

Graphitic Carbon Nitride Modified Cobalt Ferrite for Pollutant Degradation



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Dedication

*Dedicated to my Dearest Grand Mother (Late) and
Beloved Parents Mr. and Mrs. Fazal Hussain*

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*I am grateful to the Creator, **Almighty Allah**, to have guided me throughout this work and for every new thought which He setup in my mind to enhance it.*

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Abstract

Due to increasing environmental pollution, it is need of the time to develop some eco-friendly technologies that can overcome the major issue. Nanotechnology and photocatalysis provides the best way to solve the issues of environment. In the present work, we have reported the synthesis of nanoparticles of cobalt ferrite via hydrothermal method and sheets of g-C₃N₄ were produced through direct heating of melamine powder. Composites of cobalt ferrite and g-C₃N₄ were synthesized by solid state method *i.e.* grinding using agate pestle and mortar. The composites were synthesized in different concentrations by weight *i.e.* 1:3, 1:1 and 3:1 of both materials and used for the degradation of methylene blue. The samples were characterized via x-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), UV-Visible diffused reflectance spectroscopy and photoluminescence (PL). Using SEM, we came to know about the morphology of samples and particle size as well. Through XRD, phase of both materials was confirmed that their crystal system is cubic. EDS gave information about the elemental composition of the as synthesized materials. From UV-Vis spectroscopy, Tauc plot of the data was plotted for the determination of band gap. Photodegradation studies of methylene blue were carried out using bare cobalt ferrite, g- C₃N₄ and their nanocomposites. . The higher photocatalytic activity of CoFe₂O₄/g-C₃N₄ in 1:1 is attributed to high charge separation and better bandgap alignment. In short, NC-2 showed the maximum degradation of methylene blue up to 94%.

Key Words: Photocatalysis, CoFe₂O₄, g-C₃N₄, Methylene Blue

Contents

Chapter No.1	7
Introduction and Literature Review	7
1.1. Energy and Environment	7
1.2 Recent Environmental Problems:.....	7
1.2.1 Environmental Pollution	8
1.3 Energy Crisis	11
1.3.1 Advantages of Fossil fuels.....	11
1.3.2 Disadvantages of Fossil Fuels.....	13
1.4 Solution of Problems.....	14
1.5 Water Contamination	16
1.5.1 Sources of Water Pollution.....	17
1.6 Strategies of Dye Degradation.....	20
1.6.1 Need of Dye Degradation.....	20
1.7 Photocatalysis: A Breakthrough.....	20
1.7.1 Enhancing the Generation of Charge Carriers	21
1.7.2 Formation of Hetero structures	23
1.7 Synthesis of Nanomaterials	24
1.7.1 Top-Down Approach	25
1.7.2 Bottom-up Approach	25
1.8 Scope of Work	30
1.9 Objectives of work	31
Chapter 2	32
Experimental Details	32
2.1 Chemicals.....	32
2.2 Synthesis of Cobalt Ferrite.....	32
2.3 Synthesis of Graphitic Carbon Nitride	32
2.4 Synthesis of Different Nanocomposites of g-C ₃ N ₄ and Cobalt Ferrite.....	32

2.5 Characterization Techniques of Nanomaterials.....	33
2.5.1 X-ray Powder Diffraction (XRPD).....	34
2.5.2 Scanning Electron Microscopy	35
2.5.3 Energy Dispersive X-ray	36
2.5.4 Diffuse Reflectance Spectroscopy	37
Chapter 3	39
Results and Discussions	39
3.1 Phase Confirmation	39
3.2 Morphological Analysis	40
3.3 Compositional Analysis	43
3.4 Alignment of Energy Level.....	45
3.5 Photocatalytic Activity.....	48
3.6 Photoluminiscence Studies	50
3.7 Stability of a Catalyst.....	51
Conclusion	54
References.....	56

List of Abbreviations

CoFe ₂ O ₄	Cobalt Ferrite
g-C ₃ N ₄	Graphitic Carbon Nitride
SEM	Scanning Electron Microscopy
EDS Spectroscopy	Energy Dispersive X-ray
UV-vis spectroscopy	Ultra Violet-Visible Spectroscopy
XRD	X-ray Diffraction
PL	Photoluminescence
e.g.	Example gratia (For example)
i.e.	Id est (That is)
eV	Electron Volts
nm	Nano-meters
M	Molarity
g/mol	Gram per mole
hr.	Hour
Conc.	Concentration
°C	Degree Centigrade
NaOH	Sodium Hydroxide
V	Volume
e ⁻	Electron
h ⁺	Hole
SHE	Standard Hydrogen Electrode
CB	Conduction Band
VB	Valence Band
·OH	Hydroxyl Radical
CO ₂	Carbon Dioxide

O₂

E_g

mg

mL

mM

NC

Oxygen

Energy gap/Band Energy

milligram

milliliter

milli molar

Nanocomposite

List of Figures

Figure 1.1 2008 distribution of global energy consumption[3]	8
Figure 1.2 Renewable resources of Energy	16
Figure 1.3 Causes of Water Pollution	17
Figure 1.4 Photocatalytic Mechanism Illustrated Graphically	21
Figure 1.5 Heterojunctions	24
Figure 1.6 Approaches for Synthesis of Nanomaterials	25
Figure 1.7 methods for the synthesis nanomaterials	26
Figure 1.8 Schematic Explanation of Synthesis of Nanomaterials by Sol-gel method	27
Figure 1.9 Sonochemical method for the Synthesis of Nanomaterials	28
Figure 1.10 Micro-emulsion method for the synthesis of nanomaterials	29
Figure 1.11 (a) Hydrothermal Synthesis (b) Autoclave	30
Figure 2.1 Pestle and Mortar	33
Figure 2.2 Schematic Illustration of X-ray Diffraction	34
Figure 2.3 Schematic Explanation of Scanning Electron Microscopy	36
Figure 2.4 Working of Energy Dispersive X-ray Spectroscopy	37
Figure 2.5 Schematic Explanation of UV-Vis Spectroscopy	38
Figure 3.1 XRD Results of (a) g-C₃N₄ (b) NC-1 (c) NC-2 (d) NC-3 (e) CoFe₂O₄	40
Figure 3.2 SEM Images g-C₃N₄ (a) 500nm), (b) 1μm, (CoFe₂O₄ (c) 500nm (d) 1μm), (NC-1 (e) 500nm (f) 1μm), (NC-2 (g) 500nm (h) 1μm)), (NC-3 (i) 500nm (j) 1μm),	42
Figure 3.3 EDS Pattern of (a) CoFe₂O₄ (b) g-C₃N₄ (c) NC-1 (d) NC-2 (e) NC-3.	44
Figure 3.4.1 UV/Vis Spectra of CoFe₂O₄ inset shows the Tauc plot of CoFe₂O₄	45
Figure 3.4.2 UV/Vis Spectra of g-C₃N₄ inset shows the Tauc plot of g-C₃N₄ Error! Bookmark not defined.	
Figure 3.4.3 Schematic illustration of alignment of energy levels of CoFe₂O₄ and g-C₃N₄	Error! Bookmark not defined.
Figure 3.5 Absorption of Methylene Blue using different photocatalysts i.e. (a) blank, (b)g-C₃N₄ (c) CoFe₂O₄ (d) NC-1 (e) NC-3 (f) NC-2	49
Figure 3.6 Photoluminescence Spectra	50
Figure 3.7.1 XRD Pattern of NC-2 Before and After Photocatalytic Activity	51
Figure 3.7.2 SEM Images of NC-2 Before and After Photocatalytic Activity	52
Figure 3.7.3 EDS Spectra of NC-2 Before and After Photocatalytic Activity	53

List of Tables

Table 2.1. Details of CoFe₂O₄/g-C₃N₄.....	40
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Chapter No.1

Introduction and Literature Review

1.1. Energy and Environment

Energy and the environment are popular themes of the new millennium because both are closely interlinked. Energy is an irreplaceable part of our life and it is highly correlated with the environment. Many decades ago, people had not pay the attention to the sources of energy. They were intended to use such sources of energy which have high calorific value and were easy to approach. Despite thinking their hazardous effects on the environment. Continuous use of such energy sources has put irreversible damage to the ecosystem. Earth is facing serious environmental issues like global warming and greenhouse effect. Imagine what it would be like if we were out of energy. It would be eerily dark and freezing. But thinking from the environmental perspective, no energy means no power generation. But this is not the way to solve the problem. Energy departments are working to make such choices which are luxurious and eco-friendly as well, which translates into less consumption of energy and fossil fuel. But due to the rapid increase in industrialization, a lot of environmental problems has been raised by excessive CO₂ emission caused by burning of fossil fuels. Photocatalysis is one of the most favorable ways to cope with all environmental issue by water splitting, degrading carbon dioxide and other pollutants. Using photocatalysis, degradation of all other pollutants like textile dyes, surfactants, and other organic pollutants can be degraded and the environment can be saved.

1.2 Recent Environmental Problems:

Coal, oil, natural gas and atomic energy can be a case in point, and these sources of energy are limited and they generate pollution. Fossil fuel, accounting for most of the current energy consumption, is never limitless. It will become deplete someday. A possibility of fossil fuel

resource lasting 40 years or 60 years does not warrant continued dependence on it if you seriously consider irreparable harm it creates to the environment. Apart from social and economic problems and climate changes[1], acid rain, globalization, industrialization, shortage of energy and ozone depletion[2] are the issues that must be resolved.

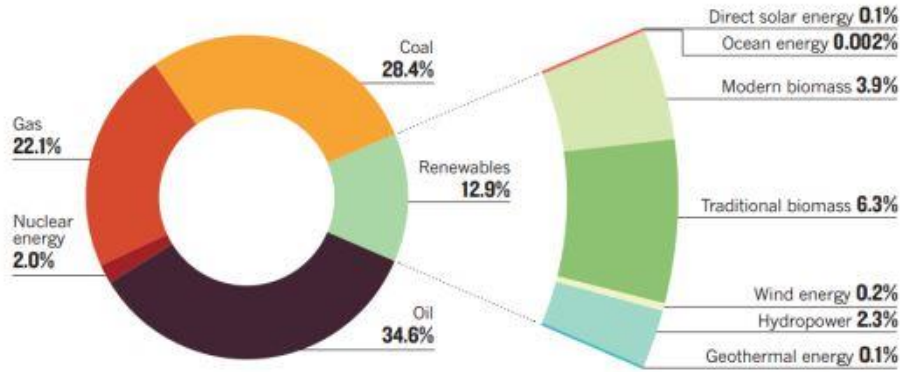


Figure 1.1 2008 distribution of global energy consumption[3]

1.2.1 Environmental Pollution

Environmental pollution has existed for centuries but only started to be significant following the industrial revolution in the 19th century[4]. Pollution occurs when the natural environment cannot destroy an element without creating harm or damage to itself. The elements involved are not produced by nature, and the destroying process can vary from a few days to thousands of years (that is, for instance, the case for radioactive pollutants). In other words, pollution takes place when nature does not know how to decompose an element that has been brought to it in an unnatural way[5].

Pollution must be taken seriously, as it has a negative effect on natural elements that are an absolute need for life to exist on earth, such as water and air. Indeed, without it, or if they were present in different quantities, animals including humans and plants could not survive. Pollution

is mainly caused due to the careless use of fossil fuels and not properly dumping of industrial waste.

- **Industrialization:**

The industry is the main source of pollution as for their running coal, gas and oil is required. In the 19th and 20th century, use of coal has rapidly increased due to its efficiency, replacing human power. The effluent from these industries is wasted without any further treatment causing severe environmental pollution. Mainly pollution is caused by those industries which generate electricity and nuclear power. Also, the transportation of this energy can harm the environment. Waste from textile industries is also a big cause of environment.

- **Transportation:**

Ever since men abandoned animal power to travel, pollution of the environment has become higher and higher. Its levels have only been increasing until now. Similarly to industries, pollution caused by transport can mainly be attributed to fossil fuels. Indeed, humans went from horse carriages to cars, trains (which, before electricity, used to be propelled by coal), and airplanes. As the traffic is increasing every day, pollution follows that evolution.

- **Agricultural Activities:**

Agriculture is mainly responsible for the contamination of water and soil. This is caused by the increased use of pesticides, as well as by the intensive character of its production. Almost all pesticides are made from chemical substances and are meant to keep diseases and threatening animals away from the crops. However, by keeping these forms of life away, harm is almost always made to the surrounding environment as well.

Furthermore, as agriculture gets more and more intensive to feed the increasing world population, more environments and ecosystems are destroyed to make space for the crops. Some of them, like rapeseed –used to make oil – demand a lot of space for a relatively small output.

- **Trading Activities:**

Trading activities including the production and exchange of goods and services. Concerning goods, pollution can be caused by packaging (which often involves the use of plastic, which is made from fossil fuels) or transport, mainly.

- **Urbanization and Globalization:**

Increasing population is the major problem of the world regarding pollution. Which also needs residential areas, residential areas provide their fair share of pollution as well. Globalization and urbanization is the also the major factor towards the pollution[1]. First, to be able to build homes, the natural environment has to be destroyed in one way or another. Wildlife and plants are driven away and replaced by human constructions. As it requires the work of industries, the construction itself is also a source of contamination of the environment. Then, when people settle in, they will produce waste every day, including a part that cannot be processed by the environment without harm yet

- **Overpopulation:**

Population growth is another basic cause of pollution[1]. Increasing pollution increases the use of resources and their excessive use cause pollution.

- **Pollutants and Their Effect on Human Health**

Pollution is a severe threat to the health of human[1, 6]. Due to water pollution, many diseases are arising like diarrhea, cholera malaria dengue[1], typhoid, HIV/AIDS. Air pollution also has

many severe effects on human health as many hazardous gases like carbon dioxide CO₂ carbon oxide CO, sulfur oxides and CFC's are released into environment unchecked[7]. Asthma, lungs cancer[8], TB and other breathing problems are arising due to air pollution. Land pollution is also caused due to the high usage of fertilizers, pesticides, herbicides, and dumping of untreated non-degradable materials like radioactive elements. Industrial waste containing textile dyes, paints, and other detergents when released unprocessed causes many serious health issues like cancer, kidney, liver and skin diseases.

1.3 Energy Crisis

Coal, oil, natural gas and atomic energy can be a case in point, and these sources of energy are limited and they generate pollution. It is a nationwide severe problem⁴. Due to increasing population, usage of energy is increasing hence leading to the depletion of energy sources. Fossil fuels are the major source of energy but due to irreversibility, the world is running with the shortage of fossil fuels which has become a large fear to the world. Coal, gas; the fossil fuels, are in high demand and they are the vast source of energy.

1.3.1 Advantages of Fossil fuels

The modern age is an age of industrialization and globalization, to meet the requirements of modern society, fossil fuels are man's best friends because they have many advantages over the others as the maximum amount of energy needs are met by fossil fuels[9].

- **Ready Availability**

Fossil fuels are present in mines and geologists tried their best to find them and make sure their availability. Many efforts had been made for the efficient extraction and refinement for the further use of fossil fuels. Owing to the increasing demand for energy due to the rapid increase in population. Geologists make their availability easier and smoother to fulfill the needs successfully.

- **Greater Energy Production**

The amount of energy released from fossil fuels is massive. Most of the engines produce a large amount of energy by combusting the fossil fuels. Due to this reason, fossil fuels are of great importance and they have the great contribution towards the industry. Energy produced from

fossil fuels depends upon the type of engine used for the combustion of fossil fuel and type of fossil fuel used in the combustion engine.

- **High Calorific Value**

The amount of heat produced by the combustion of a fuel is called the calorific value. Any kind of energy being produced has some calorific value that has a direct relationship with its efficiency. Fossil fuels have a high calorific value which makes them distinguished source of energy as compared to other energy sources available.

- **Stability**

Hydrocarbon fuels are highly stable because hydrogen and carbon show remarkable stability. Because of these perks of hydrocarbons, fossil fuels can be stored for a long period of time. In opposite to fossil fuels, current nuclear energy results from the radioactive elements as they are highly unstable and destroy with the passage of time.

- **Transportation**

Due to the high stability of fossil fuels, they are much easy to transport from one place to another place. Any kind of fuel can be transported. Their easy storage and stability make them easy to transport from one place to another. All types of fossil fuels like coal, oil or petroleum can be transported from one place to another. Even natural gas is also being transported nowadays from one place to another place.

- **Abundantly Available**

Different efforts are being made to implement the renewable energy resources and make them useable practically. In spite of all these efforts, the importance and place of fossil fuels cannot be changed. As they are abundantly available and they have the high value of energy. And the fossil fuels are the promising source of energy for the coming several decades.

- **Low Cost**

The cost-effective and economic extraction and refining procedures of the fossil fuels also make them a promising source of energy even in today's world. Their low cost of high energy production still makes them a distinguished option of energy as compared with the other energy sources.

- **Easy Set Up**

Power plants set up for the further processing of fossil fuels for the sake of use is quite easy to implant. By setting up these fuels a large amount of energy can be obtained from fossil fuels. The

resulted energy can be transported from one place to another easily.

1.3.2 Disadvantages of Fossil Fuels

Irrespective of the advantages discussed above the fossil fuels, there are some very serious and alarming limitations associated with the consumption of fossil fuels that make us think on a serious note to find some alternative energy resources. Some of the important and highly concerned disadvantages of fossil fuels are briefly discussed here.

- **Environmental Hazards.**

The main disadvantage of the fossil fuels is that they are not environment-friendly and can cause environmental pollution. Carbon dioxide, a greenhouse gas and one of the main aspects of global warming, is directly released to the environment as a result of combustion of these fossil fuels. With the increase in the consumption of these fossil fuels, the level of carbon dioxide in the atmosphere is also increasing with time. The rise in temperature as a result of global warming is the reason for melting of polar ice caps, a rise in sea levels and flooding of low lying areas. Our planet will face radical changes if this trend prevails.

- **Acid Rain.**

Sulfur dioxide is also produced as a result of their combustion and is the reason for acid rain that leads to the destruction of brickwork or marble-made monuments. The acid rain even affects the crops due to the acidification of loams and also causes health-related problems. It can cause different respiratory diseases or can make them even worse.

- **Health Issue.**

The greenhouse gases being released directly into the environment as a result of combustion of fossil fuels are also causing the depletion of ozone layer. It results in the creation of ozone holes, which lets the harmful UV rays enter the earth surface and, consequently, affects the human lives causing different diseases like cancer. Skin cancer is the major form of such disease when melanin present in the skin reacts with these high wave infra-red radiations.

- **Impact on Aquatic Life by Oil Spill.**

As previously discussed, fossil fuels are needed in huge reserves while setting up power stations. It requires their heavy transportation from one place to another via trucks, trains, ships or airplanes. During this process, some unfortunate accidents can happen, e.g., be sinking of the ships carrying large fuel reserves for their refining. It results in the disposal of large crude oil reserves that contain some toxic

substances. This crude oil, when mixed with the sea water, results in a negative impact and serious hazards on the aquatic life.

- **Depletion of Fossil Fuels.**

Other than the environmental hazards resulting from the use of fossil fuels, the biggest amongst all is their depletion. Fossil fuels have been a promising source of energy for centuries, but their rapid consumption is leading to their depletion. It is said that if we keep consuming the fossil fuels at the current rate, it will lead to their depletion, i.e., there won't be enough fuel left to fulfill our requirements after decades. Owing to the non-renewable nature of fossil fuels, it is also very likely that their prices will face a drastic hike in the near future. It might take millions of years to replace the fossil fuels. So the search to find some renewable energy sources, though expensive, is very essential.

1.4 Solution of Problems

Advancement in technology and science when come together, provides many solutions for the many issues of environment and energy. By adopting following approaches, environmental issues can be coped.

1.4.1 Usage of Clean and Reversible Sources of Energy

Using the renewable and clean energy sources is the best way to reduce energy and environmental crisis as they abundant on earth and environment friendly[10, 11].

- **Biomass**

Biomass is the biological material includes plants or plant based materials. These materials can be used further as biofuels to produce energy by their indirect or direct combustion. By direct combustion, biomass is that chemical energy which the plants obtain through photosynthesis. When plants dies, stored chemical energy in their residues converted into biomass energy by their combustion. For example, methane gas.

- **Hydropower**

Hydropower is the most environment friendly renewable source of energy. About 70% of earth is covered by water and a lot of kinetic energy is stored in water. Energy in the form of electrical

energy can be obtained through water by developing dams. The gravitational potential energy is stored in the water is converted into electrical energy using turbines next to dam barriers. This generated energy is then supplied for domestic and industrial purposes accordingly.

- **Wind Power**

Temperature variation in different regions causes the wind to move. This moving wind has a lot of kinetic energy stored in it, can be transferred into useful forms of energy using wind mills or wind turbines. Wind power generation causes no pollution generation[9], i.e., environment friendly source of energy. It has been a blessing for mankind for several centuries.

- **Solar Energy**

Solar energy is considered as an environment friendly and clean source of energy for many years because of the vast amounts of energy. Due to its most abundant nature owing to the shining sun, solar energy is thought to be the most capable renewable source of energy if efficiently harnessed by the highly modern technologies. This process to generate the solar fuels is based on the conventional concept of photosynthesis.

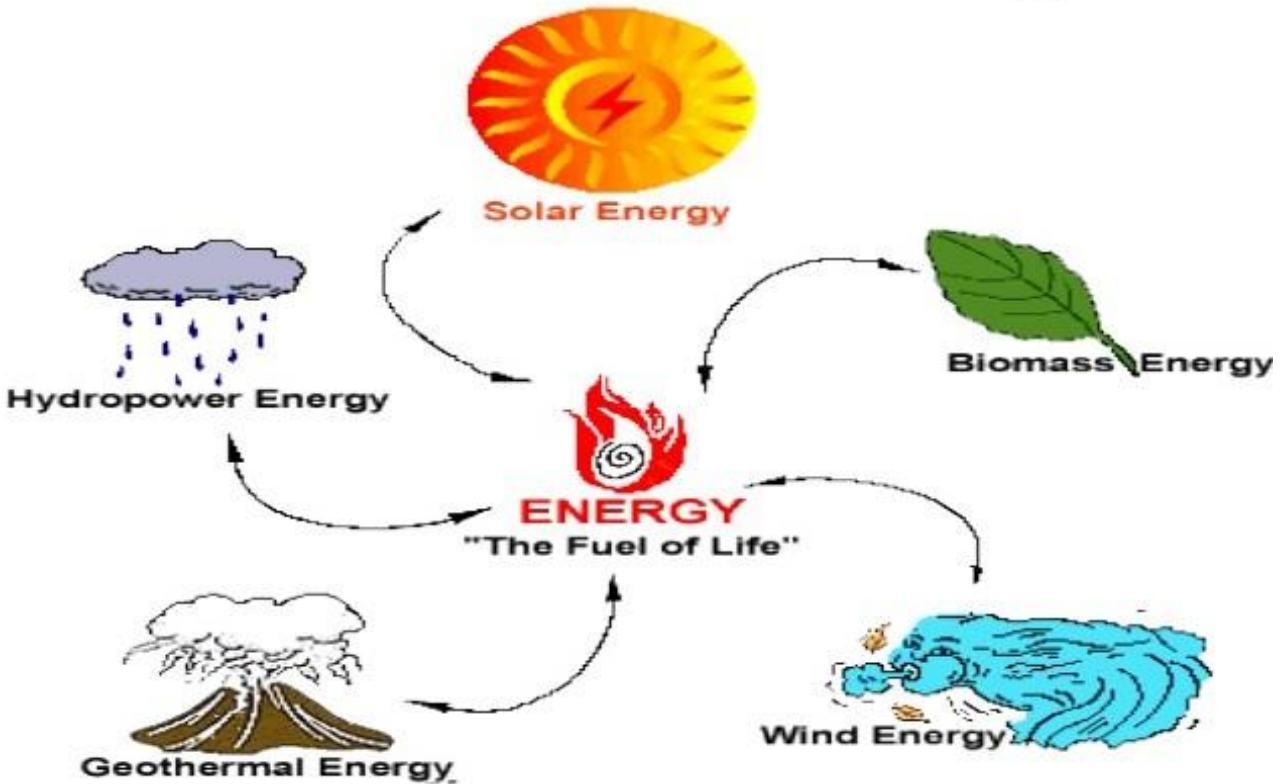


Figure 1.2 Renewable resources of Energy

1.5 Water Contamination

The importance of water in our lives can be understood from the fact that no living being can survive on earth without water. Marine water covers the major part of water on the earth which cannot be used for drinking purposes without processing. The only source of drinking water is fresh water from water bodies and from underground water. Quality of water is very important in our life as physiological activities of biological cells depend mainly on water. Water comprises 2/3 of our body and we cannot survive without water even for one day. The human brain contains 95% water[12]. A reduction of even 2% water content in body can cause dehydration. Water is required by all cells and organs of living organisms for the maintenance of their physiology and anatomy[13].

Water contamination is the addition of harmful contents to the water as it doesn't remain fit anymore for the drinking purposes as well for the survival of aquatic and marine life[14]. Water contamination is not only harmful for aquatic life but also a big danger to whole ecosystem. Water pollution has now become a major problem for global system as it is increasing day by day and it causes numerous fatal deaths. Not only industrial waste caused the water pollution but

some natural phenomena like earth quakes, storms, land sliding etc., contributing towards the lowering of water quality. There are different causes of water pollution and addition of these toxins to the water and harming the lives.

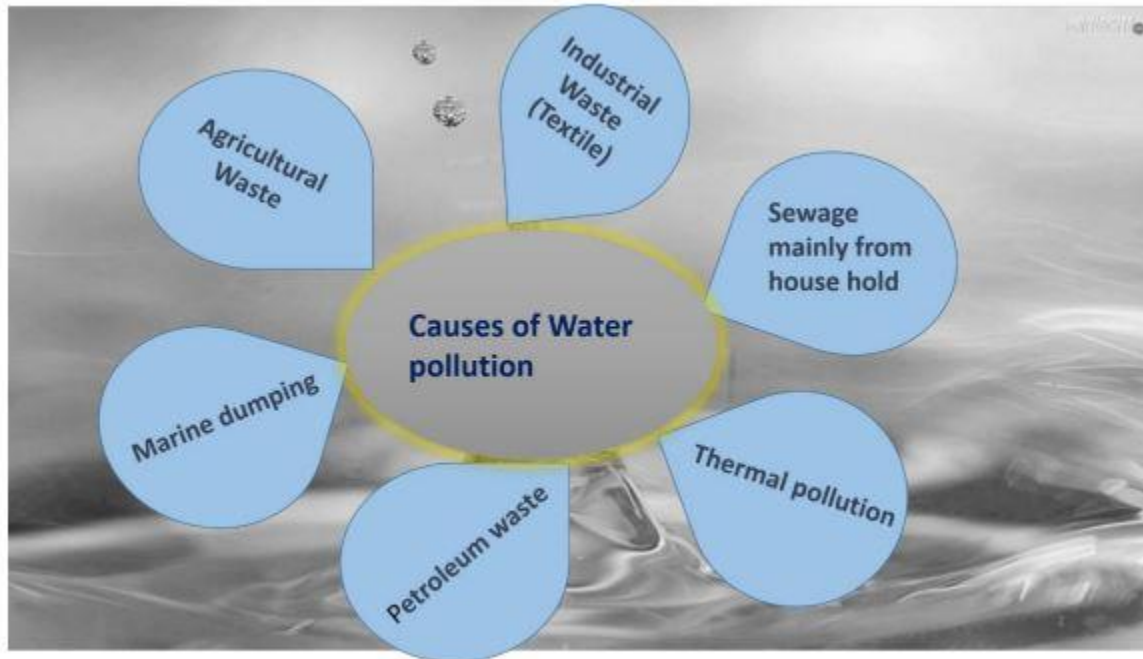


Figure 1.3 Causes of Water Pollution

1.5.1 Sources of Water Pollution

Water pollution is undesirable changes in the physical and chemical properties making it unfit for living organisms[14]. There are different sources of water contamination some of which have been discussed below;

Environment Protection Agency (EPA) published a report in 1990 which showed that more than 50% of the water pollution of water bodies is caused by the leaching of chemical from landfills where they are used to increase crop production[14]. Another source for water contamination is municipal waste. Some major sources of water pollution are pesticides and dyes. Their details are given below.

- **Pesticides**

Pesticides are those chemicals which are used to increase the production by destroying the pests in the crop[15]. Pesticides should only target pests, but they are affecting many lives including

human beings[12]. Pesticides causes many diseases in human body by causing changes in immunity and reproductive systems.

a. Insecticides

Insecticide is the type of the pesticide that is used to kill the insects in crops[16]. Since last century the use of pesticides has been increased. Insecticides can alter the whole ecosystem and are also very harmful for the humans. Degradation of pesticides is much difficult as it is not easy to reduce them immediately and harm the environment for many years. This long persistence of pesticides in the environment can cause water pollution. This can further damage the aquatic life as well those lives that are concerned with water bodies directly or indirectly[17].

b. Herbicides

Herbicides are the type of pesticides used to kill the herbs. Even their small amount in the crop can destroy the large amount of highly sensitive crop. Herbicides can be selective or non-selective. Selective herbicides harms only selected amount of plants whereas non-selective herbicides can harm many of the plants[12]. Some of the herbicides are water soluble and can enter into water causing many problems.

c. Fungicides

Fungicides are the types of pesticides used to kill fungi. In agriculture, fungicides are also used to deal with fungal infections. Fungicides are of different types including contact, translaminar, system fungicides[14]. Fungicides are available in liquid as well as in powder form. Fungicides can enter the water due to poor disposal. Some fungicides can persist to degradation in the environment and in this way they can enter into the soil and water causing their contamination[14].

- **Dyes**

Dyes are the complex aromatic molecules which are highly stable and therefore their degradation is quite difficult (65). Almost 50% of the total dyes available are for textile use. Different types of dyes includes

1. Natural dye
2. Synthetic dye

3. Food dye

Among all available dyes, mostly dyes are azo dyes. These dyes are used in different industries like pharmaceuticals, textile and cosmetics (65). Dyes are quite toxic as well so improper discharge of waste water having dyes leads to serious skin and respiratory problems. Dyes are mainly used in ink printing and textile industry.

Textile Industry:

Till 19th century only natural dyes were used as textile dyes, but later on synthetic dyes are being used in textile industry. After then, synthetic dyes are being used extensively due to their advantages like easy production and availability of dyes in different colors. The discharge of these dyes in water leads to its contamination when released untreated in water bodies. These synthetic dyes in waste water are highly carcinogenic due to the presence of harmful organic compounds like naphthalene and benzidine.

Printing Ink:

Different heavy metal are used as pigments in printing industry including titanium oxide, aluminum and brass. Leaching of these heavy metals in water causing its contaminations leading to serious health issues.

Many health hazards are caused by these dyes including;

1. When these dyes enter into water they can absorb and reflect light which can directly affect the process of photosynthesis in alga leading to the disturbance of food chains of many lives.
2. The presence of even small amount of dyes in water can affect the purity and transparency of water to a greater extent which damages aquatic environment.
3. Mostly dyes are carcinogenic and a big danger to life.
4. Textile Dyes can cause many allergic reactions in eyes, skin diseases and respiratory problems.
5. Dyes can cause the cancer of kidney, urinary bladder and liver in people working with these dyes continuously.

1.6 Strategies of Dye Degradation

Effluents from industries containing dyes products has serious effect on color and quality of water. It also affects the human health as well as aquatic life. So it is highly required to remove these dyes and pesticides from the waste water to avoid serious consequences. Following methods are being employed for the degradation of water contaminants.

1. Biological methods.
2. Chemical methods[18].
3. Physical methods.

1.6.1 Need of Dye Degradation

Although dyes have many benefits but they are also dangerous to human life in many different ways. Following are the several hazards of dyes [19]

- Dyes are most of the times soluble in water and thus they cause pollution in water. This water when discharged in to rivers, it causes severe damage to aquatic as well as human life.
- Dyes affect the absorption and reflection of sunlight from water thus affects the underwater photosynthetic activity.
- A lot of dyes are carcinogenic and some can cause irritation to skin.
- Transparency of water bodies are greatly affected by the small amount of dyes which are even undetectable by human eye. So, these harmful dyes need to be removed or better, degraded for the survival of living beings.

1.7 Photocatalysis: A Breakthrough

Photocatalysis is composed of two words, “photo” and “catalysis”. Photo means light and catalysis means the process where a substance changes the rate of chemical reaction without being consumed itself and the substance used for change the reaction rate by lowering the activation energy is called as catalyst. The catalyst used in photoreactions are called as photocatalyst and the respective chemical reaction is called as photocatalysis.

Photocatalysis is the process where sunlight is used to activate the particular substance which is used to modify the rate of chemical reaction. Photocatalysis is firstly initiated by electron-void

couples after band gap excitation. E_g is the difference of energy between VB and CB. When a photocatalyst is irradiated by light of energy comparable to or larger than E_g , the electrons which are present in outermost band can be energized to the CB and voids which carry positive charge is formed. This is photoexcited state of semiconductor. These photogenerated electron-voids pairs can recombine with the release of energy like heat and with no chemical change. If they do not recombine they induce oxidation and reduction processes in water. For photocatalytic water/air treatment, VB holes are important that prompt the oxidative breakdown of environmental toxins. This is shown in figure.

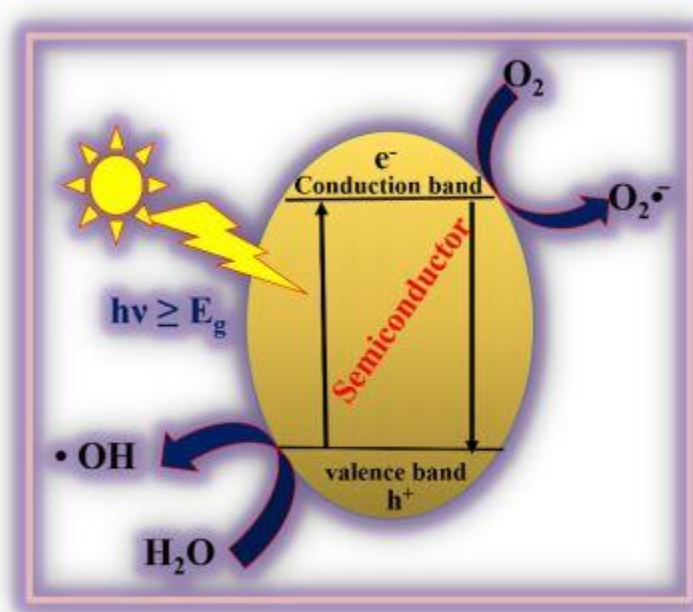


Figure 1.4 Photocatalytic Mechanism Illustrated Graphically

1.7.1 Enhancing the Generation of Charge Carriers

Photocatalytic reactions mainly occur due to the generation of electron hole pairs. The enhancement of generation of photo charge electron hole pair enhances the photo reaction[20]. The best approach for this purpose is to extend the light absorption range of semi-conductors. It can be done by following ways;

- **Integration of Plasmon**

Summing up of plasmonic metals like gold, silver and platinum with photocatalytic semiconductors also enhances the activity of photocatalyst. The mechanism of plasmonic enhancement mainly comprises light absorption and scattering, hot electron injection and induced plasmon resonance energy transfer[21]. In this way, they absorb more light, causes more electrons to excite leading to the higher efficiency.

- **Structural Defect**

One of the best way to enhance the photocatalytic activity is to create defects in the crystal. Any system can never be perfect. It can only be perfect at absolute temperature i.e. 273.16K. For any crystal to be a good conductor needs to be have some structural defects. These defects can be of two types, i.e. frenkle defects and schottky defects. Creating oxygen vacancies on the surface of semiconductor substrates can effectively tailor their electronic structure, thus leading to an enhanced visible light absorption, improved charge transport and separation and increased active sites for adsorption and photocatalytic reactions[22].

- **Sensitization**

Photocatalytic activity can be increased by increasing the sensitization of photocatalyst when approach to visible light is increased. In this way band gap of semiconductor can be sensitize. Materials which are used as sensitizers have low band gap and they absorb light more efficiently generating electron hole pair and also inhibit the recombination of electron hole pair. This was photo catalytically active.

- **Transportation of Charge Carriers**

Photocatalytic activity is being enhanced by the efficient utilization of solar energy by accelerating the charge carriers. For the good photocatalytic activity, semiconductors like TiO_2 , Fe_2O_3 , BiVO_4 , and Ta_3N_5 used having low conductivities. By reducing the size of material to nanoscale, diffusion of charged carriers can be reduced. Hence the material is 1-D and it provides large surface area, sufficient band gap to absorb incident light and shortest distance for the movement of charge carriers. Recently Dj Martin et al have reported that C_3N_4 (g- C_3N_4) nanotubes produced from direct heating of melamine powder showed enhanced photocatalytic activities compared with bulk g C_3N_4 , resulting from the fast transfer of charge carriers to the surface[23].

- **Suppression of Charge Recombination**

Photocatalytic activity depends upon the generation of photoinduced charge carrier. More the charge production, more would be the photocatalytic activity. But the problem is that these charges tends to recombine which reduces the photocatalytic activity. To enhance the photocatalytic activity, it is necessary to reduce the recombination of photoinduced charges. Hence these charges are being suppressed to recombine. Charge recombination can be suppressed by using many methods which are listed below:

1. Using scavengers which can trap electron and holes.
2. Changing the morphology of the respective photocatalyst which increases the surface area and shortens the diffusion pathway on which charge carries travel.

These properties are being achieved by the construction of heterostructures. In the designing of heterostructure the band edges of two different semiconductor photocatalyst. The designed photocatalysts efficiently suppress the recombination of photogenerated electron hole pair and prolong the life time of photocatalyst[24].

1.7.2 Formation of Hetero structures

It is also a promising technique to enhance the photocatalytic efficiency. The photocatalytic activities of ZnO/ZnSe[25], Co₃O₄/BiVO₄[24] hetero-structures, are higher as compared to individual nanomaterial. It provides better charge separation, due to the transfer of electrons from higher to a lower conducting band, and holes from lower to the higher valence band.

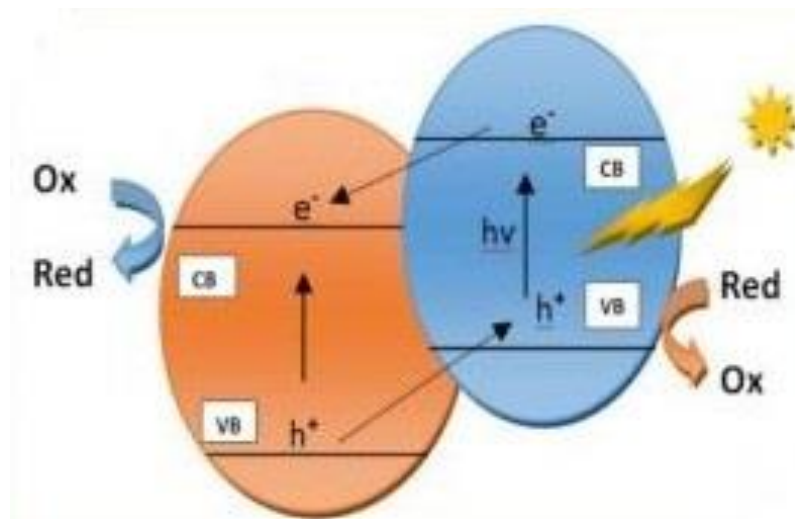


Figure 1.5 Heterojunctions

- **Type I heterojunction**

In this type of heterojunctions electrons get transferred from the more negative conduction band to the less negative conduction band and holes also move in the same direction

- **Type II heterojunction**

In this type of heterojunction electrons move from more negative conduction band to the less negative conduction band and holes move in opposite direction in valance band which is more positive hence leading to more efficient charge separation and photocatalytic activity.

- **Type III heterojunction**

It is much similar to the type II heterojunction but there is large difference in between the valance and conduction band positions of semiconductors which needs high energy driven for the charge transfer and photocatalytic activity[24].

1.7 Synthesis of Nanomaterials

In past few decades, a tremendous research has been carried out on the development of novel nanomaterials having high functionality, low cost and desirable properties. Nanomaterials are synthesized using many physical and chemical methods. By adopting these method, better control over particle size distribution can be achieved[26]. Mainly two main approaches are there for the synthesis of nanomaterials i.e. top-down approach and bottom-up approach.

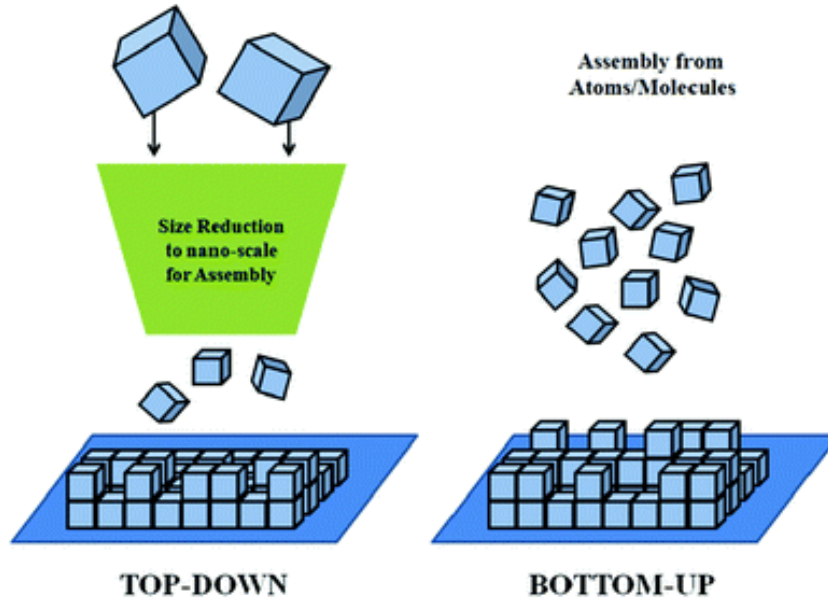


Figure 1.6 Approaches for Synthesis of Nanomaterials

1.7.1 Top-Down Approach

It is the solid state approach for the synthesis of nanomaterials. In this technique bulk material is broken into small pieces using physical methods. This method is not reliable for the material synthesis as no uniform particle size distribution is obtained using this method.

1.7.2 Bottom-up Approach

It is the wet chemical approach to synthesize nanomaterials. It is an opposite approach to synthesize the material from atomic or molecular species via chemical reactions, allowing for the precursor particles to grow in size.

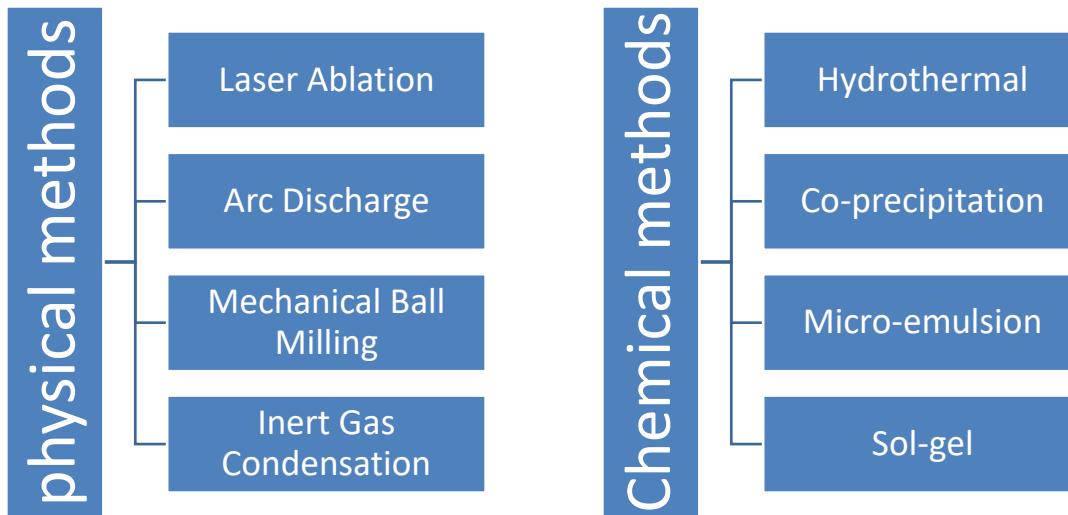


Figure 1.7 methods for the synthesis nanomaterials

- **Chemical Precipitation and Co-precipitation**

Mainly three steps are involved in the chemical precipitation method for the synthesis of nanomaterials. These steps are chemical reaction, nucleation and growth. This method of synthesis is uncontrolled. Not specific morphology can be obtained from this method. And all the processes occurring in the precipitation method are uncontrolled. Particles obtained by this method don't have narrow size distribution. Agglomeration can also occur using this method and morphology obtained by co-precipitation method is not homogenous. In co-precipitation method, inorganic salts of precursors are dissolved in water and homogenous solution is being prepared. Then pH of the solution is adjusted to basic to cause precipitation. Basically the precipitates obtained are either hydroxide or oxalates. Different parameters like pH, temperature and concentration of salts strongly effect the crystal growth. At the end of the reaction precipitates are collected as solid mass which are then washed, dried and used for further processes.

- **Sol-Gel Synthesis**

This is another method for the synthesis of nanomaterials and is one of the promising techniques for good yield of nanomaterials. The main advantage of this method is that we can obtain the

particle size of our desired shape and size. Metal Sulphides are mostly prepared by this method. In spite of all advantages of sol-gel, it is very difficult to wash the precipitates as it is much difficult to remove the residues of the reaction. Arachchige and Brock (2007) reported asolgel method for the preparation of metal sulfides. Sol-gel method is widely applied for synthesis of inorganic and organic inorganic hybrid nanomaterials to a large extent. Complete Scheme for the synthesis of nanomaterials using Sol-gel method is given below in **Fig. 1.6**

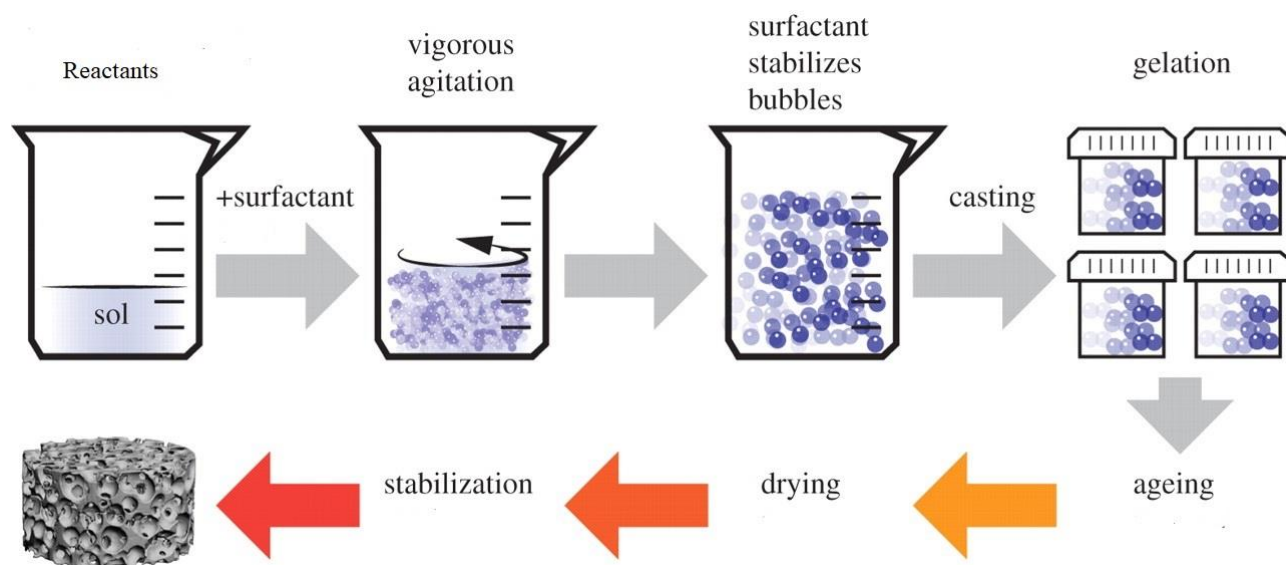


Figure 1.8 Schematic Explanation of Synthesis of Nanomaterials by Sol-gel method

- **Sonochemical Synthesis**

Both types of products either amorphous or crystalline can be obtained by using sonochemical synthesis method. In this method, synthesis is based on high temperature and pressure except for the heating and cooling rates. In this method, bubbles are formed using ultrasound waves which are then collapsed by acoustic fields. High pressure and temperature inside the bubbles causes the formation of hotspots. These hotspots are the centers for chemical reactions. The formation of crystalline or amorphous material highly depends upon the temperature and pressure inside the bubbles.

Sonochemical Method

Ultrasound radiations differ from conventional energy sources in term of duration, pressure and energy per molecule as shown in the **Fig 1.7**. Ultra-sonication methods can be effectively used for the generation of metal oxides Nano size particles.

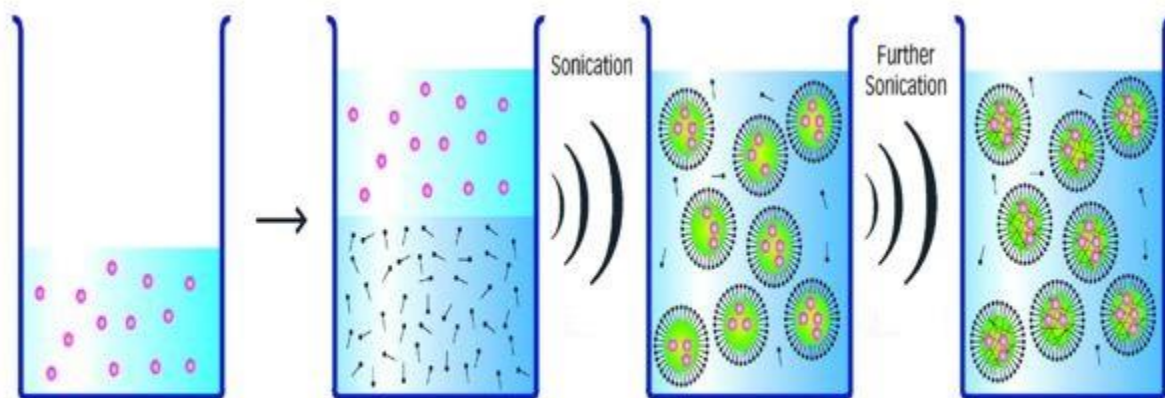


Figure 1.9 Sonochemical method for the Synthesis of Nanomaterials

- **Microemulsion Method**

Micro-emulsion is used for the controlled synthesis of nanomaterial. Using this method, nanomaterial of desired shape, size and amount can be obtained. In this method, two immiscible solvents are mixed. These immiscible solvents can be oil and water. These layers get separate and trace amount of other components can also be available. Surface tension is caused due to the presence of oil and water. The dispersion of one phase in being coated with surfactant. In this way the surface tension is being reduced with the addition of surfactant. With the addition of surfactant, the appearance of the emulsion changes to turbid or milky. Phase of the emulsion is being determined by the type of surfactant used, if the surfactant is hydrophilic, oil will be emulsified in droplets throughout a continuous water phase and vice versa. This technique has been used in past few decades for the synthesis of semiconductor photocatalyst.

Microemulsion Preparation

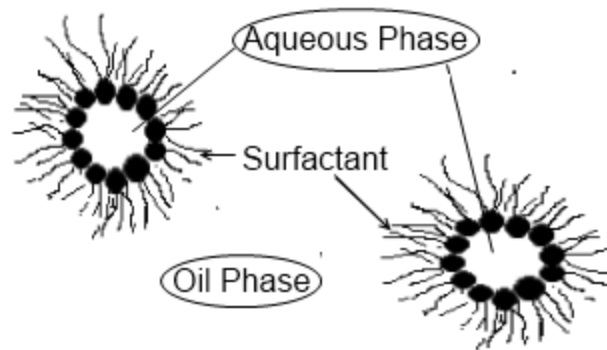


Figure 1.10 Micro-emulsion method for the synthesis of nanomaterials

- **Hydrothermal Synthesis**

In this technique the reactions are carried out under high pressure and temperature in a sealed container. The development of nanomaterials has played a significant role in the emergence of this technique. The first report on this utilization of this method was published in nineteenth century for the synthesis of quartz nanoparticles. Later hydrothermal method was widely used for the synthesis of various Nanoparticles with increase crystallinity, improved morphology and size control. Other advantages associated with this technique that it is environmental friendly, has lower energy consumption and water is used as a medium. Hydrothermal synthesis is usually carried out in pressurized vessel known as an autoclave and the reaction occurs in aqueous medium. The temperature inside the autoclave can be raised above the boiling point of water, reaching the vapors pressure. The main advantage associated with the hydrothermal method are control over (i) grain size, (ii) particle morphology,(iii) crystalline phase and surface chemistry by regulating solution composition, reaction temperature, pressure, solvent properties and aging time.



Figure 1.11 (a) Hydrothermal Synthesis (b) Autoclave

1.8 Scope of Work

In the present work, we reported the synthesis and photocatalytic application of ferrite based photocatalyst. Recent advances shows that ferrites are being used in signal transformation, inductors[27, 28], high frequency[29-33], power[34-39], electromagnetic interference (EMI) suppression[40-44] and biosensors[45-56]. However, the use of ferrites in photocatalysis[57] has opened a new gateway to energy and environment. Now ferrites are also being used for water splitting, pollutant degradation[58] and CO₂ reduction[59]. Following properties of ferrites make them more suitable for photocatalyst.

1. Large surface area.
2. Small band gap.
3. Easy to synthesize.
4. Visible light active.
5. Effective Photocatalyst

Ferrites can be prepared using different methods. Here, we reported the hydrothermal method for the synthesis of ferrites. Hydrothermal method has been used widely for the synthesis of nanomaterials[60-62]. In hydrothermal method, water is used as reaction medium in a sealed steel pressure vessel with Teflon liners as shown. The temperature is often kept higher than 100 °C so that auto genous pressure is developed in closed system. Up till now, the hydrothermal method has widely been used for the synthesis of various MCs nanostructures such as ZnSe

hollow microspheres [63], MoS₂ hollow cubic cages [64] , In₂S₃ nanoflowers [65], CuS microtubules [66], Chagas et al, reported the synthesis of Cobalt ferrite using hydrothermal method for the oxidation of CO[58]. Duangjam et al, focused on the hydrothermal synthesis of CoFe₂O₄/BiVO₄ for the photocatalytic degradation of methylene blue[57]. Sonja et al, reported the pH controlled synthesis of cobalt ferrite nanoparticles through hydrothermal process[67]. He also reported that by changing the pH the magnetic properties can be turned. Indira et al, reported the synthesis of cobalt ferrite by varying many synthesis parameters like temperature, time and pH using hydrothermal synthesis method[68]. Erik et al, studied the photocatalytic activity of cobalt ferrite by the degradation of contaminants[69]. So as to realize the full potential of cobalt ferrite as photocatalyst for the degradation of contaminations has been reported for past years. It can be used as better photocatalyst by its modification.

In our work, we have reported the synthesis of nanocomposites of cobalt ferrite with graphitic carbon nitride. Youngsheng et al, reported the synthesis of composites of cobalt ferrite with grapheme and showed it's recyclable photocatalytic activity[70]. Yao Zheng et al reported the synthesis of g-C₃N₄ and its wide application in areas of photocatalysis[71]. Generally, graphitic carbon nitride is made by breaking down of various precursors which are rich in Nitrogen, such as dicyandiamide [72], cyanamide[73, 74] , melamine derivatives[75] melamine [76] , urea [77], thiourea[78-84] and so on. The E_g has a range between 2.58 to 2.89 eV.

The synthesis of composites of cobalt ferrites and g-C₃N₄ is discussed in details in chapter 2.

1.9 Objectives of work

This thesis describes an effort to make CoFe₂O₄ nanoparticles by using hydrothermal synthesis method and formation of composites of CoFe₂O₄/g-C₃N₄ by physical method. The objective was to make a photocatalyst having minimum charge recombination rate and is visible light active and can be easily used for the degradation of dyes.

Following are detailed objectives of our work;

- Synthesis of photocatalyst having less charge recombination.
- Synthesis of CoFe₂O₄ nanoparticles by hydrothermal method.
- Synthesis of CoFe₂O₄/g-C₃N₄ by physical method
- Characterization of all the prepared samples.
- Choosing the best catalyst by performing degradation studies of Methylene Blue.

Chapter 2

Experimental Details

2.1 Chemicals

All the chemicals used for the synthesis of photocatalysts are of analytical grade and used without any further purification. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), iron nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Cetyl Trimethyl Ammonium Bromide (CTAB), Sodium Hydroxide (NaOH), melamine, Absolute Ethanol were purchased from different companies. Deionized water was used for the preparation of all materials.

2.2 Synthesis of Cobalt Ferrite

The synthesis of Cobalt Ferrite was carried out by simple hydrothermal route. For this purpose, solution of 0.85M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.425M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.85M CTAB was prepared in 35mL of deionized water. 6M NaOH was added to adjust the pH to 13. Then the mixture was transferred to the autoclaves kept at 120°C for 3 hrs. Then black precipitates were obtained which were washed with deionized water two times and with ethanol one time which were further dried in air at 70°C . The obtained black precipitates were stored for further analysis.

2.3 Synthesis of Graphitic Carbon Nitride

For the Synthesis of graphitic carbon nitride, 5g Melamine was poured into a porcelain crucible. The crucible was kept in muffle furnace and heated at 550°C ($3^\circ\text{C}/\text{min}$) then kept at ambient temperature for 2 hrs. Then yellow agglomerate was obtained which was ground to obtain powdered graphitic carbon nitride which was stored for further analysis.

2.4 Synthesis of Different Nanocomposites of g- C_3N_4 and Cobalt Ferrite

Composites of g- C_3N_4 and Cobalt ferrite were synthesized by solid state method. For the purpose, different ratios of g- C_3N_4 and Cobalt ferrite were mixed together and grinded using pestle and mortar (**Fig 2.1**). Details of CoFe_2O_4 / g- C_3N_4 Nano composites are given in **Table 3.1**:



Figure 2.1 Pestle and Mortar

Sr. no	Composite name	% of CoFe_3O_4 by weight	% of $\text{g-C}_3\text{N}_4$ by weight
1.	NC-1	75	25
2.	NC-2	50	50
3.	NC-3	25	75

Table 2.1: Details of $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$

2.5 Characterization Techniques of Nanomaterials

Once the nanomaterials are synthesized, the next step is to characterize them to confirm purity, phase, and surface morphology, thermal and optical properties. Various characterization techniques like scanning and transmission electron microscopy, X-ray diffraction, infrared

spectroscopy, DRS, photoluminescence spectroscopy can be used for the purpose. Some above mentioned techniques will be discussed briefly here.

2.5.1 X-ray Powder Diffraction (XRPD)

- **Basic Principle**

X-ray Diffraction is the most common and proficient technique for the identification and characterization of nanomaterials based on their diffraction patterns. This technique is used for the measurement of sample purity, phase composition, crystallite size, lattice constant and cell volume.

- **Mechanism**

X-rays generated by cathode tube filtered to produce monochromatic radiation. Incident X-rays interacts with matter with angle θ , called Bragg's angle. There is a path difference between two planes. If this path difference is equal to an integral multiple of the wavelength, the reflected waves will reinforce each other. Constructive interference is produced when Bragg's law is satisfied and is given as

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

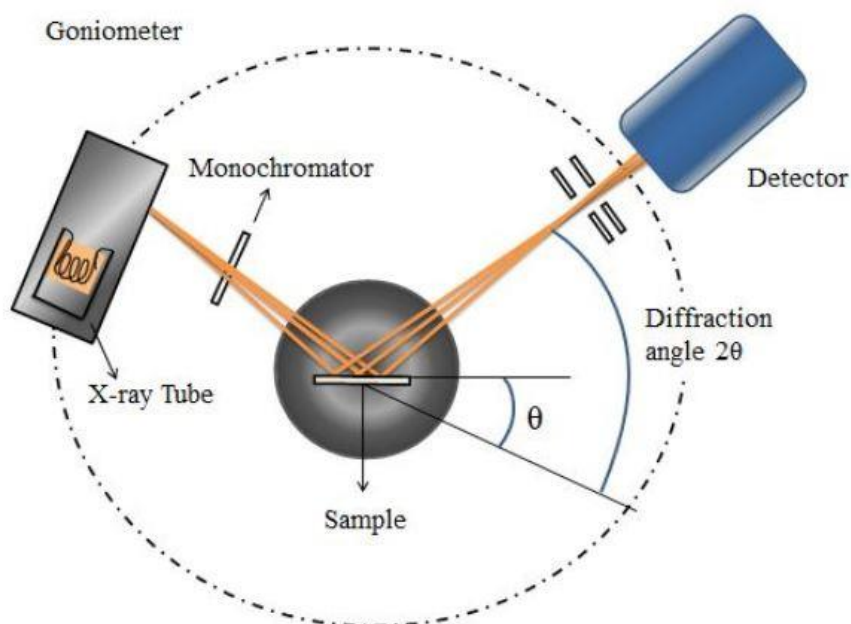


Figure 2.2 Schematic Illustration of X-ray Diffraction

The emitted characteristic x-ray are collimated and focused onto the sample. As the sample and detector are rotated, the intensity of reflected x-rays is recorded and detected by special detectors. The function of detectors is to detect and process the signals and outputs the signal on monitor. Goniometer, an instrument inside the X-ray machine is used to hold the sample and maintain the angle.

2.5.2 Scanning Electron Microscopy

In scanning electron microscopy, fast moving electrons interact with the surface atoms of sample. This interaction of electrons with the surface of sample gives the information about topology, morphology and composition of sample

- **Working**

In SEM, tungsten is used as source of electrons due to its low cost and low vapor pressure. Electron gun attached with cathode emits electrons having range from 0.5KeV to 40KeV. The whole system is processed under high vacuum. Next to electron gun, pair of condenser lenses are present whose function is to focus the electrons on the spot ranging 0.4nm to 5nm in diameter. Electron beam is deflected using deflected plates, which are able to scattered electrons to scan the specific area on sample.

Interaction of electrons with samples causes the emission of electromagnetic radiations, back scattered and secondary electron due to energy exchange between sample and electrons. The signals thus produced are then detected by special detectors results in the imaging of the sample which is displayed on computer screen.

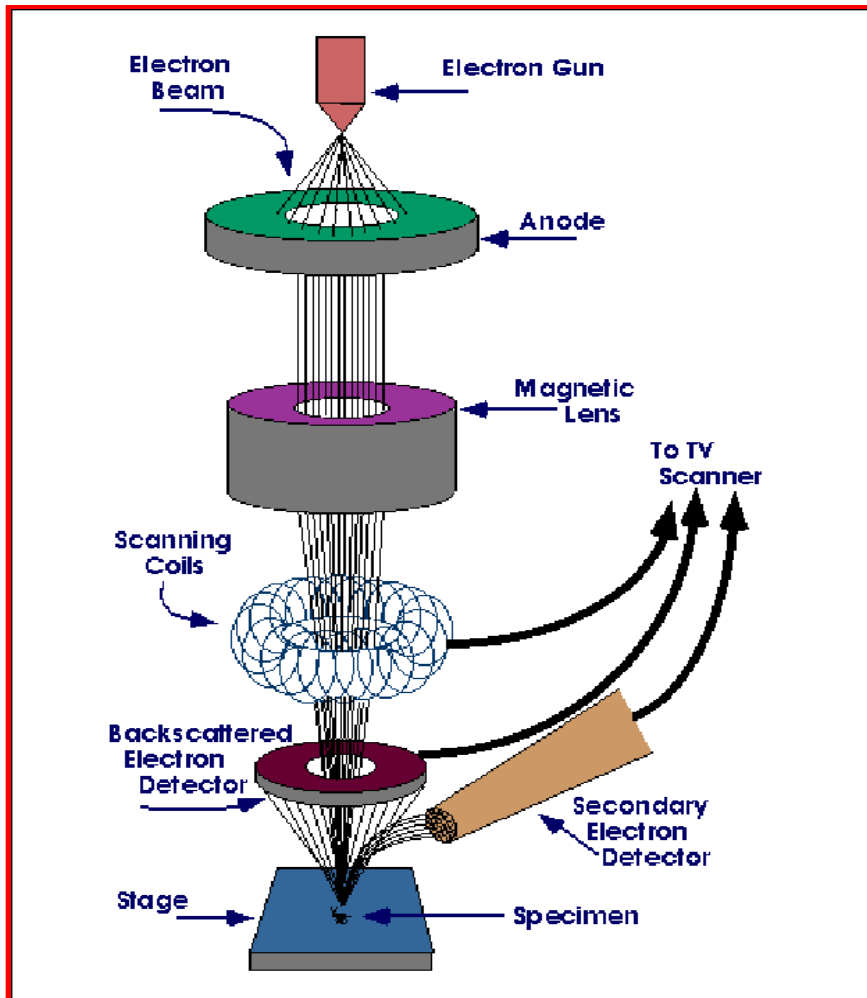


Figure 2.3 Schematic Explanation of Scanning Electron Microscopy

2.5.3 Energy Dispersive X-ray

EDX is a promising technique for the analysis of elemental composition of a sample. It is usually associated with SEM, TEM. When a high energy beam is bombarded on an atom, certain elastic and inelastic collisions occur between the beam and the electronic cloud, which may result in the knockout of interior electrons. These vacancies are filled by higher state electrons and resulted in the emission of characteristic X-rays[85]. There are two types of sources used in EDX *i.e.* electronic beam and X-rays, an electron beam is used in SEM or TEM while X-ray source is used in XRF. The detector of EDX has three parts *i.e.* a sensor, which senses the upcoming X-

ray, a preamplifier, which converts X-ray energy into a voltage, then the signal is measured by pulse processor and send to computer for further analysis and display.

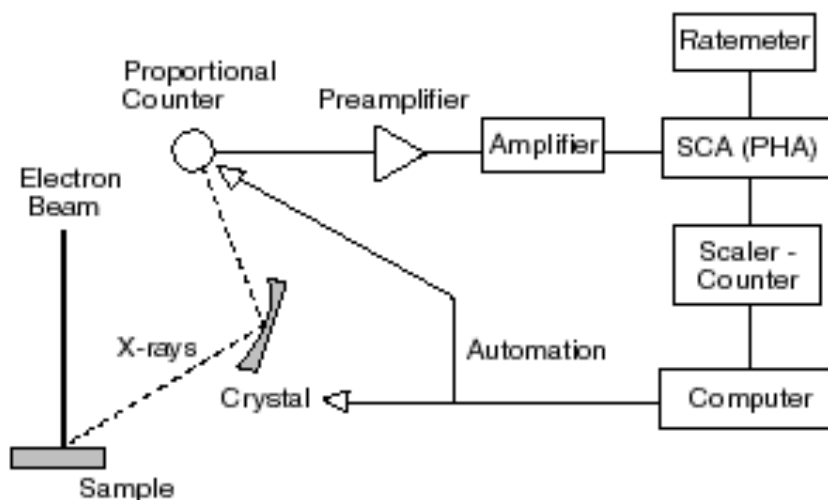


Figure 2.4 Working of Energy Dispersive X-ray Spectroscopy

2.5.4 Diffuse Reflectance Spectroscopy

Diffuse reflectance is an optical phenomenon commonly used in UV-visible and infrared (near IR; NIR, mid IR; DRIFTS) regions to obtain molecular spectroscopic data. It is commonly used to obtain spectra of powdered sample and requires minimum sample preparation. A reflectance spectrum is obtained by the analysis of surface reflected electromagnetic radiations which are collected as a function of frequency (wavenumbers cm^{-1}) or wavelength (nm). Two different types of reflections can be observed, specular or regular reflection and diffuse reflection. The specular reflection is associated with the reflection from polished or smooth surfaces like mirrors while diffuse reflection is associated with reflection from dull or rough surfaces like powders. In diffuse reflectance, the incident radiation is reflected by the sample at angles independent of the angle of incident radiation. After the interaction of the radiation with the sample, a combination of reflection, diffraction, refraction and absorption of incident radiation takes place[86].

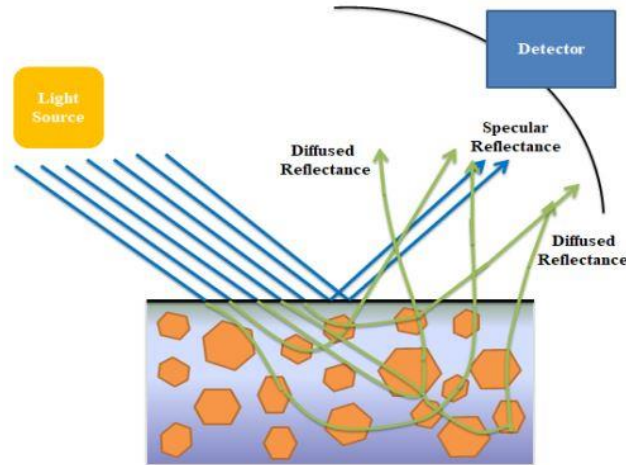


Figure 2.5 Schematic Explanation of UV-Vis Spectroscopy

These phenomena are explained by different theories but the commonly used theory to describe the diffuse reflectance spectra is the Kubelka-Munk theory which is given as:

$$F(R) = \frac{(1-R)^2}{2R}$$

Where $F(R)$ is the Kubelka-Munk function similar to extinction coefficient α and R is the reflectance. The band gap of the material can be obtained by multiplying the coefficient with the energy (eV).

$$E_g = [F(R) * hv]$$

Where exponent n is 0.5 in case of direct bandgap transitions and 2 in case of indirect band gap transitions [87].

Chapter 3

Results and Discussions

3.1 Phase Confirmation

The XRD patterns of the samples were obtained in the range 20° to 80° using a diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. All the peaks in **Fig 3.1(e)** perfectly match with available standard JCPDS 00-022-1086 and it shows the confirmation of synthesis of single phase having a cubic structure. The average crystallite size of CoFe_2O_4 is 170 \AA , is calculated from the FWHM of the (311) peak using the Scherrer formula. Similarly **Fig 3.1(a)** having a single peak at 27.3 is a characteristic interplanar stacking of aromatic system. The crystal system of $\text{g-C}_3\text{N}_4$ is cubic. Perfectly matching with available standard JCPDS (87-1526) confirms single phase synthesis of $\text{g-C}_3\text{N}_4$. The crystallite size of $\text{g-C}_3\text{N}_4$ is 294 \AA . It is clearly shown in **Fig (b),(c) and (d)** that in composite formation, peak of $\text{g-C}_3\text{N}_4$ is suppressed while decreasing its amount as compared to single phase CoFe_2O_4 .

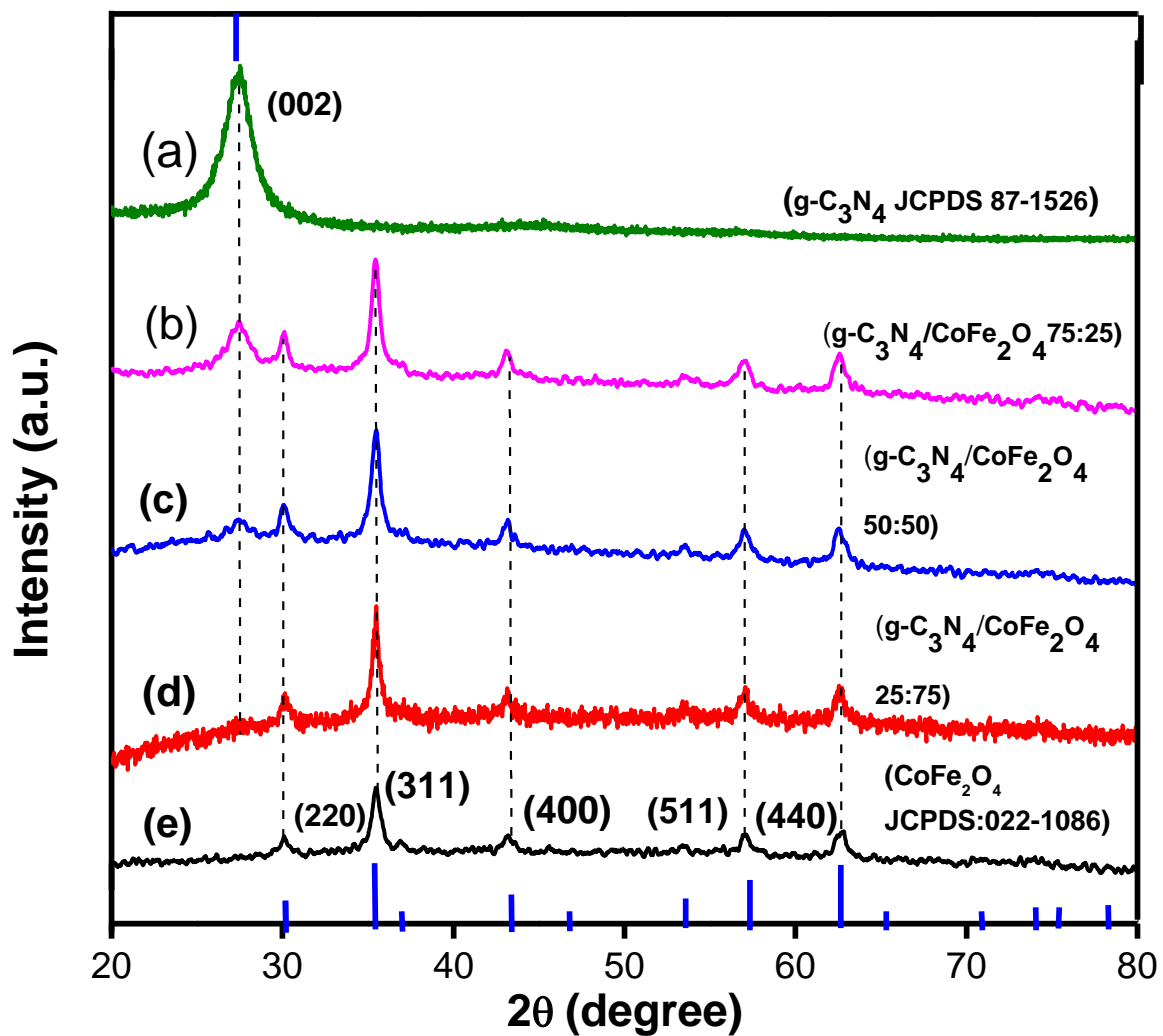
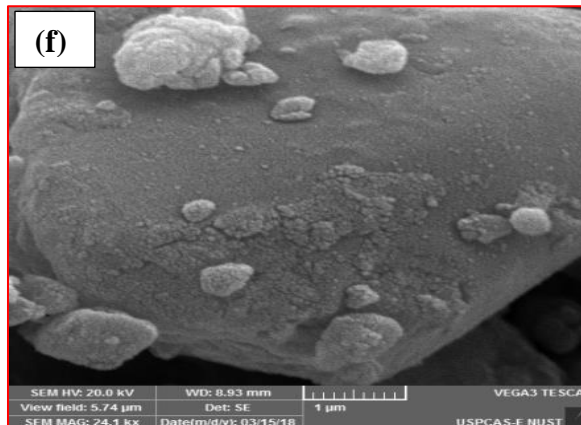
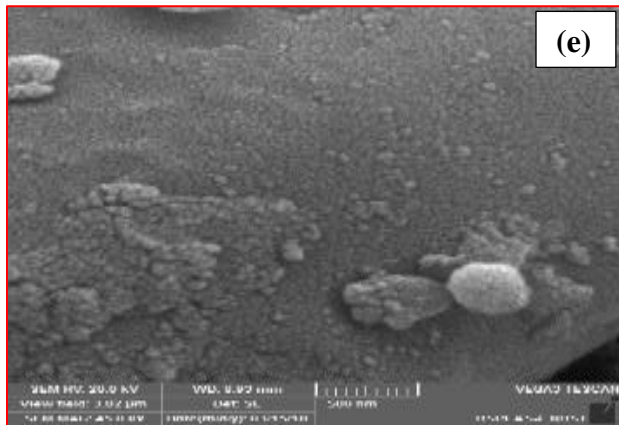
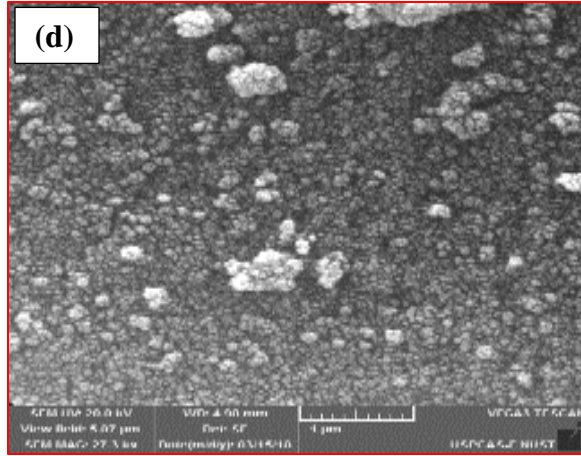
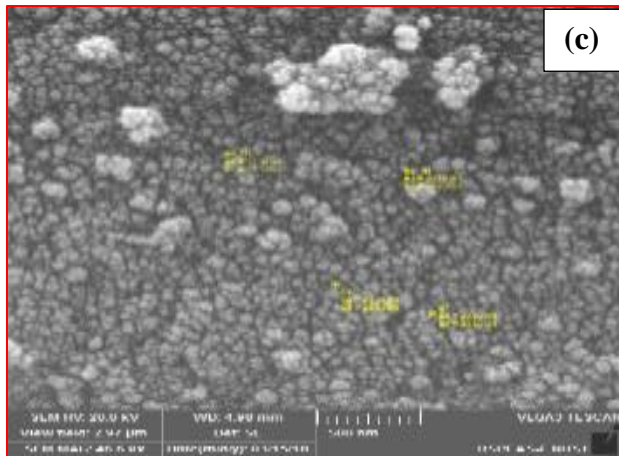
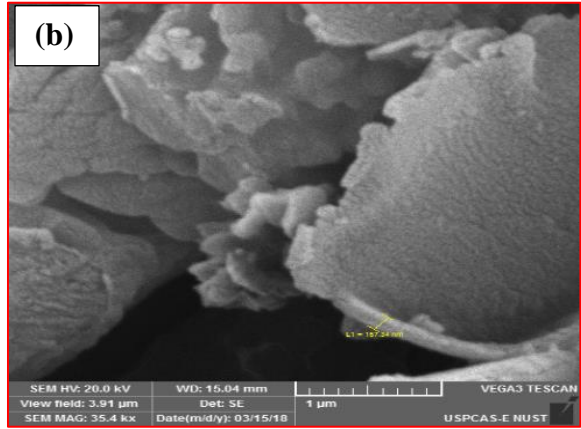
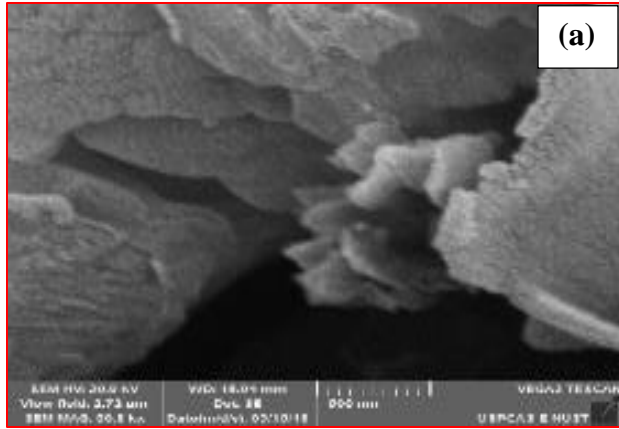


Figure 3.1 XRD Results of (a) $g\text{-C}_3\text{N}_4$ (b) NC-1 (c) NC-2 (d) NC-3 (e) CoFe_2O_4

3.2 Morphological Analysis



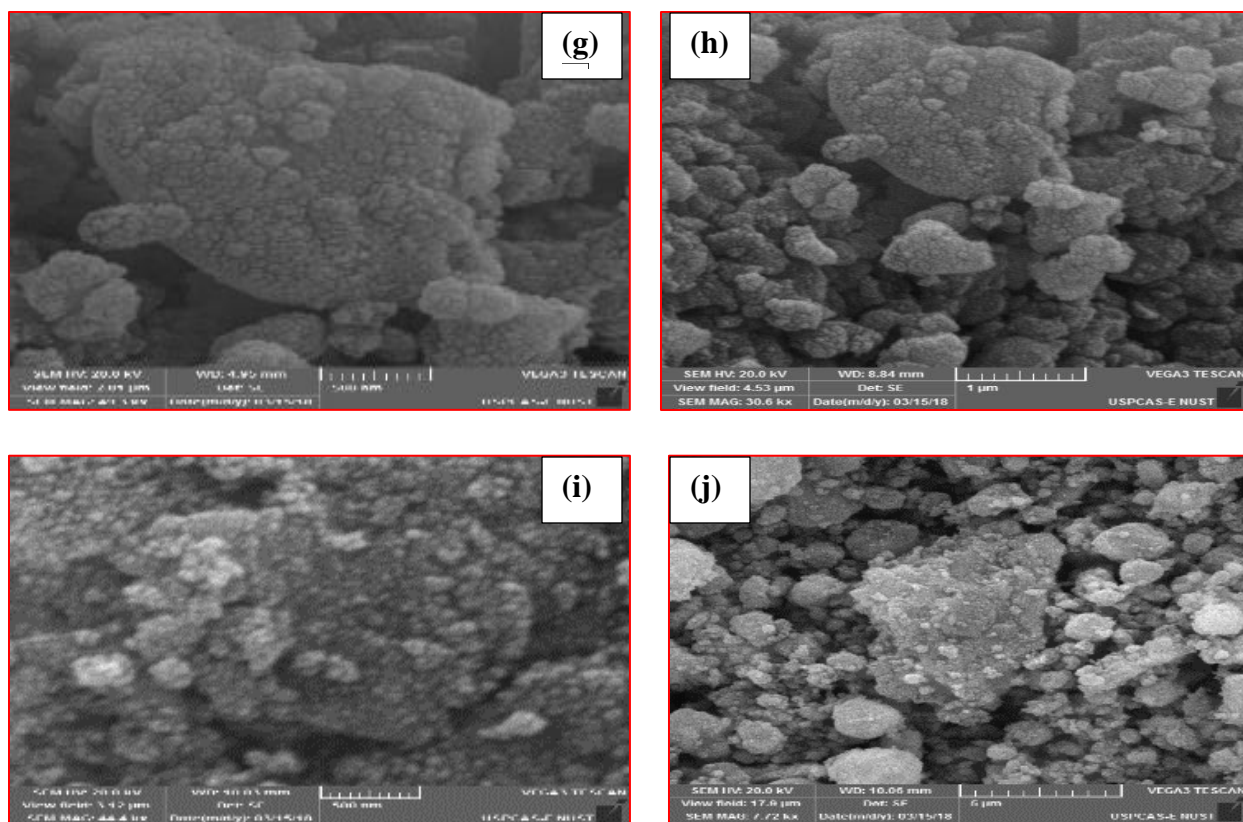
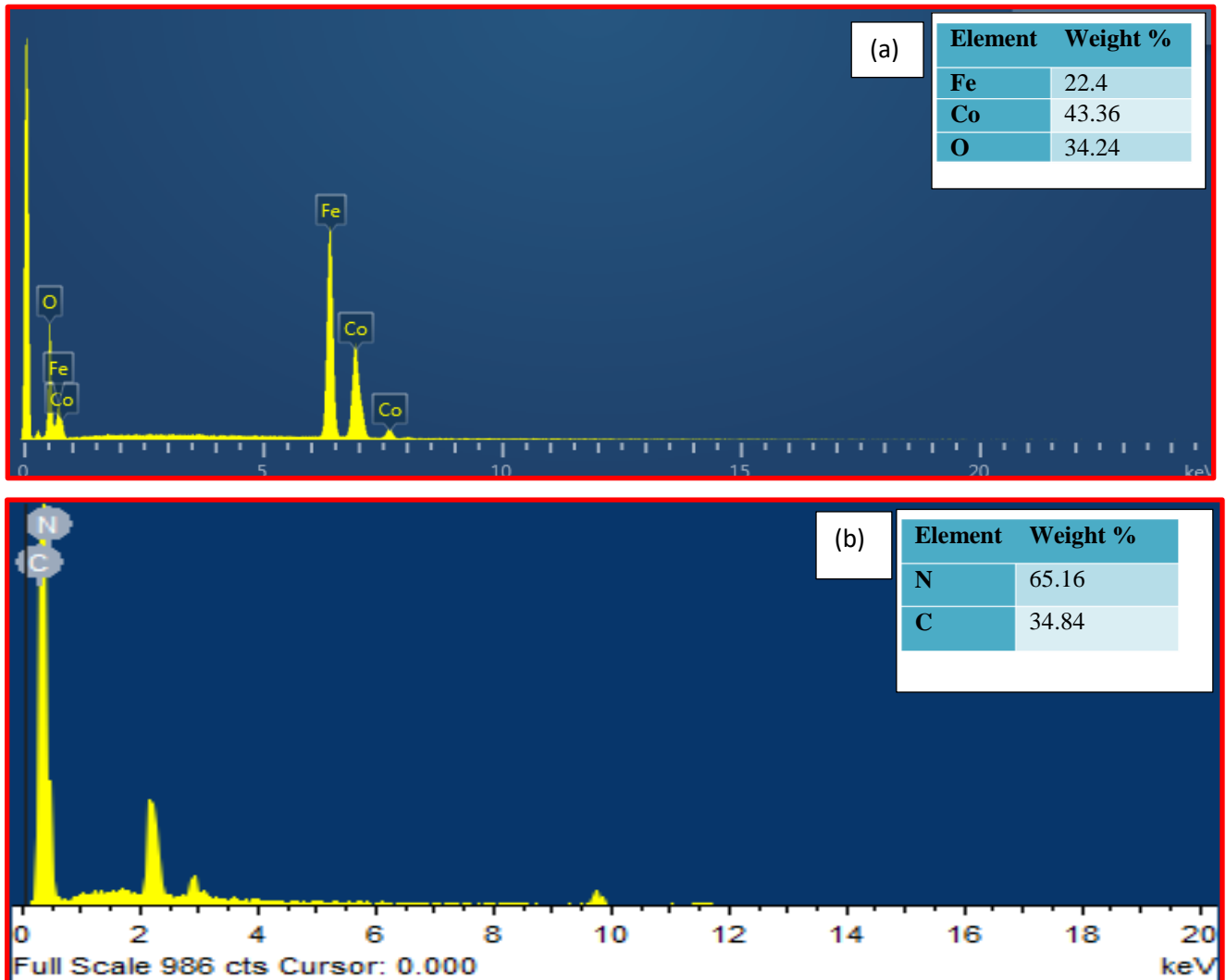


Figure 3.2 SEM Images g-C₃N₄ (a) 500nm), (b) 1µm), (CoFe₂O₄ (c) 500nm (d) 1µm), (NC-1 (e) 500nm (f) 1µm), (NC-2 (g) 500nm (h) 1µm)), (NC-3 (i) 500nm (j) 1µm),

For morphological analysis, SEM of CoFe₂O₄ and g-C₃N₄ was carried out. To analyze the morphology of synthesized materials, SEM images were taken at different scales. Irregular flakes of g-C₃N₄ (**Fig: 3.2 g-C₃N₄ (a) 500nm), (b) 1µm**) and spherical particles of CoFe₂O₄ (**Fig: 3.2(CoFe₂O₄ (c) 500nm (d) 1µm)**) and can be clearly seen through images. It can be clearly seen that size of CoFe₂O₄ is in nano range having particle size equal to 20.3nm. The deposition of CoFe₂O₄ nanoparticles on g-C₃N₄ is shown very clearly in **Fig 3.2(e), (f), (g), (h), (i), (j)**. (**Fig 3.2: (NC-1 (e) 500nm (f) 1µm)** shows the agglomeration of cobalt ferrite nanoparticles on the sheets of g-C₃N₄ and in (**Fig 3.2 (NC-2 (g) 500nm (h) 1µm)**) there is uniform distribution of CoFe₂O₄ nanoparticles over the g-C₃N₄ sheets. In **Fig 3.2 (NC-3 (i) 500nm (j) 1µm)** it can be seen very clearly that CoFe₂O₄ particles are overloaded on the sheets of g-C₃N₄.

3.3 Compositional Analysis

EDS analysis was carried out to check the percentage composition of the prepared sample. **Fig. 3.3(a)** shows the EDS pattern for CoFe_2O_4 , all peaks in the graph corresponds to Cobalt ferrite with no extra peak indicating the purity of sample. Similarly **Fig. 3.3(b)**, corresponds to the EDS pattern of $\text{g-C}_3\text{N}_4$, shows two prominent peaks of carbon and nitrogen. The EDS patterns of $\text{g-C}_3\text{N}_4/\text{CoFe}_3\text{O}_4$ composite is shown in **Fig. 3.3 (c), (d) and (e)**. It can be noted that almost all the peaks of EDS patterns of all composites are in correspondence with the desired materials. Whereas these EDS patterns are also showing the peaks of Pd and Au. It is due the sputtering of materials before analysis. Sputtering was done to increase the conductivity of electrons through the sample for better analysis.



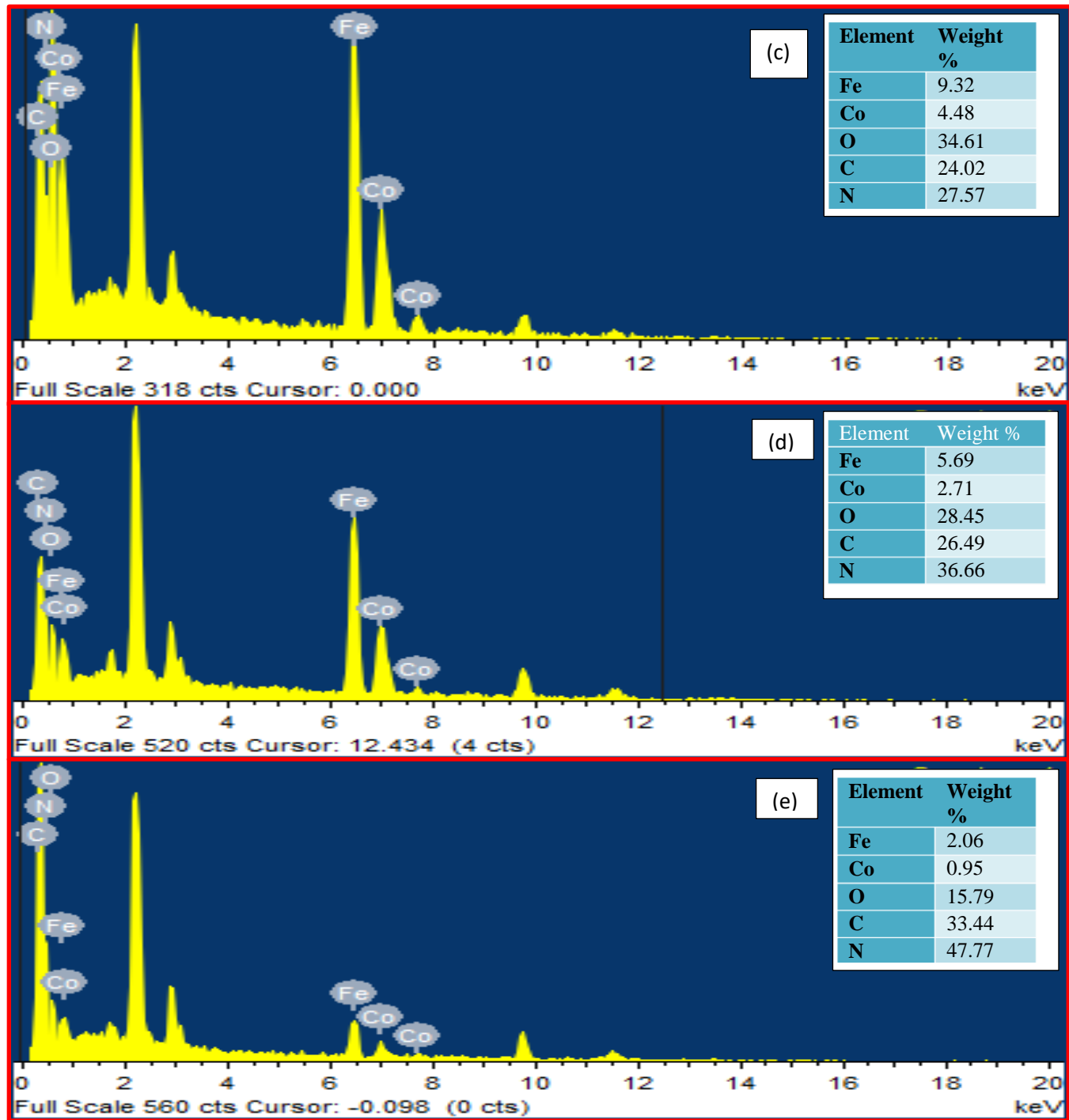


Figure 3.3 EDS Pattern of (a) CoFe_2O_4 (b) $\text{g-C}_3\text{N}_4$ (c) NC-1 (d) NC-2 (e) NC-3.

3.4 Alignment of Energy Level

The optical properties of prepared samples were evaluated by UV/Vis Spectroscopy. The corresponding results of the analysis are shown in the **Fig 3.4.1 and Fig 3.4.2**. The absorption spectra of CoFe_2O_4 exhibit a single hump at 776nm. As CoFe_2O_4 has intrinsic black color so it will absorb in wide range of 200nm to 800nm. The diffuse reflectance calculations were performed to find the equivalent absorption coefficients using Kubelka-Munk function[88]. To calculate band gap Tauc plots were plotted between $(\alpha h\nu)^2$ and photon energy as shown in **Fig 3.4.1**. As CoFe_2O_4 is direct semiconductor so the band gap value calculated using Tauc plot is 1.65eV. Tauc plot is shown in the inset. Similarly, $\text{g-C}_3\text{N}_4$ shows a single hump at 467nm. The respective tauc plot of $\text{g-C}_3\text{N}_4$ is shown in the inset of **Fig 3.4.2**

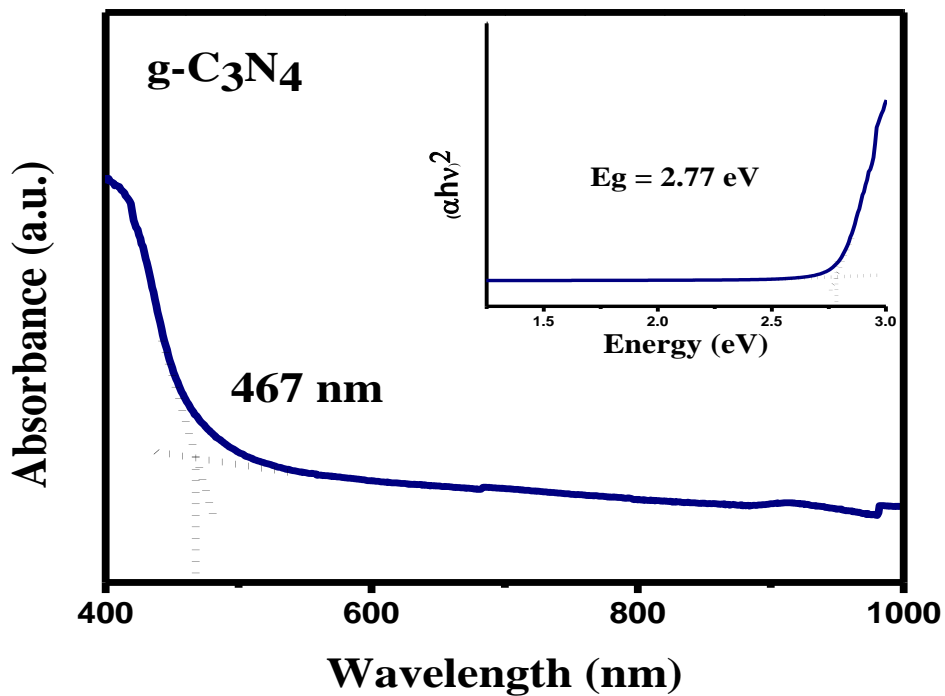


Figure 3.4.1 UV/Vis Spectra of CoFe_2O_4 inset shows the Tauc plot of CoFe_2O_4

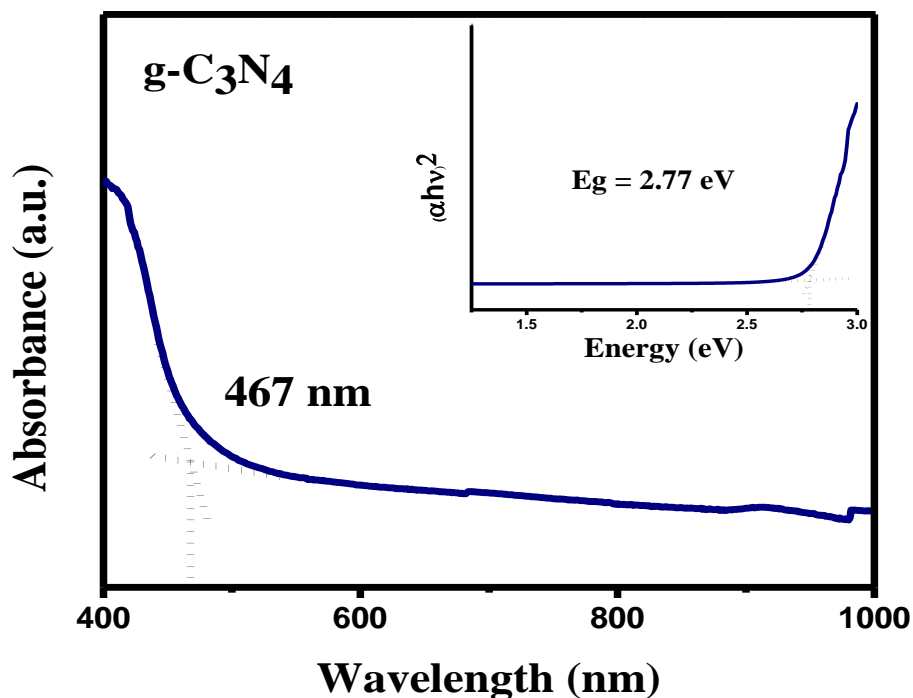


Figure 3.4.2 UV/Vis Spectra of g-C₃N₄ inset shows the Tauc plot of g-C₃N₄

The photocatalytic activity of photocatalyst is highly dependent on alignment of its energy levels. The band gap of CoFe₂O₄ and g-C₃N₄ is 1.65eV and 2.77eV respectively as calculated by their respective Tauc plots. The valence band positions of CoFe₂O₄ and g-C₃N₄ are 2.27 eV [57] and 1.58eV [89]. The corresponding conduction band positions were found -0.62eV and -1.19eV (against SHE) calculated using band gap values from Tauc plots. As XPS was not carried out so we are not affirmed about calculated conduction band values. The possible mechanism for the pollutant degradation through electron hole transfer is shown in the **Fig 3.4.3**

The electrons in the valence band of g-C₃N₄ get excited and move towards the conduction of g-C₃N₄ leaving behind the holes. As the conduction band of g-C₃N₄ is more negative than the

conduction of CoFe_2O_4 so electrons will move towards the conduction band of CoFe_2O_4 causing the reduction. And holes will remain in the VB of $\text{g-C}_3\text{N}_4$. These holes directly react with the harmful species and can degrade them into harmless species or they react with water forming hydroxyl radical which is powerful oxidizing agent and it will oxidize the harmful substances into harmless species as shown in the **Fig 3.4.3**. The cobalt ferrite might act as an electron sink as it will capture the electrons from the conduction band of $\text{g-C}_3\text{N}_4$ after excitation. In this we can get excellent charge separation and can overcome the problem of charge recombination.

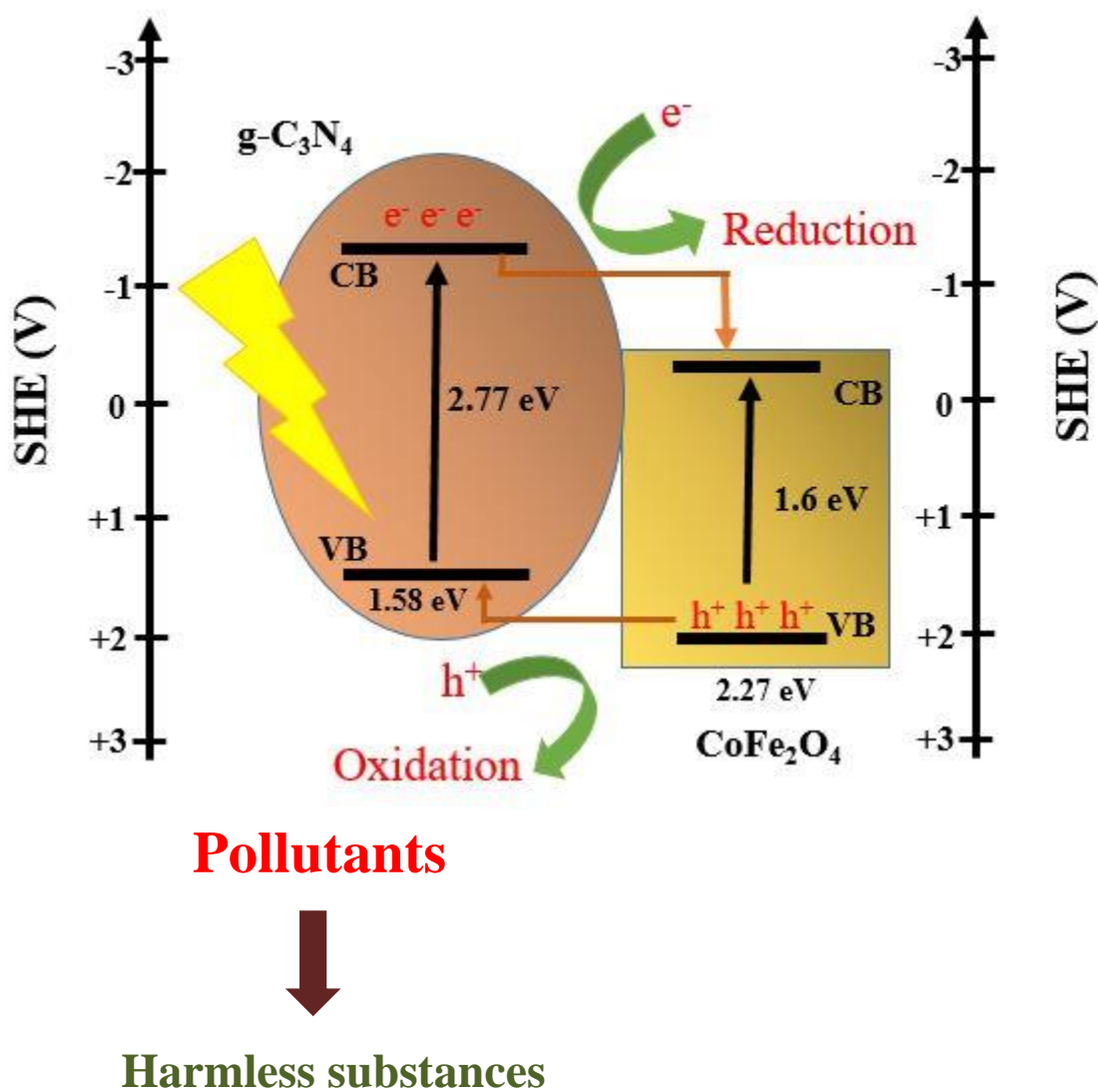


Figure 3.4.3 Schematic illustration of alignment of energy levels of CoFe_2O_4 and $\text{g-C}_3\text{N}_4$

3.5 Photocatalytic Activity

To check the photocatalytic activities of the prepared samples, all were irradiated under visible light to check the degradation against methylene blue dye. The light source used for this purpose was 300W Xe arc lamp that was placed at 30 cm from the beaker containing 100 ppm of methylene blue dye. Three controlled experiments were performed, in first light was irradiated with dye solution having no catalysts. It shows no degradation means degradation needs catalyst. In second case, 100 mg of sample was added in 100 ppm of methylene blue dye under constant stirring for 10 min and no light is irradiated i.e. under dark. This controlled experiment allows the maximum adsorption of methylene blue dye on surface of catalyst. In third experiment, light is irradiated on the system and 5mL of sample is taken out from the system for analysis of degradation using UV\Vis spectrophotometer. The same experiment was performed with all samples. The absorption graph of methylene blue dye using photocatalysts is shown in **Fig 3.5**. **Fig 3.5 (b) and (c)** shows the maximum absorption of methylene blue dye whereas it shows minimum absorption of methylene blue when both sample were mixed in equal amount as shown in **Fig 3.5 (f)**. It is due to the maximum adsorption capacity of the NC-2 and transfer of electron-hole pair between both materials.

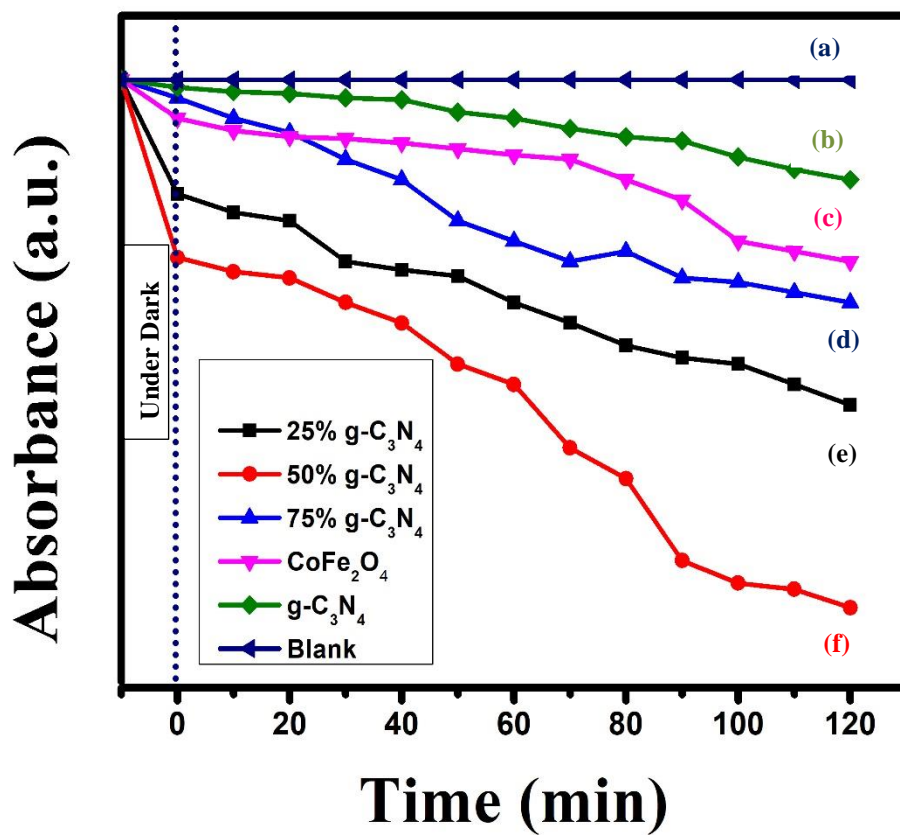


Figure 3.5 Absorption of Methylene Blue using different photocatalysts i.e. (a) blank, (b) $g-C_3N_4$ (c) $CoFe_2O_4$ (d) NC-1 (e) NC-3 (f) NC-2

3.6 Photoluminescence Studies

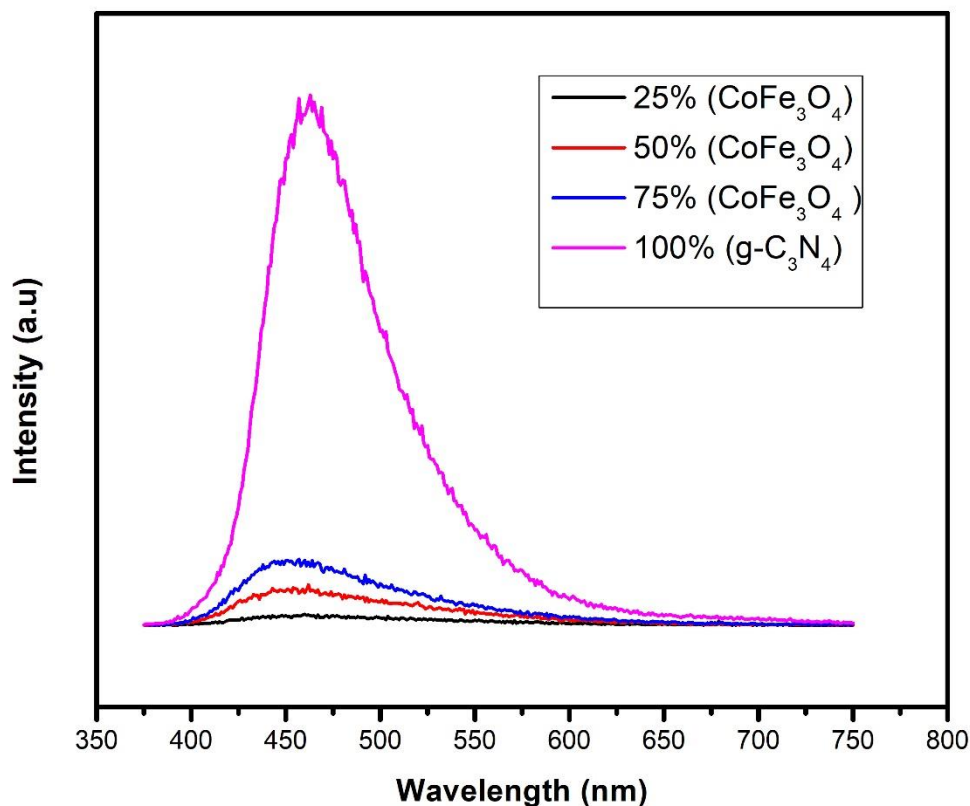


Figure 3.6 Photoluminescence Spectra

Photoluminescence spectra is the best technique for the determination of electron trapping and transfer of photo-induced charge carriers. The PL spectra of pure g-C₃N₄ and its composites with CoFe₂O₄ were clearly shown in **Fig 3.6**. The position of PL spectra of all composites of g-C₃N₄ and CoFe₂O₄ showed a strong emission peak at 450nm. The peak intensities of composites are diminished as the amount of g-C₃N₄ is decreasing showing that there is remarkable decrease in the electron-hole recombination due to the formation of heterojunction between g-C₃N₄ and CoF₂O₄ which was being illustrated in **Fig 3.4.1**. According to PL results maximum reduction in charge recombination was observed in NC-3 which is contradictory to the activity results. As the PL spectra is taken focusing the excitation wavelength of g-C₃N₄. So, PL is not the wholly-sole criteria for the judgment of activity results.

3.7 Stability of a Catalyst

A catalyst is a substance which speeds up the chemical reaction but doesn't consume during a catalyzed reaction and can be reused. Most often less amount of catalyst is required to speed up the reaction. To check either our synthesized photocatalyst is stable enough to reuse or not, its stability was confirmed using characterization techniques like XRD, SEM and EDS after the photocatalytic activity. **Fig 3.7.1** shows the XRD patterns taken before and after the photocatalytic activity of NC-2 whose efficiency was observed to be the highest. We can observe through XRD patterns that all the peaks are present even after activity confirming that phase of the photocatalyst is not changed.

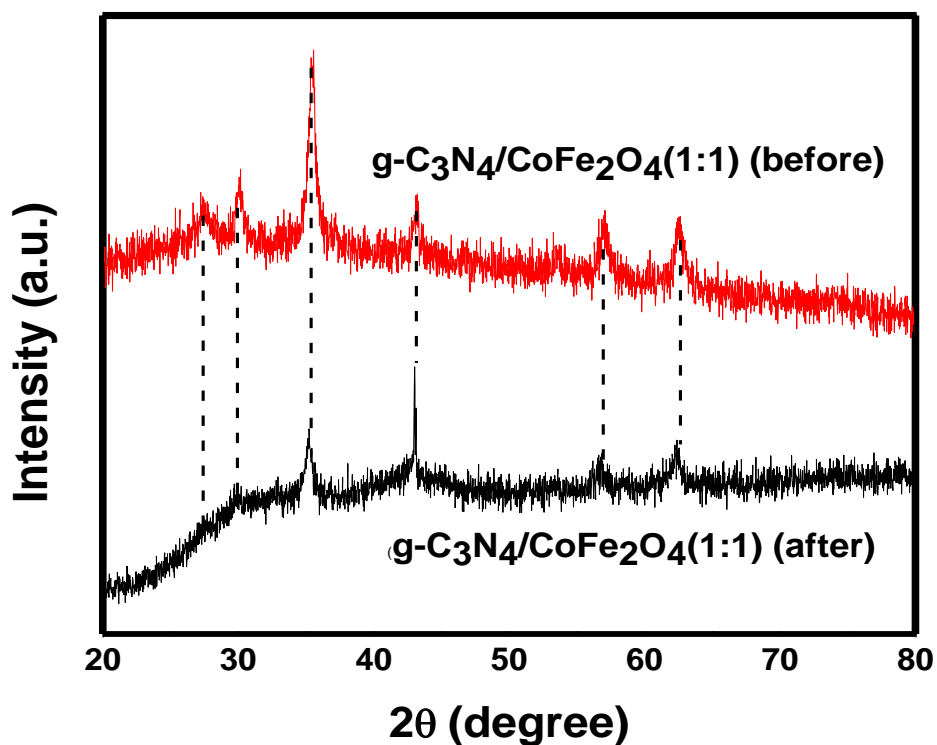


Figure 3.7.1 XRD Pattern of NC-2 Before and After Photocatalytic Activity

For the conformation of stability of the morphology of photocatalyst, SEM analysis was performed. From **Fig 3.7.2** it can be observed that the morphology of the photocatalyst is maintained after the photocatalytic activity.

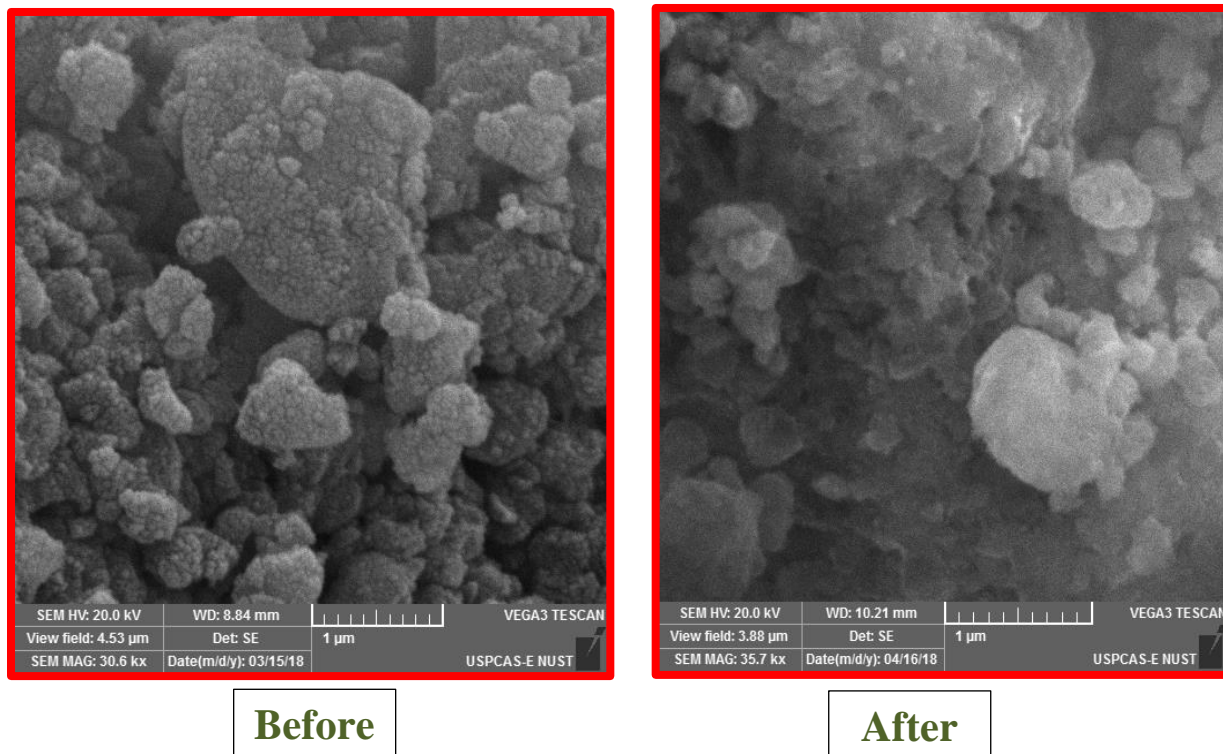


Figure 3.7.2 SEM Images of NC-2 Before and After Photocatalytic Activity

To make it sure that elemental composition of photocatalyst have no significant change, EDS analysis was carried out after performing the photocatalytic activity. **Fig 3.7.3** shows the spectra of EDS analysis of NC-2 before and after photocatalytic activity for the confirmation of stability of NC-2.

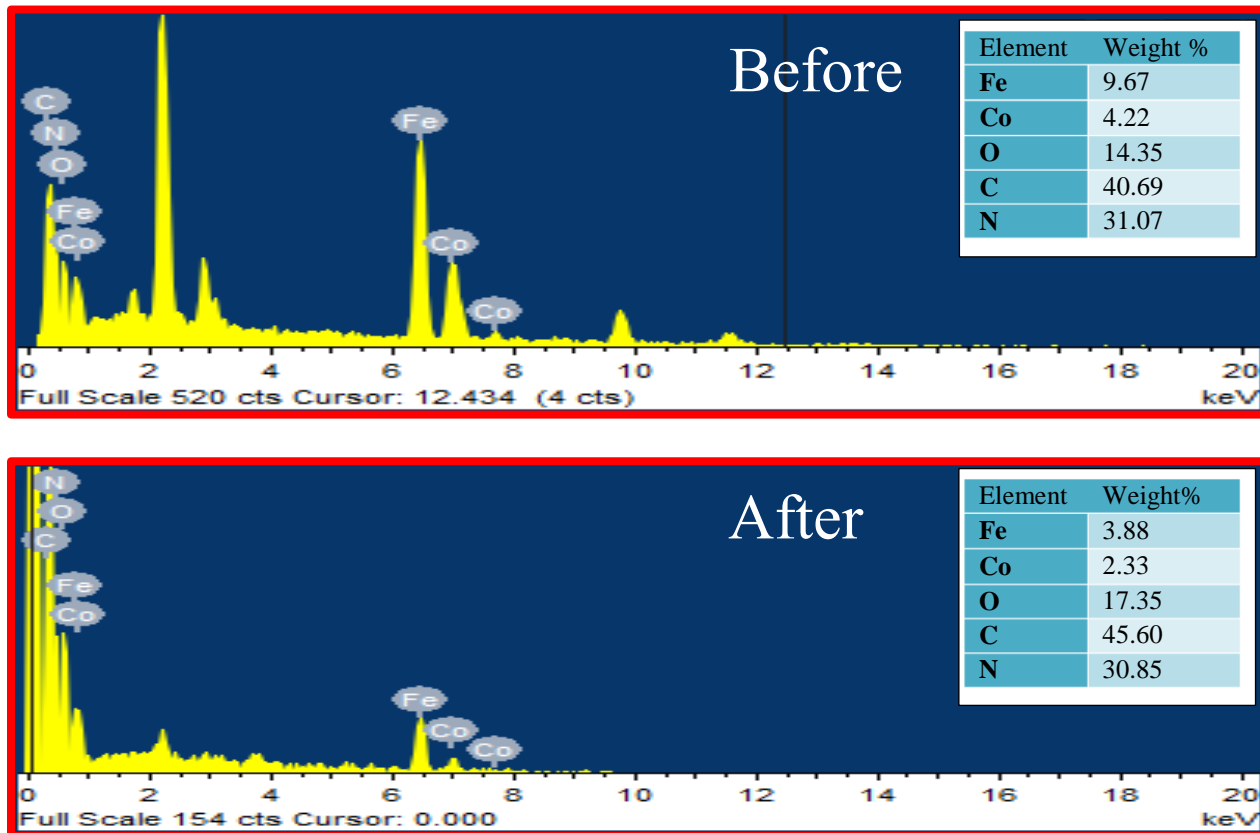


Figure 3.7.3 EDS Spectra of NC-2 Before and After Photocatalytic Activity

Conclusion

Energy and environment are the two main problems of the existing world which must be addressed on priority basis. Environmental problems are increasing day by day due to the increased industrialization, overpopulation, global warming and excessive use of fossil fuels. This not only causing the pollution but also leading to the depletion of the resources. So, the world needs to divert the attention towards the development of renewable energy sources. If we talk about the nonrenewable energy resources, sun is the infinite source of energy on the earth. Such technologies which would efficiently produce light energy and can convert it into usable form energy need to be implemented. Photocatalysis is one of most promising technique for the described purpose and to handle with all the environmental problems. Photocatalysis can degrade pollutants and can also convert CO₂ into fuel. Industrial waste consists of all of harmful materials which are drawn into the water bodies without any treatment causing the water contamination which needs attention to be reduced. So, here is this work we have reported for the synthesis of such photocatalysts which can easily reduce the harmful substances into harmless substances through pollution degradation. A large variety of photocatalysts has been reported for the pollution degradation. Many strategies have been employed to enhance the activity of these photocatalysts. In our work we have reported the fabrication of heterojunction of cobalt ferrite and graphitic carbon nitride. Graphitic carbon nitride has large number of application in the field of bio imaging, optronics and photocatalysis, due to its fluorescence and other important properties. Cobalt ferrite also has been as photocatalyst but due to having electron hole recombination, we need to synthesize its composites. In our work, we have reported the synthesis

of cobalt ferrite via hydrothermal method and its composites with g-C₃N₄ by physical method. All the characterization techniques has confirmed the formation of composite materials. It can be concluded that by forming the composites electron hole recombination has been reduced as cobalt ferrite act as electron sink. When light fall on g-C₃N₄ electrons in the valence band of g-C₃N₄ will be excited to conduction band. There electron will then be transferred to the CoFe₂O₄ and stay on the surface for some time. This process can effectively stop the charge combination and enhances the charge separation. The holes left behind in the valence band of g-C₃N₄ will promote the oxidation of harmful pollutants to harmless species. The photocatalytic activity of the material was checked for methylene blue(MB) and it was concluded that when g-C₃N₄ is mixed with CoFe₂O₄ in equal ratio (1:1), the composite (NC-2), showed the maximum degradation of MB. i.e. 94% in 2 hours as compared to bare materials and other composites i.e. NC-1 and NC-2. NC-2 showed maximum activity due to the suppression of charge recombination because of band alignment of CoFe₂O₄ and g-C₃N₄ and uniform distribution of CoFe₂O₄ nanoparticles over the surface of g-C₃N₄.

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