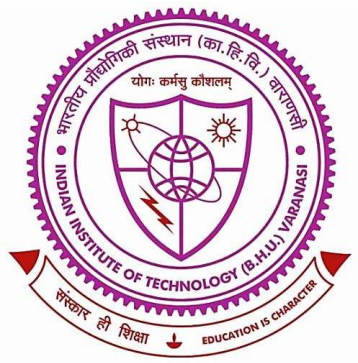
Electrodeposition of Graphitic Carbon Nitride and its Composites for Tailored Electrocatalytic Activity



Thesis submitted in partial fulfillment for the

Award of Degree

Doctor of Philosophy

By

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Chapter 5

Conclusion, Summary and Future Outlook

In summary, we effectively synthesized, tuned and electrodeposited graphitic carbon nitride and its composites onto conductive surfaces and improved its electrocatalytic activity through various modification strategies.

5.1. Major findings of each chapter

The importance of choosing gCN and the need for modification are extensively discussed in the **first chapter**. Based on the comprehensive discussion, the knowledge gap has been identified, and consequently, the problem statement and objectives of the thesis were outlined. The research efforts invested in meeting the defined objectives and the resulting outcomes were discussed in the subsequent chapters. The **second chapter** of this thesis demonstrated the exfoliation of the gCN via ball milling and further tuning by forming composites with MnO_2. The chapter has been divided into two parts. The first part demonstrated the effective electrodeposition of the gCN layer on the conductive surface, ITO, in the current case. To the best of our knowledge, this is the first report that documents the electrodeposition of gCN, deciphering step-by-step mechanistic details. The electrodeposition process resulted in a substantially increased peak current for oxidation of $K_3[Fe(CN)_6]$ (a standard redox probe) compared to the uncoated ITO substrate; however, the process exhibits a somewhat sluggish nature which was interpreted from the broad peak and a slight positive shift in the peak potential.

To further enhance the electrocatalytic activity of gCN, in-situ surface decoration of gCN with MnO_2 was attempted (**Figure 5.1**). The gCN.MnO_2 coated surface layer resulted in approximately 2.75 times higher peak current for $K_3[Fe(CN)_6]$ than the uncoated surface. The conductive surface was characterized systematically using XRD, XPS, HR-SEM, and AFM techniques, revealing the presence of a gCN.MnO_2 layer on the surface. The gCN.MnO_2 coated substrate demonstrated substantially improved electrocatalytic activity towards Dopamine oxidation exhibiting a 22% increase in sensitivity compared

to the bare electrode, along with a low limit of detection of 20 nM. In addition, the altered surface exhibits a high degree of selectivity for Dopamine, due to preferential interactions.

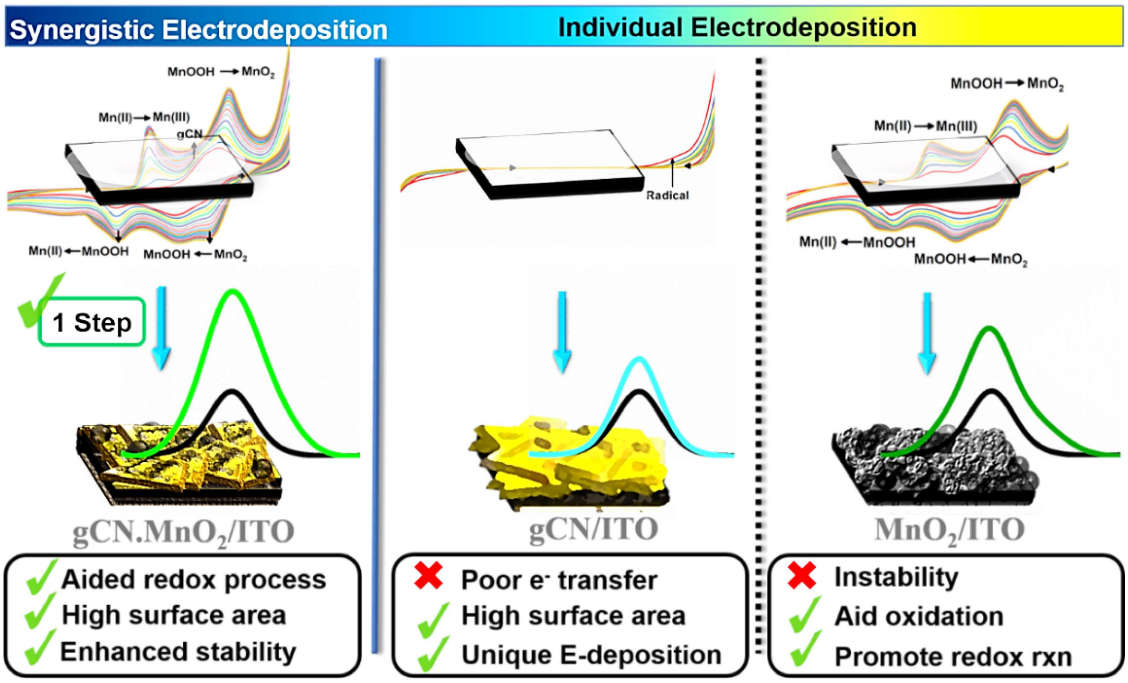

Figure 5.1: Graphical representation to summarize Chapter 2 (Part 1).

While the first part of this chapter effectively improves the electrocatalytic activity of gCN through tuning with MnO_2, several limitations were found to be associated with the process. Firstly, the synthesized gCN was in bulk form, which, following the ball-milling process, exhibited little improvement in peak current. Secondly, long sonication (~16 hours) was required to achieve a uniform suspension in the ethanol solution. Thirdly, to optimize the composite composition, it was essential to optimize the electrodeposition process for each individual component, i.e., gCN, MnO_2, and the gCN.MnO_2 composite. Moreover, large suspension volumes were required due to the larger dimensions of the ITO surface. Also, it presents difficulties in maintaining a consistent exposed surface area for each measurement.

To address all these issues, in the second part of the second chapter, we directly synthesized gCN.Mn_xO_y composite with two different weight ratios (7:3 and 9:1). The

synthesized gCN.Mn_xO_y composite demonstrated higher dispersibility. The material can readily form a suspension within 4 hours of sonication, even in deionized water. The composite was thoroughly characterized using XRD, IR, XPS, and HR-SEM techniques. Subsequently, the electrodeposition of gCN.MnO_2 using both composites was investigated, revealing that the 7:3 gCN.Mn_xO_y demonstrates superior electrocatalytic activity compared to the others. Therefore, a detailed optimization protocol was implemented, and the coated surface underwent further characterization utilizing XRD, XPS, HR-SEM, and AFM techniques. This time, instead of ITO, a screen-printed electrode was employed to test dopamine's electrocatalytic oxidation. The modified SPE with 7:3 gCN.MnO_2 exhibits a 15-fold increase in peak current and a negative potential of 0.15 V while oxidizing 100 µM of dopamine compared to the bare SPE (**Figure 5.2**). The 7:3 gCN.MnO_2 coated layer has 44 times more sensitivity for dopamine detection, resulting in a low limit of detection (LOD) of 10 nM, whereas the bare SPE demonstrates an LOD of 5.36 µM. The modified surface was subsequently employed to detect dopamine in pharmaceutical dopamine injection samples, urine samples, saliva samples, and blood serum samples. In addition, the 7:3 gCN.MnO_2 coated layer demonstrates commendable reproducibility, repeatability, and stability.

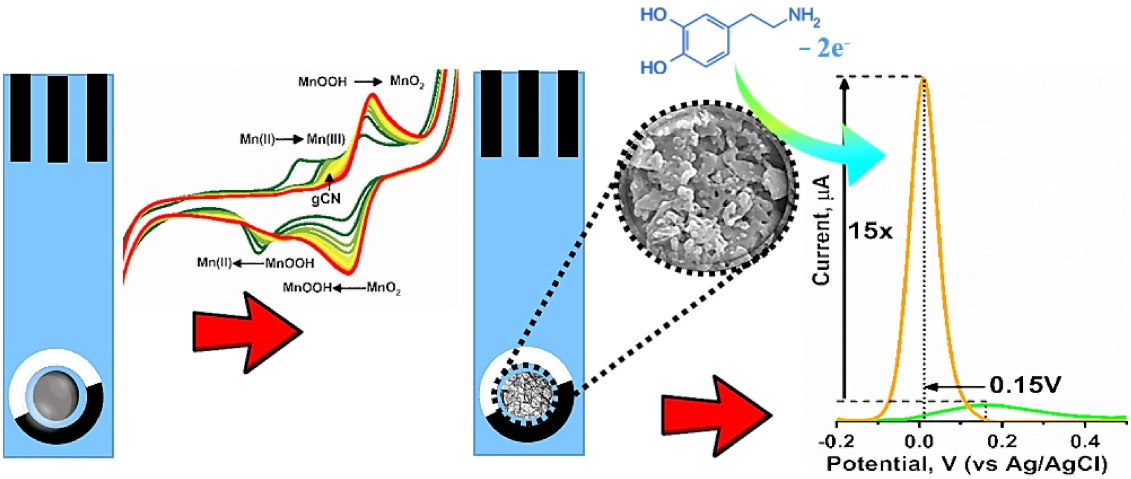

Figure 5.2: Graphical representation to summarize Chapter 2 (Part 2).

The **third chapter** of this thesis reports the use of CuO for tuning the physicochemical properties of gCN. The gCN.Cu_xO_y composite was synthesised and methodically analyzed using XRD, IR, HR-SEM, and XPS. After detailed characterisation, the electrodeposition of gCN.CuO was investigated, and a thorough mechanistic understanding was articulated. The electrocatalytic activity of the gCN.CuO composite is further tuned by modifying the cycle count and scan rate during electrodeposition. The gCN.CuO modified electrode produces more than double the peak current relative to the bare GCE for $K_3[Fe(CN)_6]$ oxidation (**Figure 5.3**). The enhanced surface was subsequently characterized using XPS and HR-SEM. The HR-SEM distinctly reveals a nanoflake morphology throughout the surface of the GCE, which differs from the initial material. This also validates the electrodeposition methodology, since its numerous optimization parameters facilitate the exfoliation of materials from bulk to nanostructures and assist in morphological development.

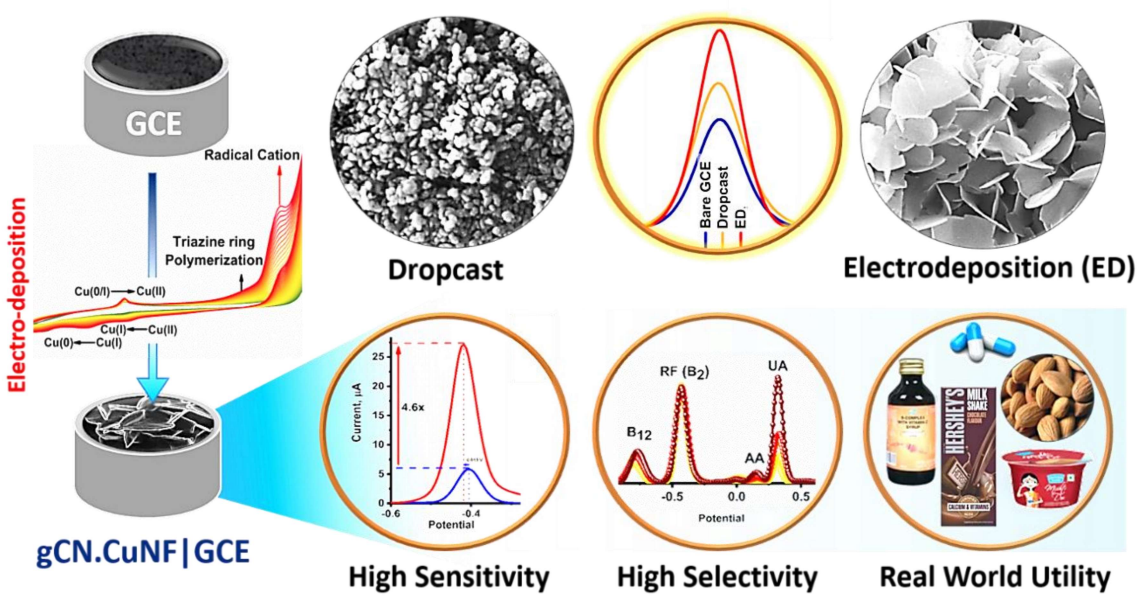

Figure 5.3: Graphical representation to summarize Chapter 3.

The electrooxidation of Riboflavin was assessed to determine the viability of the modified surface, demonstrating a 4.6-fold increase in current response with a 13 mV

negative shift relative to bare GCE at a concentration of 100 µM. Furthermore, the gCN.CuO modified surface exhibits four times greater sensitivity than the bare electrode, resulting in a limit of detection of 6 nM. The improved surface has been further investigated for selectivity, actual sample analysis, and stability assessment, demonstrating practical usefulness.

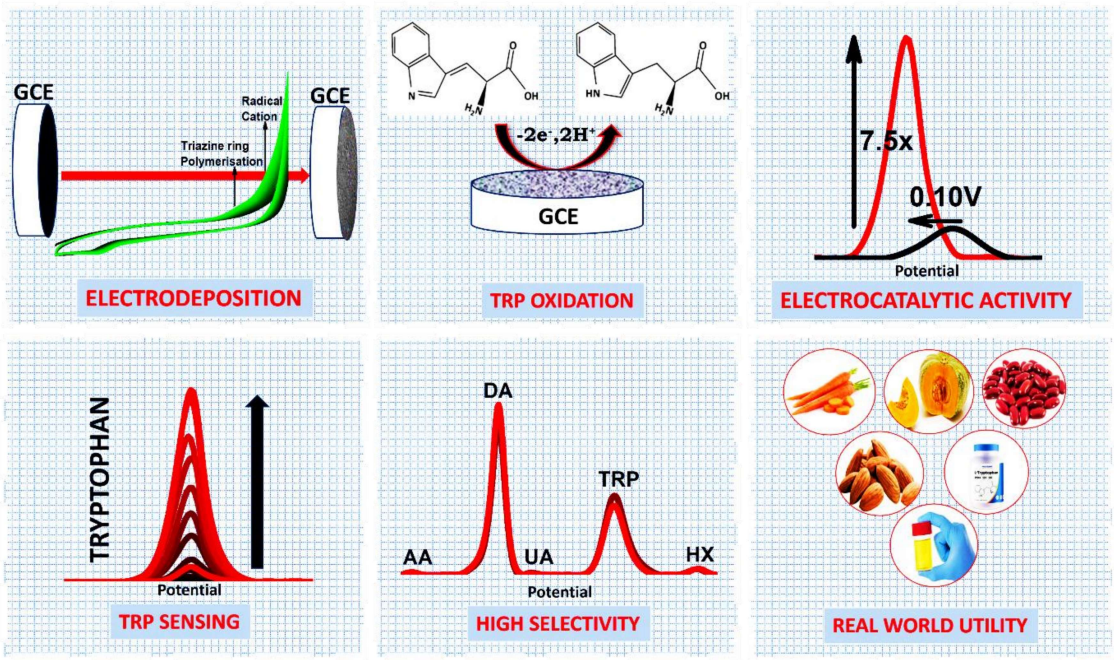

Figure 5.4: Graphical representation to summarize Chapter 4.

Following the optimization of the electrocatalytic activity of gCN by metal oxide incorporation, the **fourth chapter** addresses the enhancement of gCN via non-metal doping. Three distinct phosphorus-doped gCN samples were produced (2%, 5%, and 10%) and thoroughly characterized. The electrodeposition of all doped materials was examined, revealing that 5%-P-doped gCN has superior catalytic activity, which was further optimized for the coated interface. The altered surface was further characterized using XPS, HR-SEM, and AFM. The altered surface was evaluated for tryptophan electrooxidation. For a 100 µM TRP solution, the modified surface exhibits a current increase of 7.5 times, accompanied by a negative potential shift of 100 mV (**Figure 5.4**). Moreover, the sensitivity of the modified electrode was determined to be 7.83 times

greater than the bare electrode, with a limit of detection (LOD) of 7.1 nM. Furthermore, the modified surface was examined using interference studies, real sample analyses, and stability assessments, all of which show favourable results.

5.2. Comparative Evaluation:

5.2.1 Effect of substrate:

This thesis introduces the electrodeposition of gCN and its compound to augment the electrocatalytic activity of gCN. This thesis utilized three distinct substrates: ITO, glassy carbon electrode, and screen-printed electrode. To investigate the effect of substrate on the electrocatalytic activity of gCN, the gCN was electrodeposited on all three substrates using the same electrodeposition protocols. The SWV response of 0.5 mM solution of $K_3[Fe(CN)_6]$ as a standard redox probe was recorded using the corresponding modified and unmodified substrates. **Figure 5.5** illustrates the comparative current responses at unmodified and modified ITO, GCE, and SPE, respectively. All substrates exhibit an increase in peak current relative to the bare electrode; however, the screen-printed electrode demonstrated the highest increment, showing substantial electrocatalytic activity compared to other conductive surfaces. Interestingly, both the GCE and SPE were circular electrodes with a 3 mm diameter; still, a visible difference in electrochemical response was observed. The increased catalytic activity of gCN on the screen-printed electrodes is attributed to their greater roughness, which facilitates a more prominent electrodeposition and morphological evolution of material on its surface.

Furthermore, **Figure 5.5** also illustrates the comparison between electrodeposition and the drop-casting approach. In all instances, the electrodeposition approach results in superior electrocatalytic activity compared to the drop-casting method.

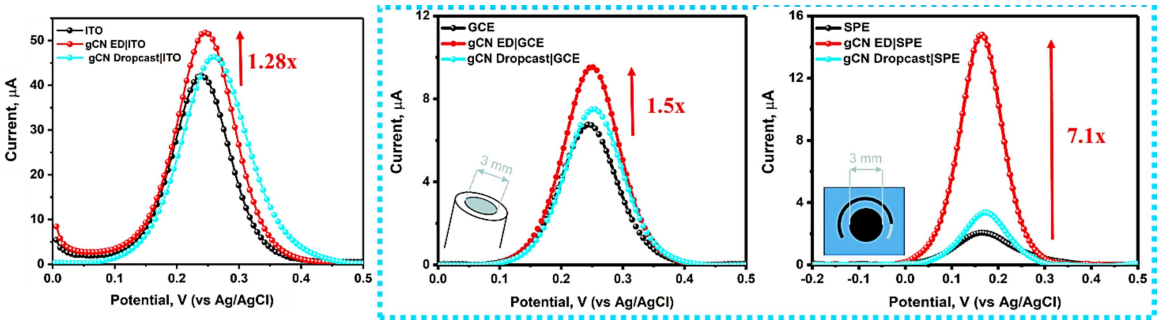

Figure 5.5: Comparative study of gCN electrodeposition and drop-casting on (a) ITO (b) GCE (c) SPE.

5.2.2 Comparison of modification strategies:

To compare the electrocatalytic activity of gCN modified using different strategies reported in this thesis, the electrodeposition of gCN, gCN.MnO_2, 7:3 gCN.MnO_2, gCN.CuO and P-gCN were carried out on GCE using 15 electrodeposition cycles at a scan rate of 100mV/s. The SWV response 0.5 mM solution of $K_3[Fe(CN)_6]$ as a standard redox probe, was recorded using all the modified and unmodified GCE. **Figure 5.6** displays the comparative SWV responses.

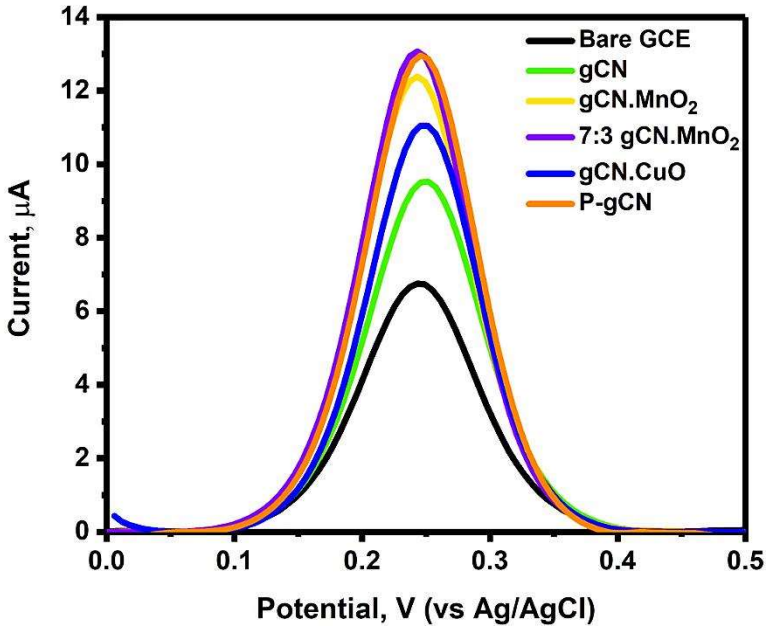

Figure 5.6: Comparative study of gCN and its composites on the glassy carbon electrode.

The figure clearly indicates that all the modification strategies improve the catalytic activity of bulk gCN. The low catalytic activity of bulk gCN is attributable to its inadequate conductivity and hindered charge transfer. Amongst all the tested materials,

the maximum current response is achieved with the electrodeposition of a 7:3 gCN.MnO_2 composite; however, P-doped gCN exhibits a comparable current response. The results unequivocally indicated that compositing with metal oxides boosts the electrocatalytic performance of gCN, whereas optimized tuning with non-metals may result in similar outcomes.

5.3. Future Perspective:

This thesis establishes a strong foundation for the use of graphitic carbon nitride (gCN) in various electrochemical applications, showcasing its potential for future advancements. Expanding beyond the scope of this work, several promising directions can be explored:

1. **Extending the gCN Modification Strategies:** The electrocatalytic activity of gCN can be further enhanced by forming composites with readily electropolymerizable conducting polymers and the use of single-atom catalysts.
2. **Morphology Engineering of gCN:** The research carried out in this thesis primarily utilizes bulk gCN; however, future work can focus on studying the effect of morphology. Using template and template-free approaches, gCN can be synthesized in several morphologies like hollow spheres, nano-rods, cubes, and flowers. Since electrochemistry is largely affected by the morphology of the catalyst, the dependency of the electrocatalytic ability of gCN on the morphology can be studied.
3. **Morphology Tuning of gCN Composites:** Through electrodeposition, the morphology of gCN and its composites can be further controlled and optimized, opening up new avenues for structural and functional enhancements in electrochemical devices.

4. **Water Splitting Applications:** Beyond analyte detection, the modified gCN electrodes developed here have potential applications in metal-free or noble-metal-free water splitting, presenting a sustainable alternative for electrocatalytic water splitting in the presence and absence of light.
5. **Supercapacitors:** The field of supercapacitors, which relies heavily on electrode modification, could greatly benefit from the strategies developed in this thesis. Optimally thick, modified gCN layers can be used to enhance energy storage capacities.
6. **Battery Applications:** Utilizing the electrodeposition of gCN and its composites, the current collectors (Cu, Al, Carbon cloth) can be uniformly coated in a binder-free approach. The coated current collectors have recently attracted research interest for mitigating corrosion issues, loss of contact, and dendritic proliferation in various battery types (Li, Na, K, etc.). Along the same line, gCN modified current collectors can potentially improve the battery stability and performance.