Chapter 1

Introduction

Graphitic carbon nitride (gCN), a metal-free polymer characterized by sp^2 hybridization and highly delocalized π-conjugated electronic structure, is a notable semiconductor material.[1–4] It is one of the most stable allotropes of carbon nitride polymers, exhibiting excellent chemical and thermal stability up to 600 ºC. It has garnered significant interest in the last decade owing to its numerous advantages, including high physicochemical stability, a unique electronic band structure with visible light responsiveness, and easy synthesis from naturally abundant precursors. Ascribed to its semiconductor nature, gCN exhibits a UV band at nearly 420 nm in the blue region of the visible light exhibiting a pale yellow colour.[5] The resulting band gap of 2.6 eV enables it to provide energy for various photocatalytic reactions. Due to these properties, gCN has emerged as a focal point of inquiry over the past decade, particularly in photochemistry, acting as a low-cost photocatalyst for water remediation[6–9], mineralization of pollutants[10,11], water splitting[12–15], and many more[16–25].

The gCN, resembling a structure similar to graphite, features a layered 2D structure that can be characterized as a unique framework of nitrogen atom-substituted graphite. This includes the π-conjugated graphitic planes formed by carbon and nitrogen heteroatoms with triazine, or tri-s-triazine rings as fundamental units. The inherent amino groups, hydrogen impurities, and -COOH functional groups arising from the incomplete polymerization of functional monomers endow enhanced electroactive sites and multiple centers for covalent and noncovalent interactions. Despite several benefits, the bulk, amorphous structure of gCN offers a limited surface area and poor mass transfer, offering a suppressed electrochemical response[26]. Its low dispersibility in most solvents and high N content are a few other problems that make bulk gCN an ineffective choice for electrochemical processes. However, the ease of surface functionalization and its ability to interact with various metals offer tremendous venues for tailoring its composition and

structure to tune the physicochemical properties of the bulk gCN as per the electrochemist's need. Very recently, the researchers started investigating various strategies to tune the composition, morphology, and electronic structure of gCN, which triggered extensive research work in modulating the semiconductor (photoelectrochemistry, electrochemiluminescence) and electronic structure (charge transfer, electrocatalytic activity) driven properties[23,27]. The notable rise in the volume of published articles annually indicates the growing realm of modified gCN with tunable properties, which needs to be extended further for electrochemical applications. Therefore, the next few sections of this chapter briefly talk about the historical progress, methods of synthesis, characterization, and modification to tailor the physicochemical and electronic properties of gCN. The major emphasis of this thesis is overcoming the aforementioned drawbacks associated with bulk gCN and tailoring its morphology, structure, and composition to tune the electrocatalytic properties. The electrocatalytic properties have been evaluated using electroanalytical sensing methods, which have been discussed at the end of this chapter.

1.1. Brief History

The scientific community considers carbon nitride (C_3N_4) to be among the oldest synthetic polymers. Its discovery goes back to 1830, when Jöns Jakob Berzelius ignited mercury (II) thiocyanate to create heptazine (tri-s-triazine; three fused triazine rings), which is the form of carbon nitride. Later on in 1834, Justus von Liebig[28] coined the word "melon" ($C_6N_9H_3$) to describe the structure that results from polymerizing heptazine units with the aid of amine linkage (NH). Based on several experiments, “Liebig concluded that the fundamental units of tri-s-triazine and triazine are melamine, melam, melem, and melon”. (see **Figure 1.1**). However, the findings were left unnoticed until 1920s, when, Franklin[29] in 1921 examined Leibig’s “melon” and deduced its molecular

formula, $H_3C_6N_9$. He asserted that polymerization of several nitrogenous compounds including guanidine, biguanide, cyanamide, dicyandiamide, and melamine, can result in melon which ultimately leads to carbonic nitride 'C_3N_4'. In 1937, "Pauling and Sturdivant[30] reaffirmed that tri-s-triazine was the fundamental unit of melon".

In 1989, "Cohen and Liu[31] published an article in Science on the crystal structure calculation of β-Si_3N_4, forecasting a carbon-nitrogen compound β-C_3N_4 with a diamond-like elastic modulus upon substituting Si with C in β-Si_3N_4." The study revealed that the hardness of β-C_3N_4 can be similar to or higher than that of diamond, hence inspiring interest in its possible uses as a semiconductor material.

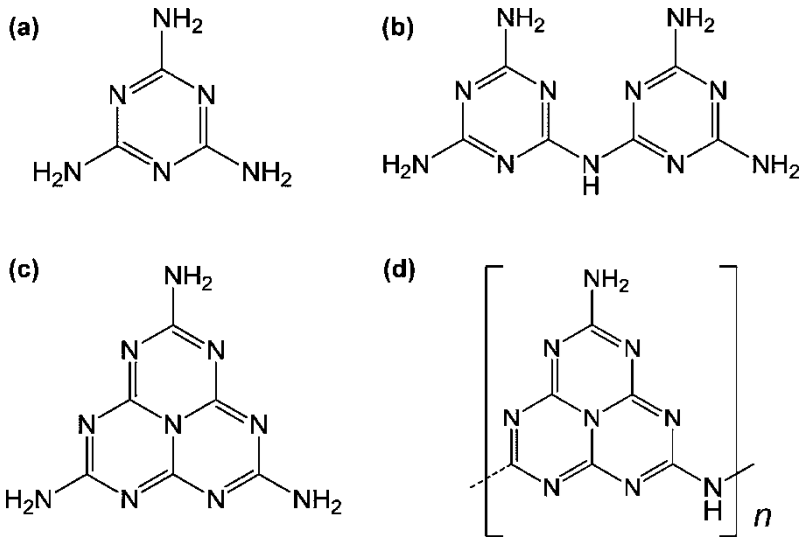

Figure 1.1: Structure of "(a) Melamine (b) Melam (c) Melem (d) Melon prepared from the pyrolysis of mercury (II) thiocyanate as described by Liebig". Reprinted from the permission from ref.[32]

In 1996, "Teter[33] re-evaluated C_3N_4 utilizing the minimal energy pseudo-potential technique and presented five probable structures of C_3N_4: a-C_3N_4, b-C_3N_4, pseudocubic-C_3N_4, cubic-C_3N_4, and g-C_3N_4, of which a-C_3N_4, b-C_3N_4, pseudocubic-C_3N_4, and cubic-C_3N_4 are identified as hard materials. According to their studies, the graphite-like C_3N_4 exhibits the most stable configuration at ambient temperature." The studies also revealed the two allotropes of gCN, one made up of triazine units (melem) and the other having tri-s-triazines as the fundamental structural unit (**Figure 1.2**). The differing nitrogen-

containing pore diameters in the structure result in distinct electron environments for the N atoms in the two gCN allotropes. "Kroke et al.[34] determined that the tri-s-triazine-based gC_3N_4 exhibits greater stability according to density functional theory (DFT) calculations". Consequently, in recent years, the tri-s-triazine structural unit gC_3N_4 has been more commonly documented. Graphitic carbon nitride crystals remain undiscovered, although carbon nitride was synthesized experimentally four years subsequent to its theoretical prediction in 2001 which resulted in increased research interest in gCN synthesis.

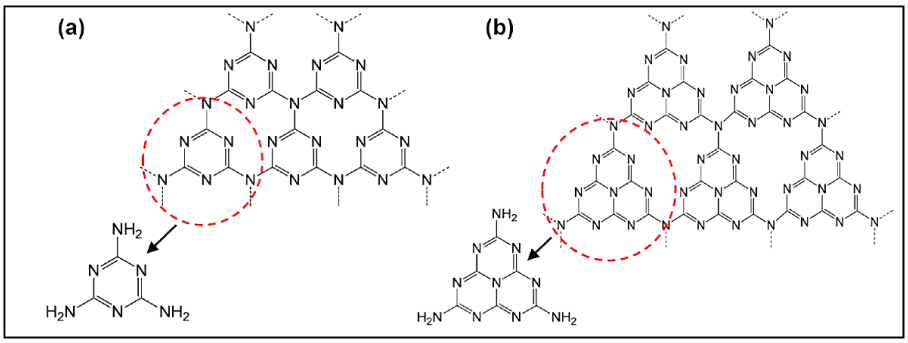

Figure 1.2: Structure of graphitic carbon nitride based on (a) s-triazine and (b) tri-s-triazine units. Incorporated with permission from ref.[23]

Table 1.1: Brief Historical progress of gCN

Year	History of gCN	Ref
1834	"Berzelius synthesized heptazine in 1830. Leibig gave it the name "melon" in 1834.	[28]
1922	Franklin coined the term "carbonic nitride" and discovered that it is the final byproduct of a number of ammonocarbonic acids, with melon serving as the starting material.	[29]
1937	Sturdivant and Pauling proposed tri-s-triazine as a monomer unit of graphitic carbon nitride.	[30]
1940	Lucas and Redemann noted similarities between the structures of graphite and melon.	[35]
1982	Leonard et al. obtained a derivative of cyameluric as the pioneer crystal structure.	[36]
1989	The hardness and bulk modulus of β-C_3N_4 was theoretically demonstrated to be on par with or higher than diamond.	[31]
1996	Hemley and Teter demonstrated that graphitic carbon nitride has five structural kinds using computational methods.	[33]
2001	Komatsu described a species with high crystallinity that was thought to be melon with a high molecular weight.	[37]
2003	Schnick et al. isolated melem and melem derivatives and determined that these were the crystalline structure of heptazine.	[38]

2006	It was found that g-C_3N_4 is a heterogeneous photocatalyst that is metal-free.	[39]
2007	Dicyclodiamide was changed into imide phase carbon nitride by Milan et al.	[40]
2009	Wang uses g-C_3N_4 to generate hydrogen in a semiconductor without the use of metal."	[41]

In 2009, "Wang and colleagues[41] revealed that g-C_3N_4 may be used as a photocatalyst to produce hydrogen in the presence of visible light". This initiated a significant historical milestone, which resulted in the publication of numerous papers and the conduct of significant research. Since then, scientists throughout the world have begun to investigate gCN. The timeline representing the detailed historical progress of gCN are documented in **Table 1.1**.

1.2. Synthesis

The thermal polymerization of N-rich molecules having a C-N bond, preferably without any C-C bond, is the most commonly used method employed for the synthesis of bulk gCN. The typical precursors include melamine, dicyandiamide, urea, cyanamide, thiourea, and their combinations.[32] **Figure 1.3** illustrates the primary precursor molecules and the temperature parameters for synthesizing gCN using thermal polymerization. The polymerization process entails the integration of polyaddition and polycondensation mechanisms, resulting in the stacking of layers of interconnected melem units. The production process from precursor to final 2D carbon nitride polymer involves many intermediate structures, resulting in a graphitic configuration (**Figure 1.4**). The choice of precursor molecules and the synthesis conditions dictate the C/N ratios, defect density, physicochemical properties, morphology, surface functionalities, and the specific surface area of the synthesized material. Thermal polymerization is the most straightforward and efficient process for the scalable and low-cost synthesis of gCN. Nevertheless, the gCN formed from thermal polycondensation has a bulk structure with

low crystallinity, aggregated particles, and low surface area (10 m^2/g). The excessive N content also results in low electrical conductivity, making them unsuitable for electrochemical applications. Over the years, researchers have synthesized bulk gCN using thermal polymerization and tuned it using the Top-down approach to achieve the desirable properties. In the Top-down approach, the bulk gCN is modified using several strategies discussed in the following sections.

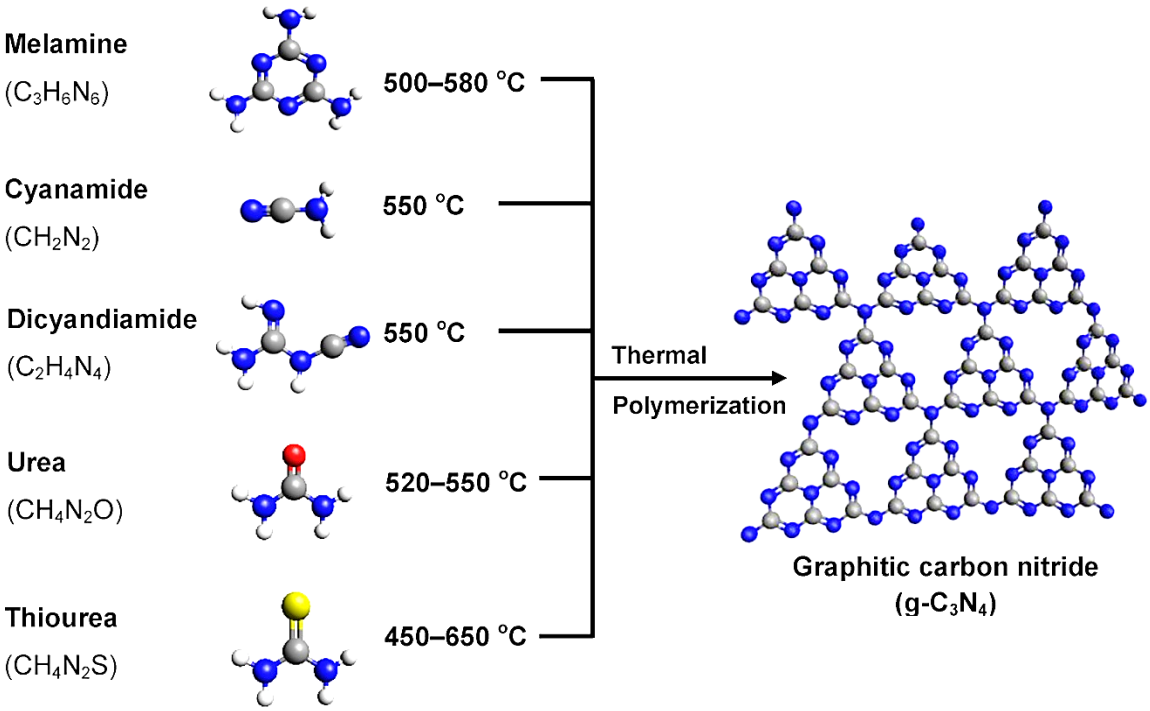

Figure 1.3: Synthesis protocol of graphitic carbon nitride using different precursors. Reprinted from the permission from ref.[32]

Additionally, a less popular, more expensive bottom-up approach exists for synthesizing gCN with enhanced crystallinity and morphological control. This approach mainly includes the structurally guided thermal polymerization of N-containing precursors in a template and template-free method[42,43]. The template method involves rigid or soft structure guiding agents, which lead to the growth of the gCN framework in the desired morphology. The hard templating uses a rigid structure with a defined morphology, like silica spheres on which the precursor was allowed to polymerize followed by template removal. In contrast, soft templating involves self-assembling precursors over self-

assembled ionic liquids, surfactants, or amphiphilic polymers. Since the additional step of template removal is not required in the soft-template method, it is considered a greener approach. On the other hand, the template-free method relies on pretreatment or, specifically, the preorganization of monomers followed by thermal polymerization/condensation.

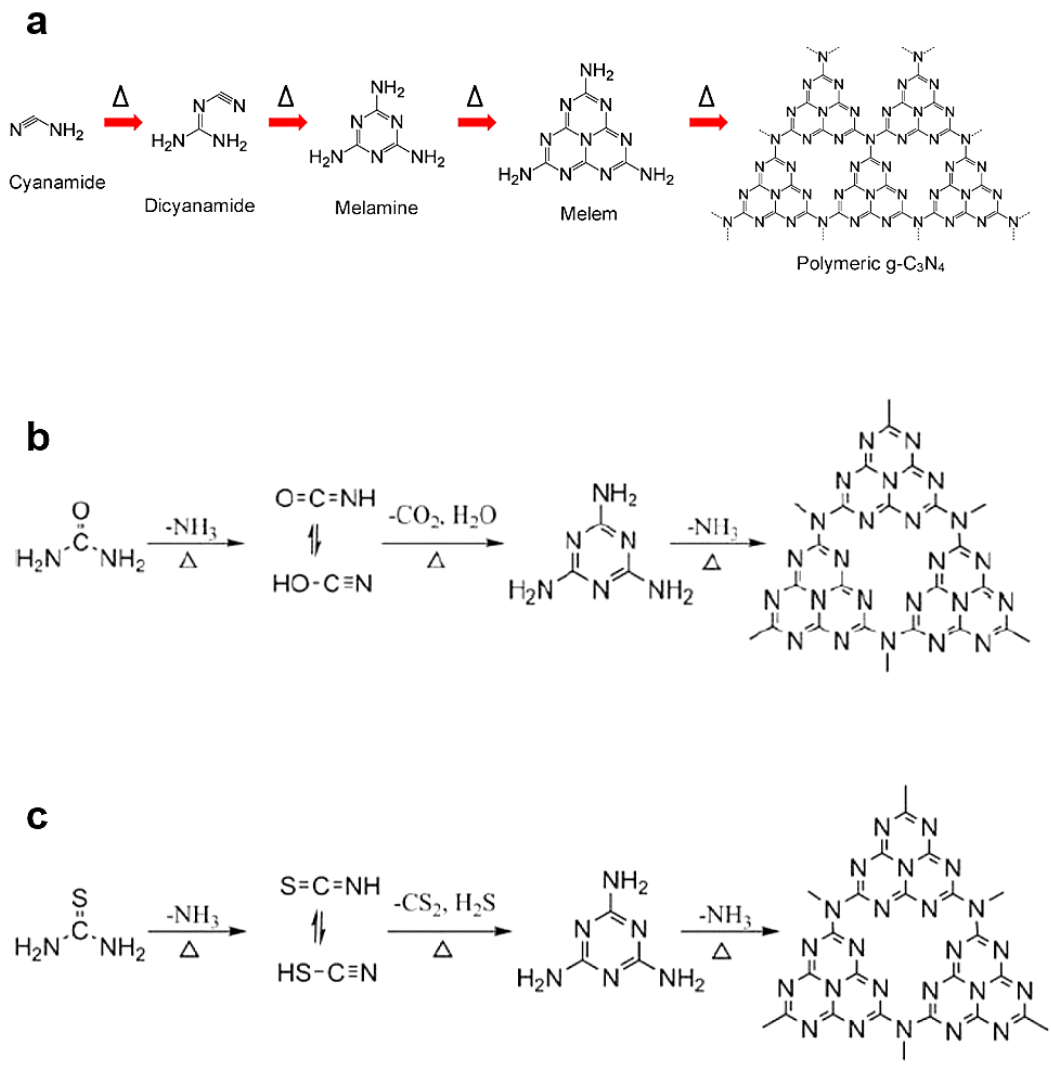

Figure 1.4: Thermal polymerization of (a) cyanamide, (b) urea, and (c) thiourea to form graphitic carbon nitride. Reprinted from the permission from ref[32]

Hydrothermal preorganization and thermal treatment of supramolecular assemblies[12,44,45] are the only two approaches that fall in the template-free category. The bottom-up approach leads to systematically controlled growth of materials, which can be tuned to induce specific morphology, porosity, or charge. However, the multi-step

procedure and expensive resources make it less useful for scalable synthesis and practical applications.

1.3. Characterization of Graphitic Carbon Nitride

Despite of a comprehensive computational and experimental insights on the structure of gCN, the low crystallinity and high disorder degree of bulk gCN poses difficulty in adequate compositional and stoichiometric analysis. This lead to generalisation of "gC_3N_4" term in majority of publications representing a defect containing polymeric gCN. In general, the synthesized gCN material can be analyzed using "X-ray diffraction (XRD)", "Fourier Transform Infrared spectroscopy (FT-IR)", and "X-ray photoelectron spectroscopy (XPS)" techniques. Additionally, "scanning electron microscopy (SEM)" coupled with "Energy-dispersive X-ray (EDX)" analysis can be used to visualise the morphology of gCN and elemental distribution on the surface of the synthesised material. The gCN doesn't exist in perfectly crystalline form though exhibits two peaks in the XRD spectra near 13.1° and 27.3°, corresponding to the (100) and (002) planes, respectively[46–48]. The peak at 13.1° is attributed to the in-plane aromatic structural packing, while the peak near 27.3° is associated with a graphitic-like stacked layered arrangement of conjugated aromatic rings. The presence of these two peaks confirms the existence of graphitic carbon nitride framework (**Figure 1.5**). IR spectroscopy can further be employed to assess the bond structure and functionalization of gCN. The gCN IR spectra may be categorized into three principal regions: 3100-3600 cm^{-1}, 1000-1600 cm^{-1}, and below 1000 cm^{-1}[49,50]. The open-ended unpolymerized structural -NH_2 group of gCN produces a peak in the range of 3100-3600 cm^{-1}. The 1000-1600 cm^{-1} range exhibits numerous vibrational modes of the C-N bond found in the triazine and heptazine rings. Near 804 cm^{-1}, gCN exhibits a characteristic IR peak attributed to the out-of-plane bending mode of the triazine ring. XPS can further be employed to verify the synthesis

of gCN[51–56]. The high-resolution deconvoluted C 1s spectra can reveal various characteristic peaks within the binding energy range of 283 eV to 300 eV. The high-resolution N 1s spectra exhibit characteristic peaks between 390 eV and 405 eV representing the pyridinic and graphitic N environment in the gCN framework. In addition to these techniques, Raman spectroscopy, atomic force microscopy, UV-Visible spectroscopy, CHN analysis are few other techniques commonly employed for characterization of gCN.

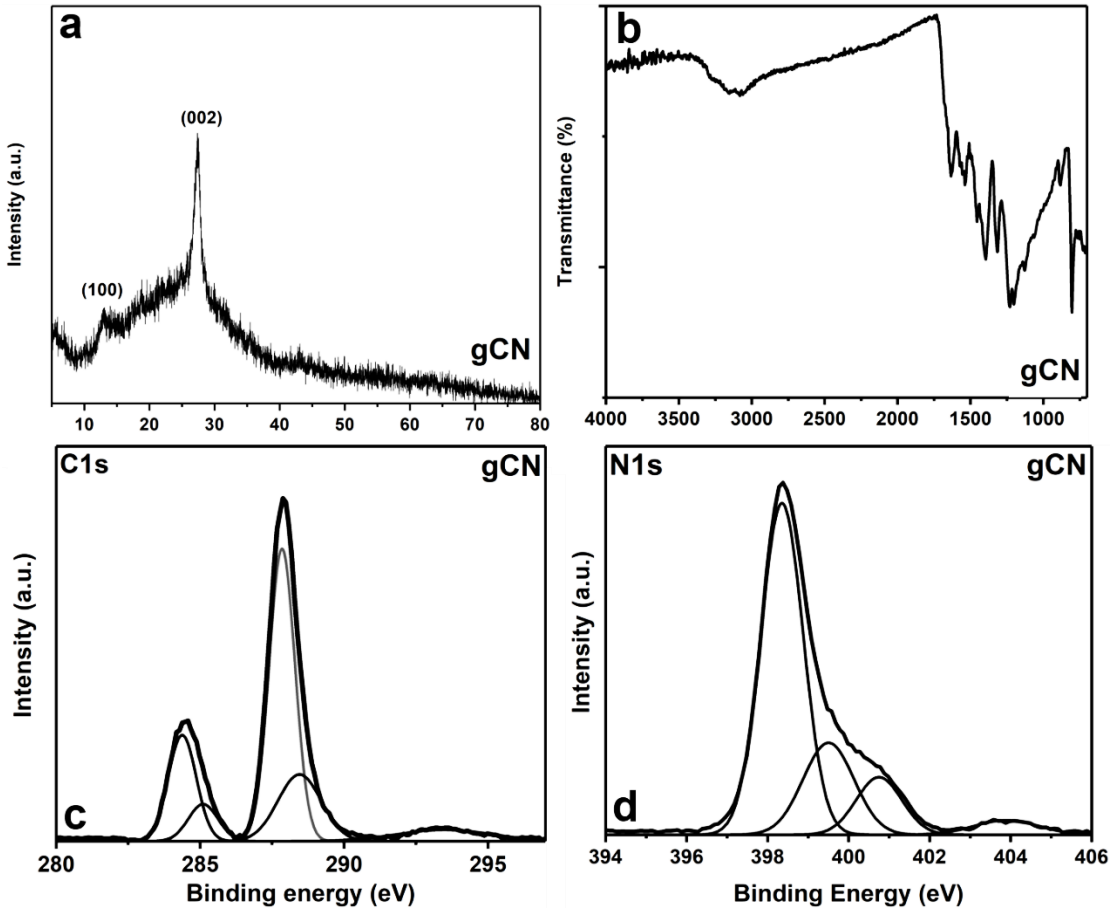

Figure 1.5: Typical (a) XRD peaks, (b) FT-IR peaks, (c) C 1s, and (d) N 1s XPS spectra corresponding to gCN.

1.4. Modifications of Graphitic Carbon Nitride

Typically, gCN in bulk or nanostructured form is unsuitable for electrocatalytic applications due to inherent structural limitations. It possesses a minimal surface area (10-15 m^2/g), low electrical conductivity, suppressed charge transfer, and inadequate

solubility in solvents, which restricts its viability as a standalone candidate[57–60]. There exist two ways to improve the electrocatalytic properties of gCN. The first involves the exfoliation/break-up of bulk carbon nitride into smaller structures. The second is to modify the surface and the polymer backbone through chemical functionalization, metal/non-metal doping, co-polymerization, or compositing.

Interestingly, the polymeric structure of gCN and the abundance of N sites offer the possibility of a wide range of interactions,[61,62] including stacking interactions, H-bonding, electrostatic interactions, and chelation, making it an ideal candidate for covalent and non-covalent functionalization (**Figure 1.6**). Consequently, the properties of gCN can be easily customized via surface engineering[63–67], hetero-junction formation[68–70], and molecular-level engineering[71,72]. Therefore, over the years, researchers have synthesized bulk gCN from facile and cost-effective thermal polymerization and tuned it to achieve the desirable properties using the following Top-Down approaches.

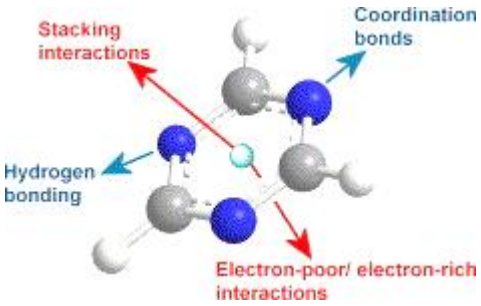

Figure 1.6: Figure representing the wide range of possible interactions for the fundamental unit of gCN. Taken with permission from Ref[61].

1.4.1 Exfoliation:

To improve the physicochemical properties of bulk gCN, it is pivotal to convert bulk structures into small, thin units. To do so, the bulk gCN is exfoliated into smaller particles using mechanical, physical, or chemical forces, commonly known as the Top-down approach. This includes ball milling, ultrasonication assisted, chemical/thermal, or electrochemical exfoliation.[26,73,74] All these methods rely on delaminating the

stacked carbon nitride layers by overcoming the weak Vander waals interaction through oxidation of the CN layers and/or intercalation of species between the layers. The resultant gCN material exhibits plate-like morphology with an abundance of –NH/–NH_2/–N/–COOH functional group, making it dispersible in water and other solvents. The exfoliation strategy increases the number of defects and N vacancies "by reducing the N species of the triazine rings (C═N═C)," ultimately resulting in surface functionalization of exfoliated gCN[67]. The exfoliated gCN exhibits higher dispersibility in water and other suitable solvents, overcoming one of the significant problems associated with bulk gCN. In addition, the exfoliation increases the surface area and reduces the material diffusion path, greatly enhancing the electrical conductivity and charge transfer dynamics[75,76]. Out of all the methods, electrochemical exfoliation is one of the most promising methods that converts the bulk gCN into thin layers due to potential-driven intercalation of charged ions and solvent molecules between the CN layers.

1.4.2 Metal/Non-metal Doping:

Introducing an external atom in the gCN framework at the molecular level is another potential method to alter its microstructure, impacting the interplanar distance, degree of graphitization, electronic structure and band gap.[73,77,78,78] Depending on the nature of the dopant (electron donating/electron accepting), different fermi levels can be generated. Though it is clearly outlined that metal/non-metal doping significantly improves the catalytic ability of the gCN, however, the understanding of the doping-induced structural changes is still in its infancy. It is generally reported that metal dopants occupy the cavities within the triazine/ s-triazine rings (**Figure 1.7**). In contrast, the non-metal dopants occupy the C or N sites in the gCN framework, generating C or N vacancies and redistributing electron clouds[78,79]. Recently, doping of multiple elements in the

gCN substrate has also been reported to improve the overall catalytic ability and adsorption efficiency of this metal-free material.

1.4.3 Composites, Co-Polymerization and Heterojunction formation:

Compositing and copolymerization is another potential strategy relying on the incorporation of metal oxides, metal-organic frameworks, conducting polymers, carbonaceous materials, and other specific compounds in the gCN framework (**Figure 1.8**). The compositing results in a heterogeneous hybrid structure having redistributed electron density in the composite material. The careful choice of the components can lead to differences in the electronegativity of the C and N atoms of gCN and the metal/non-metal centers of the additional component, resulting in the altered electron density[81].

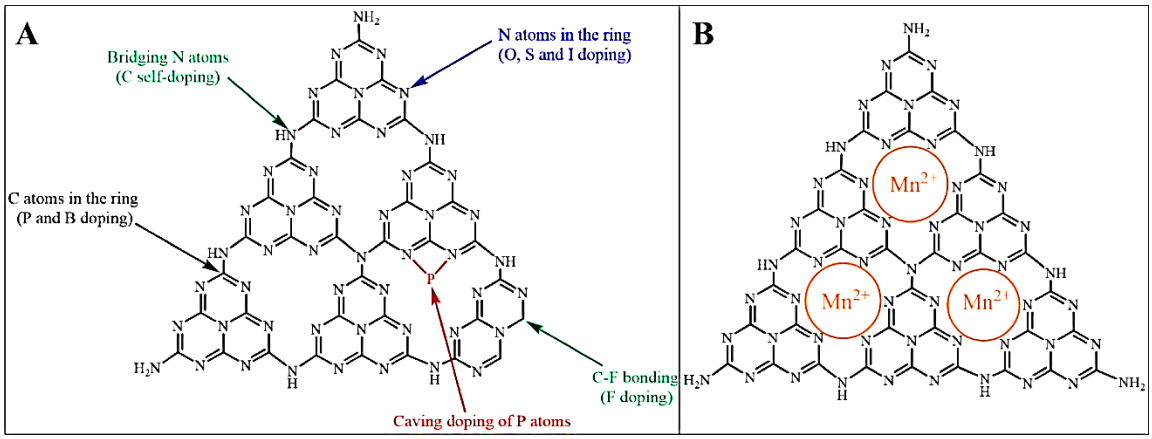

Figure 1.7: Figure illustrating various possible sites for (A) non-metal and (B) metal doping. Incorporated with permission from Ref.[80]

The altered electron density of the hybrid composite material alleviates the electrical conductivity and charge transfer efficiency, making it promising for electrochemical applications. The transition metal oxides/gCN composites are specifically important because they augment the electron density on the gCN framework through their d electrons[82,83]. In turn, the electrostatic interaction between the N centers of the gCN layers and the d orbital of the metal center synergistically stabilizes the metal oxide dissolution. The gCN-based composites are reportedly synthesized either by mixing the

precursor substances followed by thermal condensation or via the post-treatment of bulk gCN via a top-down approach. Simple dispersion, ultrasonication, and electropolymerization are commonly used strategies for post-treatment. The stability of the composite material relies on exploiting the electrostatic and stacking interactions.

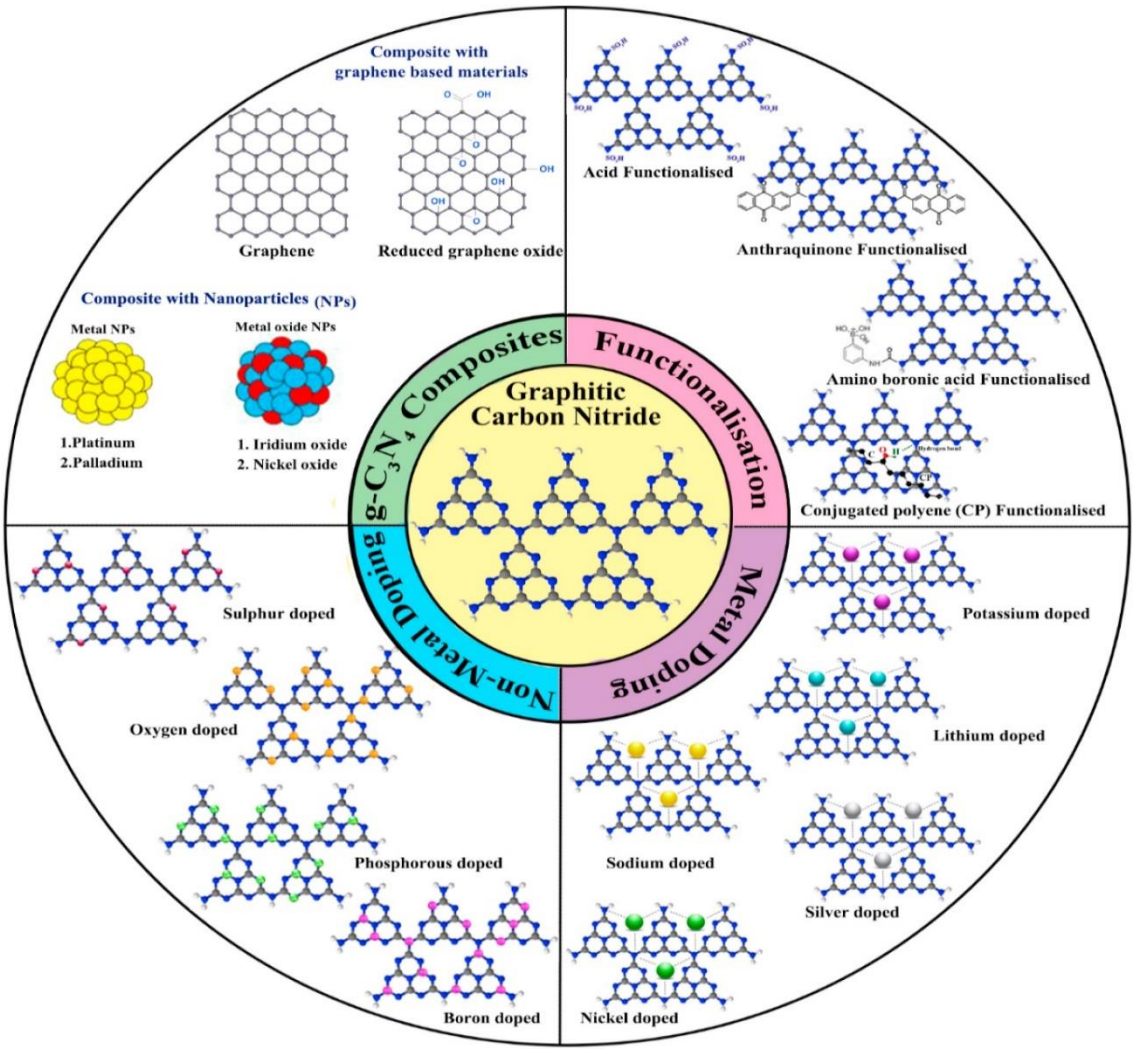

Figure 1.8: Figure summarizing the various modification strategies commonly employed for tailoring gCN. Incorporated with permission from Ref[23]

1.5. Importance of Graphitic Carbon Nitride as Electrocatalyst

The gCN modified using the abovementioned methods exhibits substantial merits compared to other class of electrocatalytic materials. A few characteristic traits are listed below

1. High surface to volume ratio with enhanced dispersibility in polar solvents

2. Pyridinic and graphitic N species endowing active sites for chemical/electrochemical oxidation
3. Abundant surface functional groups (-COOH, C-N, C=N, –NH and $–NH_2$) offering sites for transient adsorption and interaction with the substrates and the electroactive species.
4. High surface to volume ratio with enhanced dispersibility in polar solvents
5. Pyridinic and graphitic N species endowing active sites for chemical/electrochemical oxidation
6. Abundant surface functional groups (-COOH, C-N, C=N, –NH and $–NH_2$) offering sites for transient adsorption and interaction with the substrates and the electroactive species.
7. Redistributed electron density, delocalised π electron cloud, heteroatom sites of the modified gCN composites makes it suitable for selective interaction with electroactive species exploiting H-bonding, π- π stacking, and electrostatic interaction.
8. n-type, p-type doping results in facilitated charge transfer dynamics, and electronic conductivity.

All these properties lead to the improved electrocatalytic ability of modified gCN in several fields, including electrochemical water splitting, electrocatalytic CO_2 reduction, sensing, energy conversion, and storage. The electrocatalytic ability of the modified gCN is specifically relevant for electroanalytical applications as the gCN act as a versatile transducer or recognition element that promotes the interfacial interaction with wide range of electroactive biomolecules, metal ions and phenolic analyte[84–87]. The facilitated interaction of the analytes with the gCN functionalized surface facilitates the electrochemical redox processes and leads to increased sensitivity.

1.6. Immobilization of Electro-catalyst on Conductive Surfaces

To evaluate the electrocatalytic activity of a material, it is essential to immobilize the catalyst on a conductive surface with precision and optimal thickness to provide superior electrocatalytic performance. Proper immobilization of recognition element on the clean substrate is critical for the electrochemical performance. For any electrochemical process, the intimate interfacial contact between the catalyst (gCN) and the conductive substrate (working electrode) plays a pivotal role in improving the charge transfer. Therefore, several methods have been opted for the surface modification of electrodes. Few major ones include, (i) drop casting of a known volume of the nanomaterial dispersed in a particular solvent followed by drying at room temperature, (ii) Crosslinking the nanomaterials on suitable substrates with the aid of functional groups like thiol/amine, or additional cross-linker like glutaraldehyde (iii) electrodeposition/ potentiodynamic, and (iv) Spin/dip coating. Though more sophisticated methods like thermal evaporation, CVD, ALD etc have been used but such method are restricted to only few electrodes such as ITO, FTO etc. A brief literature review of the previously reported immobilization strategy of gCN is presented below.

1.6.1 Previously reported Immobilization strategies of gCN

The doctor blade method is extensively employed for applying coatings to substrates. "Zhang et al.[88,89] utilized this process by applying aqueous slurry of gCN onto an ITO surface (**Figure 1.9**)".

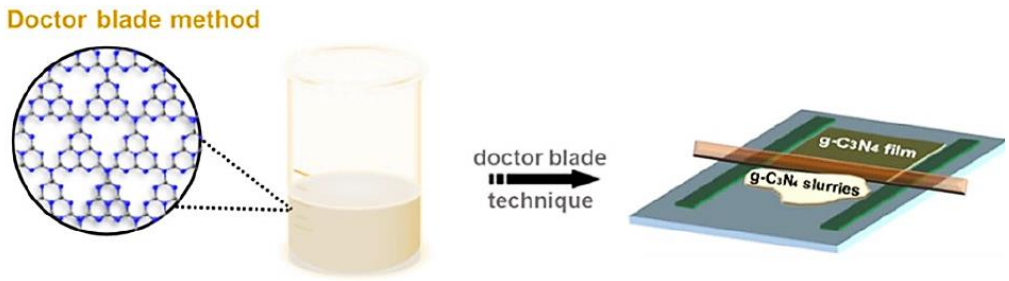

Figure 1.9: Doctor Blade method for coating of gCN slurry. Permission taken from ref[90].

Nonetheless, the deposited gCN powder employed as a "coating" suffered from poor adherence to the substrate. Subsequently, “Jiang et al.[91] documented a spin-coating technique for the development of gCN composite films with a g-C_3N_4/perovskite precursor solution”. Both the doctor blade approach and spin coating method yield homogenous immobilization of the catalyst on conducting surfaces; nevertheless, cracks and defects arise during solvent evaporation. Furthermore, stability was found to be a barrier for both systems. Binders were employed to address stability issues; nevertheless, they may affect the catalyst's activity.

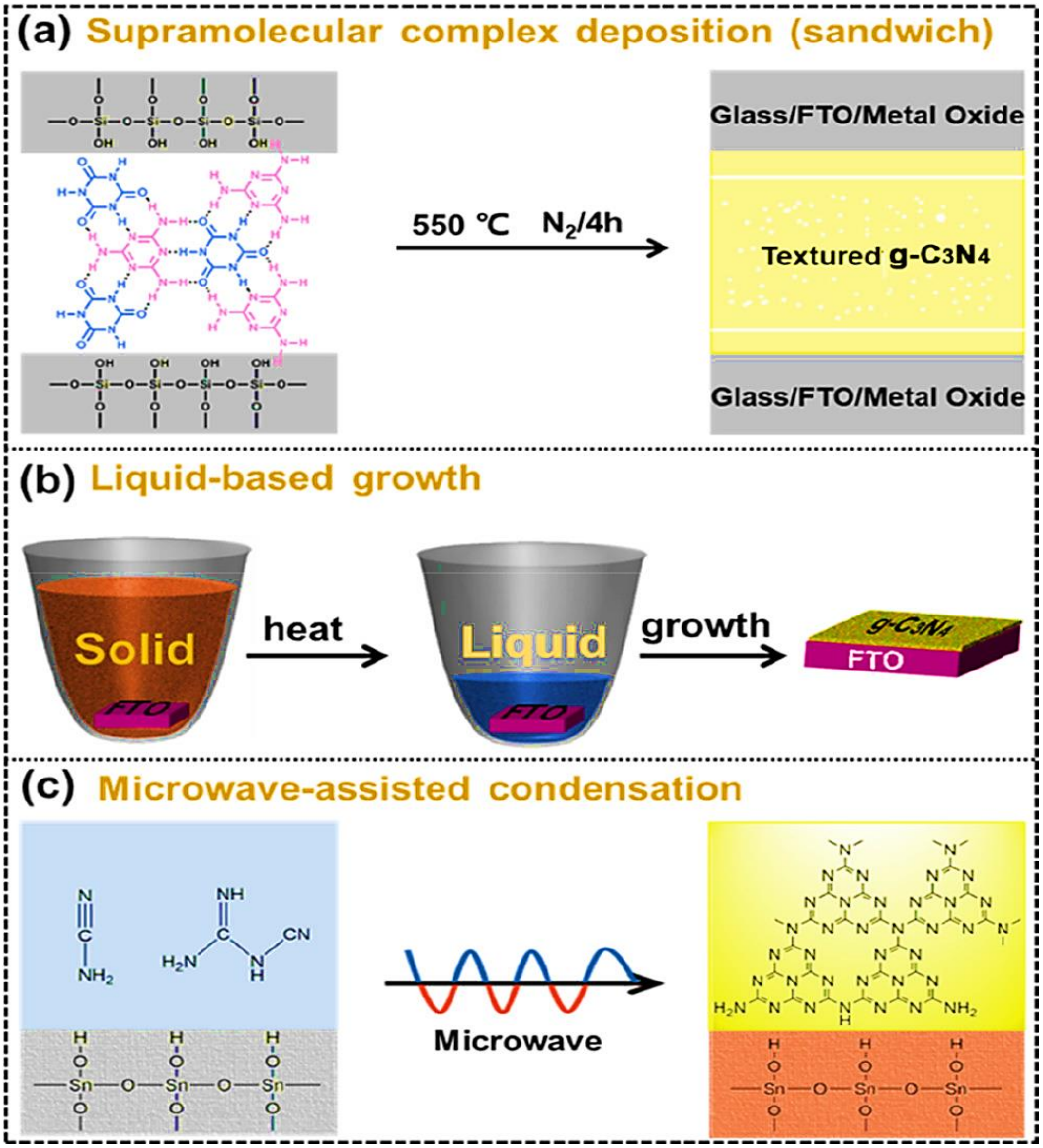

Figure 1.10: Different contact growth coating methods (a) Supramolecular Complex deposition. (b) Liquid-based growth and (c) Microwave-assisted condensation. Permission taken from ref[90].

In 2014, “Shalom et al.[92] delineated a method for the direct deposition of gCN onto diverse substrates by encapsulating a surface-attached cyanuric acid-melamine supramolecular complex within the substrates (**Figure 1.10**). This research is the first attempt to effectively cast gCN onto conductive surfaces like FTO, TiO_2, and ZnO. By interacting the supramolecular complex precursor with the glass substrate surface, a ~ 40 nm layer of organized gCN rods were synthesized”. Nevertheless, the resultant layer exhibited low catalytic activity. Subsequently, “Xu et al.[93] exhibited a liquid-based method employing a supramolecular precursor to produce continuous gCN thin films on substrates.

The authors indicate that the film consists of continuous and well-structured gCN strands”. The existence of extra precursors prevented modulation of film thickness on the substrates, which was instead influenced by the substrates' surface energy. In addition, “the fast condensation of carbon nitride onto an electrode was recorded by Zhao et al.[94] using microwaves”. A continuous layer on FTO with a near interface was produced by the microwave-assisted condensation of dicyandiamide, in contrast to the grain boundary-laden gCN coating that was created using doctor-blading.

“Arazoe et al.[95] used the revolutionary method "vacuum deposition process" (VDP) to describe a new way of reacting precursors onto target substrates in a gas-phase noncontact growth environment (**Figure 1.11**).

An open glass tube was suggested as the reaction container for the VDP technique. Precursors like guanidinium carbonate or melamine were placed at the base of the reactor tube, with the substrate placed on the opening side”. A conventional carbon nitride powder was found to coexist with a yellowish transparent membrane that was fabricated on the substrate using an appropriate heating rate under N_2 circumstances. In 2015, “Liu et al.[96] introduced a microcontact-printing-assisted technique for the fabrication of g-

C_3N_4 films on various substrates using the cyanamide precursor". The film thicknesses were found to be dependent on the ink concentrations of the precursor solution.

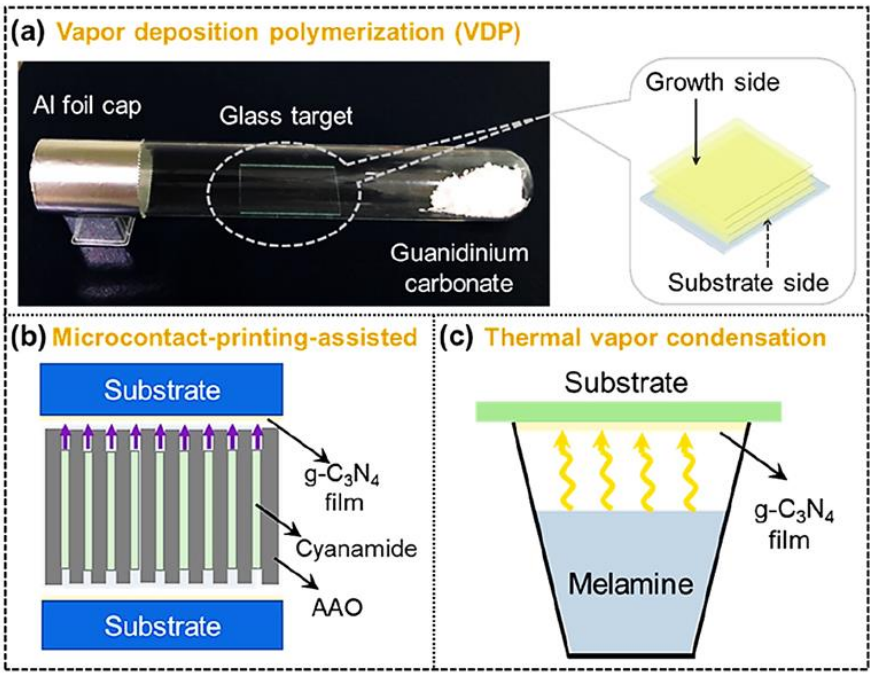

Figure 1.11: Different non-contact growth coating methods (a) Vapour deposition polymerization of precursor to gCN. (b) Microcontact-printing-assisted method of coating and (c) Thermal Vapour Condensation of precursor (Melamine) to gCN. Permission taken from ref[90].

Using the target substrates placed as a lid on top of a crucible, "Bian et al.[97] (2015) suggested a thermal vapour condensation technique to create a homogeneous and attractive g-C_3N_4 coating. The precursor in the bottom of the crucible is vaporized when the temperature is raised over 300 °C. After passing through a condensation process, the vapour was found to settle onto the "lid" substrate". The effectiveness of the method was found to be dependent on the nature of the substrate, the precursor quantity and the gap between the "lid" and the precursor level.

Despite the fact that the direct growth method yields a consistent coating, it comes with a number of drawbacks including the need for an expensive and complex instruments, issues with the coated film's durability, difficulties in optimizing the film's thickness, incomplete precursor condensation, and an excess use of precursor material. In addition

to this, all of the above-mentioned methods cannot be used for most popular working electrodes like glassy carbon electrodes, or screen-printed electrodes. On careful evaluation of literature, one can see that majorly the catalyst has been immobilised on the electrode surface using drop casting method which offers several issues as discussed below.

1.6.2 Drop-cast method

Drop cast is a commonly used technique to modify electrode surfaces in electrochemical applications. This method involves dropping a small amount of liquid with suspended particles directly onto a clean electrode surface. Though drop cast is a straightforward and facile method. Nevertheless, the concentration (mg/mL) of suspension, suspension volume, and drying conditions (time and temperature) should be optimized before pursuing drop-casting. The drop-cast method relies on the physical adsorption of the particle during the evaporation of the solvent, because of which, it suffers from irregular distribution of aggregated particles on the electrode surface, coffee ring effect, irreproducible surface decoration, and poor stability[98] (**Figure 1.12**). In order to achieve stability, the use of binders such as Nafion and chitosan has been reported, which affects the conductivity of the electrode depending on the percentage of binder used. Furthermore, the drop-cast method applies only to small circular electrodes and becomes inconsistent for larger, rectangular electrodes like ITO and FTO.

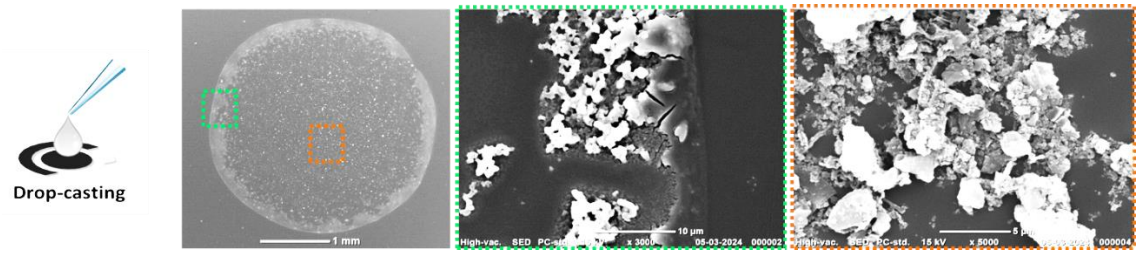

Figure 1.12: HR-SEM images of a drop casted gCN suspension on ITO surface showing different regions of non-uniform material distribution.

1.6.3 Electrodeposition/Potentiodynamic Method

Electrodeposition techniques provide optimistic solutions to the challenges associated with drop casting, thereby enabling the development of more dependable and effective electrochemical sensors and devices. To date, modification of nanomaterials by potentiodynamic method is considered as one of the robust and effective methods. The Potentiodynamic methods including electropolymerization, electrodeposition and electrophoretic deposition offers more optimization parameter leading to a precise control over the extent and uniformity of surface coverage (**Figure 1.13**). In comparison to physical adsorption in drop cast, the growth of surface layer relies on the interfacial charge transfer and chemical interactions between the electrode surface and the recognition element, thereby offering reproducible, repeatable and robust surface modification. Furthermore, it has also been shown that depending on the method, substrate, electrolyte and potential opted the morphology of the material getting deposited on the electrode can be tuned to achieve desired electrochemical performance. The change in morphology compared to the starting material can be ascribed to the effect of applied electrochemical parameters on the diffusion of active materials from the suspension to the substrate. Depending on the kinetics of diffusion and charge transfer, the ions possibly orient themselves in specific directions, which results in preferential nucleation and uniform growth with a controlled morphology. Ascribed to abovementioned advantages, electrodeposition/electropolymerization are well exploited method for the deposition of metal oxides, and polymerization of conducting polymers including melamine. Nevertheless, to the best of our knowledge no report has been published providing insights on the electrodeposition of gCN on a conducting surface and the underlying mechanism. Therefore, one of the primary aim of the research work documented in this thesis was to understand and optimize the electrochemical assisted surface immobilization of gCN and its composites. To carry out the electrodeposition and

test the efficacy of the gCN modified substrate towards the electrocatalytic oxidation of the chosen electroactive analytes, the following electroanalytical methods were employed.

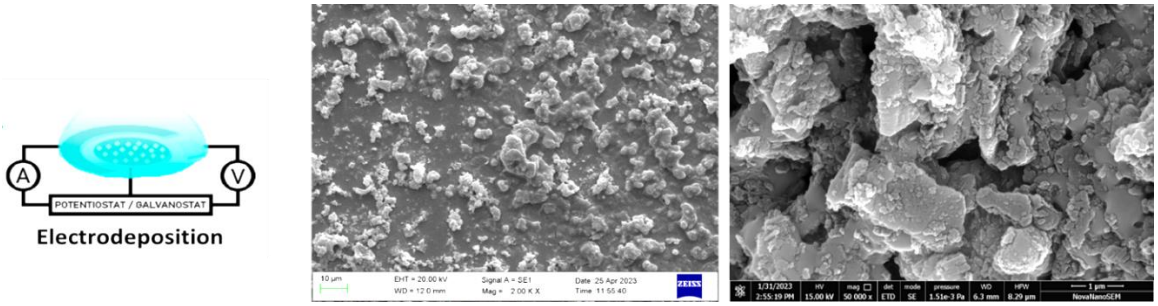

Figure 1.13: HR-SEM images of the gCN electrodeposited on ITO surface showing uniform coverage of the conducting surface.

1.7. Electroanalytical Methods

1.7.1 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) [99–106] has emerged as an important, versatile, and widely used electroanalytical technique. Its capability to provide illustrious information about the nature, thermodynamics, and kinetics of the redox behavior of a species over a wide potential window marks its effective and extensive use not only in physical, organic and inorganic chemistry but also in many diverse fields like most areas of analytical chemistry, biochemistry, etc. On closely surveying the literature, one can observe a few reports showing the applications of CV in the field of sensing in the late 80's. However, several studies demonstrating the use of CV for investigating the mechanistic aspects of CO_2 reduction[107], dopamine measurements[108,109], and other such applications[110–112] have been reported in the early 90's. CV has benchmarked its utility in qualitative analysis and thus even to date every electrochemical investigation begins with the preliminary CV studies either for interrogating the redox chemistry or for calculating any physical quantity like diffusion coefficient, number of electrons involved, etc. Thus, the fundamentals of the technique used for the present investigation have been listed below.

For a CV experiment, the typical excitation signal is a linear potential ramp from an initial potential 'E_i' to a final potential 'E_f' and then switches back to the initial potential, thereby making a triangular wave[99,101,113,114] as shown in **Figure 1.14**.

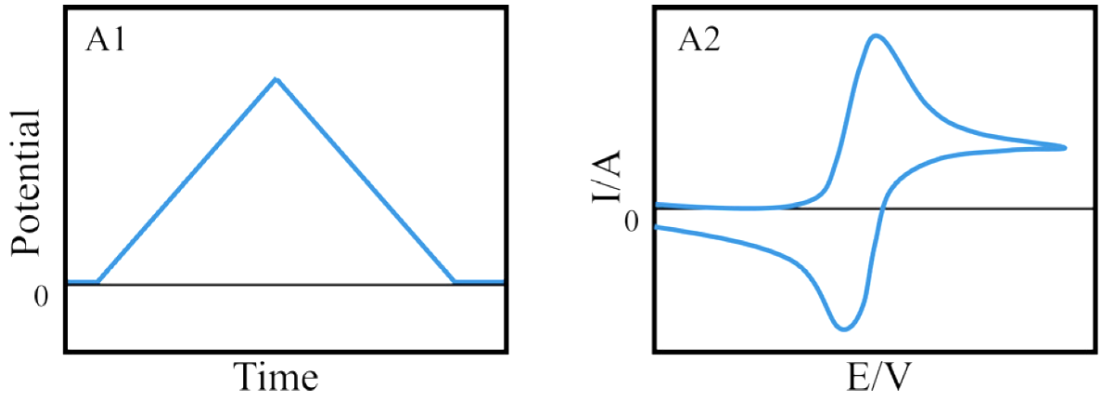

Figure 1.14: Typical excitation signal in triangular wave form and the resulting cyclic voltammogram for a reversible redox process. Taken from Biosensors 2022, 12(7), 494.[115]

The current response obtained when plotted as a function of applied potential gives the cyclic voltammogram from which a number of information can be acquired. The essential characteristics of the voltammograms are the peak potentials and peak currents. The peak current provides quantitative information like concentrations, sensitivity, and the limit of detection. The peak potential is more of a qualitative parameter of the electroactive species. The shift in peak potential to lower or higher values is a signature of the facilitated or impeded process, respectively. A redox couple that exchanges electrons rapidly with the working electrode exhibits a reversible redox process showcasing an anodic and cathodic peak.

Similarly, the peaks obtained in CV are attributed to the reduction and oxidation of the analyte species and for a reversible reaction, the current varies as a function of its concentration that can be predicted by the Randles-Ševčík equation [99,113]:

$$i_p = 0.4463\, n^{3/2} F^{3/2} A C (\upsilon D / RT)^{1/2}$$

where, n is the number of electrons transferred in the redox event, F is the Faraday's constant, A is the electrode surface area (cm^2), υ is the rate at which potential is being varied ($V.s^{-1}$), D is the analyte diffusion coefficient (in $cm^2.s^{-1}$), and C is the analyte bulk concentration (in $mol.cm^{-3}$).

Analytical chemistry has witnessed extensive use of CV for the analysis of redox systems, but its merits are of realm only for the qualitative aspects, moreover, it also suffers from certain drawbacks like much pronounced charging current, abrupt results at higher scan rates, the effect of slow electron transfer on the redox process, etc. Thus, in order to mark the niche of electrochemical analysis, more sensitive pulse techniques are used, which give the best quantitative analysis with a high level of sensitivity.

The following chapters documents the extensive use of CV for electrodeposition of gCN and its composites, for deciphering the mechanistic understanding of redox processes, estimating the electroactive surface area, and inferring the extent of electrocatalytic activity. Nevertheless, square wave voltammetry (SWV) was used for comprehensive quantitative analysis.

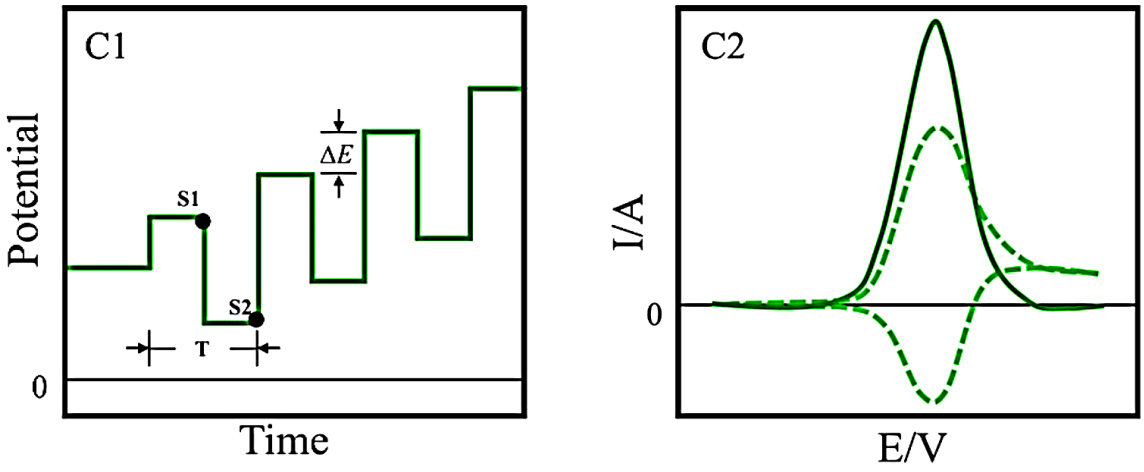

Figure 1.15: Typical excitation signal and observed response of square wave voltammetry. Taken from Biosensors 2022, 12(7), 494.[115]

1.7.2 Square Wave Voltammetry

Due to improvisation in digital and analog electronics, and invention of microprocessor-controlled potentiostats/galvanostats, square wave voltammetry (SWV)[114,116–122]

has found its practical utility in routine quantitative analyses. The past literature has revealed several reports where SWV resulted in highly sensitive[123] and specific quantification of molecules up to the femtomolar range. For an SWV experiment, a symmetrical square wave pulse of amplitude 'E_{SW}' is superimposed on the staircase wave in such a way that the forward pulse of the square wave coincides with the step of the staircase signal as shown in **Figure 1.15.**

In SWV, the current is sampled at two stages of the square wave pulse, and the difference between the forward and reverse current is taken as the net current, which is directly proportional to the analyte concentration. "The faradaic currents that flow during the positive and negative potential steps are opposite in polarity while the polarity of the charging current, which is mostly due to the ramp voltage, does not change. Thus, the component of the output current due to the faradaic signal is amplified while the component due to the charging current is reduced"[124]. Due to the aforementioned sampling procedure, the response current of the excitation signal has a negligible contribution from the charging current and thus the peak current is mainly because of faradaic processes. As a result, much enhanced sensitivity (nearly 4 times higher than DPV) and a lower limit of detection can be realized using SWV. Consequently, SWV is the most widely used voltammetric technique at present and has been deployed in almost every field where electrochemistry has some practical aspect. In this thesis, the quantitative estimation of the analytes and the immobilized layer's selectivity, stability, and repeatability were investigated using the SWV responses.

1.8. Targeted Parameters for investigating the electrocatalytic ability of modified gCN

The electrocatalytic ability of the gCN and its composites were analysed using its efficacy in improving the electrochemical redox process of an ideal redox couple, $K_3[Fe(CN)_6]$

and lately of the chosen analyte. The two major parameter tested were (i) Increase in peak current and (ii) shift in the peak potential in presence and absence of the modified gCN materials (**Figure 1.16**). Where the peak current is a direct signature of enhanced electrochemical redox process, the shift in potential to lower values indicated a facilitated charge transfer.

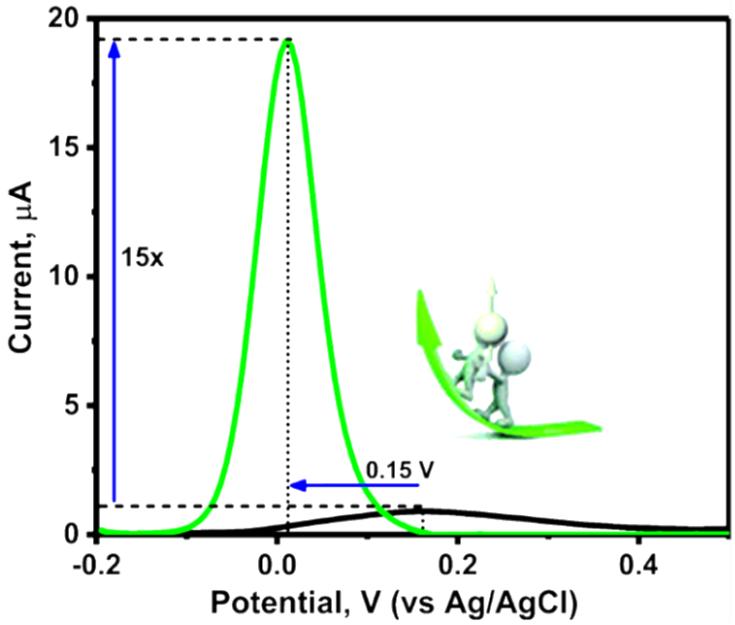

Figure 1.16: SWV plot demonstrating increase in peak current and shift in peak potential as two important parameters for analysing the electrocatalytic activity.

1.9. Purpose and layout of the Thesis

Guiding through the extensive discussion in the preceding section, it is clearly highlighted that the modification of bulk gCN is pivotal for its application as electrocatalysts in electrochemical domains. As a result, the topic of this doctoral thesis revolves around tailoring the bulk gCN synthesized from the thermal polymerization of melamine and the electrodeposition of graphitic carbon nitride and its composites for tailored electrocatalytic oxidation of biomolecules like dopamine, tryptophan, and riboflavin. The complete research work done during the doctoral tenure has been systematically summarised in the following chapters so as to provide a deep understanding of the investigations.

Chapter 1: Introduction

Chapter 2: Electrodeposition of Graphitic Carbon Nitride and MnO_2-Graphitic Carbon Nitride Composite for investigating Electrocatalytic Dopamine oxidation.

Chapter 3: In-situ Growth of CuO Nanoflakes on Graphitic Carbon Nitride Sheets: An Electro-active Interface for Electrocatalytic Oxidation of Riboflavin

Chapter 4: Electrodeposited Phosphorous Doped Graphitic Carbon Nitride for Electrocatalytic Oxidation of Tryptophan

Chapter 5: Summary, Conclusion and Future Outlook.

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