

**GREEN SYNTHESIS, CHARACTERIZATION,
MODIFICATIONS AND APPLICATIONS OF ZINC
OXIDE NANORODS**

By

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in Physics**

CERTIFICATION

This is to certify that this thesis has been read and approved as meeting the requirements of the Department of Physics, University of Ilorin, Ilorin, Nigeria for the award of Ph.D. degree.

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DEDICATION

This research work is dedicated to God Almighty, “who calleth those things which be not as though they were”. Also, to my wife, ADELEKE Abigail Olasumbo and my children especially, Inioluwa who were deprived fatherhood time for the research.

DECLARATION

I, ADELEKE, Joshua Toyin hereby declare that this thesis entitled “Green Synthesis, Characterization, Modifications and Applications of Zinc oxide nanorods” is a record of my research work. It has neither been presented nor accepted in any previous application for a higher degree. All sources of information have been specifically acknowledged.

In addition, the research work has been ethically approved by the University Ethical Review Committee.

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ABSTRACT

The demand for clean energy and clean water is becoming challenging issues having been greatly influenced by human's lifestyle and the growing world population. Nanotechnology offers promising solution through the applications of nanomaterials. The orthodox methods of synthesizing nanomaterials are expensive and generate hazardous toxic chemicals. Green method route of synthesis has become an alternative to overcome such limitations. This research work therefore aimed at synthesising a multifunctional zinc oxide nanorod through green principle route of synthesis. The objectives were to: (i) synthesize *Mangifera indica* leave extract-mediated zinc oxide nanorods (ZnO NR); (ii) synthesize spinel nickel ferrite nanorods (NF NR); (iii) modify the ZnO NR with NF NR by calcination to obtain a nickel ferrite-zinc oxide nanocomposite; (iv) characterize the synthesized nanostructures for structural, elemental composition, functional groups, morphological and optical studies using X – Ray Diffractometer XRD, Fourier Transform Infrared (FTIR), Energy Dispersive X-ray Spectrometer (EDX), Scanning Electron Microscope (SEM), UV-VIS Spectrophotometer, and Photoluminescence (PL) spectroscopy respectively; (v) examine the applications of the synthesized nanostructures for dielectric studies, solar cell nanocoating, biosensing, photodegradation and treatment of both domestic and industry waste water.

Green principle route of synthesis was used for the synthesis of zinc oxide nanorods. The zinc oxide nanorods (ZnO NR) were modified with spinel nickel ferrite nanorods (NF NR) by calcination both at 850 °C for ten hours to obtain zinc oxide-nickel ferrite (ZnO/NF) nanocomposite. Both unmodified and modified ZnO NR were characterized and examined for applications in dielectrics, solar cell nanocoating, glucose sensing, photodegradation and waste water treatment.

The findings of this research work showed that:

- (i) ZnO NR have been synthesized by green synthesis route and had been successfully modified with nickel ferrite nanorods synthesized by coprecipitation method.
- (ii) the dielectric constant ϵ' of the green synthesized ZnO NR is very high (750) with capacitance value of 0.78 pF. Its dielectric loss ϵ'' , dielectric loss angle, σ decreases with increasing frequency and then reaches a constant value, hence a good dielectric.
- (iii) the fill factor of a silver solar cell coated with the green synthesized ZnO NR by drop-casting method was enhanced showing improved solar cell efficiency up to 5%.
- (iv) the modified ZnO NR was successfully used as a biosensor for glucose.
- (v) the photocatalytic studies reveal that the ZnO/NF nanocomposite exhibits high degradation efficiency under UV light and that $\bullet\text{OH}$ and photoproduced holes h^+ are the main species in the removal of the organic dyes solution.
- (vi) for the treatment of domestic and industrial waste water, the green synthesized ZnO NR showed 93.95% and 93.95% of chemical oxygen demand (COD) reduction in 75 minutes.

This research work concluded that green synthesis route is suitable for the synthesis of ZnO NR, appropriate modification of which makes it multifunctional. It is recommended that, green synthesis method should be adopted for the synthesis of ecofriendly, cost effective and multifunctional ZnO NR.

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LIST OF ABBREVIATION AND NOTATIONS

IS	Impedance Spectroscopy
AC	Alternating Current
CVD	Chemical Vapour Deposition
DC	Direct Current
EHT	Electrical High Tension
FTIR	Fourier Transform Infrared
FWHM	Full width half maximum
FWHM	Full-Width Half Maximum
ICDD	International Center for Diffraction Data
JCPDS	Joint Committee for Powder Diffraction Standard
LASER	Light Amplification by Stimulated Emission of Radiation
LCR Bridge	Inductor-Capacitor-Resistor Bridge
LED	Light Emitting Diode
MB	Methylene Blue
CR	Congo red
RB	Rhodamine B
NPs	Nano-Particles
PVD	Physical Vapour Deposition
EDX	Energy Dispersive X-ray
SEM	Scanning Electron Microscopy
SILAR	Successive Ionic Layer Adsorption and Reaction
TCO	Transparent Conducting Oxide
TSO	Transparent Semiconductor Oxide
UV-vis spec	Ultraviolet Visible Spectrometry

XRD	X-Ray Diffractometry
NF	Nickel Ferrites
ZnO	Zinc Oxide
ZnO NR	Zinc oxide nanorods
ZnO NPs	Zinc oxide nanoparticles
NF NR	Nickel ferrites nanorods
ZnO/NF	zinc oxide / nickel ferrites nanocomposites

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

As valuable and important as clean water is to life, the major challenge to it is pollution. Water pollutants such as dyes and other organic pollutants, takes their source as waste water from industries; like: agro allied, leather, textile, photography, printing, and painting companies. These water pollutants are environmentally hazardous to the lives of microorganisms, aquatic animals and man. Another challenging issue which had been greatly influenced by people's lifestyle and the growing world population is Energy. Nanotechnology offers promising solutions through various applications of several nanomaterials. Nanomaterials are the nanostructures at the nanoscale precision – one – billionth of a meter, that is, dimension of nearly 1-100 nanometers. The nanometer scale is the molecular and atomic scale (Raj *et al.*, 2005). This is the scale range at which quantum effects takes over the physicochemical properties and behaviour of the material. In the nanoscale range, materials' properties showed size dependency. Nanomaterials have unique physicochemical properties which are significantly associated with their sizes (Nalwan, 2007). Sanvicens and Marco (2008) cited in Child (2012), gave a list nanomaterial properties to include: fluorescence, conductivity and resistivity, melting point, magnetic, chemical properties, optical, mechanical, structural properties.

Taking the advantages of the numerous properties of nanomaterials, they are applied in several areas and fields of life from life sciences, physical sciences, medical diagnostics,

drug delivery, computers, cosmetics, electronics, sensors, photo catalysts, and renewable energy especially, solar cell applications.

The removal of carcinogenic, toxic organic dyes and other pollutants (inorganic or organic) from contaminated water had led researchers into development of some methods which include; ion exchange, precipitation, sorption and reverse osmosis (Yong, *et al.*, 2016). Many nanomaterials such as graphene, alumina, silica gel and poly-materials have been used as sorbents for the treatment of polluted water. Hence nanomaterials are promising photocatalysts and sorbents for water treatment or purification.

In the area of energy applications, nanomaterials have been considered useful to have safe, efficient, cost effective and stable energy supply than fossil fuels. Nanomaterials play significant roles in lighting e.g Light emitting diodes (LED), power chips, energy storage, batteries that are more powerful and more durable. Num and Useh (2013), researched on the applications of nanomaterials in the therapeutics and diagnostics of veterinary to enhance heat production quality. Nanomaterials and nanoproducts have been used to improve health care services in medical and pharmaceuticals for diagnostics, drug delivery, implants and prostheses.

At nanoscale, among several transparent metal oxide semiconductors, zinc oxide (ZnO) is very promising because of its desirable properties which include wide energy band gap of 3.2 eV, inexpensive, abundance in nature, piezoelectricity, optical transparency, anti-reflectance sensing, electrical conductivities sensitivity, photocatalytic, low toxicity, the ratio of large surface to volume, chemical stability, and appreciable refractive index (Aneesh, *et al.*, 2007). ZnO nanostructures are materials for several applications such as solar cells, absorbance layers, transparent electrodes in touch panels, absorbents, additives in lubricants, ceramics, chemical sensors, photocatalysts, health care – drug delivery, anti-cancers, anti-bacterials and optoelectronic devices.

For better stability and more desirable qualities and properties, ZnO nanostructures are modified by doping or functionalization with metals, metal oxides or organic molecules depending on the desired application. Surface modifications of ZnO nanostructures produce highly sensitive, reflective and photocatalytic materials. A combination of dopants could significantly modify ZnO nanostructure properties appreciably (Auzans, *et al.*, 1999).

Various techniques are utilized by researchers to synthesize and deposit ZnO nanostructures. These include metal organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE), sputtering, hydrothermal, sol-gel, solvothermal, chemical bath deposition, electrochemical deposition and green synthesis (Nehru *et al.*, 2012). Among all these methods, green synthesis routes are the most beneficial. This is because the materials for green synthesis – plant (leaf) extracts, is relatively abundant in nature, hence the method is cost effective. Being natural, it is environmentally safe and compatible for biomedical and pharmaceutical applications.

This study reports the successful synthesis of zinc oxide nanorods (ZnO NRs) from the extract of mango leaves (*Mangifera indica*) and its modifications with spinel nickel ferrite nanorods (NiFe₂O₄ NR) synthesised by co-precipitation method. The modification was done to obtain zinc oxide–nickel ferrite (ZnO/NiFe₂O₄) nano-composite for better optical bio sensing and catalytic enhancement of the green synthesised ZnO NRs. The modified ZnO NRs were applied for the photodegradation of methylene blue (MB), Rhodamine B (RB) and congo red (CR) organic dyes. Further, it was used for the treatment of domestic and industry wastewaters, respectively collected from Kalasalingam University, Talmil Nadu, India and Sree Arumugham Surgicals, Virudhunagar, Tamilnadu, India. It was also used for Solar cell nano coating for solar cell efficiency enhancement and for sensing glucose.

1.2 Statement of the Problem

Increasing growth rate of world population and societal modernization have led to notable multifaceted challenges, which include attaining clean environment, water and energy. Nanotechnology has potential of ameliorating these concerns through its various applications. Nanomaterials are widely used in myriads of applications in several areas and fields of studies. Nanomaterials have applications in the detection, prevention, and even removal of pollutants (Lee *et al.*, 2005). Metal oxide nanostructures like – ZnO, TiO₂, Fe₂O₃, have been proved suitable photo catalyst for the removal of organic dyes (Nwanya *et al.*, 2015). Thus, highly potent, economical, stable, and environmental friendly photocatalysts in nanostructure forms, have found applications through nanotechnology and Nano semiconductors.

Solar cell surface modifications are considered necessary to improve efficiency and that at lower cost. A light absorbing coating can enhance efficiency significantly (Gholizadeh *et al.*, 2017) and ZnO nanostructure are also used for passivation as Anti Reflection Coatings (ARC). Among several methods of synthesising these nanostructures, the highly efficient, cost effective and ecofriendly is the green synthetic routes. Hence, the need for the study on green synthesis of zinc oxide nanorods, modification of which enhances its performance in several applications.

1.3 Motivation and Justification for the Study.

Long *et al.*, (2014) opined that among the basic needs of the modern society, are water and energy. Almost all appliances small or big from agrarian communities to the industrial communities are powered by electricity, the demand of which is far greater than the supply of fossil fuel and other non-renewable energy sources. To this electric power challenge, nanotechnology offers a cost effective stable sustainable solutions by producing electricity from sunlight through the development of photovoltaic solar cells made from

sustainable nanomaterials. Clean water is another major challenge to life and global ecosystem pollutants coming as waste water from various industries and agro allied companies. These pollutants are a threat to man and aquatic life. Many different methods have been used in the last decades to remove water pollutants. Such methods include biological chemical means, sedimentation and adsorption, notwithstanding their limitations. Out of all these methods, the most efficient, ecofriendly and cost effective is photocatalysis. Cheap and stable photocatalyst for the removal of water pollutants found their routes through nano-semiconductors such as nanostructured metal oxides in the likes of; titanium dioxide (TiO_2), zinc oxide (ZnO), ferrites (Fe_2O_3), cadmium sulphide (CdS), cadmium oxide (CdO), zinc sulphide (ZnS). ZnO is given priority due to its desirable properties – high energy band gap, non-toxic, oxidation resistance and photonic (Lai, *et al.*, 2011).

Zinc oxide nanostructures have been synthesized through various methods- physical, wet chemical, biological and green. Synthesizing through green is cheap, clean to the environment and relatively simple compared to other methods (Ravichandran, *et al.*, 2014). Hence, this work aims at synthesis of zinc oxide nanorods through green method, and modify it to obtain a unique nanocomposite – nickel ferrites/zinc oxide ($\text{NiFe}_2\text{O}_4/\text{ZnO}$) for applications in solar cell nanocoating, waste water treatment and optical biosensor.

1.4 Aim and Objectives of the Study

The aim of this study is to synthesize zinc oxide (ZnO) via green synthetic route and modify it for possible enhancement in applications for waste water treatment, solar cell nanocoating, dielectrics and sensing. Hence, the specific objectives of this research work were to:

- i. synthesize zinc oxide nanorods (ZnO NRs) and nickel ferrites nanorods (NiFe_2O_4 NRs) through green method and co-precipitation method respectively.

- ii. modify the green synthesized zinc-oxide nanorods (ZnO-NRs) with nickel ferrites nanorods (NiFe_2O_4 -NRs).
- iii. characterize both unmodified and modified ZnO-NRs for elemental, structural, morphological, optical, electrical and dielectric properties.
- iv. apply the synthesized ZnO nanorods for waste water treatment, enhancement of solar cell efficiency through nanocoating and optical biosensor for glucose.

1.5 Scope and Limitation of the Study

This research work has been limited to green synthesis, modification, characterization and a few applications of the modified zinc oxide nanorods.

1.6 Contribution to Knowledge

Zinc oxide (ZnO) nanorods have been synthesized via green method and used for solar cell nanocoating to give solar cell efficiency enhancement. Impedance spectroscopic studies have also been carried out on the green synthesized zinc oxide (ZnO) nanorods for dielectric applications. Also, in this research work, the green synthesized ZnO nanorods have been modified with spinel nickel ferrite (NiFe_2O_4) nanorods to give zinc oxide-nickel ferrite ($\text{ZnO}/\text{NiFe}_2\text{O}_4$) nanocomposite.

The $\text{ZnO}/\text{NiFe}_2\text{O}_4$ nanocomposite was used for photodegradation of some organics dyes which include: Congo Red (CR); Rhodamine B (RB); and Methylene Blue (MB). Further, it was used for the purification of domestic and industrial wastewater. The $\text{ZnO}/\text{NiFe}_2\text{O}_4$ nanocomposite was further used as an optical biosensor for glucose. Hence, this research work has added a nanomaterial that is cost effective and ecofriendly for applications in solar cell nanocoating, waste water treatment and optical biosensor. Thus, this study has shown that it is possible to use green synthetic route, which is cost effective, less

toxic, ecofriendly, abundant in nature, for the synthesis of zinc oxide nanocomposite that can be used for several applications.

CHAPTER TWO

2.0 REVIEW OF RELATED LITERATURE

2.1 Nanotechnology

Nanotechnology is a broad science where embedded in it are various fields including: materials science, biology, physics, engineering and chemistry, have shared interest at the nanoscale. The advent of nano-sized materials had begotten a world of potentialities and possibilities in a variety of industrial and scientific research endeavours. This term ‘Nanotechnology’ does not have a single, generally accepted definition. To the Russian Corporation of Nanotechnologies (RUSNANO), nanotechnology is a complex of methods and techniques that are used to research, analyse, design and produce materials, devices or systems which enables structure management and object-oriented control, chemical composition as well as interaction of their components at nanoscale (at dimensions of bellow or up to 100 nm), resulting in the improvement and development of consumer characteristics and products parameters.

In the opinion of National Nanotechnology Initiative (NNI) of U.S., nanotechnology is defined as the understanding and manipulations of matter at nanoscale dimensions (from 1 to 100 nanometers), in which relatively unique phenomena enhances novel applications in technology. It comprises of nano-sciences, engineering and advance technology as well as simulation and modelling, imaging, measuring, and manipulation of matter at nanoscale. One nanometer is $\frac{1}{1,000,000,000}$ of one meter. The thickness of a single sheet of paper is nearly one hundred thousand nanometers; the diameter of an atom of gold is around $\frac{1}{3}$ of one nanometer. This dimension – within 1 and 100 nanometers (nm) is called the nanoscale range. Unique

and special properties (– biological, chemical, and physical) usually surface in materials at this nanoscale. These properties significantly distinguishes bulk materials properties from that of single atoms and molecule in many important ways.

In their own opinion, Raj *et al.*, (2005) defined nanotechnology as the process of making, modifying, characterizing, and applying structures of materials, devices or systems by controlling and manipulating their sizes and shapes at the nanoscale so as to obtain specially unique and novel materials with superior properties. Summarily, Nanotechnology involves harnessing the unique physico-chemical properties as well as the biological properties of nanostructured substances having novel and new useful ways. The promising values of nanotechnology, economically and environmentally has birthed the experienced huge governmental and non-governmental investments globally. Almost every facet of life has been influenced by nanotechnology. These include: nanoparticles functionalized paints; nano-coated drug delivery systems in medicines; nano-fibres textiles for UV protection, wound healing and stay-clean clothing; non-toxic preservative, protective and contamination free packaging for food and agro halide industries; self-cleansing and self-healing aerospace materials for aviation and automobile industries and nanocomposites materials for applications in construction companies. (Bassett, 2006; Uriguiga, 2000).

2.2 Historical Background of Nanotechnology

The first mention of the term “nanotechnology” had been in connection with Mr. R. Feynman, the Californian professor, who described nanotechnology as a method of controlling or manipulating individual atoms and molecules to obtain smaller sets continuously down the scale. That was the first time to imagine the possibility of manufacturing nano-scaled products using atoms as building blocks. Hence, Feynman is

sometime referred to as father of nanotechnology. N. Taniguchi was the first person to introduce the word “nanotechnology” into the world of science in 1974 in an international conference with a focus on industrial production in Tokyo. This was done while he was describing the super-thin materials processing at the accuracy of nanometre scale range.

Generally, nanotechnology deals with structures of the sizes less than or equal to 100 nm and involves the development of materials and devices which are at that size range. Nanotechnology has three major elements which are:

1. Nanostructured materials exhibit uniquely special physical and chemical properties and functions, that are not easily scaled outside the range of nanometers.
2. Nanotechnology gives room for the manipulations and control of matter to enable it manifest the required properties and functions.
3. Very wide and various applications of nanomaterials permit the integration of almost every field of science, be it basic sciences, engineering, biotechnology, medicine and pharmacy, agriculture etc.

2.3 Nanostructured Materials

Particles that have dimensions between 1 and 100 nanometers drastic and novel characteristic features which are significantly different from those of bulk materials. In fact, nanometer range is the precision in which quantum effects modify the functions and properties matter. This shows the size-dependent properties of materials which are nano-scale precision. Hence, when the dimensions of particles are at nanoscale, their physical, chemical, optical as well as magnetic properties change with particle size as a determinant factor.

An explicit, simple and vivid experiment shows the phenomenon why nano-materials have large surface areas. By illustration, using a cube of a solid material which has 1 cm on a side to obtain 6 cm^2 of surface area,

$$1 \text{ cm}^3 = 6 \text{ cm}^2 \text{ surface area}$$

$$= 60 \text{ cm}^2 \text{ surface area (using cubes of 1 mm on a side} = 10^3)$$

$$= 6 \text{ m}^2 \text{ surface area (assuming cubes of 1 micrometer on a side} = 10^{12})$$

$$= 6,000 \text{ m}^2 \text{ surface area (with cubes of 1-nanometer on a side} = 10^{21})$$

Thus, the total surface area of just one cubic centimeter (cm^3) of a cube of nanoparticles give a total surface area which is one-third ($\frac{1}{3}$) bigger than a football pitch! The illustration is shown in figure 2.1. Nanoparticles have many unique and advantageous chemical and physical properties inherently associated with their size (Nalwa, 2007). Sanvicens and Marco have listed these properties as optical, magnetic, catalytic, thermodynamic and electrochemical (Sanvicens and Marco, 2008 cited in Child, 2012).

Nano materials are primarily materials that are size and dimensionally characterized. They are substances which are in the range of one nanometer, that is one- billionth of a meter (10^{-9}m). The uniqueness of these nanomaterial are evident in their properties which gives them applications in several facets of life. The unique properties of nano-scaled materials include optical, magnetic, electric, structural, chemical, physical properties mechanical properties. This is because, at nanoscale, surface to volume ratio becomes very significant. Also, quantum effects take over the normal properties and characteristics of the materials. Nanostructured materials are in use in many available commercial products – textiles, anti-uv protecting textiles, cosmetics, paints, sensors of various types, self cleaning solar cell, self healing earo materials, electronics and opto-electronics.

2.4 Categories of Nanomaterials.

Materials in nanophase exist in various forms, sizes and dimensions and are therefore classified according to:

- i. Dimensionality Siegel
- ii. Nanometer- sized structure
- iii. Bulk solids with a nanometer-scale free energy microstructure.
- iv. Equilibrium and non equilibrium

2.4.1 Siegel's Classifications of Nanomaterials

Siegel (1994), classified nanostructure substances (based on dimensionality) into four categories, viz: zero dimensional, one dimensional, two dimensional and three dimensional nanomaterials. The zero dimensional nanomaterials include clusters of atoms, filaments and cluster assemblies, nanopores and nano-particles. The one dimensional layered or laminated structures of nanomaterials include multilayers e.g layered or laminated, two dimensional such as ultrafine grained overlayers and buried layers, and three dimensional are nanophase such as equiaxed crystallites. Gleiter (2000) classified nanomaterials into three categories: materials under devices that have reduced dimensions. They are usually in form of isolated, supported (suspensions or coatings), or embedded nanoparticles or thin films. These find their applications as catalysts or semiconductor devices. The second category are nanomaterials or devices that are limited to very thin surface section of a bulk material. Example of these are quantum dots on nanowires. These have applications in high integrated circuits, memories of terabit, electron transistors, and quantum computers. The third class consists of bulk solids which have nanometer scale microstructures, these are solids whose crystallites lengths varies within a few nanometer scale all through the bulk. Based on the free energy of nanomaterials, they are also classified into equilibrium and non-equilibrium nanomaterials.

Gleiter (2000), described non equilibrium nanomaterial as consisting of heterogeneous ID crystallites of building blocks separated by boundary regions. They are characterised by chemical composition, atomic structure, shape and size which may be identical or different. Boundary region is another distinguishing microstructural feature for

non equilibrium nanomaterials. Vivid example of this is the nanocrystalline nickel (Ni powder). Nanomaterial can also be classified into polymeric and non-polymeric based on their chemical composition. Semicrystalline polymers consist of crystallites and interfacial regions of same chemical composition e.g Cu. The polymeric nanomaterials are made from high molecular weight polymer-long, flexible molecular chains. The crystallisable or amorphous of a tactic polystyrene blocks are examples of a block copolymer.

2.5 Transparent Conducting Oxides

Transparent conducting oxides (TCO) are materials that are transparent in the visible region and reflecting in the infrared region of the electromagnetic spectrum (Lam *et al.*,2008) TCO have been given considerable attention over the years due to their application prospects in the field of LCD (Liquid Crystalline Display). Due to their promising properties like good electrical conductivity as well as large transmittance in the visible region, TCO have direct applications in opto-electrical devices like as solar cells and flat panel. Such transparent conducting oxides include: Tin doped indium oxide (ITO), metallic doped SiO₂ and ZnO (Crissy *et al.*,2007).

2.6 ZnO Nanostructure

Zinc Oxide (ZnO) is one of the group II-IV semiconductors that has unique and fascinating characteristic features which include, direct and wide energy band gap of 3.37eV at ambient temperature. Other unique properties of Zinc Oxide nanostructure are its high exciton and binding energy of about 60 meV at ambient temperature, its radiation hardness, it is bio-safe, piezoelectric, biocompatible, photoelastic. Zinc Oxide nanostructure is very stable at room temperature, it has bipolar crystallographic planes giving it higher c-axis growth rate. Zinc Oxide nanostructures shared three main identified crystal structures, Viz; the wurtzite,

zinc blende and the rock salt. Zinc oxide is a multifunctional metal oxide semiconductor which finds has many applications in antireflection coatings, sensors, electrodes for solar cells, piezoelectric transducers, photo catalysts, optoelectronics, drug delivery uv-protection and medical applications. In this study, zinc oxide nanorods were modified with nickel ferrites and the result nanocomposite were used for dielectric studies, solar cell nanocoating, glucose sensing, photodegradation of organic dyes and further used for the purification of domestic and industry waste water.

Metal oxides have large number of atoms which are responsible for their attracting characteristic properties including antibacterial, antiviral, antifungal, magnetic, electrical and photo-catalytic activities (Ayyakannu *et al.*, 2015). Thus, metal oxide nanoparticles play significant roles have become a focus of study in the area of nanoscience research and management as an emerging field nanotechnology (Roopan *et al.*, 2014). The choice of ZnO nanoparticles (NPs) for this research work may be attributed to its various area of applications in several fields such as electronics, opto-electronics, medical, biological, environmental as well as in antimicrobial activities (Maryanti *et al.*, 2014).

Zinc oxide (ZnO) has highly stable mechanically and thermally and also has high radiation hardness (Burlacu *et al.*, 2008). Structurally, ZnO has a wurtzite structure similar to that of GaN (Özgür *et al.*, 2005), which makes it a useful nanomaterial in high performance optoelectronic devices. Undoped and doped zinc oxide nanoparticles have many attracting properties, such as, high transparency in the visible region and high reflectivity in the infrared region (Ismail *et al.*, 2001), excellent piezoelectrical properties (Liu, *et al.*, 2005), hexagonal wurtzite structure n-type conductivity (Natsume, *et al.*, 2000), etc. All these good properties give them wide area of applications in several fields, such as, transparent conductors, solar cells (Chen *et al.*, 2005), electrical, piezoelectric or luminescent devices and also as gas sensors, chemical sensors, surface acoustic wave devices (Wang *et al.*, 2015), UV laser and

catalysts. Several researchers have studied extensively on the photodegradation of organic pollutants by semiconductor catalysts, the results of which had been positive on the purification of waste water (Kaneva *et al.*, 2011).

The ZnO nanostructure is among the semiconducting materials that belongs to the space group P63. In the visible region of the electromagnetic spectrum, ZnO has high transparency, good absorbing and light trapping properties. Also, it is environmentally safe being less toxic, economically effective because of its relative abundance in nature, and a good photocatalysis due to its good optical properties (Mallika *et al.*, 2014). Thus ZnO Nanoparticle is a major role player in toxicity processes as it inhibits the immune cells (Roy *et al.*, 2015).

ZnO nanoparticles have gained attentions of nanomaterials scientists due to its novel properties such as such as unique semiconducting properties, special antibacterial, antiviral and antifungal properties, as well as its UV filtering, photo catalytic, and wound healing properties (Ramesh *et al.*, 2014 and Elumalai *et al.*, 2015). Other physic-chemical properties of zinc oxide nanoparticles include its direct and wide energy band gap of 3.4eV at ambient temperature and its high exciton binding energy of 60 meV (Mohammad *et al.*, 2009). Moreover, among other transparent semiconducting metal oxides like calcium oxide (CaO) and magnesium oxide (MgO), ZnO nanoparticles had been reported as having strong resistance against microorganisms (Tamanna *et al.*, 2015). The amazing functions and applications of zinc oxide nanoparticles have been attributed to reactive oxygen as the photo generated species from the surfaces of these metal oxides (Nagajyothi *et al.*, 2014). Zinc oxide have amazing application in diagnostics, biomolecular detection, micro electronics (Gunabalan *et al.*, 2015).

2.6.1 Types of ZnO – n type and p-type ZnO

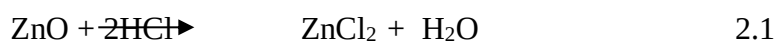
The two major types of zinc oxide are the n - type and p – type. When zinc (Zn) in the zinc oxide is substituted with group three elements like aluminium (Al), gallium (Ga), or indium (In), or when the oxygen is substituted with group VII elements like chlorine or iodine, then n – type zinc oxide is obtained (Kato, 2002). Due to the inhomogeneity of P – type ZnO, doping of ZnO remains difficult and its measurement is intrinsically complex (Ohgaki, 2008).

2.6.2 Properties of ZnO

Zinc oxide appears in white powdery form. It is an inorganic compound. In materials science, ZnO is often referred to as group II-VI semiconductor. The ZnO powder has many applications in materials industries for products like plastics additives, ceramics, glass, cements, rubbers, lubricants, paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants, first aid tapes etc (Hernandez *et al.*, 2008).

2.6.3 Chemical Properties of ZnO

When crystalline ZnO is heated, it changes its colour from white to yellow and on cooling in air, it reverts back to white. Zinc oxide is amphoteric and slightly soluble in both water and alcohol, but readily dissolves in most acids (Wilberg and Holleman, 2001).



Soluble zincates are obtained from the reactions of zinc oxide with bases or alkalai.

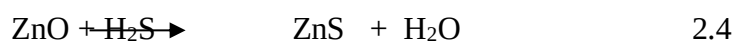


The reactions of ZnO with fatty acids and oil produces the corresponding carboxylates. When reacting with a strong aqueous solution of ZnCl₂ or phosphoric acid, it forms a phosphoric cement-like product (Zn₃(PO₄)₂.4H₂O which is useful in dentistry.

At a temperature of about 1975 °C, ZnO decomposes into zinc (Zn) vapour and oxygen only. This is a prove of its stability. The reaction of ZnO with carbon is a reduction reaction, reducing the metal oxide to the metal.



Violent reactions, fire or explosion Hazard may be caused when a mixture of ZnO reacts violently with the mixture of aluminium (Al) and magnesium (Mg) powders, chlorinated rubber and linseed oil are heated. ZnO reacts with hydrogen sulphide to give the zinc sulphide (hence used as a deodorant)



2.6.4 Physical Properties of ZnO

ZnO crystallizes exists in three forms, viz: hexagonal (Wurtzite), Cubic (Zinc blende), and the cubic (Rock salt) which is seldom observed at high pressures of about 10GPa (Ozgur *et al.*, 2005). The lattice constants are $a=3.25\text{\AA}$ and $c = 5.2 \text{\AA}$ their ratio $c/a = 1.60$ which is in the range of the ideal hexagonal cell $c/a = 1.633$. The Zn – O bond in ZnO is highly ionic, which explains its strong piezoelectricity: thus it has many piezoelectric uses such as various pressure transducers, acoustics and acoustic-optical devices (Singh, 2010; Dal *et al.*, 1994).

2.6.5 Optical and Electrical Properties of ZnO

Zinc oxide has direct and wide energy band gap of 3.3 eV which is large enough transmit most of the useful solar radiation (Buba *et al.*, 2010). The transparency of ZnO in the visible and near-ultraviolet region of electromagnetic spectrum is high. It has high conductivity and changes under photo reduction / oxidation environment (Mondal *et al.*, 2008). ZnO is an n-type, transparent and wide band gap semiconductor ($E_g = 3.2 \text{ eV}$), the large exaction binding energy of 60 MeV at ambient temperature. The electrical conductivity of ZnO is attributed to its defects that are both intrinsic and extrinsic. Former defects of ZnO

(like excess Zn at the interstitial point in the absence of oxidation) aids its conductivity. Thin films of pure ZnO has high sensitivity to oxidation. Absorption of oxygen in the ZnO thin films tends to decrease its electrical conductivity. Like many extrinsic semiconductor, dopants plays significant roles on ZnO electrical conductivity. Doping of ZnO with several and different dopants, enhances its electrical properties by extrinsic defects. Moreover, varying annealing temperatures under reducing environments and doping conditions modify the electrical properties of ZnO nanostructures (Kumpika *et al.*, 2007). The novel properties of ZnO - optical and electrical properties gave it a variety of applications, especially in solar cell nano coating, self-healing and self-cleaning nanomaterials, sensors of different types, UV photo detectors and bulk wave resonators.

2.6.6 Zinc Oxide Nanocomposites

Nanocomposites are nanomaterials which that incorporate various nanoscaled particles into a matrix of standard material. Nanocomposites are obtained from the addition of different nanoparticles in specified proportions which modifies drastically and improve the properties of the starting materials. Such properties include mechanical strength, malleability, corrosion hardness, toughness, elasticity, thermal, electrical and electrochemical conductivity. The effectiveness of the nanoparticles is such that the amount of material added is normally only between 0.5 and 5% by weight. Nanocomposites can dramatically improve properties like: Mechanical properties including, strength, modulus and dimensional stability, Electrical conductivity, Decreased gas, water and hydrocarbon permeability, Flame retardancy, Thermal stability, Chemical resistance, Surface appearance, Optical clarity (AZO Nano). Recently nanocomposite materials have become one of the most extensively studied material all over the world as they have shown to possesses several technological application such as effective quantum electronic devices, magnetic recording materials sensors etc. Moreover nanocomposite material composed of conducting polymers & oxides have open

more field of application such as drug delivery, conductive paints, rechargeable batteries, toners in photocopying, smart windows, etc (Ganesh, 2012).

Zinc oxide nanoparticles tend to aggregate, owing to a large surface area and high surface energy (Hong *et al.*, 2009). For applied systems, the homogenous dispersion of nanoparticles in the different matrices is necessary. In order to prevent nanoparticle aggregation and improve dispersion, a number of novel synthetic approaches have been developed. Recently, the fabrication of inorganic nanoparticles in nanofibular materials has merited substantial attention because of their significant potential applications in the fields of catalysts, electronic nanodevices, optoelectronics, sensors, and nanocomposites bioresources (Azizi *et al.*, 2013).

ZnO nanoparticles can be used as part of organic/ inorganic nanocomposite coatings in numerous industrial sectors, including food, textiles, packaging, environmental, health care, and medical care. ZnO nanoparticles have been incorporated with methyl cellulose (MC) (Perez *et al.*, 2013), starch, acrylic binder, alginate, chitosan, and polyimide (Nafchi *et al.*, 2013) to show strong antibacterial activity, dielectric properties, and UV absorbance (Jinxia *et al.*, 2016). The physical size of the host polymer and the embedded particles of the composite are both in the submicrometer or nanometer range, so that the typical large surface area of nanofiber materials and nanoparticles is maintained. Furthermore, these nanocomposites have been proven to have both the advantages of polymers (such as being lightweight, flexible, and moldable) and of inorganic particles such as special functionality, high strength, and thermal stability (Wang *et al.*, 2015).

2.7 Synthesis Approaches

There are two main approaches to the synthesis of nanomaterials as propounded by Feynman (1959). They are; “Bottom Up” and “Top Down” approaches. In “Bottom Up” approach, the finished products (larger structures) are obtained from small building blocks

which are produced and assembled. Here, the determinant factors or variable parameters are crystallinity, chemical composition, morphology, and grain size,. The synthesis routes suitable for this are the wet-chemical methods. In “Top Down” approach, large materials are modified to produce smaller ones. Appropriate synthesis methods for this include: mechano-chemical method, mechanical methods, lithography, etching technology, etc. The major reason for the dramatic changes in the properties of materials at nano scale is due to increase in surface to volume ratio. Hence, the basis for synthesis routes which are commonly done in any of these three phases. Viz; Liquid-phase synthesis, Gas-phase synthesis and Vapour-phase synthesis.

2.7.1 Synthesis at the Liquid-Phase

Under liquid - phase synthesis, the methods usually employed are: Co-precipitation, Sol-gel, Micro-emulsions, Hydrothermal/Solvo-thermal, Microwave, Sono-chemical Synthesis, and so on.

2.7.2 Synthesis at the Gas-Phase

This involves vapourizing a material to super-saturation to form the background gas, after which the gas is cooled. Here, the precursors could be solids, liquids or vapours. If solids, the methods adopted for synthesis include; inert gas condensation, pulsed laser ablation, spark discharge generation, and ion sputtering. If the precursors are liquid or vapour, commonly used methods are; chemical vapour synthesis (CVD), spray pyrolysis, photochemical synthesis, thermal plasma methods, low-temperature reactive methods.

A few methods of synthesizing ZnO nanostructures are discussed here, being the basis for the choice method for this research work - Green synthesis route.

2.8 Synthesis Routes of Zinc Oxide Nanostructures

Literature is replete with several synthesis routes for zinc oxide nanostructures. One of the first synthesis method of crystals of metals and their alloys is gas condensation. Tissue and Yuan (2003) had earlier on reported in gas phase condensed Cu^{3+} : Y_2O_3 Nano phosphorous. The demerits of gas condensation method include very slow processes, incompatibility of precursor, high temperature for the formation of gas phase.

Chemical Vapour Deposition (CVD) is another technique of depositing nanostructures. It is modified to deposit metal oxide where the precursors may involve organic materials and in such ease of metal-organic or organo-metallic precursor, the method is called metal-organic chemical vapour deposition (MOCVD) or organometallic vapour-phase epitaxy (OMPVE). Several other researcher had investigated and reported the synthesis and deposition of ZnO nanostructures by MOCVD especially with plasma enhanced (Kim *et al.*, 2010). Ataev *et al.*, (2001) reported the crystal growth of ZnO by VPE using hydrogen gas as the carrier. Here, the zone for evaporation was kept at 170°C a pressure of 133Pa setting the flow rate to 40ml/min.

Several other methods have been employed by various researchers to obtain ZnO nanoparticles of different shapes, sizes and spatial structures. These methods include; vapour deposition, sol-gel process precipitation, hydrothermal, emulsions and mechanochemical processes. Nanostructured materials can have significantly different properties, depending on the chosen fabrication route. Each method offers some advantages over other techniques while suffering limitation from the others. Green principle method of synthesis is the focus of this research work.

2.9 Biosynthesis of Nanoparticle Using Plant Extracts

Plant extracts have been reported as reducing, capping and stabilizing agents for the biosynthesis of nanomaterials such as zinc oxide, gold and silver nanoparticles. Kora *et al.*, (2010) reported the synthesis of mono-dispersed silver nanoparticles with spherical shape and sized 3 nm using gum kondagogu (non-toxic polysaccharide, an exudate obtained from the bark of *Cochlospermum gossypium*). They suggested that carboxylate and hydroxyl groups were involved in complexation and bioreduction of silver ions into nanoparticles. This method is compatible with green chemistry principles as the gum serves a matrix for both bioreduction and stabilization of the synthesized nanoparticles. Due to the relative abundance in nature and cost effectiveness of plant derived biopolymer, green synthesis method could be adopted for large scale production of stable monodispersed nanoparticles. These nanoparticles were reported to have potential and effective antibacterial properties against *Bacillus cereus* and *S. aureus*. In another study, Manjunath and Venkataraman, (2010) reported the green synthesis of silver nanoparticles with an average size of 57 nm from 10 ml of *Moringa oleifera* leaf extract and 90ml of 1mM aqueous of AgNO₃, heated at 60–80 °C for 20 min. The nanoparticles obtained had antimicrobial activity against pathogenic microorganisms, which include *S. aureus*, *Candida tropicalis*, *K. pneumoniae*, and *C. krusei*. It has also been reported by Kumar *et al.*, (2010) that green synthesized silver nanoparticles (~20 nm) from natural extracts of *Eucalyptus citriodora* and *Ficus bengalensis* loaded with cotton fibers had very good antibacterial activities against gram-negative *E. coli* bacteria. These fibers have potential applications in burn/wound healing and in antibacterial textiles and finishings. The leaf extracts of *Garcinia mangostana* had been reported as reducing agent in the synthesis of silver nanoparticles. The aqueous silver ions when exposed to leaf extract were reduced and silver nanoparticles with an average size of 35 nm were obtained.

2.10 Green Synthesis of ZnO Nanostructures

To overcome the limitations and negative impacts of the orthodox methods of synthesizing nanostructured materials, researchers now prefer the use of green methods for the synthesis eco-friendly nanoparticles, and of various metal and metal oxide nanoparticles for biological medical and pharmaceutical applications (Akl *et al.*, 2012). Generally, chemical methods such as sol-gel process, micelle, chemical precipitation, chemical bath deposition (CBD), hydrothermal method, spray pyrolysis, chemical vapour deposition (CVD) etc. generate some toxic chemical which are environmentally hazardous and hence, adverse effect on medical applications. In some of the physical and chemical method of synthesis, some reactions demand high temperature or high pressure to initiate the reaction. Some reactions require inert atmosphere protection, and toxic matters used as template, stabilizer and precursors (Manish *et al.*, 2012). Biological approaches using microorganisms and plants or plant extracts for metal, metal oxide nanostructures synthesis are now given attentions as valuable alternatives to chemical methods. Myriads of biological systems such as bacteria, yeast and fungi have been used in synthesis of ZnO nanoparticles (Alagumuthu *et al.*, 2012). The procedural processes involved in using microorganisms for biological method of synthesis are elaborated as it requires maintenance of cell cultures, several purifications and intracellular synthesis. Hence, employing “green” methods for the synthesis of zinc oxide nanostructures has attracted attentions of researchers since conventional chemical and physical methods are expensive and non-ecofriendly (Cynthia *et al.*, 2012; Vidya *et al.*, 2013). Table 2.1 summarizes some of the reported synthesis of nanoparticles from plant extracts.

Table 2.1: Synthesis of nanoparticles from plant extracts (Kavitha *et al.*, 2013)

S/No	Plant	Bimolecular Involved	Nanoparticle	Size
1	<i>Allium cepa</i>	Vitamin C	Au	~100 nm
2	<i>Allium sativum</i>	Sucrose and fructose	Ag	4.4 ± 1.5 nm
3	<i>Achyranthus aspera</i>	Polyols	Ag	20-30 nm
4	<i>Anacardium occidentale</i>	Polyols and proteins	Au, Ag, Au-Ag allow and Au core-Ag shell	-
5	<i>Andrographis paniculata</i> Nees	Hydroxyflavones catechins	Ag	28 nm
6	<i>Astragalus gummifer</i> Labill.	Proteins	Ag	13.1 ± 1.0 nm
7	<i>Azadirachta indica</i> A. Juss	Salanin, Nimbin, Azadirone and Azadirachtins	Au	2 - 100 nm
8	<i>Camellia sinesis</i>	Polyphenolic compounds	Au	25 nm
9	<i>Carica papaya</i>	Hydroxyflavones and catechins	Ag	15 nm
10	<i>Centella asiatica</i>	Terpenoid, flavonoid	Ag	-
11	<i>Chenopodium album</i>	Oxalic acid	Ag, Au	12 nm, 10 nm
12	<i>Coleus aromaticus</i>	Flavonoids	Ag	40 - 50 nm
13	<i>Cinnamomum zeylanicum</i> Blume	Terpenoids	Pd	15 - 20 nm
14	<i>Cinnamomum camphora</i>	Polyols, hererocyclic components	Pd	3.2 - 6.0 nm
15	<i>Citrullus colocynthis</i>	Polyphenols with aromatic ring and bound amide region	Ag	31 nm
16	<i>Datura metel.</i>	Plastohydroquinone or plastrocohydroquinol	Ag	16 -40 nm
17	<i>Desmodium triflorum</i> .	Water-soluble antioxidative agents like ascorbic acids	Ag	5-20 nm
18	<i>Diopyros kaki</i>	Terpenoids and reduced sugars	Pt	2-12 nm
19	<i>Doscorea bulbera</i>	Ployphenols or flavonoids	Ag	8-20 nm Average 75 nm
20	<i>Dioscorea oppositifolia</i>	Polyphenols with aromatic ring and bound amide region	Ag	14 nm

2.11 Mango (*Mangfera indica*) leaves

In this research work, mango (*Mangfera indica*) leaves extracts were examined for the synthesis of zinc oxide nanorods. Pharmaceutical industries have been using extracts of medicinal plants intensively as raw materials. Demand for the use of medicinal plants is

increasing at alarming rate due to the effects of these plants on living systems. Plants are the major sources of raw materials for treatments used by traditional healers in many communities. Even, developed countries are now going “green”. Nunez-Selles, (2005) opined that some plants have sedatives, analgesic, antipyretics, cardio-protective, anti-inflammatory, antioxidants, antispasmodics, and immune-modulatory functions. The mango tree (*Mangifera indica* Linn Anacardiaceae) is readily available in Nigeria, West Africa. Oliver-Baver, (1986) reported that the tree originated from India and spread to West Africa. The bark and leaves of mango tree have astringent properties and are therefore used as pain relief for toothache, sore throat, sore gums. It is also used for the treatment of dysentery, malaria and diarrhea (Donatus *et al.*, 2008). Researchers had reported that all the organs of the plants, *Mangifera indica* are rich in phytochemicals. The phytochemical constituents of the leave extract include; tannins and flavonoids. These phytochemicals play vital roles in health promotion, prevention of diseases and production of medicines. They are antioxidants which exhibit a wide range of biological functions like anti-carcinogenic and anti-mutagenic effects (Uriguiga and Leighton, 2000).

Senthilkumar and Sivakumar, (2014) reported that these phytochemicals in plants act as capping and reducing agents. The phenolic compounds (in plants) exhibit higher antioxidant potential which are very good reducing agents of metal ions, thus favouring the green synthesis of nanoparticles. Moreover, the growth of nanoparticles are stabilized and particles agglomeration are inhibited by the phytochemicals hence this research work aimed at the synthesis of *Mangifera indica* - mediated ZnO nanorods.

2.12 Modifications of ZnO nanostructures

Despite all the interesting properties of ZnO and its applications, pure ZnO thin films lack stability in terms of thermal ageing in air or corrosive environments (Jimenez, 1997). Group II and group III metal ions such as indium (In), aluminium (Al), gallium (Ga), copper

(Cu), cadmium (Cd) etc due to their high absorption and photonic properties, have been used as dopants for polycrystalline ZnO for enhancement in structural, optical and electrical properties (Cao *et al.*, 2006). Modification is particularly done to get high transparency, stability and high conductivity. Aluminium doping is particularly suitable for this purpose (Mondal *et al.*, 2008).

2.13 Methods of Morphological Modifications of zinc oxide

The desire for new and more possible applications of zinc oxide, the need to reduce its content in rubber mixtures, and the major problem of its tendency to form significant agglomerations have encouraged researchers in recent years to carry out numerous studies to find an optimum method of modifying the surface of the compound without impairing its physicochemical properties. Modification is always carried out so as to improve its performance properties, and thus its various applications.

Evidently, the applications of a nanomaterial depends to a large extent on its compatibility and surface properties. Hence, to obtain more desirable and improved performance of a nanomaterial, there is need for their surface functionalization or modification (Vasilev *et al.*, 2010). There have been various possible approaches to the modification of surfaces of metallic materials which had improved their surface properties. In this present section, surface modification methods for zinc oxide will be reviewed. These include mechanical, chemical and physical methods used for morphological modifications. Generally, the aim is to improve zinc oxide bioactivity, photocatalysis, biocompatibility, stability, wear and corrosion resistance. The summary of methods of modification is given in table 2.2 as reported by Siavash, (2013).

Table 2.2: Summary of Methods of Morphological Modifications of zinc oxide (Siavash, 2013)

Modification method	Type Modifiers	Modifying agents	Effect of modification	Result	Application
Calcination	Inorganic and organic	silica and trimethyl siloxane (TMS)	ultrafine particles of ZnO, a solution to the problem of their agglomeration	The silica reduced its photocatalytic activities, while its compatibility was increased by hexamethyldisilazane (HMDS)	UV radiation protection
controlled precipitation	Inorganic	triethanolamine $N(CH_2CH_2OH)_3$ (TEOH) and containing silanol ($\equiv Si-OH$) and siloxane ($\equiv Si-O-Si\equiv$)	clusters of ZnO on the silica surface	Improved aggregation and reduced average particle size	photocatalysis
Sol-gel	Inorganic	calcium phosphate, TiO_2 and silica	Improved biocompatibility	Improved Bioactivity	Thin films bone conductivity
Biochemical methods	Organic	photochemistry,	Self assembled Monolayers		Induced specific cell and tissue Response
Mechanical methods - Grinding Polishing Machining Blasting Attrition	Inorganic	Nanophase surface layers on zinc oxide	higher hydrophilicity.	gives improved surface topographies; Improved adhesion in bonding.	nanophase surface layers, enhanced purity, improved tensile properties and surface hardness of

					ZnO
hydrothermal method (microwave dehydration)	Organic	Octadecyltrimethoxysilane	an increase in the degree of cross-linking of the vulcanizates,	an increase in vulcanization reversion and a decrease in prevulcanization time	vulcanization reversion
Electro-spinning method	Inorganic	silver ions. As the ZnO:Ag mass ratio was increased, there was a change in the product's surface area and particle size. obtained a		ZnO-Ag composite with particles measuring approximately 120–250 nm and with a surface area of 3–6 m ² /g.	Antibacterial, antimicrobial and other medical applications
plasma-enhanced chemical vapour deposition (PE-CVD).	Inorganic	LiCoO ₂ . ZnO	Zinc oxide covered with a layer of LiCoO ₂ was obtained. favourable effect of ZnO on the electrochemical yield and thermal stability of LiCoO ₂	an increase in the surface area of the functionalized ZnO (from 0.4 to 1 m ² /g).	Li-ion batteries, electronic devices, catalysts and high-performance sensors.
Biological method	Organic	<i>Sepia officinalis</i> cephalopod mollusk	β-chitin as a template for biomimetic ZnO deposition	β-chitin	biomimetic ZnO deposition

Polymerization	Organic	Poly methyl methacrylate (PMMA)	increased lyophilicity of the inorganic surface and reduced aggregates formation	inorganic-polymer composites	ZnO/PMMA composite
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Other methods of physical morphology modification include processes such as thermal spraying, physical vapour deposition, ion implantation and glow discharge plasma treatment, where chemical reactions do not occur. The surface modified layer, film or coating obtained on the titanium substrate is mainly a product of the thermal, kinetic, and electrical energy involved.

2.14 Application of ZnO nanoparticles

2.14.1 Biological Applications

Zinc oxide nanoparticles have several biological applications such as sensing, biological labeling, gene and drug delivery, nanomedicines and pharmaceuticals. This is made possible because of their environmentally friendliness, non-toxicity. Bauermann *et al.*, (2006). It has been reported that for biological applications, the basis is water solubility of the nanomaterial, which is obtained by surface functionalization as reported by Wang *et al.*, (2007) who synthesised a water-soluble ZnOAu nanocomposite with dual functionality - fluorescence and bioconjugation. Reddy *et al.*, (2007) had reported the biomedical and antibacterial applications due to the toxic nature of ZnO nanoparticles to bacterial systems. In their report, zinc oxide nanoparticles showed total inhibition of *E. coli* and *S. aureus* growth respectively but minimal effects on primary human T cell. The killing of cancerous cells and human T cells by zinc oxide nanoparticles was also reported by Hanley *et al.*, (2008).

2.14.2 Solar Cells Applications of ZnO Nanostructures

Some researchers had reported the application of ZnO nanoparticles in solar cells. Here, zinc oxide (ZnO) is always prepared as thin films functioning as absorbance layer in dye-sensitized ZnO solar cells. A very high solar cell efficiency of 4.4% was obtained by the use of polydispersed zinc oxide nanostructured aggregates as reported by Suliman *et al.*, (2007). In their report, ZnO nanoparticles were chemically synthesised using the precursor zinc chloride, NaOH as a base in a PVP solution of water at 160 °C for 8 h by hydrothermal method.

The silicon wafer reflects up to 35% of the incident beam of sunlight striking its surfaces due to its luster property. Coating the light sensitive surface of the solar cell with an Anti Reflection Coating (ARC) will definitely increase its life span and efficiency (Kolton, 1981). Anti-Reflection Coating is put on the surface of the silicon wafer of the solar cell to reduce the amount of solar light loss. Several methods have been used to eliminate energy losses due to reflection of light. These include modification of solar cell surfaces with gold nanomesh and the combination of silver nanocubes scattered over a thin gold layer (Beau *et al.*, 2017, [Venkatesha](#), 2016). Other methods developed for reflectivity reduction of solar cells include the use of light absorbing nanowires, graphene, photonic crystals, plasmonics, nanocones, as sub-wavelength structures in solar cell materials. Good and conventional Anti Reflection Coatings (ARC) are Titanium dioxide (TiO₂) and silicon oxide (SiO₂). These give high photocurrent of minimized reflectance. In the present, ZnO is also used for passivation as ARC because of their properties like high refractive index, wide energy band gap, safety-nontoxic, and cost effective (Ellmer *et al.*, 2007; Gangopadhyay *et al.*, 2004).

The focus of this research work in this section is the effect of coating a silver solar cell with zinc oxide nanoparticles on its efficiency.

2.14.3 Photocatalytic and environmental application of nanostructured ZnO

As valuable and important as clean water is to life, the major challenge to it is pollution. The major sources of water pollutants like dyes and other organic pollutants, come as waste water from industries like; textile, photography, printing, painting, leather, agro allied companies – pesticides, insecticides' fertilizer, etc. These water pollutants pose environmental hazards to man, aquatic animals and microorganisms. Generally, it is a threat to the ecosystems due to its toxicity and the carcinogenic effect (Shameem *et al.*, 2017). Removal of these pollutants had begat several methods which include; sedimentation, adsorption, chemical precipitation, advanced oxidation processes (AOPs) and some biological means but for their limitations. Thus, highly efficient, cost effective, eco friendly and stabile photocatalysts have found their routes through semiconductors in nano forms. TiO_2 , ZnO , Fe_2O_3 and CdS , CdO , ZnS have been proved suitable photocatalysts for the removal of organic water pollutants (Nwanya *et al.*, 2015). Among all these and other photocatalysts, TiO_2 is commonly used yet, ZnO have gained more attentions due to its desirable properties – electric, photonic and oxidation resistance, non-toxic, high band gap ($E_g = 3.37\text{eV}$). (Ravichandran *et al.*, 2014). The photocatalytic activities of ZnO nanoparticles were also determined by decomposition of Orange II dye in aqueous solution under UV irradiation of 365 nm wavelength. Samples kept at 700_C exhibited a good photocatalytic activity, $k = 0.0379 \text{ min}^{-1}$ (k for P25 Degussa is 0.0222 min^{-1}) as reported by Houskova *et al.*, (2007).

2.14.4 Photoluminescence (PL) and Sensor Application of ZnO nanoparticles

Bourlinos *et al.*, (2006) synthesised, examined and reported a modified ZnO nanoparticles that shows liquid-like behavior and their PL properties. ZnO nanocrystals (3–7 nm) were firstly synthesised by alkaline hydrolysis of zinc acetate in the presence of LiOH · H₂O in absolute ethanol medium for 4–5 days. The as-prepared ZnO colloids were precipitated by adding heptane in excess, followed by centrifugation and drying at room temperature. Surface modification of ZnO nanoparticles with charged organosilane [(CH₃O)₃Si(CH₂)₃N⁺(CH₃)(C₁₀H₂₁)Cl[−]] was done in an alkaline environment.

The PL quantum yield of the ZnO sulfonate nanosalt (0.065 mgmL^{−1} in acetonitrile), corresponding to the green-yellow emission band, was measured relative to that rhodamine 6G (R6G, 30 m in methanol). This property could lead to other possible applications in optics and photonics. dopants concentration, calcination temperature, calcination period, and precursor are factors controlling the crystallization of ZnO nanoparticles—which is useful for increasing the PL properties. The authors believed that this novel process can be useful for an advanced technology with strong growth potential for PL devices.

2.14.5 Applications of Green Nanotechnology

Green Nanotechnology involves fabricating novel nanomaterials that are beneficial to the environment directly or indirectly for water treatments - surface water, groundwater and wastewater which have been contaminated by hazardous metal ions, organic and inorganic solutes and micro-organisms (Vishnu *et al.*, 2013). The need for environmental non-toxic synthetic protocols for nanoparticles synthesis leads to the developing interest in biological approaches which are free from the use of toxic chemicals as by-products. Thus, there is an increasing demand for “green nanotechnology”. Nanoparticles produced from plants extracts are more stable and the synthesis rate is faster than in the case of other biological methods.

Green nanotechnology has been described as the development of clean technologies, to minimize potential environmental and human health risks associated with the manufacture and use of nanotechnology products and to encourage replacement of existing products with new nano products that are more environmentally friendly throughout their lifecycle (Minna and Steven, 2012). It uses existing principles of green chemistry and green engineering to make nanomaterials and nano-products without toxic ingredients.

The goal of green nanotechnology is to produce nanomaterials with little energy and renewable inputs at low temperatures, aiming at protecting the environment not only by cleaning it up but also by inventing novel chemical process which do not corrupt. Green synthesis route of nanoparticle depends on plant source and the organic compound in the crude plant extract. Zinc oxide nanoparticles produced by green method have been studied for applications in the field of optical devices, sensors, catalysis, biotechnology, DNA labeling, drug delivery, medical, chemical and biological sensors and as catalyst. Nanostructured ZnO has been used in sun screen coatings and paints because of its high UV absorption efficiency and transparency to visible light (Reed and Hutchison, 2000). Fan and Lu, (2005) had highlighted some applications of nanomaterials produced by green synthesis routes. They are:

1. Solar steam light is a successful invention of nanotechnology due to the scarcity of electricity which is useful in case of the wide application of water purification and disinfecting of the dental instruments.
2. The nano engineered polymer matrix is used for light tubes with high efficiency which is shatter proof and has the capability of efficiency of compact fluorescence light bulbs.
3. The carbon nanotubes are used in the blades of windmill which are strong and also with lower weight. The blades of longer size which are filled with a huge amount of carbon nanotubes are able to produce more electricity.

4. The wires with carbon nanotubes are lower resistance than the wires of electric transmission grid. The radical change of the electricity distribution grid is now possible by nanotechnology.
5. The graphene are useful for the increase in the binding energy of hydrogen in a fuel tank with respect to the surface of the graphene layers which produces a higher amount of hydrogen for storage which is of very lighter weight for the fuel tank.
6. Sodium borohydride nanoparticles are also useful for the storage of oxygen.
7. The piezoelectric nanofibers are more flexible for woven into clothing. The fibers are capable to modify the normal motion into electricity especially for the mobile like electronic devices.
8. The energy consumption produced by friction can be reduced by the use of various lubricants which are used by the inorganic bucky balls.
9. Now-a-days nanotech solar cells are developed which are comparatively of lower cost than the conventional solar cells.
10. Currently, the batteries are also made of nanomaterials.
11. The efficiency of the membranes in fuel cells are separated by the hydrogen ions from the other gases like oxygen is now possible only for the advancement of the nanotechnology.
12. The fossil fuels like petrol, diesel and gasoline are produced by the low grade raw materials to increase the functionality of various machines and engines by the wonder of nanotechnology and it can also produce fuels from the normal raw materials which are more efficient.
13. Nanotechnology is also useful for reducing the cost of the fuel cells by changing the spacing between the platinum atoms which can be used in the fuel cells to increase the catalytic ability of the platinum. It allows the fuel cell to function with about 80% less platinum which can appreciably and considerably reduce the cost of the fuel cell.

14. The nanoclusters are valuable for the control of chemical waste materials from industries to control various pollutions. For this purpose, the nanoclusters act as catalysts to reduce the polluting waste byproducts which are generated in the process accustomed to produce propylene oxide. Propylene oxide is utilized for the production of common materials like plastics, paint, detergents.
15. Nanoparticles are effective in cleaning up the organic solvents which are polluting the ground water.
16. Nanostructured membranes are designed to control carbon dioxide in the exhaust stacks of power plants which cause air pollution.
17. Volatile organic compounds are cleared from the air by using a catalyst which helps in the breakdown of volatile organic compounds at room temperature. The catalyst consists of porous manganese oxide.
18. The nanoparticles are the miracle of nanotechnology which creates a miracle in the field of medical science especially in cancer cells. The engineered nanoparticles can be delivered to the target site which attracts by the diseased cells for allowing the direct treatment of the cells. For example, nanoparticles which deliver chemotherapy drugs directly to the cancer cells are under development.
19. The chemotherapy drugs can also be delivered to the cancer cells with applying the heat to the cells. For example, gold nanorods to which DNA strands are attached. The DNA strands act as a scaffold which holds together the nanorods and the chemotherapy drug. When the infrared light illuminates the cancer cells, the infrared light is absorbed by the gold nanorod which turns into heat. The produced heat releases the chemotherapy drug and destroys the cancer cells.

20. Nanoparticles are also developing to defeat the viruses. The nanoparticles delivers an enzyme that prevents the reproduction of viruses in the patient's bloodstream instead of destroy the viruses.
21. Some nanoparticles are developed which can be delivered across the brain barrier to tackle neurologic disorders.
22. Immune response can be developed by vaccines by attaching the vaccine molecules to a DNA nanostructure which delivers the vaccine molecules to the specific cells that are in key triggering white blood cells to an immune response.
23. Sound waves are the powerful events which are mainly for the noninvasive surgery which is used by a carbon nanotubes coated lens to convert the light from a laser to focused sound waves. This developed invention by the researchers develop a method which can blast the tumor cells or to the other diseased sites without damaging the healthy tissues.
24. Bismuth nanoparticles are used for the radiation therapy for the treatment of cancer The preliminary results specify the bismuth nanoparticles can increase the dose to the tumor by 90 percent.
25. Nanoparticles consist of polyethylene glycol-hydrophilic carbon clusters (PEG-HCC) which have been shown to absorb the free radicals at a much higher rate than the proteins out body uses for this function. They have the ability to absorb free radicals may reduce the harm which is caused by the release of the free radicals after a brain injury.
26. Targeted heat therapy is being developed to destroy the breast cancer tumors. In this methodology of treatment the antibodies are strongly attracted to proteins produced in one type of breast cancer cell which are also attracted to the nanotubes for the accumulation towards the tumor. Infrared light from a laser is absorbed by the nanotubes and also produces heat which incinerates the tumor.
27. Nanofibers can also stimulate the construction of the cartilages in the damaged joints

28. Nanoparticles are also used in the early detection of the cancer tumors. When the nanoparticles attach to cancer tumors, the nanoparticles release the biomarkers molecules known as the peptides. In this technique, the each nanoparticle carries several peptides of a very high concentration of these markers which will occur at very early stages of cancer and also allowing the early detection of the disease.
29. The magnetic nanoparticles can attract and attach to the cancer cells in the blood stream. These types of nanoparticles may allow the doctors to easy removal of the cancer cells before they can ascertain the new tumors.
30. The early detection method for brain cancer under the development uses magnetic nanoparticles and NMR technology. The magnetic nanoparticles attach to the particles in the blood stream known as microvesicles which originate in brain cancer cells. The NMR technique is used to detect these microvesicles or magnetic nanoparticle clusters which allows the early diagnosis.
31. The iron nanoparticles can be used to improve the MRI technique of the cancer cells. The nanoparticles coated with a peptide which binds to a cancer tumor cells. Once the nanoparticles are attached to the cancer tumor cells, then the magnetic property of the iron oxide enhances the images from the MRI scan.
32. The carbon nanotubes and gold nanoparticles are being used in a sensor which detects proteins investigative of the oral cancer.
33. The nanoparticles coated with the proteins can attach to damaged portions of the arteries. This technique provides the delivery of drugs to the damaged regions of arteries to fight against the cardiovascular disease.
34. The diagnosis of early detection of the kidney damage is being developed by the use of gold nanorods which are functionalized to attach the proteins generated by the damaged kidneys. The color of the nanorod changes when protein accumulates on the nanorod.

35. Nanorods are useful in case of the diagnostic system are being used to separate the microorganisms like viruses, bacteria and other foreign substances of blood sample allows the Raman spectroscopy signals of the components which has been demonstrated to allow the identification of viruses and bacteria in less than one hour.
36. The earliest nano-medicine application was the use of nanocrystal which acts as an antimicrobial agent for the treatment of wounds. The most common silver nanocrystal is used as an antimicrobial agent for the treatment of wounds.
37. A nanoparticle cream has been shown to fight against the infections. The nanoparticles contain nitric oxide gas is well recognized as to kill the bacteria. Research on animal model like mice have shown that the use of the nanoparticle cream releases the nitric oxide gas at the site of staph eruption significantly reduced the infections.
38. Burn dressings are treated by the nano-capsules containing antibiotics. The infection produced by the harmful bacteria in the wound causes the breaking of the nano-capsules for the release of antibiotics which allows a quicker treatment of an infection and reduces the number of frequencies of dressing.
- 39 Catalysis : Chemical catalysis benefits especially from nanoparticles, due to the extremely large surface to volume ratio. The application potential of nanoparticles in catalysis ranges from fuel cell to catalysis converters and photocatalytic device. Catalysis is also important for the production of chemicals. Platinum nanoparticles are now being considered in the next generation of automotive of platinum required. (<http://www.en.wikipedia.org>)

CHAPTER THREE

METHODOLOGY

3.0 Introduction

Zinc oxide nanorods (ZnO NR) were synthesised through green synthesis method from leave extract of mango leaves (*Mangifera indica*). The synthesised ZnO NR was modified with nickel ferrite (NiFe_2O_4) nanorods to obtain nickel ferrite/zinc oxide ($\text{ZnO}/\text{NiFe}_2\text{O}_4$) nanocomposite. Both modified and unmodified zinc oxide nanorods were characterized for elemental components, structural, optical electrical and dielectric properties. Scan electron microscope (SEM) and X-ray Diffractometer (XRD) were used to determine their morphology and structure, energy dispersive x-ray spectrometer (EDX) and Fourier transform infrared (FTIR) were used to obtain their elemental composition and functional groups. UV-Vis was used for the optical studies, impedance spectroscopy was used to determine their dielectric properties while four point probes were used to get the electrical conductivity of the synthesised ZnO NR.

The nanocomposite ($\text{NiFe}_2\text{O}_4/\text{ZnO}$) was used for the treatment of both domestic and industrial waste waters after successful photodegradation of organic dyes (MB, CR and RB). A silver solar cell was coated with the ZnO NR for efficiency enhancement which was determined from I-V characterization taken from the solar cell Kit. Photoluminescence studies of the nanocomposite ($\text{NiFe}_2\text{O}_4/\text{ZnO}$) was carried out to determine its bio sensitivity.

3.1. Materials and Chemicals

The starting materials for the synthesis for the synthesis of ZnO nanoparticles, are; leave extract of mango leaves (*Mangifera indica*), anhydrous zinc acetate $[\text{Zn}(\text{O}_2\text{CCH}_3)_2]$, Sodium hydroxide pellets and ethanol. The precursors for the modifier, Nickel Ferrite nanorods (NiFe_2O_4 NR) are; iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$),

sodium hydroxide (NaOH) and polyvinylpyrrolidone [PVP – (C₆H₉NO)_n]. All were of pure analytical grade purchased from Sigma Aldrich and distilled water was used as solvent for all the experiments.

3.2 Green Synthesis of ZnO NPs

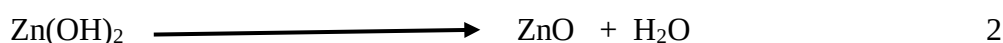
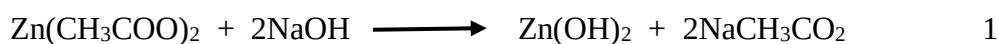
3.2.1 Leave Extract Preparation.

Mango (*Mangifera indica*) leaves were collected within the compounds of Osun State University, Osogbo, Nigeria. The leaves were air dried until constant mass was obtained and it was blended into powder. 50g of the powdered leaves was boiled at 70 °C in 100 ml of distilled water for about 30 minutes until the colour changed. After cooling, the mixture was filtered, centrifuged and the supernatant solution was collected as the leave extract.

3.2.2 Preparation of zinc oxide nanorods (ZnO NR)

0.4 M solution of zinc acetate dihydrate [(CH₃COO)₂Zn.2H₂O] was prepared with 50 ml of distilled water. The solution was stirred for about 20 minutes. 5 ml of the leave extract was added to the solution under continuous stirring. 0.3 ml of 2.0 M sodium hydroxide (NaOH) was added in drops to the mixture to enhance precipitation and to maintain a pH of 12. The whole mixture was stirred further for 1 hour. The precipitate was taken out, washed repeatedly with distilled water and then washed with ethanol to remove impurities, after which it was dried in air at 60 °C for six hours to yield white ZnO NR. The synthesized ZnO NR was calcinated for one hour in air tight oven at 100 °C .

3.2.3 Equation of Reaction for the synthesis of ZnO NR



3.3 Synthesis of nickel ferrite nanorods (NF NR)

0.4 M solution of hydrated iron chloride [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$] and 0.2 M solution of hydrated nickel chloride [$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$] were prepared. Equal volumes of the two different solutions were mixed and stirred vigorously on magnetic stirrer for 1 h at 80 °C. Then, 3 mg of polyvinylpyrrolidone [PVP – $(\text{C}_6\text{H}_9\text{NO})_n$] was added in to the solution as a capping agent after which 3.0 M sodium hydroxide (NaOH), was added in drops to the solution kept under constant stirring until brown precipitate is formed. The solution was allowed to cool, filtered and washed repeatedly with deionized water to obtain a pH of 7 and dried at 150°C for 2 hours. The NiFe_2O_4 NR formed was then milled by mortar and pestle to fine powder.

3.4 Modification of zinc oxide nanorods (ZnO NR) with nickel ferrite nanorods (NF NR)

The synthesis route used here was solid synthesis. Nickel ferrite nanorods (NiFe_2O_4 NR), zinc oxide nanorods (ZnO NR) and thiourea were mixed in ratio 1:20:10 respectively. The mixture was calcinated in a furnace at 800 °C for 8 hours after which $\text{NiFe}_2\text{O}_4/\text{ZnO}$ hybrid nanocomposite was observed to have been formed.

3.5 Physical Measurements

The elemental composition of each of the green synthesised ZnO NR, co-precipitated NiFe_2O_4 NR and modified ZnO NR, that is, calcinated $\text{NiFe}_2\text{O}_4/\text{ZnO}$ nanocomposites were analyzed using Energy Dispersive Spectroscopy (EDX) - BRUKER-X Flash 6130, and Fourier Transform Infra-Red (FTIR) spectroscopy - by SHIMADZU - IR TRACER 100 using KBr pellet method at room temperature through the wave range 400 - 4000 cm^{-1} . The structural properties were characterized using X-Ray Diffraction (XRD) machine - D8

advance ECO XRD systems with SSD160 1D Detector, with Cu-K α 1 and K α 2 radiation of wavelength 1.5406 and 1.54438Å. The Spectroscopic electron morphology (SEM) - ZEISS-EVO 18 Research was used to investigate the surface morphology of the samples while the optical properties of the samples were studied using VISIONlite 061408 UV – VIS (1600 series) spectrophotometer and the optoelectronic nature by photoluminescence (PL) spectroscopy. These physical measurements were taken at the International Research Centre of Kalasalingam University, Taminil Nadu, India.

3.6 Applications

3.6.1 Impedance Spectroscopic Studies

For dielectric studies, ZnO NR powdered sample was compressed into pellets of 13.01 mm diameter and 0.082 mm thickness by using a very high pressure (5 Ton). The pelletized ZnO NR was characterized by an alternating current (AC) Impedance Spectroscopy (HIOKI 3532 – 50 LRC HiTESTER model) measurements were obtained in the 40 Hz to 10 MHz frequency range, at a constant voltage of 1.0V and different temperatures 100 - 155 °C.

3.6.2 Solar Cell Nanocoating with ZnO NR

To examine the solar cell application of the synthesized ZnO NR, a solar cell characteristic apparatus was used. The kit consists of a silicon ($1.5 \times 6 \text{ cm}^2$) solar cell, made by the INSIF ELECTRONICS AN ISO 9001:2008, India. The conducting surface of the solar cell was coated by the ZnO NR via drop-casting method. The ZnO NR suspension was prepared by dissolving 2.5 mg of ZnO NR in 50 cm³ of ethanol and mixed thoroughly by a sonicator for 10 min. Then, droplets of the ZnO NR suspension was deposited on the surface.

The *I*–*V* characteristics of Si solar cells were determined before coating and after coating with ZnO NR.

3.6.3 ZnO NR for Biosensing

The sensing properties of the modified ZnO NR by green synthesis was studied using a room-temperature JASCO spectrofluorimeter by exciting the modified ZnO NR at 370 nm excitation wavelength. The PL measurements were taken at room temperature for different concentrations (0.1mM, 0.2mM and 0.3mM) of glucose solutions added.

3.6.4 Photodegradation Application

3.6.4.1 Photocatalytic Activity at Varying Amount of Catalyst

The photocatalytic activity of the ZnO/NF nanocomposite was evaluated by photodegradation of an aqueous methylene blue (MB) dye. The experiment was carried out in a photo reaction chamber – (HEBER multilamp Photoreactor Model – HML-MP88) using four 360 nm UV lamps of 8 W. The catalytic experiments were carried out with 100 mL solution of 5×10^{-5} M MB and 20 mg, of the ZnO/NF nanocomposite (catalyst) under constant stirring. About 4 mL of the aliquot solution was withdrawn at predetermined time intervals (10 minutes) from the reaction mixture, centrifuged and the decrease in absorbance values were monitored at the maximal absorption wavelength of methylene blue (664 nm) with the time of irradiation by VISIONlite 061408 UV – VIS (1600 series) spectrophotometer. The experiment was repeated for different amount of catalyst - 40 mg, 50 mg and 75 mg keeping the concentration of the dye solution constant at 5×10^{-5} M. The whole procedure was repeated for the photo degradation of two other organic dyes – Congo Red (CR) and [Rhodamine](#) B (RB). A control

experiment was also carried out under identical experimental condition using commercial MB without catalyst.

3.6.4.2 Photocatalytic Activity at Different pH

The procedure in 3.6.4.1 above was repeated for 50 mg of catalyst with the mixture solution at pH of 3.0 and pH of 9.0. Likewise, about 4 mL of the aliquot solution was withdrawn at predetermined time intervals (10 minutes) from the reaction mixture, centrifuged and the decrease in absorbance values were monitored by spectrophotometry.

3.6.5 Wastewater Treatment Applications

The industry wastewater used for this research work was collected from Sree Arumugham Surgicals, 8/178 E-8 Srivilliputhur road, Sankarapandiapuram, Chatrapatti-626 102, Virudhunagar, Tamil Nadu, India. The domestic wastewater was collected from the wastewater tank of Kalasalingam University, Tamil Nadu, India. Both domestic and industry wastewaters collected were treated with the green synthesized zinc oxide nanorods (ZnO NR) under UV absorbance and chemical oxygen demand (COD) measurements.

The batch experiment studies were carried in Photocatalytic Reactor - a photo reaction chamber – (HEBER multilamp Photoreactor Model – HML-MP88) using four 360 nm UV lamps of 8 W. Each tube was filled with 50 ml of solution of 5×10^{-5} M Methyl Red solution. Aeration is given to get the maximum efficiency and complete reaction on the Catalyst. The reactor has been started with various dosage of catalyst and samples were collected within 15 minutes interval of time and the absorbance of samples was measured by a UV–Vis spectrophotometer and COD (Chemical Oxygen Demand).

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Characterization Analysis

4.1.1 The Energy Dispersive Spectroscopy (EDX) Analysis

The Energy Dispersive Spectroscopy spectral of the green synthesized ZnO nanorods and the co-precipitated Nickel ferrite nanrorods are shown in fig. 4.1a, and 4.1b respectively. Fig. 4.1a revealed that only zinc (Zn), and oxygen (O) signals were detected and no other signal of secondary phase or impurity was detected. This implies the high purity chemical composition of the green synthesized ZnO NR. This is supported by Thema *et al.*, (2015) who in their own case reported the Green synthesis of ZnO nanoparticles via *Agathosma betulina* natural extract.

The EDX spectrum in Fig. 4.1b revealed that only Nickel (Ni), Iron (Fe) and oxygen (O) signals were detected and no other signal of secondary phase or impurity was detected. This implies the high purity chemical composition of the synthesized nickel ferrite nanorods (NF NR).

4.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra measurement of ZnO NR is shown in figure 4.2a. The spectra peaks observed the transmittance waveband from 430.0 cm^{-1} to 420.48 cm^{-1} corresponds to the metal-oxygen bonds may be due to Zn - O. The stretch around $860 - 900\text{ cm}^{-1}$ implies aromatic ring -1,3- distribution of metal. The spectra peaks between $1529.55 - 1500.31\text{ cm}^{-1}$ and $1260 - 1031.92\text{ cm}^{-1}$ indicates O-H in-plane and out-of-plane bonds respectively. The

broad peaks around $3700 - 3000 \text{ cm}^{-1}$ is due to O-H stretch which corresponds to the hydroxyl groups. Hence, the FTIR analysis confirmed the participation of biological (organic) molecules in bio-reduction reactions, formation, capping and stabilization of the nanoparticles.

The FTIR measurement of nickel ferrite nanorods (NF NR) at room temperature through the wave range $400 - 4000 \text{ cm}^{-1}$ is as shown in Fig. 4.2b. The stretch for NF NR was at 420.48 cm^{-1} which corresponds to the metal-oxygen bonds due to Ni - O and Fe - O. This is in good agreement with Auzans *et al.*, (1999). The peak at 1068.56 cm^{-1} which was found to be around $1260-1050 \text{ cm}^{-1}$ give cyclohexane ring vibration, C-F stretching, C-O stretching alcohols, carboxylic acids, esters, ethers (David, 2011). The peaks between $1537.80 - 1500.31 \text{ cm}^{-1}$ indicates O-H in-plane and out-of-plane bonds and appeared at 1512.19 cm^{-1} . The peak at 1357.89 cm^{-1} indicates aliphatic nitro compound, methyne C-H bending. The peak at 2374.37 cm^{-1} indicates $\text{-C}\equiv\text{O}$ absorption. The peak 2827.64 indicates methylamino, N-CH_3 , C-H stretching. The peaks around $3700 - 3000$ were observed at 3452.58 cm^{-1} leading O-H which corresponds to the hydroxyl groups attached by the hydrogen bonds to the iron oxide surface and the water molecules chemically adsorbed to the magnetic particle surface (associated water content).

The FTIR spectra of ZnO/NF hybrid nanocomposite is as shown in fig. 4.2c, the transmittance waveband from 430.0 cm^{-1} to 420.48 cm^{-1} , which corresponds to the metal-oxygen bonds may be due to Zn - O, Ni - O and Fe - O. The stretch around $860 - 900 \text{ cm}^{-1}$ implies aromatic ring -1,3- distribution of metal (Coates, 2000). This is in good agreement with Kandasamy *et al.*, (2010). The spectra peaks between $1529.55 - 1500.31 \text{ cm}^{-1}$ and $1260 - 1031.92 \text{ cm}^{-1}$ indicates O-H in-plane and out-of-plane bonds respectively. The broad peaks around $3700 - 3000 \text{ cm}^{-1}$ is due to O-H stretch which corresponds to the hydroxyl groups which had been be completely removed when the sample is sintered at temperatures $\geq 973\text{K}$

as reported by Dey and Ghose, (2003). Hence, the FTIR analysis confirmed the formation of the ZnO/NF nanocomposite.

4.3 X-ray Diffraction (XRD) Analysis

The crystal structural properties of the green-synthesized ZnO NPs, co-precipitated NF NRs and the calcinated ZnO/NF nanocomposite were analysed with XRD. Fig. 4.3a shows the X-ray Diffraction (XRD) pattern of the green-synthesized ZnO nanorods. The ZnO NR diffraction peaks shows highly oriented and crystalline structure of zinc oxide nanorods. The sharp and narrow diffraction peak positions with 2θ values of 31.78, 34.43, 36.27, 47.55, 56.62, 62.88, 66.40, 67.97, 69.11, 72.59, 76.99, 81.41, 89.64 were indexed as (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104) and (203) hkl crystal planes. The peak intensity profiles were in good agreement with those of powder ZnO obtained from the International Centre of Diffraction Data card (JCPDS) card No. 89 - 0510. This confirmed the formation of a crystalline hexagonal wurtzite structure of the ZnO NR.

The X-ray Diffraction pattern of the nickel ferrite nanorods (NF NR) synthesized by co-precipitation method is as shown in Fig.4.2d The NF NR diffraction peaks show highly oriented and crystalline structure. The sharp and narrow diffraction peak positions with 2θ values of 21.389, 35.325, 41.701, 43.610, 50.807, 55.768, 63.387, 67.732, were indexed as (111), (220), (311), (222), (400), (331), (422) and (511) hkl crystal planes. The peak intensity profiles were in good agreement with those of smooth powdered NF NR obtained from the International Centre of Diffraction Data card (JCPDS) card No. 10-035.

The crystal structures of the modified green-synthesized ZnO nanoparticles that is, ZnO/NF nanocomposites studied with XRD machine is as shown in Fig.4.3c. The XRD pattern of ZnO/NF nanocomposite gives the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104) and (203) crystal peaks which belong to hexagonal wurtzite

ZnO phase while the (220), (222), (400), (331) and (422) peaks correspond to spinel NiFe₂O₄ phase. It was observed that there is no extra diffraction peaks of other phases, which implies its phase purity no obvious other peaks of impurity are observed except for the peaks of both ZnO and NiFe₂O₄ and a weak peaks of NiFe₂O₄ at the 2θ values of 22.349, 31.628 and 83.893° for (111),(311), (511) respectively, disappeared in ZnO/NF nanocomposites. The average grain size of the synthesized ZnO NRs, NF NRs and ZnO/NF nanocomposite were calculated as 7.56nm, 6.67nm and 7.67nm respectively, by using Debye-Scherrer's Eq. (1).

$$D = \frac{K\lambda}{\beta \cos \theta} \text{ \AA} \quad (1)$$

Where D is the average crystallite size in Å, K is the shape factor, λ is the wavelength of X-ray (1.5406 Å) Cu -Kα radiation, β is the full width at half maximum of the diffraction peak, and θ is the Bragg angle (Cullity, 1978).

4.4 Scanning Electron Microscope (SEM) Analysis

The scanning electron microscope (SEM). The SEM micrograph images as shown in fig. 4.4a revealed that the morphology of the green synthesized ZnO NR have hexagonal shaped nanorods with granular nano-sized range 10 nm – 25 nm. From fig. 4.4b, the scanning electron micrograph (SEM) micrograph image of the nickel ferrite nanorods (NF NR) shows prismatic hexagonal shape with granular nano sized range of 10 nm – 20 nm. Fig. 4.4c the micrograph image of the ZnO/NF nanocomposites shows high degree of agglomeration and different surface morphologies which may be due to the magnetic attraction between nickel ferrite and zinc oxide layers. This is in agreement with the report of Yang and Zeng, (2004).

4.5 Optical Properties

Figures 4.5a shows the maximum absorption spectra of the green synthesized ZnO NR at 204 nm wave band and Fig. 4.5b shows its energy band gap to be 3.7 eV contrary to the standard value of 3.4 eV reported in literatures. Reasons may be attributed to the presence of organic molecules with higher absorption ability.

The approximate band-gap values of ZnO, NF and ZnO/NF hybrids are $\sim 3.12\text{eV}$, $\sim 1.60\text{eV}$ and $\sim 1.71\text{eV}$ respectively. These results suggest that modification with NF enhances the optical absorption property of ZnO nanoparticles. This is supported by the reports of Zhu *et al.*, (2016) who calculated the band gaps using $E_g = 1240/\lambda$ equation; and that of Rahmayeni *et al.*, (2016) who reported the band gap values of ZnO, NF and ZnO/ NF as 3.12, 1.64 and 2.78eV respectively. It should be noted that the band gap of ZnO/ NF had values lower than ZnO leading to better photo-catalytic performance.

Optical studies and photo-catalytic activities of the green synthesized ZnO NR and ZnO/NF nanocomposite have been analysed using photo degradation of methylene blue (MB) dye solution with two conditions: (i) in the absence of photo-catalysts, that is, self-photo degradation and (ii) in the absence of UV irradiation. It is observed and as supported by literatures that ZnO/NF nanocomposite has higher photocatalytic activities than ZnO and NF. Reducing the band-gap of the photocatalyst by doping enhances its performances.

4.6 Applications of Green Synthesized ZnO NR to dielectrics

4.6.1 The Impedance Spectroscopic (IS) study of ZnO NR

4.6.2 Frequency Domain Responses

The applied ac voltage signal is given by

$$V(t) = V_0 e^{i\omega t} \quad 2$$

for a single frequency $f = \omega/2\pi$. The resulting steady state of measured current in the electrical network is given by

$$I(t) = I_0 e^{(i\omega t + \phi)} \quad 3$$

where $\omega = 2\pi f$ and ϕ is the phase angle – phase difference between the applied voltage and the current. The implication of this is that for a purely resistive substance, $\phi = 0$ when $Z(\omega) = Z'(\omega)$. In such case, the impedance is completely independent of frequency. In this IS study, our ZnO NR proved not completely resistive over a range of frequency as shown by its Cole-Cole plot in Fig. 4.6a. This is in support of Kronig-Kramer's relation which connects the real and imaginary parts, ensuring that Z'' and θ cannot be zero over all frequencies (Barsoukov and Macdonald, 2005). The frequency dependent spectroscopic plots of the green synthesized ZnO NR are shown in Fig. 4b. From fig. 4.6b(i), it is observed that dielectric constant (ϵ') decreases with increase in frequency (f). The decrease in the value of dielectric constant on increasing frequency may be attributed to a combined contribution due to electronic, ionic, and interfacial polarization. The large value of the dielectric constant ϵ' obtained at lower frequencies is caused by the oxygen vacancies, and grain boundary defects. The observed dielectric dispersion at low frequencies can be explained on the basis of the Maxwell-Wagner theory of interfacial polarization (Muhammad *et al.*, 2010, Geethalakshmi *et al.*, 2014). When frequency increases, polarization decreases until it disappears except ionic and electronic polarization, which makes dielectric constant decrease rapidly (Baljinder

et al., 2016). The dielectric loss (ϵ'') is also a function of frequency as it can be seen from fig. 4.6b (ii). It also decreases with increase in frequency. When frequency increases, the increase in hopping electrons results in local displacement in the direction of the extent electric field . This leads to an increase in electric polarization and therefore aids dielectric loss. (Hassouna *et al.*, 2012, Aparna *et al.*, 2016). The behaviour of tangent of dielectric loss angle ($\tan \delta$) as a function of frequency for ZnO NRs is shown in fig. 4.6b(iii). For this sample, $\tan \delta$ is also observed to be decreasing with increasing frequency. This occur when the jumping rate of charge carriers lags behind the alternating electric field beyond a certain critical frequency. At low frequencies, more energy is required for electron transfer or ion exchange, small energy is required at high frequency for ion exchange. Low dielectric losses are desirable being the energy dissipation in the dielectric system. (Muhammad *et al.*, 2009)

4.6.3 A.C. Conductivity and Time Domain Responses

In the time domain, the relationship between the properties of the material sample and response to alternating voltage or current is complex. The response of capacitive element is

$$i(t) = \left(\frac{dv(t)}{dt} \right) C \quad 4$$

That of inductive element is

$$v(t) = \left(\frac{di(t)}{dt} \right) L \quad 5$$

The equations transform into

$$I(j\omega) = C \cdot \omega \cdot j \cdot v(j\omega)$$

$$I(j\omega) = - \frac{v(j\omega)}{L \cdot \omega \cdot j} \quad (j = \sqrt{-1})$$

Thus, $v(j\omega) = V_m \pi$

$$I(j\omega) = I_m \pi \cdot \exp(\theta j)$$

This is a form of Ohm's law

$$I(j\omega) = -\frac{V(j\omega)}{Z(j\omega)}$$

$$\text{For capacitance, } Z(j\omega) = -\frac{1}{(Z.\omega.j)} \quad 6$$

$$\text{For inductance, } Z(j\omega) = L.\omega.j \quad 7$$

The complex quantity $Z(j\omega)$ is the impedance function. From Fourier Transform,

$$Z(j\omega) = -\frac{F[V(t)]}{F[i(t)]} \quad 8$$

Thus the complex number, $Z = a + jb$ $j \equiv \sqrt{-1} \equiv \exp\left[\frac{j\pi}{2}\right]$

$$\text{The impedance vector is } Z(\omega) = Z' + Z'' \quad 9$$

The relaxation time also called time constant, τ , of a ‘parallel RC element’ is given by

$$\tau = RC \quad 10$$

At maximum frequency,

$$\omega_{max}RC = 1 \quad 11$$

The Cole–Cole plot shown in fig.4.6a confirms the distribution of relaxation time. Also, the periodic conductivity σ in the ZnO NR is observed to increase with increasing frequency. The relaxation is equally observed in the whole frequency range as a gradual increase in conductivity with increasing frequency as shown in fig. 4.6c below due to the hopping electrons which are responsible for electronic polarization. This is supported by the report of Ziaul *et al.*, 2011 and Tripathi *et al.*, 2009

4.6.4 Impedance Domain

Impedance is a complex quantity which is only real at $\theta = 0$ and therefore, $Z(\omega) = Z'(\omega)$ for a purely resistive behaviour.

$$Z(\omega) = |Z|\exp(-i\phi)$$

$$Z(\omega) = |Z|\cos\phi - i|Z|\sin\phi$$

$$Z(\omega) = z'(\omega) - iZ''(\omega)$$

12

Z' is the real while Z'' is the imaginary part of the complex impedance. It is only when $Z(\omega) = z'(\omega)$ that $Z' = R$ which is an ordinary linear resistance, that $Z(\omega)$ is purely real. Here, the relaxation time is given by $\tau = RC$ where at maximum frequency of loss, $\omega_{max} RC = 1$

These impedance responses help to give information on the nature of the conducting species, within the sample itself and whether conduction is by ions or electrons as reported by John *et al.*, (1990). The spectroscopic plots of some impedance responses of the ZnO NR are shown in Fig.4.6 d - e

From fig. 4.6d, the imaginary Z'' impedance plotted against real (Z') shows a semicircle from which the resistance R and capacitance C values may be obtained. The intercepts on the Z' axis give the value of R , while the value of C can be calculated by applying equation $\omega_{max} RC = 1$ to the frequency at the peak of the semicircle. In this sample – ZnO NRs, the value of the resistance is 4.125 (M Ω) as shown in the characteristic graph Fig.4.6d. The capacitance value is calculated to be 7.79×10^{-11} or 0.78 pF. This value is for the bulk capacitance of a sample. The variation of the real part of impedance (Z') with frequency at different temperatures shown in fig. 4.6e, revealed that dielectric loss Z'' decreases in value with increasing frequency at all the temperatures. It also decreases with temperature which indicates increase in the a.c. conductivity. Hence, these may be interpreted in terms of the bulk response of the sample and a single parallel RC element. There is no 'electrode spike' in the curve at low frequency therefore, there was no impedance barrier to charge transfer between the metal electrode and the sample, so the conducting species were electrons which is in agreement with the reports of John *et al.*, (1990) and Ziaul, *et al.*, (2011).

4.7 Solar cell efficiency enhancement by ZnO NR nanocoating

In fig. 4.7, the I-V characteristics curves of a photovoltaic cell give series of information on the cell's performance. The graphs of output voltage versus current for different levels of insolation and temperature for both uncoated and coated cells revealed the effect of ZnO coating on the cells. The parameters used are short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and efficiency (η), which are summarized in tables 4.1, 4.2 and 4.3.

Table 4.1: I-V characterization before ZnO nanocoating

V(mV)	I (mA)
19	45
25	41
28	37
30	34
33	28
35	22
36	18
38	0

Table 4.2: I-V characterization After ZnO nanocoating

V(mV)	I (mA)
-------	--------

8	57
10	56
15	53
16	52
19	50
28	41
30	38
33	34
35	26
37	18
38	0

	Parameter	I _{mp}	I _{sc}	V _{oc}	V _{max}	P _{in} (	P _{max} (mW)	FF	η (%)
Before nanocoating	output	34	51	29	38	986	0.986	0.37	7.04
After nanocoating		36	60	32	38	1151.4	1.151	0.51	11.63

Table 4.3: The comparison of I – V characterization before and after ZnO nanocoating

The common characteristic factor of a solar cell is the fill factor, defined as

$$FF = \frac{I_{max}V_{max}}{(V_{oc})(I_{sc})} \quad (4.2)$$

$$FF = \frac{P_{max}}{(V_{oc})(I_{sc})} \quad (4.3)$$

The efficiency, η of the solar cell was also obtained before and after ZnO NR coating by using the formula

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{sc}V_{oc}FF}{P_{in}} \quad (4.4)$$

Where,

V_{OC} = the open-circuit voltage, that is, the maximum voltage of the cell when the circuit is still open

I_{SC} = short-circuit current – this is the maximum current the cell gives in a short circuit condition.

$P_{\max}$ = maximum power point of the solar cell, which relates the point where the power supplied by the cell is connected to the load at its maximum value. At this point, $P_{\max} = I_{\text{mp}} \times V_{\text{max}}$.

FF = fill factor, the ratio of the maximum power to the product of the open-circuit voltage and the short-circuit current, $(V_{\text{oc}} \times I_{\text{sc}})$.

$\eta \%$ = percentage efficiency of a solar cell, is the ratio of the maximum electrical power that the photovoltaic cell can produce to the amount of solar irradiance incident on the cell surfaces.

In this research work, the solar cell which was coated with the green synthesized ZnO NR shows a better performance compared to the uncoated solar cell. The short-circuit current (I_{sc}) in the uncoated and coated cell increases in value from 34 mA to 36 mA respectively. The fill-factor FF also increases from 0.37 to 0.51, and hence, the efficiency enhancement from 7.04% to 11.52% respectively. The increase of I_{sc} may be due to high absorption rate of solar irradiation, as an effect of the drop-casting of ZnO NR on the conducting surface of the solar cell. This result agreed with the results of Gholizadeh *et al.*, (2017), who in their research work examined the Charge transport in hybrid nanorod-polymer composite photovoltaic cells and the effect of ZnO nanostructure assisted Si solar cell on Efficiency enhancement based on fill factor enlargement and down-shifting of UV-blue spectral of the cell.

4.8 The sensing activities of the modified nanostructure (ZnO/NF)

The optoelectronic nature of modified semiconductor nanoparticles has been widely studied using the photoluminescence (PL) spectroscopy. For instance, it is used to observe the efficacy of charge carrier trapping and to understand the electron–hole pair recombination of semiconductors nanoparticles. Semiconductor material like ZnO normally shows PL

signals owing to surface oxygen vacancies, recombination of electron–hole pair and defects of semiconductor particles, similar to that which was reported by Pawinrat *et al.*, (2009). As shown in the figures 4.8 a - d, ZnO/NF + Gl and Gl photoluminescence has high intensity band peak. The PL spectra shows maximum yellow and orange emission band at 580, 590 and 600 nm for ZnO/NF solution, mixture of 1.0 mM of glucose and 2.0 mM of glucose respectively. The PL spectra also show peaks at 350 and 700 nm for all the solutions. The intensity of this peak at 700 nm is reduced when a calculated amount of glucose was added to ZnO/NF solution. As glucose concentration increases, the sensing activity intensity has peaks in the UV region of 350 nm, the intensity increases in the yellow and orange emission spectrum and decreases in the red emission spectra of 700 nm. A possible reason for the decrease in the intensity may be due to the suppression of recombination of electron–hole pairs occurred by loading ZnO/NF solution with glucose solution. Generally, lower intensity of PL band peak confirms the lower electron hole pair recombination which enhances the sensing activity of the as synthesized sensor. During the sensing reactions, the excited electrons are transferred to glucose from ZnO/NF and thereby reducing the electron hole recombination rate in a significant manner which further improves the sensing activity, in conformity with the report of Senthilraja *et al.*, (2016).

4.9 Modified nanostructure (ZnO/NF) as a photocatalyst

4.9.1 Photocatalytic degradation of organic dyes:

The photocatalytic activities of the ZnO/NF nanocomposites on the degradation of three organic dyes which include; (i) methylene blue (MB), congo red (CR) and Rhodamine B (RB) were evaluated by the photodegradation of the dyes under UV light, and recorded at different irradiation times in the presence of different amount of the photocatalyst (ZnO/NF) – 20 mg, 40 mg, 50 mg and 75 mg as shown in Fig. 4.9 a-d, respectively. It can be clearly

seen that in the photodegradation processes of MB, the absorbance decreases gradually with the increase in time of irradiation and that 50 mg of the photocatalyst is the most efficient. A close observation of the Fig.4.9 a-d clearly suggests that the photodegradation efficiency of 50 mg of the photocatalyst is higher when compared with that of others. Hence, 50 mg of the catalyst was used for the photodegradation of both congo red (CR) and rhodamine B (RB). Figures 4.10a-b shows the absorption spectral of photo-reaction of congo red and rhodamine B respectively. In comparison, rhodamine B degraded least, while methylene blue was the most photo-degraded. Also for optimization, the best solution media for the photocatalytic reactions were also examined and found to be the basic medium as shown in figures 4.11a and 4.11b. The photocatalytic reactions at pH of 9 was better than those at pH of 5. This may be attributed to the presence of basic ionic medium which is able to absorb a part of either excitation or the emission energy. The structural formulae of the dyes are shown in fig. 4.13f – h.

4.9. 2 Photodegradation Efficiency

The de-colorization efficiency can be calculated using equation 2,

$$\eta = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \quad 2$$

where C_0 and C are the dye's initial concentration and the concentration after the irradiation time 't', respectively and A_0 and A are the corresponding absorbance values. The plots of $\ln(A_0/A)$ against irradiation time drawn for all the samples (varying amount of catalysts in methylene blue) are shown in Fig. 4.12a-b. The degradation rate constants (k) were calculated from the slope of the straight line drawn using the linear regression according to the first-order kinetic law $\ln(A_0/A) = kt$. The calculated k values and the corresponding linear fitting with a linear regression coefficient degree (R^2) values are shown in Table 4.4. The values of k

and R^2 clearly indicate that 75.0 mg of the ZnO/NiFe₂O₄ nanoparticles exhibits better photocatalytic performance which may be attributed to the presence of larger number of reacting ions (species). The Calibration plots of the photodegradations of the organic dyes, methylene blue (MB), congo red (CR) and rhodamine B (RB) and their combined linear fittings are shown in figures 4.13a-d. It was observed that methylene blue was the most degraded, while rhodamine B degraded least which may largely be attributed to the structural formulae of the dyes (shown in fig. 13f – h) and the favourable media solutions. These results are supported by the findings of Li *et al.*, (2015) in their similar work, “Synthesis of highly permeable Fe₂O₃/ZnO hollow spheres for printable photocatalysis”

Table 4.4: Photocatalytic reaction parameters of ZnO/NiFe₂O₄ nanoparticles

Amount of Catalyst (mg)	Rate constant (k), min⁻¹	R²
20.00	0.0289	0.9315
40.00	0.0617	0.9597
50.00	0.0779	0.9656
75.00	0.0896	0.9897

Moreover, the close interphase contact coupling of NiFe₂O₄ and ZnO nanoparticles in ZnO/NiFe₂O₄ nanoparticles should play an important role in enhancing the photoreactivity as opined by Lai *et al.*, (2011). Generally, the close coupling of ZnO/NiFe₂O₄ nanoparticles results in enhancing the electron transfer rate between interfaces and hindering the recombination of photo-generated electrons and holes. The active species involved in the reaction of photocatalytic degradation of MB dye solution are hydroxyl radicals ($\bullet$ OH), photogenerated holes (h^+), and superoxide radical anions ($O_2^{\bullet-}$). Thus, $\bullet$ OH and h^+ play

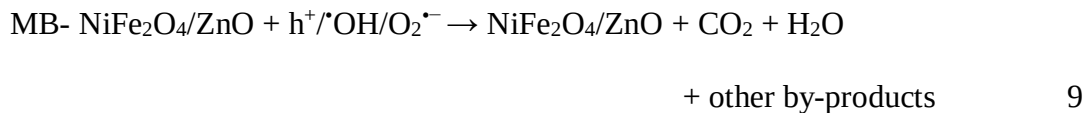
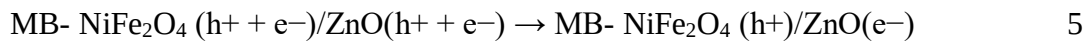
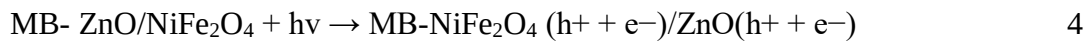
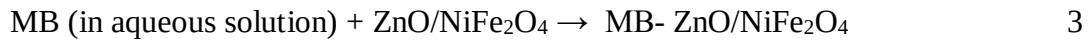
important roles in the photocatalytic degradation of organic pollutants by ZnO/NiFe₂O₄ nanoparticles under UV light which is in accordance with the reports from literatures. In similar works of Hua-Yue *et al.*, (2016), Zhu *et al.*, (2015) and Tang *et al.*, (2015), the findings of this research work on photocatalytic activities of the synthesized ZnO/NF are supported.

Fig. 4.13 (e) shows the self-photo degradation of MB dye under UV irradiation without ZnO/NF. It also shows the ZnO/NF photocatalytic performance in the absence of UV irradiation. When comparing both of these activities, ZnO/NF has slightly degraded the MB dye in the absence of UV irradiation. In the case of self-photo degradation of MB dye under UV irradiation, there is no significant activity in dye degradation. It is also observed from this comparison study that ZnO/NF shows more photodegradation performances than ZnO NR.

4.9.3 Photocatalytic Reaction Mechanism

The first reaction is the adsorption of MB dye molecules on ZnO/NiFe₂O₄ nanoparticles shown in equation 3 which in turn leads to dye-sensitization of ZnO in NiFe₂O₄/ZnO nanoparticles. Under UV light, electrons (e⁻) in the valence band (VB) of dye-sensitized ZnO and NiFe₂O₄ will be excited to the CB while the same amount of holes (h⁺) in the VB is produced (Eq. 4). The CB potential of ZnO is more positive than that of the NiFe₂O₄ while the VB potential of NiFe₂O₄ is more negative than that of the ZnO. Therefore, the photoelectrons (e⁻) photo-produced in NieFe₂O₄ were transferred across the interface of the NiFe₂O₄/ZnO nanoparticles to the surface of ZnO (Eq. 5). At the same time, some holes (h⁺) are transferred injected quickly from ZnO to NiFe₂O₄ due to the more negative VB potential of NiFe₂O₄ than that of the ZnO and the close interphase contact of NiFe₂O₄ and ZnO. The fast migration of h⁺ and e⁻ lead to the improved lifetime and transfer of photo-generated charge carriers as opined by Hou *et al.*, (2011). The dissolved oxygen (O₂) in

aqueous solution acting as the electron scavenger reacts with electrons to yield active free radicals ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, etc.) [Eqs. (6) and (7)]. The separated holes will react with electron donors (H_2O) to yield active $\bullet\text{OH}$ free radicals [Eq. (8)]. Subsequently, the surface-adsorbed CR molecules were attacked by the generated h^+ and other free radicals ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, etc.), leading to the degradation and opening-ring reactions (Eq. 9) as suggested by Yao *et al.*, (2015) in their similar work, where they used one-pot approach for synthesis of N-doped $\text{TiO}_2/\text{ZnFe}_2\text{O}_4$ hybrid as an efficient photocatalyst for degradation of aqueous organic pollutants.



4.10 Domestic and Industry Wastewater Treatment Applications

4.10.1 Industry Wastewater Treatment

UV absorbance and chemical oxygen demand (COD) measurements were used for the determination of industry wastewater treatment efficiency using 0.02 – 2 mg/L concentrations of ZnO/NF nanocomposites. The raw industry wastewater containing methyl red dye had a UV absorbance and COD values of 0.303 and 2480 mg/L respectively prior to treatment. The UV absorbance and COD results of the raw industry wastewater are presented in Figures 4.14a and 4.14b respectively. Within the treatment period of 75 minutes, the UV absorbance showed consistent reduction in values from 0.303 to 0.197, 0.169, 0.144, 0.141 and 0.086 for industry wastewater treated with 0.02, 0.5, 1, 1.5 and 2 mg/L concentrations of the ZnO nanorods respectively. There was no significant difference between the UV absorbance values for the industry wastewater treated with 1 and 1.5 mg/L concentrations of the ZnO nanorods. Similarly, reduction in COD values from 2480 mg/L to 1360, 800, 480, 240 and 160 mg/L was obtained for the industry wastewater samples treated with 0.02, 0.5, 1, 1.5 and 2 mg/L concentrations of ZnO nanorods respectively within the treatment period of 75 minutes as shown in table 4.4. Figures 4.14a-c showed that the UV absorbance values were correlated with respective COD values. The 2 mg/L concentration of the ZnO nanorods had the highest industry wastewater treatment efficacy (COD of 93.54%) compared to other concentrations used.

Table 4.5: The UV-Vis and COD of Industry wastewater at varying amount of catalyst

0.02 mg/L	TIME (min.)	UV	COD mg/L
	0.0	0.303	2480
	15.0	0.281	2320
	30.0	0.256	2000
	45.0	0.248	1920
	60.0	0.234	1600
	75.0	0.197	1360
0.5 mg/L	TIME	UV	COD mg/L
	0 min	0.303	2480
	15 min	0.266	2080
	30 min	0.214	1600
	45 min	0.192	1280
	60 min	0.176	800
	75 min	0.169	800
1 mg/L	TIME	UV	COD mg/L
	0 min	0.303	2480
	15 min	0.262	1760
	30 min	0.212	1200
	45 min	0.186	800
	60 min	0.146	560
	75 min	0.144	480
1.5 mg/L	TIME	UV	COD mg/L
	0 min	0.303	2480
	15 min	0.231	1760
	30 min	0.201	960
	45 min	0.194	720
	60 min	0.149	240
	75 min	0.141	240
2 mg/L	TIME	UV	COD mg/L
	0 min	0.303	2480
	15 min	0.212	1760
	30 min	0.164	640
	45 min	0.096	160
	60 min	0.089	160
	75 min	0.086	160

Similarly, The UV absorbance and COD results of the raw domestic wastewater are presented in table 4.5. The reduction in COD values from 476.8 mg/L to 28.8 mg/L was obtained for the domestic wastewater samples treated with 0.02, 0.5, 1, 1.5 and 2 mg/L

concentrations of ZnO nanorods respectively within the treatment period of 75 minutes. The results showed that the 2 mg/L concentration of the ZnO nanorods had the highest domestic wastewater treatment efficacy of 93.95% of COD reduction in 75 minutes as shown in figure 4.13c.

Table 4.6: The UV-Vis and COD of domestic wastewater at varying amount of catalyst

0.02 mg/L	TIME	COD mg/L
	0 min	476.8
	15 min	475.2
	30 min	363.2
	45 min	292.6
	60 min	270.4
	75 min	268.8
0.5 mg/L	TIME	COD mg/L
	0 min	476.8
	15 min	468.8
	30 min	320.0
	45 min	230.4
	60 min	172.8
	75 min	176.0
1 mg/L	TIME	COD mg/L
	0 min	476.8
	15 min	331.2
	30 min	236.8
	45 min	142.4
	60 min	44.8
	75 min	43.2
1.5 mg/L	TIME	COD mg/L
	0 min	476.8
	15 min	297.6
	30 min	152
	45 min	86.4
	60 min	33.6
	75 min	32
2 mg/L	TIME	COD mg/L
	0 min	476.8
	15 min	278.4
	30 min	105.6
	45 min	32
	60 min	28.8

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS.

5.1 Summary of the Findings

Zinc oxide nanorods (ZnO NR) have been successfully synthesized through green synthesis route. The results of characterization of the zinc oxide nanostructure confirmed the formation of a crystalline hexagonal wurtzite structure of the ZnO NR with average grain size of 6.67 nm. It also revealed the participation of biological (organic) molecules in bio-reduction reactions, formation, capping and stabilization of the nanoparticles and that revealed that only zinc (Zn), and oxygen (O) signals were detected and no other signal of secondary phase or impurity was detected. This implies the high purity chemical composition of the green synthesized ZnO NR. The ZnO NR has low dielectric losses which makes it desirable in the dielectric system.

Spinel nickel ferrite nanorods (NF NR) were also successfully synthesized by co-precipitation chemical method. From the characterization results, it was revealed that the structure of the synthesized nickel ferrite NF were prismatic hexagonal shape with granular nano sized range of 10 nm – 20 nm with elemental compositions of only nickel (Ni), iron (Fe) and oxygen (O), indicating its purity.

Similarly, zinc oxide / nickel ferrite nanocomposites were successfully synthesized. The results of its characterization revealed the high degree of agglomeration and different surface morphologies which may be due to the magnetic attraction between nickel ferrite and zinc oxide layers and that the average grain size of the synthesized ZnO/ NF nanocomposites were obtained to be 7.67 nm.

The impedance spectroscopic (IS) studies of the green synthesized zinc oxide nanorods (ZnO NR) revealed that it has high dielectric constant (750), and low dielectric loss angle, σ which makes it desirable for the systems.

A silver solar cell have been successfully coated with the synthesized ZnO NR by drop casting method. As a result, the fill-factor FF was increased from 0.37 to 0.51, and hence, the efficiency enhancement of 4.48%.

The bio-sensing ability of the modified ZnO NR was revealed by the photoluminescence (PL) spectroscopy which showed that as the glucose concentration increases, the sensing activity intensity has peaks in the UV region of 350 nm, the intensity increases in the yellow and orange emission spectrum and decreases in the red emission spectra of 700 nm.

The photocatalytic studies reveal that the ZnO/NF nanocomposite exhibits high degradation efficiency under UV light and that $\bullet\text{OH}$ and photoproduced holes h^+ are the main species in the removal of the organic dyes solution.

For the treatment of domestic and industrial waste water, the green synthesized ZnO NR showed 93.95% and 93.95% of chemical oxygen demand (COD) reduction in 75 minutes.

5.2 Conclusions

It can be inferred from this study that, green (plant extract mediated) synthetic routes is a suitable technique for synthesis of zinc oxide nanostructures. This is an environmental friendly and cost effective route for the synthesis of zinc oxide nanostructures. The study further demonstrated that, zinc oxide nanorods could be modified with nickel ferrites to obtain a multifunctional ZnO/NF nanocomposite for application in dielectric systems, solar cell nanocoating, bio-sensing, photodegradation of organic dyes and for wastewater treatments.

5.3 Recommendations

It is recommended that, green synthesis method should be adopted for the synthesis of eco-friendly, cost effective and multifunctional ZnO NR. The study therefore recommend further research on more plant extracts for the synthesis of zinc oxide nanostructures to improve their properties for onward applications.

5.4 Suggestions for further studies

There are needs to carry out further research on the synthesis and modifications of multifunctional zinc oxide nanostructures in order to improve their applicability. Some of the areas to look into include among others:

The need to research into the green synthesis techniques and conditions of synthesis that can come out with zinc oxide nanostructures with improved properties.

There is also the need to study the active chemical components of plant extracts that acts as reducing and capping agents in the synthesis of metal oxide nanoparticles.

More research has to be done on methods and means of modifications of zinc oxide nanostructures for more and better applications.

Magnetic properties of the nanocomposite can also be looked into for possible electronic applications in further study.

FIGURES

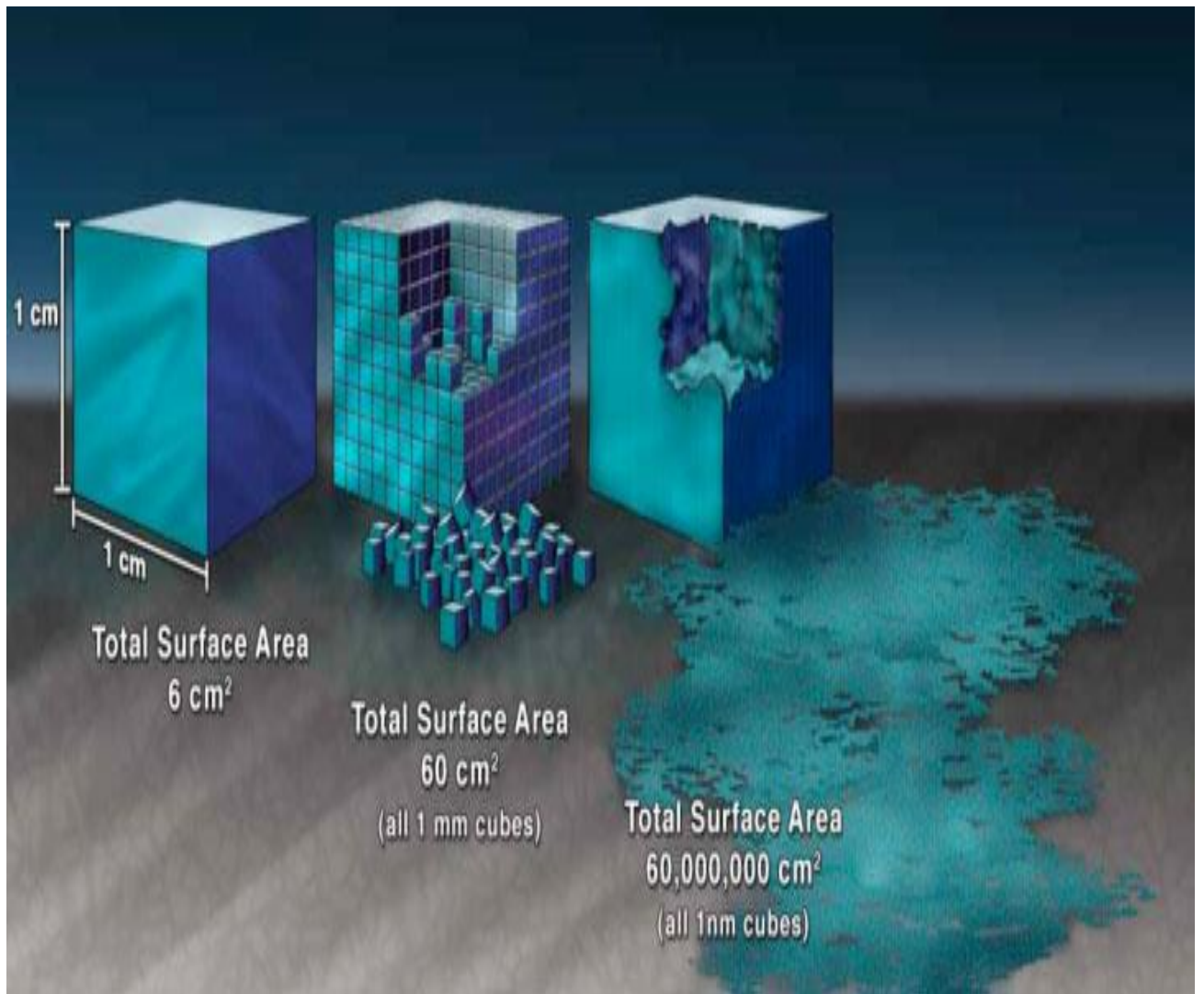


Fig.1.1: Illustration on the effect of the increased surface area of nanostructured materials (source: <https://www.nano.gov/nanotech-101/special>, accessed 01/04/2017)

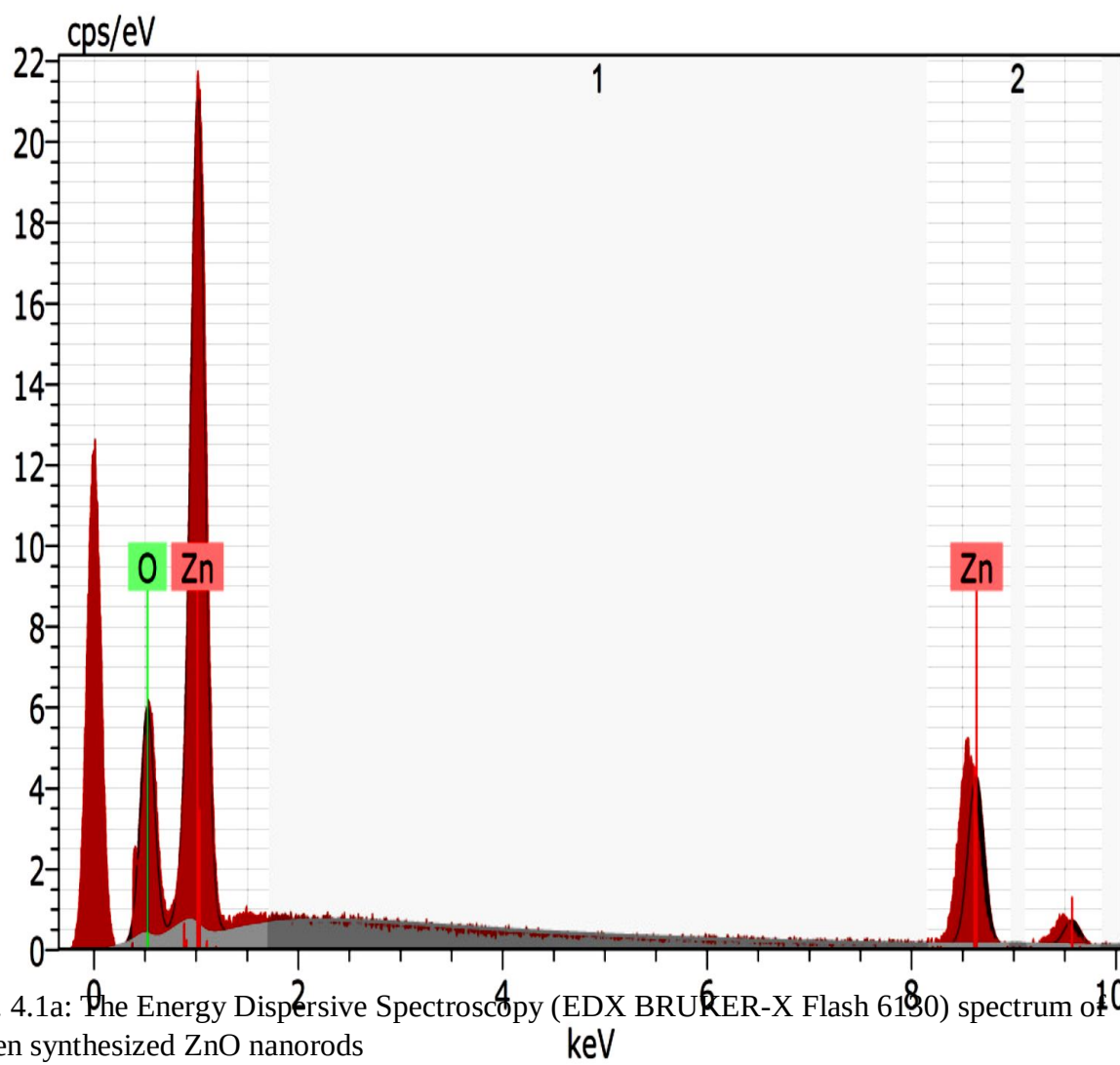


Fig. 4.1a: The Energy Dispersive Spectroscopy (EDX BRUKER-X Flash 6130) spectrum of green synthesized ZnO nanorods

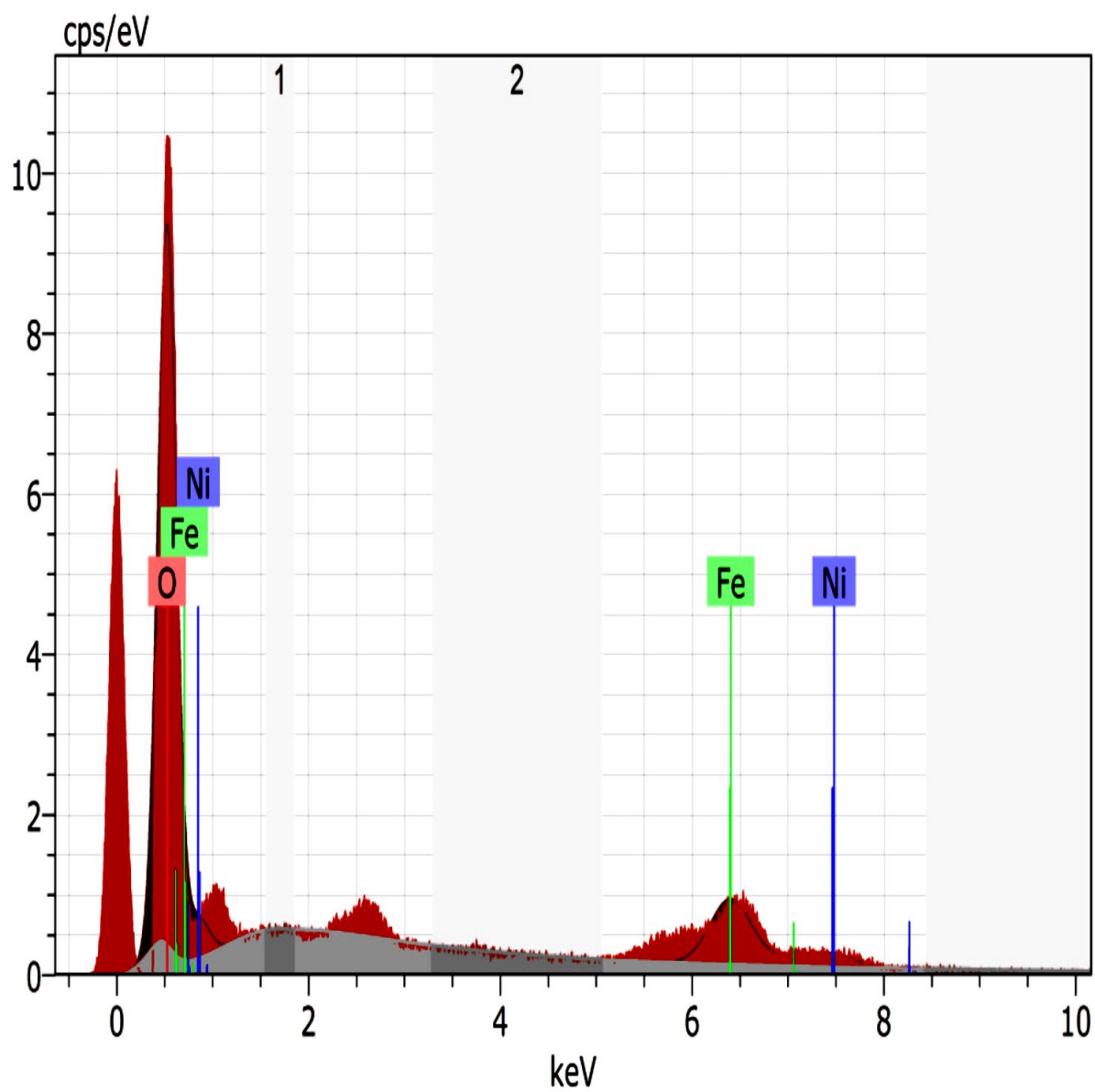


Fig. 4.1b: The Energy Dispersive Spectroscopy (EDX BRUKER-X Flash 6130) spectrum of nickel ferrites nanorods (NF NR)

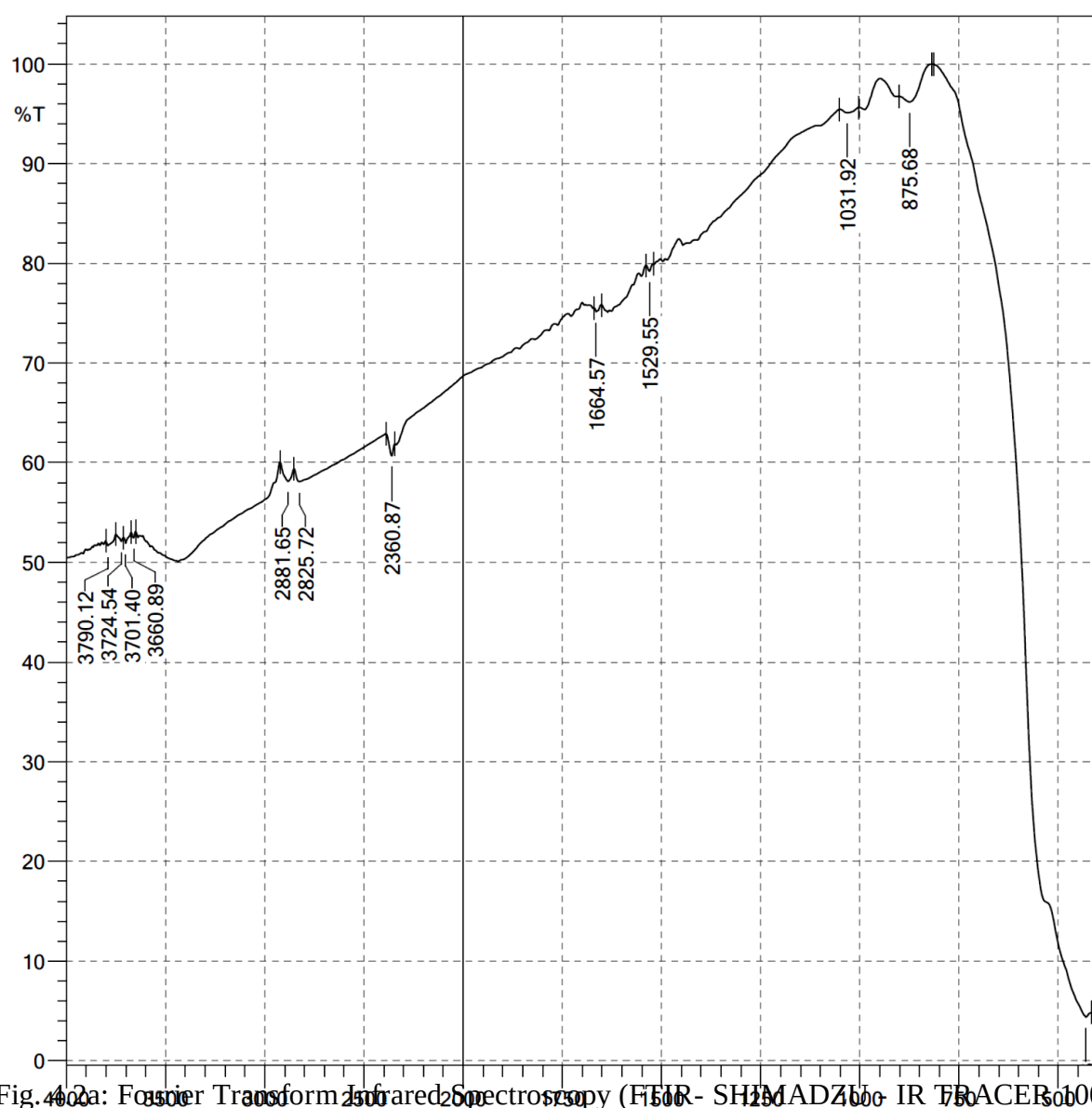


Fig. 4.2a: Fourier Transform Infrared spectroscopy (FTIR- SHIMADZU IR TRACER 100) of Green Synthesized ZnO NR

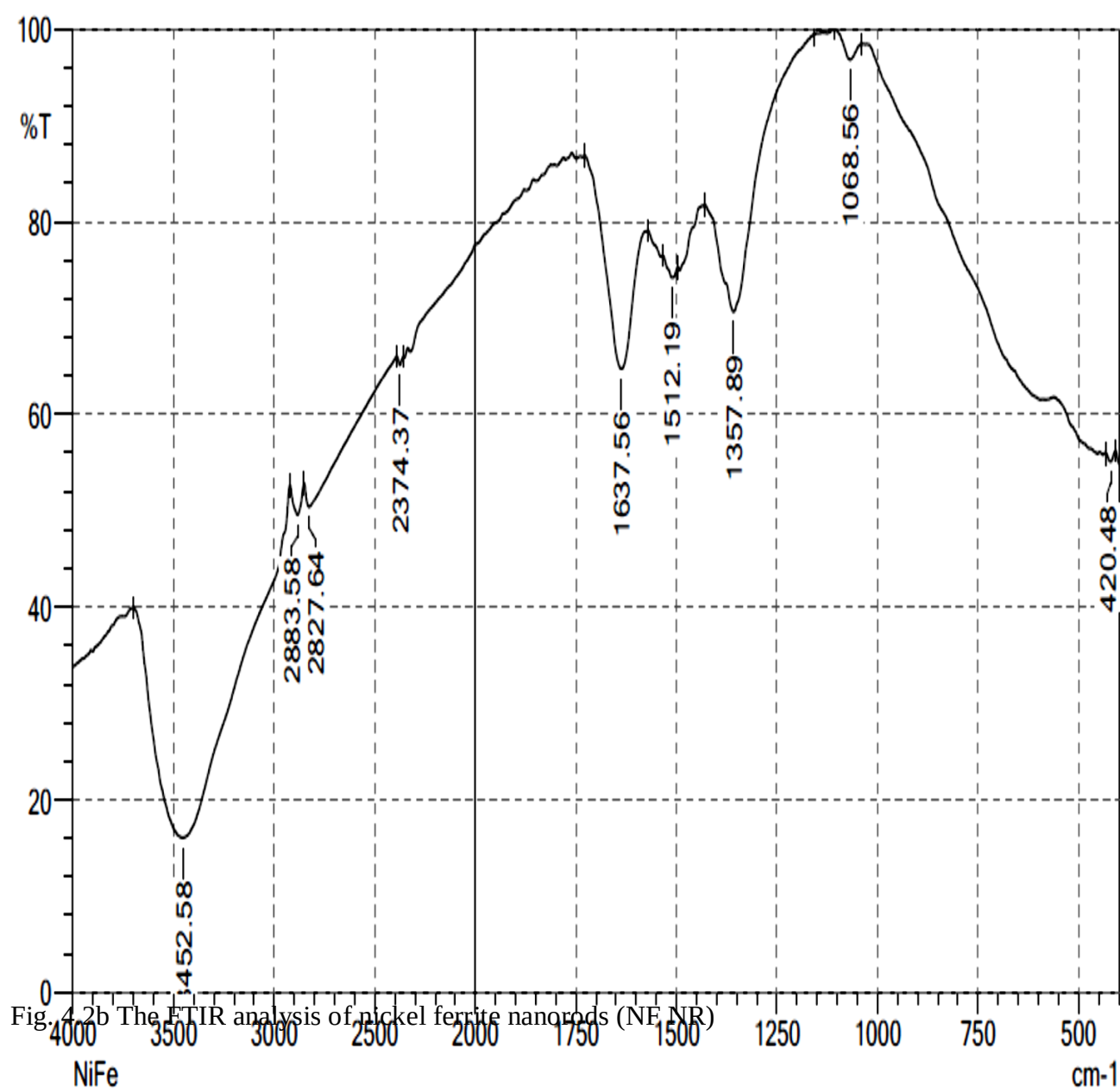


Fig. 4.2b The FTIR analysis of nickel ferrite nanorods (NE-NR)

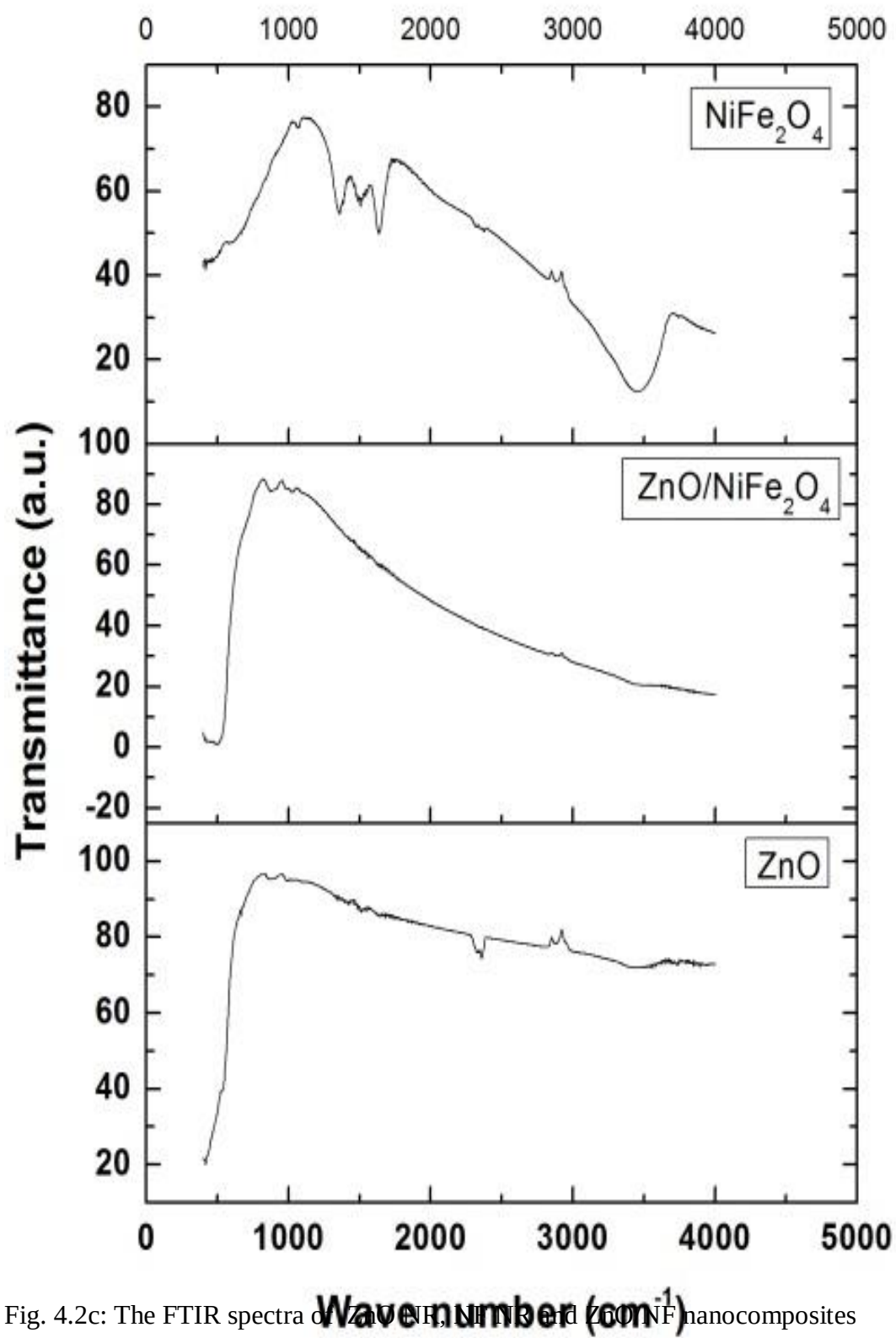


Fig. 4.2c: The FTIR spectra of ZnO/NiFe₂O₄, NiFe₂O₄ and ZnO/NiFe₂O₄ nanocomposites

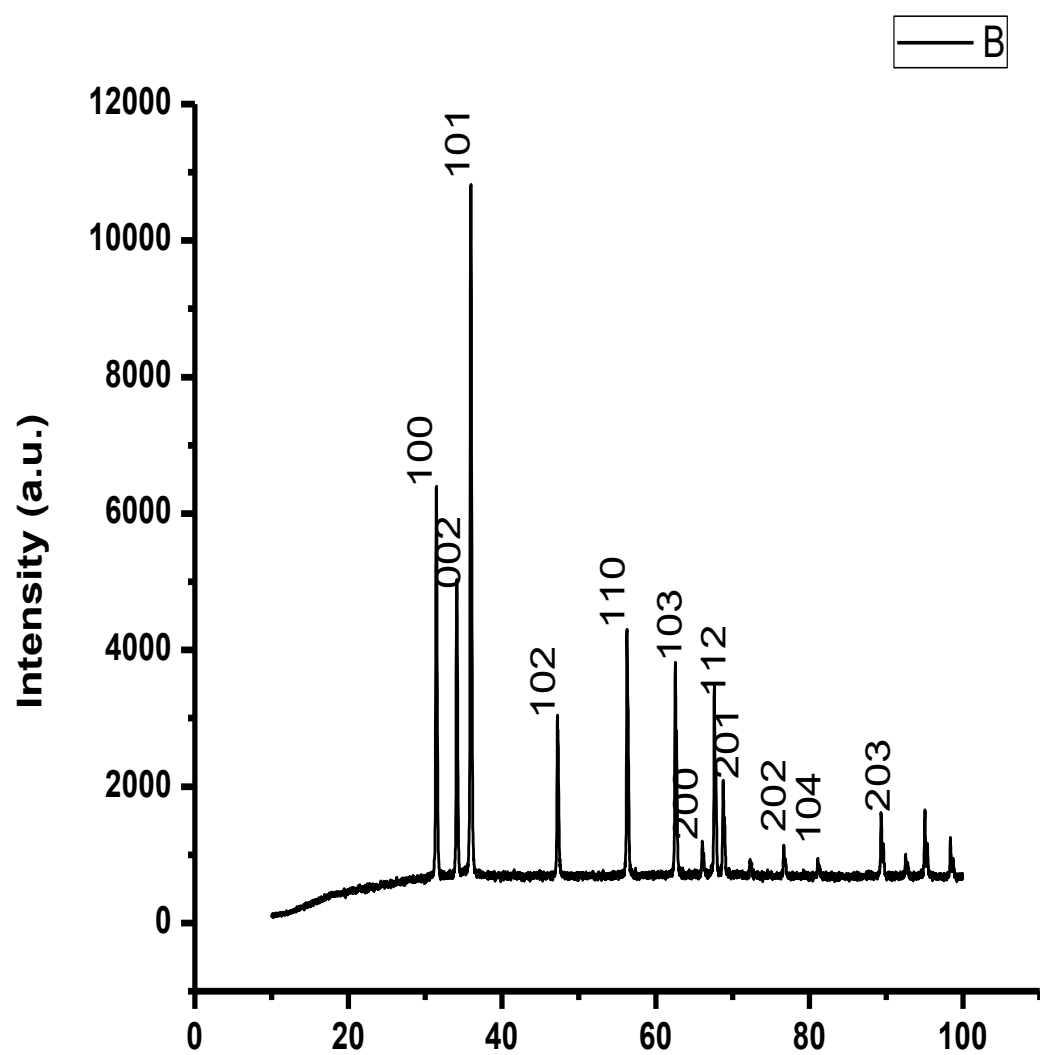


Fig. 4.3a: The X-ray Diffraction (XRD - D8 advance ECO, SSD160 1D Detector) Spectra pattern of the green-synthesized ZnO nanorods

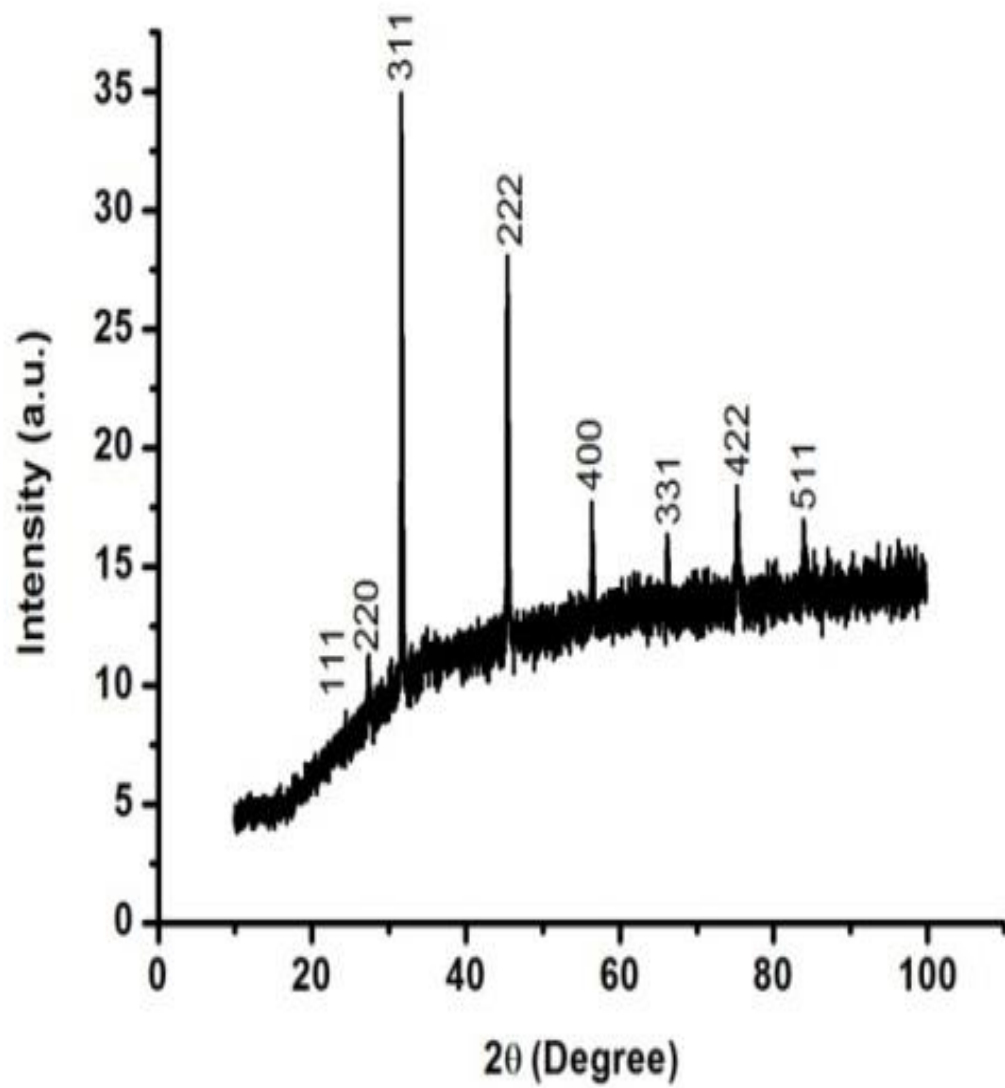


Fig. 4.3b: X-ray diffraction (XRD) pattern of nickel ferrite nanorods (NF NR)

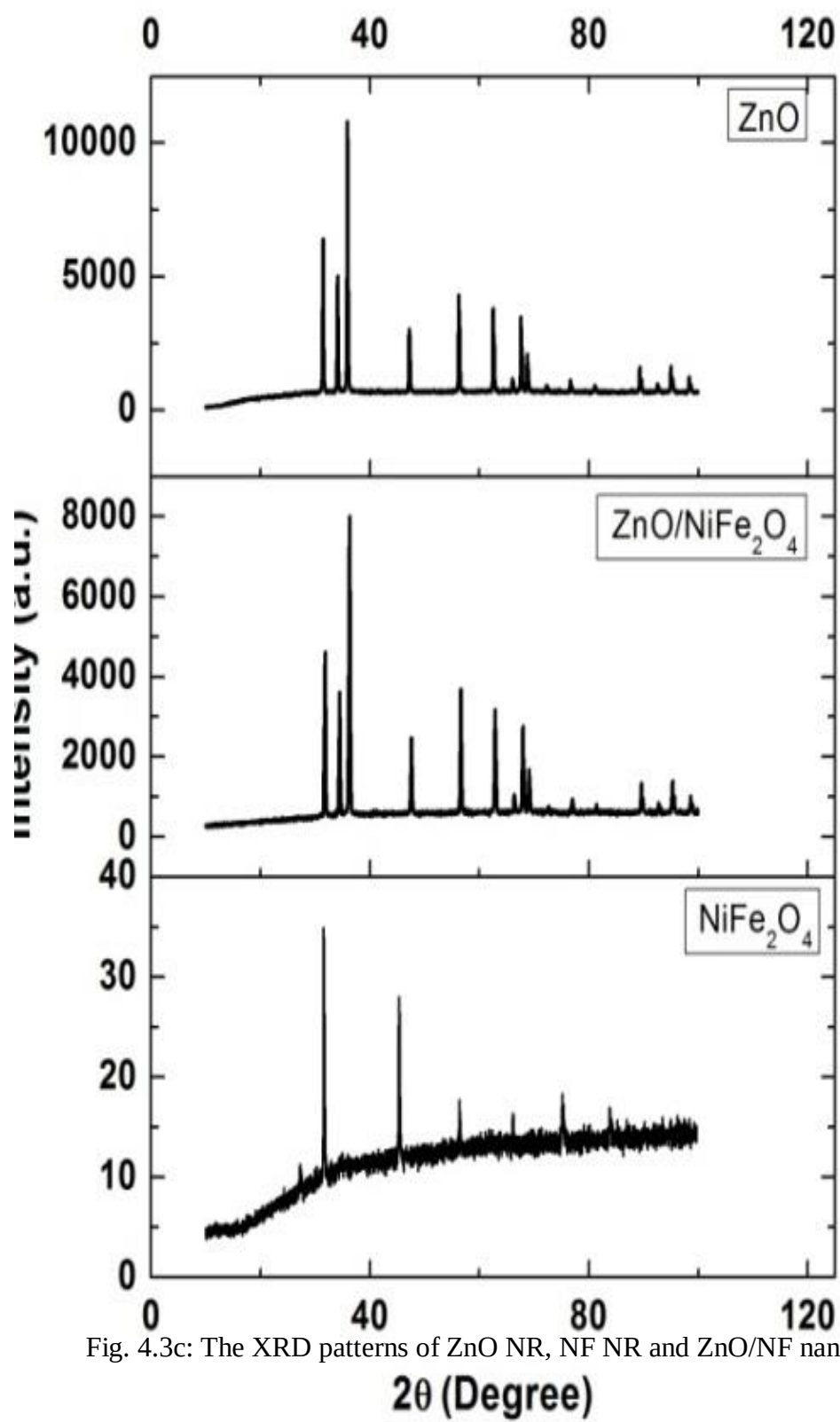


Fig. 4.3c: The XRD patterns of ZnO NR, NF NR and ZnO/NF nanocomposites

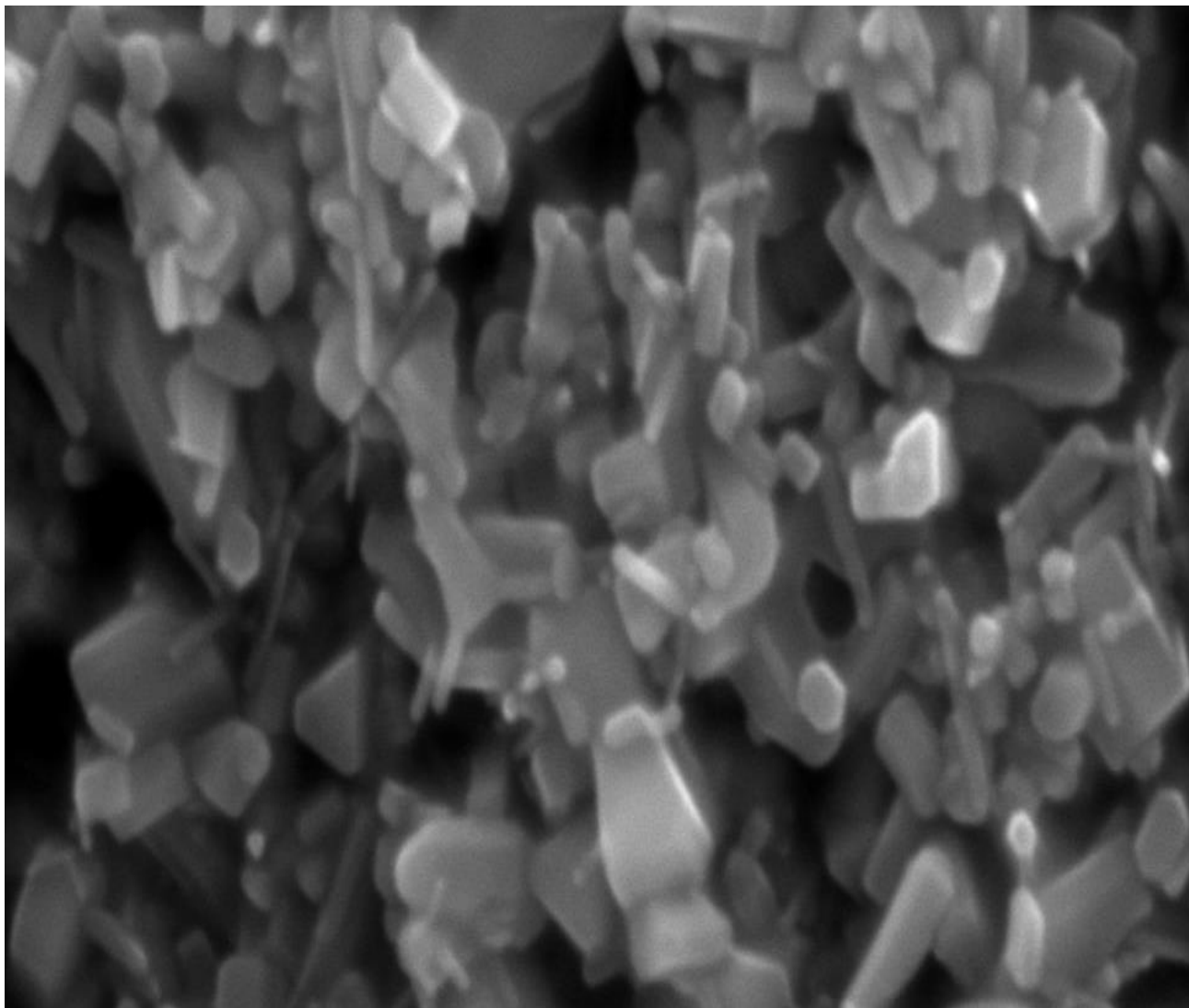


Fig. 4.4a: The scanning electron microscope (SEM, ZEISS-EVO 18 Research) green synthesized ZnO NR



Fig. 4.4b: The scanning electron micrograph (SEM, ZEISS-EVO 18 Research) of nickel ferrite nanorods (NF NR)

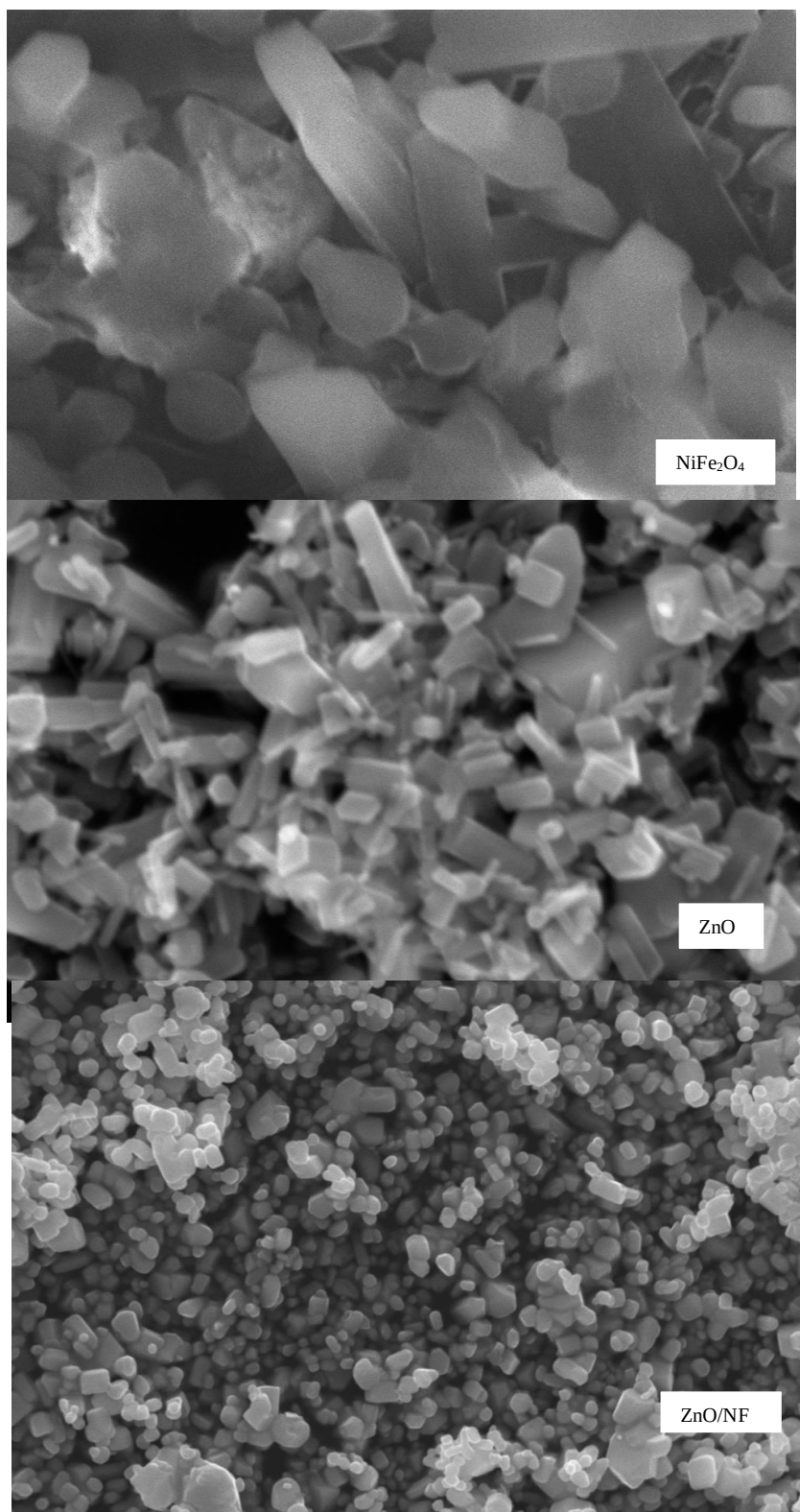


Fig. 4.4c The SEM images of NF NR, ZnO_NR, and ZnO/NF nanocomposites

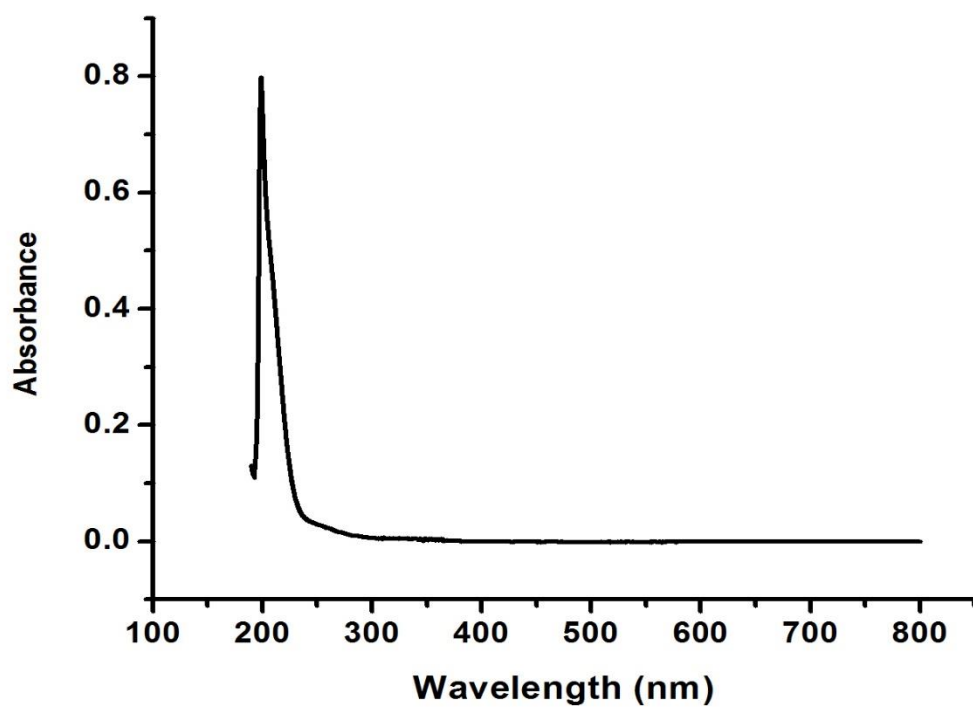


Fig.4.5 a: UV – VIS of Green Synthesized ZnO NR

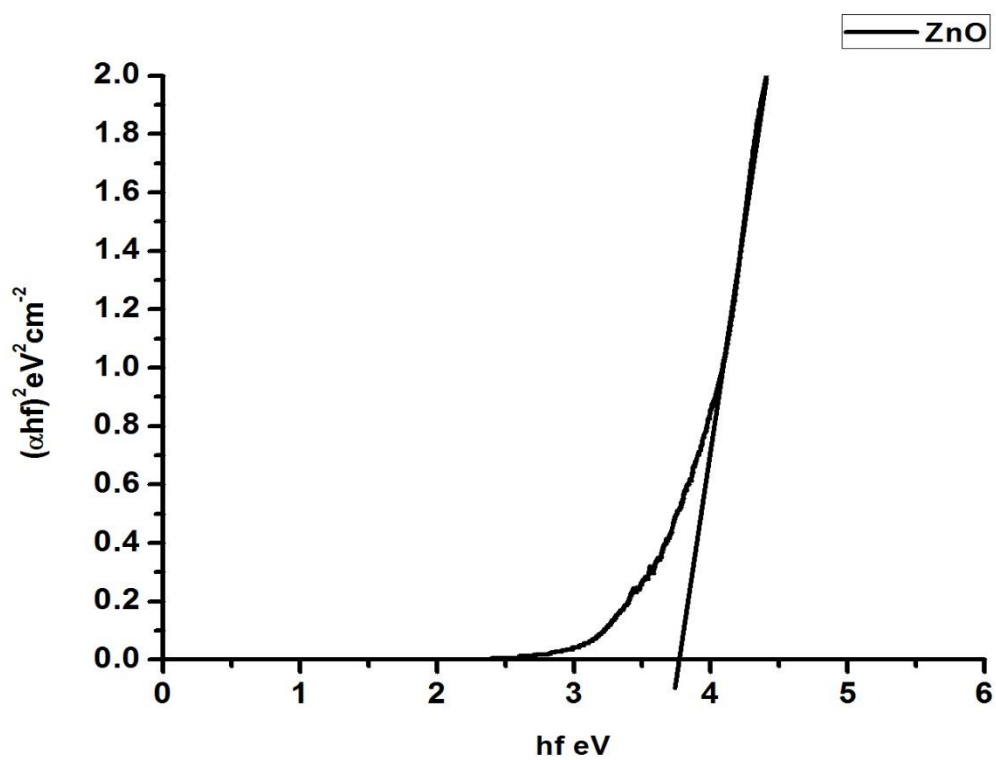


Fig.4.5b: Optical Band Gap of Green ZnO

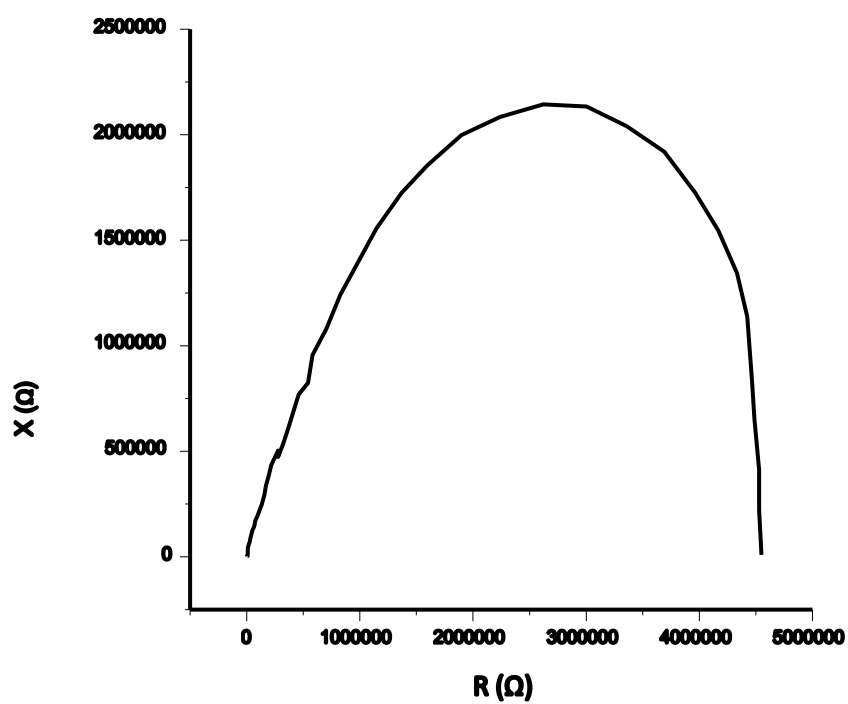


Fig. 4.6a The Cole-Cole plot of bio-synthesized ZnO NPs

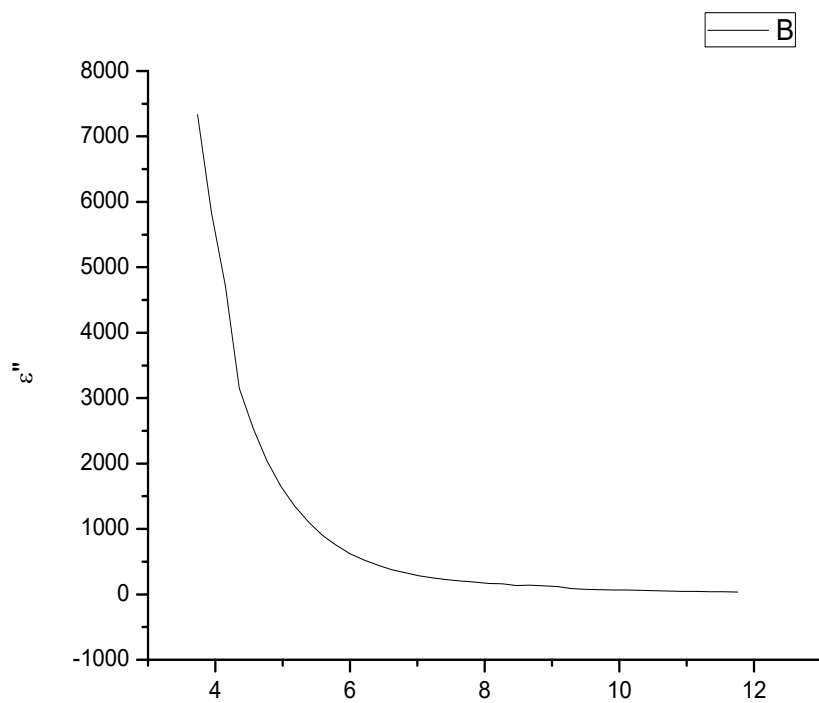


Fig. 4.6b A plot of ϵ'' against $\ln f$

(i)

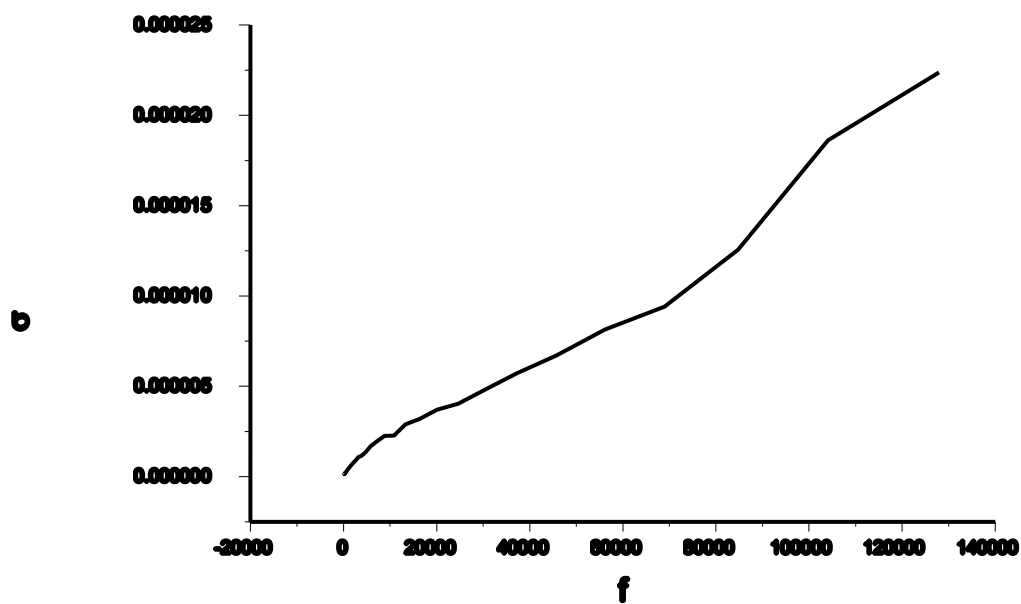


Fig.4.6c: A plot of electrical conductivity against frequency

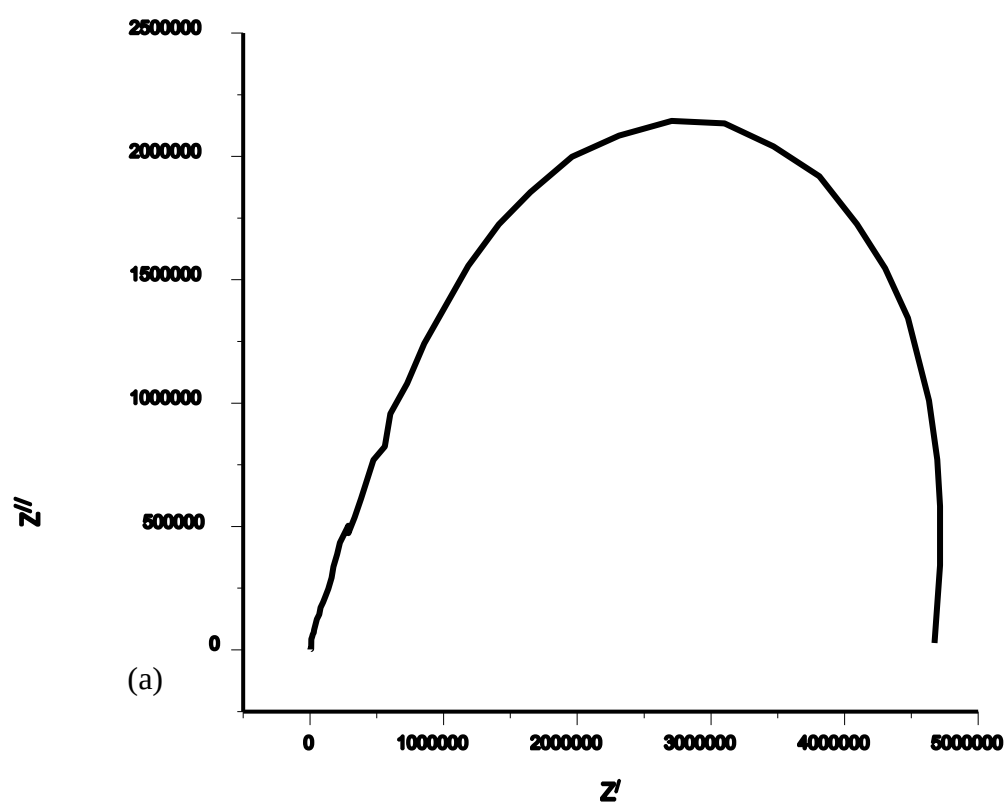


Fig.4.6 (d) Imaginary impedance Z'' versus real impedance

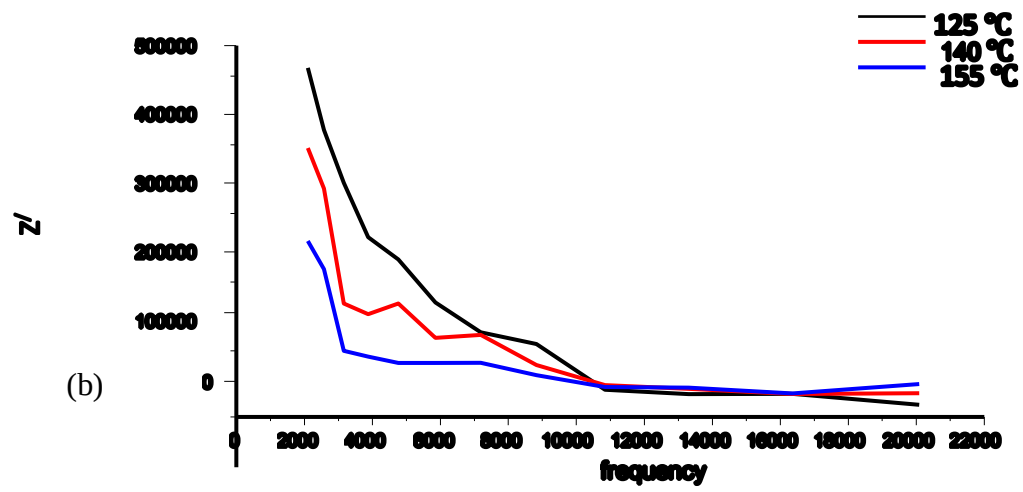


Fig.4.6 (e) Variation of real part of impedance of ZnO NR with frequency at different temper

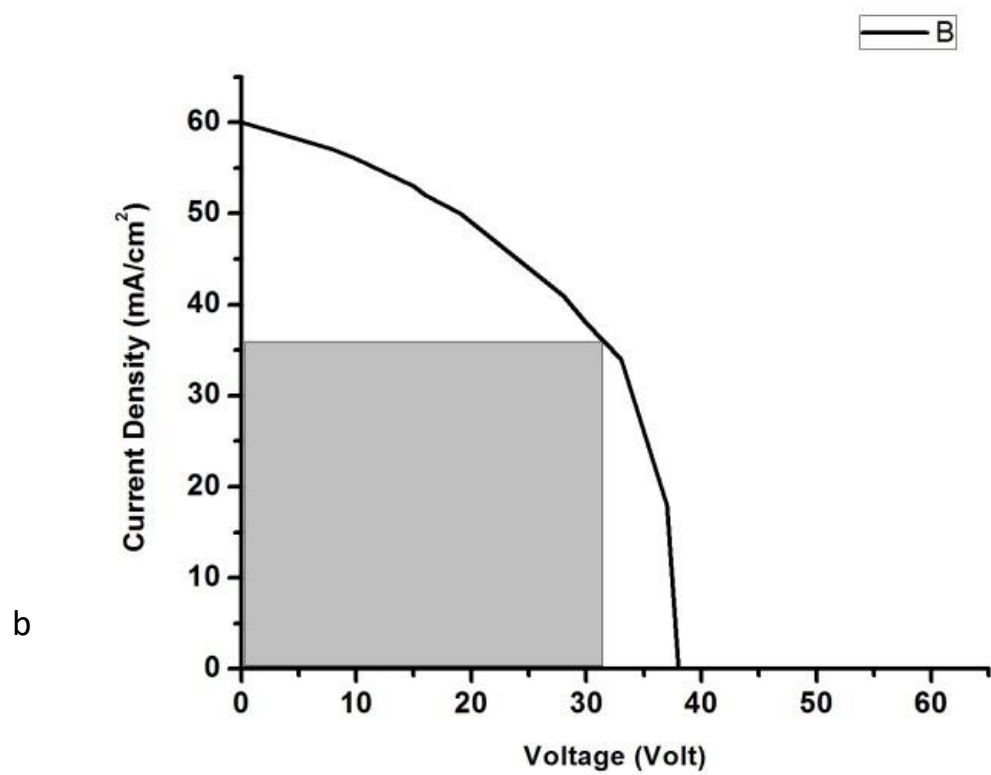
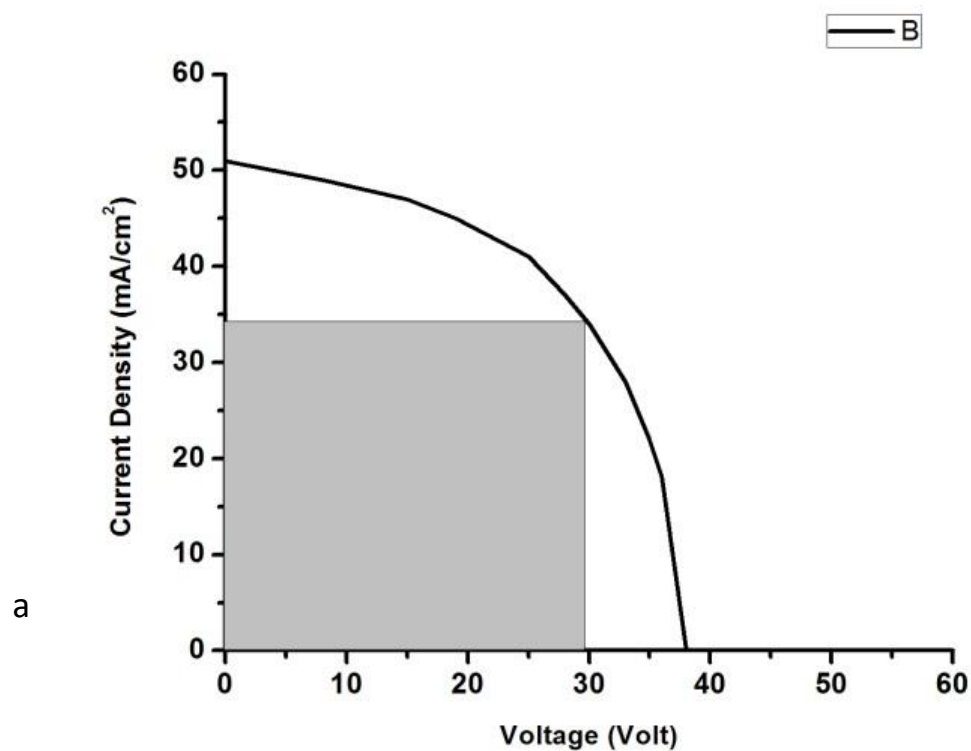


Fig. 4.7 I – V characteristics of the (a) uncoated and (b) coated solar cell samples under solar irradiation (100 mW cm^{-2}).

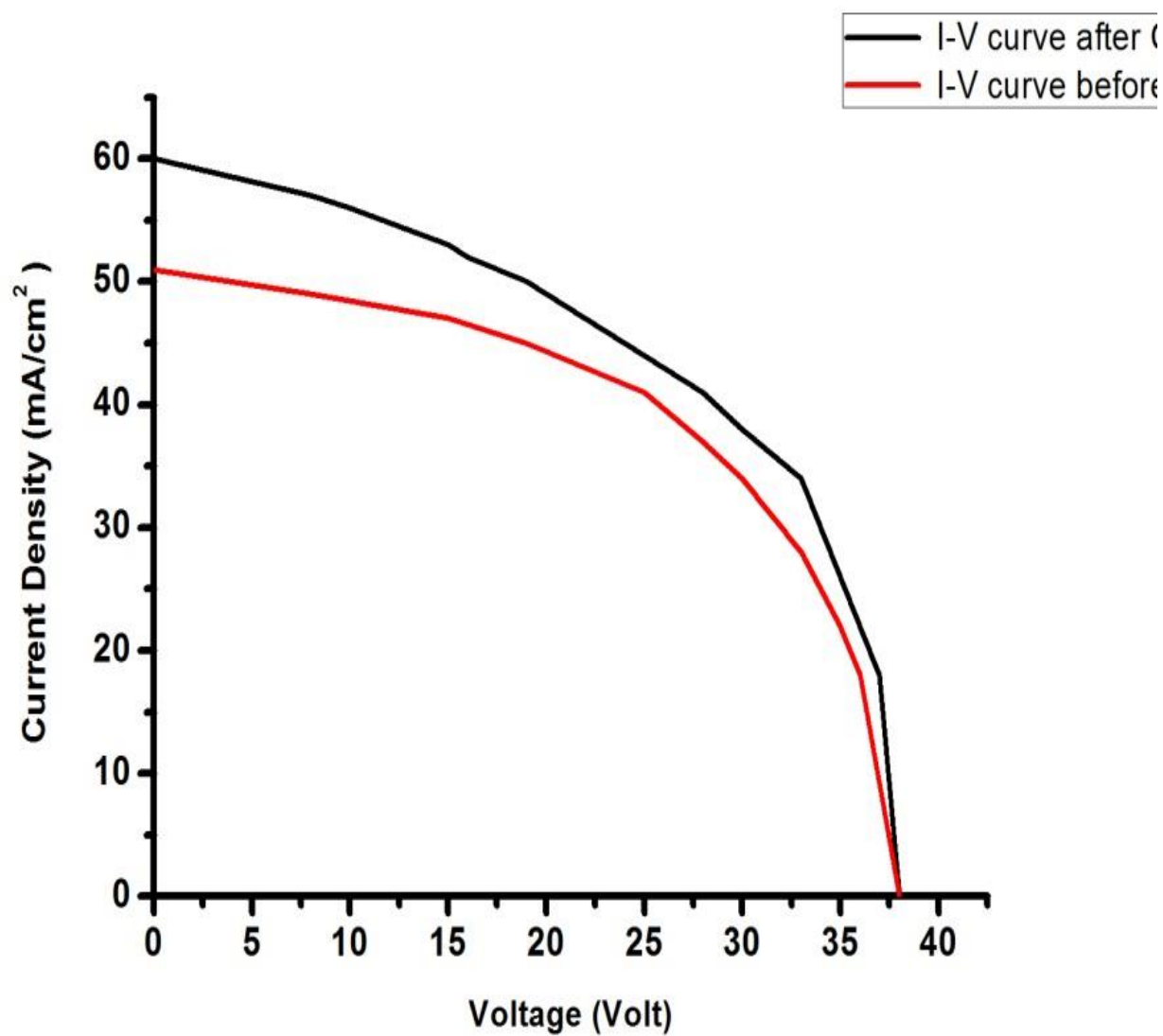


Fig. 4.7c The overlaid I – V characteristics of the (a) uncoated and (b) coated solar cell samples under solar irradiation (100 mW cm^{-2}).

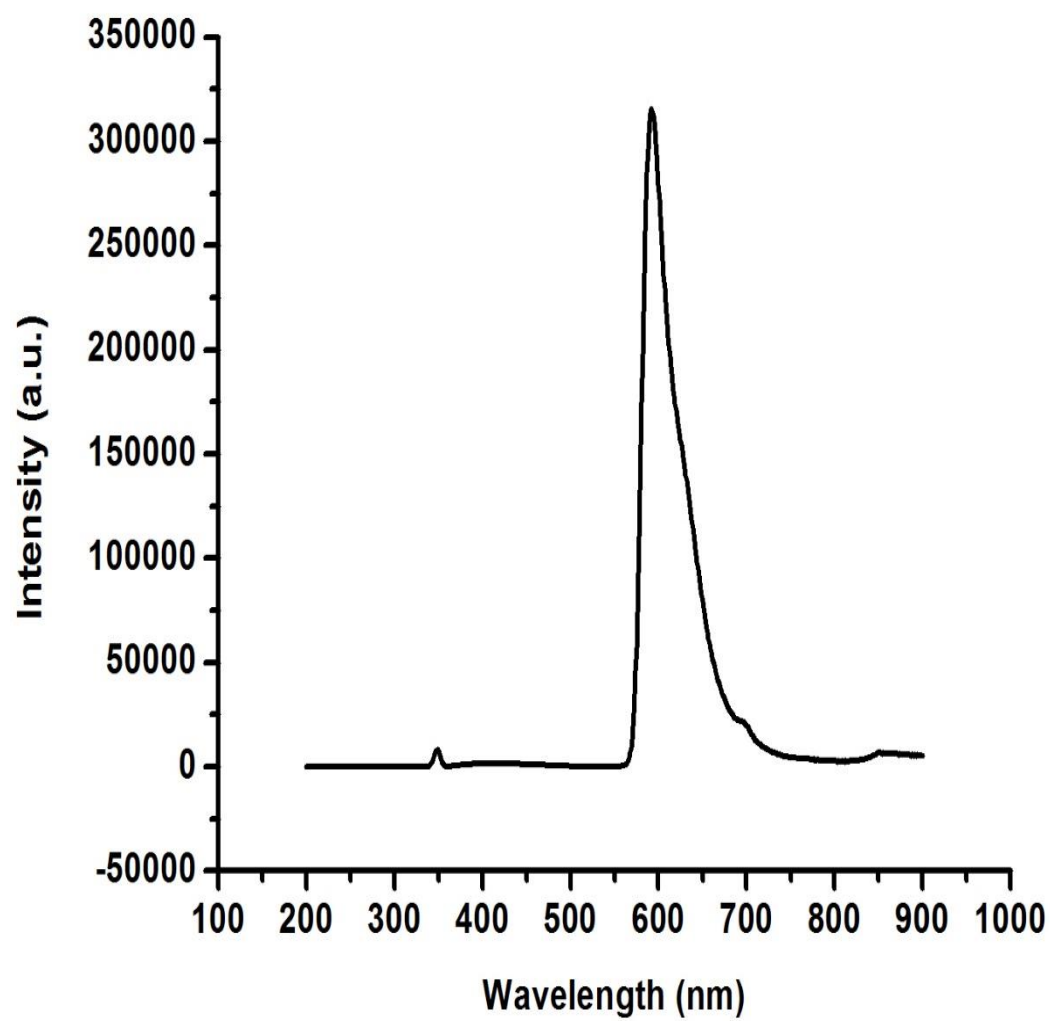


Fig. 4.8a : The Photoluminescence (PL) spectra of ZnO/NF solution - (D)

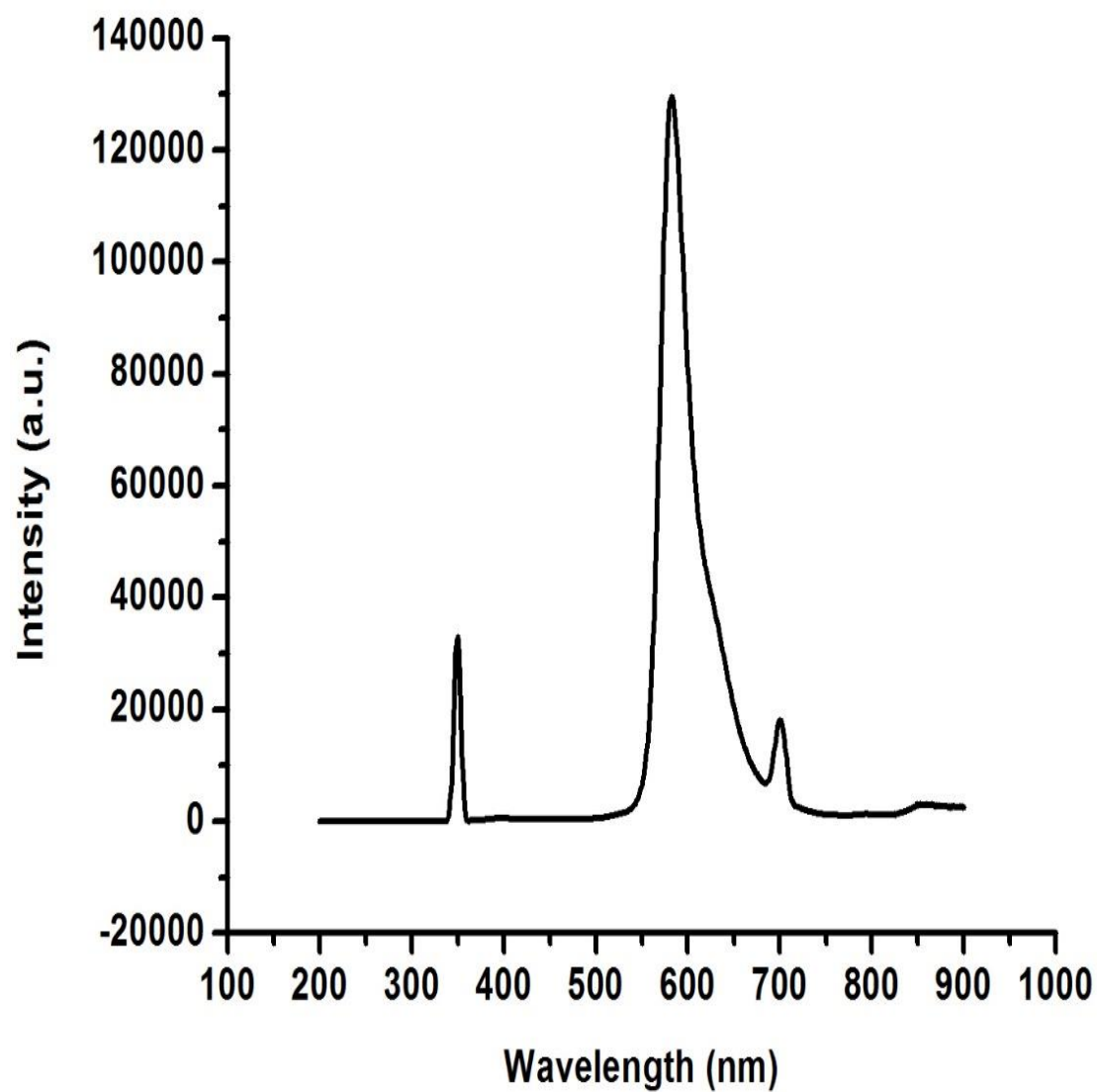


Fig. 4.8b : The Photoluminescence (PL) spectra of ZnO/NF solution + 0.1 mM glucose solution (D₁)

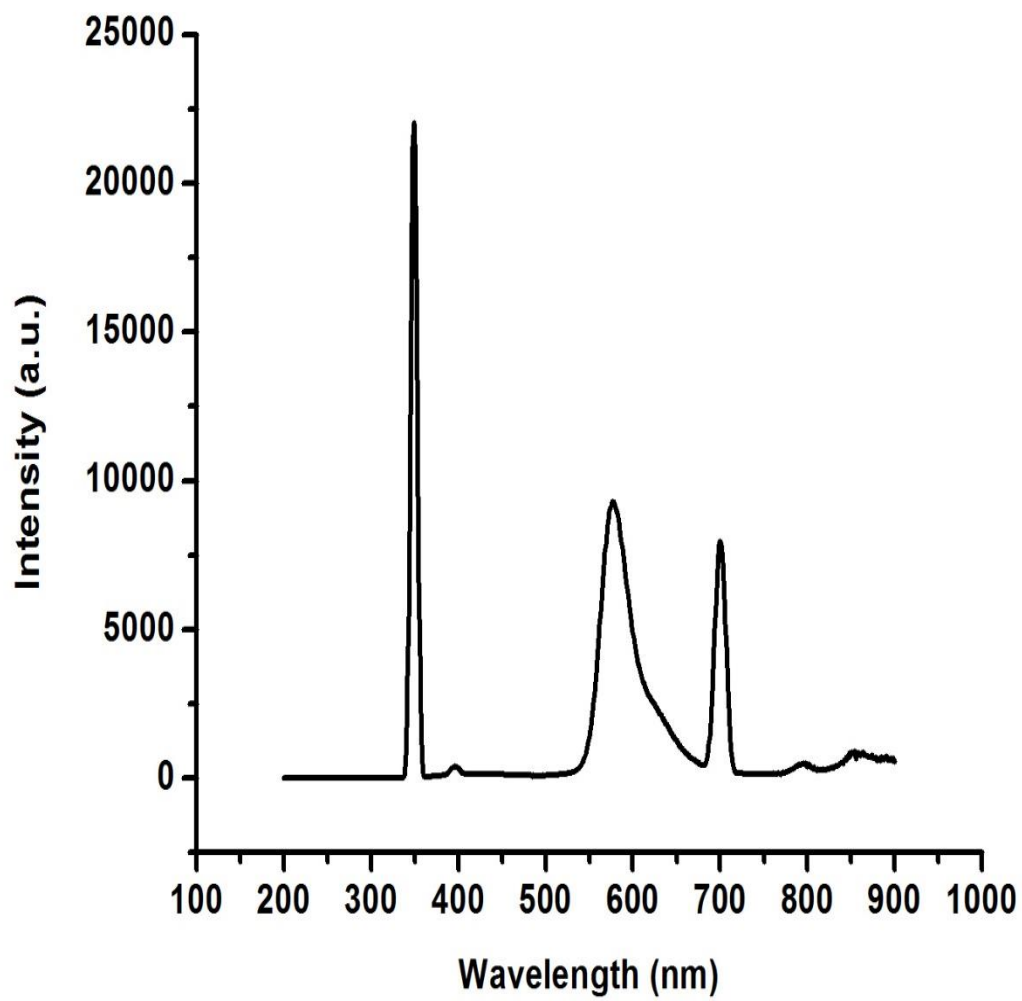


Fig. 4.8c : The Photoluminescence (PL) spectra of ZnO/NF solution + 0.2 mM glucose solution (D₂)

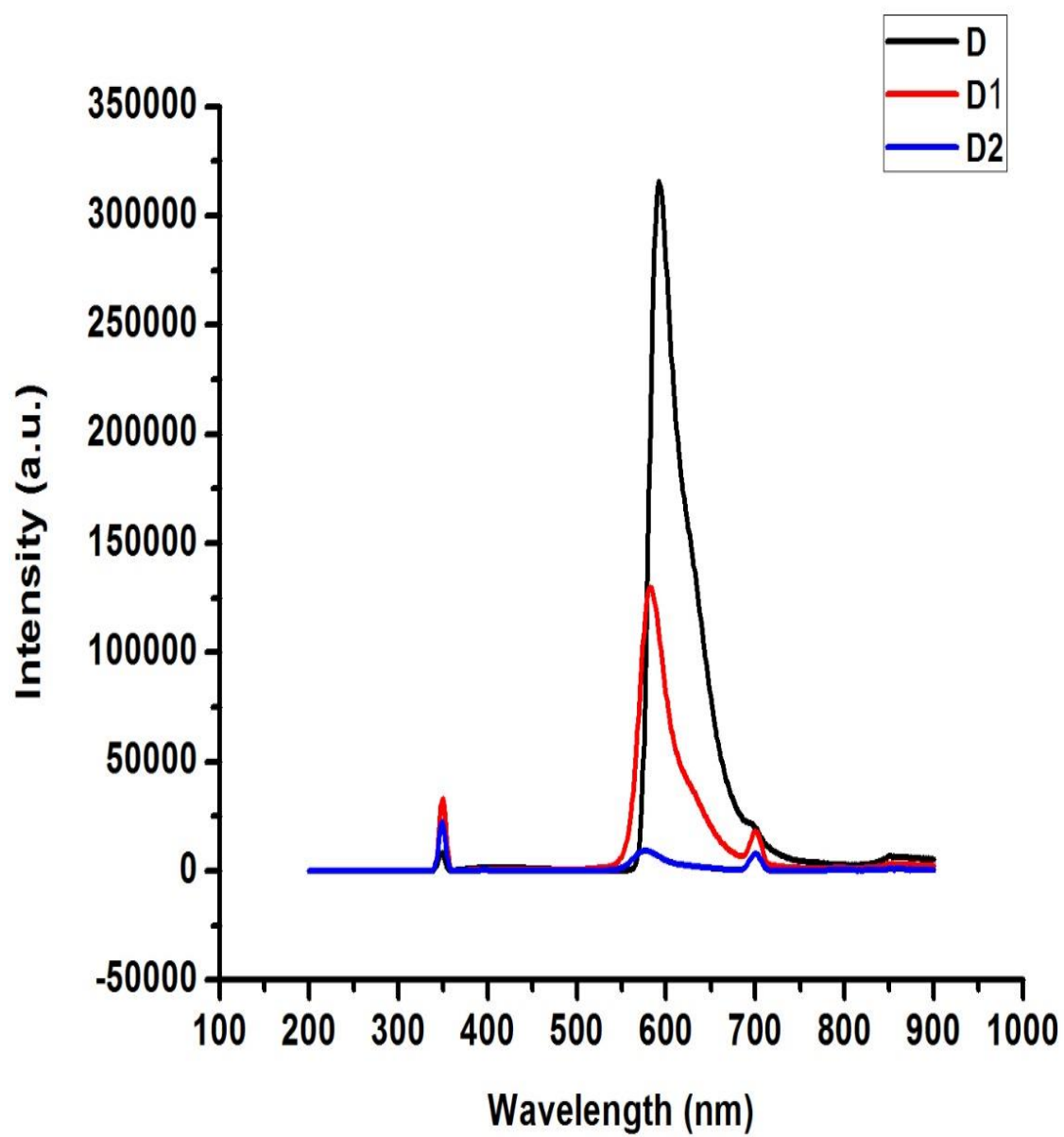


Fig. 4.8d: The Photoluminescence (PL) spectra of ZnO/NF solution + 0.1 mM and 0.2 mM glucose solutions overlaid

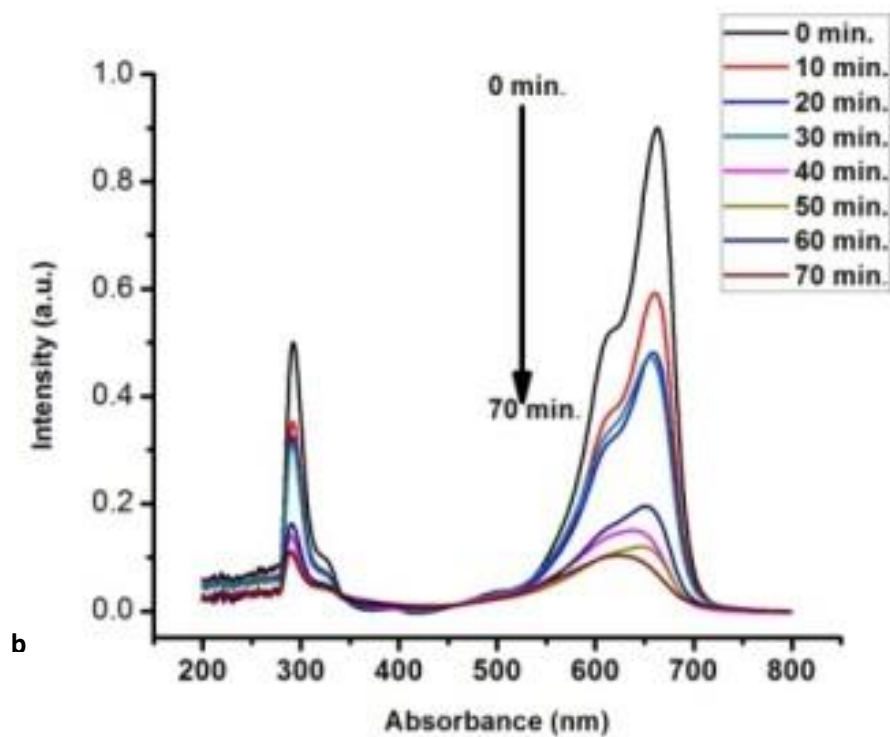
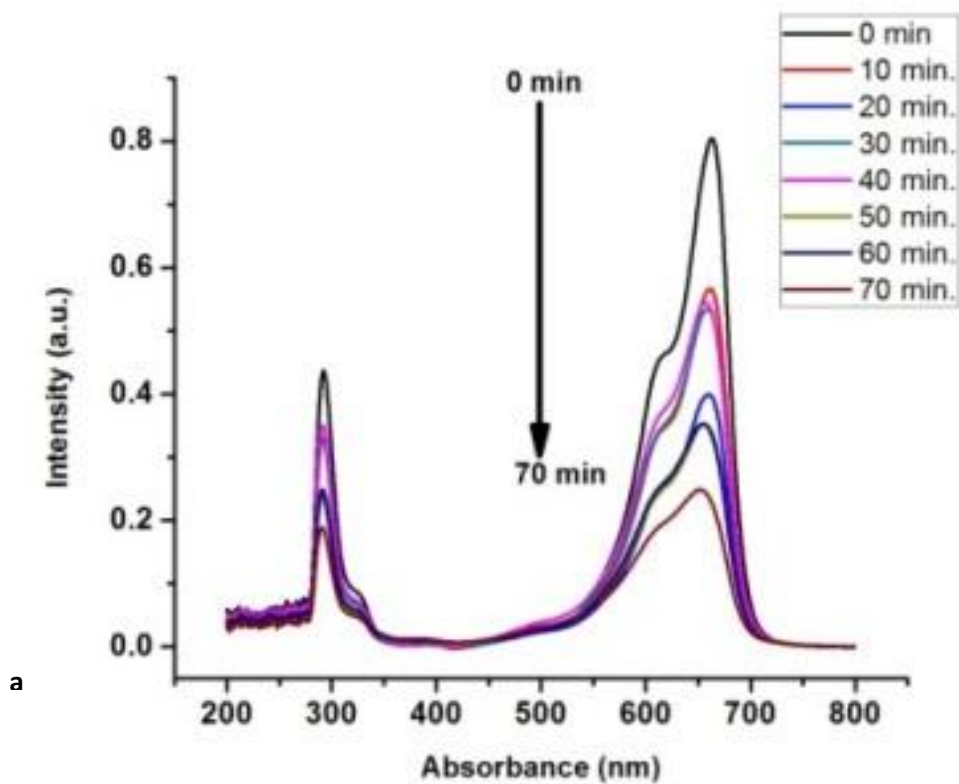


Fig. 4.9a-b: Absorbance spectra of Methylene Blue (MB) dye solution containing (a) 20 mg (b) 40 mg (c) 50 mg and (d) 75 mg of ZnO/NF nanoparticles

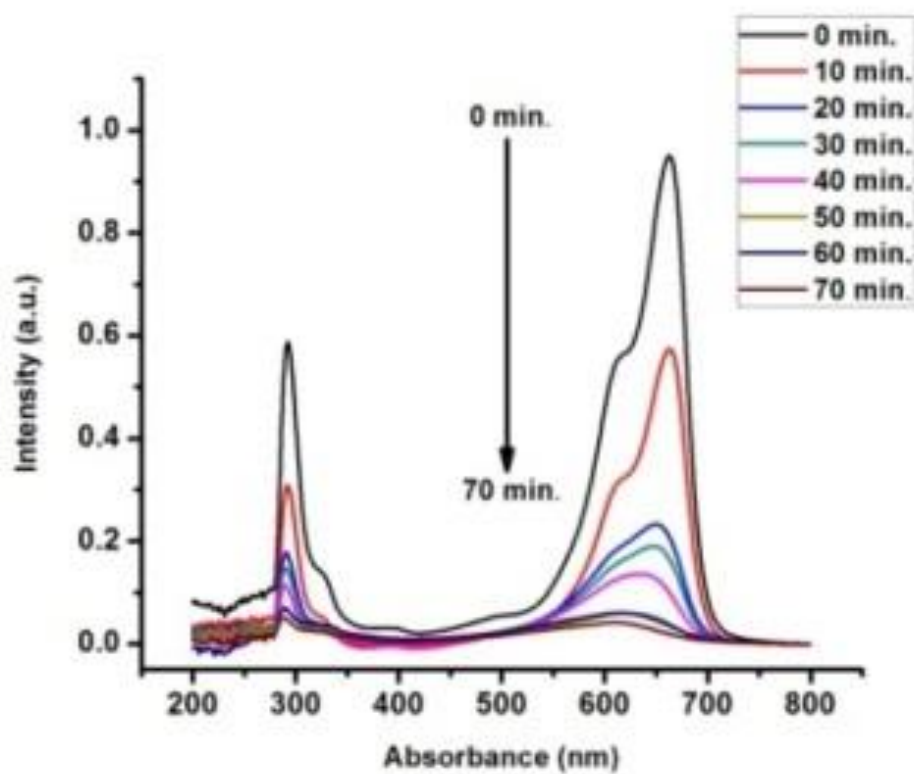
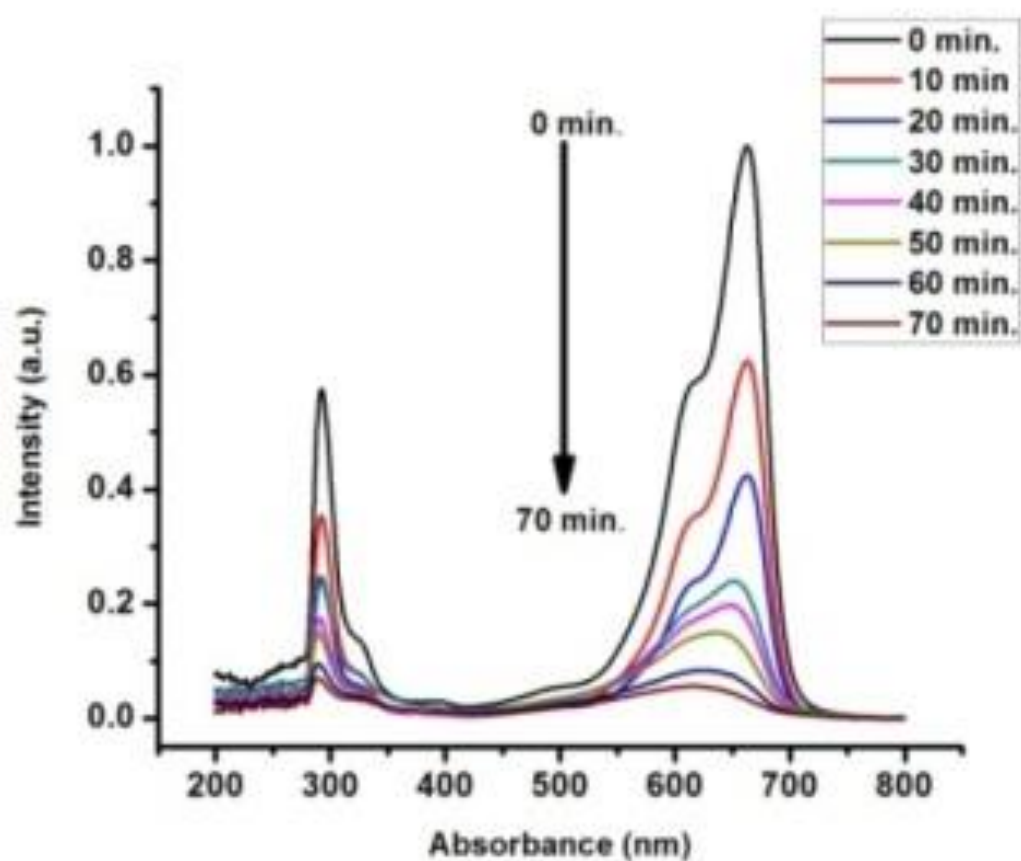


Fig. 4.9c-d: Absorbance spectra of Methylene Blue (MB) dye solution containing (c) 50 mg and (d) 75 mg of ZnO/NF nanopartic

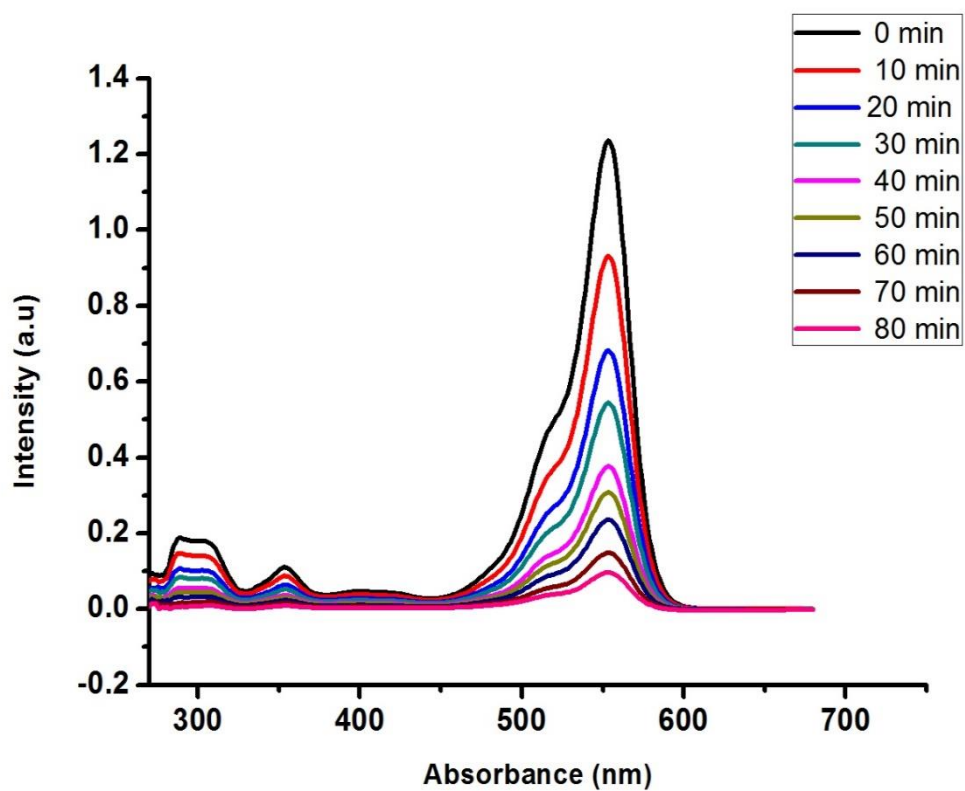


Fig. 4.10a: The absorption spectra of photodegradation of congo red (CR) dye

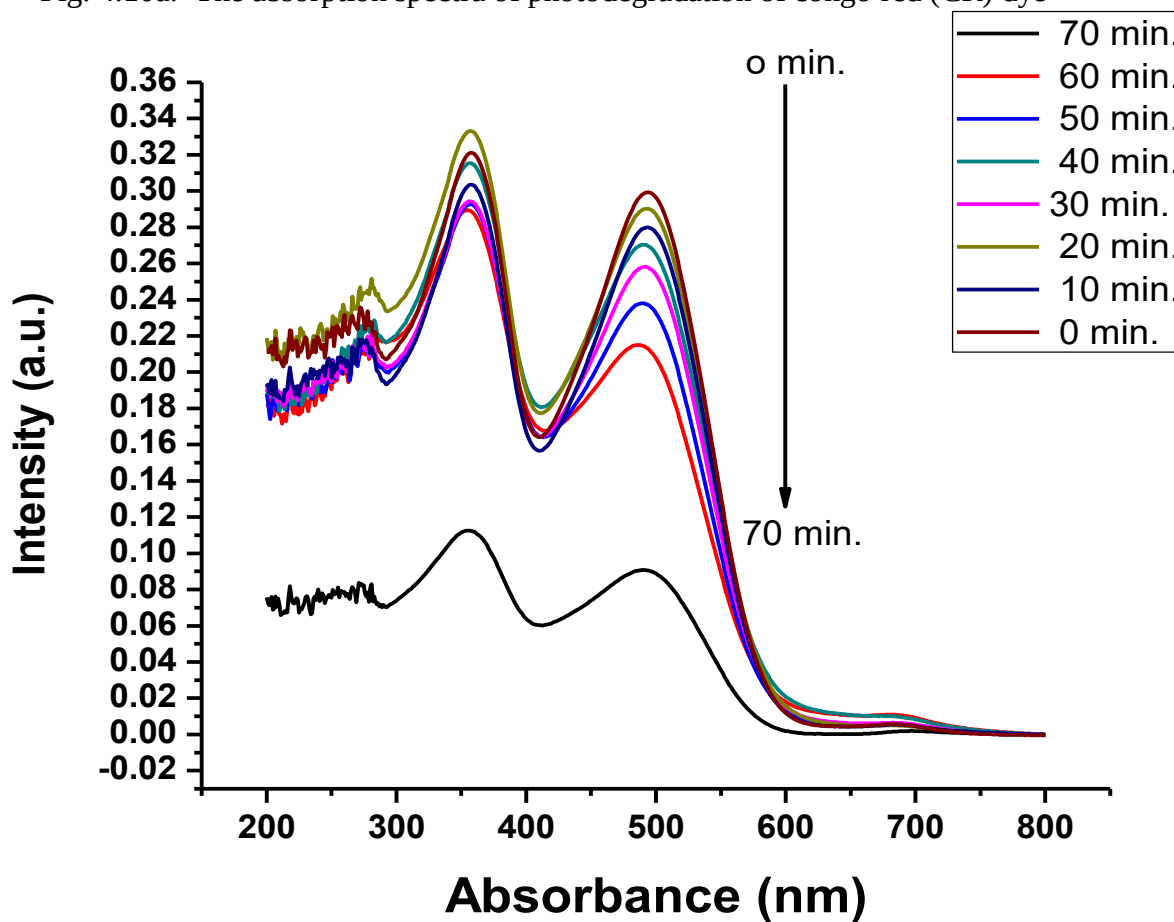
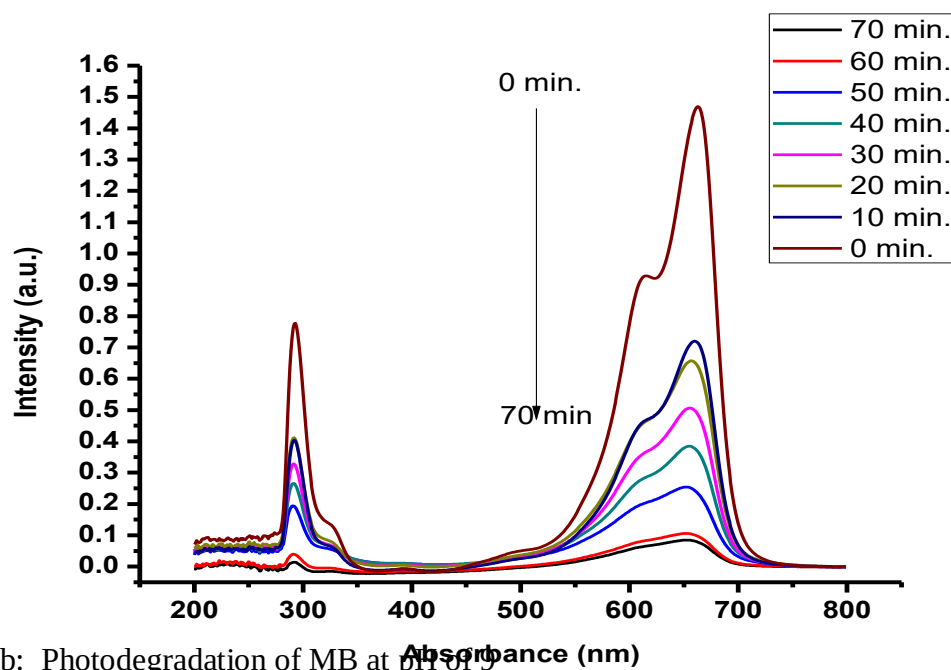
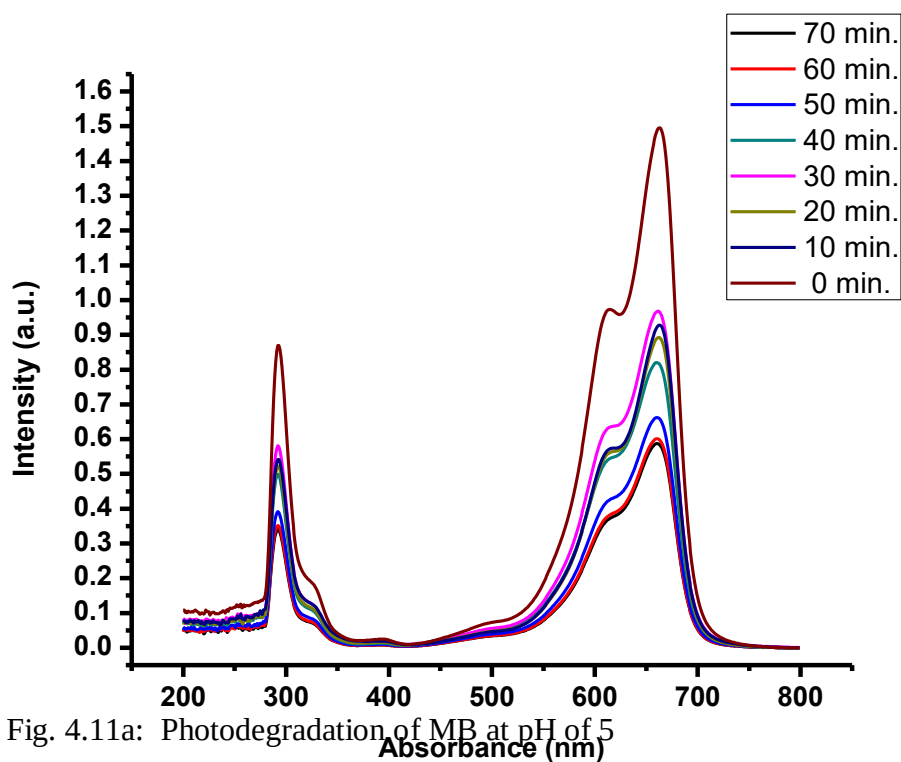


Fig. 4.10 b: The absorption spectra of photo-reaction of Rhodamine B (RB)



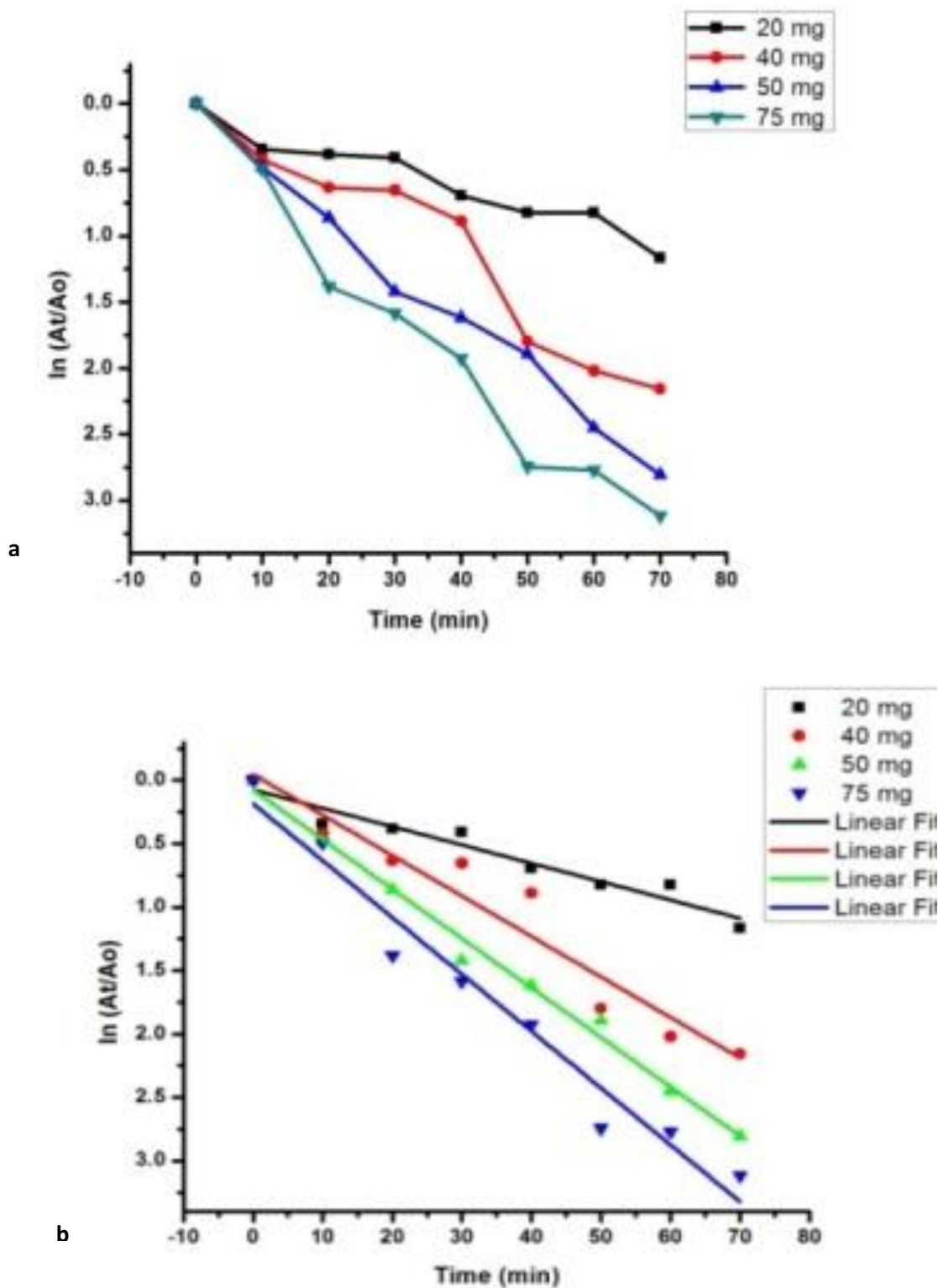


Fig. 4.12: (a) The combined Calirarion plots of MB (b) the linear fitting of the Calirarion plots of absorbance spectra of Methylene Blue (MB) dye solution containing (a) 20 mg (b) 40 mg (c) 50 mg and (d) 75 mg of ZnO/NiFe₂O₄ nanoparticles

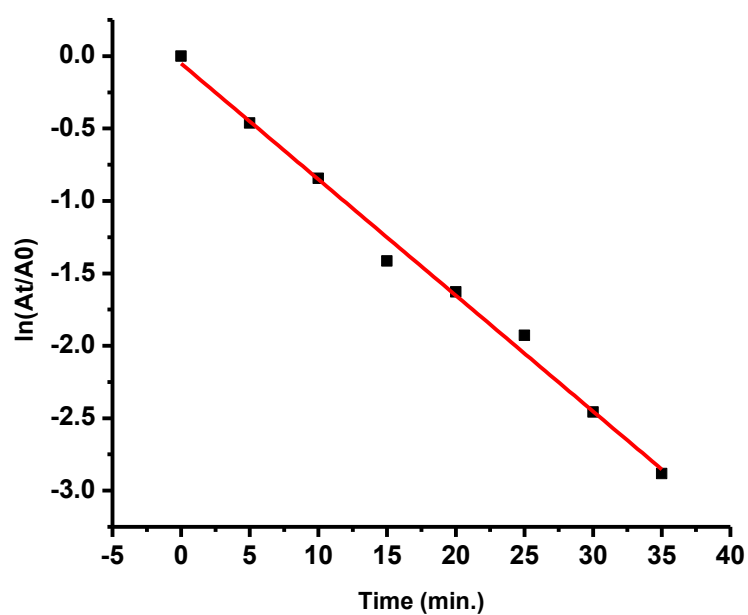


Fig. 4.13a: Calibration Plot for Photodegradation of Methylene Blue (MB) Dye

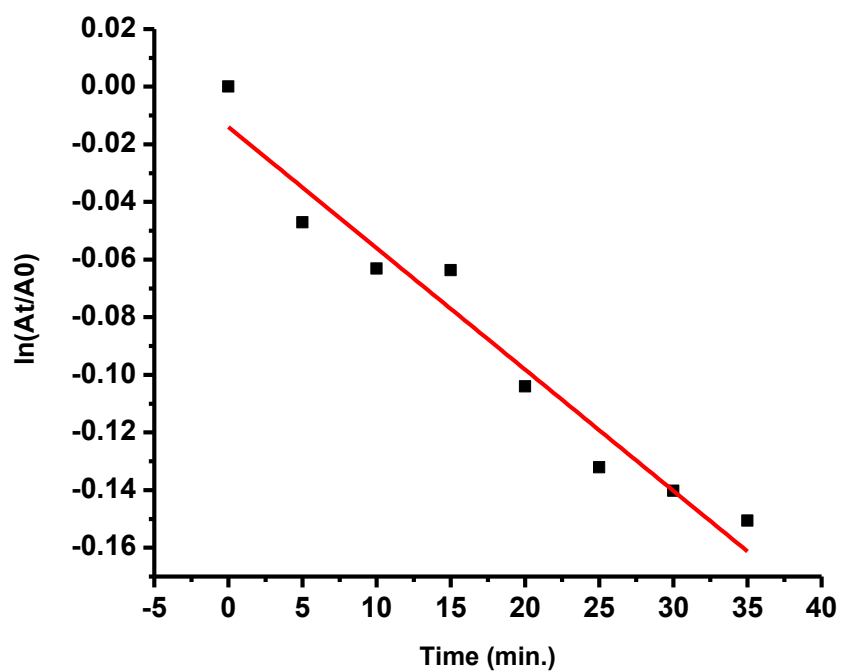


Fig. 4.13b: Calibration Plot Photodegradation of Congo Red Dye

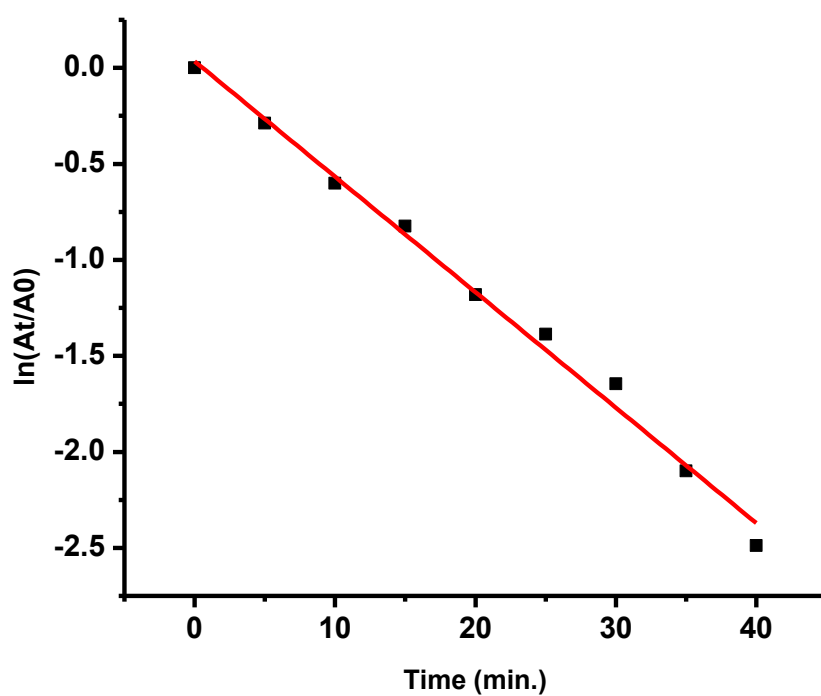


Fig. 4.13c: Photo degradation of Rhodamine B (RB) dyes

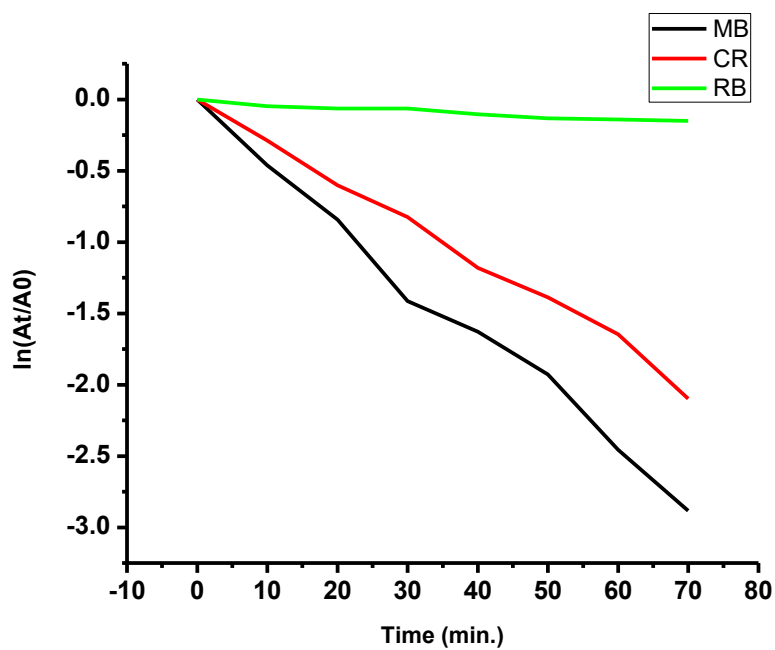


Fig.4.13d: A Comparison of Calirarion Plots for Photodegradation of MB. CR and RB dyes

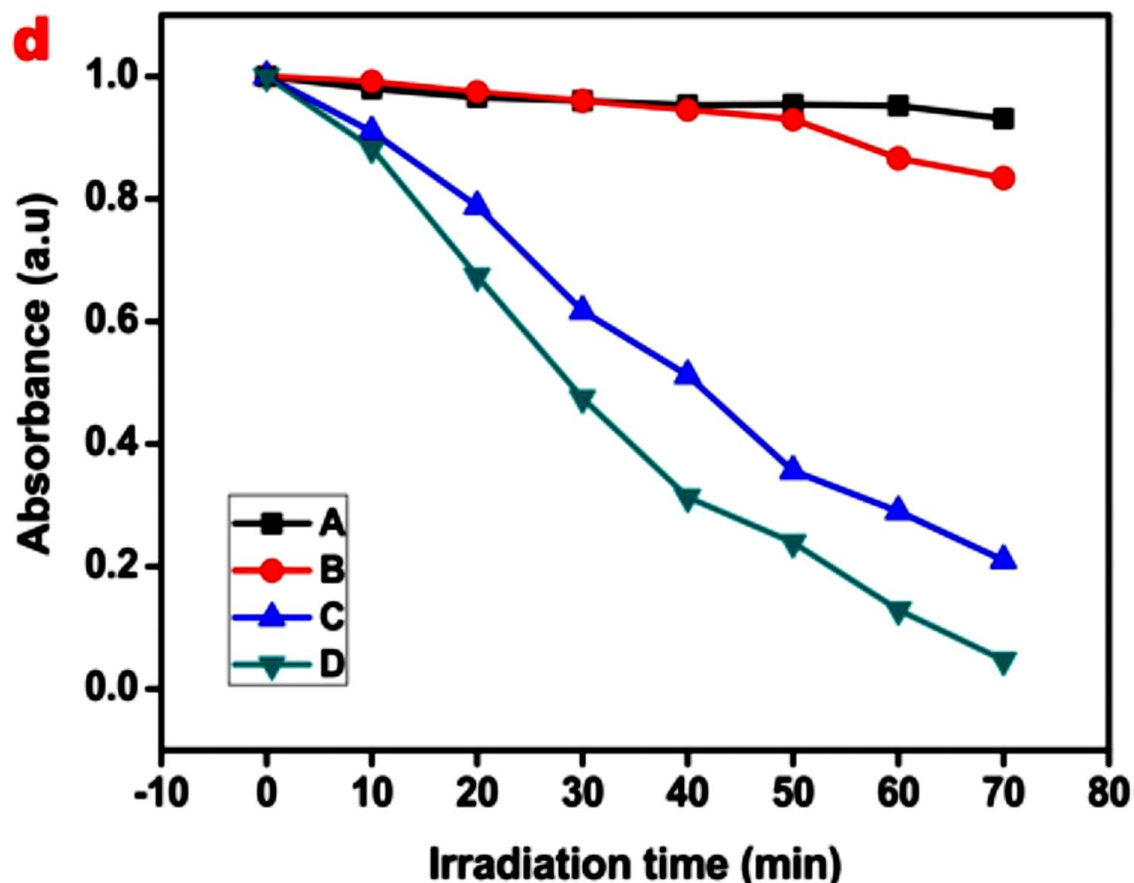


Fig.4.13 e: Photo-degradation & photocatalytic performances. (A) self-photo degradation of MB dye-with UV irradiation & absence of photo-catalysts (B) MB dye and 75mg of ZnO/NF -absence of UV irradiation with stirring (C) 75mg of ZnO NR with MB dye (D) 75mg of ZnO/NF nanopowder with MB dye.

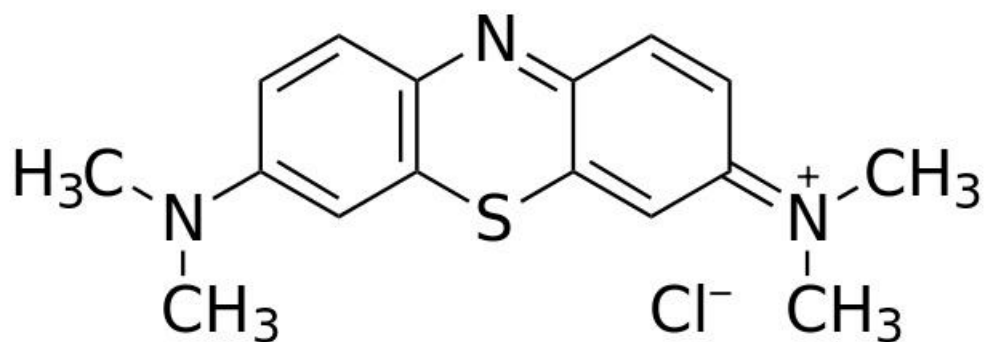


Fig. 4.13 f : The structural formula of Methylene blue dye

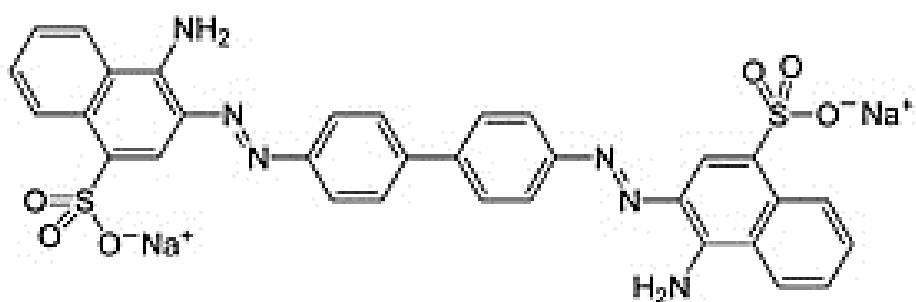


Fig. 4.13 g : The structural formula of Congo red dye

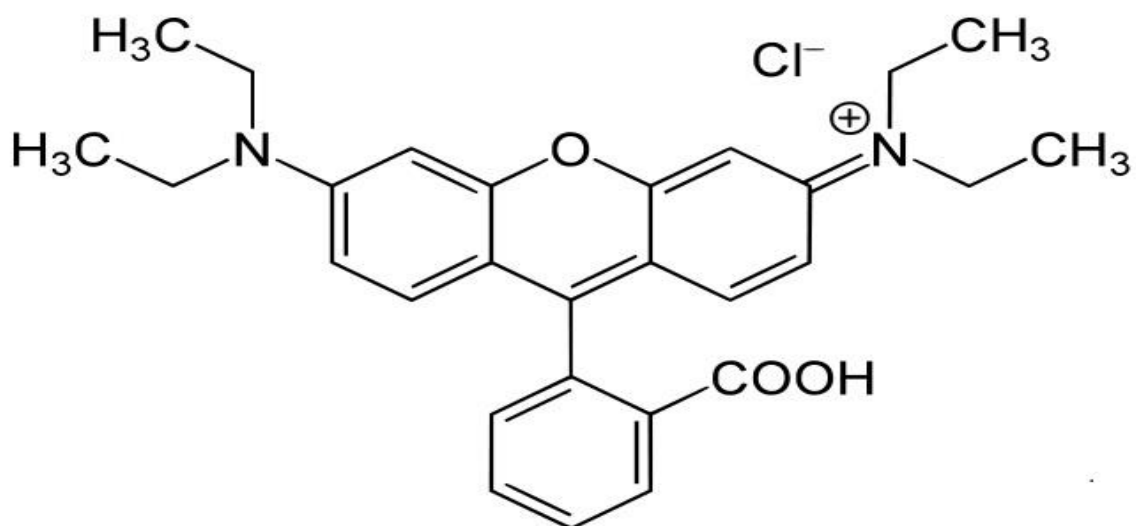


Fig. 4.13 h : The structural formula of Rhodamine B dye

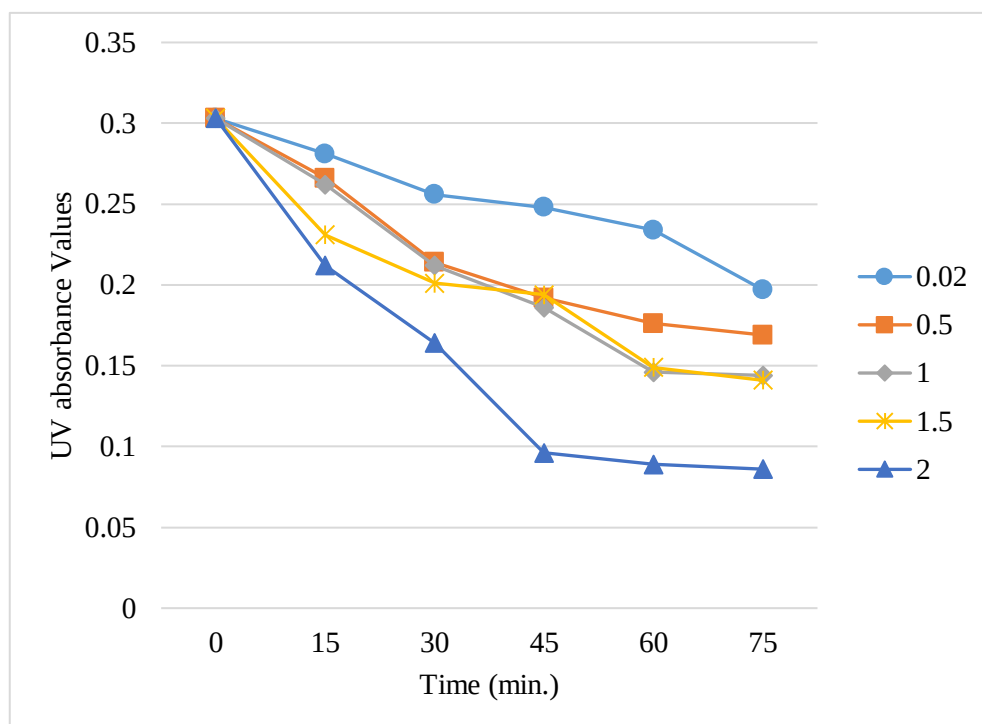


Figure 4.14a: UV Absorbance of Industry Wastewater Treated with ZnO Nanoparticles

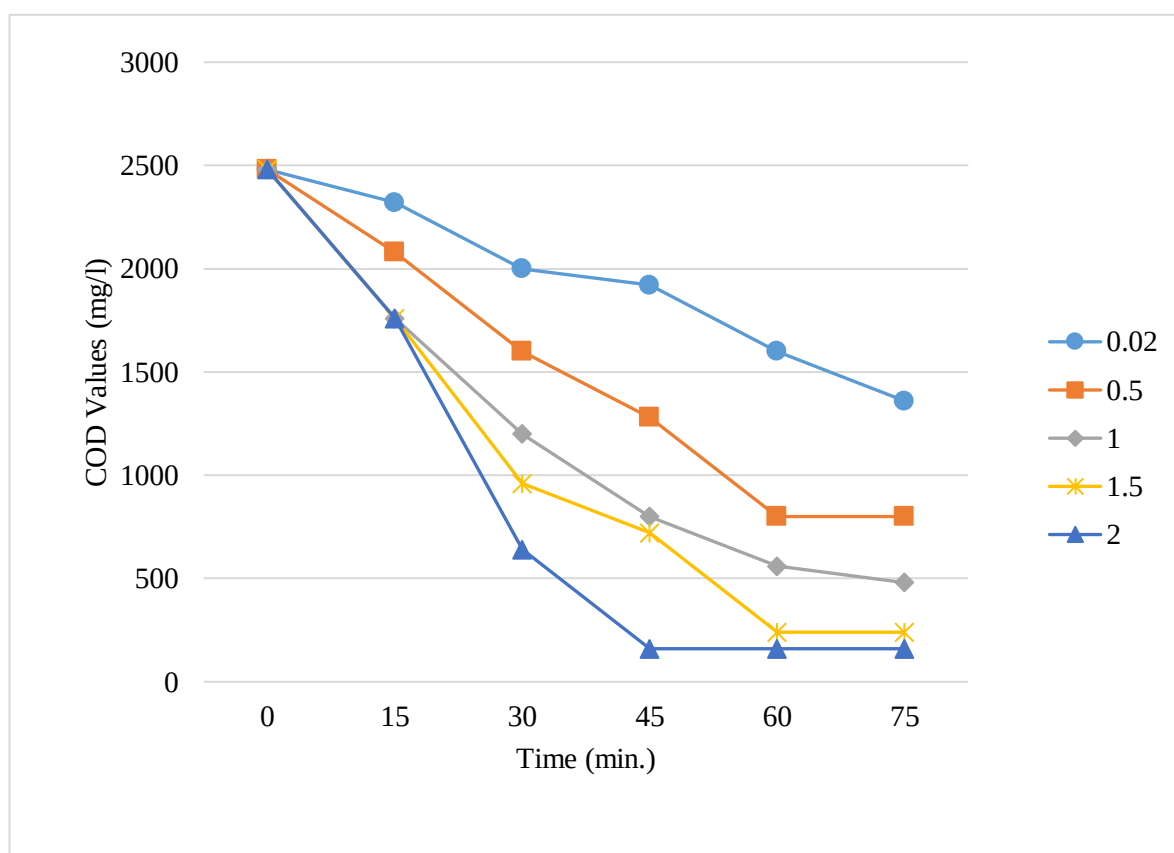


Figure 4.14b: COD of Industry Wastewater Treated with ZnO Nanoparticles

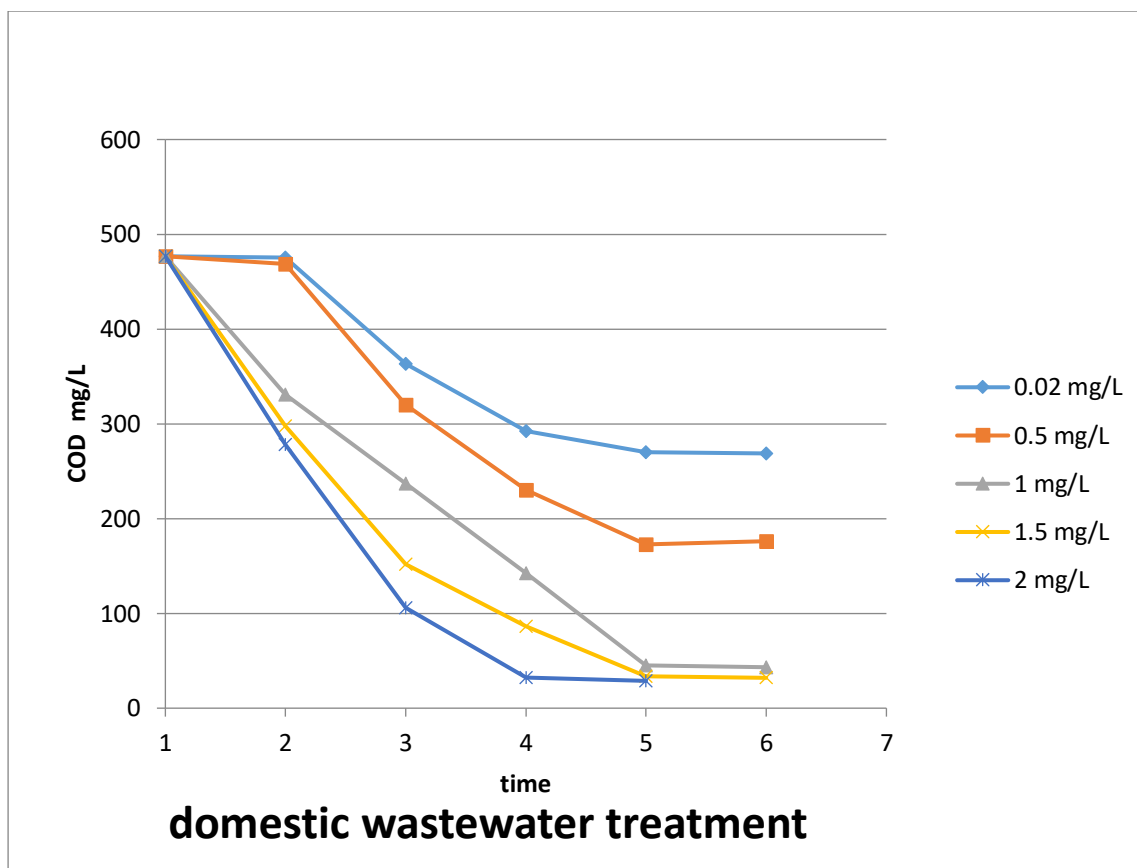


Figure 4.14c: COD of Domestic Wastewater Treated with ZnO Nanoparticles

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