CHAPTER

1

INTRODUCTION

1. Motivation and problem statement

Dyes are mostly used in paints, textiles, leather, pulp and paper, food and pharmaceutical industries. These industries are very significant because they generate valuable items. The bulk of industrial activities use organic dye to colour their products, which are subsequently discharged into freshwater reservoirs like rivers and streams that eventually open out into the ocean ((Abdulhosseinzadeh et al., 2015) and (Adhikari et al., 2014)). Twenty percent of these dyes are wasted and wind up in streams, which is bad for the ecosystem. Furthermore, the ecosystem finds it challenging to decompose these contaminants due to their structures. Furthermore, according to Ahmed, these pollutants can have serious detrimental impacts on human health, such as liver problems, genetic abnormalities, eye irritation, and skin allergies (Ahmed et. al., 2018). Towards the end of the 19th century, synthetic dyes drastically altered the composition of many natural dyes; as a result, a natural dye must be safe and free of toxins, carcinogens, mutagens, and allergens. However, textile dyes are linked to the majority of reported cases of unexpected garment adverse effects. A number of food dyes, such as butter yellow, are known to cause cancer. Because these colours are less commonly reported in textiles than in food or cosmetics, it can be difficult to discover the right blend for them. A sizable amount of the organic colours present in industrial effluent is lost.

Effluent causes environmental problems and grave harm to aquatic life during its synthesis and processing (Akram et al., 2018; Allen et al., 2010). Significant amounts of dyes, especially organic ones, are released by a number of industries, including textile, cosmetics, plastics, leather, pharmaceutical, and others (Alshehri et al., 2012; Amano et al., 2013). The textile industry's significant water emissions and chemical load make it the main environmental issue. These dyes that have leaked are dangerous and carcinogenic to the environment, according to reports. Scientists are trying to figure out how to decompose dyes before releasing them into the environment since they are toxic. These colours can irritate the skin, eyes, and respiratory tract in both humans and animals, making ingestion risky (An et al., 2014). Many approaches, including as biological, chemical, physical, and electrochemical oxidation, have been developed, especially for treating dyes in wastewater systems (Atout et al., 2017; AZ–OM, 2013). However, common wastewater treatments are usually more costly, and the degrading process requires a larger space. Thus, a simple, inexpensive method can be used to eliminate the organic dyes. One method to perhaps turn these drawbacks into better outcomes is by the use of photocatalysis (Balavi et al., 2013; Bharathkumar et al., 2015).

The paper and textile dyeing industries commonly use congo red, a noteworthy class of azo dyes, as a colourant. For this reason, it is believed to be more important to degrade congo red from wastewater via photocatalysis (Bharathkumar et al., 2015; Bhatti et al., 2017). Semiconductor nanoparticles (NPs) are now one of the most promising materials for degrading dyes as a photocatalyst. Graphitic carbon nitride (g–C_3N_4), in comparison to other semiconductor nano–particles, demonstrates superior photocatalytic behaviour due to its low cost, outstanding thermal stability, low toxicity, and ability to oxidise a variety of organic contaminants (Bindu and Thomas, 2014; Blitz, 1998). However, as g–C_3N_4 is triggered by UV light, as well as visible light. Nonetheless, it is quite likely that visible light will cause g–C_3N_4 NPs to activate (Bourdo et al., 2008). Taking into account that metal or nonmetal doping.

Presently, g–C_3N_4's increased activity in VL absorption is of interest. It has been discovered that doping of transition metals into g–C_3N_4 can increase the material's absorption of visible light. So far, several remarkable photocatalytic materials have shown exciting photocatalytic activity. Furthermore, research into new materials with higher reactivity of known potential photocatalysts is essential to the development of technologies (X. Chen et al., 2016). Consequently, the main goal of the current study is to develop g–C_3N_4 photocatalyst that degrades organic colours when exposed to visible light.

This visible light driven photocatalysis has many advantages over dye degradation and doesn't further contaminate the environment. However, it's crucial to obtain the degraded products that don't damage biological systems (Ding et al., 2011). In addition to dyes, the sometimes effluents contain various chemical intermediates that are far more dangerous than the parent compounds. Nonetheless, the chemical evaluation of the toxicological potential of the treated water has many limitations, the most important of which is the inability to estimate the bioavailability of the contaminants (Dutta et al., 2016, 2015). Thus, more investigation is needed to confirm the purity of the treated water. Survival analysis is one of the many treatment methods that may be utilised to verify the species and capacities for survival of the plants and animals in the treated industrial wastewater. Under certain conditions, it can be used to a wide range of species, such as fish, crabs, algae, bacterial cells, plants, daphnias, and ceriodaphnias. Among other species, brine prawns, or Artemia salina, are small crustaceans that can survive in hostile conditions and low oxygen levels (Feng et al., 2018; Fu et al., 2016). All the data recommended the usage of *Artemia Salina (AS)* and *Moong bean (Vigna Radiata)* as model species for survival assessment.

Energy and environmental difficulties are the two primary development concerns of the modern period (Y. S. Fu et al. 2012). Since industrialization began, pollution has become an unavoidable part of contemporary life. Industrialization has increased the pace of pollution and wastewater output, and there is little sign that this pollution will decrease very soon. Since India is a developing country, it is expected that boosting the industries' total output capacity many times over will support the national economy and help India maintain its position in the international market. Since there are two sides to every coin, it stands to reason that pollution will increase in tandem with productivity. Since controlling environmental pollution is a difficult problem to solve, efforts must be made to create plans and techniques for managing the pollution together with secure waste disposal. Due to the increased demand for water due to an expanding population, water pollution is one of the primary challenges that needs to be tackled with the utmost care since a clean water source is essential for life. There are numerous locations where water can be found, such as lakes, rivers, ponds, seas, ground water, etc. It serves a wide range of functions, from significant industrial and agricultural use to modest household needs. The various sectors' global water use is categorised in Figure 1.1. It's clear that agriculture and industry use 90% of the water resources. Water supply pollution also originates from the household, industrial, and agricultural sectors—all of which use water in different ways. The textile industry is one of the major global water polluters, consuming large amounts of water and discharging large volumes of contaminated water into the environment, ((R.–C. Chen et. al., 2013) and Corma et al. (2004)). According to Adhikari et al. (2014) and Amano et al. (2013), 10–15% of the 0.7 million tonnes of dyes generated annually for use in dying textiles, plastics, leather, paint, and other materials are lost as effluents during the dye manufacturing process.

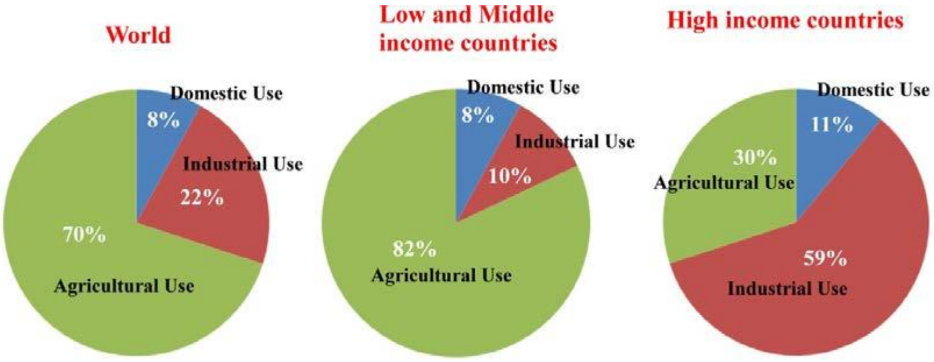

Figure 1.1 Worldwide consumption of water. (Data courtesy: wikipedia.com)

The large quantity of dyes injected into the water system cause it to become colored, preventing sunlight from passing through. In addition, it produces eutrophication and disturbance, alters pH, turns poisonous and turbid water, has a greater concentration of COD and BOD, and endangers both the environment and aquatic life. These dyestuffs in water have dangerous impacts on the ecosystem, and drinking such tainted water can harm people's health as well. In order to meet the demand for a clean water source, decolorization, purification (wastewater treatment), or recycling of this contaminated water has consequently grown to be a serious concern and an urgent need for a sustainable environment. The bulk of the country's textile sector is located in the districts of Bhadohi and Mirzapur in Uttar Pradesh, which is one of the states that produces the greatest number of textiles. This has therefore led to a growing amount of concern regarding the condition of the surrounding water bodies, which is what motivated me to look into this topic for my thesis.

2. Problems caused by the industrial dye effluents

Textile dyes are extremely dangerous and carcinogenic; they have been connected to numerous human and animal diseases as well as environmental harm (Chen et al., 2010). This is due to the fact that industrial pollutants are mixed with textile colors in large quantities. Anoxic deposits in public water supply systems are caused by dye accumulation in soil and sediment in aerobic conditions, especially in traditional treatment facilities. (L. Chen et al., 2016; R. C. Chen et al., 2013) These deposits might be partially replaced or distorted. It is also possible that intermediate synthetic compounds break down into compounds that combine to produce dyes and other chemicals that are carcinogenic and mutagenic.

A substantial amount of industrial waste is continuously poisoning the water sources near populated regions, posing a threat to the aquatic environment and human health. The food and beverage, leather, textile, and biological filtration industries employ a wide range of chemicals, some of which are industrial byproducts like dye. These substances have the potential to directly or indirectly harm our bodies or the environment. Thus, it is crucial to get rid of this contamination from water (Chen et al., 2010).

3. Dye

Dyes are utilized as coloring chemicals in a wide variety of commercial industries, including pigments, clothing, cosmetics, and artworks (R. C. Chen et al., 2013). Dyeing is essential to the production of these products. The production of synthetic dye is expected to reach 7 lakh tonnes per year, according to projections made by Corma et al. (2004), Deluga et al. (2004), and Denchak (2018). It is possible to classify synthetic dyes into three primary categories. through the use of dyes that are non–ionic, cationic, and anionic. Disperse and vat dyes are examples of non–ionic dyes that dissolve in organic solvents, whereas ionic dyes, which include anionic and cationic dyes, often dissolve in water. Furthermore, cationic dyes are classified as base dyes, whereas ionic dyes are divided into three distinct groups: direct dyes, acid dyes, and reactive dyes (Ding and associates, 2014).

The dye production in the commercial textile industry is approximately 10,000 tons per year on average. A little more than ten to fifteen percent of the contaminated dye that is produced is discharged into water bodies such as rivers, lakes, and ponds (Zhu et al., 2012). In addition to being toxic to humans, dyes frequently have detrimental effects on polluted aquatic life and can trigger allergic reactions. The creation of poisonous dyes that are easily absorbed by the environment occurs when dye waste water is not managed in an effective manner. The dye molecule's absorption of solar light slows the rate of photosynthesis in aquatic plants.

3.1 Types of dye

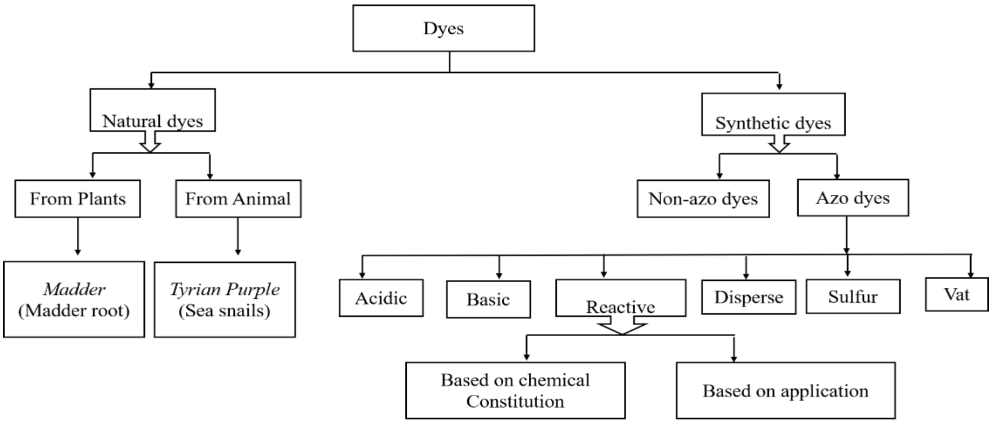

Figure 1.2 Classification of dyes based on chemical constitution

3.1.1. Basic dyes (Cationic dye)

Cationic dyes, which are widely used to dye acrylic, wool, nylon, and silk, have distinct chemical structures that are based on different atomic groups. These dyes are classified as hazardous pigments and have the potential to induce cancer, mutations, allergic dermatitis, and skin irritation. These dyes, which are often hydrochloride or zinc chloride complexes that rely on the positively charged ion, are referred to as basic dyes. Cationic dyes are water soluble, create colored cations in solution, and have a positive charge on their molecule. The primary dyes exhibit high color brightness and intensity, as well as strong visibility. As seen in Figure 1.3, it is frequently utilised as a model in dye absorption investigations including dyes like *Methylene blue (MB)* and *Rhodamine blue (RhB)* the textile sector. Acute *MB* exposure can cause heart palpitations, shock, nausea, jaundice, and other symptoms.

3.1.2. Methylene blue

Methylthioninium chloride is also referred to as *methylene blue* (MB, $C_{16}H_{18}ClN_3S$, M.W 319.85 g/mol). Compared to other dyes in its class, this heterocyclic thiazine chemical, which appears to be odorless and is a dark green powder that dissolves in water to generate a navy-blue color, is used in enormous quantities in the textile industry. MB is a highly toxic chemical that is mostly employed as a dye and is widely used in many different industries, including the paper, painting, leather industries and mostly in textile. MB is mostly utilised in the pharmaceutical industry and can result in hemolytic anemia, infantile skin desquamation, hypertension, chest pain in the abdomen, fever, and bluish staining of the skin, among other side effects. However, MB irritates the eyes severely and, at high concentrations, can cause conjunctive injury and blindness. For this reason, it must be removed from the water stream (Zhao et al., 2015; Zhou et al., 2013).

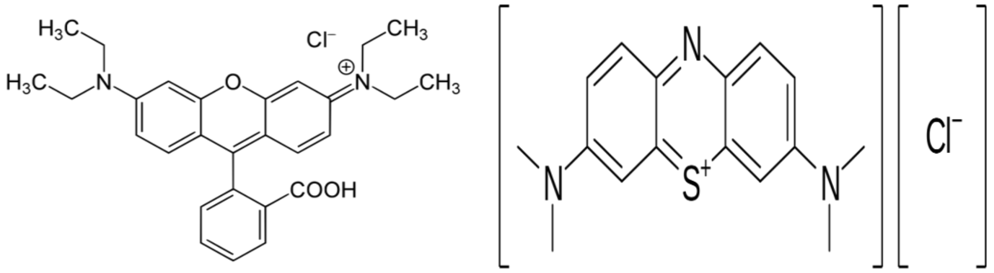

Figure 1.3 Structure of Rhodamine blue and Methylene blue dye (image courtesy: wikipedia.com)

3.1.3 Rhodamine blue

Basic cationic dye *Rhodamine Blue* (RhB, $C_{28}H_{33}ClN_2S_{32}$, M.W. 479.02 g/mol) is used extensively in the paper, paint, and leather industries to impart red color in aqueous solution. Therefore, it is crucial to remove RhB from effluents before releasing them into a water stream to safeguard public health, the environment, and aquatic life. Because its carcinogenicity, toxicity to reproduction and development, and neurotoxicity, RhB is frequently used as a biological stain in medical laboratories, despite the fact that it is hazardous to both humans and animals (Zhang et al., 2011).

3.1.4 Anionic dyes

Anionic dyes consist of several chemicals from widely different dye families and are mostly reliant on negatively charged ions. Although their structures differ significantly, as shown in azoic and nitro dyes, they all have the characteristic of being ion replacements that are soluble in water. Chemically speaking, most reactive dyes are members of the anionic azo dye family, which also includes direct dye. When reactive dyes come into contact with cotton and wool, most of them form covalent patterns. Such dyes should not be released back into the environment due to their limited stability, which is caused by the reaction groups' hydrolysis in the aqueous phase. X. Y. Zhang et al. (2010) state that acids are used in the dyeing process of hydrophilic fibers such silk, wool, polyamide, modified acrylic, and polypropylene.

Reactive azo dyes are harmful due to their toxicity, carcinogenicity and environmental persistence. When these dyes are released into water systems, they can contaminate aquatic ecosystems, harming aquatic life and potentially entering the human food chain. Some reactive azo dyes contain hazardous aromatic amines, such as benzidine, which are carcinogenic. Effective treatment processes are necessary to mitigate these risks, and there is a gradual shift for safer, environmentally friendly alternatives in industries like textiles to reduce the impact on human health and the environment. Apart from AOPs; Physical and Chemical treatment processes are in use. Some biological methods are being used.

3.1.5 Acid blue 113

A sort of direct dye, *acid blue 113* (AB 113, $C_{32}H_{21}N_5Na_2O_6S_2$, M.W.681.65 g/mol) is a powder with a pale greenish–black hue. When it dissolves in water, it seems to be purple/blue in color. It is used for dyeing silk, wool and polyamide fibers. Direct dyes mixed with bath–dyed wool and stick–blend fabric can also be used for biological shading, leather, and paper. Since acid dyes are made of organic sulfonic acids, they are toxic to people. Figure 1.4. shows the *Acid blue 113* structure.

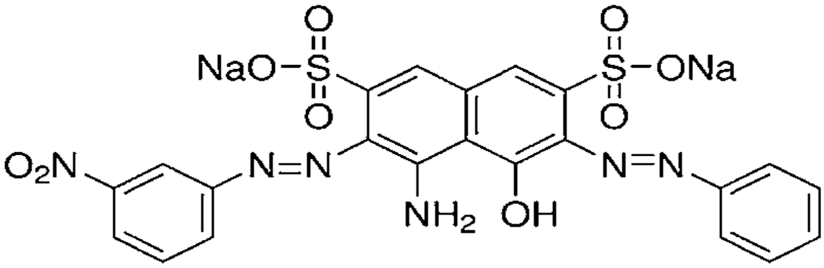

Figure 1.4 Structure of Acid blue 113 (image courtesy: wikipedia.com)

3.1.6 Toxicity of dyes

The primary factors that encourage the possibility of textile dye contamination are their potential toxicity and the potential carcinogen. It has been established that the toxicity of dyes and intermediates can cause mutations in both aquatic and human species. primarily cause: benzidine and other aromatic chemicals, which are proven carcinogens, are used to make a lot of colors. Azo dyes make up around 70% of reactive dyes; certain azo dyes might cause cancer or cause mutations in aquatic species (Zhang et al., 2012).

Azo dyes, particularly those containing benzidine and other aromatic chemicals, pose significant risks to public health and the environment due to their toxicity and carcinogenic potential. These dyes can contaminate water sources, harming aquatic ecosystems and potentially entering the human food chain.

Water containing colors or decaying materials can lead to serious kidney, liver, reproductive, and central nervous system damage, as well as nausea, bleeding, skin, and mucous membrane ulcers. In general, MB results in myocardial depression, elevated arterial blood pressure, hypertension, etc.

3.1.7 Consumption of dye effluents

Cotton textiles are widely used in both domestic and commercial settings on a regular basis. Textile textiles require a high oxygen demand, have a mild odor, do not degrade, and are prone to microbiological contamination, which can have a negative impact on human and animal health as well as increase the toxicity of wastewater discharged by the textile sector. Fabrics have been dyed using a variety of organic dyes, including *rhodamine blue* (RhB) and *methylene blue* (MB). According to L. Zhang et al. (2016), wastewater treatment and dye degradation are therefore more significant environmental issues that seriously harm both terrestrial and aquatic wildlife. The ideal solution to this issue is to use metal oxide nanoparticles, which are used in the current work and are stated below as the nanoparticles used to remove such colors from our surroundings.

3.2 Nanotechnology towards environmental remediation

The field of nanoscience and nanotechnology is a rapidly developing field of study that deals with systems, devices, and structures that have unique characteristics and uses due to the way their atoms are arranged on a scale of 1 to 100 nm. In 1959, Nobel Prize–winning American physicist Richard Fenyman introduced the idea of nanotechnology. Nanotechnology is widely employed with photocatalysts to eliminate pollutants from water. Several scientific theories state that photocatalysts are nanoparticles (NPs) with advantageous electronic structures, light absorption, charge transfer, and other semiconducting features (Chaktavorty and Roy, 2024). In the wastewater treatment process, metal oxide nanoparticles (NPs) such as TiO_2, WO_3, ZnO, $ZnFe_2O_4$, N–doped ZnO, S–doped ZnO, Bi_2WO_6, Fe_3O_4, V_2O_5, and other zero–valent metal nanoparticles (NPs) of Ag, Fe, Zn, and other elements have been widely used in recent years (Zhang et al., 2015). The nanomaterials exhibit excellent absorption and photocatalytic efficiency due to their small size and large surface to volume ratios.

3.3 Metal oxide nanoparticles

Metal oxide NPs are important class of nanomaterials which play a very significant role in many areas of science and technology (Pan et al., 2014; Song et al., 2017; J. Zhang et al., 2016). Metal oxide NPs can adopt a vast number of structural geometries with electronic structures that can exhibit metallic, semiconductor or insulator character. Metal oxide nanoparticles have intrinsic charge separation capabilities that differentiate from metal NPs. The synthesis of metal oxide NPs with desired properties was initiated since 1980 (Krishnapriya et al., 2015). The major advantages of metal oxide NPs are:

(i) cell parameters and lattice symmetry of metal oxide NPs are changing with structural changes,

(ii) high electrochemical characteristics of metal oxide NPs as compared to the bulk counterpart because of the quantum confinement effect

(iii) change in band gap of metal oxide NPs with change in surface properties and size, which influence the chemical activity and conductivity. Semiconductor metal oxides have found diverse applications ranging from solar cells, passing through their integration in electronic devices, lithium–ion batteries (X. Chen et al., 2013; Lim et al., 2015; Villaseñor et al., 2002), photocatalyst agent and as sensors (Lim et al., 2015).

Nanocrystalline spinel ferrites, typical representatives of magnetic materials with magnetic permeability and electrical resistivity have attracted great attention due to their broad applications in many fields like magnetic materials, energy, biomedicine and diverse catalytic processes. Recently, the development of magnetic photocatalyst has interested a multitude of researchers, especially for MFe_2O_4 (M= divalent metal ion e.g.

Zn, Ni, Co, Cu etc.) materials due to their easily recycling capability. Magnetic nanomaterials also exhibit great efficiency for the removal of trace pollutants from an aqueous medium.

Among the spinel ferrites, zinc ferrite ($ZnFe_2O_4$) has drawn a lot of attention due to its relatively narrow band gap for visible–light response, high sensitivity, stable chemical and photo–chemical properties. Bulk $ZnFe_2O_4$ is a completely normal spinel structure where Zn ions in the tetrahedral or A sites and Fe ions in the octahedral or B sites. As zinc ion has no magnetic moment, bulk $ZnFe_2O_4$ has a weak antiferromagnetic behavior with a Neel temperature of 10.5 K and paramagnetic behavior at higher temperature. However, redistribution of zinc cations into octahedral sites resulted in ferromagnetic behavior in zinc ferrite.

The transition metal oxides such as WO_3, ZnO, TiO_2 and its composite materials have drawn a lot of attention towards photocatalytic environmental remediation. Amongst the transition metal oxides, tungsten oxide (WO_3), a n–type semiconductor with a band gap of 2.4 – 2.8 eV is one of the most interesting materials exhibiting unique optical, thermal, physiochemical and electrical properties (F. Fu et al., 2012). This leads to an extensive diversity of applications in chemical selective catalysis, sensors, fuel cell, chromism and adsorption of pollutants. WO_3 has emerged one of the interesting semiconductor materials for photodegradation of micropollutants under visible–light irradiation as well as photocatalytic water splitting reaction.

3.3.1 Graphitic carbon nitride (g–C_3N_4) nanomaterial photocatalyst

Following the report by Ragupathy et al. (Ragupathy and Sathya, 2017), there has been a lot of interest in graphitic carbon nitride (g–C_3N_4), a novel, metal–free polymeric material with intriguing properties like a narrow band gap of 2.7 eV, ease of synthesis, high physico–chemical stability, nontoxicity, low cost, and earth abundance (He et al., 2015). It turns out that this semiconductor material is the most reliable allotrope among different carbon nitride in ambient settings, with a structure resembling graphite and made up of tri–s–triazine subunits joined in a layer by planar tertiary amino groups. As shown in Figure 1.5, g–C_3N_4 offers rich surface features that are crucial to catalysis, including basic surface functions, electron–rich properties, H–bonding motifs, and more, because of the presence of hydrogen and the fact that nitrogen has one extra electron than carbon.

Furthermore, it is a promising green metal–free photocatalytic material for photo–splitting water, photo–decomposition of various organic contaminants, visible–light assisted photosynthesis process, CO₂ activation, transesterification, oxygen reduction, hydrogen production, etc. because of its high thermal stability up to 600°C and perfect acid–alkali resistance. However, bulk g–C_3N_4's low specific surface area and high recombination rate continue to limit its photodegradation efficacy likelihood of charge carriers that are photoexcited. It is crucial to develop g–C_3N_4 as a promising visible–light driven photocatalytic material. A number of methods, including metal deposition, non–metal doping, the creation of

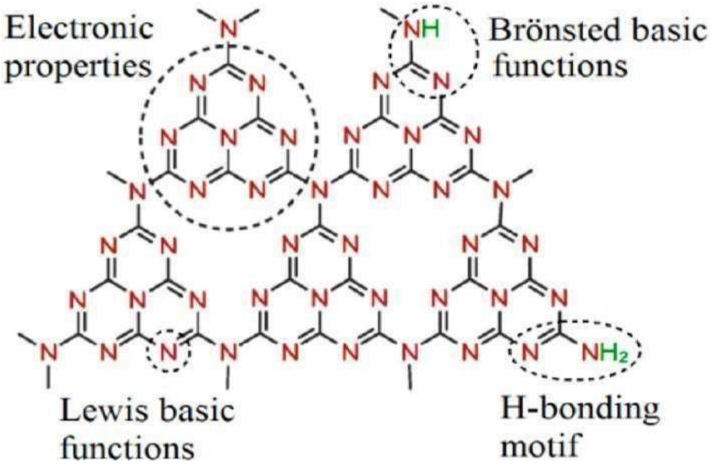

Figure 1.5 g–C_3N_4 exhibits several surface functions

nano/mesoporous structures, and coupling with other semi–conductors, have recently been used to improve the photodegradation efficiency of g–C_3N_4 (Wu et al., 2016).

When compared to g–C_3N_4, the surface area of nanostructures based on g–C_3N_4 can also be significantly developed and the nanocomposites can have special qualities. For instance, mixing g–C_3N_4 with Fe_3O_4 produces magnetic characteristics that make catalyst recycling easier. As previously indicated, because of its distinct electrical structure and suitable band gap of 2.7 eV, g–C_3N_4 essentially possesses all the necessary components for heterogeneous photocatalysts. It's interesting to note that this band gap not only overcomes the endothermic nature of catalytic reactions but also makes it easier to integrate with other materials to create and manipulate superior photoelectro–catalytic attributes. According to Figure 1.6, carbon nitride nanocompounds may be broadly classified into two groups: optimization design with metal–free elements and metal elements and in all application aspects.

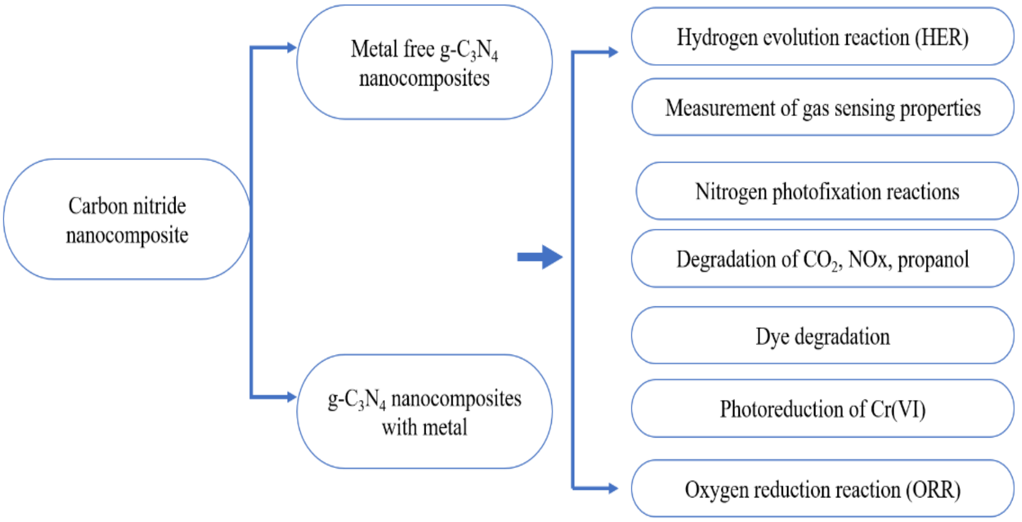

Figure 1.6 Carbon nitride nanocompounds: kinds and applications

In particular, the metal-free carbon nitride nanocompounds are primarily doped by elements such as sulphur, phosphorus, boron, and fluorine, particularly with carbon.

As is common knowledge, nonmetal materials are less expensive and easier to manufacture than noble metals, making them advantageous for widespread application in real industrial production (Yuan et al., 2017). Additionally, the g–C_3N_4 nonmetal–synthesized nanocomposites can prevent excessive oxidation of molecular oxygen and reduce or even completely abolish the quantity and inertness of C–H bonds in organic structures, which can have a significant impact on molecular selectivity. More significantly, doping nonmetal elements into g–C_3N_4, which is thought to be the framework, can modify the shape and location of molecular orbitals, adjust electronic characteristics, and significantly increase ionic conductivity—all of which indicate a significant promotion of photocatalytic performances. Currently, g–C_3N_4 nanocompounds, particularly mesoporous g–C_3N_4/Carbon, are widely used for highly efficient photoelectrochemical catalytic reactions like water splitting, energy conversation, and the oxygen reduction reaction because of their exceptional biocompatibility, stability, and remarkable electronic conductivity.

At the moment, the primary source of carbon nitride nanocompounds is a combination of many materials used as precursors using a particular technology (He et al., 2015; Yu et al., 2015). Table 1.1 lists several methods that can be used in the synthesis of carbon nitride nanostructures. As an example, the contents of the graphene–based mesoporous silica nanosheets (Xue et al., 2022) or highly ordered mesoporous carbon would both benefit from the insertion of carbon nitride for improved conductivity (Ravichandran et al., 2022). Furthermore, a very common way of generating graphene is the chemical vapour deposition method (CVD) (Mukherjee et al., 2018; Nguyen et al., 2014; Xiong et al., 2010). This process uses the atomic structure of the metal substrate to rationally inoculate and develop graphene. Additionally, Ref. provides more thorough descriptions for the various synthesize methods (Table 1.1) (Asadi et al., 2019; Guan et al., 2020; Kunnamareddy et al., 2021; J. Zhang et al., 2010).

In summary, these techniques not only guarantee the advancement of the research but also aid in enhancing the dispersion and conductivity of the composite materials, resulting in improved catalytic performances.

Table 1.1 Methods of synthesizing carbon nitride nanocompounds

Methods of synthesis	**Advantages**	**Disadvantages**	**Ref**
The silica microspheres as hard template method	Effortlessly managing the look of the product	Hazardous at work and unsuitable for the surroundings	(Bagherzadeh and Kaveh, 2018)
The chemical vapor deposition method (CVD)	Preserving the material's high level of purity	Sustained pressure and altitude are hard to maintain	(Han et al., 2014)
Solvent thermal polymerization method	Displaying a remarkable high surface area and total porosity	Reducing the effectiveness of diffusion and transmission	(Deng et al., 2017)
The microcontact printing technique	Low equipment cost and ease of use	Confined to the submicron range	(Yang et al., 2014)
The facile calcination method	Can significantly increase the sample's mechanical strength	It is difficult to monitor and regulate the process of a compound's thermal dissociation or crystal transition	(Ding et al., 2018; ElSayed, 2004; Khan et al., 2017; Priyadharsan et al., 2019;

			Wang et al.,2018, 2011)
The facile solid–state method	The prepared samples show excellent stability and purity	High demands on the equipment	(A.Priyadharsan et al., 2018)
The ultrasound assisted liquid phase exfoliation method	To quickly move the reactants to the electroactive sites, the sample might be made with big, multi–sized holes	Sample morphology is difficult to regulate precisely	(Malavika et al., 2021)
The sample vacuum filtration method	The samples exhibit good flexibility and high purity	There are strict limitations on sample preparation conditions and expensive equipment requirements	(Sirelkhatim et al., 2015)
The melt blending method	It is simpler to see the synergistic distribution effect amongst various hybrids	Controlling sample morphology is a difficult task	(J. Arun et al., 2022)

The facile hydrothermal method	The synthetic sample particles exhibit good dispersion and great purity	It is challenging to watch the sample's growing progress	(Zawadzki. 2022)

Several methods of measurement have been used to characterize the synthesized carbon nitride nano composites in order to examine their shape and characteristics. The two primary characterizations of characterization methods that are covered in this review are structural characterization and performance characterization. A variety of spectrograms or morphology data, such as Fourier transform infrared spectrometer (FT–IR) techniques, energy–dispersive X–ray spectroscopy (EDS) patterns, scanning electron microscopy (SEM), X–ray diffraction (XRD) patterns, and so on, are more frequently used by the former to illustrate structural properties. Table 1.2 presents a specific introduction to characterization methods.

3.3.2 Metal oxide–graphitic carbon nitride (g–C_3N_4) nanocomposite photocatalysts

A quick and easy method to enhance g–C_3N_4's photodegradation capabilities is to build a heterostructure based on the compound. Additionally, compared to 0D/2D and 1D/2D hetero–structures, it has been demonstrated that a two–dimensional / two–dimensional (2D/2D) heterostructure is the most effective and stable nanostructure (Morris et al., 2003). Two types of 2D materials can form a large interfacial region by intimate face–to–face contact, which results in low photogenerated charge recombination rate and high specific surface areas. Additionally, the coupling contact between a 2D g–C_3N_4 nanosheet and another 2D semiconductor is critical for creating intact heterojunction interfaces that facilitate effective electron–hole shuttling, extending charge carrier lifespan and boosting photocatalytic effectiveness. According to detailed engineering research, the 2D/2D nanohybrids' close heterointerfaces at the molecular level will produce intriguing findings for modifying the bare g–C_3N_4's current molecular structure. This will increase the mobility of electron–hole pairs, which will then boost the photocatalytic redox ability. The g–C_3N_4 based composite photocatalytic materials, such as Fe_3O_4/g–C_3N_4, BiOBr/g–C_3N_4, ZnO/g–C_3N_4, N–TiO_2/g–C_3N_4, Bi_2WO_6/g–C_3N_4, BiOI/g–C_3N_4, $BiVO_4$/g–C_3N_4, WO_3/g–C_3N_4, CdS/g–C_3N_4, MoS_2/g–C_3N_4, TaON/g–C_3N_4, Ag_3PO_4/g–C_3N_4, $ZnWO_4$/g–C_3N_4, S–TiO_2/g–C_3N_4, TiO_2/g–C_3N_4, $SrTiO_3$/g–C_3N_4, $CuCr_2O_4$/g–C_3N_4.

Table 1.2 Methods of characterization and their functions

Method of characterization	**Function**
Scanning electron microscopy (SEM)	Showing specific morphology and nanostructure, as well as the surface dispersion of nanoparticles, stacking situation of sample.
Energy dispersive X–ray spectroscopy (EDS)	Investigating the element composition and distribution of sample.
X–ray diffraction (XRD)	Demonstrating the characteristic peak and lattice constant (crystal surface peak).
Thermogravimetry–differential thermal analysis (TG–DTA)	Presenting the change of sample weight with increasing temperature to obtain the optimum temperature for the best properties.
Fourier transform infrared spectrometer (FT–IR) techniques	Exhibiting the heterocyclic stretches of typical structure and the chemical composition formation.
Brunauer–Emmett–Teller (BET) models	The specific surface areas and pore size distribution plots were calculated according to the BET

etc. (V. Arun et al., 2022; Manikandan et al., 2022; Manimegalai et al., 2023; Paul et al., 2021, 2021; Saranya et al., 2021; Velu and Nae Yoon, 2022).

Coupling of g–C_3N_4 with another semiconductor which exerts a substantial influence in modifying the electronic band structure as well as construction of favourable surface structure in semiconductors, resulting in high quantum efficiency for the photodegradation of environmental pollutants. The metal oxide–g–C_3N_4 nanocomposite shows excellent photocatalytic efficiency due to the direct transfer of photo–generated charge from metal oxide NPs to the g–C_3N_4 surface, which in turn accelerates the separation of photo–excited charge carriers and generation of additional ●OH radicals.

3.4 Semiconductor Photocatalysis

In recent years, researchers have concentrated on the utilization of semiconductor photocatalysts to photodegrade dangerous dyes since they show the capacity to completely degrade such colorant**.** Through the activation of a catalyst, the acceleration of chemical transformations is brought which is referred by semiconductor photocatalysis, involving a semiconductor either alone or in combination with metal/organic/organometallic promoters, with ensuing charge through light assimilation as well as energy transfers to adsorbed species. In establishing, whether a change is really photocatalytic, it is consequently essential to establish the photons are consumed by the catalyst rather than adsorbates (Rochkind *et al.* 2015; Barbero *et al.* 2016), furthermore, noticing that the immediate activation of reactants and intermediates through light assimilation is the domain of photochemistry.

Photoexcited charge carriers drive the change of water and carbon dioxide into hydrogen, carbon monoxide, methane, methyl alcohol and related oxygenates and hydrocarbons, in the photocatalytic creation of so–called “Solar Cells”. Sunlight consumed by chlorophyll in plants develops starch and oxygen generation from CO_2 and

H_2O and consequently are termed artificial photosynthesis, yet the above such procedure parallel those in nature. The complete oxidation (mineralization) of organic pollutants such as those experienced in aquatic environments are actuated either photoexcited charge carriers by directly or through the formation of potent oxidants such as hydroxyl radicals (Nosaka *et al.* 2017). From the valence band into the conduction band, semiconductor photocatalysis is started by excitation formation following photon absorption and excitation of electrons (step I). Either the bulk of the semiconductor or at the surface, the subsequent electron hole pairs may recombine with the related energy discharged through either fluorescence or thermal excitation of the lattice (step II). After photon capture, recombination is the essential procedure that limits photocatalyst proficiency. With adsorbates, for example, water, oxygen and other organic or inorganic species, electrons (and holes) that move to the surface of the semiconductor and do not experience fast recombination may participate.

3.4.1 Heterogeneous photocatalysis towards removal of water contaminant

The pollution of surface as well as ground water has drawn a lot of attention in industrial society towards development of some green techniques for cleaning up polluted aquifers available for industrial facilities. Semiconductor photocatalysis has drawn a lot of attention as a low cost, environment friendly and sustainable treatment technology to remove persistent organic compounds and microorganisms in water. Photocatalytic oxidation reactions have the potential to completely mineralize organic compounds to CO_2, water vapor and inorganic substances by solar light and to lead us to a clean and green purification technology for treatment of polluted air and water. The initial interest in heterogeneous photocatalysis was started when **Fujishima and Honda** discovered in 1972 the photochemical splitting of water into hydrogen and oxygen with TiO_2. TiO_2 is generally, the common choice as a photocatalytic material for environmental remediation because of its outstanding stability, low cost and non–toxic nature. Photocatalysis may be regarded as photo–induced reaction, accelerated by the presence of a catalyst. In semiconductor based photocatalysis, the photocatalytic degradation process is initiated by the absorption of a photon by the photocatalyst in presence of different light sources (mainly sunlight, visible–light and UV light) resulting in the excitation of an electron from the *valence band* (VB) to the *conduction band* (CB). The hole generated in the VB can come into contact with a water molecule in an aqueous medium which results in the formation of hydroxyl radical (●OH). An electron in the CB can contact with dissolved molecular oxygen resulting in the formation of superoxide radical anion ($\bullet O_2^-$), which reacts with water molecule to form ●OH radicals, an extremely powerful and indiscriminate oxidant, which oxidizes organic contaminants to the respective inorganic harmless anions and molecules such as NO_3^-, SO_4^{2-}, Cl^-, CO_2, H_2O etc. (Figure 1.7). The following reaction steps are generally involved in the semiconductor–based metal oxide photocatalytic process.

The chemical reactions that can occur at the surface of the photocatalysts are expressed below:

$$\text{Semiconductor (Photocatalyst)} + h\nu \rightarrow \text{Semiconductor } (e^-_{CB} + h^+_{VB}) \quad (1)$$

$$\text{Semiconductor } (h^+_{VB}) + H_2O \rightarrow \text{Semiconductor} + H^+ + OH\bullet \quad (2)$$

$$\text{Semiconductor } (h^+_{VB}) + OH^- \rightarrow \text{Semiconductor} + OH\bullet \quad (3)$$

$$\text{Semiconductor } (e^-_{CB}) + O_2 \rightarrow \text{Semiconductor} + O_2^{-\bullet} \quad (4)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet} \quad (5)$$

$$\text{Pollutant} + OH\bullet / h^+_{VB}/e^-_{CB} \rightarrow \text{degradation/redox–products} \quad (6)$$

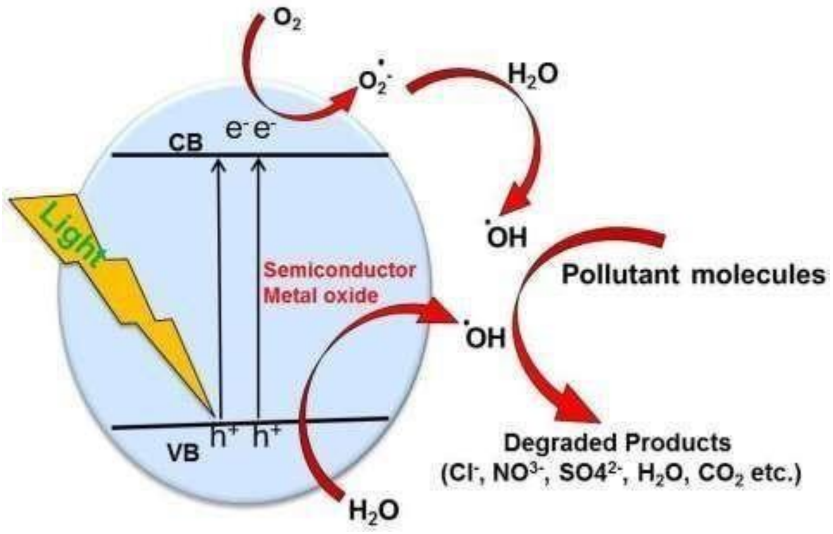

Figure 1.7 Schematic representation of the photocatalytic degradation.

The UV region constitutes only 4–6% of the solar spectrum, whereas the visible region accounts for up to 45%. However, due to TiO_2's wide band gap (3.2 eV for anatase), wavelengths below 388 nm are needed to excite electrons from the valence band to the conduction band. This limits the utilization of solar energy, as TiO_2 exhibits photo-inefficiency. Thus, developing efficient photocatalytic materials for water treatment technology has become an active research focus.

A novel photocatalyst must exhibit a strong visible-light response, high photodegradation efficiency, and chemical stability. Incorporating photoactive nanomaterials onto g–C_3N_4 inhibits the electron-hole recombination process, allowing excited electrons in the conduction band to reach reaction sites and generate oxidative species. Consequently, g–C_3N_4-supported nanomaterials demonstrate enhanced photocatalytic activity. Accordingly, various g–C_3N_4-based metal oxide semiconductor photocatalysts have been developed for environmental remediation applications, leveraging these properties to address environmental challenges effectively.

3.5 Different theories of photocatalysis

Exist on the transformation of the positive hole from which the most important ones are the ●OH free radical theory and direct oxidation theory.

3.5.1 ●OH free radical theory

According to the ●OH free radical theory, the hole is transformed into a hydroxyl radical through the reaction with water on the TiO_2 surface. This highly active oxidant takes part in the oxidation of a series of organic compounds. Several authors tried to prove this theory by detecting intermediate species and products of oxidation. Mills and Jishun (1998) reported the hydroxylated product at photo mineralization of 4–chlorophenol in an oxygen–saturated solution where 4 chlorocatechol was expected to be formed by oxidation with ●OH free radical.

3.5.2 The direct oxidation theory

This theory suggests the oxidation of substrates directly by positive holes. Several indirect proofs were given for this theory. Richard et al (1997) found that the production of hydroquinone by the photocatalytic transformation of 4 hydroxybenzyl alcohol was little affected in the presence of ●OH free radical quencher. In two other studies, extra absorption bands observed by time–resolved diffuse reflectance spectroscopy were assigned to the cationic radicals of photocatalytically oxidized compounds. All the above–mentioned studies were performed in aqueous solutions using microscale techniques but little attention has been paid to gaseous substrates. This publication, therefore, focuses on the photocatalytic oxidation of gaseous ethanol using a macroscale method that should provide the discrimination of mechanisms based on the two theories. A special reaction cell with small clearance was designed to diminish the dispersion influence and assure the experimental accuracy. Moreover, the formation and degradation of an intermediate, acetaldehyde, was also studied, which should help in the elucidation of the mechanism of ethanol photocatalytic oxidation.

3.6 Literature survey of g–C_3N_4 based photocatalyst

3.6.1 Dyes

Kansal et al. (2009) investigated the degradation of Reactive Black 5 (RB5) and Reactive Orange 4 (RO4) dyes using a heterogeneous photocatalytic process, evaluating the photocatalytic activity of semiconductors such as TiO_2 and ZnO. The study varied pH levels, catalyst amounts (0.25–1.5 g L^{-1}), and initial dye concentrations. Results indicated that the ZnO/UV system outperformed the TiO_2/UV system, with complete decolorization of RB5 achieved within 7 minutes using ZnO, compared to only 75% with TiO_2. For RO4, the ZnO/UV system achieved 92% decolorization, while the TiO_2/UV system reached 62% in the same timeframe.

Rong et al. developed a ternary TiO_2/g–C_3N_4/hectorite nanocomposite, which demonstrated excellent stability and repeatability across four consecutive photocatalytic discoloration tests. This enhanced performance is attributed to the synergistic effects of improved visible light absorption, effective charge separation, and lower regeneration rates. Hydroxyl and superoxide active species contribute to the process, while holes play a crucial role in the high decolorization efficiency of Rhodamine B (RhB).

3.6.2 Phenols

The photocatalytic degradation of resorcinol in a ZnO batch reactor has been investigated under visible light by Pardesi et al (2009). In that study, the effect of pH on COD reduction was shown to be significant, with neutral or alkaline pH proving more suitable. Mediators of the photocatalytic reaction were identified by Fourier transform infrared spectroscopy (FTIR) and gas chromatography coupled to mass spectrometry

(GC/MS), as 1,2,4–trihydroxy–benzene and 1,2,3–trihydroxy–benzene. The final results showed complete removal of resorcinol (with an initial concentration of 100 ppm) and its mineralization on the surface of the ZnO photocatalyst by sunlight.

3.6.3 Pesticides

Pesticides and toxicants are major pollutants in the agro–chemical industry. In one study by Alalam et al. (2015), the removal of pesticides from industrial wastewater was targeted. For this, nano TiO_2 was employed, and the monitored pollutants in the samples were chlorpyrifos, lambda–cyhalothrin, and diazinon. COD was also measured as a parameter regarding the level of pollution in the wastewater. The independent variables of initial pH, irradiation time, and chemical dose were altered to observe their effects on the dependent variable. The maximum removal of COD with the photo–Fenton process was 90.7%, while with photocatalytic treatment it was 79.6%.

Kushniarou et al. (2019) conducted a study to photocatalytically degrade 12 conventional pesticides for vegetables, grapes, citrus fruits, and fruit crops in an aqueous suspension of TiO_2 and Na_2 S_2O_8 in a semi–industrial unit under natural sunlight in Murcia, Spain. The optical decomposition of all pesticides can be modeled by assuming quasi–first–order kinetics. The time required to remove 90% of the contaminants in the summer was reported to be less than 4 hours, except for cyproconazole which was reported to be 4.9 hours.

P. Xia and et al reported 2D/2D g–C_3N_4 heterostructure photocatalyst was prepared by in–situ growth of MnO_2 nanosheets on to the surface of g–C_3N_4 by wet chemical method. Z scheme heterojunction formed between $MnO_2$and g–C_3N_4 nanosheets, in which photoinduced electrons in the MnO_2 combine with the holes in the g–C_3N_4 for use as enhanced charge carrier extraction and utilization upon photoexcitation (Dhiman and Kondal, 2022).

A meso/macroporous NiO/g–C_3N_4 hybrid photocatalyst was synthesized by ammonia evaporation–induced method. The 3D hierarchical honey comb–like the structure of the composite was encoded as $Ni(OH)_2$, films on the surface of g–C_3N_4 and its thermal decomposition to NiO. As prepared hybrid photocatalyst enhances the better photocatalytic activity compared to bare NiO and g–C_3N_4. This could happen due to the optical absorption, the good absorption capacity of organic contaminants, and the low desorption capability of the photocatalytic electron–hole pair on the well–defined structure at the heterojunction (Paul et al., 2021).

Guo et al reported $CuBi_2O_4$ is a P–type metal oxide semiconductor with a bandgap of 1.6 eV. $CuBi_2O_4$ was doped with g–C_3N_4 shows enhanced visible light absorption further degrades Tetracycline hydrochloride (TC). The optimal content of 70% wt of $CuBi_2O_4$/g–C_3N_4 exhibited the highest performance.

Gebrehiwot group reported a ternary $NiFe_2O_4$/rGO/g–C_3N_4 composite, where GO acts as an electron mediator to bind $NiFe_2O_3$ and g–C_3N_4 by chemical bond and p–p stacking, rGO, and p–p stacking. GO accelerates interfacial charge carrier between g–C_3N_4 and $NiFe_2O_3$. The use of $NiFe_2O_4$ nanoparticles as a photosensitizer can improve the light absorption of g–C_3N_4 and electron mediated graphene sheets improve charge separation and optimal light and stability.

Gao et al synthesized 0D Co_3O_4 QDs /2D g–C_3N_4 nanosheet heterostructure. The clear lattice fringe showed the confinement of g–C_3N_4 inhibiting the growth of Co_3O_4 NPs, indicating the formation of a 0D/2D heterostructure. Under visible light irradiation, it showed excellent degradation performance for TC with a removal rate of 98.7% in the presence of peroxomonosulfate (PMS). The degradation mechanism is due to the synergistic effect of free radicals H^+, $\bullet O_2^-$, $\bullet OH$ and SO_4^{2-} in the catalytic reactions.

3.7 Aims and objectives of this thesis

From the above discussion, it is observed that graphitic carbon nitride acts as good photocatalyst and since it is having only carbon and nitrogen, it is totally biodegradable and its activity can be further enhanced by doping of metals molecules.

- To synthesize particles of g-C_3N_4.
- To synthesize particles of g-C_3N_4 doped with iron, doped with cobalt and doped with nickel (g–C_3N_4/Fe, g–C_3N_4/Co and g–C_3N_4/Ni).
- To characterize the as-synthesized metal doped graphitic carbon nitride with physico–chemical characterization techniques.
- To investigate the activity of as–synthesized catalyst towards degradation of pollutant dye in water.