dependent on their structure. Of about 90% of solid materials are crystalline in nature and each crystalline has a significant X-ray diffraction pattern which can be used as fingerprint to detect the material [2].

Diffraction pattern is obtained only when the X-rays are interacted with the crystal. Information like symmetry of the unit cell, stress, strain, size of crystallite and growth orientation etc. are obtained from the diffraction patterns [2].

When a material is irradiated with a monochromatic light of wavelength around the inter atomic distance of the material, light gets dispersed by the atoms and interfere to give rise to diffracted light with a higher intensity. Intensity of the scattered light is directly proportional to the arrangement of atoms in the material. If wavelength of light is λ and the incident angle is θ and the constructive interference is obtained at an angle 2θ from the incident beam of light if Bragg's equation is satisfied [42].

Bragg's equation is given by,

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

where, n is diffraction order, d is the distance between the diffracting planes and θ is Bragg's angle.

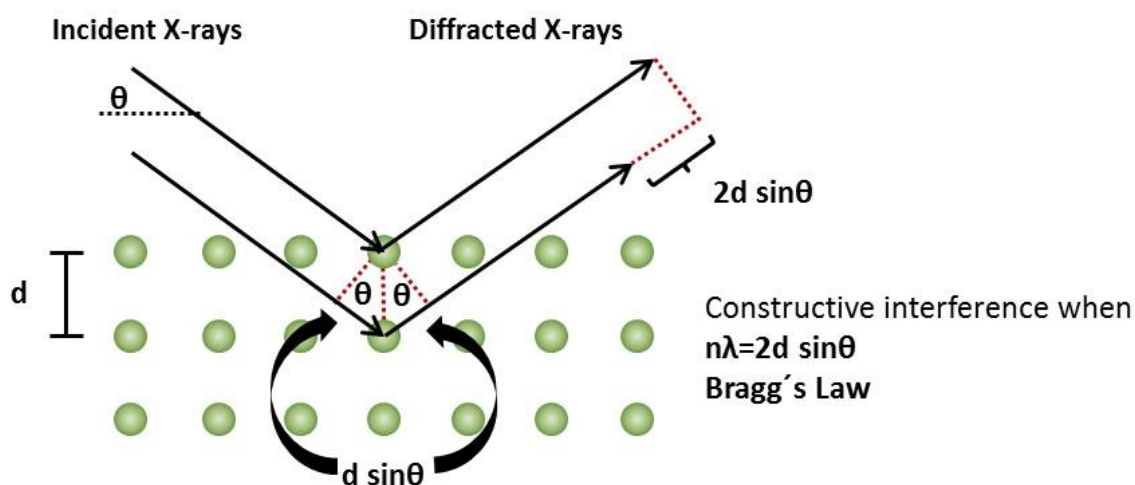


Figure 4.4 Schematic representation of Bragg's Law

Generally, in XRD Cu- $K\alpha$ is the incident light for which the $\lambda = 1.5405$ nm. Distance between the diffracting planes is calculated according to Bragg's equation and indexed by comparing it with the d spacing of the material from the Joint Committee on Powder Diffraction Standards (JCPDS) data.

4.3.2 SCANNING ELECTRON MICROSCOPE (SEM):

High resolution scanning electron microscope (SEM) is very useful for the characterization of size and shape of the nanoparticle. The sample preparation and acquisition of images are relatively easy and convenient. Since the SEM image is a two-dimensional (2D) representation of three-dimensional (3D) structures from a certain viewing angle, it does provide a certain amount of 3D detail that can be used to recreate the shape of a basic structure with sub-nm precision using model-based measurement. Secondary electrons (SEs) and/or backscatter electrons (BSE) produced when the sample is bombarded by the primary electron (PE) beam provide the signal that causes a SEM image to be created. A SEM's overall accelerating voltage is usually 30 kV. The SE has a limited escape depth in the region of a few nm owing to their low energy below 50 eV, while the BSE has a slightly higher escape depth in the range of a few nm [43].

The demand for SEM in laboratories to characterise nanoparticulate materials is increasing because of the application of nanoparticles in the commercial products [44].

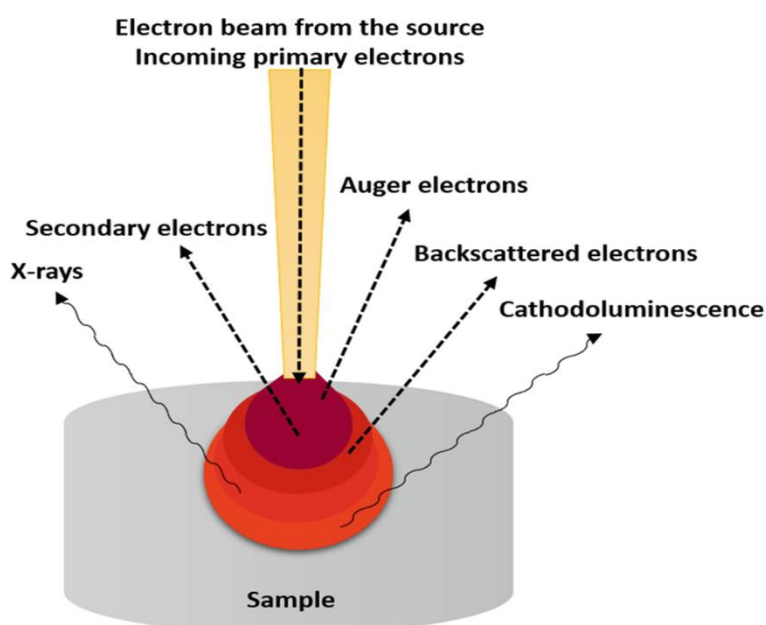


Figure 4.5 Working of SEM

4.3.3. FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR):

Fourier transform infrared (FTIR) spectroscopy is a very efficient non-destructive characterization technique for surface characterization of nanoparticles' surfaces, providing a specific setup is connected to the spectrometer. The chemical structure of the nanoparticles' surface and the surface reactive sites responsible for surface reactivity can be determined under particular conditions [45].

The structure and bands of the synthesised nanoparticles, as well as the stretch of bonds, were revealed by FTIR. FTIR may be used to test a variety of components, including bulk or thin films, liquids, solids, pastes, powders, fibers, and other materials. FTIR analysis may be used for quantitative (amount) analysis as well as qualitative (identification) analysis of materials where appropriate criteria are used. FTIR can test samples up to 11 mm in diameter and weigh in bulk or the top 1 mm of the sample [46].

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

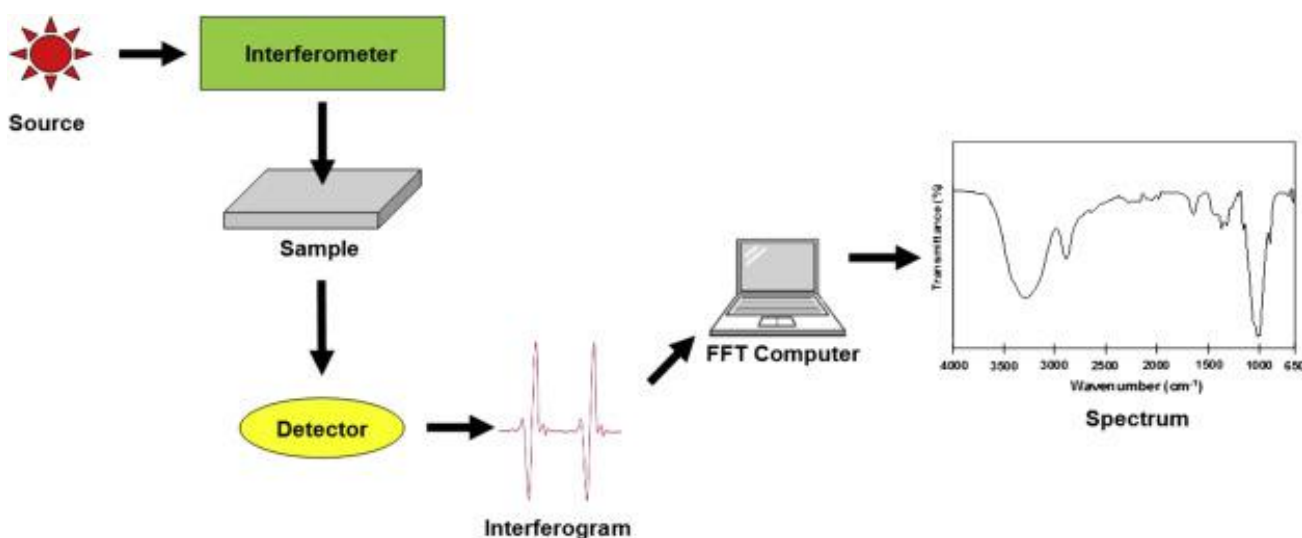


Figure 4.6 Working of FT-IR

CHAPTER-5

RESULTS AND DISCUSSION

Crystal structure, morphology, compositional information, organic functional groups on the surface and photocatalytic application of the synthesized nanoparticles were characterized using the following instruments. These include X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infra-red spectroscopy (FTIR). These highlighted techniques are presented in this project work. Given below figure 5 (a) is the photocopy of NiO which is black in colour and figure (b) is a green coloured sample that shows the presence of Ni(OH)₂. A brief information about the above techniques has been discussed in the following section.



Figure 5.1 (a) NiO Sample



(b) Sr/Ni(OH)₂ sample

5.1 X-RAY DIFFRACTION (XRD)

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

Bragg's equation is given by,

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

where, n is the diffraction order, d is the distance between the diffracting planes and θ is the Bragg's angle.

Generally, in XRD Cu- $K\alpha$ is the incident light for which the $\lambda = 1.5405$ nm. Distance between the diffracting planes is calculated according to Bragg's equation and indexed by comparing it with the d spacing of the material from the Joint Committee on Powder Diffraction Standards (JCPDS) data.

NiO spheres exhibits several well-defined diffraction reflections at 19.01° , 31.72° , 38.63° , 45.458° , 51.97° , 59.21° and 75.18° . The XRD of bare Ni substrate, which shows peaks at 45° , 55° and 75° . The diffraction peaks for NiO are shown in planes of (111), (200), (220), (311) and (222) are shown in Figure 4.1. All these diffraction peaks can be perfectly indexed to the cubic (FCC) crystalline structure of NiO, and also their relative intensity of the characteristic peaks, which is in accordance with the standard spectrum (JCPDS, No. 04-0835).

The XRD pattern reveals that the samples are single phase, with no other diffraction peaks other than the characteristic peaks of the cubic lattice of NiO. This result indicates that the physical phases of NiO nanoparticles are pure, and were prepared and discussed in detail [47].

Strontium doped nickel hydroxide shows peaks at (001), (100), (101), (110), (111), (200) planes.

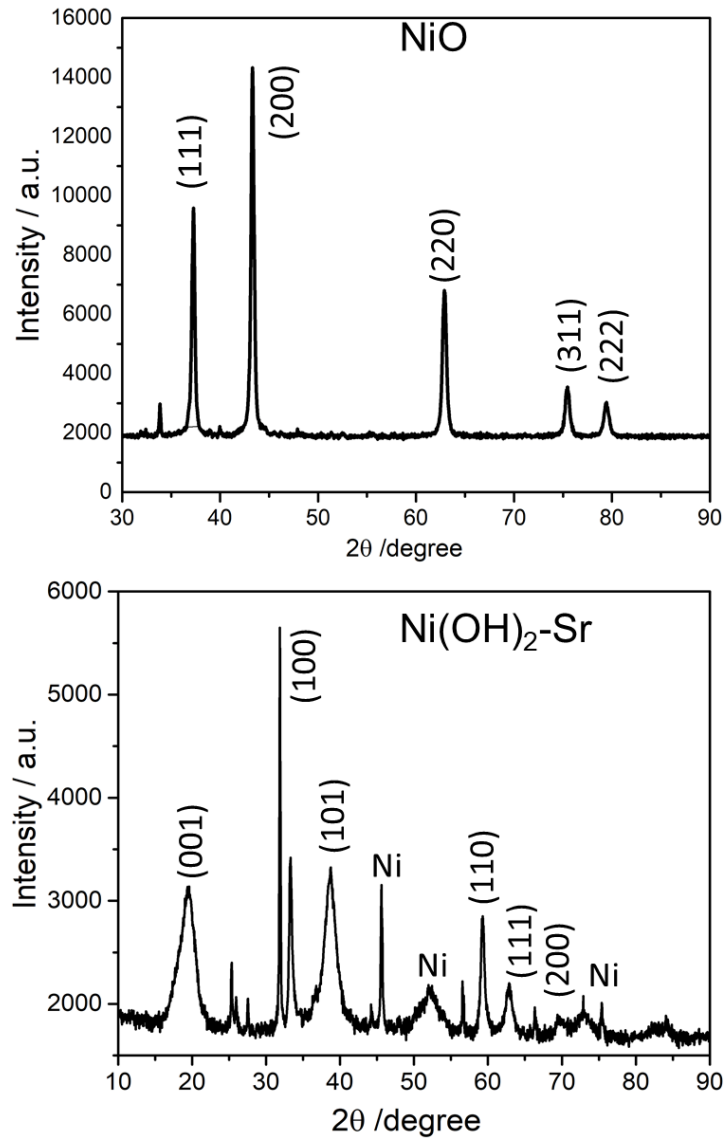


Figure 5.2 XRD peak for NiO and Sr/Ni(OH)₂

The crystallite size of the Strontium doped nickel hydroxide nanoparticle is found out using Debye-Scherrer's formula,

$$D = k\lambda/\beta \cos \theta$$

Where k is the empirical constant which is equal to 0.9, λ is the wavelength of X-ray radiation (1.5405 Å for Cu-K α), β is the full width at half maximum of the diffraction peak and θ is the peak position [17].

The crystallite sizes of Sr/Ni(OH)₂ samples is found to be 8.7 nm which was calculated from the measured values from the data.

5.2 SCANNING ELECTRON MICROSCOPE (SEM)

High-resolution scanning electron microscope (SEM) is excellent for nanoparticle size and shape characterization, because the required sample preparation and image analysis is relatively quick and simple.[48] The scanning Electron Microscopy (SEM) images allowed a detailed study on the morphological structure of the nanoparticles [49].

The scanning electron microscope operates in the same manner as an optical microscope, but instead of detecting photon, it detects electrons scattered from the sample. The wavelength of electrons can be made shorter than that of photons because electrons can be accelerated by an electric potential. As a result, the SEM will magnify pictures up to 200.000 times [50].

The morphological variations in the synthesised sample nanoparticles were detected and analysed. Nickel oxide analysed by SEM is shown in figure 5.3 (a). Sr doped nickel hydroxide nanoparticles thus synthesised at low temperature was analysed and the images are displayed in Figure 5.3 (b).

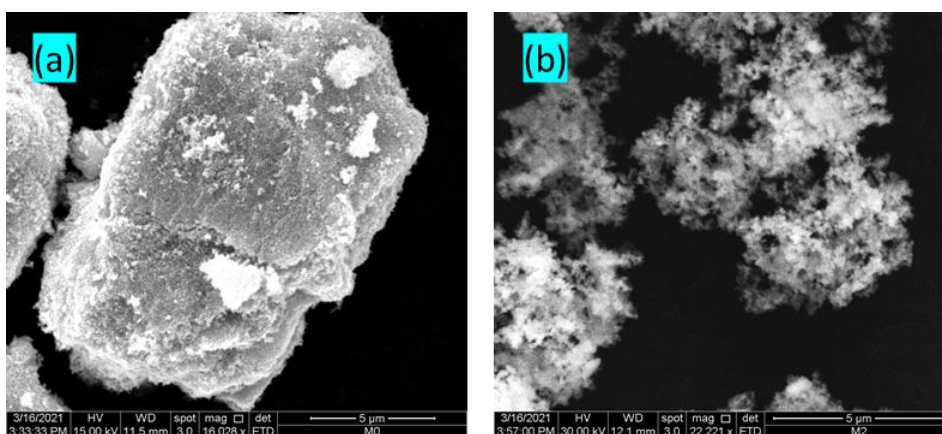


Figure 5.3 (a) Scanning electron microscopy (SEM) image of pure NiO nanoparticles and (b) SEM image of Sr doped Ni(OH)₂ nanoparticles. The SEM images were measured for both the powder samples (NiO and Sr doped Ni(OH)₂). The powder samples were pasted on the carbon tape for measuring the SEM images

Nickel oxide shows high surface energy than the strontium doped nickel hydroxide because it is agglomerated [51].

Compared to pure nickel oxide, strontium doped nickel hydroxide shows finite structures. Results show that the synthesised NiO nanoparticles are smooth, spherical in shape and some are agglomerated as they have high surface area to volume ratio and has less cohesive energy compared to the bulk materials. SEM photographs of strontium doped nickel hydroxide are spherical. Strontium doped nickel hydroxide shows small size compared to the pure nickel oxide due to its high dispersion [52].

When calcinated to higher temperature of about 160°C nickel oxide can be de-agglomerated [53]. The size according to the SEM images of strontium doped nickel hydroxide maybe below 10nm.

5.3 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY:

The FTIR analysis of nickel oxide and strontium doped nickel hydroxide is shown in the figure 5.4 below. The formation of the nanoparticles can be observed from its colour change. The vibrational peak at 3488 cm⁻¹ is due to the O-H stretch and the peak around 578 cm⁻¹ is described as the Ni-O stretching vibration.

The broad absorption band in the region 500-600 cm⁻¹ is the Ni-O stretching vibration. The size of the samples used in this study is less than the bulk forms of NiO. The broad spectrum at 3450 cm⁻¹ is due to the O-H stretching vibrations and a weak band at 1645 cm⁻¹ is the H-O-H bending vibrations [54].

The broad band at 3440 cm⁻¹ is the stretching vibration of water molecules present in the nickel hydroxide nanoparticle. The figure 5.4 (B) shows the peaks of FT-IR of strontium doped nickel hydroxide.

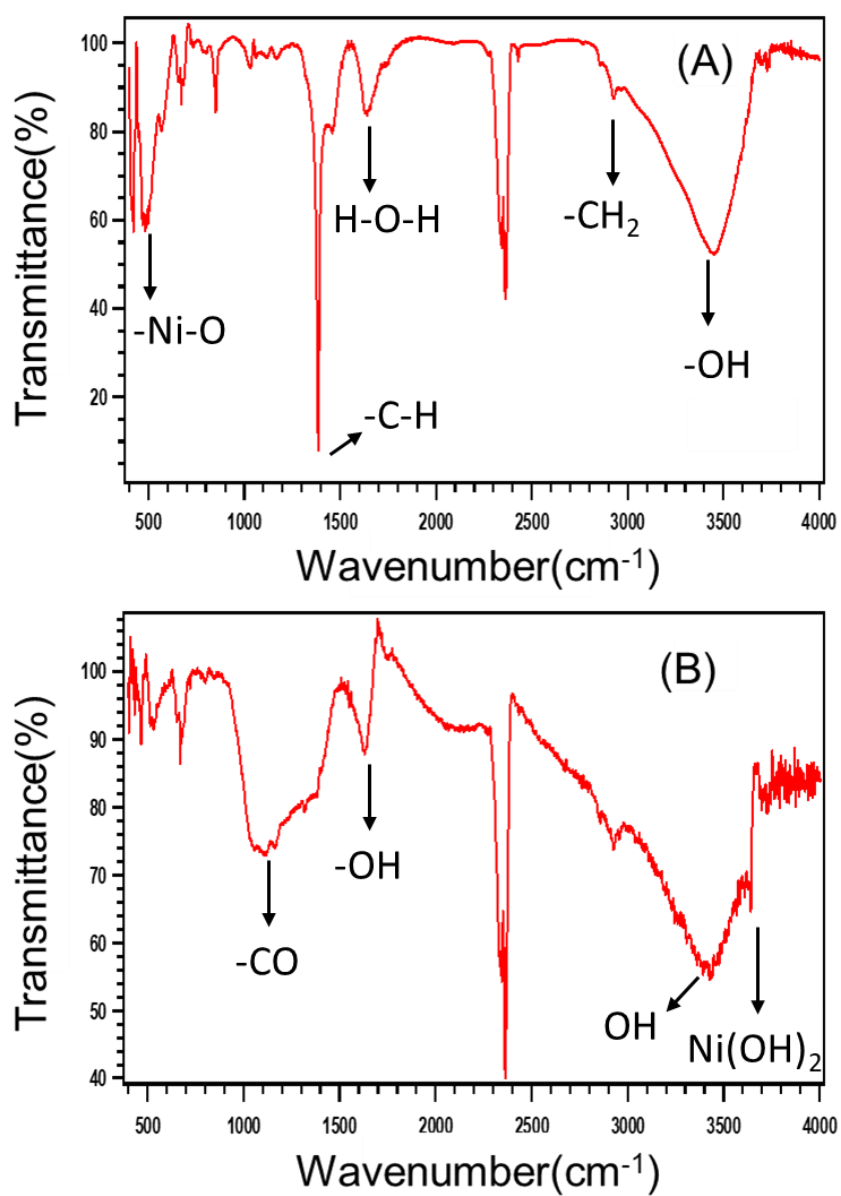


Figure 5.4 (A) FT-IR peak of NiO (B) FT-IR peak of Sr/Ni(OH)₂

5.4 PHOTOCATALYTIC ACTIVITY TEST

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

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

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

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

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

Where, k = rate of reaction constant and t is time. The Photocatalytic dye degradation activity were performed during the well sun shining between 11:00 AM to 2:00 PM in clear sky. The average solar light intensity was measured about $1.00 \times 10^5 \text{ lux}$. Likewise, the effect of some other important operational parameters such as pH of dye solution and catalyst dosage study were performed. In the pH test, dye solution pH was adjusted by the addition of 0.1 M hydrochloric acid solution and 0.1M of sodium hydroxide solution.

5.5 PHOTOCATALYTIC ACTIVITY

The photocatalytic degradation efficiency of as prepared catalysts of NiO, and Sr/Ni(OH)₂ nanoparticles were resolved by the deprivation of FG dye under irradiation of Sun light. When irradiating the FG dye solution, the concentration of the dye was noticeably reduced and it was confirmed by the significant color variation.

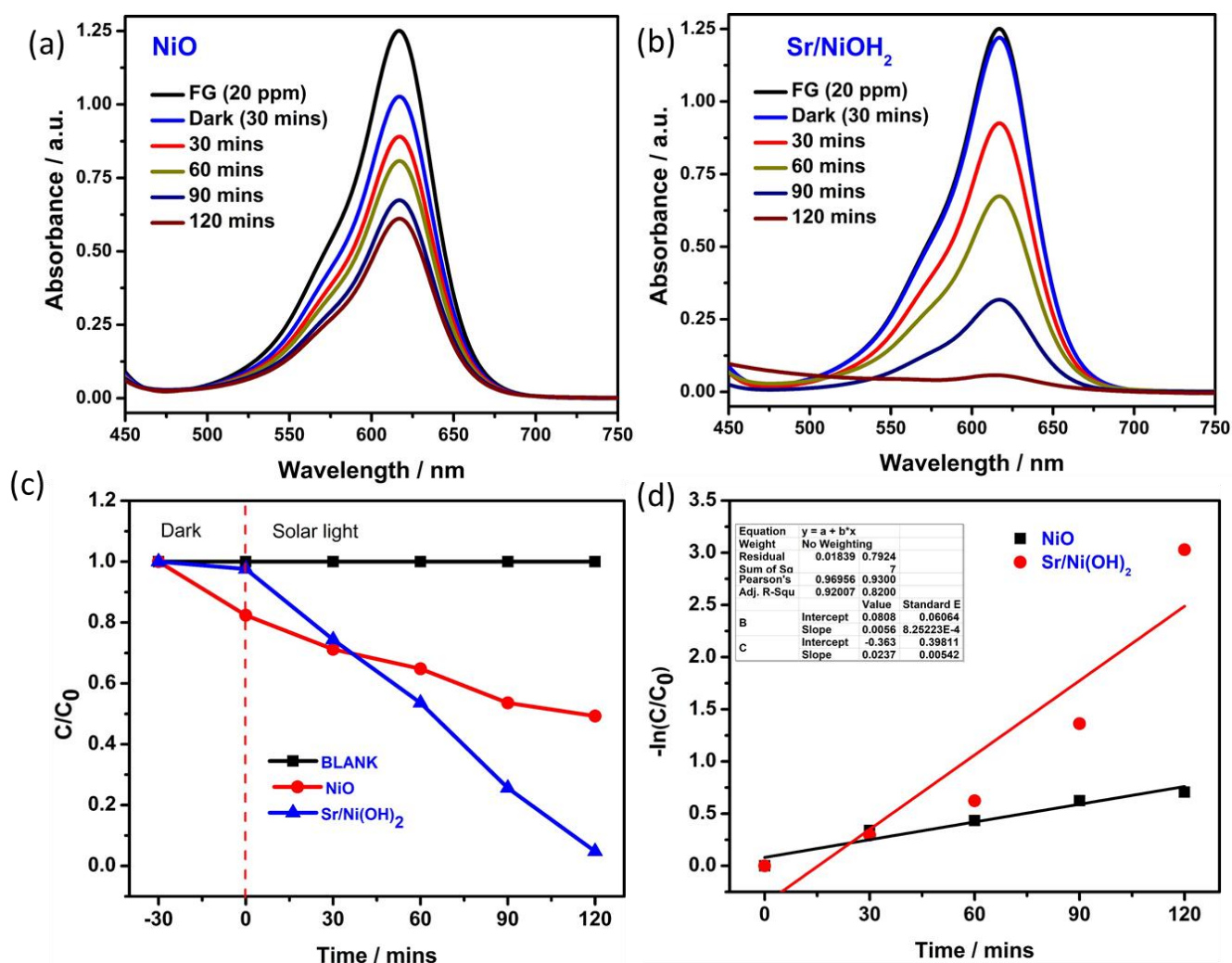


Figure 5.5 (a-b) represents the UV-visible spectra for the FG with occurrence of catalysts NiO, and Sr/ Ni(OH)₂ were irradiated by sun light for 120 minutes. (c) C/C_0 versus time interval plot of FG dye (d) $-\ln(C/C_0)$ versus time interval plot of FG dye

For NiO catalyst, the catalyst influences the organic molecule to achieve the efficiency of about 50.64% within 120 mins. The photocatalyst experiment was further extended to doped samples. The degradation reaction of Sr/ Ni(OH)₂ samples were performed by the same process. The rate of electron-hole pair recombination was delayed by doping the metal ions into the NiO structure results increased the degradation efficiency. Compared to NiO catalyst, Sr/Ni(OH)₂ catalysts reached high efficiency of degradation of 95.2%, respectively [55].

The significant improvement of the degradation efficiency is due to the doping effect of Sr ion at the Ni²⁺ lattice sites, it reduce recombination of excited charge carriers (electron-hole pair).

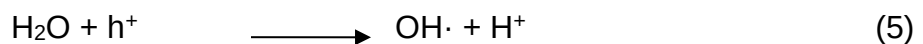
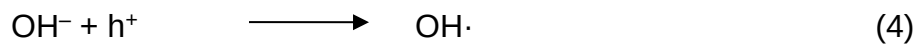
Figure.5.5 c depicts the changes in initial and final concentration of dye in the presence and absence of photocatalyst against the light irradiation with respect to time (t) for the FG dye solution. The Sr/Ni(OH)₂ catalyst shows highest degradation ability due to the fact that sub energy-level act as traps for recombination. Based on the sub energy level of the conduction band helps to produce a large number of reactive oxygen species (ROS). In addition the investigation of pseudo-first order kinetics studies shown in Figure.5.5 d the degradation rates were 0.0112 min⁻¹ and 0.0375 min⁻¹ for NiO, and Sr/ Ni(OH)₂ nanoparticles against FG dye, respectively. From the studies rate constant value and R² values are listed in Table.1. The Figure 5.5 shows schematic diagram illustrating the mechanism of charge separation, generation of reactive oxygen species (ROS) and photocatalytic activity of photocatalyst under sunlight irradiation [56].

The mechanism of FG dye degradation for the Sr/Ni(OH)₂ catalyst is described as follows,

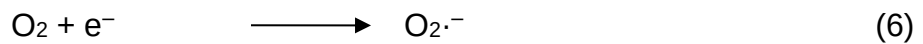
(i) Formation of electron hole pair



(ii) Formation of hydroxyl radicals



(iii) Formation of superoxide radicals



(iv) Photo degradation of crystal violet and rhodamine B dye

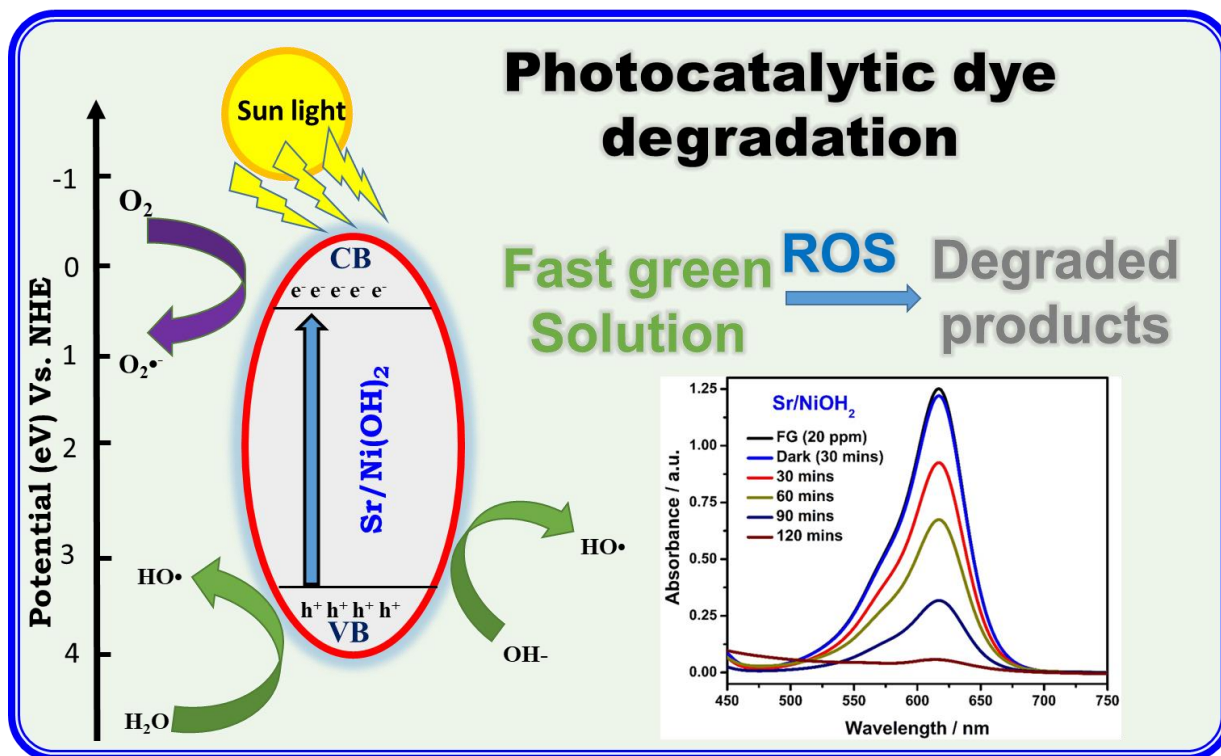


Figure. 5.6 Schematic diagram illustrating the mechanism of charge separation and photocatalytic activity of photocatalyst under the sunlight irradiation

Table 1 Photocatalytic activity result of NiO, and Sr/ Ni(OH)₂ nanoparticles.

S.No	Catalyst	Band gap (eV)	Degradation efficiency (%) (120 minutes)	K (min ⁻¹)	R ²
Fast green (20 ppm)					
1	NiO	3.21	50.64	0.012	0.920
2	Sr/Ni(OH) ₂	2.82	95.2	0.054	0.820

SUMMARY AND CONCLUSION

- Nickel based metal oxides have attracted much attention due to its applications in catalysis, dye degradation, battery cathodes, antiferromagnetic layers, p-type transparent conducting films, and electrochromic films.
- Polyvinylpyrrolidone was used as surfactant to reduce particle size.
- Herein, high temperature based cubic phase of NiO nanoparticles were synthesized. At first, the Ni(OH)_2 was synthesized by chemical precipitation method and then the wet sample was calcinated at 450°C for 4 hours at air atmosphere.
- Low temperature based hexagonal structure of Sr (5%) ion doped Ni(OH)_2 nanoparticles were synthesized using the chemical precipitation method.
- Crystallite structure and size were confirmed by XRD. The size of the crystallite was calculated using Debye Scherrer formula, the size was found to be 14.3 nm and 8.7 nm for NiO and Sr doped Ni(OH)_2 nanoparticles, respectively.
- The SEM microscopy demonstrated the synthesized nanoparticles were in the nanoscale region with a spherical shape.
- Organic functional groups present on the surface of the nanoparticles were identified using FT-IR spectroscopy.
- The investigated photocatalytic result demonstrated that Sr doped Ni(OH)_2 showed excellent dye degradation of Fast green (FG) than the pure NiO nanoparticles due to its effective charge carriers creation and followed by the free radical formation during the light irradiation.
- Thus, the prepared cost effective and low temperature based Sr doped Nickel hydroxide nanoparticle Sr/Ni(OH)_2 could be the suitable candidate for water purification, through the photocatalysis process.

REFERENCES

- [1] Runowski, Marcin. "Nanotechnology–nanomaterials, nanoparticles and multifunctional core/shell type nanostructures." *Chemik* 68, no. 9 (2014): 766-775.
- [2] Ealia, S. Anu Mary, and M. P. Saravanakumar. "A review on the classification, characterisation, synthesis of nanoparticles and their application." In *IOP Conference Series: Materials Science and Engineering*, vol. 263, no. 3, p. 032019. IOP Publishing, 2017.
- [3] Cartaxo, Ana Luísa Pécurto. "Nanoparticles types and properties–understanding these promising devices in the biomedical area." (2010).
- [4] Khan, Ibrahim, Khalid Saeed, and Idrees Khan. "Nanoparticles: Properties, applications and toxicities." *Arabian journal of chemistry* 12, no. 7 (2019): 908-931.
- [5] Bayda, Samer, Muhammad Adeel, Tiziano Tuccinardi, Marco Cordani, and Flavio Rizzolio. "The history of nanoscience and nanotechnology: From chemical–physical applications to nanomedicine." *Molecules* 25, no. 1 (2020): 112.
- [6] Kumbhakar, Pathik, Suprakas Sinha Ray, and Andey L. Stepanov. "Optical properties of nanoparticles and nanocomposites." (2014).
- [7] Akbarzadeh, Abolfazl, Mohammad Samiei, and Soodabeh Davaran. "Magnetic nanoparticles: preparation, physical properties, and applications in biomedicine." *Nanoscale research letters* 7, no. 1 (2012): 1-13.
- [8] Guo, Dan, Guoxin Xie, and Jianbin Luo. "Mechanical properties of nanoparticles: basics and applications." *Journal of physics D: applied physics* 47, no. 1 (2013): 013001.
- [9] Jadhav, S. D., and I. A. Shaikh. "Synthesis of Nanoparticles an Overflow, a Review Article." (2019).
- [10] Krishna, R. Nivesh, R. Gayathri, and Vishnu Priya. "Nanoparticles and their applications-A review." *Journal of Pharmaceutical Sciences and Research* 9, no. 1 (2017): 24.
- [11] Tiquia-Arashiro, Sonia, and Debora Rodrigues. "Application of nanoparticles." In *Extremophiles: Applications in Nanotechnology*, pp. 163-193. Springer, Cham, 2016.

- [12] Fernández-García, Marcos, and José A. Rodriguez. "Metal oxide nanoparticles." *Encyclopedia of inorganic and bioinorganic chemistry* (2011).
- [13] Galstyan, Vardan, Manohar P. Bhandari, Veronica Sberveglieri, Giorgio Sberveglieri, and Elisabetta Comini. "Metal oxide nanostructures in food applications: Quality control and packaging." *Chemosensors* 6, no. 2 (2018): 16.
- [14] El-Kemary, M., N. Nagy, and I. El-Mehasseb. "Nickel oxide nanoparticles: synthesis and spectral studies of interactions with glucose." *Materials Science in Semiconductor Processing* 16, no. 6 (2013): 1747-1752.
- [15] Theivasanthi, T., and M. Alagar. "Chemical capping synthesis of nickel oxide nanoparticles and their characterizations studies." *arXiv preprint arXiv:1212.4595* (2012).
- [16] Ohtani, Bunsho, and Tsukasa Torimoto. "Photocatalysts.", 2016.
- [17] Ameta, Rakshit, and Suresh C. Ameta. *Photocatalysis: principles and applications*. 2016.
- [18].Chiu, Yi-Hsuan, Tso-Fu Mark Chang, Chun-Yi Chen, Masato Sone, and Yung-Jung Hsu. "Mechanistic insights into photodegradation of organic dyes using heterostructure photocatalysts." *Catalysts* 9, no. 5 (2019): 430.
- [19]. Brown, M.A.; De Vito, S.C. Predicting azo dye toxicity. *Crit. Rev. Environ. Sci. Technol.* 1993, 23, 249–324.
- [20]. Chen, S.; Zhang, J.; Zhang, C.; Yue, Q.; Li, Y.; Li, C. Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from *Phragmites australis*. *Desalination* 2010, 252, 149–156.
- [21]. Daneshvar, N.; Salari, D.; Khataee, A.R. Photocatalytic degradation of azo dye acid red 14 in water: Investigation of the effect of operational parameters. *J. Photochem. Photobiol. A Chem.* 2003, 157, 111–116.
- [22]. Ledakowicz, S.; Gonera, M. Optimisation of oxidants dose for combined chemical and biological treatment of textile wastewater. *Water Res.* 1999, 33, 2511–2516.

- [23]. Grzechulska, J.; Morawski, A.W. Photocatalytic decomposition of azo-dye acid black 1 in water over modified titanium dioxide. *Appl. Catal. B Environ.* 2002, 36, 45–51.
- [24]. Haque, E.; Jun, J.W.; Jhung, S.H. Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235). *J. Hazard. Mater.* 2011, 185, 507–511.
- [25]. Shi, B.; Li, G.; Wang, D.; Feng, C.; Tang, H. Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species. *J. Hazard. Mater.* 2007, 143, 567–574.
- [26]. Galindo, C.; Jacques, P.; Kalt, A. Photooxidation of the phenylazonaphthol AO20 on TiO₂ : Kinetic and mechanistic investigations. *Chemosphere* 2001, 45, 997–1005.
- [27]. Aleboyeh, A.; Aleboyeh, H.; Moussa, Y. "Critical" effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: Acid Orange 8, Acid Blue 74 and Methyl Orange. *Dyes Pigments* 2003, 57, 67–75.
- [28]. Ayodhya, D.; Veerabhadram, G. A review on recent advances in photodegradation of dyes using doped and heterojunction based semiconductor metal sulfide nanostructures for environmental protection. *Mater. Today Energy* 2018, 9, 83–113.
- [29] Chaturvedi, Shalini, and Pragnesh N. Dave. "Environmental application of photocatalysis." In *Materials Science Forum*, vol. 734, pp. 273-294. Trans Tech Publications Ltd, 2013.
- [30] Bhati, Indu, Pinki B. Punjabi, and Suresh C. Ameta. "Photocatalytic degradation of fast green using nanosized CeCrO₃." *Macedonian Journal of Chemistry and Chemical Engineering* 29, no. 2 (2010): 195-202.
- [31] Anwer, Hassan, Asad Mahmood, Jechan Lee, Ki-Hyun Kim, Jae-Woo Park, and Alex CK Yip. "Photocatalysts for degradation of dyes in industrial effluents: Opportunities and challenges." *Nano Research* 12, no. 5 (2019): 955-972.
- [32] Yang, Xiaogang, and Dunwei Wang. "Photocatalysis: from fundamental principles to materials and applications." *ACS Applied Energy Materials* 1, no. 12 (2018): 6657-6693.

- [33] Bhati, Indu, Pinki B. Punjabi, and Suresh C. Ameta. "Photocatalytic degradation of fast green using nanosized CeCrO₃." *Macedonian Journal of Chemistry and Chemical Engineering* 29, no. 2 (2010): 195-202.
- [34] Prasad, Rishi, Pravin S. Walke, and Shekhar D. Bhame. "Structural and optical studies on flowerlike strontium doped zinc oxide synthesized by hydrothermal method." *Materials Research Express* 6, no.11 (2019)
- [35] Teoh, Lay Gaik, and Kun-Dar Li. "Synthesis and characterization of NiO nanoparticles by sol–gel method." *Materials Transactions* 53, no. 12 (2012)
- [36] Waghmare, Suraj S., Prashant B. Patil, Shiva K. Baruva, Madhuri S. Rajput, Ramesh J. Deokate, and Sarfraj H. Mujawar. "Hydrothermal synthesis of β -Ni (OH)₂ and its supercapacitor properties." In *AIP Conference Proceedings*, vol. 1942, no. 1, p. 140059. AIP Publishing LLC, 2018.
- [37] Banerjee, Arghya Narayan, Sang Woo Joo, and Bong-Ki Min. "Photocatalytic degradation of organic dye by sol-gel-derived gallium-doped anatase titanium oxide nanoparticles for environmental remediation." *Journal of Nanomaterials* 2012 (2012).
- [38] Wahab, A., M. Imran, M. Ikram, M. Naz, M. Aqeel, A. Rafiq, H. Majeed, and S. Ali. "Dye degradation property of cobalt and manganese doped iron oxide nanoparticles." *Applied Nanoscience* 9, no. 8 (2019): 1823-1832.
- [39] Rahimi, Rahmatollah, Mohammad Bozorgpour, and Mahboubeh Rabbani. "Synthesis of Fe-doped Nickel oxide nanostructures via a simple mechanochemical route and its application for photocatalytic removing of MB." In *17th International Electronic Conference on Synthetic Organic Chemistry*. 2013.
- [40] Rivera-Chaverra, María J., Elisabeth Restrepo-Parra, Carlos D. Acosta-Medina, Alexandre Mello, and Rogelio Ospina. "Synthesis of Oxide Iron Nanoparticles Using Laser Ablation for Possible Hyperthermia Applications." *Nanomaterials* 10, no. 11 (2020): 2099.

[41] Sarkar, Shrabana, Nidia Torres Ponce, Aparna Banerjee, Rajib Bandopadhyay, Saravanan Rajendran, and Eric Lichtfouse. "Green polymeric nanomaterials for the photocatalytic degradation of dyes: a review." *Environmental Chemistry Letters* (2020): 1-12.

[42] Kumar, P. Vijaya, A. Jafar Ahamed, and M. Karthikeyan. "Synthesis and characterization of NiO nanoparticles by chemical as well as green routes and their comparisons with respect to cytotoxic effect and toxicity studies in microbial and MCF-7 cancer cell models." *SN Applied Sciences* 1, no. 9 (2019): 1-15.

[43] Vladár, András E., and Vasile-Dan Hodoroaba. "Characterization of nanoparticles by scanning electron microscopy." In *Characterization of Nanoparticles*, pp. 7-27. Elsevier, 2020.

[44] Hodoroaba, Vasile-Dan, Steffi Rades, T. Salge, Johannes Mielke, Erik Ortel, and R. Schmidt. "Characterisation of nanoparticles by means of high-resolution SEM/EDS in transmission mode." In *IOP Conference Series: Materials Science and Engineering*, vol. 109, no. 1, p. 012006. IOP Publishing, 2016.

[45] Baraton, Marie-Isabelle, and Lhadi Merhari. "Dual contribution of FTIR spectroscopy to nanoparticles characterization: surface chemistry and electrical properties." In *Nanomaterials Synthesis, Interfacing, and Integrating in Devices, Circuits, and Systems II*, vol. 6768, p. 676806. International Society for Optics and Photonics, 2007.

[46] Preetha Devaraj, Prachi Kumari, Chirom Aarti, and Arun Renganathan, Synthesis and Characterization of Silver Nanoparticles Using Cannonball Leaves and Their Cytotoxic Activity against MCF-7 Cell Line; Journal of nanotechnology, 2013

[47] Qiao, Hongxia, Zhiqiang Wei, Hua Yang, Lin Zhu, and Xiaoyan Yan. "Preparation and characterization of NiO nanoparticles by anodic arc plasma method." *Journal of Nanomaterials* 2009 (2009).

[48] Vladár, András E., and Vasile-Dan Hodoroaba. "Characterization of nanoparticles by scanning electron microscopy." In *Characterization of Nanoparticles*, pp. 7-27. Elsevier, 2020.

- [49] Halder, Mita, Md Mominul Islam, Pritam Singh, Anupam Singha Roy, Sk Manirul Islam, and Kamalika Sen. "Sustainable Generation of Ni (OH) ₂ Nanoparticles for the Green Synthesis of 5-Substituted 1H-Tetrazoles: A Competent Turn on Fluorescence Sensing of H₂O₂." *ACS omega* 3, no. 7 (2018): 8169-8180.
- [50] Hashem, Manal, Elias Saion, Naif Mohammed Al-Hada, Halimah Mohamed Kamari, Abdul H. Shaari, Zainal Abidin Talib, Suriati B. Paiman, and Mazliana A. Kamarudeen. "Fabrication and characterization of semiconductor nickel oxide (NiO) nanoparticles manufactured using a facile thermal treatment." *Results in physics* 6 (2016): 1024-1030.
- [51] Heera, P., and S. Shanmugam. "Nanoparticle characterization and application: an overview." *Int. J. Curr. Microbiol. App. Sci* 4, no. 8 (2015): 379-386.
- [52] Srihasam, Saiganesh, Krishnan Thyagarajan, Mallikarjuna Korivi, Veeranjaneeya Reddy Lebaka, and Siva Pratap Reddy Mallem. "Phytogenic generation of NiO nanoparticles using Stevia leaf extract and evaluation of their in-vitro antioxidant and antimicrobial properties." *Biomolecules* 10, no. 1 (2020): 89.
- [53] Yang, Chun-Chen. "Synthesis and characterization of active materials of Ni (OH) ₂ powders." *International Journal of Hydrogen Energy* 27, no. 10 (2002): 1071-1081.
- [54] Kovalenko, Vadym, and Valerii Kotok. "The popcorn effect": obtaining of the highly active ultrafine nickel hydroxide by microwave treatment of wet precipitate." (2018): 12-20.
- [55] Sun S, Zhang Y-Chao, Shen G, Wang Y, Liu X, Duan Z, Pan L, Zhang X, Zou J-Jun, Photoinduced Composite of Pt decorated Ni(OH)₂ as Strongly Synergetic Cocatalyst to Boost H₂O Activation for Photocatalytic Overall Water Splitting, *Applied Catalysis B: Environmental* 243 (2019) 253-261.
- [56] Kumar DR, Ranjith KS, Nivedita LR, Asokan K, Rajendra Kumar RT Swift heavy ion induced effects on structural, optical and photo-catalytic properties of Ag irradiated vertically aligned ZnO nanorod arrays. *Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms* 450 (2019) 95–99.