

**EFFECT OF ALKALI METALS DOPING ON GRAPHITIC CARBON
NITRIDE (G-C₃N₄)**

Submitted in partial fulfilment of the requirements for the award of

Master of Science in Chemistry

by

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DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

CATEGORY -1 UNIVERSITY BY UGC

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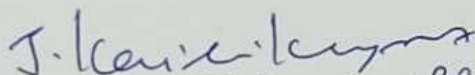
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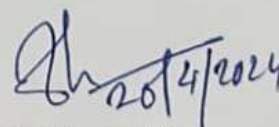
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DECLARATION

I am **K. NAWIN KUMAR (42910013)** hereby declare that the Project Report entitled **“EFFECT OF ALKALI METALS DOPING ON GRAPHITIC CARBON NITRIDE (G-C₃N₄)”** done by me under the guidance of **Dr. SAHELI KARMAKAR M.Sc., PhD.**, Assistant Professor, Department of Chemistry, Sathyabama University is submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Chemistry.

DATE:

PLACE:

SIGNATURE OF THE CANDIDATE

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ABSTRACT

In this study, we crafted Pure Graphitic Carbon Nitride (GCN) and variants doped with Alkali Metals using a two-step synthesis involving Hydrothermal and Thermal Polymerization techniques. The strategic infusion of metallic atoms into the lattice of graphitic carbon nitride (g-C₃N₄) is a recognized method to enhance its light-induced catalytic prowess. Our focus was on embedding Lithium (Li), Sodium (Na), and Potassium (K) within the g-C₃N₄ matrix, which markedly bolstered its photocatalytic capabilities. We meticulously examined the synthesized pure GCN and its alkali metal-doped counterparts through a suite of analytical techniques. **Fourier Transform Infrared Spectroscopy (FTIR)** was employed to decipher the molecular vibrational signatures, **X-Ray Diffraction (XRD)** illuminated the crystalline architecture and compositional essence, **Scanning Electron Microscopy (SEM)** revealed the surface morphology, **Ultraviolet Diffuse Reflectance Spectroscopy (UV-DRS)** elucidated the electronic band structure and light absorption characteristics, and **Photoluminescence (PL) Spectroscopy** was utilized to evaluate the materials' Photocatalytic Catalytic Activity.

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CHAPTER 1

INTRODUCTION

1.1 GRAPHITIC CARBON NITRIDE

Graphitic carbon nitride, or g-C₃N₄, is a polymeric semiconductor composed of Carbon (C), Nitrogen (N), and a small amount of Hydrogen (H). These elements are linked together in a structure featuring tris-triazine motifs. Unlike most carbon-based materials, g-C₃N₄ is rich in electrons, has alkaline surface features, and can form hydrogen bonds. The architecture of each stratum in graphitic carbon nitride is characterized by a network of carbon-nitrogen ring structures. These rings manifest as either triazine (C₃N₃) or heptazine (C₆N₇) configurations, interconnected via nitrogen atoms bonded in a sp² fashion or through NH groups. Such a distinctive structural feature endows g-C₃N₄ with its photocatalytic capabilities, opening avenues for its deployment in diverse fields, notably in the purification of the environment. Therefore, it's considered a promising alternative to traditional carbon materials for various applications. Industrial activities release hazardous substances that pose a significant risk to our environment. Consequently, innovative strategies are essential for the efficient eradication of these contaminants. Graphitic carbon nitride (g-C₃N₄) emerges as a promising solution for this challenge. Its surface is rich in chemical properties, particularly amino groups, making it suitable for ion removal.

Graphitic Carbon Nitride-based compounds are recognized for their ability to effectively adsorb dyes. g-C₃N₄ is making waves as a photocatalyst that doesn't require metals and responds to visible light, making it a game-changer in the realm of solar energy transformation and environmental cleanup. It's being harnessed for synthetic photosynthesis and purifying the environment. Its exceptional attributes such as economical production, robustness, catalytic prowess, and harmlessness are being scrutinized. g-C₃N₄ has found its place in a variety of catalytic uses, including acting as a catalyst-free of base metals for NO breakdown, serving as a benchmark in distinguishing oxygen activation sites for oxidation reactions on supported catalysts, and as a functional substance for the creation of nanoparticles.

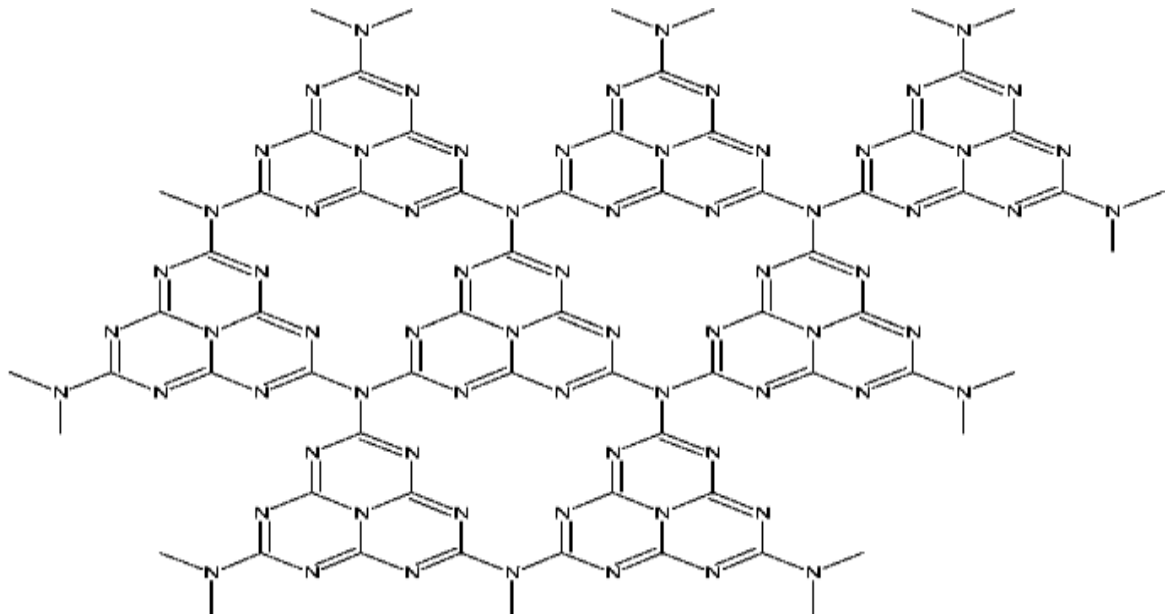


Fig:1.1: Structure of g-C₃N₄

1.2 DOPING

Doping involves deliberately adding foreign elements to a pure semiconductor to enhance its electrical, optical, and structural characteristics. These added elements, termed dopants, may possess more or fewer electrons than the semiconductor itself. The significance of this process is its capacity to boost semiconductor efficiency at standard temperatures. Since undoped semiconductors perform inadequately at ambient temperatures and cannot be utilized at extremely high temperatures, doping is essential for the practical use of semiconductor devices at normal temperatures. Introducing metal ions into a substance's framework to adjust its attributes is known as metal doping. This method can profoundly transform the material's electrical, optical, and structural traits. In sustainable energy, metal doping is pivotal. Within nanotechnology, transition metals are frequently employed as dopants to imbue nanocrystals with novel properties. In essence, metal doping is a multifaceted approach with applications spanning electronics, renewable energy, and nanotechnology, serving as a fundamental instrument for customizing material properties for specific uses.

1.3 METAL DOPED GRAPHITIC CARBON NITRIDE

Introducing metallic elements into graphitic carbon nitride (g-C₃N₄) is a widely adopted technique to boost its photocatalytic efficiency. This method entails embedding metal atoms within the g-C₃N₄ matrix. The presence of metal atoms can inhibit the fusion of photo-induced electron-hole pairs in semiconductor matrix. Metal incorporation can lead to the formation of novel active locales, potentially heightening the selectivity of reactions. The infusion of metals can modify the electronic configuration of g-C₃N₄, potentially broadening the spectrum of light absorption and improving the material's surface characteristics. Such alterations can markedly elevate the photocatalytic prowess of g-C₃N₄. Consequently, metal-infused g-C₃N₄ may be regarded as a comprehensive photocatalyst since it amalgamates the roles of both the photocatalyst and the cocatalyst within a single entity. This significantly bolsters the efficiency of charge segregation and its exploitation, culminating in superior photocatalytic performance.

1.4 ALKALI METALS

The S-block elements, the alkali metals, are positioned on the periodic table's far left. These elements are known for their extreme reactivity and tendency to donate electrons, ranking them among Earth's most reactive substances. They exhibit an **ns¹** electron configuration. The S-block elements are Lithium, Sodium, Potassium, Rubidium, Cesium and Francium. Characterized by their malleability, lustrous appearance, and low melting points, these metals are univalent and highly electropositive.

Lithium (Li): With an atomic number of 3, it has an atomic radius of 152 picometres.

Sodium (Na): It is defined by an atomic number of 11 and an atomic radius of 186 picometres.

Potassium (K): This element has an atomic number of 19 and an atomic radius of 227 picometres.

1.5 ALKALI METALS DOPED GRAPHITIC CARBON NITRIDE

Incorporating alkali metals into graphitic carbon nitride's framework, by doping augments its characteristics significantly. Such enhancement curtails the fusion of photogenerated electron-hole pairs, broadens the spectrum of light the material can harvest, and thus, amplifies its photocatalytic performance. These

improvements render alkali metal-doped graphitic carbon nitride a versatile candidate for diverse uses, spanning from light-driven catalysis to biosensing and nano enzyme applications. In our work we concentrate only on Lithium (Li), Sodium (Na), and Potassium (K) doped g-C₃N₄.



Fig:1.2: Electronic configuration of Lithium, Sodium, Potassium.

Research on modified graphitic carbon nitride, enhanced with lithium, sodium, or potassium, reveals its potential in breaking down colorants like crystal violet and methyl orange when illuminated by sunlight. These findings suggest that this modified material could be an effective catalyst activated by solar energy for the breakdown of various colorants. Upon exposure to sunlight, this semiconductor material can produce pairs of electrons and holes. These mobile charges then drive chemical reactions that degrade pollutants. This property positions the lithium, sodium, or potassium-enhanced graphitic carbon nitride as a viable option for catalysing the production of hydrogen gas using solar energy. Additionally, its ability to effectively use electrons makes it suitable for decomposing dyes.

CHAPTER 2

LITERATURE SURVEY

The pressing issues of energy scarcity and environmental pollution have brought attention to a potential global crisis that humanity must confront. Among the diverse technologies aimed at mitigating these challenges, photocatalysis has garnered significant interest for its promising applications, leveraging the abundant energy from natural sunlight or artificial indoor illumination. Photocatalysis finds widespread use in hydrogen production and the decomposition of organic contaminants. To employ this technique effectively, a proficient photocatalytic material is essential. The ideal material should feature a moderate band gap, effectively absorbing visible light and efficiently managing charges for chemical processes. Additionally, non-toxicity, abundance, and affordability are crucial factors for an ideal photocatalyst. Recently, graphitic carbon nitride (g-C₃N₄) has drawn considerable attention due to its potential applications as a photocatalyst, electrode material for fuel cells, catalyst for organic synthesis, hydrogen storage material, CO₂ capture material, and more (Devina et.al.,)

Graphitic carbon nitride (GCN), functioning as a metal-free layered polymeric semiconductor, has emerged as a potential photocatalyst owing to its distinctive optical, electronic, and physiochemical characteristics. Despite its inherent properties, the current photocatalytic efficiency of pristine GCN remains suboptimal for practical applications. Consequently, it becomes crucial to enhance GCN's photocatalytic activity through modifications. Elemental doping stands out as a straightforward and effective method for such improvements, with alkali metal ions being frequently introduced into GCN to boost its photocatalytic performance. In the realm of non-noble metal ion-doping studies for GCN, Na⁺ and K⁺ are the preferred ions, given that Li⁺ has a strong affinity for water, and Cs⁺ is too large to form a stable product. Various approaches, including calcination of a mixture of carbon nitride precursors with alkali halide and combinations involving GCN and alkali halide or alkali metal hydroxide, have been employed to intercalate Na⁺ or K⁺ into GCN. These processes have consistently shown that alkali metal ion doping contributes to increased surface area, improved crystallinity, and enhanced light absorption in GCN (Siyu Hu et.al.,)

Graphitic carbon nitride (g-C₃N₄), a metal-free polymeric semiconductor, stands out as a crucial two-dimensional material with significant potential in photocatalytic applications. However, the intrinsic g-C₃N₄ has a limitation in effectively harnessing solar energy due to its light absorption threshold around 460 nm. Elemental doping, particularly introducing alkali metal ions into g-CN, proves to be a simple and effective approach to alter the semiconductor's electronic structure. Current research predominantly explores the effects of lithium, sodium, and potassium doping on g-CN in the context of enhancing its photocatalytic properties. The inherent low photocatalytic activity of bulk g-C₃N₄ prompted the exploration of various strategies to enhance its performance. In this study, a solvothermal method was employed to prepare Na and O co-doped g-C₃N₄, effectively modifying its band structure. The introduction of oxygen into the g-C₃N₄ lattice resulted in improved light absorption and a red shift. Simultaneously, Na doping enhanced the separation and migration of photo-generated carriers under visible light. Additionally, the high surface electronegativity of (Na, O)-g-C₃N₄ facilitated its well-dispersion in pure water. This tailored approach significantly boosted the photocatalytic H₂ production activity of (Na, O)-g-C₃N₄, particularly under visible light, with an impressive apparent quantum yield of 22.3% at 420 nm (Zhitong Ge et.al.,)

GCN acting as a polymeric semiconductor material, emerges as a promising photocatalyst driven by visible light, attributed to its moderate band gap (2.7 eV) and favourable band edge positions. The common method of preparing g-C₃N₄ involves the thermal condensation of organic precursors rich in carbon and nitrogen, resulting in a multilayered structure with weak interlayer van der Waals interaction and strong intralayer covalent bonding. However, inherent challenges such as a high recombination rate of photogenerated charge carriers and a scarcity of surface active sites limit the photocatalytic efficiency of graphitic carbon nitride. To overcome these limitations, various approaches have been suggested, including doping, manipulating microstructure and morphology, coupling with other semiconductors and noble metals, and forming isotype g-C₃N₄/g-C₃N₄ junctions. Leveraging its distinctive structure, post-growth thermal treatment is commonly employed to enhance the structural and photocatalytic properties of GCN. This includes the creation of porous structures and nanosheets with diverse surface

functional groups through thermal exfoliation of bulk g-C₃N₄ in different atmospheres like air, NH₃, and oxygen (Wenjian Fang et.al.,)

Graphitic carbon nitride, denoted as g-C₃N₄, constitutes a polymeric structure comprising carbon, nitrogen, and trace amounts of hydrogen, interconnected through tris-triazine-based patterns. Distinguishing itself from the majority of carbon materials, g-C₃N₄ possesses electron-rich characteristics, basic surface functionalities, and hydrogen-bonding motifs owing to the presence of nitrogen and hydrogen atoms. Consequently, it is considered a promising alternative to traditional carbon materials in various applications. This provides a concise overview of g-C₃N₄, covering its synthesis methods with diverse textural structures and surface morphologies, and delving into its physicochemical properties. The focus then shifts to exploring four catalytic applications of g-C₃N₄: serving as a base metal-free catalyst for NO decomposition, acting as a reference material to discern oxygen activation sites in oxidation reactions over supported catalysts, functioning as a functional material for synthesizing nanosized metal particles, and operating as a metal-free catalyst for photocatalysis. The rationale behind employing g-C₃N₄ in these applications is elucidated, with the anticipation that this review will spark further exploration of novel applications for g-C₃N₄ in catalysis and beyond. Recent years have witnessed extensive exploration of g-C₃N₄ applications in catalysis, establishing its efficacy across a diverse range of reactions. This review endeavours to avoid redundancy by categorizing the applications of g-C₃N₄ in heterogeneous catalysis into three distinct perspectives (Yan Xu et.al.,)

Firstly, g-C₃N₄ is examined as a metal-free catalyst, specifically for catalysing reactions such as NO decomposition. Secondly, it serves as reference material to distinguish oxygen activation sites during oxidation reactions on supported catalysts. The 3rd aspect highlights its utility as a high surface support with abundant functional groups, facilitating the preparation of small and stable metal nanoparticles. Nano-Catalysis stands out as an exhilarating niche within nanoscience, focused on crafting catalysts at the nanoscale to govern reaction activity and selectivity. A widely acknowledged principle is that catalysts formulated at the nanoscale exhibit catalytic efficacy compared to their bulk counterparts, primarily attributable to quantum confinement effects (Junjiang Zhu et.al.)

A potassium-doped graphitic carbon nitride with tunable band gap and improved mineralization capability was synthesized using dicyandiamide monomer and potassium hydrate as precursors. Establishing an energy level match between two semiconductors is a significant factor for forming heterojunctions. The control of semiconductor nanocrystal band gaps through the grain size, known as the quantum size effect, is crucial in this context. While the size-dependent band gap of quantum dots has been extensively explored, the conventional preparation of quantum dots often involves rigorous conditions and complex procedures. An alternative, straightforward, and adaptable approach involves doping. Regular discharge of diverse organic and inorganic pollutants into the environment poses a significant threat to the food chain, impacting human, plant, and animal health. Nitrite (NO_2^-) is a noteworthy inorganic pollutant known for its high carcinogenicity to both human health and the environment (Shaozheng Hu et.al.,)

Commonly used in various applications such as additives, corrosion inhibitors, vasodilators, food preservatives, and fertilizers, nitrite concentration in drinking water should not surpass $65\text{ }\mu\text{m}$ according to WHO standards. In soil, inorganic nitrogen compounds constitute less than 5% of the total nitrogen content, prompting the addition of nitrogen-rich fertilizers to promote plant growth. Nitrite is widely recognized as a food preservative, employed in items like cheese, cured meats, fish, beer, cosmetics, and certain drugs. Alkali-metal-doped (Na^+/K^+) graphitic carbon nitride has been employed for electrochemical nitrite detection, utilizing alkali metal as an eco-friendly doping source. Graphitic carbon nitride, a polymeric semiconductor well-explored for applications like dye photodegradation, water splitting for hydrogen or oxygen production, and electrochemical chemosensors, previously faced challenges in its extensive use as an electrochemical sensor due to low conductivity (Jigyasa et.al.,)

Photocatalysis technology stands out as a promising solution to address the dual challenges of resource and environmental crises triggered by fossil fuels. The pivotal factor influencing the efficiency of photocatalysis lies in the semiconductor-based photocatalyst, requiring high activity and stability. An ideal photocatalyst should possess the capability to absorb visible light, facilitate rapid charge carrier transfer, and exhibit stability, non-toxicity, and abundance. Graphitic carbon nitride (g-C₃N₄), a recently developed polymer semiconductor with a band gap of 2.78 eV, has garnered attention for its promising features, including good visible light response activity, suitable band positions, and chemical stability. However, two main drawbacks hinder its photocatalytic activity: the relatively large band gap limits visible light absorption to wavelengths smaller than 450 nm, and the fast charge carrier recombination stemming from its organic π -conjugated polymer structure restricts its overall photocatalytic performance. Consequently, developing a novel g-C₃N₄-based photocatalyst with a narrower band gap and improved charge separation and migration is crucial.

A comprising potassium-functionalized graphitic carbon nitride (KGCN) and reduced graphene oxide (RGO), was synthesized through a straightforward hydrothermal method. This nanocomposite served as an efficient heterogeneous catalyst for Knoevenagel condensation and the sustainable synthesis of aryl-substituted chromenes. Comprehensive characterization through techniques such as powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, and BET surface area analysis validated the structure of the KGCN–RGO nanocomposite. In the catalytic application, this nanocomposite demonstrated excellent recyclability for the synthesis of various aryl-substituted chromo-enes in ethanol. The catalytic protocol showcased high atom economy and a low E-factor, underscoring its environmentally friendly and sustainable nature.

Nanotubes, with their versatile applications spanning various fields, especially in catalysis, have garnered significant attention. In this study, we devised a straightforward synthesis method for producing sodium-doped g-C₃N₄ nanotubes (Na-CNTs). The process involves hydrothermal synthesis of an intermediate, followed by treatment through microwave irradiation heating (Shan Wu et.al.,)

The technique leverages the self-assembly of melamine and cyanuric acid in a NaOH solution, resulting in the formation of a Na-doped melamine cyanaurate supramolecular intermediate. Subsequently, this supramolecular intermediate undergoes direct microwave irradiation heating with carbon fibers acting as microwave absorbers. Comprehensive characterizations confirm the convenient formation of uniform one-dimensional (1D) nanotubes in the shape of Na-CNTs, and successful sodium doping is achieved through this direct microwave irradiation process. Furthermore, sodium doping enhances the charge attractive force between layers and induces more structural defects in Na-CNTs. Photodegradation experiments using rhodamine B (RhB) as a model pollutant reveal that the obtained Na-CNTs exhibit significantly improved photocatalytic performance. In just 20 minutes, the degradation rate reaches nearly 91.43%, and the photodegradation velocity of Na-CNTs is 3.2 times higher compared to pure g-C₃N₄ (PCN).

Na ions were incorporated into the triangular vacancies within the aromatic ring plane of g-C₃N₄ nanowires, creating an electronic bridge that enhances the transfer and separation of photogenerated electron-hole pairs. Experimental findings and theoretical calculations confirmed the integration of Na atoms into the g-C₃N₄ matrix, altering the density of states distribution and migration path of photo-generated carriers. Consequently, this modification improves the photocatalytic hydrogen production activity of g-C₃N₄.

Numerous prior investigations suggest that the incorporation of alkali metals can alter the energy band structure of semiconductor photocatalysts. In 2015, Hu et al. outlined two approaches for alkali metal-doped CN photocatalysts. The first method involves thermally polymerizing dicyandiamide and KOH thoroughly mixed as the CN precursor and K source, respectively. In the second method, pre-synthesized CN is dispersed in a KOH solution, with water removal by heating and stirring. A comparison reveals that, in the post-treatment synthesis, K species predominantly reside on the CN surface, and the photoluminescence intensity remains unchanged, indicating no enhancement in photogenerated carrier efficiency.

Metal ion doping proves instrumental in modifying g-C₃N₄'s structure, as evidenced by examples involving lithium, sodium, potassium, magnesium, iron, cobalt, copper, and silver. A comprehensive review delves into the intricacies of g-C₃N₄ doping, showcasing its impact on hygroscopic properties, photocatalytic performance, energy storage, and catalytic capabilities. Doped g-C₃N₄ finds application in diverse sensors, with your recent paper being the sole source on its adsorption performance. Consequently, this research focuses on synthesizing and exploring the adsorption capabilities of g-C₃N₄ doped with lithium, sodium, potassium, magnesium, calcium, strontium, and barium, potentially unveiling novel adsorbents.

Graphitic carbon nitride (g-CN) has gained prominence as a visible-light-activated photocatalyst in energy and environmental applications. While most studies focus on enhancing its photocatalytic performance, exploring its adsorption capabilities not only broadens its application range but also unveils valuable insights into surface interactions. In this study, sodium-doped g-CN (Na(x)-CN) is synthesized through one-step pyrolysis involving melamine and sodium carbonate (Na₂CO₃). Na(x)-CN exhibits remarkable adsorption capacities, reaching a maximum of 1319 mg/g for methylene blue—approximately 650 times higher than pristine g-CN. It effectively addresses the common issues of selectivity and slow adsorption kinetics seen in conventional adsorbents. The exceptional adsorption performance is predominantly attributed to π - π interactions and electrostatic forces. Additionally, the synthesis route assisted by Na₂CO₃ enhances optical properties and photocarrier separation efficiency, further improving contaminant removal through photodegradation.

Research on modified g-C₃N₄, enhanced with Li, Na, K reveals its potential in breaking down colorants like crystal violet and methyl orange when illuminated by sunlight. These findings suggest that this modified material could be an effective catalyst activated by solar energy for the breakdown of various colorants. Upon exposure to sunlight, this semiconductor material can produce pairs of electrons and holes. These mobile charges then drive chemical reactions that degrade pollutants. This property positions the Li, Na, K-enhanced g-C₃N₄ as available option for catalysing the production of hydrogen gas using solar energy (Yamei Pang et.al.,)

CHAPTER 3

AIM AND SCOPE

The dissertation primarily focuses on the synthesis, detailed analysis, and various uses of Alkali metal-doped Graphitic Carbon Nitride. This material is crucial in numerous fields of study, including catalysis, sensors and photo catalytic activities and possesses many additional attributes as documented in scholarly articles.

To characterize the compound using

- ❖ Fourier Transform Infrared Spectroscopy
- ❖ X-Ray Diffraction Spectroscopy
- ❖ UV-Visible Spectroscopy
- ❖ Photo Luminescence Spectroscopy
- ❖ Scanning Electron Microscope Spectroscopy.

**PHOTOCATALYTIC
ACTIVITY**

**PHOTO
LUMINESCENCE**

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS

All the chemicals used in this experiment were of analytical grade and is used without any further purification. Melamine (99%), Lithium Chloride Anhydrous (99%), Sodium Chloride (99%), Potassium Chloride (99%), Deionised water, Ethanol (99.9%), Beaker, Silica Crucible with Lid, Magnetic Stirrer.

4.2 EXPERIMENTAL METHODS

4.2.1 Synthesis of Pure Graphitic Carbon Nitride (g-C₃N₄)

The pure g-C₃N₄ is synthesised by “Hydro-Thermal Method” followed by “Thermal Polymerisation Method”. The Pure g-C₃N₄ was synthesized using Melamine as precursor. 2 grams of Melamine is taken and transferred into a Silica Crucible and closed using lid and then it is kept in muffle Furnace for 4hrs at 550°C. The resultant compound is the pure g-C₃N₄. It is then washed with water for 3 times and with ethanol for 3 times to get the purified form.

4.2.2 Synthesis of Lithium doped Graphitic Carbon Nitride (Li-GCN)

The Lithium doped g-C₃N₄ is synthesised by “Hydro-Thermal Method” followed by “Thermal Polymerisation Method”. Li-doped g-C₃N₄ was synthesized using Lithium Chloride Anhydrous and Melamine as precursors taken in 1:5 ratio respectively with 5ml of Deionised water and stirred up to 5hrs at 100°C using magnetic stirrer. After getting solid dried sample it is grounded to fine powder using mortar and pestle. Then it is transferred to Silica Crucible and closed using lid and then it is kept in muffle Furnace for 4hrs at 550°C. The resultant yellow coloured compound is the Li-doped g-C₃N₄. It is then washed with water for 3 times and with ethanol for 3 times to get the purified form.

4.2.3 Synthesis of Sodium doped Graphitic Carbon Nitride (Na-GCN)

The Sodium doped g-C₃N₄ is synthesised by “Hydro-Thermal Method” followed by “Thermal Polymerisation Method”. Na- doped g-C₃N₄ was synthesized using Sodium Chloride and Melamine as precursors in 1:5 ratio respectively with 5ml of Deionised water and stirred up to 5hrs at 100°C using magnetic stirrer. After getting solid dried sample it is grounded to fine powder using mortar and pestle. Then it is transferred to Silica Crucible and closed using lid and then it is kept in muffle Furnace for 4hrs at 550°C. The resultant yellow coloured compound is the Na-doped g-C₃N₄. It is then washed with water for 3 times and with ethanol for 3 times to get the purified form.

4.2.4 Synthesis of Potassium doped Graphitic Carbon Nitride (K-GCN)

The Potassium doped g-C₃N₄ is synthesised by “Hydro-Thermal Method” followed by “Thermal Polymerisation Method”. K-doped g-C₃N₄ is synthesized using Potassium Chloride and Melamine as precursors taken in 1:5 ratio respectively with 5ml of Deionised Water and stirred up to 5hrs at 100°C using Magnetic Stirrer. After getting solid dried sample it is grounded to fine powder using mortar and pestle. Then it is transferred to Silica Crucible and closed using lid and then it is kept in Muffle Furnace for 4hrs at 550°C. The resultant yellow coloured compound is the K-doped g-C₃N₄. It is then washed with water for 3 times and with ethanol for 3 times to get the purified form.

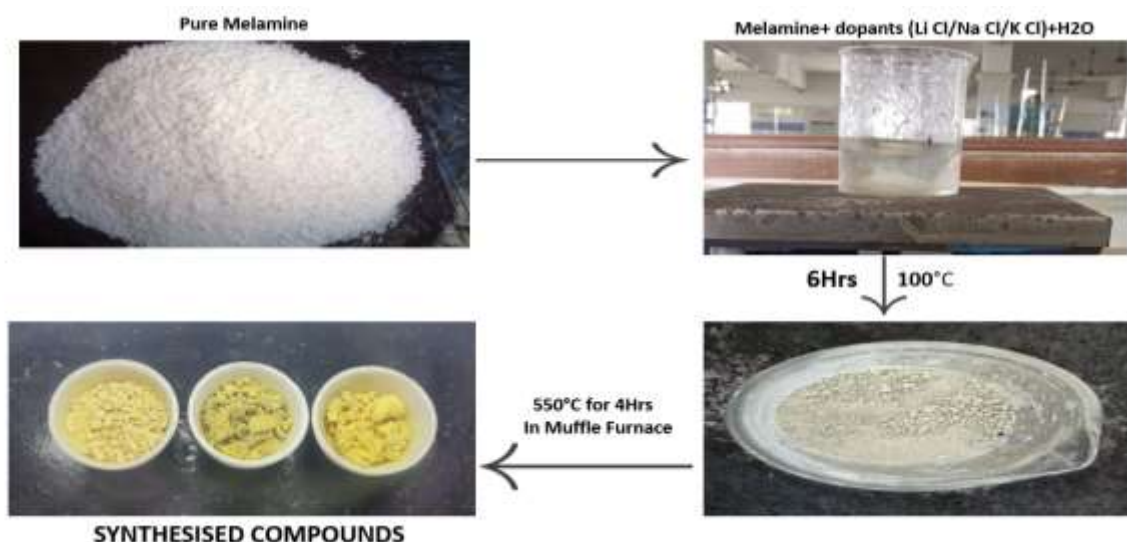


Fig:4.1: Synthesis Scheme

4.3 CHARACTERISATION TECHNIQUES

4.3.1 FTIR SPECTROSCOPY

FTIR spectroscopy, which stands for Fourier-transform infrared spectroscopy, is a powerful analytical technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. It works by passing IR radiation through a sample and measuring the radiation that is absorbed and transmitted, creating a unique molecular fingerprint of the sample. FTIR can determine the structure of unknown chemical substances by comparing their spectral data with known reference spectra. Every chemical compound has a unique infrared absorption spectrum, akin to a molecular fingerprint. FTIR can identify compounds by matching their spectra with known references. It helps in identifying functional groups within a molecule by analysing specific absorption bands, which correspond to different types of chemical bonds.

4.3.2 POWDER XRD ANALYSIS

X-ray diffraction (XRD) is a multifaceted diagnostic method that examines the physical attributes of samples in various states powder, solid, or liquid. It assesses aspects like phase makeup, crystalline configuration, and directional orientation. Bragg's Law provides the mathematical relationship for X-ray scattering by crystals:

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

- **(d)** signifies the distance between atoms within a crystal lattice,
- **(θ)** denotes the X-ray's angle of entry,
- **(n)** represents an integer value, and
- **(λ)** is the X-ray's wavelength.

Bragg's Law elucidates the specific angles at which crystals reflect X-ray beams. A pronounced reflection occurs when the waves bouncing off consecutive layers of the crystal lattice have a path difference that's a whole number multiple of the wavelength, a process known as Bragg reflection. In the realm of chemistry, XRD stands out as a robust instrument with broad applications.

Powder XRD, in particular, is invaluable for analysing powdered crystalline substances. It's instrumental in pinpointing the crystalline phases within a sample, leveraging unique diffraction patterns that can be matched against a reference database for identification. The technique also allows for the assessment of sample purity and the detection of any adulterants. Furthermore, powder XRD facilitates the measurement and refinement of a crystal's lattice parameters a key factor in comprehending its characteristics. The Scherrer equation links the breadth of the diffraction pattern's peak to the size of the particles, providing a means to ascertain this dimension.

4.3.3 UV-DRS ANALYSIS

UV Diffuse Reflectance Spectroscopy (UV DRS) also known as Absorption Spectroscopy is an essential method in the field of chemistry, widely applied for various purposes. It serves as a technique to investigate the optical characteristics of newly created compounds. It is used for solid samples. In the realm of catalysis, UV DRS is utilized to examine the molecular structure, electronic configuration, and bonding environment of the metal in focus. Additionally, it scrutinizes how the metal interacts with its base during the stages of catalyst formation, conditioning, and chemical reactions.

Furthermore, UV DRS is a critical instrument for evaluating the photocatalytic performance in chemical processes.

UV-Visible Spectroscopy: This approach quantifies the alteration in light's transmittance when it traverses a liquid medium. It's chiefly employed for scrutinizing solutions that permit the passage of light, capturing the spectrum of light absorption at diverse wavelengths to deduce the sample's molecular makeup.

UV Diffuse Reflectance Spectroscopy (UV DRS): Diverging from the above, UV DRS gauges the shift in light that bounces back from a material's exterior, making it ideal for examining powdered or solid substances with non-smooth textures. This method captures the diffusion and rebound of light on the material's facade, offering a window into the surface characteristics of the sample, including the crucial band gap energies essential for photocatalytic processes.

To encapsulate, the core distinction is based on the sample interaction: UV-Visible Spectroscopy is concerned with light's journey through a sample, whereas UV DRS is focused on the light that is mirrored off the sample's exterior.

4.3.4 PHOTO LUMINESCENCE SPECTROSCOPY

Photoluminescence analysis, also known as Emission Spectroscopy, is a technique that observes the light a material releases after it has soaked up some form of energy. This light show can reveal a lot about what's happening inside the material, like where there might be flaws or how the atoms are arranged. It's particularly good at showing us how electrons jump around between different energy spots within the material. It allows scientists to investigate the electronic structures of various materials without making physical contact or altering their state. By shining light on a material, it absorbs the energy and becomes photo-excited.

This method is particularly valuable for examining the optical and electronic characteristics of semiconductors and molecular compounds. During the photoluminescence process, the material absorbs light, which elevates electrons to a higher energy state. Following this excitation, the electrons undergo several relaxation processes that eventually lead to the emission of light. The duration from when the light is absorbed to when it's emitted can be extremely brief, from femtoseconds, or it can last for much longer periods. UV-Visible Diffuse Reflectance Spectroscopy (UV-DRS), on the other hand, tells us about the energy levels that electrons can't reach. It does this by measuring the light that bounces off (is reflected by) the material instead of being absorbed. When you put these two techniques together, it's like having a full map and a flashlight to explore the world of a material's electrons. You get to see where the electrons can go, where they can't, and how they move between their allowed spaces – all of which paints a detailed picture of the material's optical characteristics.

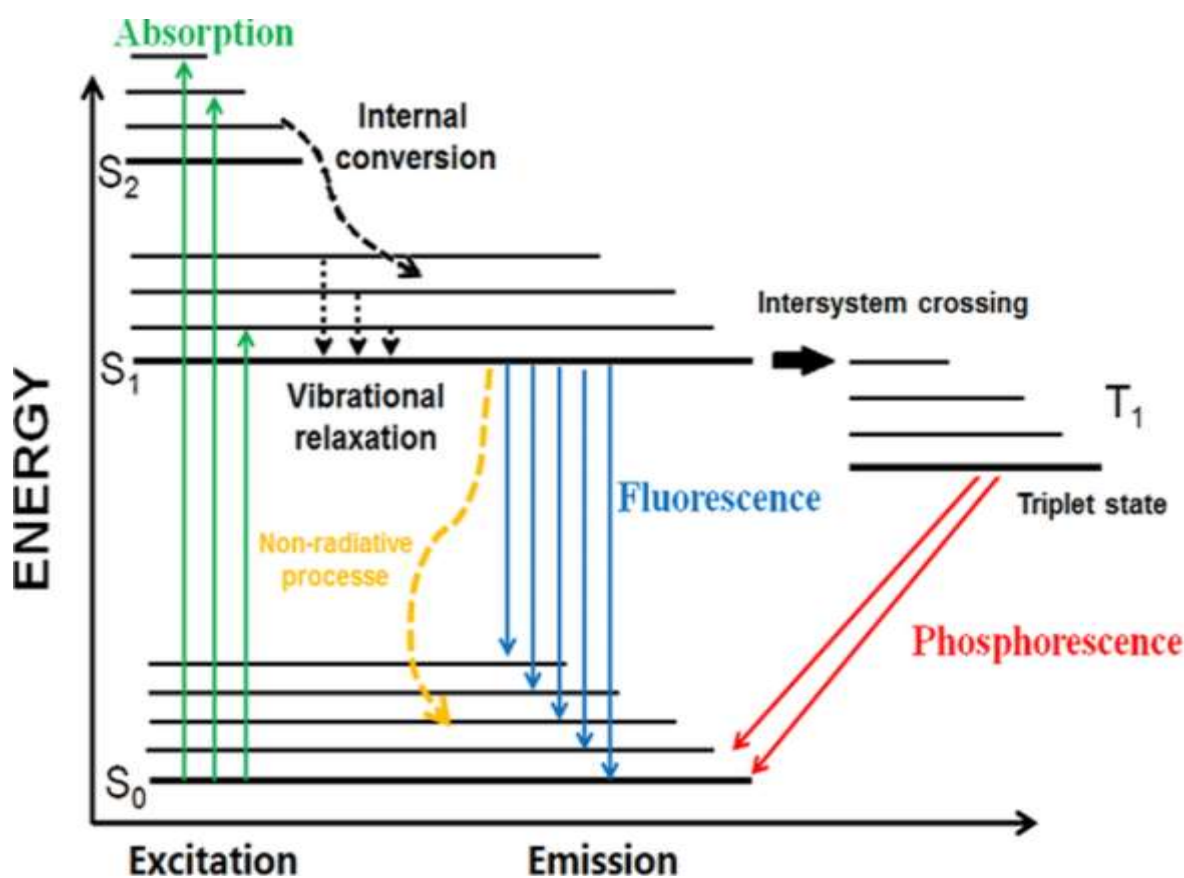


Fig:4.2: Jablonski Diagram representing the formation of Fluorescence

4.3.5 SEM ANALYSIS

A Scanning Electron Microscope (SEM) is a specialized form of electron microscope that produces images of a sample by rastering it with a dense electron beam. The interaction between the electrons and the atoms in the sample gives rise to signals that provide data about the sample's surface texture and composition. In the realm of nanotechnology, especially in chemistry, SEM holds significant importance. It is one of the most potent tools for examining and understanding the shape and chemical makeup of nanostructures. It offers high-definition images that aid in comprehending the structure and composition of nanomaterials. With the progression of nanotechnology, SEM has become an essential instrument for the creation of new nanomaterials. It assists in refining synthesis methods and achieving superior quality images. SEM is employed for the detection of nanoparticles and is seen as a potential replacement for existing silicon-based electronic chips. Scanning Electron Microscopy (SEM) is employed to analyse the diverse physical attributes of nanomaterials. It also serves as a tool for real-time engineering and alteration of nanomaterials. Energy Dispersive X-ray Spectroscopy (EDS) detectors, when used in conjunction with SEM, allow for the examination of the elemental composition of a sample's surface. This process is often referred to as microanalysis.

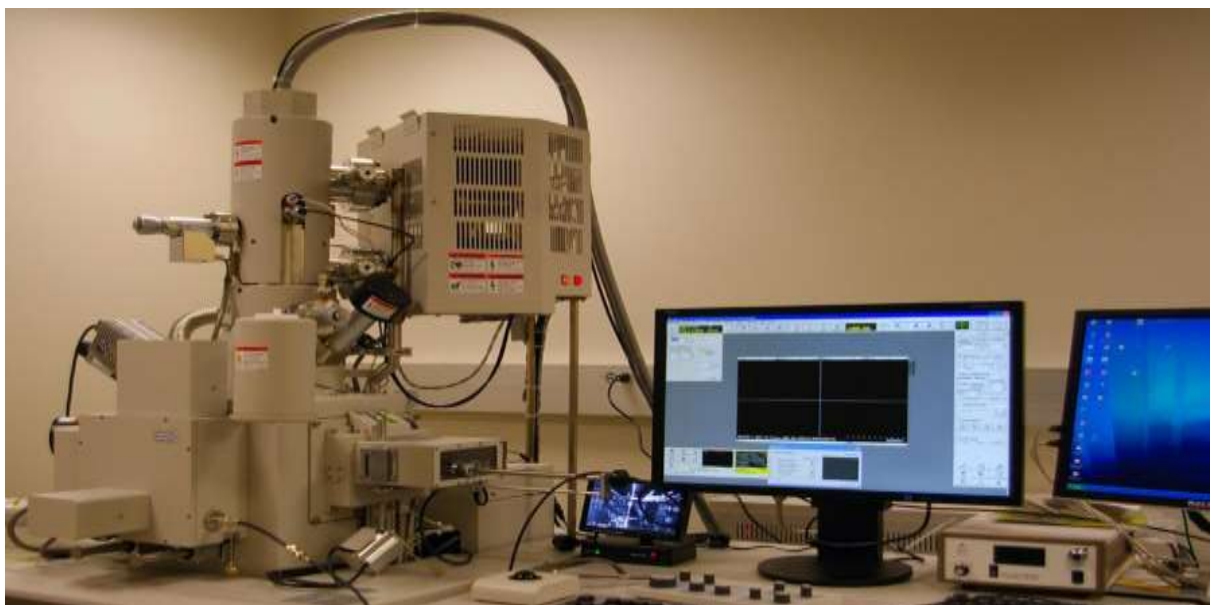


Fig:4.3: Scanning Electron Microscope

CHAPTER 5

RESULT AND DISCUSSION

The synthesised pure g-C₃N₄ and Li/Na/K-doped g-C₃N₄ were analysed for their crystal structure, shape, composition, surface organic functional groups, and catalytic potential using a variety of instruments. These instruments include Powder X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet Diffuse Reflectance Spectroscopy (UV DRS) and Photo Luminescence Analysis (PL). The techniques emphasized in this project are showcased within. A concise overview of these methods is provided in the subsequent segment.



Fig:5.1: Synthesised Pure g-C₃N₄ And Doped g-C₃N₄

5.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The Effect of Alkali Metals on the structural properties were investigated by FTIR Spectroscopy (JASCO, FTIR 6600 Spectrophotometer, JAPAN). The FTIR spectra of all the samples are similar to each other, The spectra consist of bands characteristic for g-C₃N₄. The FTIR spectra of all the samples show comparable characteristic bands at 803 cm⁻¹ and 1200–1800 cm⁻¹ region are due presence of Heptazine units and stretching Vibration modes of Aromatic C-N Heterocyclic ring of GCN, respectively, this confirms that alkali metals only interrupt the intralayer long-range periodic arrangement without modifying the basic atomic building blocks. This witness the formation of C-N-C bond which is a distinct property of Graphitic

materials having alternative N and C Atoms. However the intensity of these units are reduced for Li/Na/K Samples due to lesser systematic packing of triazine units.

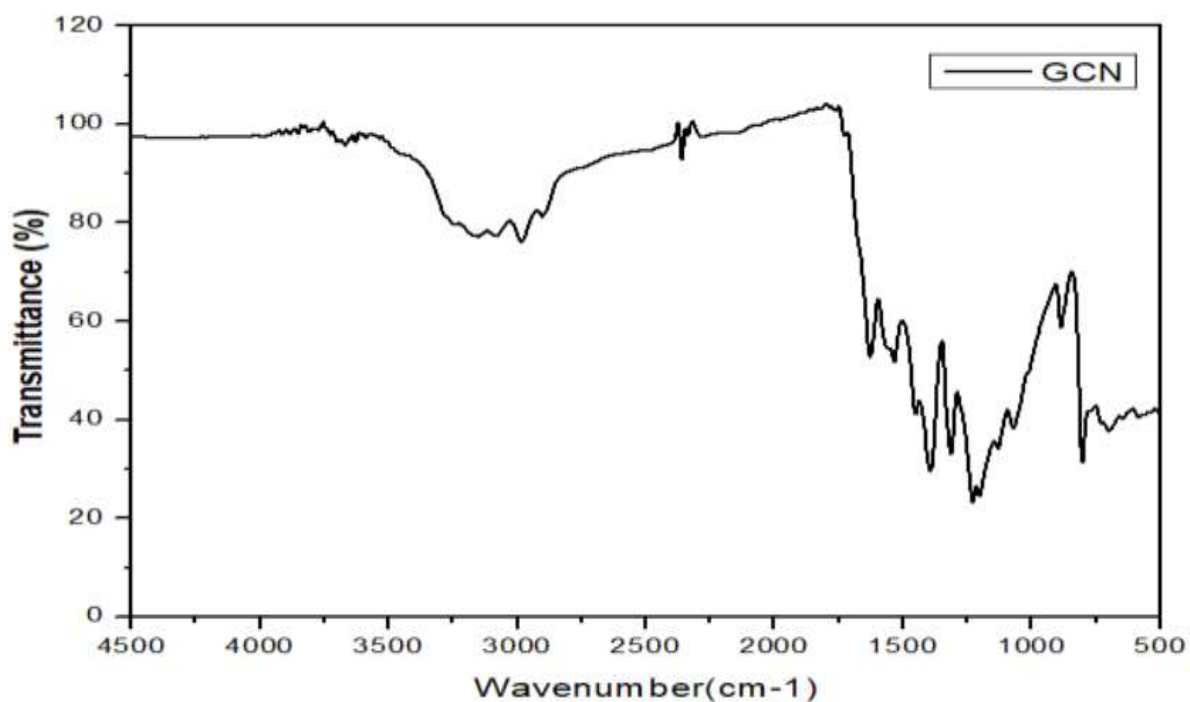


Fig:5.2: (a) FTIR of Pure GCN

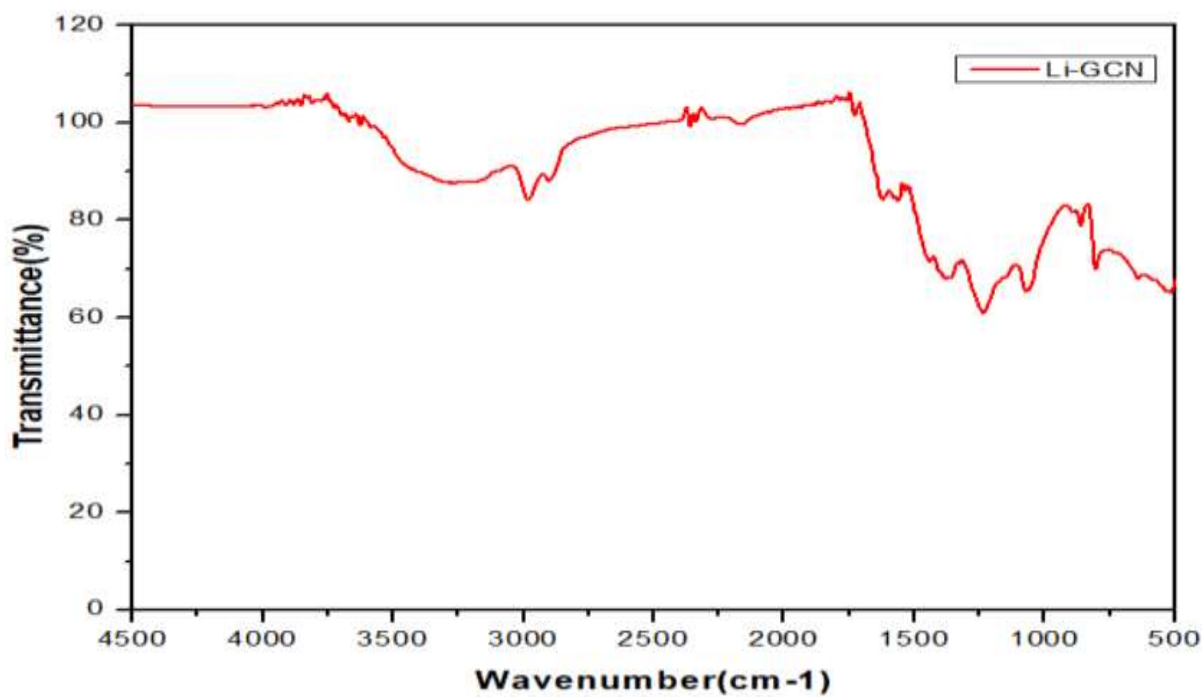


Fig:5.2: (b) FTIR of Lithium doped GCN

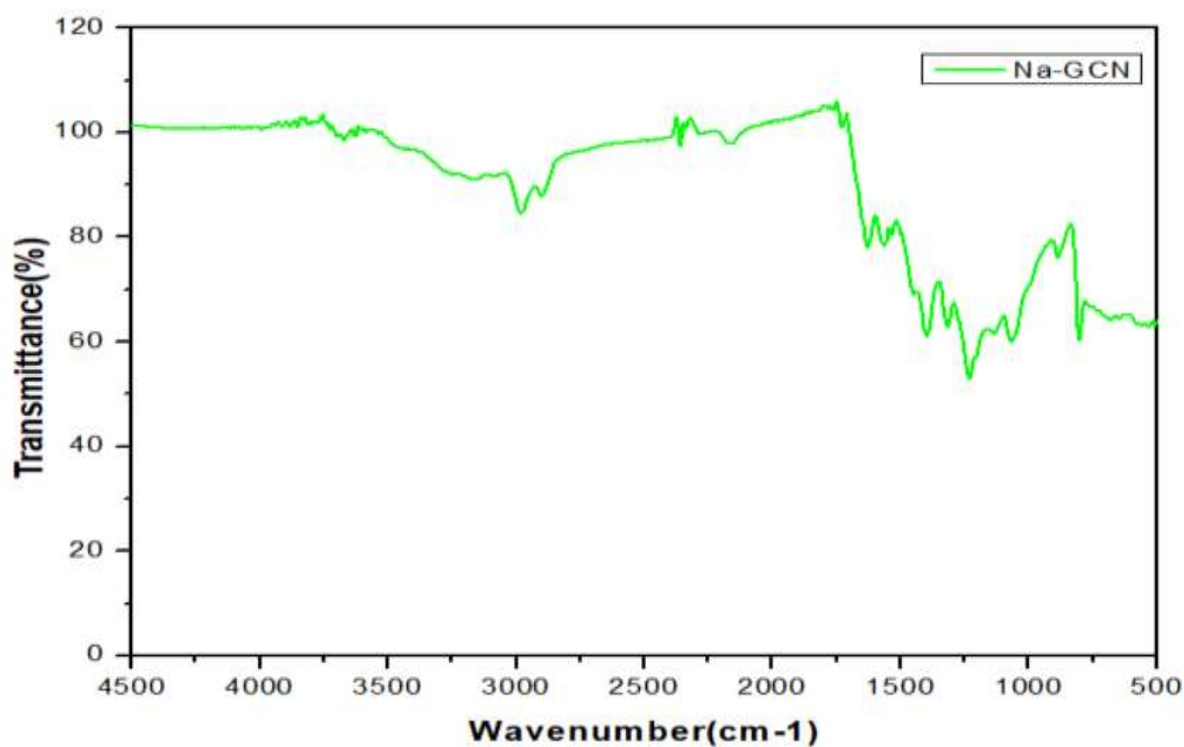


Fig:5.2: (c) FTIR of Sodium doped GCN

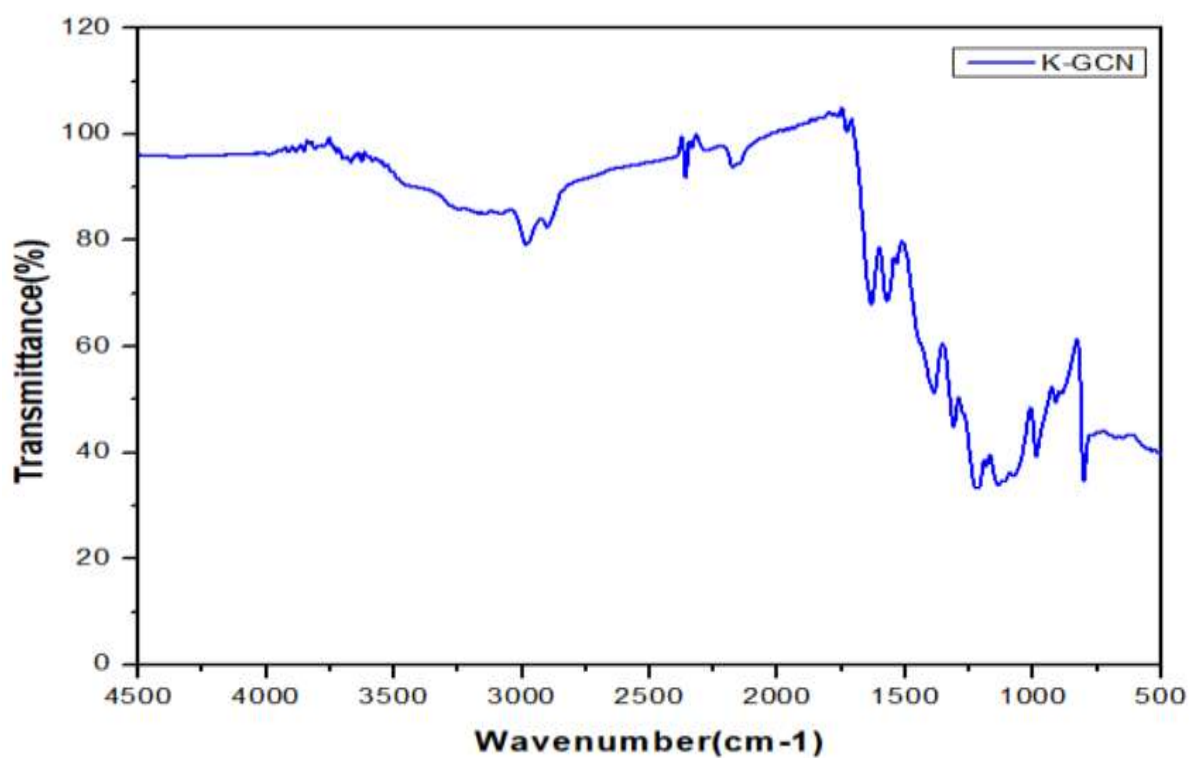


Fig:5.2: (d) FTIR of Potassium doped GCN

S.NO	WAVENUMBER (cm ⁻¹)	FUNCTIONAL GROUPS
1	1627, 1533	C=C
2	2984, 1450, 1395	C-H
3	2282	CYANO
4	1200 -1800	C-N, C=N
5	3200 - 3600	O-H
6	3000 - 3500	-NH, -NH ₂

Table:5.1: Spectral Data of all above FTIR

5.2 POWDER X-RAY DIFFRACTION ANALYSIS (POWDER XRD)

The Powder XRD patterns of pure g-C₃N₄ and Alkali Metals doped are analyzed (ARO EQUINOX 3000, Thermo Fisher Scientific). The XRD pattern of Pure g-C₃N₄ exhibited two characteristic diffraction peaks at $2\theta=13.0^\circ$ and $2\theta=27.3^\circ$. The former can be assigned to the (100) crystal plane, representing the in-plane long-range periodic packing or in-plane structural Tri-S-Triazine units and the another is associated with the (002) crystal plane, representing the interlayer stacking of conjugated aromatic systems. The gradual decrease and absence of 13.0° peak for GCN-Li, GCN-Na, and GCN-K shows that GCN synthesized in the media of alkali metals has reduced in-plane ordering. There is a shift in peak at (002) plane towards higher angle side is observed, this is due to the incorporation of alkali metals, mentioned as below.

$$2\theta = 27.3^\circ \rightarrow 27.4^\circ \rightarrow 27.6^\circ \rightarrow 27.8^\circ$$

Pure GCN Li Na K

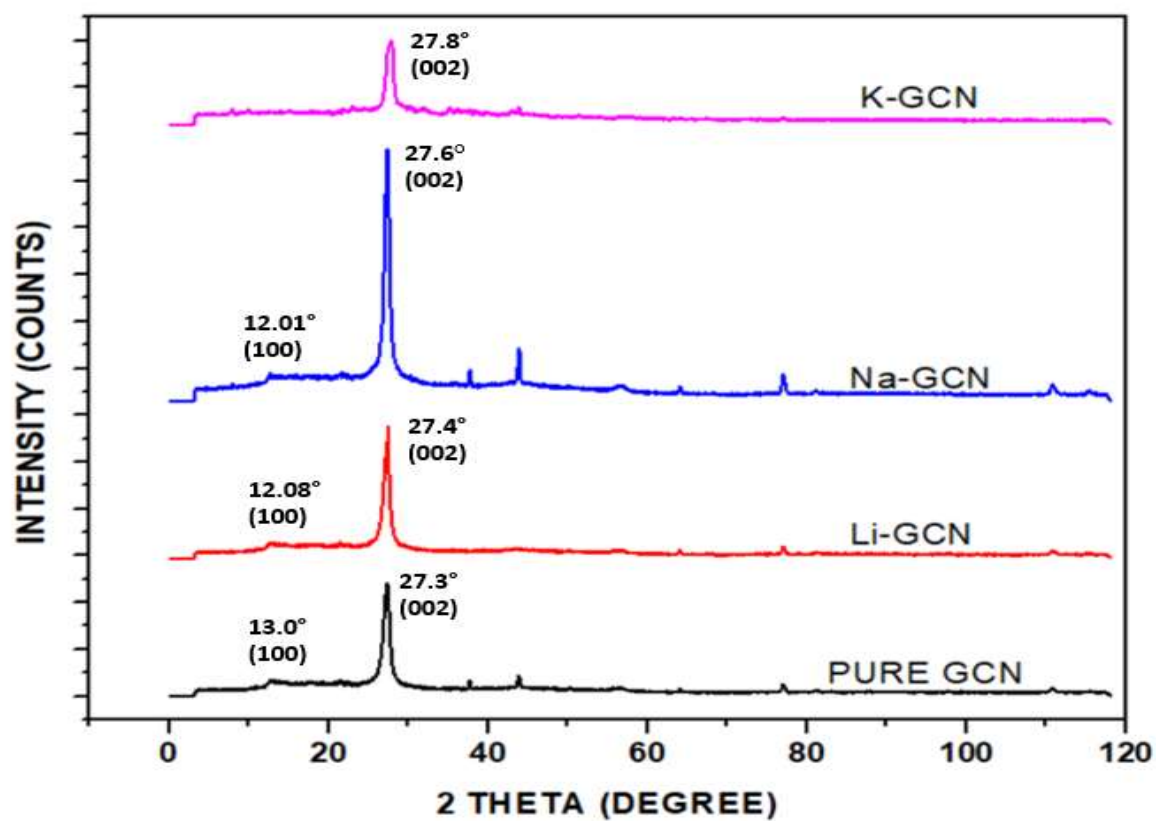


Fig:5.3: (a) Powder XRD Patterns of Pure GCN and Alkali metals doped GCN

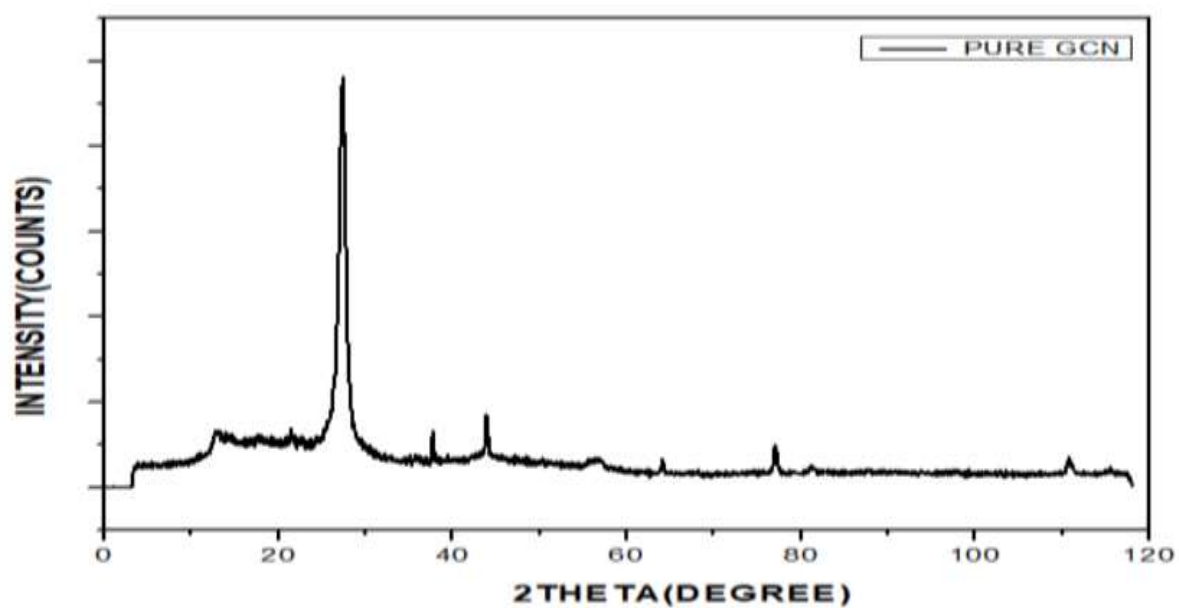


Fig:5.3: (b) Powder XRD Patterns of Pure GCN

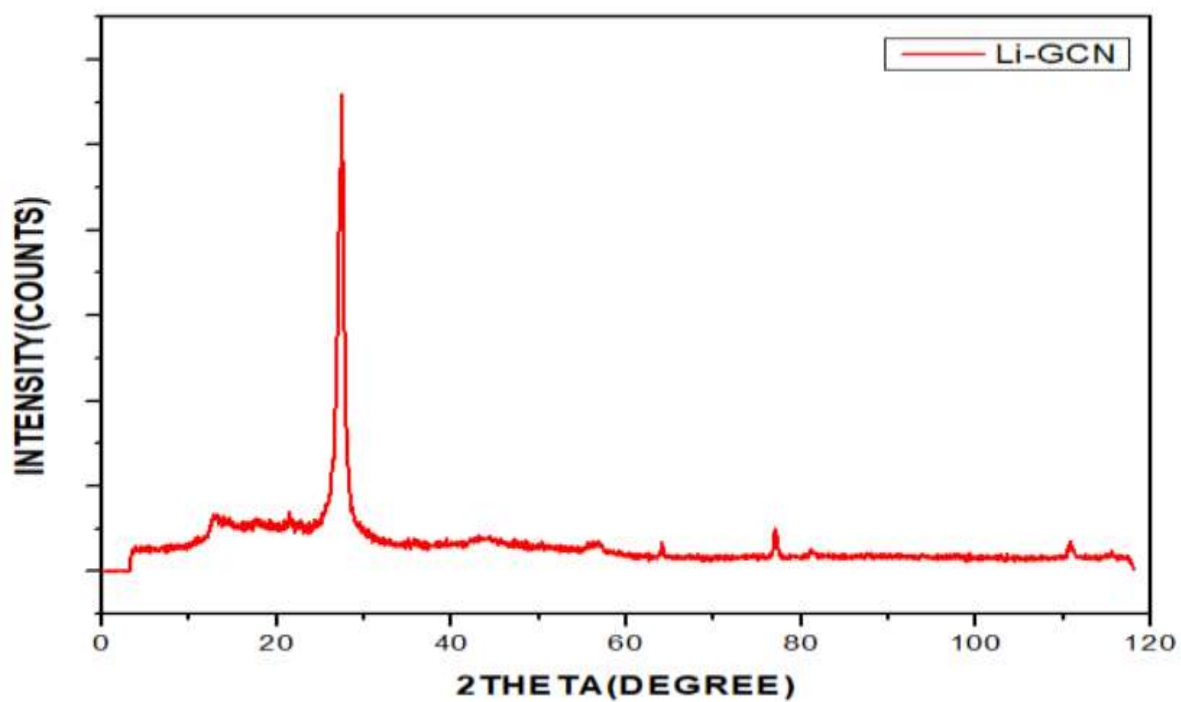


Fig:5.3: (c) Powder XRD Patterns of Li-doped GCN

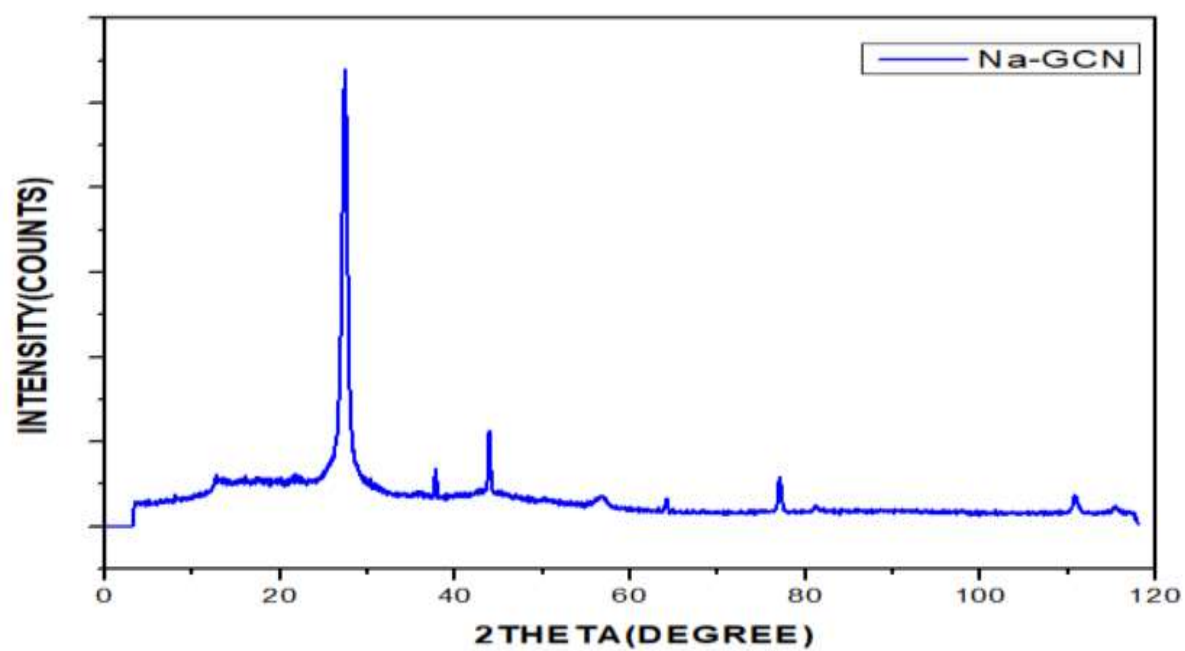


Fig:5.3: (d) Powder XRD Patterns of Na-doped GCN

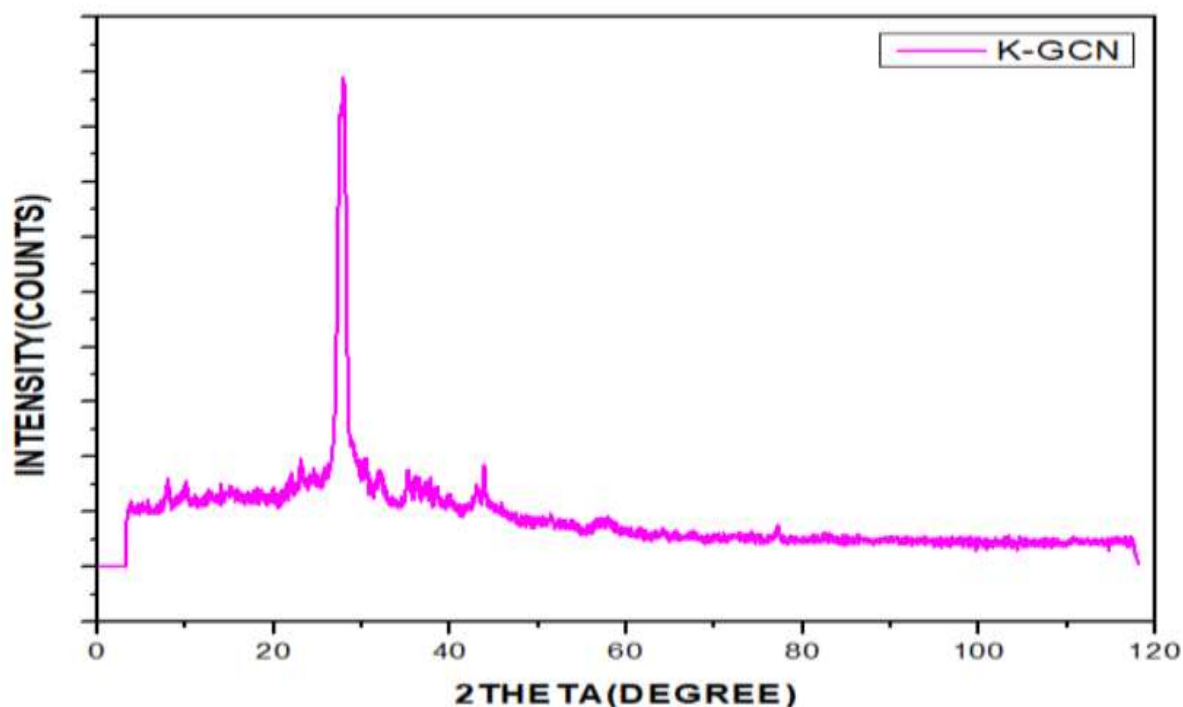


Fig:5.3: (e) Powder XRD Patterns of K-doped GCN

5.3 SCANNING ELECTRON MICROSCOPE ANALYSIS (SEM)

The Scanning Electron Microscopy (SEM) images of the Graphitic Carbon Nitride (GCN) and its alkali metal-doped variants (Li-doped, Na-doped, and K-doped GCN) provide visual evidence of the changes in the structural morphology due to the doping process.

Lamellar Morphology of GCN: The SEM image of the undoped GCN shows a typical lamellar (layered) morphology with large-sized, irregular flakes. These flakes are formed due to the aggregation of GCN nanosheets.

Effect of Alkali Metals: The introduction of alkali metals (Lithium, Sodium, and Potassium) into the GCN structure causes a transformation in the morphology. The large-sized GCN nanosheets change to smaller nanosheets, which appear like nano flakes in the SEM images of the Li-doped, Na-doped, and K-doped GCN.

Structural Changes at High Dopant Amount: At high dopant amounts, the structure of GCN undergoes further changes. Multiple cracks and pores appear, and there is an aggregation of irregular-shaped nanoparticles. This is evident in the SEM images of the Li-doped, Na-doped, and K-doped GCN.

Confirmation of Incorporation: These changes in the structural properties of GCN confirm the successful incorporation of the alkali metals (Lithium, Sodium, and Potassium) into the GCN structure.

Tuning of Properties: The incorporation of these alkali metals could potentially tune the optical and electronic properties of GCN, enhancing its performance in various applications.

In summary, the SEM images provide a visual justification for the structural changes in GCN due to alkali metal doping, confirming the successful incorporation of the Dopants and suggesting potential enhancements in the material's properties.

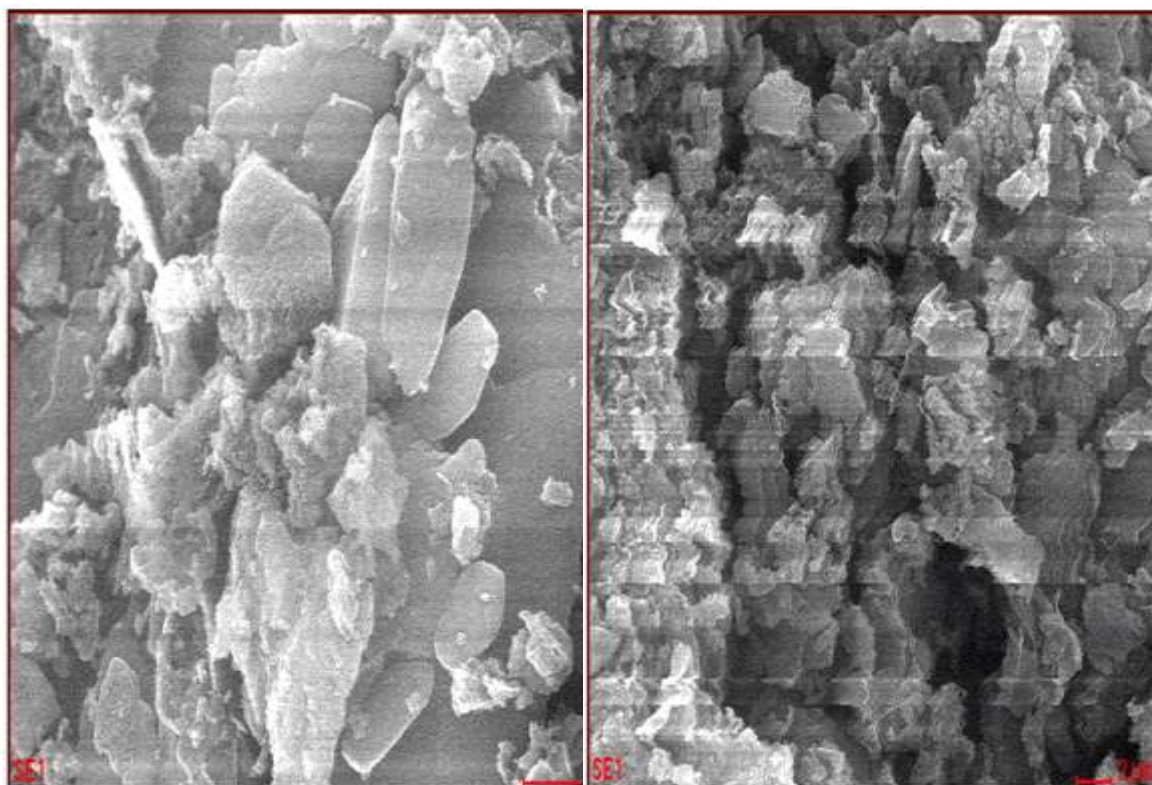


Fig:5.4: SEM Image of Pure g-C₃N₄ representing the Nanoflakes structure

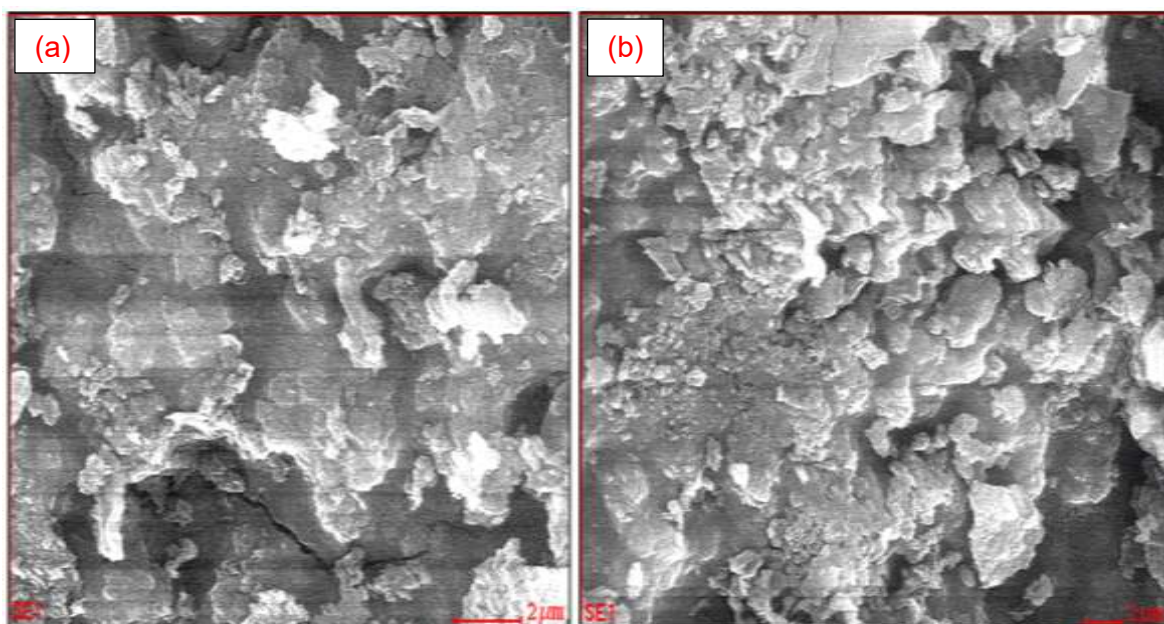


Fig:5.5: (a), (b) are SEM Images of K- doped g-C₃N₄

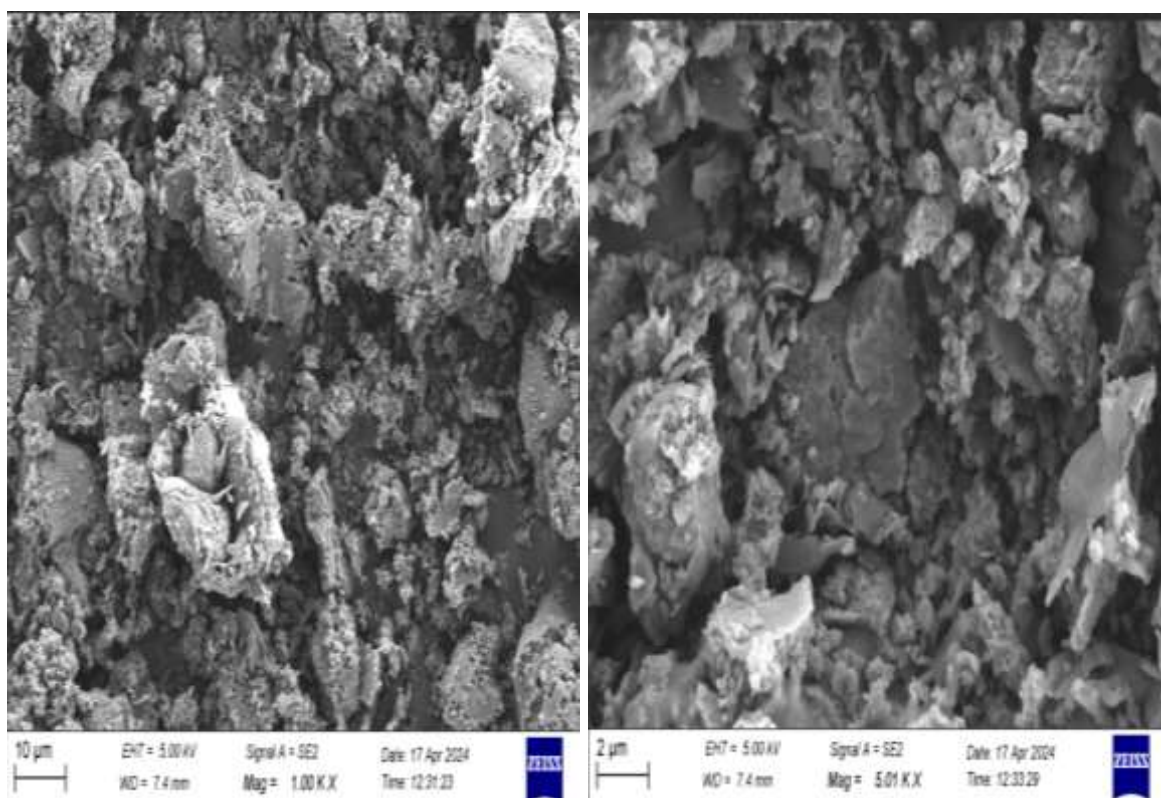


Fig:5.6: (a), (b) are SEM Images of Na-Doped g-C₃N₄

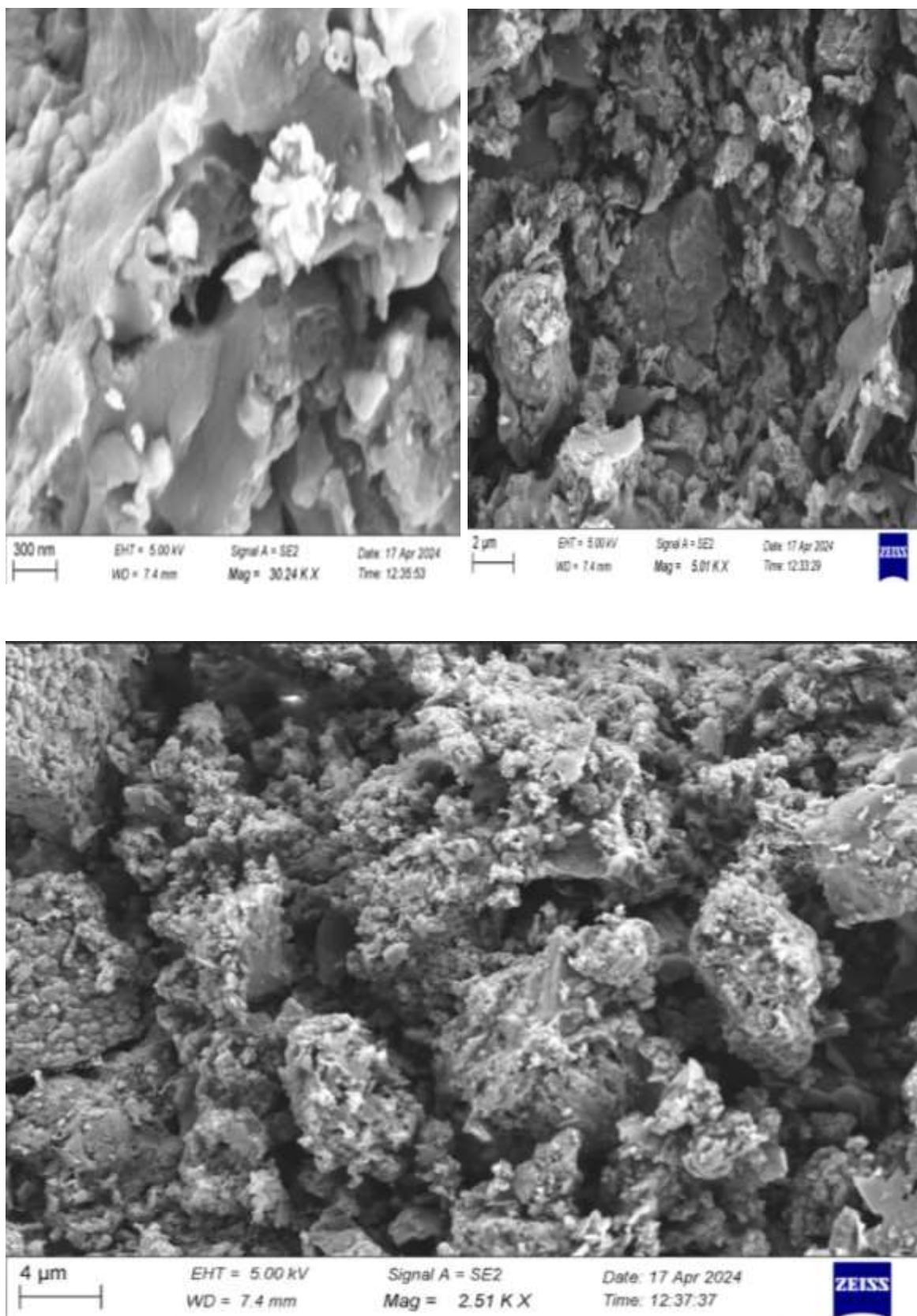


Fig:5.6: (c), (d) and (e) are SEM Images of Na-Doped g-C₃N₄

5.4 ULTRA VIOLET DIFFUSE REFLECTANCE SPECTROSCOPY (UVDRS)

The optical absorption of prepared samples are measured using UV-DRS. The UV-Visible absorption spectra for the materials pure g-C₃N₄, Li-GCN, Na-GCN, and K-GCN are presented. In pure g-C₃N₄, photoexcitation leads to the generation of photoelectrons that move from the valence band, which is composed of the N 2p orbital, to the conduction band, made up of the C 2p orbital, demonstrating the characteristic absorption behaviour of semiconductors. Upon doping with alkali metals, notable shifts towards longer wavelengths (from 376 nm to 412 nm) are noticeable in the absorption spectra for Na-GCN and K-GCN.

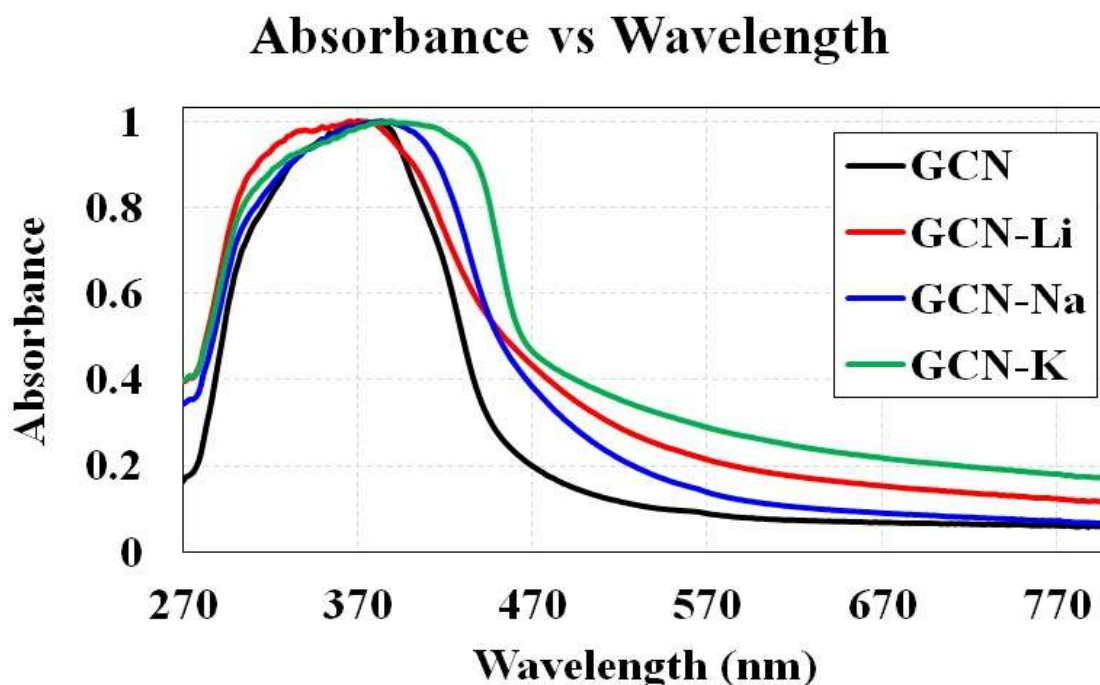


Fig:5.7. UV DRS of Pure GCN and Alkali metals doped GCN

This also reveals that the pure g-C₃N₄ is light yellow in colour. Colour of the alkali metals doped g-C₃N₄ gradually deepens with the increase in size of the dopant. The visible light absorptivity increases gradually on doping from lithium to potassium.

SAMPLES	λ_{MAX}
Pure GCN	370
Li-GCN	376
Na-GCN	382
K-GCN	390

Table:5.2: Spectral Data of all above UV DRS Analysis

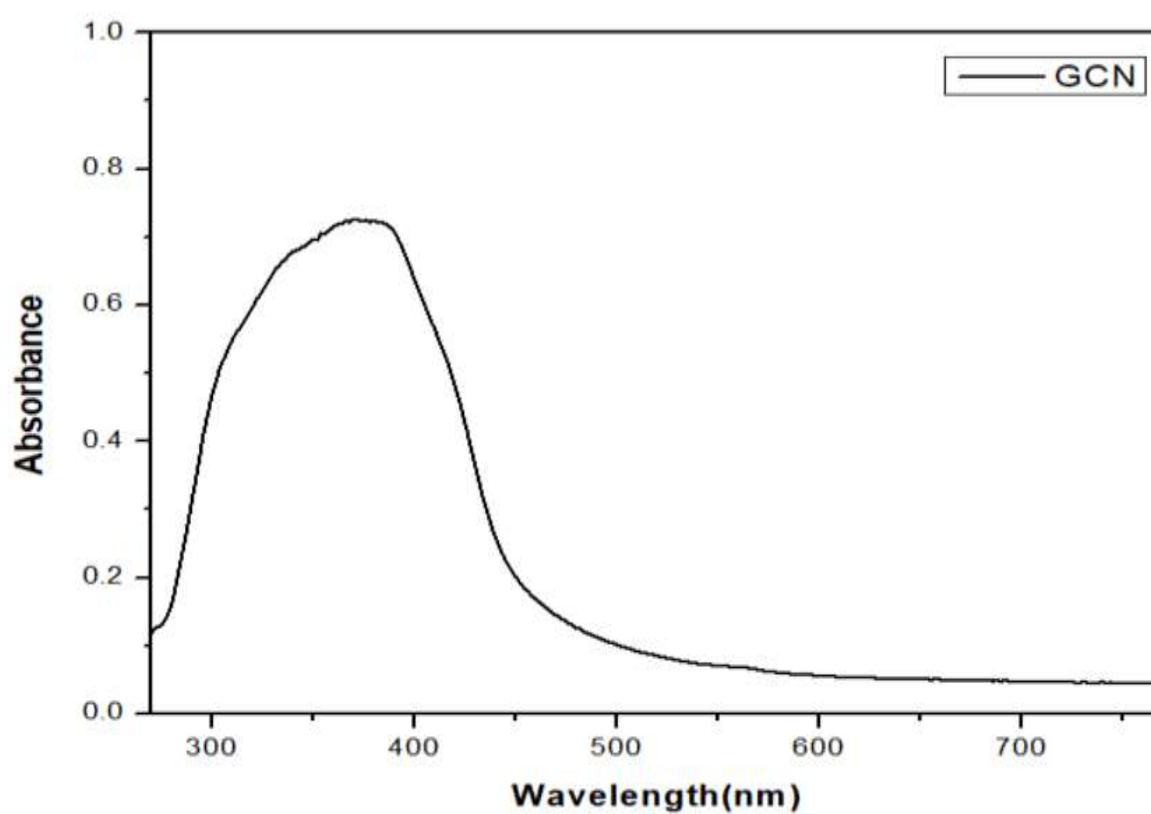


Fig:5.8. (a) UV DRS of Pure GCN

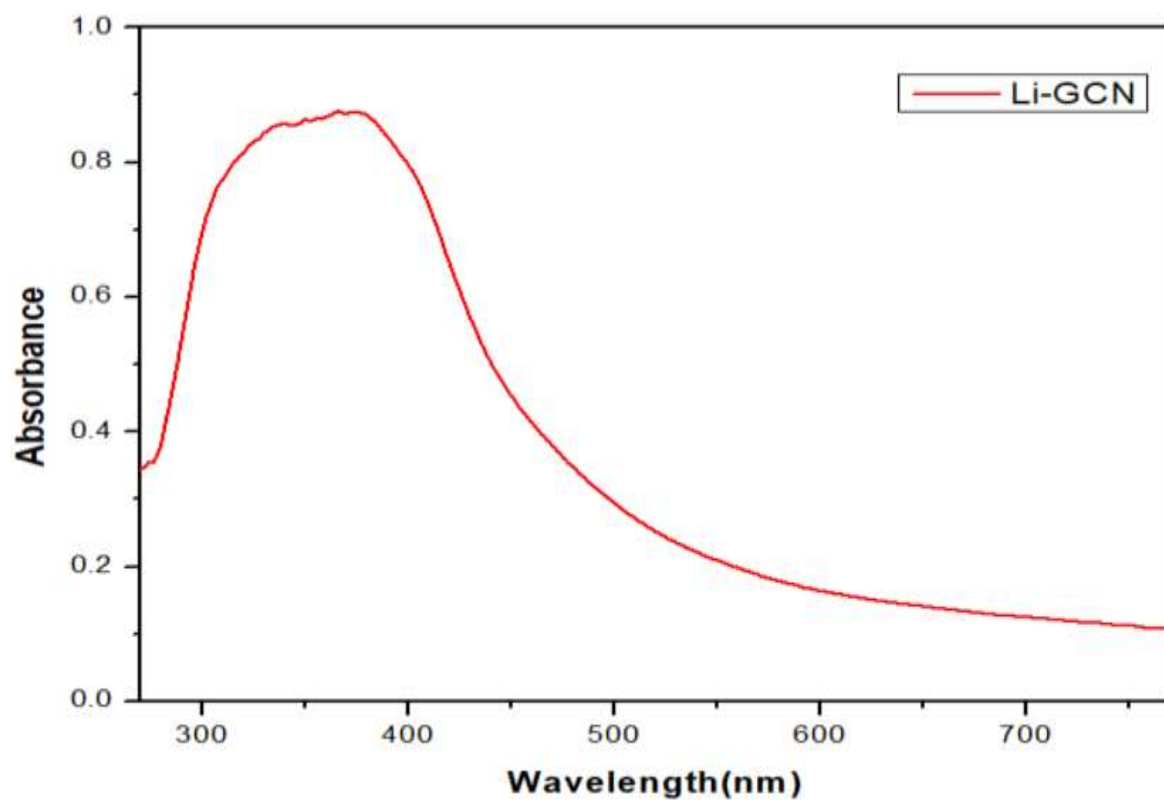


Fig:5.8. (b) UV DRS of Li-doped GCN

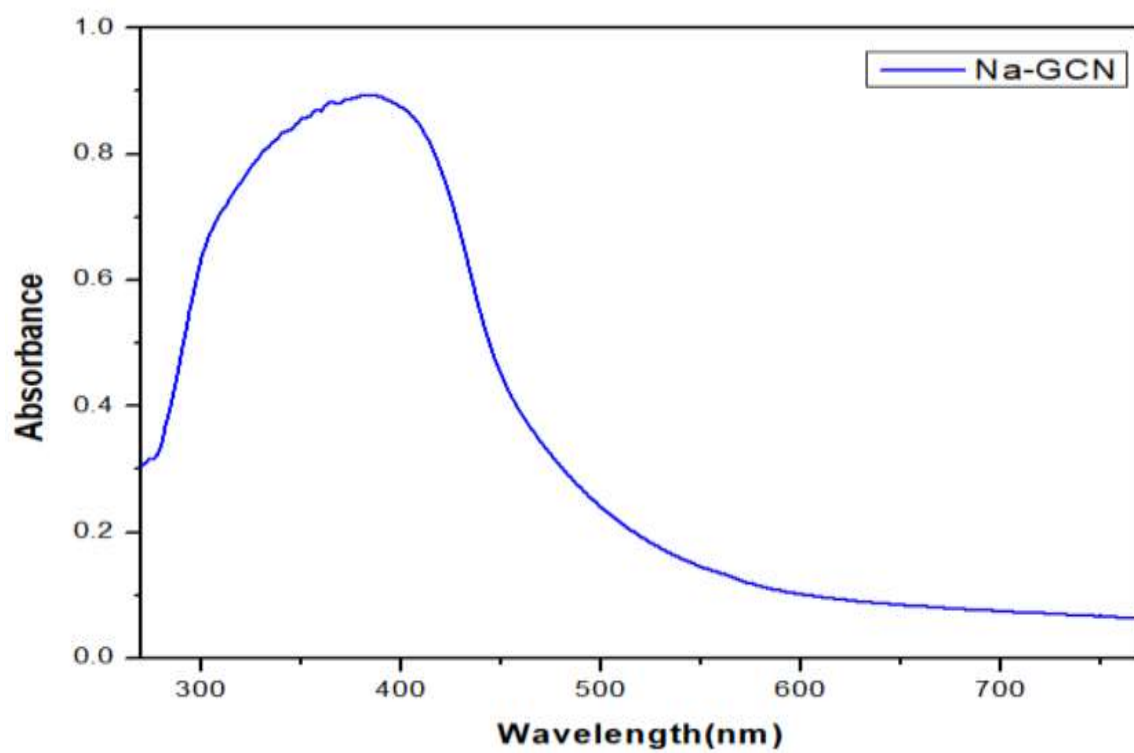


Fig:5.8. (C) UV DRS of Na-doped GCN

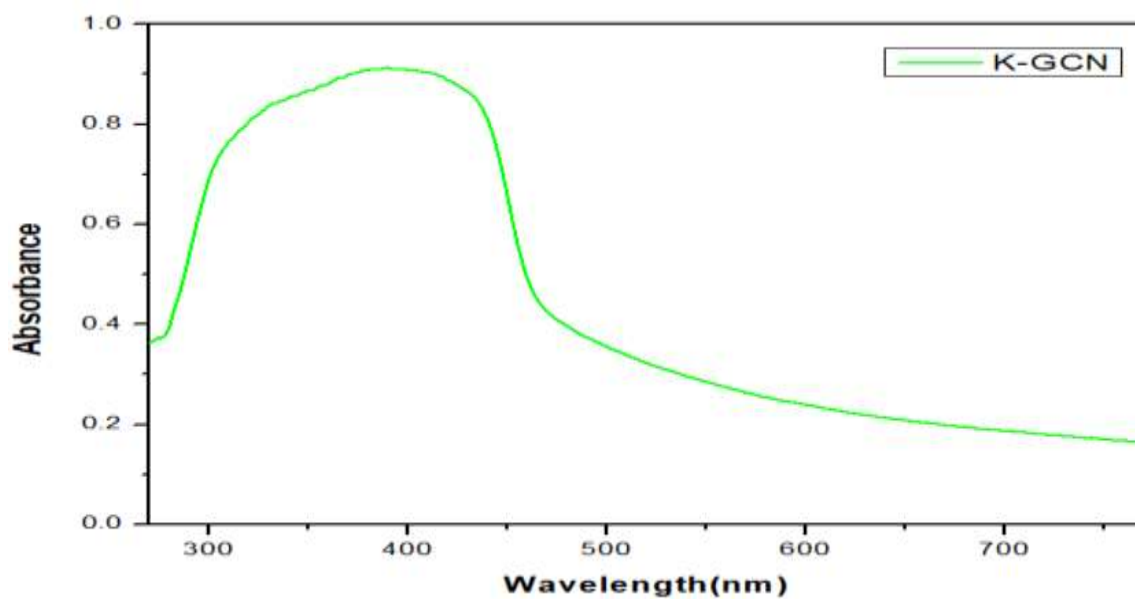


Fig:5.8. (d) UV DRS of K-dopped GCN

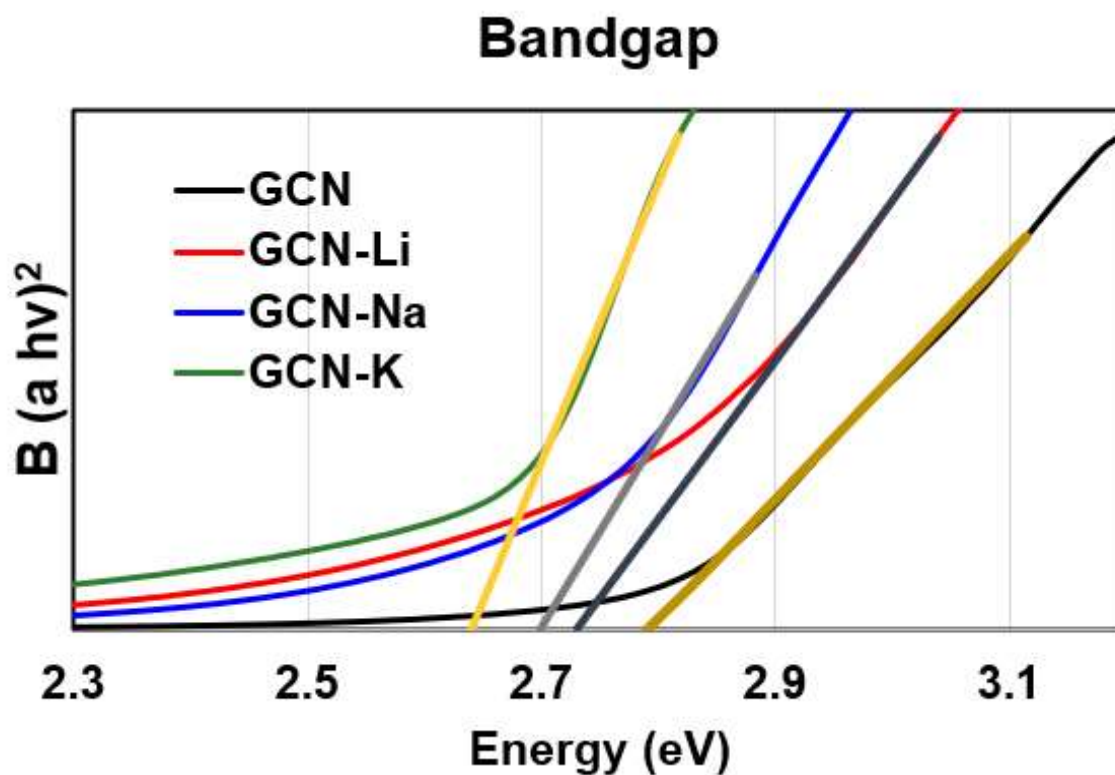


Fig:5.9: bandgap diagram

The band gaps have been calculated using the tangent lines on the graphs that plot the square root of the Kubelka–Munk function versus the photon energy. These calculations reveal that the band gaps for bulk g-C₃N₄, Li-GCN, Na-GCN, and K-GCN are **2.79 eV**, **2.73 eV**, **2.70 eV**, and **2.64 eV**, respectively.

5.5 PHOTOLUMINESCENCE SPECTRUM ANALYSIS

The PL spectrum analysis of prepared samples is carried out under the excitation wavelength of 370 nm at room temperature. For Pure GCN, the broad Photo Luminescence (Emission) band is around 465 nm. Such PL signal is mainly results from the $n-\pi^*$ electronic transitions involving lone pairs of nitrogen atoms in Pure GCN. In this case the obvious BLUE SHIFT is observed for the prepared samples.

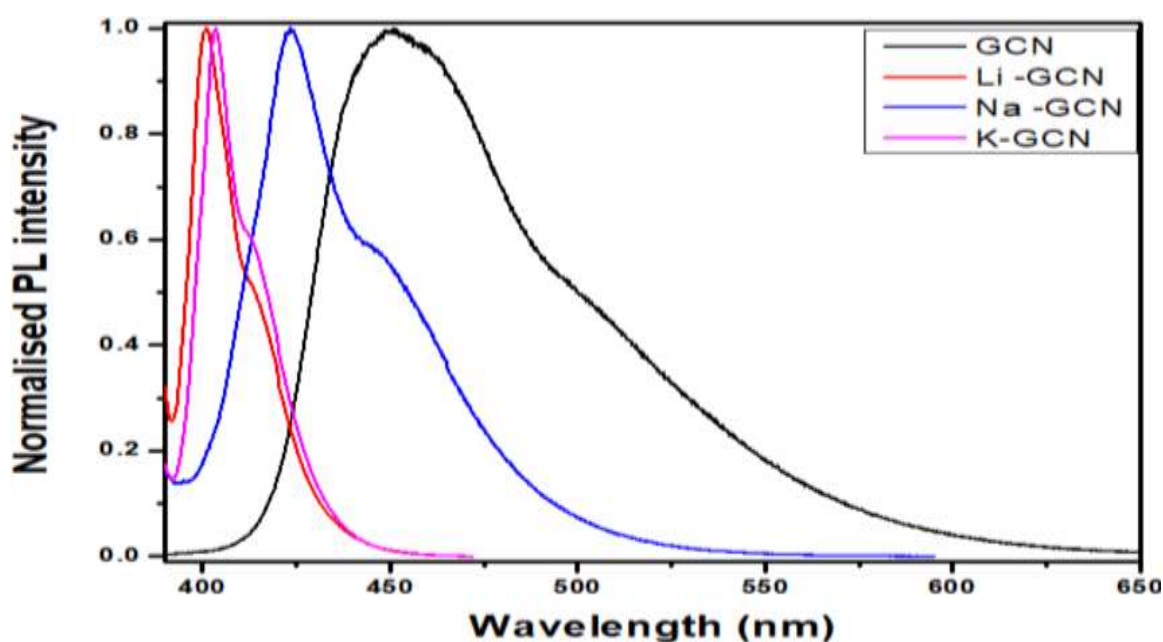


Fig:5.10. PL Spectrums of Pure GCN and Alkali metals doped GCN

SAMPLES	λ_{MAX}
Pure GCN	452
Li-GCN	401
Na-GCN	423
K-GCN	403

Table:5.3: Spectral Data of all above Photoluminescence Analysis

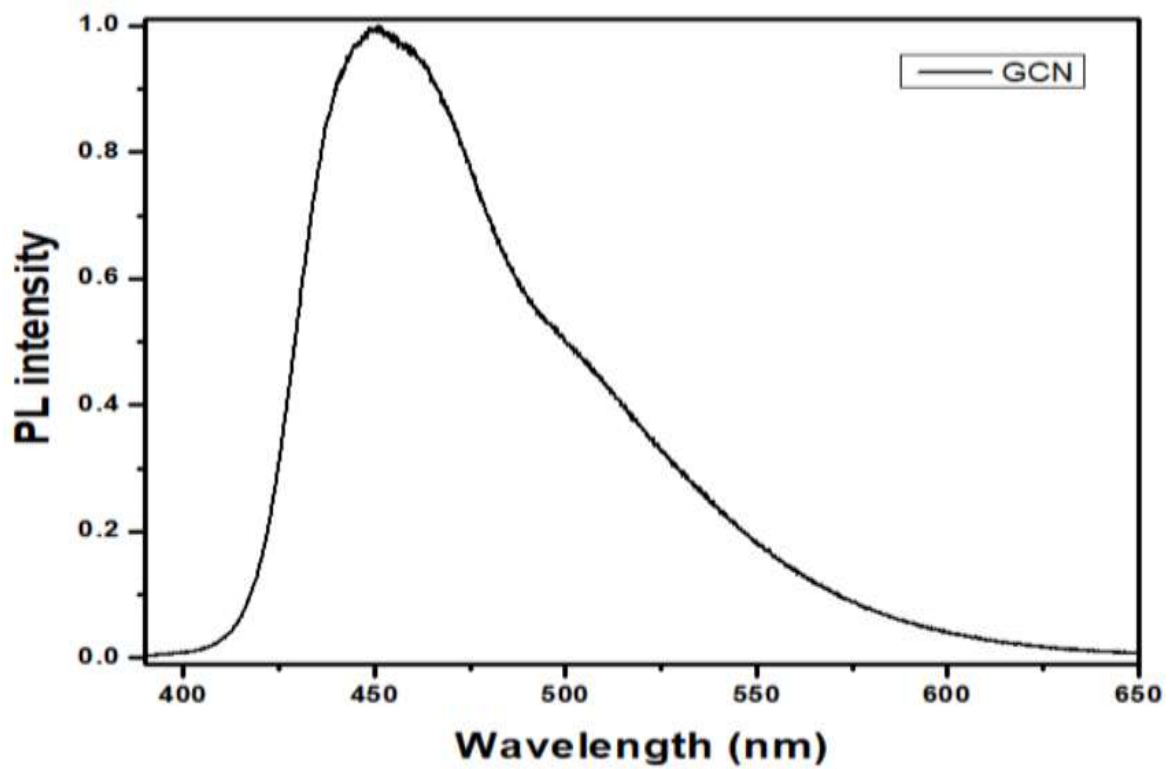


Fig:5.11. (a) PL Spectrum of Pure GCN

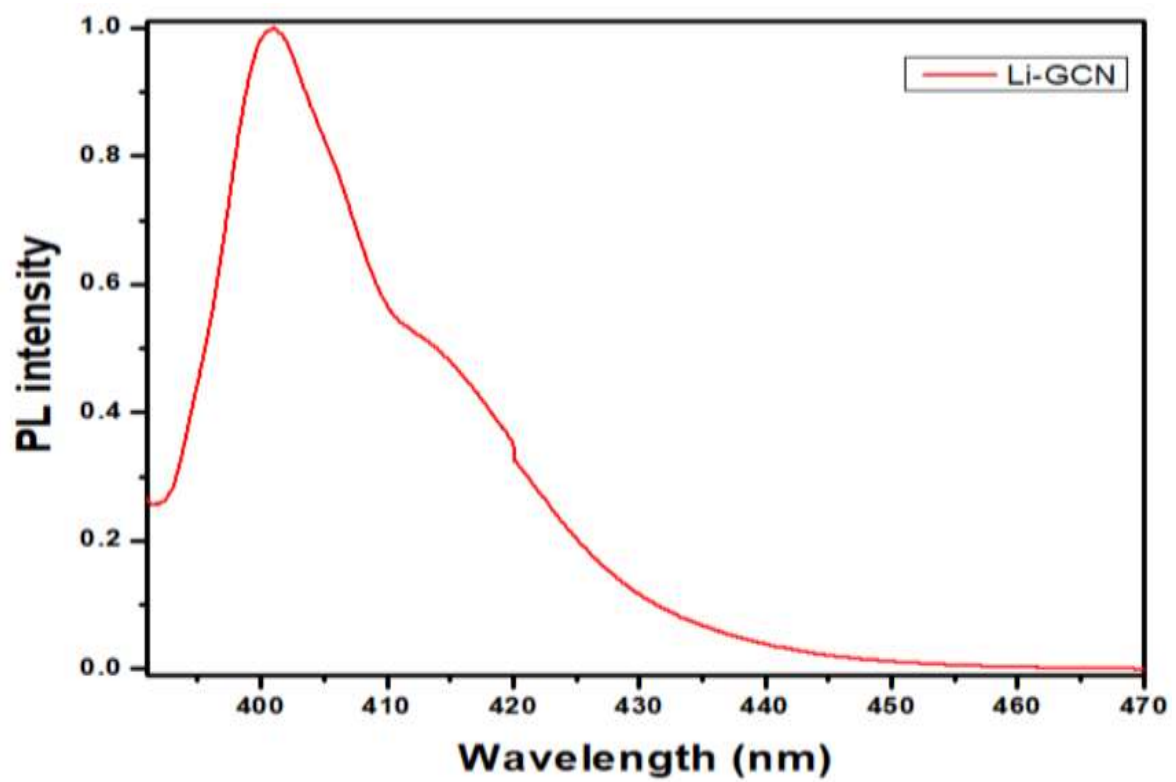


Fig:5.11. (b) PL Spectrum of Li-doped GCN

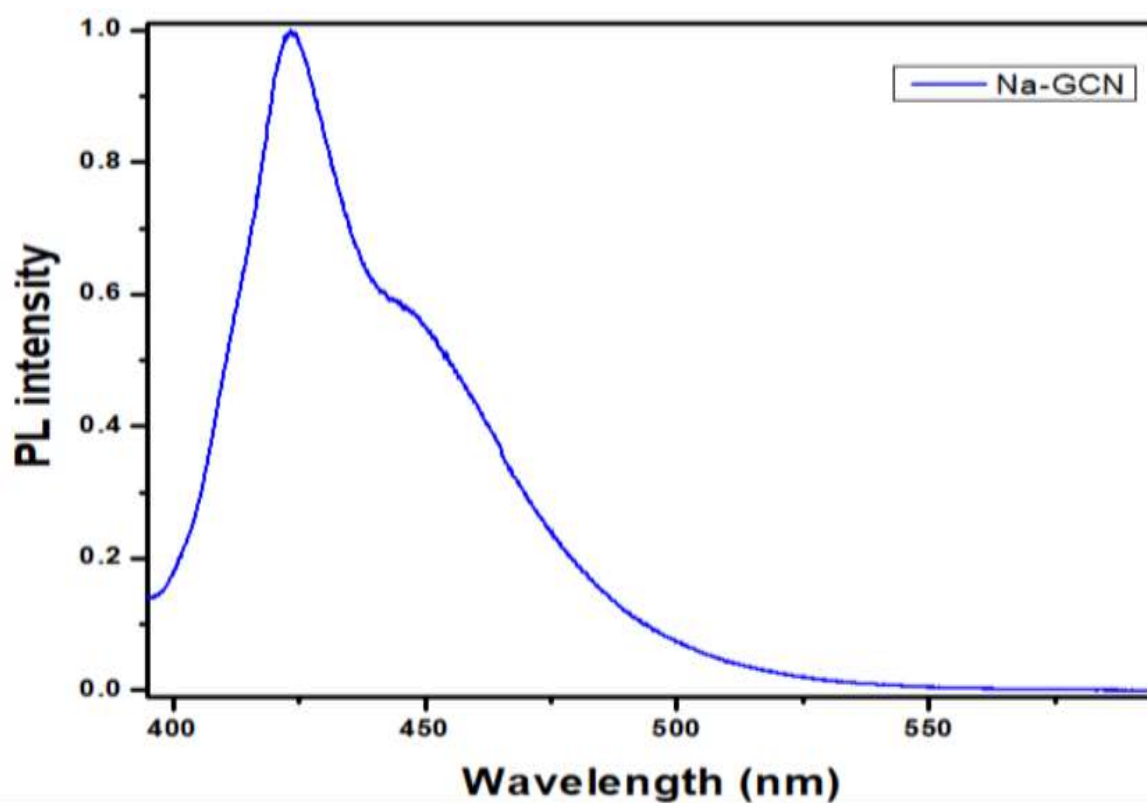


Fig:5.11. (c) PL Spectrum of N-doped GCN

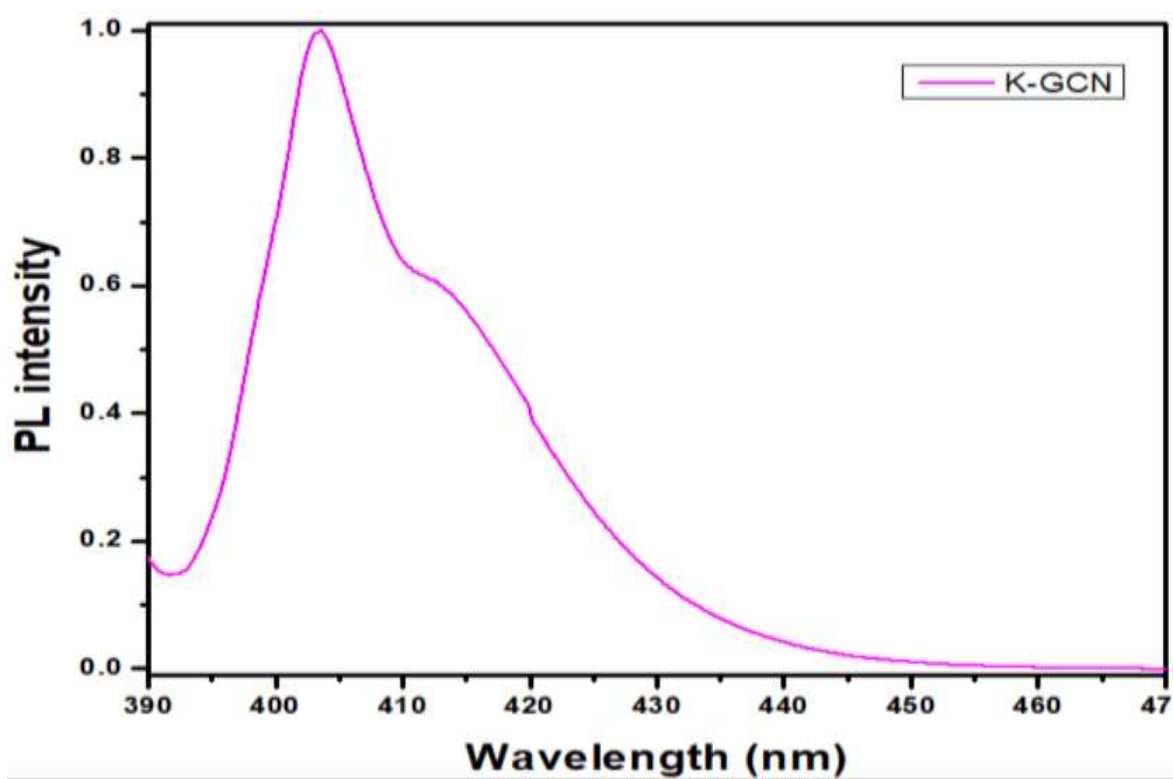


Fig:5.11. (d) PL Spectrum of K-doped GCN

CHAPTER 6

SUMMARY AND CONCLUSION

An economical and straightforward method was employed to create both Pure Graphitic Carbon Nitride (GCN) and its variants doped with Alkali metals. Scanning Electron Microscopy (SEM) revealed that the synthesized GCN and its lithium, sodium, and potassium-doped counterparts all exhibited nano flake-like structures, akin to the pure form. The prepared GCNs displayed numerous layered and folded flake-like configurations. X-Ray Diffraction (XRD) analysis verified the successful production of Pure GCN and its Alkali metal-doped versions, with diffraction peaks at **27.3°**, **27.4°**, **27.6°**, and **27.8°** corresponding to the (002) plane of Pure GCN, Li-doped GCN, Na-doped GCN, and K-doped GCN, respectively. Fourier-Transform Infrared Spectroscopy (FTIR) showed similar characteristic bands at **803 cm⁻¹** and the **1200–1800 cm⁻¹** range, attributed to the presence of Heptazine units and the stretching vibrations of the aromatic C-N heterocyclic rings in GCN. This indicates that the Alkali metals disrupted the interlayer periodicity without altering the fundamental atomic structure, confirming the formation of the C-N-C bond, a hallmark of graphitic materials with alternating nitrogen and carbon atoms. Ultraviolet-Diffuse Reflectance Spectroscopy (UV-DRS) measured the optical absorption, noting a RED SHIFT in the absorption band from **370 nm to 412 nm**, signifying that pure g-C₃N₄ is pale yellow, with the colour intensifying as the dopant size increases, enhancing visible light absorption from lithium to potassium. Photoluminescence (PL) spectrum analysis under an excitation wavelength of **370 nm** showed a broad PL band around **465 nm** for Pure GCN, indicative of n- π^* electronic transitions involving nitrogen's lone pairs. A BLUE SHIFT was observed in the doped samples. These synthesized materials are promising for applications in sensing, batteries, and bioimaging, and as non-toxic, eco-friendly photocatalysts.

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