

CARBON NANOMATERIALS FOR PHOTOCATALYTIC HYDROGEN GENERATION

Submitted in partial fulfillment of the requirements for the award of

Bachelor of Science

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SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC

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BONAFIDE CERTIFICATE

This is to certify that the Project Report is the bonafide work of D. KARTHIK (40030016), K. KEERTHIPRIYA (40030017), S.A. MASTHAN BEE (40030022) who carried out the project entitled "CARBON NANOMATERIALS FOR PHOTOCATALYTIC HYDROGEN GENERATION" under my/our supervision from June 2022 to April 2023.

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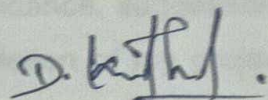
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DECLARATION

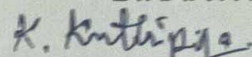
We D. Karthik, K. Keerthipriya, and S.A. Masthan bee, hereby declare that the project report entitled **CARBON NANOMATERIALS FOR PHOTOCATALYTIC HYDROGEN GENERATION** done by us under the guidance of **Dr. V. KAVITHA M.Sc., M.Phil., Ph.d.**, Professor Department of chemistry, Sathyabama Institute of Science and technology is submitted in partial fulfillment of the requirement for the award of Bachelor of Science degree in chemistry in April 2023.

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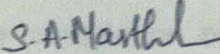
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ABSTRACT

Graphitic carbon nitride (g-C₃N₄) photocatalysis for solar hydrogen generation, thiourea, a sulfur-containing compound is a starting material for the synthesis of graphitic carbon nitride semiconductors. The conversion of thiourea into g-C₃N₄ is characterized by X-Ray Diffraction, FTIR spectroscopy. The assynthesized g-C₃N₄ samples, further modified with carbon nanoparticles, were capable of splitting water under visible light ($\lambda > 420$ nm) in the presence of triethanolamine as an electron donor with the aid of cocatalyst Pt . Nanoparticles of g-C₃N₄ doped with carbon uses visible light for water splitting in the presence of sacrificial agent, triethanolamine. The photogenerated holes oxidize the sacrificial reagent, which enrich the electrons in a photocatalyst, allowing a swift delivery of photo-generated electrons and holes layers independently. Holes then separate water molecules and generate protons in the outer g-C₃N₄. Owing to electrostatic attraction, protons penetrate through g-C₃N₄ to bind with photo-generated electrons present and to create hydrogen molecules on the Pt surface. This results in a high photocatalytic efficiency for the development of H₂. The evolution of photocatalytic hydrogen from water is a promising and sustainable approach for converting solar energy to chemical energy.

KEYWORDS: Carbon, Graphitic Carbon nitride, Triethanolamine, Photocatalytic hydrogen activity.

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LIST OF ABBREVIATIONS AND SYMBOLS

S. NO	ABBREVIATIONS AND SYMBOLS	DEFINITION
1.	g-C ₃ N ₄	Graphitic Carbon Nitride
2.	TEOA	Triethanolamine
3.	H ₂	Hydrogen
4.	Pt	Platinum
5.	TiO ₂	Titanium dioxide
6.	NH ₄ OH	Ammonium hydroxide
7.	NaBH ₄	Sodium Borohydride
8.	°C	Degree centigrade
9.	G	Gram
10.	ml	Millilitre
11.	mm ²	Millimeter square
12.	μm	Micrometer
13.	μ	Micro
14.	XRD	X-Ray Diffraction
15.	FTIR	Fourier Transformed Infrared
16.	DRS	Diffuse Reflectance Spectroscopy

CHAPTER 1

INTRODUCTION

The search for new photocatalytic systems working under solar light for hydrogen production is increasingly triggering the interest of the scientific community. In the framework of novel photocatalysts, graphitic carbon nitride (g – C₃N₄) has emerged in the last decade as one of the most promising material to run H₂ photoproduction from water under visible light, due to cost-effective and easy synthesis, chemical stability, narrow band-gap and band potentials suitable to perform relevant redox reactions in aqueous solution. Its intrinsic limitations, namely relatively high charge carriers recombination, low surface area and restricted light harvesting in the visible region, have been in part compensated by several strategies. For instance, metal and non-metal doping, structural and morphological modifications, dye-sensitization and combination with co-catalysts of different nature (e.g., carbon nanotubes, carbon dots) have proved to be rewarding in terms of enhanced photocatalytic activity towards H₂ generation from water also in the presence of sacrificial agents.

Respectively g-C₃N₄, providing new micro-sized composites with excellent photocatalytic properties towards H₂ production from triethanolamine (TEOA) aqueous solution; in particular , up to 20-fold increase of hydrogen evolution rate (HER) was achieved compared to g-C₃N₄ alone, due to a synergic effect between the constituents in the composite , essentially due to improved charge carrier separation. Such an effect results from the positive band-alignment with the semiconductor namely g-C₃N₄ is selected based on its bandgap in order to exploit this synergic effect.

Carbon nitrides are a class of polymeric materials consisting mainly of carbon and nitrogen. They can be obtained from carbon materials, through substitution of the carbon atoms by nitrogen.

Graphitic carbon nitride (g – C₃N₄) is not only the most stable allotrope of carbon nitrides at ambient atmosphere, but it also has rich surface properties that are attractive for many applications, including catalysis, due to the presence of basic surface sites and is an emerging material as an organic semiconductor photocatalyst active for various kinds of reactions such as water splitting, CO₂ reduction and degradation of harmful organic compounds, because of its non-toxic, stable and earth-abundant nature. In these systems, structural properties of g-C₃N₄ such as specific surface area and porosity have a strong impact on activity, because they strongly affect the efficiency of electron/hole utilization to the surface chemical reaction.

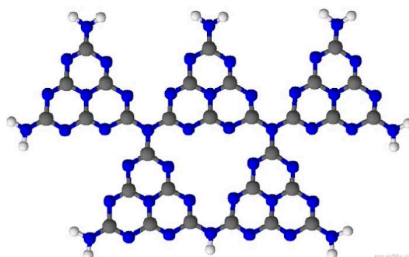


Fig 1.1 Graphitic Carbon Nitride

Graphitic carbon nitride, g-C₃N₄, is a polymeric material consisting of C, N and some impurity H, connected via tris-triazine-based patterns. Compared with the majority of carbon materials, it has electron-rich properties, basic surface functionalities and H-bonding motifs due to the presence of N and H atoms. It is thus regarded as a potential candidate to complement carbon in material applications. In this project, a brief introduction to g-C₃N₄ is given, the methods used for synthesizing this material with different textural structures and surface morphologies are described, and its physiochemical properties are referred.

As is known to all, converting solar energy to chemical energy, especially hydrogen energy, has been becoming the research focus, owing to energy crisis and environment pollution. The hydrogen energy can be directly used as fuel without any harmful pollutants emitting and has high energy yield (122kJ/g), which is three times higher than that of gasoline (40kJ/g). However, the present methods of industrial hydrogen production, including steam reforming and gasification, not only expend a great deal of fossil fuels, but also emit carbon dioxide which is primarily greenhouse gas. Since, the solar light and water are abundant and renewable. In the past decades, a great deal of efforts has been made to research the photocatalysts to produce hydrogen from low cost and environmentally friendly process.

Converting solar energy into hydrogen gas by water splitting is considered as a long-term solution address global energy environmental problems. Great efforts has been devoted to the search for abundant systems for the purpose of efficient capture, conversion, and storage of solar energy in a cost-effective manner. To further advance the recently-developed carbon nitride photocatalysis for solar hydrogen generation, thiourea, a sulfur-containing compound, was used as a cheap and easily-available starting material for the synthesis of graphitic carbon nitride semiconductors.

As-prepared photocatalysts were subjected to several characterizations, and the results showed that the heating temperature and the presence of sulfur motifs offer a facile chemical pathway for the control of the condensation / polymerization of carbon nitride, and thus adjusting their textural and electronic properties. Photocatalytic activity experiments demonstrated that the g-C₃N₄ synthesized from thiourea exhibited a much higher H₂ production rate of g-C₃N₄ prepared activity can be further enhanced by increasing the condensation temperature.

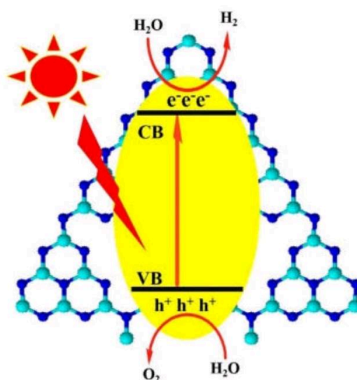


Fig 1.2 Photocatalytic activity

Catalytically splitting water by sunlight to produce hydrogen gas has attracted worldwide attention due to increasing energy demands and growing greenhouse gas emissions. Since the discovery of H_2 production by water splitting in Pt/TiO_2 photoelectrochemical cells have been made to establish stable, efficient and affordable heterogeneous photocatalytic systems for solar to chemical conversion.

In times of rapid change, a hydrogen-led economy has the advantage that it is very flexible as it is applicable to diverse energy sources, production processes, transportation and storage models. Hydrogen is a basic chemical building block which can be transformed and used in variety of ways.

The generation of photocatalytic hydrogen via water splitting under light irradiation is attracting much attention as an alternative to solve such problems as global warming and to increase interest in clean energy. However, due to the low efficient and selectivity of photocatalytic hydrogen production under solar energy, a major challenge persists to improve the performance of photocatalytic hydrogen production through water splitting. However, the fast recombination of photoexcited electron-hole pairs limits the rate of hydrogen evolution and various methods such as modification, heterojunctions with semiconductors, and metal and non-metal doping, and heterojunctions, and we summarize recent achievements in their application as hydrogen production photocatalysts.

CHAPTER 2

LITERATURE SURVEY

1. Title: Polycondensation of thiourea into carbon nitride semiconductors as visible light photocatalysts

Authors: Guigang Zhang, JinshuiZhang, Mingwen Zhang and Xincheng Wang

Journal and year: Journal of materials chemistry, February 2012.

Inference: Recently developed carbon nitride photocatalysis for solar hydrogen generation, thiourea, a sulfur-containing compound, a starting material for the synthesis of graphitic carbon nitride semiconductors. Photocatalytic activity experiments demonstrated that the g-C₃N₄ synthesized from thiourea exhibited a much higher H₂ production rate than the g-C₃N₄ prepared from dicyanamide or urea and this activity can be further enhanced by increasing the condensation temperature.

2. Title: Graphitic Carbon Nitride materials for photocatalytic Hydrogen Production via water splitting.

Authors: Seong Jun Mun and Soo-Jin Park

Journal and year: Catalysts, September 2019

Inference: Graphitic Carbon Nitride has emerged as an attractive material for photocatalytic hydrogen production. The fast recombination of photoexcited electron-hole pairs limits the rate of hydrogen evolution.

3. Title: Reductive modification of Carbon Nitride by metals – The Influence on structure and photocatalytic hydrogen evolution

Journal and year: Materials, January 2022

Inference: Pt, Ru, and Ir were introduced onto the surface of graphitic carbon nitride. A reduction of these photocatalysts with hydrogen causes several changes, such as significant increase in the specific surface area, a C/N atomic ratio, a number of defects in the crystalline structure of g-C₃N₄ and the contribution of nitrogen bound to the amino and imino groups. The structural changes significantly enhanced the photocatalytic activity in the production of hydrogen through the reaction.

4. Title: Recent development in graphitic carbon nitride based photocatalysis for hydrogen generation

Authors: Muhammad Salman Nasir, Guorui Yang, Iqra Ayub, Shengjie Peng

Journal and Year: Applied Catalysis B. Environmental, June 2019

Inference: The graphitic carbon nitride has an attractive band structure, good chemical stability, earth abundant and significantly easily fabricated which makes an application for the generation of hydrogen by water splitting. Future development of the different strategies of water splitting using graphitic carbon nitride (g-C₃N₄) for hydrogen generation.

5. Title: Photocatalytic hydrogen evolution from biomass conversion

Authors: Kayla Alicia Davis, Sunghoon Yoo, Benjamin D. Sherman

Journal and Year: Nano convergence 2021

Inference: Hydrogen evolution from photocatalytic biomass conversion not only produces valuable carbon-free energy in the form of molecular hydrogen. This photocatalytic hydrogen evolution from bioass and bioass-derived substrates.(including ethanol, glycerol, formic acid, glucose and polysaccharides).

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

The aim of the project is to develop an efficient photocatalyst using graphitic carbon nitride and carbon materials which is prepared from the solid wastes.

3.2 SCOPE

Using renewable resource such as solar energy, the hydrogen can be produced from an environment-friendly and low-cost water-splitting technology through a photocatalytic process which requires nanomaterials, which can fulfil the future requirements of energy. Nanomaterials are highly efficient as a photocatalyst possessing high surface area, necessary to attain high solar-to-hydrogen (STH) conversion efficiency

The main objective of the study

- To prepare carbon materials (CNDs) from green pea pod.
- To prepare an heterojunction photocatalytic material using g-C₃N₄ and Carbon.
- To characterize the prepared catalyst by Fourier Transform – Infrared Spectroscopy (FT-IR), Powder X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM) and Diffuse Reflectance Ultraviolet Spectroscopy (DRUV).

To utilize the catalyst for water splitting reactions for hydrogen generation

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS:

Thiourea, Triethanolamine (TEOA), Methanol, Sodiumborohydride, Hexachloroplatinate, Ammonium Hydroxide are the chemicals which is used for the entire experiment.

4.2 METHODS:

4.2.1 Preparation of g – C₃N₄:

g– C₃N₄ can be synthesized by thermal polymerization in a closed air volume, using thiourea as a precursor. To synthesize g– C₃N₄, 20g of thiourea was placed in porcelain crucibles, tightly closed with a cover and subjected to thermal treatment at 275°C, 300°C and 350°C for 2 hours. The crucibles were left for cooling. A porous, brittle yellow material formed inside the crucible after the heat treatment of thiourea at different temperatures and the resulting material was then ground into powder in an agate mortar. The powder formed during the process is shown in 4.2.1 a) Thiourea 275°C b) Thiourea 300°C c) Thiourea 350°C

TEMPERATURE	YIELD
275°C	4.03g
300°C	5.50g
350°C	6.10g

Table 4.2.1 Yield of thiourea at different Temperatures



Fig 4.2.1A) THIOUREA 275°C B) THIOUREA 300°C C) THIOUREA 350°C

4.2.1.1 Preparation of Carbon from Green Pea:

The fresh green pea peel was taken and dried in sunlight for 2-3 days till become yellow brittle. The green pea was grinded and sieved in 150 μ . 10g of green pea powder is accurately weighed and mixed with 20mL of Ammonium Hydroxide solution. The mixture is soaked for 24 hours. The mixture was placed in silica crucibles, tightly closed with cover and subjected to thermal treatment at 300°C, 400°C for 4 hours. The crucible were left for cooling. A black material formed inside the crucible after the heat treatment of the mixture at different temperature and the resultant material was then grounded into powder in an agate mortar. The powder formed during the process is shown in fig 4.2.1.1 a) at 300°C b) at 400°C



A)



B)

Fig 4.2.1.1 A) Preparation of carbon material from pea pod at 300°C

B) Preparation of carbon material from pea pod at 400°C

4.2.2 Preparation of photocatalyst:

4.2.2.1 Carbon doped g-C₃N₄:

0.2g of g-C₃N₄ (prepared from 275°C) is accurately weighed, 0.01g of carbon (prepared from 400°C) and added 10mL of water. A magnetic pellet is used to stir the mixture in a magnetic stirrer. The mixture has to run for 2-3 hours at room temperature. After the running time, the mixture undergoes decantation process by removing the liquid layer at the top. The solid layer is poured in watchglass and kept in oven at 50°C for 15-20 minutes. The powder formed during the process is shown in fig 4.2.2.1

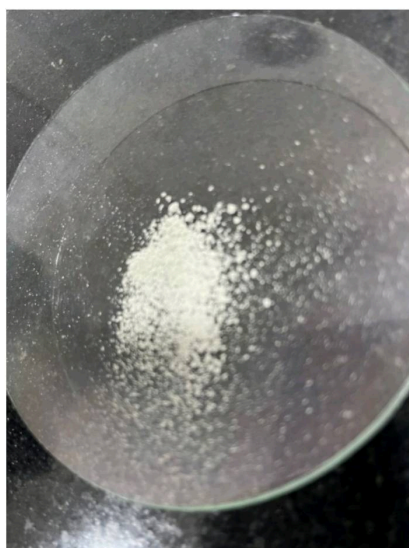


Fig 4.2.2.1 Carbon doped g-C₃N₄

4.2.2.2 Using Graphitic Carbon Nitride (g-C₃N₄) loaded with Pt

0.2g of g-C₃N₄ (prepared from 275°C) is accurately weighed and added 4mL of Hexachloroplatinate solution in a beaker. A magnetic pellet is used to stir the mixture in a magnetic stirrer. 8mL of sodiumborohydride solution was applied to the mixture slowly which is used to reduce the platinum. The mixture has to run for 2-3 hours at room temperature. After the running time, the mixture undergoes decantation process by removing the liquid layer at the top. The solid layer is poured in watchglass and kept in oven at 50°C for 15-20 minutes. The powder formed during the process is shown in fig 4.2.2.2



Fig 4.2.2.2 g-C₃N₄ loaded with Pt

4.2.2.3 Carbon induced Graphitic Carbon Nitride (g-C₃N₄) loaded with Pt

0.2g of g-C₃N₄ (prepared from 275°C) is accurately weighed, 0.01g of carbon (prepared from 400°C) and added 4mL of Hexachloroplatinate solution in a beaker. A magnetic pellet is used to stir the mixture in a magnetic stirrer. 8mL of sodiumborohydride solution was applied to the mixture slowly which is used to reduce the platinum. The mixture has to run for 2-3 hours at room temperature. After the running time, the mixture undergoes decantation process by removing the liquid layer at the top. The solid layer is poured in watch glass and kept in oven at 50°C for 15-20 minutes. The powder formed during the process is shown in fig 4.2.2.3



Fig 4.2.2.3 Carbon induced g-C₃N₄ loaded with Pt

4.3 Characterization techniques:

4.3.1 XRD (X-Ray Diffraction):

X-ray diffraction is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition and physical properties of materials. It is usually well known for qualitative and quantitative analyses for crystalline phases in materials, far more information can be obtained from a careful analysis of the diffraction patterns or by using specific XRD settings: i.e., characterization of solid solutions, crystalline size and shape, crystal orientation, internal elastic stresses/strains at different levels etc.

When a beam of monochromatic X-rays is incident on a crystal/ composed of unit cells of regularly arranged atoms, the X-rays that are scattered by different atoms interfere with each other, resulting in strong XRD in some special directions. The orientation and intensity of the diffraction lines in space are closely related to the crystal structure. The substance's composition, crystal form, intramolecular bonding mode, molecular configuration and so on determine the specific diffraction pattern of the substance. By comparison with the XRD spectra of known crystalline substances, the composition and structure of the sample, the phase composition of the sample can be quantitatively analyzed. The size of a solid sample required for XRD must be greater than 10x10 mm², the thickness must be greater than 5 μm, and the surface must be flat.

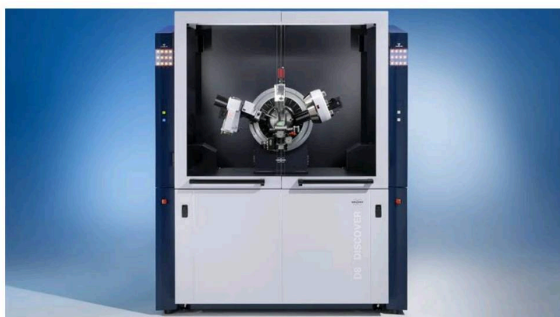


Fig 4.3.1 XRD (X-Ray Diffraction)

4.3.2 FTIR (Fourier transform infrared spectroscopy):

FTIR stands for Fourier transform infrared, the preferred method of infrared spectroscopy. FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. The spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

Fourier transform infrared Spectroscopy relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. It is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. This simultaneously collects high-spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelength at a time.



Fig 4.3.2 FTIR (Fourier Transform Infrared Spectroscopy)

4.3.3 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy, or diffuse reflection spectroscopy, is a subset of absorption spectroscopy. Chemical reactions in dry reagent elements are most commonly monitored by diffuse reflectance spectroscopy. These elements can be illuminated by either a direct or a diffuse light source. Both sources of light will provide specular and diffuse reflection. Specular reflection is defined as the reflection from the surface of the element, where the angle of incidence equals the angle of reflectance. It is not a good indicator of the progress of reactions occurring within the element and thus is of minimal value in making these measurements.

Diffuse reflection, which arises from the interaction of light with various chemical and physical factors within the reaction volume of the element, is the major component of the measurement. These interactions include the absorption, transmission, and scattering properties of the illuminated element. A layer in which a chromophore is being generated or degraded is illuminated at a suitable wavelength in order to make a measurement. The amount of diffuse light recovered in an element which contains a reflective function is used to measure the progress of the reaction.



Fig 4.3.3 Diffuse Reflectance Spectroscopy

4.4 EXPERIMENTAL PROCEDURE

4.4.1 FABRICATION OF PHOTOREACTOR

The batch photoreactor is a cylindrical reactor borosilicate glass with a total volume of 250mL. It has a length of 15cm and internal diameter of 3cm.

The reactor has two ports namely, one at the middle and the other at the side of the reactor. The middle and side ports are 3cm & 2.5cm in length and 1.5cm & 1cm of internal diameter respectively. The side port is used for transferring the solutions and for purging the gas in order to remove dissolved oxygen from the solution. In the middle port a 10mL syringe is inserted for volume measurements at an head space of 3 cm. The whole reactor is sealed proof with teflon tape at the ports to prevent any leakage of gases. The volume of the gas liberated is observed by the pressure induced movement of the syringe.



Fig: 4.4.1 Borosilicate Glass Photo reactor

4.4.2 PHOTOCATALYTIC EXPERIMENT

The water splitting reaction was tested within a 250mL Borosilicate glass reactor. 0.5g of photocatalyst is added to a 100 mL containing 10% triethanolamine (TEOA) and it is closed with rubber cork to prevent the leakage of gas. the reactor was purged with N_2 gas for 20 min to remove the dissolved oxygen. The solution is stirred continuously in order to keep the catalyst particles in suspension state and the reaction takes place under the solar light for 6h. The volume of generated H_2 gas is measured using a glass syringe.

4.4.3 CALCULATIONS

The rate of hydrogen production is calculated from the volume measured in the experimental procedure as

$$n = PV/RT \text{ (mol L}^{-1} \text{ h}^{-1}\text{)}$$

where,

P is Pressure (1 atm)

V is volume (L)

R is Gas constant (0.08206 L atm mol⁻¹ K⁻¹)

T is Temperature (kelvin)

n is no. of moles (mol L/h)

The rate of hydrogen production in mol g⁻¹ h⁻¹ is given by,

Hydrogen = n / catalyst weight (mol g⁻¹ h⁻¹)

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Photocatalytic activity for Hydrogen Generation:

Improving the photocatalytic activity of g-C₃N₄ by introducing various nanoparticles Surface modifications of the catalytic structure and morphology has the potential to promote charge separation and narrow the band gap due to increased surface area and efficient charge-carrier separation. The graphitic carbon nitride was introduced in the reactor which exhibits significantly improved the light-harvesting ability mainly due to the multiple scattering effect. A 4h reaction was performed to confirm the hydrogen production ability of g-C₃N₄ under visible-light irradiation.

5.2 CHARACTERIZATION:

5.2.1 XRD:

From the fig 5.2.1 the graphitic carbon nitride showed the strongest XRD peak at 27.4°, corresponding to 150 nm, is due to the stacking of the conjugated aromatic system. The CN/Pt and CN/C/Pt shows the strong XRD peak at 27° corresponds to 99 nm and 50 nm, calculated using Debye Scherrer equation. The structure of the prepared graphitic carbon nitride and carbon nanodot/graphitic carbon nitride composites were characterized by XRD. displays the XRD patterns of the CND/CN hybrid photocatalysts with different contents of CNDs, and the pure CN. All the photocatalysts exhibited two distinct diffraction peaks at 27.7° and 13.2°, which is indexed to graphitic carbon nitride as the (002) and (100) crystal surfaces (JCPDS 87-1526).

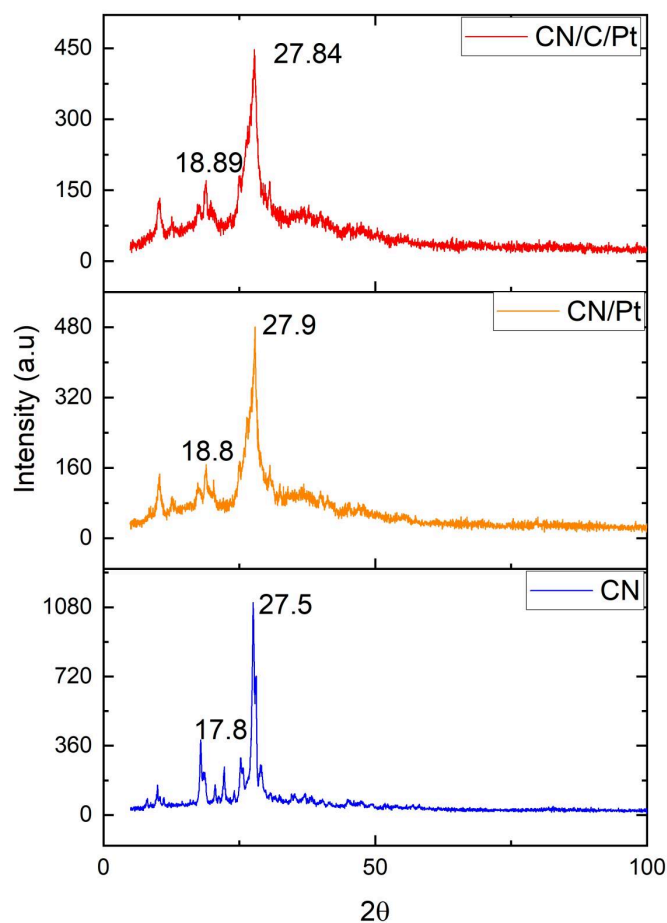


Fig 5.2.1 XRD for Carbon Nitride

5.2.2 FTIR:

Fig: 5.2: displays the FTIR spectra of the pure graphitic carbon nitride (CN), Carbon (Cs) and 1% Pt (CN/C/Pt). The absorption peaks between 3600 and 3000 cm^{-1} are due in detail to the stretching of N-H, some hydrogenated N atoms in the $g\text{-C}_3\text{N}_4$. Normal absorption peaks of 1700 to 1200 cm^{-1} are the stretching vibrational modes of $\text{C}=\text{N}$ and $\text{C}-\text{N}$. Both the CN/C/Pt and the CN / C also displays the sharp peak of triazine units at 810 cm^{-1} . The as-prepared graphite carbon nitride and CNDs / CN nanocomposite's chemical composition is approximately consistent with $g\text{-C}_3\text{N}_4$.

VIBRATIONAL PEAKS (cm^{-1})	FUNCTIONAL GROUPS
3600 – 3000 cm^{-1}	N – H
2940 cm^{-1}	C – H
2870 cm^{-1}	- COOH
1700 cm^{-1}	C = N
1200 cm^{-1}	C – N
810 cm^{-1}	Triazine units

Table 5.2.2 Vibrational peaks and their functional groups

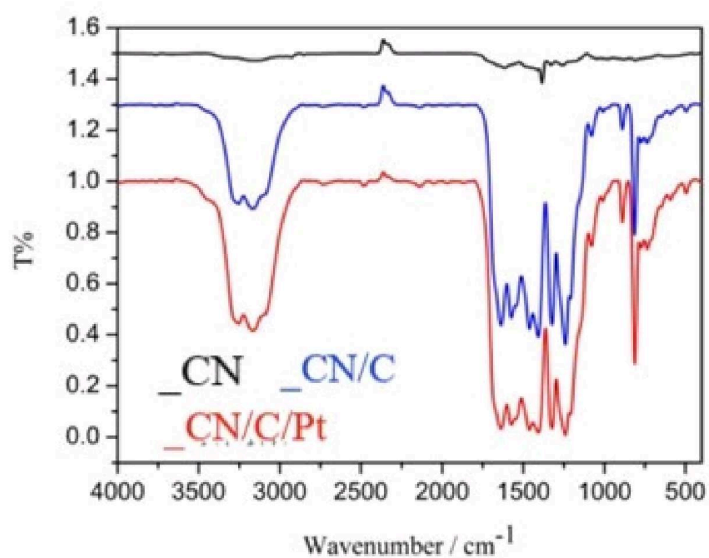
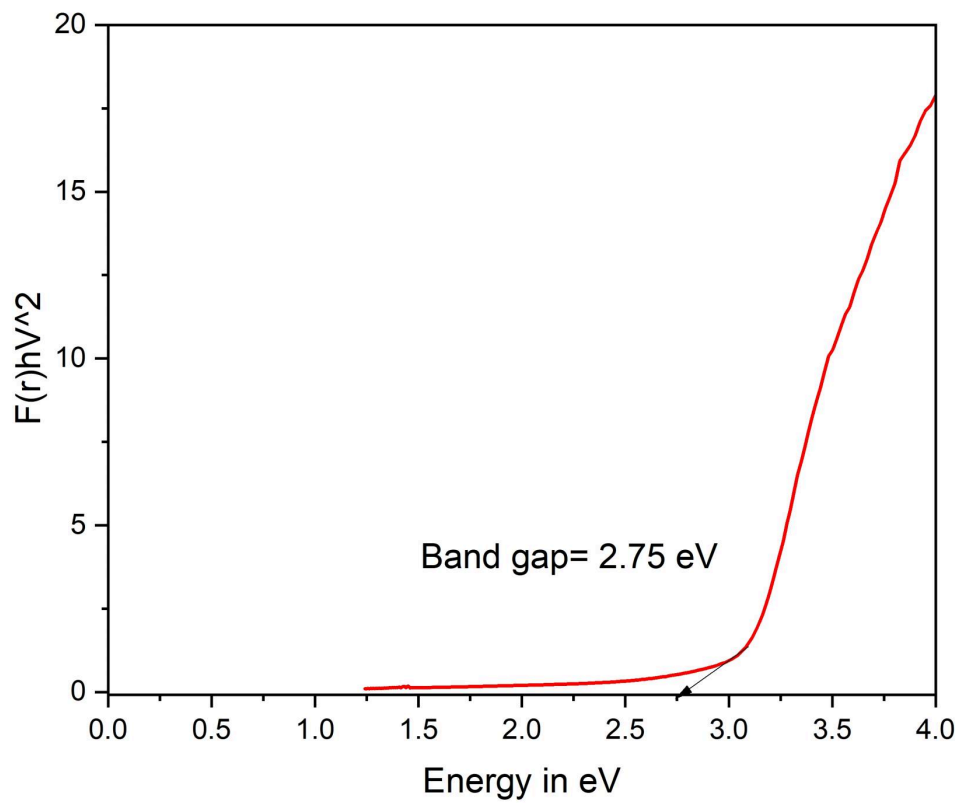


Fig: 5.2.2: FTIR spectra of the pure graphitic carbon nitride (CN), Carbon (Cs) and 1% Pt (CN/C/Pt).

5.3 DRS

The band gap for C_3N_4/C doped material is calculated using Kubelka-Munk function from Diffuse reflectance data. It is seen from the fig 5 3, the band gap was found out to be 2.75 eV.



5.4 PHOTOCATALYTIC ACTIVITY

The photocatalytic experiment was performed for 6hrs. The pure graphitic carbon nitride shows low hydrogen activity of $6.8205 \mu\text{molg}^{-1}\text{h}^{-1}$. This is because of the recombination of holes and electrons. But the CN/C/Pt catalyst shows $31.37 \mu\text{molg}^{-1}\text{h}^{-1}$ of hydrogen activity which is the highest among all the other photocatalyst used. This confirms that the electron-hole pairs produced doesn't combine rapidly as in the case of pure graphitic carbon nitride due to the presence of carbon materials.

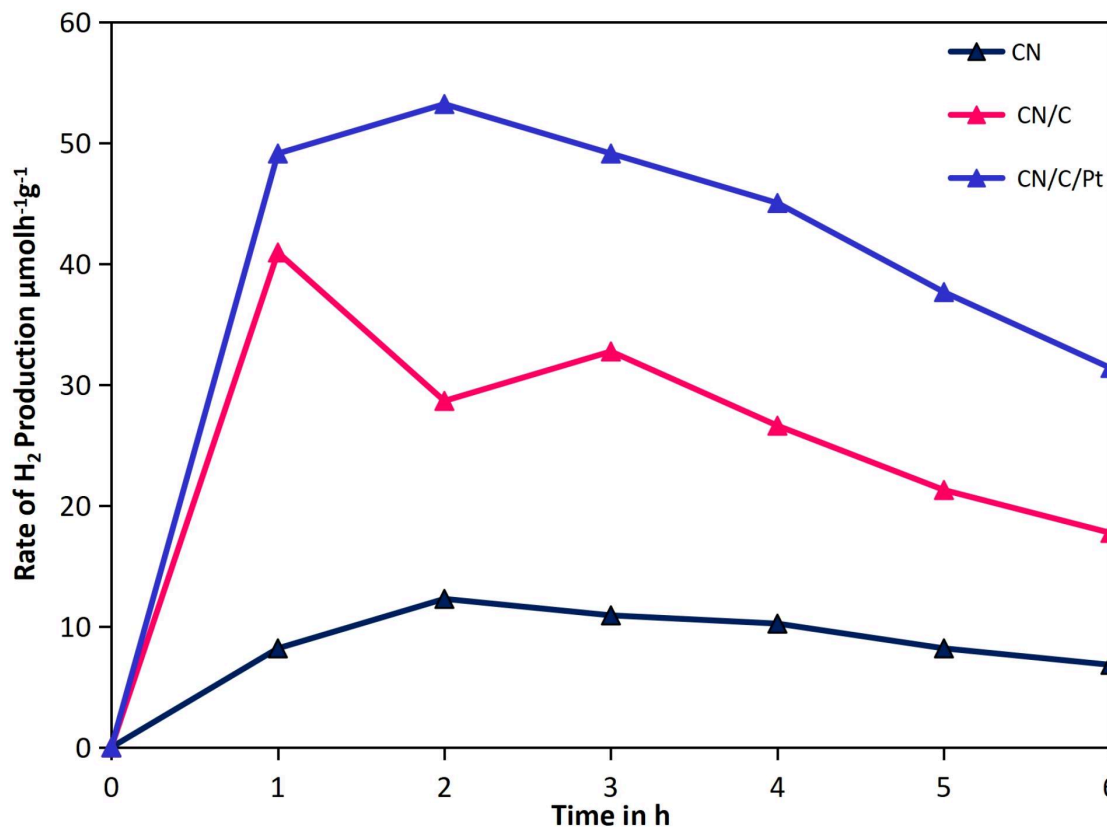
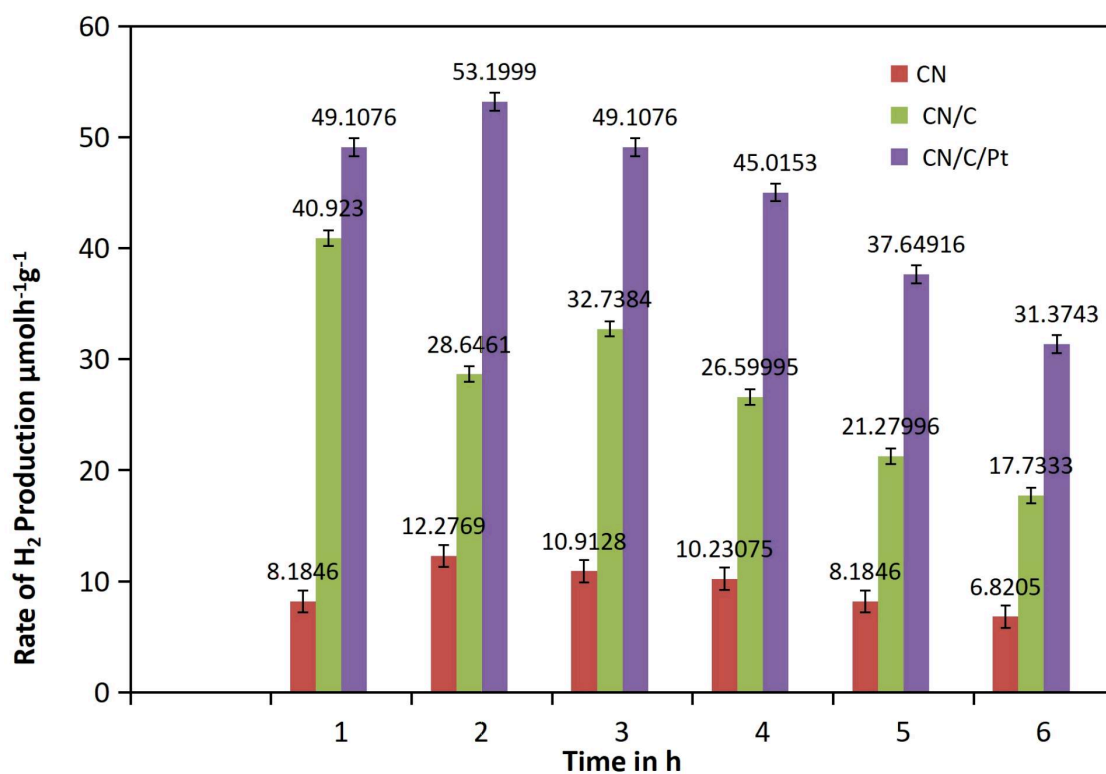


Fig. 5.4: represents the comparison of hydrogen activity of the various nanocomposites and pure graphitic carbon nitride.

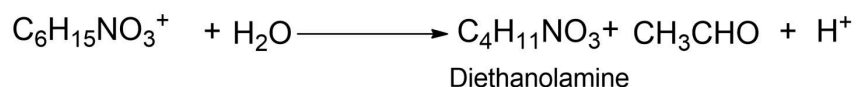
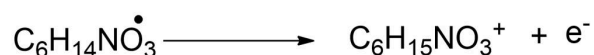
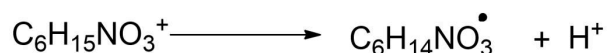
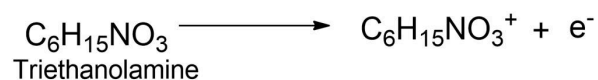
CN/C/Pt shows a elevated hydrogen evolution at the 2 hours of light irradiation having an activity of $53.1999 \mu\text{molg}^{-1}\text{h}^{-1}$. Similarly, the CN/C catalyst peaked the hydrogen evolution of $40.923 \mu\text{molg}^{-1}\text{h}^{-1}$ at the 1 hour of irradiation. During the 6-hour process the hydrogen activity for the photocatalyst tends to increase in the beginning but decreases eventually at the end.



5.5. PHOTOCATALYTIC MECHANISM

In the process of H₂ evolution reaction over C/g-C₃N₄ photocatalyst, the g-C₃N₄ in CN/C/Pt is excited under the irradiation of visible light and then produces electron-hole pairs. In g-C₃N₄ the problem found to be the rapid recombination of electron-hole pairs, but in this nanocomposite the photogenerated electrons in the conduction band (CB) of g-C₃N₄ would be easily transferred to the surface of Carbon n and reduction of H₂O to H₂ in the C/C₃N₄/Pt composite takes place due to the intimate contact with the Carbon nanodots. The holes in the valence band (VB) of g-C₃N₄ are quickly quenched by a TEOA sacrificial agent. The presence of CNDs accelerates the separation and transfer of photogenerated electrons of g-C₃N₄. Thus resulting in the enhanced photocatalytic activity in the H₂ generation reaction.

Triethanolamine as sacrificial agent



The triethanolamine acts as a sacrificial agent which scavenges the holes and gets oxidized there and enriching the electrons in the photocatalyst. The water is oxidized at the holes to produce protons. This process is repeated to produce more no. of protons which then due to electrostatic attraction combines to produce hydrogen.

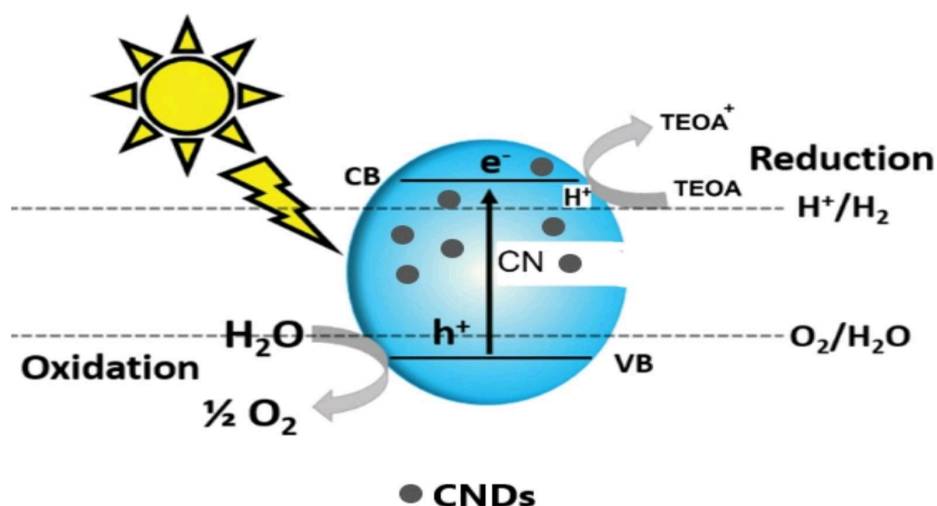


Fig: 5.5 Schematic water splitting mechanism by CN/C/Pt nanocomposite in the presence of TEOA under visible solar light

CHAPTER 6

SUMMARY AND CONCLUSION

Composite photocatalysts based on g-C₃N₄ and CNDs were prepared by assembling Cs with g-C₃N₄ by hydrothermal approach, the photocatalytic generation of H₂ over g-C₃N₄/Cs composites under visible light increased dramatically.

- The X-ray diffraction of the sample shows the peaks at 27.7 and 13.2°
- The FTIR shows the vibrational frequencies 3600-3000, 2940, 2879, 1700, 1200, 810 of functional groups N-H, C-H, -COOH, C=N, C-N, Triazine units respectively.
- SEM image displays lamellar structure of graphitic carbon nitride and graphitic carbon nitride possess tri-s-triazine structure.

The optimized composite catalyst, C₃N₄/C/Pt exhibited the higher photocatalytic performance than pure the g-C₃N₄. The dramatically improved photocatalytic performance was attributed to the fact that the CNDs act as electron reservoirs to trap the electrons for improving charge separation efficiency and light harvesters to enhance the visible light absorption. With the help of triethanolamine as a sacrificial agent that scavenges the holes and preventing the recombination of the H₂ and O₂ molecules and thereby increasing the photocatalytic performance. This study demonstrates that CNDs are active components for improving photocatalytic performance of g-C₃N₄ and provides novel inspiration in developing g-C₃N₄-based hybrid photocatalysts by loading other nanodots materials.

REFERENCES

1. Alwin, E., Kočí, K., Wojcieszak, R., Zieliński, M., Edelmánová, M., & Pietrowski, M. (2020). Influence of high temperature synthesis on the structure of graphitic carbon nitride and its hydrogen generation ability. *Materials*, 13(12), 2756.
2. Colmenares, Juan C., Agnieszka Magdziarz, Maria A. Aramendia, Alberto Marinas, José M. Marinas, Francisco J. Urbano, and José A. Navio. "Influence of the strong metal support interaction effect (SMSI) of Pt/TiO₂ and Pd/TiO₂ systems in the photocatalytic biohydrogen production from glucose solution." *Catalysis Communications* 16, 1, 2011, 1-6
3. Denisov, N. M., Evgenii Borisovich Chubenko, V. P. Bondarenko, and V. E. Borisenko. "Synthesis of oxygen-doped graphitic carbon nitride from thiourea." *Technical Physics Letters* 45 (2019): 108-110.
4. Guangxia Li, Hongmei Cao, Hongmei Zeng, Kewei Liu, Yu Zhang, Huihua Gong, , Lin Zhong, , , Hongjian Yan, Synthesis of graphitic carbon nitride by heating mixture of urea and thiourea for enhanced photocatalytic H₂ production from water under visible light, *International Journal of Hydrogen Energy*, 42, 2017, 143-151.
5. Konstantinos C. Christoforidis, Zois Syrgiannis, Valeria La Parola, Tiziano Montini, Camille Petit, Elias Stathatos, Robert Godin, James R. Durrant, Maurizio Prato, Paolo Fornasiero, Metal-free dual-phase full organic carbon nanotubes/g-C₃N₄ heteroarchitectures for photocatalytic hydrogen production, *Nano Energy*, 50, 2018, 468-478,
6. Li, Yuexiang, Kai Zhang, Shaoqin Peng, Gongxun Lu, and Shuben Li. "Photocatalytic hydrogen generation in the presence of ethanolamines over Pt/ZnIn₂S₄ under visible light irradiation." *Journal of Molecular Catalysis A: Chemical* 363 (2012): 354-361.

7. Lin, Wen-Churng, Wen-Duo Yang, I-Lun Huang, Tser-Son Wu, and Zen-Ja Chung. "Hydrogen Production from Methanol/Water Photocatalytic Decomposition Using Pt/TiO₂- x N x Catalyst." *Energy & Fuels* 23, no. 4 (2009): 2192-2196.
8. Malik, R., & Tomer, V. K. (2021). State-of-the-art review of morphological advancements in graphitic carbon nitride (g-CN) for sustainable hydrogen production. *Renewable & Sustainable Energy Reviews*, 135, 110235,
9. Sheng Xiong, Rongdi Tang, Daoxin Gong, Yaocheng Deng, Jiangfu Zheng, Ling Li, Zhanpeng Zhou, Lihua Yang, Long Su, Environmentally-friendly carbon nanomaterials for photocatalytic hydrogen production, *Chinese Journal of Catalysis*, 43, 2022, 1719-1748.
10. Yuan, L., Han, C., Yang, M. Q., & Xu, Y. J. (2016). Photocatalytic water splitting for solar hydrogen generation: Fundamentals and recent advancements. *International Reviews in Physical Chemistry*, 35(1), 1-36.
11. Zhang, Guigang, et al. "Polycondensation of thiourea into carbon nitride semiconductors as visible light photocatalysts." *Journal of Materials Chemistry* 22.16 (2012): 8083-8091.
- 12 Zhou, Meihua, Yuexiang Li, Shaoqin Peng, Gongxuan Lu, and Shuben Li. "Effect of epimerization of d-glucose on photocatalytic hydrogen generation over Pt/TiO₂." *Catalysis Communications* 18 (2012): 21-25.