Original Article

http://www.tjbac.tmu.ac.in

TMU Journal of Basic & Applied Chemistry
Vol.2
January-December, 2022: pp. 1-12.
ISSN 2583-1518 (Online)

Nanostructured Graphitic Carbon Nitride: A Novel Material for Water Purification

Abstract
Graphitic carbon nitride (GCN) is a material of potential in the field of water purification. Due to the favourable structures and functional groups present, the material becomes very effective in removing different toxic dyes from water by catalysis and adsorption techniques. In recent time GCN has attracted the attention of the researchers because of different important features like its two dimensional structure with very high surface area low cost and high production yield synthesis techniques and other. In this work, efforts have been given to understand the negative impact of over using textile dyes in different industries like paper, textile, paint or other. Also the common ways and means by which these dyes may be removed from water mainly by adsorption as well as photo-catalysis have been investigated.
Substantial study has been done in order to understand basic theories behind both the processes and to study the basic reaction kinetics involved in such processes. In this regards graphitic carbon nitride has been chosen as a material of potential and its use as water purifier has been described in depth.

Keywords : graphitic carbon nitrides, nanostructure, water pollution, dyes, catalysis, adsorption

A. Ved*

Corresponding Author Affiliation
Department of Physics
Faculty of Engineering and Computing Sciences
Teerthanker Mahaveer University
Moradabad, UP 244001
E-mail: ayushved342@gmail.com
Ph No.+919528793915

Received on 06.11.2021
Accepted on 31.12.2021

Introduction

Nanotechnology is an interdisciplinary science in which material scientists, mechanical and electronic engineers, biologists, chemists & physicists work together to extend the nanoscale boundaries. Nano is a Greek word, which means micro or small. Every particle, whose size is 100 nm or smaller is considered a nanoparticle. Nanoscience is the study of the fundamental principles of molecule and structure with at least one dimension roughly between 1 & 100nm.

Nanomaterials found its application in several fields of extreme importance that include energy, defence, communication, medicine, construction, filtration and many more. Another very important aspect of nanotechnology is its environmental aspect. Nanotechnology can solve the problem of environmental pollution specially the problem of water pollution. There are several nanomaterials which have proved its potential in the field of environment specially in addressing the water pollution problem. These materials include carbon nanotube, graphene, zinc oxide, titanium di-oxide and many more. Graphitic carbon nitride (GCN) is one of the materials of extreme interest in this regard. The water pollutant may be classified into organic large molecules, heavy metals, textile dyes and others.

The presence of amine groups at the edges of the GCN motif due to deficiency in polymerization and condensation reactions during synthesis process render structural defects in GCN [Zhu Jet.al,2014; Das Det.al,2017] making it favourable for removal of different water contaminant. As stated by Zhu et al., these defects encourage delocalization and relocalization of electrons on the GCN surface thereby rendering its impressive surface properties including Lewis base functionalities and electron-rich characteristics (Zhu Jet.al,2014) . All these properties accompanied with thermal and chemical stability are the primary reasons behind the catalytic activity of GCN.

Owing to the suitable wide band gap semiconductor nature along with appropriate CB and VB redox edge potentials and ability to harvest photons corresponding to the visible range. GCN acts as an efficient photocatalyst material for degradation of dyes. However, bulk GCN suffers from rapid electron-hole charge carriers' recombination, moderate surface area, and low quantum efficiency along with not enough utilization of solar light, all of which adversely affects its photocatalytic efficiency (Sun and Liang, **2017**). This is compensated by structural and morphological modifications as performed and reported by many researchers.

Paul et al. showed that pristine GCN synthesized from urea at a temperature of 550°C could effectively degrade 10 ppm of MB dye aqueous solution with a rate constant 'k' value of 0.0081 min^{-1} and GCN dosage of 0.01 g/100 mL under visible light irradiation (200W Xenon lamps) (Paul DR et.al,2019) . Similarly another report by Paul et al. revealed the extensive utilization of pure GCN in degradation of both cationic (RhB and MB) and anionic (MO) dyes (Paul DR,2020). Gu et al. synthesized hierarchically porous GCN from melamine exhibiting an impressive surface area of 109.3 m^2/g for effective visible-light assisted degradation of MO with a 'k' value of 0.69 h^{-1} (Gu S, et.al.2014).Metal nanoparticles suffer from many drawbacks which restrict their practical applicability. Nobel metal nanoparticles are difficult to synthesize, not at all cost-effective, poorly available, unstable under chemical conditions, and most importantly cannot be reused or regenerated due to their high tendency of agglomeration (Veisi H,2019). These disadvantages led to the incorporation, immobilization and anchoring of these metal nanoparticles into carbon-based polymeric matrix to improve their functionality and stability (Veisi H et.al.,2019; Li J et.al.,2012; Zhang P et.al.,2011).

GCN in its pristine and functionalized forms has been extensively applied for the complete removal of dye pollutants from water environment following adsorption technique. However, the moderate surface area of bulk GCN is not suitable enough for the effective adsorption of dyes on its surface. This led to the fabrication of mesoporous GCN and GCN nanosheets with increased surface area and surface-active sites.

Yousefi et al. performed oxidation of GCN nanosheets by Hummer's method and subsequently utilized these samples for the removal of various textile dyes like MB, RhB, MO and others (Yousefi M,2019). Bhowmik et al.,2015, supported Au nanoparticles on GCN sheet which were effectively employed for the removal of cationic MB and RhB and anionic MR from water environment (Bhowmik T et.al,2015). Removal efficiency of 91% in 380 min and 90% within 420 min was achieved for RhB and MB respectively. Zou et al. fabricated a novel composite of GCN and β-cyclodextrin which showed improved adsorption of MO dye at an acidic pH compared to pristine GCN (Zou Y et.al.2016).In this mini review the different aspects of GCN for water purification have been studied. Here I have mainly studied the efficiency of GCN in removing textile dyes from water.

Basic Ideas of Textile Dyes

What are Dyes?

The substance which coloured the substrate through chemically bonds to the substrate on which applied is called Dye. These dyes are distinguished from the pigment which is not chemically bond to the material which we want to colour. Chemical structure of indigo dye and its corresponding digital images has been shown in **Fig.1**

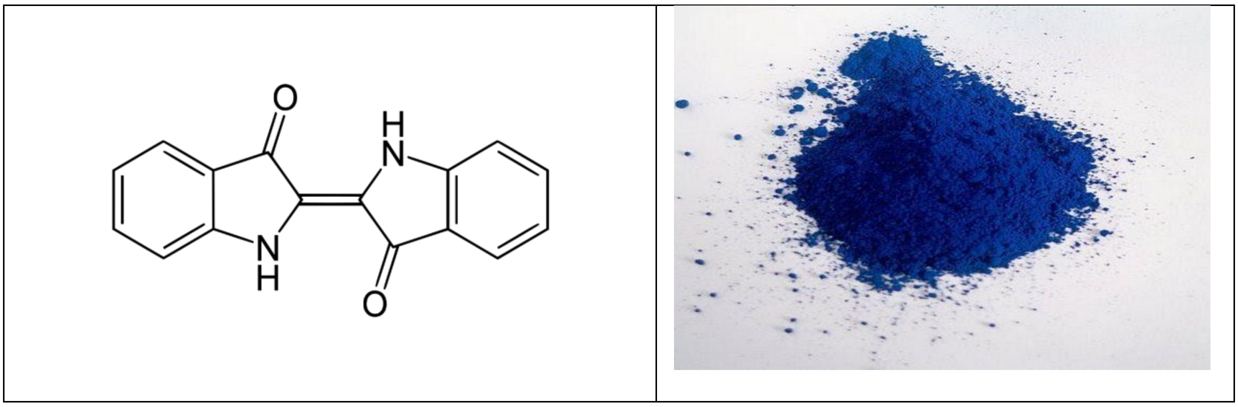

Fig.1: Chemical structure of indigo dye and its corresponding digital images

The dyes may be divided into two types one is natural and other is synthetic or man-made.   natural dyes are mainly derives from different plant sources- roots, berries, bark of tree, leaves, wood, fungi and lichens etc. and we are depending on the nature to get dyes to dye the substance like cloths, tomb, building, caves etc until 1800 A.D. After this man can able to make synthetic dyes. Today we are mainly use synthetic dyes because synthetic dyes production is taken less time to that of making process of natural dyes. Synthetic dyes are mainly obtained from the petrochemicals and this method is the first man-made synthetic dye. This method firstly used by J. Puller and Sons in Scotland. **Chart 1** describes the broad classification of textile dyes.

Water pollution by Textile dyes

Human activities over the last few decades have led to the exponential increase in the environmental crisis that the world is facing right now. Rapid emergence of numerous industries in order to meet the needs of the fast growing world population has resulted in severe negative impacts on the natural resources of the planet. Water resource, the most important resource for the survival of all living organisms, is currently being drown in chemical wastes emitted from countless manufacturing industries. Toxic chemical compounds discharged from textile, printing, tannery, dye manufacturing, food-processing and cosmetic industries are the primary sources of hazardous effluents with apparel industries solely contributing to approximately one-fifth of the planet's total water pollution.

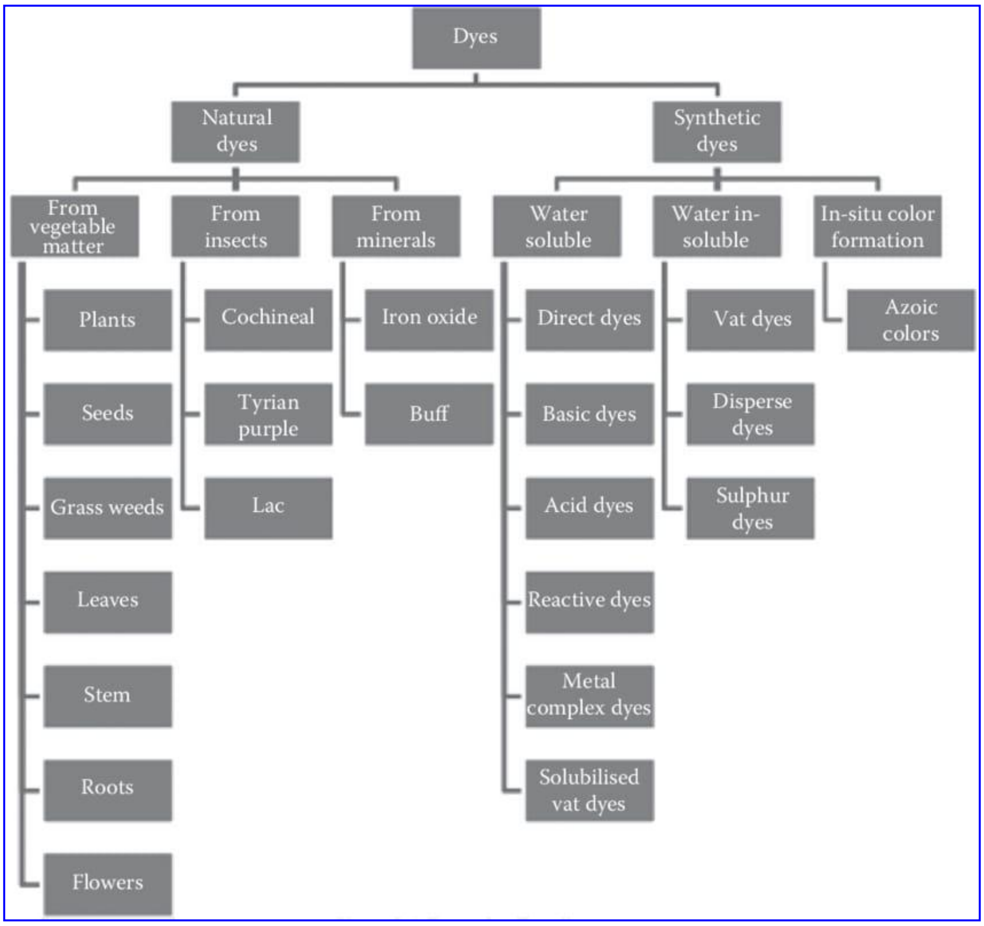

Chart 1: Classification of dyes and their characteristics

Textile dyes are considered to be the most perilous pollutants among the numerous types of complex organic chemical compounds that comprise the wastewaters emitted from textile industries which when released into the environment without proper treatment results in drastic fatal effects on aquatic ecosystem and human beings. The synthetic non-biodegradable dyes can cause acute detrimental effects on aquatic bio-organisms and aquatic plants by blocking the sunlight from reaching the depths of water-bodies, causing hindrance to the photosynthetic activities, depleting the oxygen level required for their survival, and stimulating the growth of unwanted algae on water surface. The effects these pollutants can cause on human health are of grave concern. While most of the commonly used textile dyes reportedly cause dysfunctions of the vital human organs like kidney, liver, brain, and reproductive system, many are also found to be mutagenic and carcinogenic in nature. Along with these, dyes can also lead to allergic dermatitis, skin itching and irritation, and in cases of excessive exposure can significantly hamper the central nervous system. **Table 1** summarizes basic classifications of few commonly used dyes.

Table 1: Basic classifications of few commonly used dyes

Types of dyes	Classification of Dyes		Characteristics	Examples
Cationic	Dyes with delocalized charge	Methine	Undergo dissociation into positive ions under soluble condition. Composed of substituted aromatic groups Exhibit superior solubility in water Possess bright colour shade They are types of alkaline dye	Rhodamine B, Methylene Blue, Crystal Violet, Basic Blue 41 etc.
		Streptocyanine		
		Hemicyanine		
		Enamine		
	Dyes with localized charge	Azo		
		Anthraquinone		
		Phthalocyanine		
		Perinone		
		Nitro		
Anionic	Direct Dyes		In aqueous medium they behave as acids Form negative ions upon undergoing dissolution Highly soluble in aqueous media Exhibit complex structures They have components of acidic groups like SO_3H and COOH	Methyl Orange, Rose Bengal, 4-Nitrophenol, Congo Red etc.
	Acid Dyes			
	Reactive Dyes			
Non-Ionic	Disperse Dyes		They do not form any charged ions when dissolved in aqueous medium Low solubility in water	Disperse Red 60, Direct Green 97

Approximately, 40 % all over the world used chlorine contained colorants that are commonly known as colorants contain organically bound chlorine a known carcinogen. In the wastewater there are mostly organic material are present, there are many elements which is used to disinfect the water but chlorine is the best element to disinfectants the harmful material, it is best primary element for textile industry for the water treatment. These chemicals get evaporated and are inhaled during breathing causing several serious disease especially to kids and infants even before their birth. **Fig.2** shows how the unorganized use of dyes polluting the environment

Fig.2: Unorganized use of dyes polluting the environment

Processes for removing textile dyes from water

Photo-catalysis

Photocatalysis (PC) is the speeding up of a photon induced reaction in the presence of a catalyst. In catalysed photocatalysis, light is absorbed by an absorbed substrate. It is the process in which light source is interact with surface of semiconductor materials this is photocatalysis. It produces the electron pair in conduction band and hole pair in valence band when the catalyst interacts with light of sufficient energy.

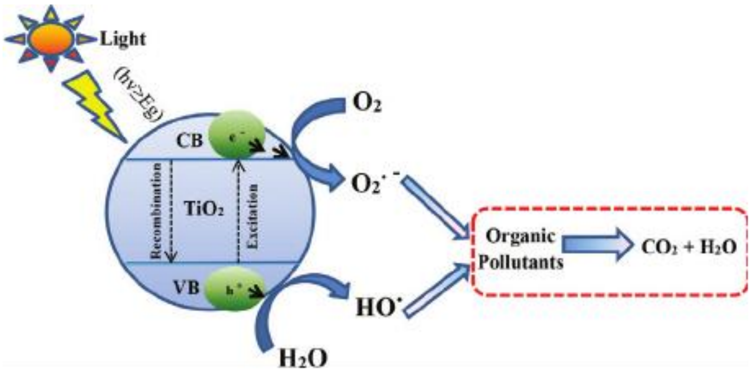

Fig.3: Schematics of basic photocatalysis process

It is to be noted that it is the one of the best solutions for producing H_2 from the water and to remove the organic pollutant material from the environment by the use of sunlight. TiO_2 is the best and cheaper nanomaterial for the process photocatalysis. **Fig.3** shows the basic catalysis process schematically

As we discuss above, the photocatalysis is produce electron-hole pair when a photocatalyst absorb photons. When the light is illuminated the electrons becomes excited which are present in the valence band. These excited electrons thus transfer excess energy to the electrons reciding in the conduction band of the catalyst creating electron hole pair through the process called photo excitation. The electron and hole which are produced react with the absorbed oxygen and water on the surface of catalysis to form reactive oxidizing molecules that again react with the pollutants and oxidize into Carbon Dioxide and H_2O through the few intermediate steps. The photochemical reaction does not modify the catalyst, and it is not consumed by it.

Adsorption

Adsorption is the process in which the molecular species deposit on the surface. The substances which absorbed on the surface is called absorbate while the substance absorbed is called adsorbent. The adsorbed are remove from the surface of substance is called desorption. The phenomena of adsorption are surface phenomena i.e., this process takes place only on surface of adsorbent. Adsorption is affected by the temperature; this process is exothermic. In simple word, deposition of substance on the surface is known as adsorption. There are two types of adsorption on the basis of interaction force between adsorbate and adsorbent: Physical adsorption (known as physisorption) and chemical adsorption (known as chemisorption).

Adsorption study is one of the easiest processes to test the dye removal of a certain material by the process under interest. It simply requires the uniform contact between the remover and the water with contaminations for a certain time. During this contact the dyes get adsorbed onto the material and the water slowly becomes contamination free. The process depends on time and other several parameters like material itself, material shape and size, material amount, initial dye concentration, types of dyes and sometimes on the pH value of water as well. The basic laboratory process for measuring the adsorption is rather simple and doesn't differ much from that of photo-catalysis. The process simply needs a closed container and the contaminated water sample is taken into a beaker placed in magnetic stirrer. A small part of the contaminated water (may be 10 ml around) is kept before addition of the sample which will work as reference sample i.e. the sample with initial concentration of contamination. Then as stated before the sample is added to the contaminated water and thoroughly stirred in order to uniform dispersion of the sample into the water. After a certain interval (that depends on the response of the certain dye to the certain remover but may be 30 minutes for instance) a small part of the sample (may be 10 ml) is filtered and the filtrate is kept for further use. In this way the process gets continued. The qualitative confirmation of the removal performance can easily be estimated from the visual colour change of the water sample just like in the process of photo-catalysis. The quantification of the removal performance may be done with the help of a UV-Visible spectroscopy. The reason is that every dye materials have specific colors in visible range and thus all of them have sharp absorption peak somewhere in the visible region. The intensity of this peak will be decreased as per the relative presence of the dyes in the water.

Another important aspect of the entire process is the initial concentration of the dye. It has been seen that the removal efficiency of any material through adsorption is very much dependent on the initial concentration of the dye and gets decreased when the initial concentration gets higher. Now if the work is a field based work then there is no restriction on the concentration of the contaminant however for laboratory based work there is a universally accepted initial concentration and the corresponding process involves taking raw dyes then diluted it to the stock solution and further diluted it up to the test solution of suitable molarity and use it for actual experiment purpose. The detail process is as follows (though there are reports that many groups do not follow the same and set their own initial concentration level):

Adsorption Isotherm

Generally, adsorption theory is explained by isotherms. It is because the temperature plays important role during the adsorption process. There several isotherms are explained below:

Freundlich Theory

Freundlich adsorption is one of the most widely used technique to quantify the adsorption process which involves the adsorption of fluids by solid as a function of system's pressure. The expression of Freundlich theory's equation:

$$\frac{x}{m} = kP^{\frac{1}{n}} \qquad (1)$$

n>1; x = adsorbed gas mass; m= adsorbent mass; p= pressure; n= constant at a given temperature.

In above equation, taking logarithm on both sides,we get,

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log P \quad (2)$$

The graph of above equation is plotted as in the below **Fig.4.**

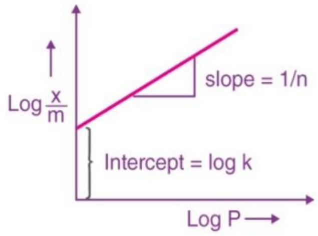

Fig.4: Graphical representation of Freundlich isotherm

Langmuir theory

This theory was proposed in 1916 by Irving Langmuir. He proposed that adsorption of a gas on the solid surface one by one at a particular site of preference. It's predicted that all adsorption sites are identical and the molecule of gas show the ability to bind with one site which is independent of may or may not occupied the neighbouring sites. It's also expected that there's a dynamic equilibrium between adsorbed and non-adsorbed gas molecules. A linear adsorption as well as maximum surface coverage is predicted by Langmuir isotherm especially at low adsorption densities.

Adsorption Mechanism

The situation on the surface edge of any material is not the same as the situation in interior. For example, molecules in a liquid's interior are entirely surrounded on all sides by other molecules and therefore the molecules exerted intermolecular force in all direction shown in below figure (a). Schematics of adsorption mechanism has been shown in **Fig.5**

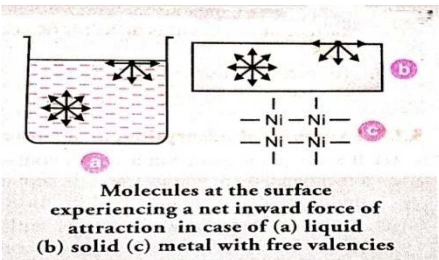

Fig.5: Schematics of adsorption mechanism

Since, the molecule on the surface of liquid is surrounded by a large molecule in the liquid phase and some molecules in the vapour phase that is at the surface of liquid. From this, the molecule, at the surface of liquid experience some attraction force (say inward direction force) which may due to the surface tension. So, the force of attraction is experience by the molecule at the surface of solid shows in figure (b). Besides this, in case of some solid like transition metal (say Nickel), there are no utilize of free valencies at the surface which show in figure (c). Liquids and solids have the ability of attracting molecules of other substances come into contact due to residual inward direction force of attraction or some free vacancies at the surface.

Introduction to Graphitic Carbon Nitride (g-CN)

The general formula of g-CN is g-C3N4. It is material that contains carbon, nitrogen and little hydrogen as impurity. These are connected through tris- triazine-based pattern. It is very important organic material which is used mostly as semiconductors. It is an allotropes of carbon nitride with very high stability due to its unique structure and is hard than the other carbon nitride and also show chemical stability at more than temperature 500 centigrade. It is a novel nanomaterial which has many uses in solve the problem of environmental pollution and also used for water filtrations. It has some unique optical properties that make it a material of high potential in the field of opto-electronics. The colour of the crystals of graphitic carbon nitride is pale yellow.

There are two structures are proposed by the scientists which act as smallest building unit of g-CN. In one type g-CN is made of triazine and the other is made of the tris-s-triazine as shown in **Fig.6**. The red dotted parts show in figure (a) & (b) the basic unit of the graphitic carbon nitride: - Triazine and Tri-s-Triazine (Heptazine) respectively. The structure of Graphitic Carbon Nitride with the Tri-S-Triazine is most stable than the structure with the triazine so Tri-S-Triazine is most accepted as the basic unit of Graphitic Carbon Nitride.

Preparation of g-CN

The building block of g-CN is developed by reaction between cyanamide, dicyandiamide and bases. The first off shaped chemical compound C_3N_4 structure, melon, with pendant amino teams, may even be extremely ordered chemical compound any reaction which leads to additional condensed and there are defects in few C_3N_4 molecule, connected through tri-s-triazine (C_6N_7) units.

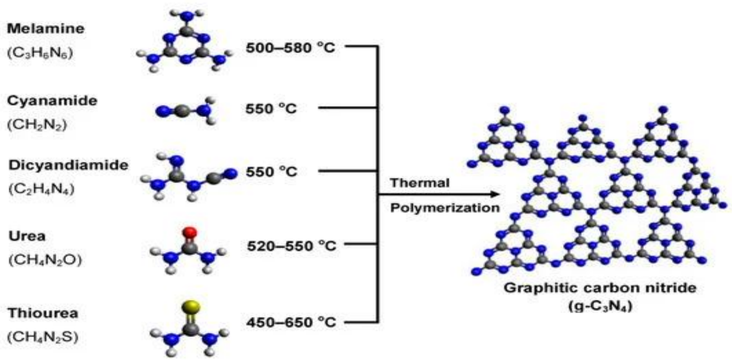

Fig.6: Basic techniques for synthesizing g-CN

Graphitic carbon contains mainly carbon and nitrogen. It is very stable polymeric semiconductor. There are many ways to synthesize $g-C_3N_4$. It is prepared by condensation at high temperature with nitrogen rich organic compound such as melamine, urea etc. and the method to prepare $g-C_3N_4$ are given below:

In below Image (**Fig.6**) there are presently several methods to prepare g-C_3N_4 by heating nitrogen rich organic compound at high temperature and undergo thermal polymerization then we get g-C_3N_4.Melamine is used as a cheap single source of the synthesis of g-CN by thermal condensation of melamine. This method is low cost and effective alternative which can help to produce g-C_3N_4 on large scale. Other method of synthesizing g-CN involves reaction between $C_3N_3Cl_3$ and $NaNH_2$ at a temperature as low as 200 ^oC for around 10 h or electro- deposition of suitable precursor on silicon substrate.

Properties of g-C3N4

Metal free catalyst: From the very beginning g-CN being a metal free catalyst, attracted the interest of researchers. The material contains only C and N with small amount of H as defects. Optical properties: The optical properties of g-CN are studied in details by employ UV-Vis DSR and PL spectroscopy. g-CN absorption pattern similar to organic compound with optical gap around 2.07 and thus an adsorption edge at around 420 nm. Stability: By the analysis of thermogravimetric of graphitic carbon nitride, this material shows the stability up to the 600°C. Due to this property of GCN is used as heterogenous catalysis under extreme condition.Graphitic Carbon Nitride is highly porous material unlike graphene. It is non-toxic, low-cost, metal free element.

Application of g-CN

g-CN shows fascinating optical and other properties as well as excellent chemical and thermal stability. It is material of low cost and high yield and found its application in many purposes such as photocatalyst, for sensing, for imaging, for g-C3N4 based LED, etc.It is commercially available in market by the name of brand-Nicanite. As per the report it is best storage material to store hydrogen. Due to it micro sized graphitic form it is used for coating such as tribological, biocompatible medical, chemically inert etc. and it is used for coating insulators. It is also used for the energy battery storage. Carbon Nitrides has special properties of semiconductor, with very good catalytic efficiencies. There are important applications are stated as follows:

(a) Carbons Nitride can shows photocatalysis and thus give rise water splitting. (b) g-CN acts as a catalyst for oxidation reaction. (c) Carbon Nitride has applications in Hydrogenation reactions. (d) Carbon Nitride can act as a basic catalyst. (e) Carbon Nitride has application in NO decomposition. (f) Carbon Nitride can activate π-bonds and Aromatic systems.

Conclusion

In this work I have tried to summarize the extensive applications of g-CN in the areas of water purification. It has been shown that g-CN is one of the most effective materials in the field of removal of dye from water and thus in water purification. In this context, along with the reported result from other workers few of our mentor's own experimental data has been shown that have more rigidly established our claim. Adsorption properties of Graphitic carbon nitride has been shown that it is one of the best nanomaterial to remove organic pollutants. In all the cases, the material shows its efficient properties. All these results as summarized here clearly indicated that researchers should put systematic effort to think about the development of Graphitic Carbon Nitride based water filter and adsorption that they will certainly be as effective as any of the currently used material with further advantages in its easy and cost-effective technique.

References

Bhowmik T, Kundu MK, Barman S.2015. Ultra small gold nanoparticles–graphitic carbon nitride composite: an efficient catalyst for ultrafast reduction of 4-nitrophenol and removal of organic dyes from water. *RSC Adv.*, *5*(48):P 38760-38773.

Das D, Banerjee D, Pahari D, Ghorai UK, Sarkar S, Das NS. **2017.** Chattopadhyay, K. K. Defect induced tuning of photoluminescence property in graphitic carbon nitride nanosheets through synthesis conditions. *J. Lumin.*, *185:* 155-165.

Gu S,Xie J, Li CM.2014. Hierarchically porous graphitic carbon nitride: large-scale facile synthesis and its application toward photocatalytic dye degradation. *RSC Adv.*, *4*(103): 59436-59439.

Li J, Liu CY, Liu Y.2012. Au/graphene hydrogel: synthesis, characterization and its use for catalytic reduction of 4-nitrophenol. *J. Mater. Chem.*, *22*(17): 8426-8430.

Paul DR, Sharma R, Nehra SP,Sharma A. **2019.**Effect of calcination temperature, pH and catalyst loading on photodegradation efficiency of urea derived graphitic carbon nitride towards methylene blue dye solution. *RSC Adv.*, *9*(27): 15381-15391.

Paul DR, Nehra SP.2020. Graphitic carbon nitride: a sustainable photocatalyst for organic pollutant degradation and antibacterial applications. *Environ. Sci. Pollut. Res.* .

Sun S, Liang S. **2017.** Recent advances in functional mesoporous graphitic carbon nitride (mpg-C_3N_4) polymers. *Nanoscale*.*9*(30): 10544-10578.

Veisi H, Kazemi S, Mohammadi P, Safarimehr P, Hemmati S. **2019.**Catalytic reduction of 4-nitrophenol over Ag nanoparticles immobilized on Stachys lavandulifolia extract-modified multi walled carbon nanotubes. *Polyhedron*, *157*: 232-240.

Yousefi M, Villar-Rodil S, Paredes JI, Moshfegh AZ.2019. Oxidized graphitic carbon nitride nanosheets as an effective adsorbent for organic dyes and tetracycline for water remediation. *J. Alloys Compd.809:* 151783.

Zhang P, Shao C, Zhang Z, Zhang M, Mu J, Guo Z, Liu Y.2011. In situ assembly of well-dispersed Ag nanoparticles (AgNPs) on electrospun carbon nanofibers (CNFs) for catalytic reduction of 4-nitrophenol. *Nanoscale*, *3*(8): 3357-3363.

Zhu J, Xiao P., Li H. **2014.**Carabineiro, S. A. Graphitic carbon nitride: synthesis, properties, and applications in catalysis. *ACS Appl. Mater. Interfaces*, *6*(19): 16449-16465.

Zou Y, Wang X, Ai Y, Liu Y, Ji Y, Wang H, Wang, X.2016. β-Cyclodextrin modified graphitic carbon nitride for the removal of pollutants from aqueous solution: experimental and theoretical calculation study. *J. Mater. Chem. A*, *4*(37): 14170-14179.