Synthesis and Characterisation of Sulphur Doped Graphitic Carbon Nitride and it's Photocatalytic Activity

A dissertation report submitted
In the partial fulfilment of requirement of degree
Masters of Science In Chemistry

Submitted by:
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July, 2023

CERTIFICATE

This is to certify that the thesis entitled “Synthesis and Characterisation of Sulphur Doped Graphitic Carbon Nitride and it’s Photocatalytic Activity" being submitted by Ms. Meghana Goel (Roll No. 302102009) in partial fulfilment of the requirements for the award of degree of Masters of Science in Chemistry, Thapar Institute of Engineering and Technology, Patiala, Punjab is a Bonafede work carried out under the supervision and conception of Dr. Davinder Kumar and that no part-of this thesis has been submitted for the award of any other degree.

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DECLARATION

I hereby declare that the work being presented in thesis entitled “Synthesis and Characterisation of Sulphur Doped Graphitic Carbon Nitride and it’s Photocatalytic Activity" is submitted in partial fulfilment of requirements for the award of degree of Master in Chemistry, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala in my laboratory during the period of January 2023 to July 2023, under the conception and supervision of Dr. Davinder Kumar, Associate Professor, School of Chemistry and Biochemistry (SCBC). Thapar Institute of Engineering and Technology, Patiala. I have not submitted the matter embodied in this thesis for award of any other degree.

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ACKNOWLEDGEMENT

I would like to thank Dr. Davinder Kumar, Assistant Professor, Thapar Institute of Engineering and Technology, Patiala for providing me with his guidance throughout the period of my dissertation. I got to learn a lot of new things about research in the field of chemistry. Thus, I offer my sincere appreciation definitely added up to my experiences.

I am grateful to Thapar institute of Engineering and technology for providing me with endless support so that I can learn well in my master's course. I am thankful to all my professors who has helped me to gain an opinion about the field. I am always looking forward for the constant subsistence.

I am extremely thankful to Dr. Satnam Singh, Professor and Head, School of Chemistry and biochemistry for providing me with the resources for my experiments. It is totally my pleasure that I got to meet and learn from everybody in the department. I give everyone all the credits for making this term a beautiful experience for me. I will always cherish this in my life.

I would also like to thank my family and friends for their constant support and always backing me with all the resources so that I can learn well. I am grateful to them for always respecting my choices and keeping their faith in me. I am hoping to make them proud of me.

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LIST OF ABBREVIATIONS

Abbreviation	**Word**
g-C_3N_4	Graphitic-carbon nitride
S- gC_3N_4	sulphur-doped graphitic carbon nitride
e-	Electron
h_+	Holes
HOMO	Highest occupied molecular orbital
LUMO	Lowest occupied molecular orbital
nm	Nanometre
g	Gram
2θ	2 theta degree
°C	Degree Celsius
SCN	sulphur-doped graphitic carbon nitride
C	Final concentration
C_0	Initial concentration
k	Rate constant
eV	Electron Volt
EBT	Eriochrome Black T

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ABSTRACT

Graphitic-carbon nitride (g-C_3N_4) has gained interest due to its applications in photocatalysis, semiconductors, and sensing. To increase performance, g-C_3N_4 has undergone a variety of alterations, including additions of metals, metal oxides, alkali metals, non-metals, graphitic carbon nitride/nanotubes, and their hybrids. In this study, to create the sulphur-doped graphitic carbon nitride (Sg-C_3N_4) an efficient template assisted calcination technique has been applied. A variety of analytical and spectroscopic techniques were used to determine the structural and crystalline characteristics of the nanosheets as formed. For the removal of hazardous dyes like Eriochrome Black T, the synthesised catalyst has been used. The process of photocatalytic degradation has been used and the activity of Sg-C_3N_4 and has been compared with respect to bulk g-C_3N_4 to degrade the dye in presence of sunlight. The bulk g-C_3N_4 has low surface area therefore has less photocatalytic activity. To enhance the efficiency, sulphur doping of g-C_3N_4 has been done due to which surface area increases and the process of physical adsorption on the surface of catalyst amplifies. Doping is also effective as it narrows the band gap and fastens the process of charge transfer, which increases the light absorption and charge carrier lifetime.

Keywords- Doping, Eriochrome Black T, Graphitic carbon nitride, Photocatalysis, Sunlight,

Chapter 1

Introduction and Objectives

1.1 Introduction

Graphitic Carbon nitride g-C_3N_4 is the most stable allotrope amongst other carbon nitrides. [1] It has gained immense popularity due to it's structural and morphological characteristics as well as it's applications in fields like semiconductors, sensing and photocatalysis. [2] Broadly it has been explored because of the chemical and physical stability and a comparatively narrower band gap of 2.7ev which facilitates the photocatalysis and it's other applications as well. g-C_3N_4 has a polymeric structure with tri-s-triazine units connected to tertiary ammines (Figure-1). [3] Each layer in it's graphite is strengthened by C-N covalent bonding and weak Vander- Waals forces. [1] g-C_3N_4 is considered earth abundant as is primarily made up of atoms Carbon and Nitrogen which are plenty on earth. It is easy to synthesise with various methods like thermal condensation, solution mixing, hydrolysis, sol-gel, solvothermal, microwave assisted heating, mechanical grinding. [4] O_2 and N_2 rich precursors like urea, thiourea, dicyandiamide, cyanamide, melamine which are comparatively low prices thus owes to the inexpensive preparation of the polymer. [4] It's physical and chemical features are controllable as depends on factors like method of preparation, type of precursor chosen, atmospheric conditions like pressure, temperature, and doping. [5]

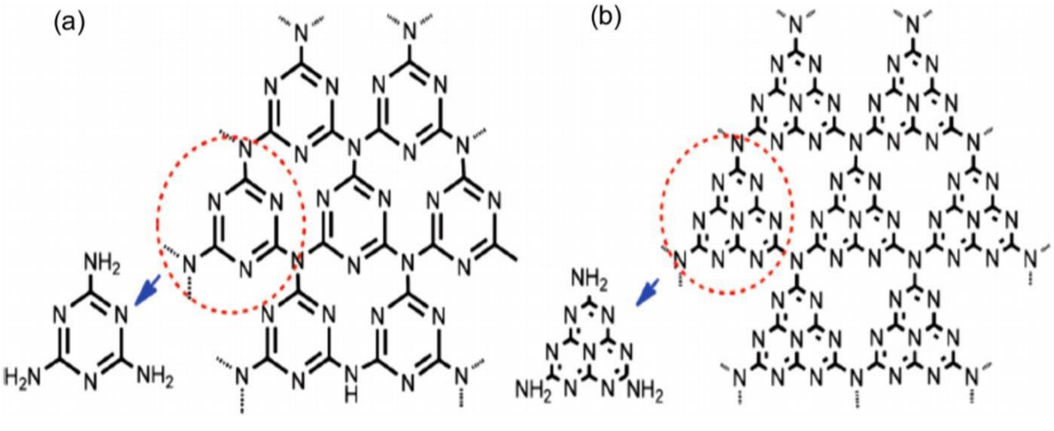

Figure-1 (a) s- triazine (b) tri-s-triazine

The photocatalytic activity of this g-C_3N_4 has been a keen topic of research interest. Considering it has it's applications in removal of dyes from water, removal of pollutants from wastewater, degradation of contaminants like organic and inorganic ions in water solution. [6] This reaction of photocatalysis can be oxidative or reductive depending upon the catalyst involved. When this catalyst is exposed to light, there is a transfer of electrons from valence band to conduction band which creates electrons (e^-) and holes (h^+). [7] For this photodegradation process, the active species like OH^- radicals, h^+ and O_2^- radical are the primary oxidants. Scavengers obstruct the charge carrier recombination and increase the photocatalytic efficiency of the catalyst. In absence of such species, these photogenerated electrons recombines with the hole and thus decreases the activity. [4]

This redox reaction of photocatalysis takes place with the initiation of formation of electrons and holes on photonic excitation of the catalyst. On this generation of electrons, ionisation of water takes place, which forms OH^- ions which further oxidises to OH* radical. The proton formed from water splitting protonates the superoxide O_2^- radical to form HO^{2-} ion. This ion so formed reacts with another proton to construct hydrogen peroxide (H_2O_2). [4] On further reaction of this hydrogen peroxide with electron, formation of OH^- radical takes place. Now, three active species i.e., OH radical, e^- and h^+ are formed and these leads to photodegradation on reacting with the substance of interest. The OH radical forms the degradation product, e^- forms the reduction product and h^+ forms the oxidation product as required by the reaction scheme depicted below. [8] (Figure-2)

The activation of this whole scheme of reaction depends on the initiation by the photon So the photon is required to have enough energy for excitation of the catalyst. The electronic structure of g-C_3N_4 has been studied by Wang et al. and the band gap of HOMO- LUMO was around 2.6 eV. [9] UV light irradiation activates it because of its wide band gap. Sunlight is an inexpensive source of light because it contains both UV and visible light. Some modifications are made on g-C_3N_4 to control the band gap and make it effective under visible light as well. [10] The carbon P_z orbitals (photogenerated h+ present) and nitrogen P_z orbitals (photogenerated e- present) in the polymer g-C_3N_4 participate in the conduction band and valence bands, respectively. These characteristics make graphitic carbon nitride an intriguing nanomaterial with several applications in photocatalysis. [11]

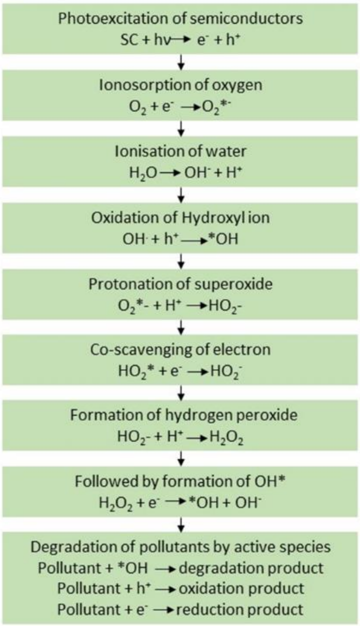

Figure-2 Reaction scheme of photocatalytic degradation

Although photocatalytic applications of g-C_3N_4 have been proven by various researchers but it is somewhat inappropriate because of multiple drawbacks. It has been proven to have low surface area of ~$10m^2g^{-1}$ due to high degree of condensation of monomers. The rate of recombination of charge is also high i.e., electron and hole pairs generated by photon activation recombine very fast in the polymer g-C_3N_4 as the particle boundary effects due to which there is an interruption in the delocalisation of electrons. [12] The limited spectrum of light that may be used by this allotrope because it can only absorb blue light decreases it's spectrum of applications as well. Therefore, decreasing the photocatalytic efficiency of it as a catalyst. To overcome this limitation, modifications in the g-C_3N_4 has been made. [7]

To enhance the photocatalytic activity of catalyst g-C_3N_4, co-catalysts can be coupled to it. [13] As the efficiency of photodegradation depends on various factors like size and structure of the particle, surface area, number of surface-active sites and the light harvesting capacity. [1] To achieve maximum efficiency various routes have been optimised. Making changes in the structural definitions of the polymer like creation of nanorods, 2-dimensional nanosheets, ultrathin structures etc. Incorporating nonmetals like B, C, N, O, S, P and noble metals like silver (Ag), platinum (Pt), gold (Au), palladium (Pd) has proven to be an effective approach to enhance the photocatalytic activity of g-C_3N_4. [14] (Figure-3) Another approach is the preparation of heterojunction like transition metal/ metal oxides, graphene oxide (GO), reduced graphene oxide (rGO), carbon dots etc. [15] For accelerating the surface of g-C_3N_4 doping has been proved to be extremely useful and success rates are also high. All the limitations are covered up like increment in surface area by modifying pore surface, optimising surface sensitisation to increase the light harvesting and to obtain a red shift of it’s absorption range band gap engineering has been used so that range of absorption can be increased. [16]

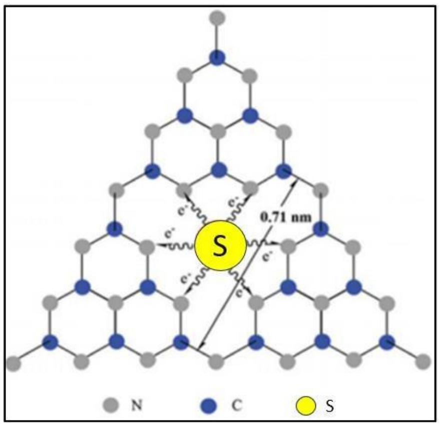

Figure-3 Possible doping site for Sulphur in doped graphitic carbon nitride

The mechanism of heterogenous photocatalysis is similar to what explained for plain g-C_3N_4. There are majorly 4 stages for heterogenous photocatalysis. (Figure-4) First is the generation of electron-hole pairs by absorption of light on the surface of catalyst. [17] Next is the excitation of charge and then there is separation of charge with it’s migration to surface and recombination in the bulk. At last, then we have electrocatalytic reaction of degradation of our pollutant of interest at the surface. [18] The pollutant to undergo degradation can be anything like organic compounds, waste water, dyes like Rhodamine B, Methylene blue, Erichrome Black- T, methyl orange, aziridine dye etc. [19]

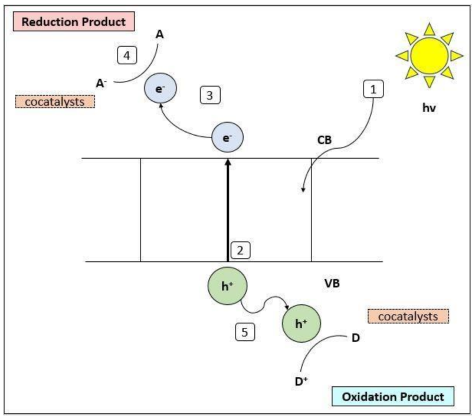

Figure-4 Mechanism of photocatalysis

1.2 Aim & Objectives

The Aim and objectives of our research is explained as follows:

- Optimisation of synthesis: Create a streamlined, repeatable process for the high yield, high purity synthesis of Sg-C_3N_4 with controlled sulphur doping levels.
- Characterisation: Determine the crystal structure, surface morphology, and elemental composition of the Sg-C_3N_4 material using various analytical techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and other spectroscopic methods.
- Analysing the photocatalytic activity: Examine the synthesised Sg-C_3N_4 photocatalytic activity by looking at its capacity to break down organic contaminants or promote water splitting when exposed to artificial sunlight or visible light irradiation.

  And eventually learning more about the mechanisms underlying the increased photocatalytic activity caused by sulphur doping in Sg-C_3N_4. Examine how sulphur affects the material's charge carrier dynamics, surface reactivity, and redox characteristics.

Chapter-2

Literature review and Research Gaps

2.1 Literature review

Graphitic carbon nitride/ metal doped modifies carbon nitride has various applications. To list them all down starting from CO_2 / NO_2 / O_2 reduction, degradation of dyes and drugs, photocatalytic disinfection to medical applications like artificial enzyme development, wound healing application, bone regeneration and fracture healing, photodynamic therapy and bioimaging, applications in drug delivery. It also has utilisation in sensing technologies, biosensing and gas sensing, water splitting, hydrogen evolution, oxygen evolution. [20] Energy storage devices like Supercapacitors, fuel cells, lithium metal batteries, sodium ion batteries, vanadium redox flow batteries, lithium magnesium batteries, zinc air batteries, lithium oxygen batteries, lithium-ion batteries, and lithium sulphur batteries have all been produced using graphitic carbon nitride. [21] Instead of using toxic metals to prepare quantum dots, researchers have also reported the use of graphitic carbon nitride for the synthesis of Quantum dot light emitting diode. As vast as it is, the usage of graphitic carbon nitride and it's modifications to enhance the applications has gained wide interest. In this study we will be focusing on the photocatalytic activity of this catalyst to degrade various dyes. [22]

Kumar et al. synthesised CeO_2/g-C_3N_4/ V_2O_5 heterojunction nanostructures using simple hydrothermal method. The structure and properties of the photocatalyst were characterised by XRD, SEM, TEM, XPS, PL, EIS and UV-DRS. The photocatalytic activity was checked for the degradation of carcinogenic hexavalent Chromium (VI) ions in the presence of infrared and visible light. It depicted an activity of 99% reduction within 1 hour and 40 minutes. Whereas the reaction completes in just 30 mins under visible light, in the presence of tartaric acid as a scavenger. The dominant active species were found to be photogenerated electrons and then O_2^- radicals. [23]

Das et al. reported the use of semiconducting materials g-C_3N_4 and Ag_2ZrO_3 to fabricate a nanocomposite which reportedly depicts good photocatalytic activity as well as photoinactivation of bacteria. Completion of formation and morphological evidences were collected using multiple characterisation techniques. When the Ag_2ZrO_3 nanoparticles were covered with 30wt% of g- C_3N_4, the heterojunction so formed shows photocatalytic efficiency of 99.70% for the decomposition of Rhodamine-B dye under visible light source. It is also found to me more than 48% effective for photoinactivation of microorganisms like *Escherichia coli* and *Bacillus subtilis.* [24]

Zhang et al. describes a study for the synthesis of Bi_2O_4/g-C_3N_4 nanosheets using the integration of calcination and hydrothermal method. Formation, composition and other physicochemical properties were analysed using various characteristic techniques. The catalyst as prepared shows a 95% efficiency to degrade Tetracycline in the presence of solar light, which is superior to that of pure g-C_3N_4. This increase in activity is broadly attributed to increase in surface area and thus enhancing the no. of reaction sites, on modification. They claim that the change increases the separation effectiveness of electron hole pairs. [25]

Borthakur et al. synthesised a WO_3/g-C_3N_4 nanocomposite using hydrothermal calcination method and characterisation was performed using various techniques to analyse and confirm the formation of proposed heterojunction. To judge the photocatalytic performance degradation of Rhodamine- B dye was performed in the presence of H_2O_2 under irradiation of solar light. To ensure the best activity loading of WO_3 was optimised and reportedly exhibits highest degradation i.e., 99.5% concentration of dye, at 2wt% of WO_3 over g-C_3N_4. This degradation process follows pseudo first order kinetics and the rate constants with modified has been found to be 2.6 and 7.7 times higher as compared to pure g-C_3N_4. [26]

Sutanto et al. used sol gel techniques to fabricate ZnO_2/TiO_2 sol with varying molar ratios followed by calcination to complete the synthesis of proposed catalyst i.e., g-C_3N_4/-3ZnOc-$Zn_2Ti_3O_8$. The one with ratio 3ZnO_2: 1TiO_2, reportedly shows good photocatalytic activity with 82% degradation of methylene blue dye within 45minutes in the presence of visible light. And when this 3:1 is loaded with 10wt% of g-C_3N_4, it shows 99% degradation of methylene blue on illumination of sunlight. This improvement in degradation of methylene blue from 1.8 to 2.2% is attributed to enhancement in adsorption of organic molecules due to more no. of surface OH^- ions. [27]

Junqi et al. prepared a ternary composite of g-C_3N_4/Au/$BiPO_4$ using hydrothermal process. Thiourea has been used a precursor for the synthesis of g-C_3N_4. A comparison of photoelectrochemical and photocatalytic activity has been made in between gC_3N_4/Au/$BiPO_4$, g-C_3N_4, $BiPO_4$ and g-C_3N_4/$BiPO_4$. Au here served as electron mediator and could also adsorb photons. Such modifications increase the charge separation thus decreasing the electron hole pair recombination which in turn improves the electron transport property. On modification, they have reported a 14% enhancement in photocatalytic activity for the degradation of methyl orange. [28]

Yan et al. used chemical precipitation method to synthesise Ag_3PO_4/ GO/g-C_3N_4 where Ag_3PO_4 acts as photosensitiser, GO as the cocatalyst and these promotes the photocatalytic activity of g-C_3N_4. These modifications have been done as single component g-C_3N_4 has a low quantum efficiency due to fast recombination of charge. This ternary photocatalyst depicts an enhancement in absorption in visible region. The rate of degradation of this catalyst against Rhodamine-B dye was found to be 94.8% in 50 minutes. [29]

Zhao et al. prepared BiOCl/Bi_2MoO_6/g-C_3N_4 nanocomposite using facile refluxing process. A comparison has been made between the photocatalytic activity of nanocomposites that differ with the number of g-C_3N_4 loadings. To confirm the interactions between g-C_3N_4 and BiOCl/Bi_2MoO_6 a series of characterisation techniques have been used. An improved activity was observed by the nanocomposite with the loading of o.10 g-C_3N_4. These catalysts can be practically used as recyclable photocatalyst. They have reported a 78.82% degradation of Rhodamine B dye. [30]

Mousavi et al. used ultrasonic heat treatment and synthesised a g-C_3N_4/Fe_3O_4/BiOI using melamine powder as precursor. This acts as a photocatalyst in presence of visible light. The results show that amount of BiOI has substantial effect on the photodegradation of Rh-B. To check the photocatalytic activity, it has been used for the degradation id Rhodamine-B, Methylene blue and methyl orange. They have reported that g-C_3N_4/Fe_3O_4/BiOI nanocomposites shows about 10-, 22- and 21-fold higher activity for the degradation of Rh-B, MB and MO. [31]

Hong Wu et al. created a nanojunction GO/g-C_3N_4/MoS_2 using solvothermal method. Thiourea and Melamine have been used as precursors. This heterostructure has a flower structure which leads to improvement in collection of electrons in MoS_2 and holes in gC_3N_4. Here GO helps to increase the electrical conductivity. It acts as a photocatalyst in presence of solar light. To check the activity photodegradation of MB, Rh-B, CV has been studied. They have reported that the prepared material has more adsorption and response sites and the photocatalytic activity of GO/g-C_3N_4/MoS_2 is 3.54 times higher than that of g-C_3N_4/MoS_2. [32]

2.2 Research Gap

The potential research gap in this study with respect to the studies made as of yet are:

- Understanding the effects of doping: More research may be needed to fully understand how sulphur doping affects the photocatalytic activity of graphitic carbon nitride. The particular methods by which sulphur doping affects the electrical band structure, charge separation, and surface characteristics of sg-C3N4 might have been the subject of research.
- Mechanism of photocatalysis: While sg-C3N4 has demonstrated potential as a photocatalyst, it's possible that a thorough understanding of the underlying mechanisms for photocatalysis was lacking. Clarifying the paths of photogenerated charge carriers and finding the important reactive species in charge of the photocatalytic activity were two areas that may have been the subject of additional study.
- Comparing with other catalysts: To learn about the benefits and drawbacks of sgC3N4 in terms of photocatalytic activity and efficiency, researchers may have compared it to other semiconductor photocatalysts like TiO2 and ZnO.
- Impact on environment: Understanding the potential environmental effects of sgC3N4 and its photocatalytic compounds may have been a research topic of interest, as it is with any novel material.
- Applications in real world: The photocatalytic activity of sg-C3N4 may have been shown in laboratory experiments, but practical use in real-world settings might have been difficult. A potential area of research was the stability, recyclability, and effectiveness of sg-C3N4 in various environmental settings.
- Research methodology: It could be interesting to look at different precursors, reaction conditions, and catalysts for synthesis. The relationship between the material's structural characteristics and its photocatalytic efficiency might have used more research.

Chapter-3

Materials and Methodology

3.1 Apparatus and chemicals used

Melamine and thiourea were used for the preparation of catalyst. Ammonium sulphate has been used as catalyst in the preparation of Sulphur doped graphitic carbon nitride (Sg-C_3N_4). Ethanol is used as solvent and for purification purposes. Distilled water was used throughout for all the experiments and washing etc. The dye has been procured from the department labs and is used to check the photocatalytic activity of the catalyst so prepared. Overall, the apparatus used includes crucible, petri dishes, test tubes, falcon tubes, glass voiles, spatulas, wash bottles, mortar and pestle, Eppendorf, beakers, measuring cylinders.

3.2 Synthesis

For the synthesis of Bulk Graphitic carbon nitride, melamine as purchased has been put up for calcination at 550° Celsius for 4 hours and the polymer has been prepared. Then for the synthesis of heterojunction, pure melamine and thiourea as purchased without any further purification has been used. To prepare multiple catalysts for comparison of photocatalytic activity, multiple ratios of thiourea to melamine has been used. [33] Three variations of the doped catalyst have been used with 0.1 %, 0.2% and 0.3% sulphur doping as confirmed from the characterisation techniques. For this preparation thiourea to melamine has been used in a ratio of 2:3, 3:2 and 4:1 weight by weight.

Accordingly different weights of thiourea and melamine have been crushed in mortar and pestle to make it a fine powder, ammonium sulphate $(NH_4)_2SO_4$ has been added to it. Then it is calcined at 550° Celsius at a heating rate of 5°C/ min in a muffle furnace for 4 hours. [33] (Figure-5) $(NH_4)_2SO_4$ acts as a catalyst to enhance polymerisation of melamine. As $(NH_4)_2SO_4$ increases the process of mass transfer and formation of bubbles. These bubbles release gases such as H_2O, SO_2, NH_3. So, basically it is proposed to show enhancement in photocatalytic activity depending upon the loading of different amounts cocatalyst. [33]

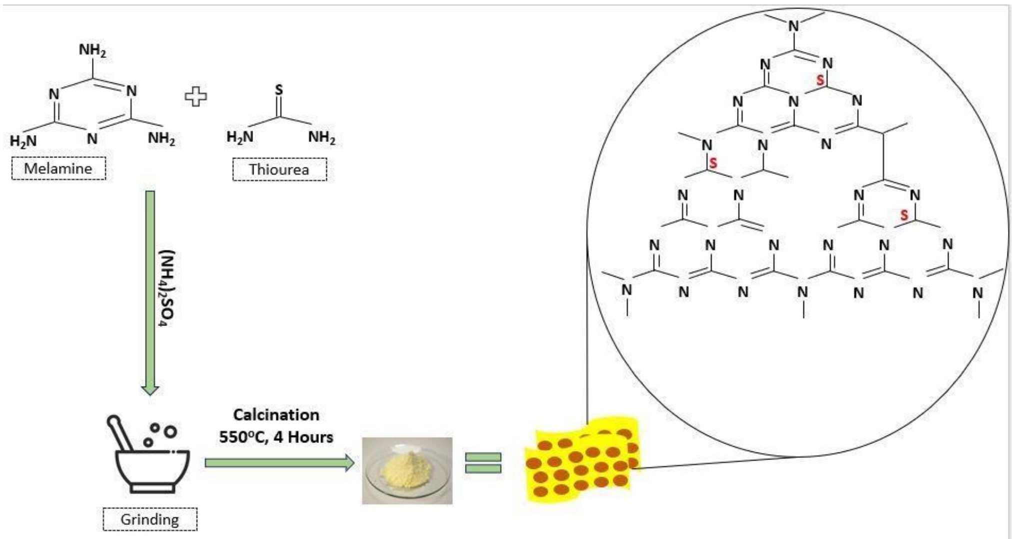

Figure-5 Process followed for the synthesis of g-C_3N_4 & S-g-C_3N_4

3.3 Instrumentation

To study the chemical identity and features of the prepared g-C_3N_4 & S-g-C_3N_4 (0.1 SCN, 0.2 SCN & 0.3 SCN). X- ray diffraction (**XRD**) has been done using Rigaku Smart Lab SE X-Ray diffractometer with HyPix -400 (2D HPAD) with Cu Kα radiation. XRD is performed for indexing the peaks corresponding to the features of g-C_3N_4 & S-g-C_3N_4. To analyse the surface of the catalyst and to examine the constituents as well field emission scanning electron microscopy (**FE-SEM**) was done using Carl Zeiss Sigma 500 FEG-SEM with 0.8 nm resolution at 15 kV, samples for the same have been prepared with gold sputter coating by Quorum technologies, Q150R. Chemical composition was measured by energy dispersive X-ray spectrometer (**EDS**) using Bruker, QUANTAX 200 using SSD detector with Energy resolution < 129 eV. Photoluminescence (**PL**) emission spectra was measured on Horiba Labram HR Confocal Micro-Raman spectrometer to analyse the optical fluorescence of the compound as a function of wavelength. Fourier transform infrared spectroscopy (**FT- IR)** was recorded to determine the presence of proposed elements in the compound prepared.

3.4 Preparation for photocatalytic reaction

The activity of the prepared catalyst is examined by the degradation efficiency of EBT dye under sunlight. A comparison has been made to check the capability of all the variations synthesised of S doped g-C_3N_4 (S-g-C_3N_4) i.e. (0.1%, 0.2%, 0.3% SCN) and the bulk g-C_3N_4. Solar light has been used as the light source for photocatalytic reaction. For the experiment EBT dye solution of 10 ppm i.e., 2mg of dye suspended in 200 ml water has been prepared. 10ml of this solution has been taken in the test tubes and 0.2 g of each catalyst i.e., 0.1% SCN, 0.2% SCN, 0.3% SCN and bulk g-C_3N_4 has been added to it. The reaction has been put up on magnetic stirrer in the dark for 60 minutes and then for 2 hours in sunlight. An aliquot of 5 ml has been taken and centrifuged to remove the catalyst still suspended in the solution. Thereafter, the solutions were measured with UV-Visible spectrophotometer. The changes in the concentration were calculated by C/C_0 where C_0 is initial concertation of the dye and C is the amount of dye remaining after degradation. [34] The proposed reaction for photocatalytic degradation of EBT using our modified catalyst is as below. (Figure-6)

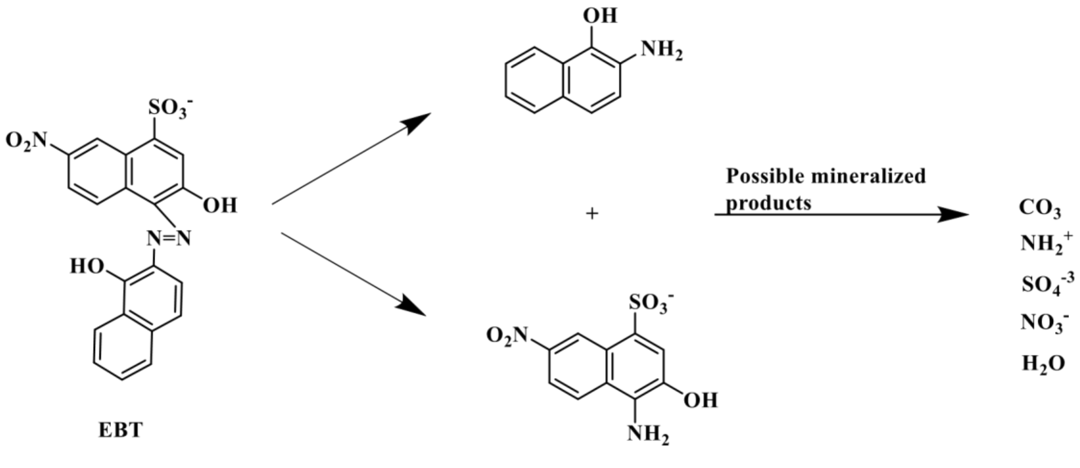

Figure-6 Photocatalytic degradation of EBT dye

Chapter-4

Results and Discussion

4.1 Characterisation

4.1.a Field Emission Scanning Electron Microscopy (FESEM)

To examine the morphology of the catalyst prepared FESEM was used. The prepared samples of S-gC_3N_4 have layered structure and pore channels are also visible due to copolymerisation of melamine of thiourea. A characteristic stacked lamellar structure was observed for the S-gC_3N_4 as can be seen in figure. A sheet structure was prominently observed as the method of synthesis is used to prepare a doped nanosheet. The observation of porous structure can be attributed to the process of calcination i.e., due to the release of H_2S gas from thiourea. [35] (Refer Figure-7).

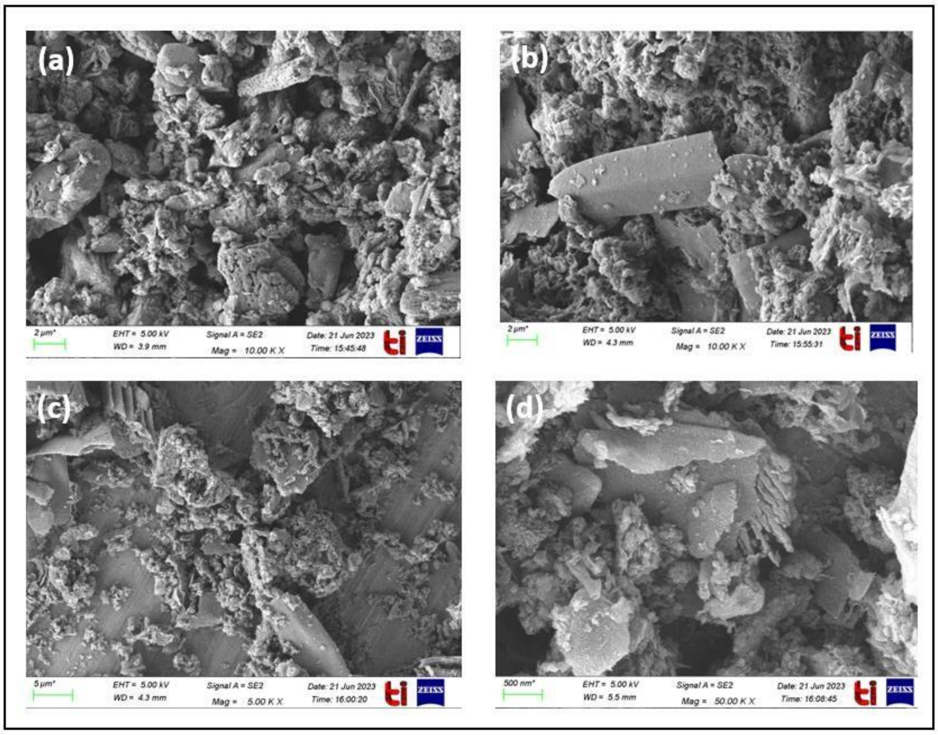

Figure-7 FESEM of (a) bulk g-C_3N_4, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN

4.1.b Energy dispersive spectroscopy (EDS)

EDS was conducted to determine the composition and distribution of elements. WE can observe the peaks for all the proposed elements i.e., Carbon and Nitrogen in bulk along with Sulphur in doped variations of the catalyst. (Figure-8) The amounts by percentage of Carbon, Nitrogen and Sulphur for all the catalysts to be compared is depicted by graphs (Figure-9) below which is sample 1 (a) bulk g-C$_3$N$_4$ with no Sulphur content, sample 2 (b) with 0.1% Sulphur then sample 3 (c) with 0.2% Sulphur and sample 4 (d) with 0.3% sulphur. Thus named the samples depicting the percentages of dopant which is eventually found to increase i.e., from 0.1 to 0.2 to 0.3 %. The shading in the area mapping also determines the amount of Carbon, Nitrogen and Sulphur. [36]

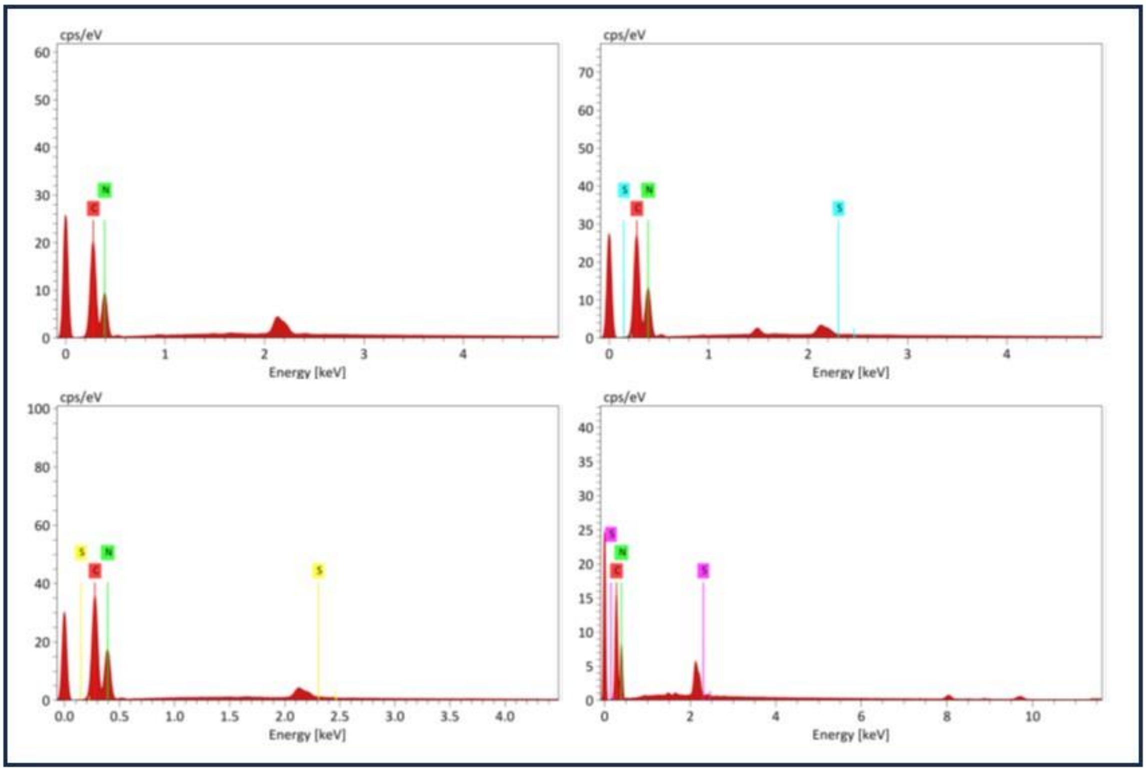

Figure-8 EDS spectra; Peaks depicted by elements Carbon, Nitrogen, Sulphur in (a) bulk gC$_3$N$_4$, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN

Table 1- Percentages of elements Carbon, Nitrogen and Sulphur in samples bulk g-C$_3$N$_4$, 0.1% SCN, 0.2% SCN, 0.3%SCN

Sample	Carbon	Nitrogen	Sulphur
Bulk gC3N4	33.6	66.64	0
0.1SCN	32.91	66.97	0.1
0.2SCN	32.51	67.23	0.2
0.3SCN	31.83	67.88	0.3

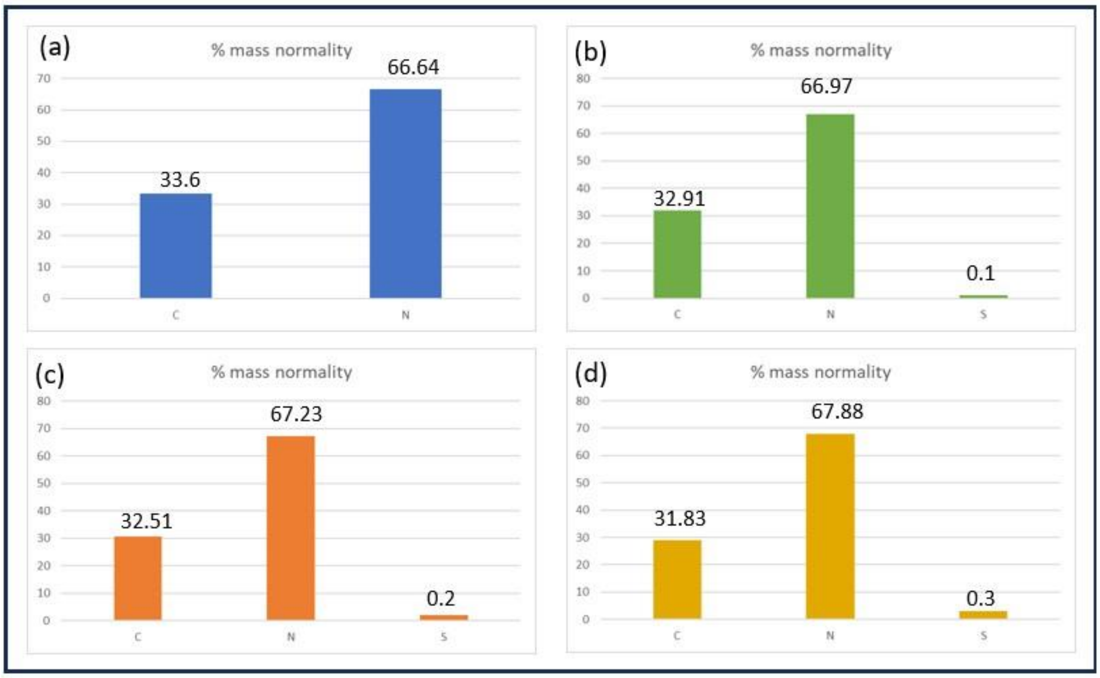

Figure-9 EDS spectra; Percentages of elements Carbon, Nitrogen, Sulphur in (a) bulk g-C_3N_4, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN

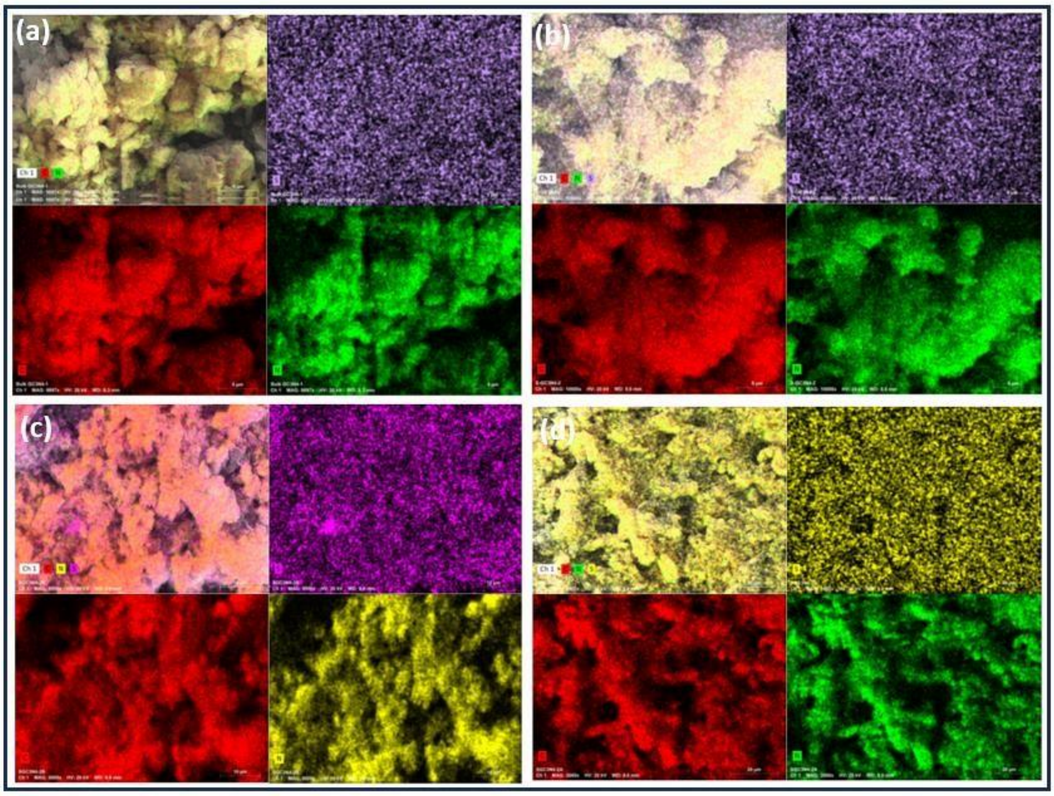

Figure-10 EDS Area mapping of (a) bulk g-C_3N_4, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN

4.1.d Fourier Transform- Infrared Spectroscopy (FT-IR)

For samples containing various quantities of sulphur, FT-IR spectra were taken and are shown in Figure. O-H and N-H stretching vibration from water that has been absorbed and sustained amino groups correlate to the broad band between 3300 and 3600 cm^{-1} in the spectrum for bulk g-C3N4. Between 1300 and 1700 $cm^{-1,}$ the stretching vibration modes of the carbon nitrogen heterocycles produced a series of notable peaks. The tris triazine units are thought to be responsible for the peak's strength at 800 cm-1. The doped samples 0.1% SCN, 0.2% SCN and 0.3%SCN shows similar characteristic to that of g-C_3N_4 but there is a change in intensity depending upon the percentage of sulphur. Therefore, the incorporation of Sulphur is verified due to the increase in intensity of bands observed in FT-IR spectra. [33]

4.1.c X-ray Diffraction study (XRD)

To examine the crystallinity of the samples prepared, XRD was recorded and is given in figure. We can observe that all the 4 samples i.e., bulk g-C_3N_4, 0.1% SCN, 0.2% SCN and 0.3%SCN shows diffraction peaks at 2θ = 12.8 corresponding to (100) plane and 2θ = 27.6 which is attributed to (002) plane. These peaks are characteristic to the graphitic carbon nitride g-C_3N_4 structure. The peak at 2θ = 27.6 is because of the conjugated aromatic structure of g-C_3N_4 and the interlayer stacking of the structure and at 2θ = 12.8 is the smaller peak related to tri-s-triazine structural units and the in plane structural packing. [37] Peaks are similar for the Sulphur doped g-C_3N_4. But with increase in sulphur doping i.e., from 0.1% to 0.25 to 0.35 Sulphur doping the width of these peaks increases eventually. On incorporation of the dopant into the g-C_3N_4, the crystallinity of the structure reduces due to which intensity of these peaks in XRD graphs also decreases. In S-gC_3N_4, there is enhancement in the contact between the layers due to which the interlayer distance shortens which strengthens the Vander Waals force between the heptazine layers of S-gC_3N_4. [33]

4.1.e Photoluminescence (PL)

Photoluminescence spectra (P.L.) was recorded to study the recombination of charge carriers. It was excited at 340 nm. In comparison for bulk g-C_3N_4, a low fluorescence intensity can be observed for all the samples of sulphur doped i.e., 0.1% SCN, 0.2% SCN and 0.3%SCN. This indicates a that the photogenerated pairs of electron ad hole in the modified catalyst increased separation efficiency in turn supports the special structure of the doped g-C_3N_4, because it has been demonstrated that photon absorption and charge carrier collection can be separated by the nanosheet structure in orthogonal spatial directions.[38] Because of its thin thickness, the porous structure also shortens the distance required for charge carriers to move from the interior to the exterior and prevents recombination of photogenerated electron hole pairs during immigration. Increased porous structure can also be the cause of the decrease in fluorescence intensity of S-g-C3N4 seen with higher heating temperatures. [39]

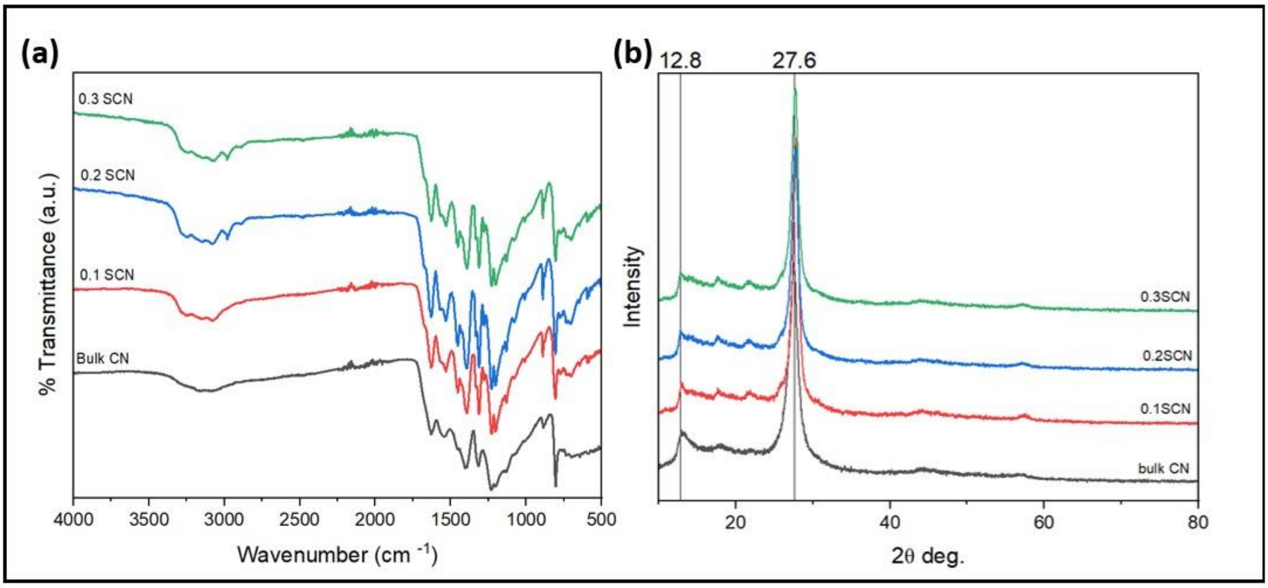

Figure-11 (a) FTIR spectra bulk g-C_3N_4, 0.1% SCN, 0.2% SCN and 0.3%SCN. (b) XRD pattern of bulk g-C_3N_4, 0.1% SCN, 0.2% SCN and 0.3%SCN.

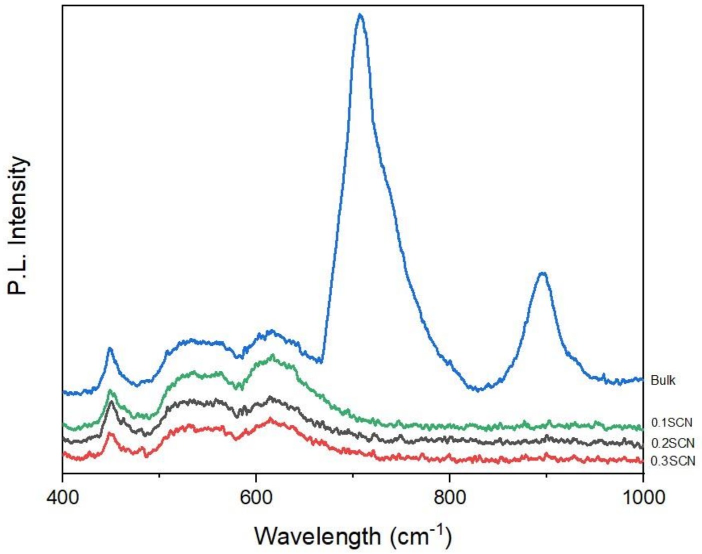

Figure-12 PL spectra of samples bulk g-C_3N_4, 0.1% SCN, 0.2% SCN and 0.3%SCN

4.1.f UV- Visible Diffuse Reflectance spectroscopy. (UV-DRS)

To justify the photocatalytic catalytic activity UV- vis diffuse absorbance spectra was compared between bulk g-C_3N_4 and 0.1% SCN, 0.2% SCN and 0.3%SCN. All doped samples show refined optical absorption particularly at the range of 620-685 nm. The graph in Figure 12(a) depicts the absorbance v/s wavelength i.e., Kubelka-Munk function plots of our samples and on making the necessary calculations we have plotted the Tauc plot (Figure 12 (b)) to determine the band gap values. It is also justified from the Tauc plot that S- g-C_3N_4 exhibit narrower band gap than that of bulk. This is because in porous structure of nanosheets there is a multiple reflection of incident light which in turn increases the path length which is effective for absorption of incident light. [40]. The table below has the values of band gap for the samples prepared bulk g-C_3N_4 and 0.1% SCN, 0.2% SCN and 0.3%SCN. With the increase in doping content, the HOMO-LUMO band gap eventually decreases because sulphur is more electronegative than carbon and nitrogen, so there is more electron density in the lattice therefore less energy is required for the transfer of charge due to which on increasing the amount of Sulphur doping the band gap value decreases. As this facilitates the fast charge transfer and thus supports the enhancement in rate of photocatalytic reaction. The table below has the values of band gap for the samples prepared.

Table-2 Band gap values for bulk g-C_3N_4 and 0.1% SCN, 0.2% SCN and 0.3%SCN

Sample	Band gap
Bulk gC3N4	2.79
0.1SCN	2.76
0.2SCN	2.77
0.3SCN	2.75

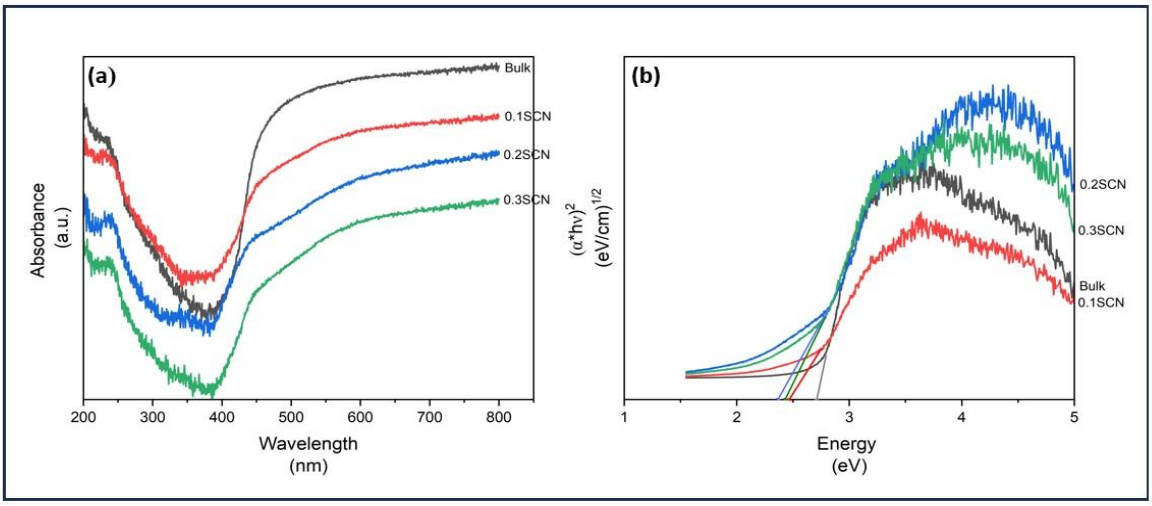

Figure 13 (a)UV-vis DRS spectra (a) Kubelka-Munk function plots (b) Tauc plot

4.2 Photocatalytic activity

To check the photocatalytic activity of bulk g-C_3N_4 and S-g-C_3N_4 (0.1% SCN, 0.2% SCN and 0.3%SCN), we have checked it's efficiency of degradation for Erichrome Black T dye (EBT) in the presence of solar light. To make a comparison between bulk g-C_3N_4 and all the modified versions of S-g-C_3N_4, 0.2g of each catalyst has been added to 10ppm solution of the dye. The reaction has been set up in four different test tubes and on a magnetic stirrer. The reaction takes place for 60minutes in the dark and for 120 minutes in solar light. To the visible eyes a significant change of colour can be seen. First, when the reaction is set up in dark the shades of blue get lightened and then in the presence of sunlight the blue shades in the test tube disappear.

To confirm the degradation of dye, UV-visible absorption spectra has been recorded for each sample which confirms the degradation of the dye. The maximum absorption for EBT dye is in the range of 620nm- 685nm. Specifically, at 625nm we observe the maximum absorption in our sample with no catalyst and just shows absorption by the solution of EBT dye (with 10ppm concentration). Then we observed the absorption spectra of samples with varying amounts of catalyst i.e., bulk g-C_3N_4 and 0.1% SCN, 0.2% SCN and 0.3%SCN. From the data recorded we did the necessary first order reaction calculations using the first-order equation: $\ln(C/C0) = -kt$, where k is the reaction rate constant (min^{-1}). We have plotted a graph between ln C/C_0 v/s time. We have recorded the values of rate constants (k value) in Table-3. It is observed that values of rate constant increases as the amount of doping increases i.e., the reaction of photocatalytic degradation of EBT dye by our catalyst samples is fastest when the rate constant is high depicting enhanced rate of reaction on doping. It can be concluded that the catalyst with maximum amount of doping shows maximum degradation activity for EBT dye. So, from the results it has been analysed that Sulphur doped variations show maximum degradation of dye and especially the modified catalyst with 0.3% Sg-C3N4.

Table-3 Value of rate constants for photocatalytic degradation of EBT by our catalysts.

Sample	k value (min^{-1})
Bulk gC3N4	0.00737
0.1SCN	0.00778
0.2SCN	0.00726
0.3SCN	0.00828

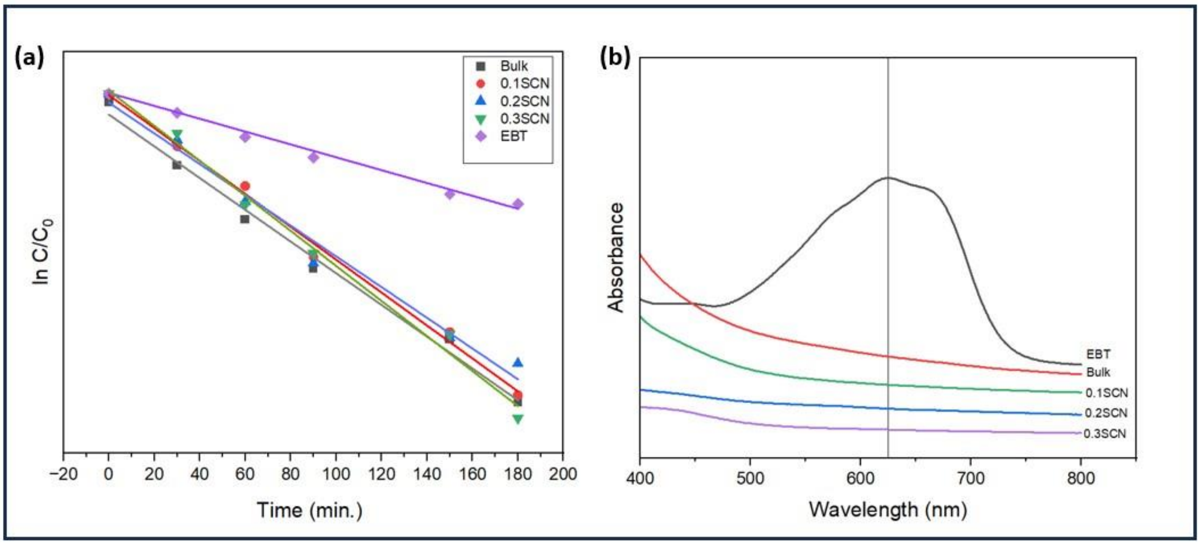

Figure-14 (a) Reaction rate curves for samples under visible light (b) UV- visible absorption spectra bulk g-C_3N_4, 0.1% SCN, 0.2% SCN and 0.3%SCN

There are multiple reasons for better photocatalytic activity of S-g-C_3N_4 then g-C_3N_4. The bandgap of g-C3N4 becomes smaller when sulphur doping is added. A narrower bandgap is advantageous for photocatalysis because it enables sg-C3N4 to absorb a wider range of visible light. The photocatalytic activity of bulk g-C3N4, in contrast, is only active in the ultraviolet (UV) portion of the spectrum due to its greater bandgap. Sg-C3N4 is able to absorb an increased amount of visible light, which makes up a significant component of the solar spectrum, because of the narrower bandgap and the presence of sulphur dopants. This improved light absorption makes Sg-C3N4 a more effective visible-light-driven photocatalyst by allowing it to use sunlight for photocatalytic processes more effectively. [6]

Furthermore, the separation of photogenerated charge carriers (electron-hole pairs) is improved by sulphur doping in g-C3N4. To stop photoexcited electrons from recombining with holes, sulphur functions as an electron acceptor and has the ability to catch them. This better charge carrier separation raises the possibility of redox reactions occurring on the surface of the material, which results in increased photocatalytic activity. The Sg-C3N4 lattice develops defects in structure as a result of sulphur doping. These defects may serve as charge carrier trap sites, further lowering the recombination rates of the carriers and increasing the total photocatalytic efficiency. New active sites for catalytic reactions are introduced by the presence of sulphur dopants on the surface of S-g-C3N4. Compared to bulk g-C3N4, these active sites encourage the adsorption of reactants and enhance surface redox reactions, which improves photocatalytic efficacy. [6,41]

The enhancement in the photocatalytic efficiency of S-g-C3N4 over bulk can be attributed to various reasons like the S-g-C3N4 structure's -conjugation network may grow as a result of sulphur doping. Charge carriers' mobility is improved by this increased conjugation, enabling them to move more freely inside the substance and take part in photocatalytic events more successfully. In S-g-C3N4, sulphur doping can change the energy levels of the valence and conduction bands, moving them in relation to the reaction species' redox potentials. This alteration can promote photocatalytic activity by facilitating electron transport and redox reactions. [41]

Conclusion

Overall, the synthesis, characterisation, and assessment of sulphur-doped graphitic carbon nitride's photocatalytic activity have made significant advances in the field of photocatalysis. In our research we have we have attempted to create a Sulphur- doped graphitic carbon nitride, characterising it’s morphological and chemical properties and comparing the photocatalytic activity between the bulk g-C_3N_4 and the variations of catalyst to be prepared. The results underline how important sulphur doping is for modifying the characteristics of S-g-C3N4 for improved solar-light-driven photocatalysis. The potential for further enhancing sg-C3N4's efficiency and broadening its application range is encouraging as our understanding of its photocatalytic mechanisms deepens. The results highlight its potential for useful applications, encourage additional research into enhancing its functionality, and open up new opportunities for utilising sg-C3N4 in cutting-edge environmental and energy-related technology. In the end, this research adds to the overarching objective of creating creative and sustainable materials for a more sustainable future. However, it is crucial to understand that this field of study is still in its early stages, and subsequent research will build on these results to develop sg-C3N4based photocatalysis's potential even further. the findings of this study make a substantial contribution to the creation of effective and long-lasting photocatalytic materials, taking us one step closer to a cleaner and greener future.

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ABSTRACT

Graphitic-carbon nitride (gC3N4) has gained interest due to its applications in photocatalysis, semiconductors, and sensing. To increase performance, gC3N4 has undergone a variety of alterations, including additions of metals, metal oxides, alkali metals, nonmetals, graphitic-carbon nitride/nanotubes, and their hybrids. In this study, to create the sulphur-doped graphitic carbon nitride (SgC3N4) an efficient template assisted calcination technique has been applied. A variety of analytical and spectroscopic techniques were used to determine the structural and crystalline characteristics of the nanosheets as formed. For the removal of hazardous dyes like Eriochrome Black T, the synthesised catalyst has been used. The process of Photocatalytic degradation has been used and the activity of S- gC3N4 and has been compared with respect to bulk gC3N4 to degrade the dye in presence of sunlight. The bulk gC3N4 has low surface area therefore has less photocatalytic activity. To enhance the efficiency, sulphur doping of gC3N4 has been done due to which surface area increases and the process of physical adsorption on the surface of catalyst amplifies. Doping is also effective as it narrows the band gap and fastens the process of charge transfer, which increases the light absorption and charge carrier lifetime. Keywords- Doping, Eriochrome Black T, Graphitic carbon nitride, Photocatalysis, Sunlight,

Chapter 1 Introduction and Objectives

1.1 Introduction

Graphitic Carbon nitride g-C3N4 is the most stable allotrope amongst other carbon nitrides. [1] It has gained immense popularity due to it's structural and morphological characteristics as well as it's applications in fields like semiconductors, sensing and photocatalysis. [2] Broadly it has been explored because of the chemical and physical stability and a comparatively narrower band gap of 2.7ev which facilitates the photocatalysis and it's other applications as well. g- C3N4 has a polymeric structure with tri-s-triazine units connected to tertiary ammines (Figure-1). [3] Each layer in it's graphite is strengthened by C-N covalent bonding and weak Vander- Waals forces. [1] g-C3N4 is considered earth abundant as is primarily made up of atoms Carbon and Nitrogen which are plenty on earth. It is easy to synthesise with various methods like thermal condensation, solution mixing, hydrolysis, sol-gel, solvothermal, microwave assisted heating, mechanical grinding. [4] O2 and N2 rich precursors like urea, thiourea, dicyandiamide, cyanamide, melamine which are comparatively low prices thus owes to the inexpensive preparation of the polymer. [4] It's physical and chemical features are controllable as depends on factors like method of preparation, type of precursor chosen, atmospheric conditions like pressure, temperature, and doping. [5]

Figure-1 (a) s- triazine (b) tri-s-triazine

The photocatalytic activity of this g-C3N4 has been a keen topic of research interest. Considering it has it's applications in removal of dyes from water, removal of pollutants from wastewater, degradation of contaminants like organic and inorganic ions in water solution. [6] This reaction of photocatalysis can be oxidative or reductive depending upon the catalyst involved. When this catalyst is exposed to light, there is a transfer of electrons from valence band to conduction band which creates electrons (e-) and holes (h+). [7] For this photodegradation process, the active species like OH- radicals, h+ and O2- radical are the primary oxidants. Scavengers obstruct the charge carrier recombination and increase the photocatalytic efficiency of the catalyst. In absence of such species, these photogenerated electrons recombines with the hole and thus decreases the activity. [4] This redox reaction of photocatalysis takes place with the initiation of formation of electrons and holes on photonic excitation of the catalyst. On this generation of electrons, ionisation of water takes place, which forms OH- ions which further oxidises to OH* radical. The proton formed from water splitting protonates the superoxide O2- radical to form HO2- ion. This ion so formed reacts with another proton to construct hydrogen peroxide (H2O2). [4] On further reaction of this hydrogen peroxide with electron, formation of OH- radical takes place. Now, three active species i.e., OH radical, e- and h+ are formed and these leads to photodegradation on reacting with the substance of interest. The OH radical forms the degradation product, e- forms the reduction product and h+ forms the oxidation product as required by the reaction scheme depicted below. [8] The activation of this whole scheme of reaction depends on the initiation by the photon So the photon is required to have enough energy for excitation of the catalyst. The electronic structure of g-C3N4 has been studied by Wang et al. and the band gap of HOMO- LUMO was around 2.6 eV. [9] UV light irradiation activates it because of its wide band gap. Sunlight is an inexpensive source of light because it contains both UV and visible light. Some modifications are made on g-C3N4 to control the band gap and make it effective under visible light as well. [10] The carbon Pz orbitals (photogenerated h+ present) and nitrogen Pz orbitals (photogenerated e- present) in the polymer g-C3N4 participate in the conduction band and valence bands, respectively. These characteristics make graphitic carbon nitride an intriguing nanomaterial with several applications in photocatalysis. [11]

Figure-2 Reaction scheme of photocatalytic degradation

Although photocatalytic applications of g-C3N4 have been proven by various researchers but it is somewhat inappropriate because of multiple drawbacks. It has been proven to have low surface area of ~10m2g-1 due to high degree of condensation of monomers. The rate of recombination of charge is also high i.e., electron and hole pairs generated by photon activation recombine very fast in the polymer g-C3N4 as the particle boundary effects due to which there is an interruption in the delocalisation of electrons. [12] The limited spectrum of light that may be used by this allotrope because it can only absorb blue light decreases it's spectrum of applications as well. Therefore, decreasing the photocatalytic efficiency of it as a catalyst. To overcome this limitation, modifications in the g-C3N4 has been made. [7] To enhance the photocatalytic activity of catalyst g-C3N4, co-catalysts can be coupled to it. [13] As the efficiency of photodegradation depends on various factors like size and structure of the particle, surface area, number of surfaceactive sites and the light harvesting capacity. [1] To achieve maximum efficiency various routes have been optimised. Making changes in the structural definitions of the polymer like creation of nanorods, 2-dimensional nanosheets, ultrathin structures etc. Incorporating nonmetals like B, C, N, O, S, P and noble metals like silver (Ag), platinum (Pt), gold (Au), palladium (Pd) has proven to be an effective approach to enhance the photocatalytic activity of g-C3N4. [14] Another approach is the preparation of heterojunction like transition metal/ metal oxides, graphene oxide (GO), reduced graphene oxide (rGO), carbon dots etc. [15] For accelerating the surface of g-C3N4 doping has been proved to be extremely useful and success rates are also high. All the limitations are covered up like increment in surface area by modifying pore surface, optimising surface sensitisation to increase the light harvesting and to obtain a red shift of it's absorption range band gap engineering has been used so that range of absorption can be increased. [16]

Figure-3 Possible doping site for Sulphur in doped graphitic carbon nitride The mechanism of heterogenous photocatalysis is similar to what explained for plain g-C3N4 There are majorly 4 stages for heterogenous photocatalysis. First is the generation of electron-hole pairs by absorption of light on the surface of catalyst. [17] Next is the excitation of charge and then there is separation of charge with it's migration to surface and recombination in the bulk. At last, then we have electrocatalytic reaction of degradation of our pollutant of interest at the surface. [18] The pollutant to undergo degradation can be anything like organic compounds, waste water, dyes like Rhodamine B, Methylene blue, Erichrome Black- T, methyl orange, aziridine dye etc. [19]

Figure-4 Mechanism of photocatalysis 1.2 Aim & Objectives The Aim and objectives of our research is explained as follows: •

Optimisation of synthesis: Create a streamlined, repeatable process for the high yield, high purity synthesis of Sg-C3N4 with controlled sulphur doping levels. • Characterisation: Determine the crystal structure, surface morphology, and elemental composition of the SgC3N4 material using various analytical techniques like

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X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and

other spectroscopic methods. • Analysing the photocatalytic activity: Examine the synthesised Sg-C3N4 photocatalytic activity by looking at its capacity to break down organic contaminants or promote water splitting when exposed to artificial sunlight or visible light irradiation. And eventually learning more about the mechanisms underlying the increased photocatalytic activity caused by sulphur doping in Sg-C3N4. Examine how sulphur affects the material's charge carrier dynamics, surface reactivity, and redox characteristics.

Chapter-2 Literature review and Research Gaps

2.1 Literature review

Graphitic carbon nitride/ metal doped modifies carbon nitride has various applications. To list them all down starting from CO2 / NO2 / O2 reduction, degradation of dyes and drugs, photocatalytic disinfection to medical applications like artificial enzyme development, wound healing application, bone regeneration and fracture healing, photodynamic therapy and bioimaging, applications in drug delivery. It also has utilisation in sensing technologies, biosensing and gas sensing, water splitting, hydrogen evolution, oxygen evolution. [20] Energy storage devices like Supercapacitors, fuel cells, lithium metal batteries, sodium ion batteries, vanadium redox flow batteries, lithium magnesium batteries, zinc air batteries, lithium oxygen batteries, lithium-ion batteries, and lithium sulphur batteries have all been produced using graphitic carbon nitride. [21] Instead of using toxic metals to prepare quantum dots, researchers have also reported the use of graphitic carbon nitride for the synthesis of Quantum dot light emitting diode. As vast as it is, the usage of graphitic carbon nitride and it's modifications to enhance the applications has gained wide interest. In this study we will be focusing on the photocatalytic activity of this catalyst to degrade various dyes. [22] Kumar et al. synthesised

CeO2/g-C3N4/ V2O5 heterojunction nanostructures using simple hydrothermal method. The structure and properties of the photocatalyst were characterised by

XRD, SEM, TEM, XPS, PL, EIS and UV-DRS. The photocatalytic activity was checked for the degradation of carcinogenic hexavalent Chromium (VI) ions in the presence of infra-red and visible light. It depicted an activity of 99% reduction within 1 hour and 40 minutes. Whereas the reaction completes in just 30 mins under visible light, in the presence of tartaric acid as a scavenger. The dominant active species were found to be photogenerated electrons and then O2- radicals. [23] Das et al. reported the use of semiconducting materials g-C3N4 and Ag2ZrO3 to fabricate a nanocomposite which reportedly depicts good photocatalytic activity as well as photoinactivation of bacteria. Completion of formation and morphological evidences were collected using multiple characterisation techniques. When the Ag2ZrO3 nanoparticles were covered with 30wt% of g- C3N4, the heterojunction so formed shows photocatalytic efficiency of 99.70% for the decomposition of Rhodamine-B dye under visible light source. It is also found to me more than 48% effective for photoinactivation of microorganisms like Escherichia coli and Bacillus subtilis. Yang et al. describes a study for the synthesis of Bi2O4/g-C3N4 nanosheets using the integration of calcination and hydrothermal method. Formation, composition and other physicochemical properties were analysed using various characteristic techniques. The catalyst as prepared shows a 95% efficiency to degrade Tetracycline in the presence of solar light, which is superior to that of pure g-C3N4. This increase in activity is broadly attributed to increase in surface area and thus enhancing the no. of reaction sites, on modification. They claim that the change increases the separation effectiveness of electron hole pairs. Borthakur et al. synthesised a WO3/g-C3N4 nanocomposite using hydrothermal calcination method and characterisation was performed using various techniques to analyse and confirm the formation of proposed heterojunction. To judge the photocatalytic performance degradation of Rhodamine- B dye was performed in the presence of H2O2 under irradiation of solar light. To ensure the best activity loading of WO3 was optimised and reportedly exhibits highest degradation i.e., 99.5% concentration of dye, at 2wt% of WO3 over g-C3N4. This degradation process follows pseudo first order kinetics and the rate constants with modified has been found to be 2.6 and 7.7 times higher as compared to pure g-C3N4. Sutanto et al. used sol gel techniques to fabricate ZnO2/TiO2 sol with varying molar ratios followed by calcination to complete the synthesis of proposed catalyst i.e., g-C3N4/-3ZnO-c-Zn2Ti3O8. The one with ratio 3ZnO2: 1TiO2, reportedly shows good photocatalytic activity with 82% degradation of methylene blue dye within 45minutes in the presence of visible light. And when this 3:1 is loaded with 10wt% of g-C3N4, it shows 99% degradation of methylene blue on illumination of sunlight. This improvement in degradation of methylene blue from 1.8 to 2.2% is attributed to enhancement in adsorption of organic molecules due to more no. of surface OH- ions. Junqi et al. prepared a ternary composite of g-C3N4/Au/BiPO4 using hydrothermal process. Thiourea has been used a precursor for the synthesis of g-C3N4. A comparison of photoelectrochemical and photocatalytic activity has been made in between g-C3N4/Au/BiPO4, g-C3N4, BiPO4 and g-C3N4/BiPO4. Au here served as electron mediator and could also adsorb photons. Such modifications increase the charge separation thus decreasing the electron hole pair recombination which in turn improves the electron transport property. On modification, they have reported a 14% enhancement in photocatalytic activity for the degradation of methyl orange. Yan et al. used chemical precipitation method to synthesise Ag3PO4/ GO/g-C3N4 where Ag3PO4 acts as photosensitiser, GO as the cocatalyst and these promotes the photocatalytic activity of g-C3N4. These modifications have been done as single component g-C3N4 has a low quantum efficiency due to fast recombination of charge. This ternary photocatalyst depicts an enhancement in absorption in visible region. The rate of degradation of this catalyst against Rhodamine-B dye was found to be 94.8% in 50 minutes. Zhao et al. prepared BiOCl/Bi2MoO6/g-C3N4 nanocomposite using facile refluxing process. A comparison has been made between the photocatalytic activity of nanocomposites that differ with the number of g-C3N4 loadings. To confirm the interactions between g-C3N4 and BiOCl/Bi2MoO6 a series of characterisation techniques have been used. An improved activity was observed by the nanocomposite with the loading of o.10 g-C3N4. These catalysts can be practically used as recyclable photocatalyst. They have reported a 78.82% degradation of Rhodamine B dye. Mousavi et al. used ultrasonic heat treatment and synthesised a gC3N4/Fe3O4/BiOI using melamine powder as precursor. This acts as a photocatalyst in presence of visible light. The results show that amount of BiOI has substantial effect on the photodegradation of Rh-B. To check the photocatalytic activity, it has been used for the degradation id Rhodamine-B, Methylene blue and methyl orange. They have reported that g-C3N4/Fe3O4/BiOI nanocomposites shows about 10-, 22- and 21-fold higher activity for the degradation of Rh-B, MB and MO. Hong Wu et al. created a nanojunction GO/g-C3N4/MoS2 using solvothermal method. Thiourea and Melamine have been used as precursors. This heterostructure has a flower structure which leads to improvement in collection of electrons in MoS2 and holes in g-C3N4. Here GO helps to increase the electrical conductivity. It acts as a photocatalyst in presence of solar light. To check the activity photodegradation of MB, Rh-B, CV has been studied. They have reported that the prepared material has more adsorption and response sites and the

photocatalytic activity of GO/g-C3N4/MoS2 is 3.54 times higher than that of g-C3N4/

MoS2.

2.2 Research Gap The potential research gap in this study with respect to the studies made as of yet are: • Understanding the effects of doping: More research may be needed to fully understand how sulphur doping affects the photocatalytic activity of graphitic carbon nitride. The particular methods by which sulphur doping affects the electrical band structure, charge separation, and surface characteristics of sg-C3N4 might have been the subject of research. • Mechanism of photocatalysis: While sg-C3N4 has demonstrated potential as a photocatalyst, it's possible that a thorough understanding of the underlying mechanisms for photocatalysis was lacking. Clarifying the paths of photogenerated charge carriers and finding the important reactive species in charge of the photocatalytic activity were two areas that may have been the subject of additional study. • Comparing with other catalysts: To learn about the benefits and drawbacks of sg-C3N4 in terms of photocatalytic activity and efficiency, researchers may have compared it to other semiconductor photocatalysts like TiO2 and ZnO. • Impact on environment: Understanding the potential environmental effects of sgC3N4 and its photocatalytic compounds may have been a research topic of interest, as it is with any novel material. • Applications in real world: The photocatalytic activity of sg-C3N4 may have been shown in laboratory experiments, but practical use in real-world settings might have been difficult. A potential area of research was the stability, recyclability, and effectiveness of sg-C3N4 in various environmental settings. • Research methodology: It could be interesting to look at different precursors, reaction conditions, and catalysts for synthesis. The relationship between the material's structural characteristics and its photocatalytic efficiency might have used more research.

Chapter-3 Materials and Methodology

3.1 Apparatus and chemicals used

Melamine and thiourea were used for the preparation of catalyst. Ammonium sulphate has been used as catalyst in the preparation of Sulphur doped graphitic carbon nitride(S-g-C3N4). Ethanol is used as solvent and for purification purposes. Distilled water was used throughout for all the experiments and washing etc. The dye has been procured from the department labs and is used to check the photocatalytic activity of the catalyst so prepared. Overall, the apparatus used includes crucible, Petri dishes, test tubes, falcon tubes, glass voiles, spatulas, wash bottles, mortar and pestle, Eppendorf, beakers, measuring cylinders.

3.2 Synthesis

For the synthesis of Bulk Graphitic carbon nitride, pure melamine as purchased has been put up for calcination at 550° Celsius for 4 hours and the polymer has been prepared. Then for the synthesis of heterojunction, pure melamine and thiourea as purchased without any further purification has been used. To prepare multiple catalysts for comparison of photocatalytic activity, multiple ratios of thiourea to melamine has been used. Three variations of the doped catalyst have been used with 0.1 %, 0.2% and 0.3% sulphur doping as confirmed from the characterisation techniques. For this preparation thiourea to melamine has been used in a ratio of 2:3, 3:2 and 4:1 weight by weight. Accordingly different weights of thiourea and melamine have been crushed in mortar and pestle to make it a fine powder, ammonium sulphate (NH4)2SO4 has been added to it. Then it is calcined at 550° Celsius at a heating rate of 5°C/ min in a muffle furnace for 4 hours. (NH4)2SO4 acts as a catalyst to enhance polymerisation of melamine. As (NH4)2SO4 increases the process of mass transfer and formation of bubbles. These bubbles release gases such as H2O, SO2, NH3. So, basically it is proposed to show enhancement in photocatalytic activity depending upon the loading of different amounts cocatalyst. [1] Figure-5 Process followed for the synthesis of g-C3N4 & S-g-C3N4 3.3 Instrumentation

To study the chemical identity and features of the prepared g-C3N4 & S-g-C3N4 (0.1 SCN, 0.2 SCN & 0.3 SCN). X- ray diffraction (XRD) has been done using Rigaku Smart Lab SE X-Ray diffractometer with HyPix -400 (2D HPAD) with Cu Kα radiation. XRD is performed for indexing the peaks corresponding to the features of g-C3N4 & S-g-C3N4. To analyse the surface of the catalyst and to examine the constituents as well field emission scanning electron microscopy (FE-SEM) was done using Carl Zeiss Sigma 500 FEG-SEM with 0.8 nm resolution at 15 kV, samples for the same have been prepared with gold sputter coating by Quorum technologies, Q150R. Chemical composition was measured by energy dispersive X-ray spectrometer (EDS) using Bruker, QUANTAX 200 using SSD detector with Energy resolution > 129 eV. Photoluminescence (PL) emission spectra was measured on Horiba Labram HR Confocal Micro-Raman spectrometer to analyse the optical fluorescence of the compound as a function of wavelength. Fourier transform infrared spectroscopy (FT- IR) was recorded to determine the presence of proposed elements in the compound prepared. 3.4 Preparation for photocatalytic reaction

The activity of the prepared catalyst is examined by the degradation efficiency of EBT dye under sunlight. A comparison has been made to check the capability of all the variations synthesised of S doped g-C3N4 (S-g-C3N4) i.e. (0.1%, 0.2%, 0.3% SCN) and the bulk gC3N4. Solar light has been used as the light source for photocatalytic reaction. For the experiment EBT dye solution of 10 ppm i.e., 2mg of dye suspended in 200 ml water has been prepared. 10ml of this solution has been taken in the test tubes and 0.2 g of each catalyst i.e., 0.1% SCN, 0.2% SCN, 0.3% SCN and bulk g-C3N4 has been added to it. The reaction has been put up on magnetic stirrer in the dark for 60 minutes and then for 2 hours in sunlight. An aliquot of 5 ml has been taken and centrifuged to remove the catalyst still suspended in the solution. Thereafter, the solutions were measured with UV-Visible spectrophotometer. The changes in the concentration were calculated by C/C0 where C0 is initial concertation of the dye and C is the amount of dye remaining after degradation.

Figure-6 Phototcatalytic degradation of EBT dye

Chapter-4 Results and Discussion

4.1 Characterisation 4.1.a FESEM To examine the morphology of the catalyst prepared FESEM was used. The prepared samples of SgC3N4 have layered structure and pore channels are also visible due to copolymerisation of melamine of thiourea. A characteristic stacked lamellar structure was observed for the S-gC3N4 as can be seen in figure. A sheet structure was prominently observed as the method of synthesis is used to prepare a doped nanosheet. The observation of porous structure can be attributed to the process of calcination i.e., due to the release of H2S gas from thiourea.

Figure-6 FESEM of (a) bulk g-C3N4, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN 4.1.b EDS EDS was conducted to determine the composition and distribution of elements. The amounts by percentage of Carbon, Nitrogen and Sulphur for all the catalysts to be compared is given in table below bulk g-C3N4, 0.1% SCN, 0.2% SCN and 0.3%SCN. Here, thus named depicting the percentages of dopant which is eventually found to increase i.e., from 0.1 to 0.2 to 0.3 %. The shading in the area mapping also determines the amount of Carbon, Nitrogen and Sulphur.

Figure-7 EDS spectra; Peaks depicted by elements Carbon, Nitrogen, Sulphur in (a) bulk g-C3N4, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN

Figure-8 EDS spectra; Percentages of elements Carbon, Nitrogen, Sulphur in (a) bulk g-C3N4, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN Figure-9 EDS Area mapping of (a) bulk g-C3N4, (b) 0.1% SCN, (c) 0.2% SCN, (d) 0.3%SCN

4.1.d FT-IR For samples containing various quantities of sulphur, FT-IR spectra were taken and are shown in Figure. O-H and N-H stretching vibration from water that has been absorbed and sustained amino groups correlate to the broad band between 3300 and 3600 cm-1 in the spectrum for bulk g-C3N4. Between 1300 and 1700 cm-1, the stretching vibration modes of the carbon nitrogen heterocycles produced a series of notable peaks. The tri-s triazine units are thought to be responsible for the peak's strength at 800 cm-1. The doped samples 0.1% SCN, 0.2% SCN and 0.3%SCN shows similar characteristic to that of g-C3N4 but there is a change in intensity depending upon the percentage of sulphur. Therefore, the incorporation of Sulphur is verified due to the increase in intensity of bands observed in FT-IR spectra. 4.1.c XRD To examine the crystallinity of the samples prepared, XRD was recorded and is given in figure. We can observe that all the 4 samples i.e., bulk g-C3N4, 0.1% SCN, 0.2% SCN and 0.3%SCN shows diffraction peaks at 2θ = 12.8 corresponding to (100) plane and 2θ = 27.6 which is attributed to (002) plane. These peaks are characteristic to the graphitic carbon nitride g-C3N4 structure. The peak at 2θ = 27.6 is because of the conjugated aromatic structure of g-C3N4 and the interlayer stacking of the structure and at 2θ = 12.8 is the smaller peak related to tri-s-triazine structural units and the in plane structural packing. Peaks are similar for the Sulphur doped g-C3N4. But with increase in sulphur doping i.e., from 0.1% to 0.25 to 0.35 Sulphur doping the width of these peaks increases eventually. On incorporation of the dopant into the g-C3N4, the crystallinity of the structure reduces due to which intensity of these peaks in XRD graphs also decreases. In S-gC3N4, there is enhancement in the contact between the layers due to which the interlayer distance shortens which strengthens the Vander Waals force between the heptazine layers of S-gC3N4. Figure-10 (a) FTIR spectra bulk g-C3N4, 0.1% SCN, 0.2% SCN and 0.3%SCN. (b) XRD pattern of bulk g-C3N4, 0.1% SCN, 0.2% SCN and 0.3%SCN. 4.1.e PL Photoluminescence spectra (P.L.) was recorded to study the recombination of charge carriers. It was excited at 340 nm. In comparison for bulk g-C3N4, a low fluorescence intensity can be observed for all the samples of sulphur doped i.e., 0.1% SCN, 0.2% SCN and 0.3%SCN. This indicates a that the photogenerated pairs of electron ad hole in the modified catalyst increased separation efficiency in turn supports the special structure of the doped g-C3N4, because it has been demonstrated that photon absorption and charge carrier collection can be separated by the nanosheet structure in orthogonal spatial directions. Because of its thin thickness, the porous structure also shortens the distance required for charge carriers to move from the interior to the exterior and prevents recombination of photogenerated electron hole pairs during immigration. Increased porous structure can also be the cause of the decrease in fluorescence intensity of S-g-C3N4 seen with higher heating temperatures. 4.1.f UV- DRS To justify the photocatalytic catalytic activity UV- vis diffuse absorbance spectra was compared between bulk g-C3N4 and 0.1% SCN, 0.2% SCN and 0.3%SCN. All doped samples show refined optical absorption particularly at the range of 450-600 nm. It is also justified from the tauc plot that S- g-C3N4 exhibit narrower band gap than that of bulk. This is because in porous structure of nanosheets there is a multiple reflection of incident light which in turn increases the path length which is effective for absorption of incident light. Figure-11 PL spectra of samples bulk g-C3N4, 0.1% SCN, 0.2% SCN and 0.3%SCN

4.2 Photocatalytic activity To check the photocatalytic activity of bulk g-C3N4 and S-g-C3N4 (0.1% SCN, 0.2% SCN and 0.3%SCN), we have checked it's efficiency of degradation for Erichrome Black T dye (EBT) in the presence of solar light. To make a comparison between bulk g-C3N4 and all the modified versions of S-g-C3N4, 0.2g of each catalyst has been added to 10ppm solution of the dye. The reaction has been set up in four different test tubes and on a magnetic stirrer. The reaction takes place for 60minutes in the dark and for 120 minutes in solar light. To the visible eyes a significant change of colour can be seen. First, when the reaction is set up in dark the shades of blue get lightened and then in the presence of sunlight the blue shades in the test tube disappear. To confirm the degradation of dye, UV-visible absorption spectra has been recorded for each sample which confirms the degradation of the dye. The maximum absorption for EBT dye is in the range of 620nm- 685nm. We have done the calculations by the first-order equation:

$\ln(C/C0) = -kt$, where k is the reaction rate constant (min^{-1}). So, it has been analysed that Sulphur doped variations show maximum degradation of dye. The table as depicted by Figure- 12.

Figure-13 UV- visible absorption spectra for bulk g-C3N4, 0.1% SCN, 0.2% SCN and 0.3%SCN There are multiple reasons for better photocatalytic activity of S-g-C3N4 then g-C3N4. The bandgap of g-C3N4 becomes smaller when sulphur doping is added. A narrower bandgap is advantageous for photocatalysis because it enables sg-C3N4 to absorb a wider range of visible light. The photocatalytic activity of bulk g-C3N4, in contrast, is only active in the ultraviolet (UV) portion of the spectrum due to its greater bandgap. Sg-C3N4 is able to absorb an increased amount of visible light, which makes up a significant component of the solar spectrum, because of the narrower bandgap and the presence of sulphur dopants. This improved light absorption makes sg-C3N4 a more effective visible-light-driven photocatalyst by allowing it to use sunlight for photocatalytic processes more effectively

Furthermore, the separation of photogenerated charge carriers (electron-hole pairs) is improved by sulphur doping in g-C3N4. To stop photoexcited electrons from recombining with holes, sulphur functions as an electron acceptor and has the ability to catch them. This better charge carrier separation raises the possibility of redox reactions occurring on the surface of the material, which results in increased photocatalytic activity. The S-g-C3N4 lattice develops defects in structure as a result of sulphur doping. These defects may serve as charge carrier trap sites, further lowering the recombination rates of the carriers and increasing the total photocatalytic efficiency. New active sites for catalytic reactions are introduced by the presence of sulphur dopants on the surface of S-g-C3N4. Compared to bulk g-C3N4, these active sites encourage the adsorption of reactants and enhance surface redox reactions, which improves photocatalytic efficacy. The enhancement in the photocatalytic efficiency of S-g-C3N4 over bulk can be attributed to various reasons like the S-g-C3N4 structure's -conjugation network may grow as a result of sulphur doping. Charge carriers' mobility is improved by this increased conjugation, enabling them to move more freely inside the substance and take part in photocatalytic events more successfully. In S-g-C3N4, sulphur doping can change the energy levels of the valence and conduction bands, moving them in relation to the reaction species' redox potentials. This alteration can promote photocatalytic activity by facilitating electron transport and redox reactions. Conclusion

Overall, the synthesis, characterisation, and assessment of sulphur-doped graphitic carbon nitride's photocatalytic activity have made significant advances in the field of photocatalysis. In our research we have we have attempted to create a Sulphur- doped graphitic carbon nitride, characterising it’s morphological and chemical properties and comparing the photocatalytic activity between the bulk g-C3N4 and the variations of catalyst to be prepared. The results underline how important sulphur doping is for modifying the characteristics of S-g-C3N4 for improved solar-light-driven photocatalysis. The potential for further enhancing sg-C3N4's efficiency and broadening its application range is encouraging as our understanding of its photocatalytic mechanisms deepens. The results highlight its potential for useful applications, encourage additional research into enhancing its functionality, and open up new opportunities for utilising sg-C3N4 in cutting-edge environmental and energy-related technology. In the end, this research adds to the overarching objective of creating creative and sustainable materials for a more sustainable future. However, it is crucial to understand that this field of study is still in its early stages, and subsequent research will build on these results to develop sg-C3N4-based photocatalysis's potential even further. the findings of this study make a substantial contribution to the creation of effective and longlasting photocatalytic materials, taking us one step closer to a cleaner and greener future.

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CeO2/g-C3N4/ V2O5 heterojunction nanostructures using simple hydrothermal method. The structure and properties of the photocatalyst were characterised by	CeO2/g-C3N4/V2O5 heterojunction (CCGV) was rationally synthesized by simple hydrothermal method. The crystal structure, morphology, and optical properties of the photocatalysts were characterized by

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