Nickel-Doped Carbon Nitride for Applications in Electrochemical Energy Systems

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ABSTRACT

Alkaline fuel cells and supercapacitors have attracted considerable attention over the last decades, mainly because these systems offer the possibility to produce and store energy in a sustainable manner. Since the current limitations of these technologies requires the development of highly conductive materials with enhanced stability, this project aims to explore the uses of modified graphitic carbon nitride (GCN) as both OH^- conductive fillers and pseudocapacitive electrode materials.

In order to reach the project's goal, GCN was fabricated from melamine and then doped with nickel via wet chemistry. GCN was also doped with Ni in-situ for comparative purposes.

FTIR and UV-vis spectra for both GCN and NiDGCN indicate that these materials were successfully fabricated. The results also indicate that the in-situ method is more effective at introducing nickel into the GCN's structure. Also, a band gap reduction in Ni-doped samples suggests that the presence of metal in the GCN structure, enhances its electrical conductivity.

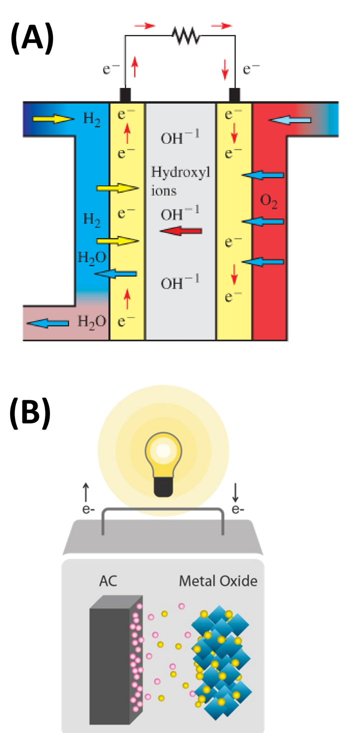
INTRODUCTION & BACKGROUND

Electrochemical energy systems are playing an important role in our changing energy landscape.[1] For example, alkaline fuel cells are very promising since these high-efficiency devices can produce energy (sustainable electricity) from hydrogen and oxygen, without generation of emissions.[2] Also, fuel cells can be sized to fit a wider variety of applications, ranging from stationary to mobile energy production.[3]

In the case of supercapacitors, these are used in applications requiring many rapid charge-discharge cycles (*e.g.* elevators, trains, cranes and regenerative braking).[4]

Supercapacitors and batteries combined offer the best solution for many energy systems. Supercapacitors allow batteries not only to perform better but also extend their lifetime.

Figures A and B are schematics of an alkaline fuel cell and a supercapacitors, respectively.[3, 4]



Device	Advantages	Limitations
Alkaline fuel cell	Allows the use of non-precious metals as catalysts	Membranes suffer degradation over time
Supercapacitors	High power density	Low energy density and degradation over time

To overcome the limitations described above, this research project aims to explore the possibility of using modified graphitic carbon nitride nanosheets (GCN) in the fabrication of: (1) chemically and mechanically stable polymer nanocomposite anion-exchange membranes and (2) nanostructured supercapacitor electrodes with high performance.

Hypothesis: The structure of GCN will facilitate the formation of metal ion complexes which could increase the OH- conductivity of the fabricated membranes. Also, the presence of nickel, in addition to a high nitrogen density could increase the pseudo-capacitance of the electrodes.

OBJECTIVES

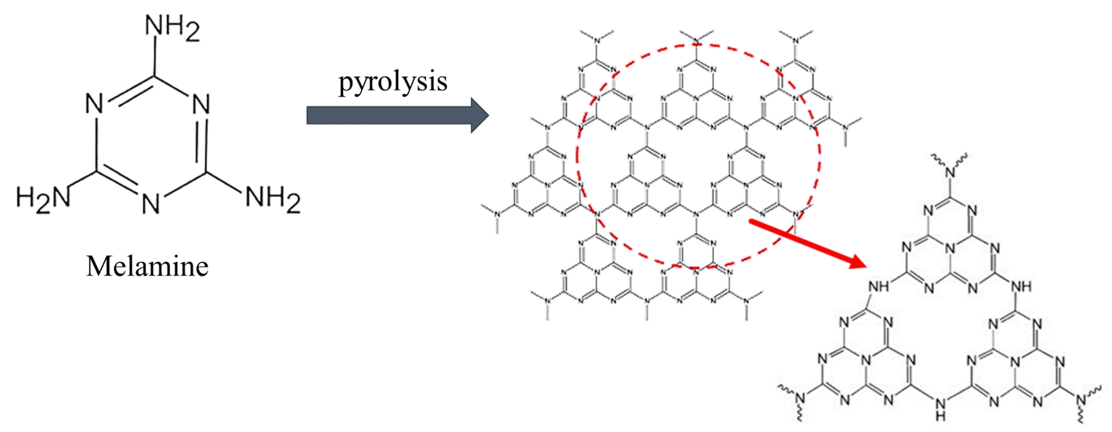
The **objectives** of this research project are:

1. Fabricate and characterize nickel-doped graphitic carbon nitride nanosheets (NiDGCN)
2. Fabricate and characterize polymer nanocomposite anion-exchange membranes using NiDGCN as fillers
3. Fabricate and characterize NiDGCN-based supercapacitor electrodes

METHODOLOGY

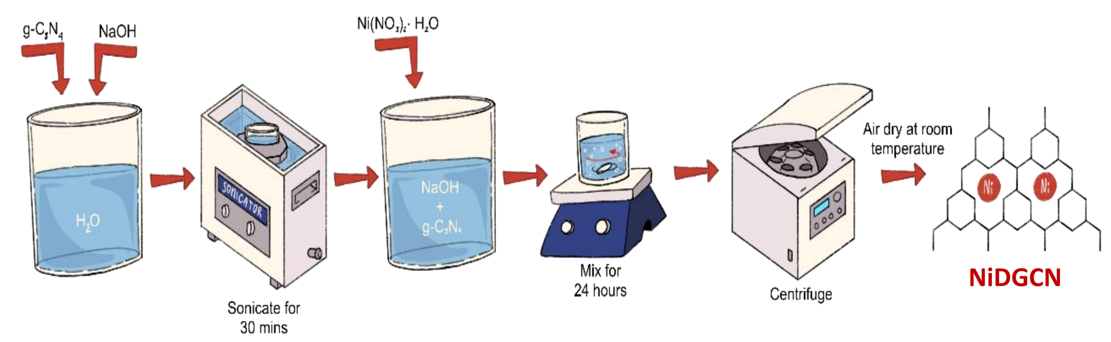
Graphitic Carbon Nitride Fabrication

Graphitic carbon nitride was fabricated by subjecting a precursor (melamine) to pyrolysis at 550 °C, which enables the polymerization of melamine into graphitic carbon nitride. The polymerization process that takes place is depicted in the figure below.



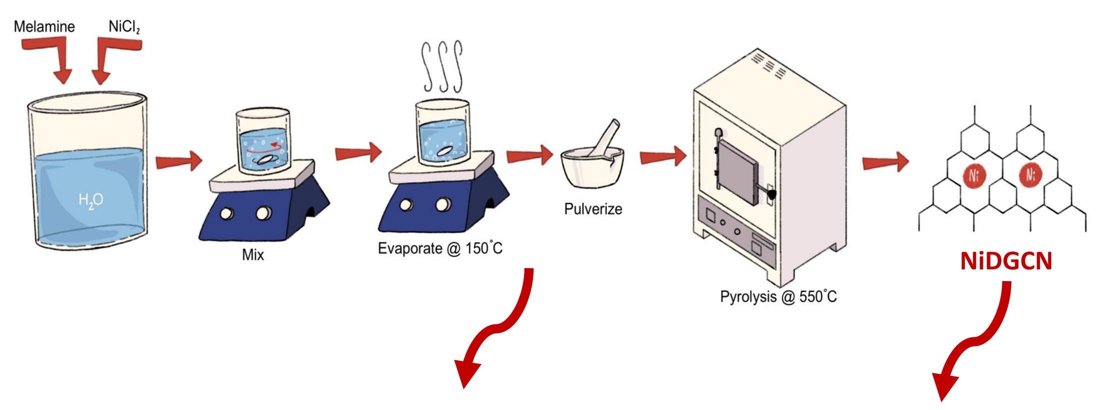
Ex-situs Nickel-Doped Graphitic Carbon Nitride Fabrication

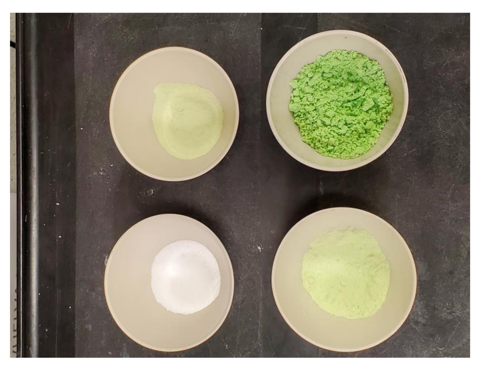
The ex-situs fabrication method consists of fabricating graphitic carbon nitride (GCN = $g\text{-}C_3N_4$) nanosheets and then adding it to solutions with different concentrations of nickel nitrate hexahydrate under stirring for 24 hours.



In-situs Nickel-Doped Graphitic Carbon Nitride Fabrication

The in-situs fabrication method consists of the addition of nickel chloride into a solution containing melamine under stirring. After water evaporation, nickel-doped graphitic carbon nitride is produced via pyrolysis.



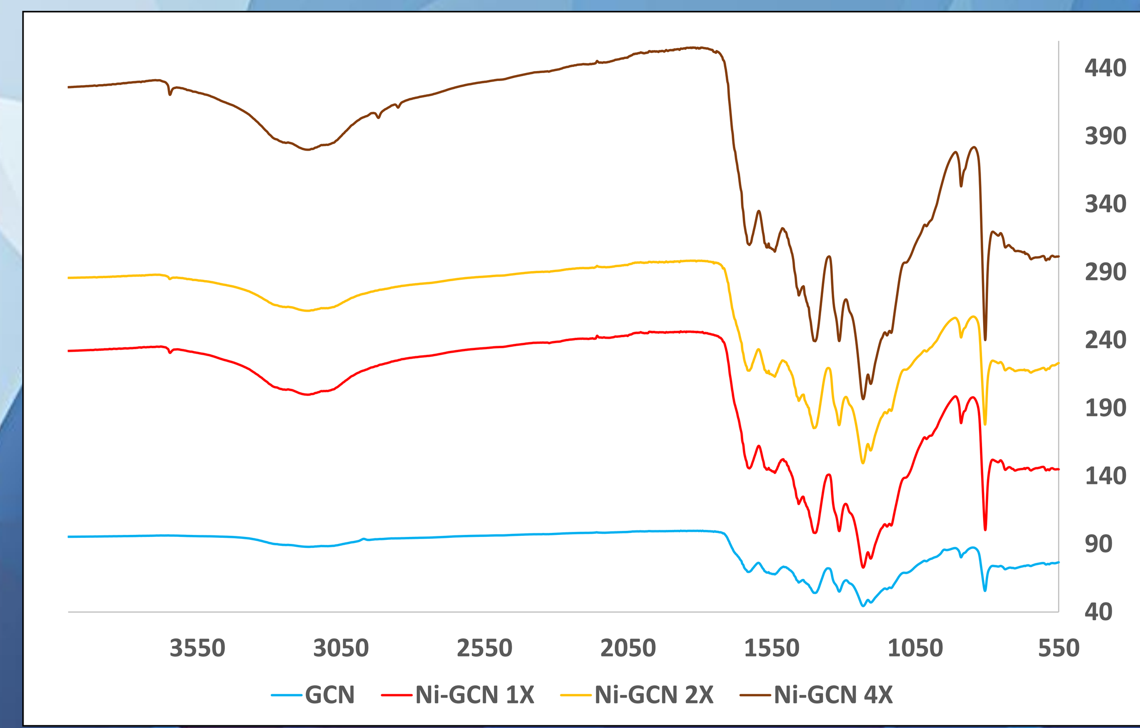


Dried samples of mixtures containing nickel chloride (at different wt %) and melamine

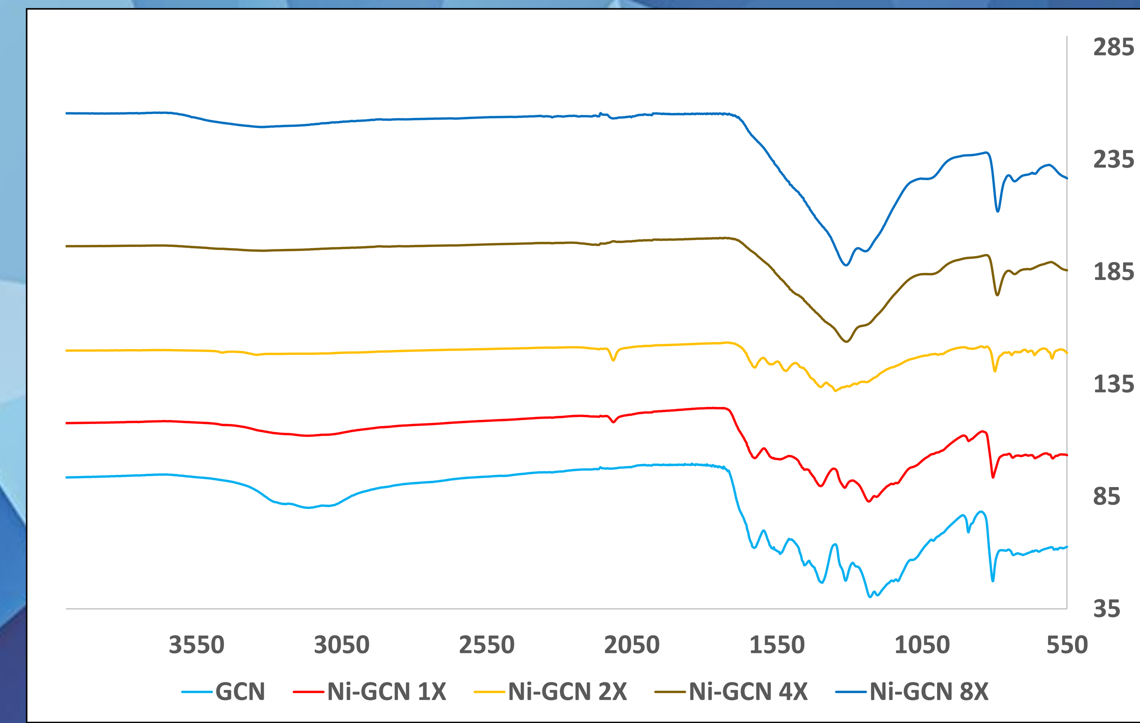
NiDGCN prepared with different amount of nickel chloride
X = Grams of the nickel chloride used in the synthesis

RESULTS

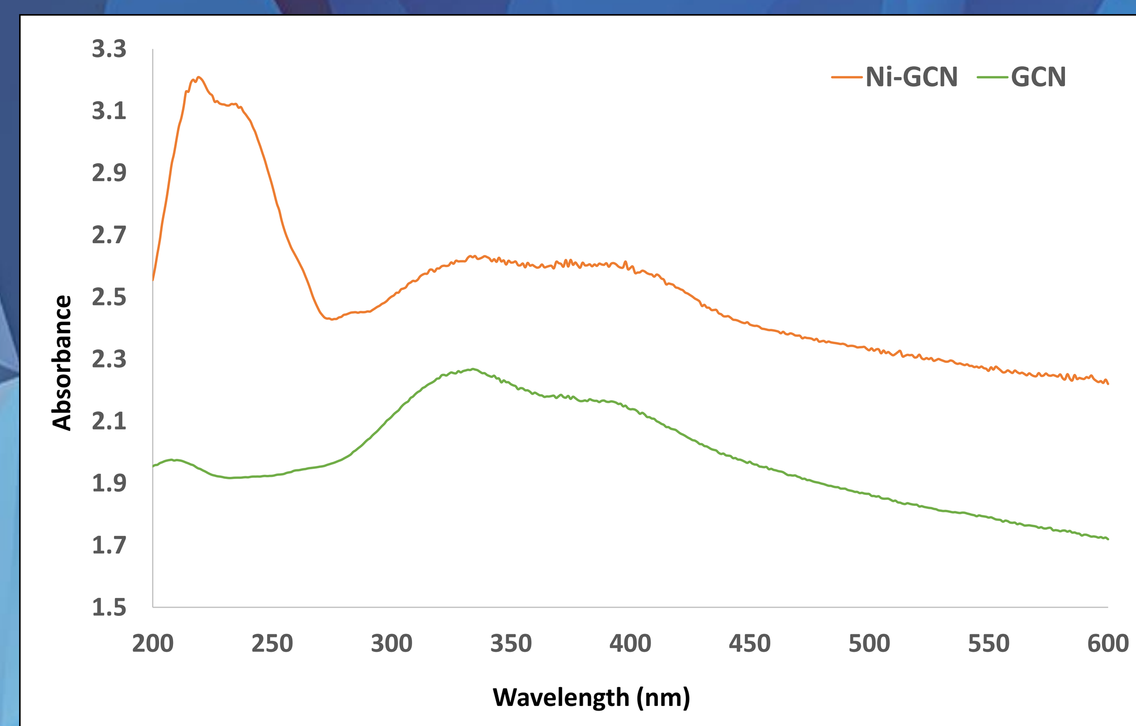
FTIR Spectra For Ex-situ Fabricated Samples



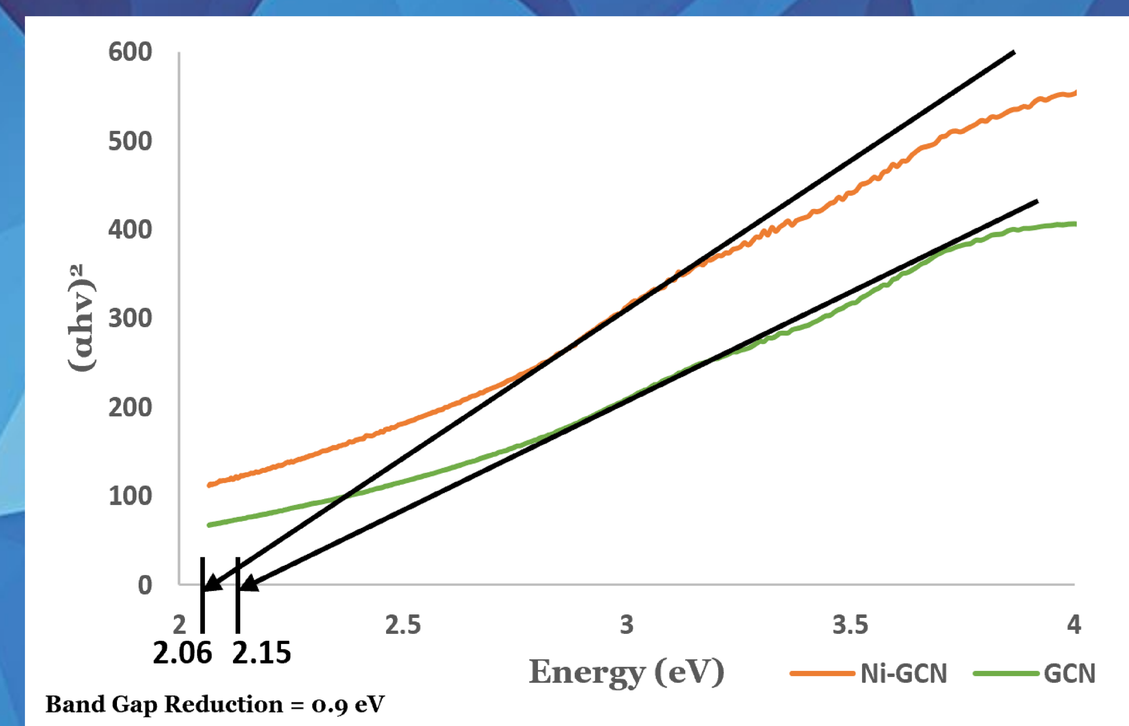
FTIR Spectra For In-situ Fabricated Samples



UV-Vis Spectra



TAUC Plots



FUTURE WORK

- ✓ Complete the NiDGCN characterization: AFM, XRD, RAMAN and SEM
- ✓ Fabricate and characterize polymer nanocomposite anion-exchange membranes using NiDGCN as fillers
- ✓ Fabricate and characterize NiDGCN-based supercapacitor electrodes

CONCLUSIONS

- ✓ FTIR and UV-vis spectra for GCN and NiDGCN indicate that these materials were successfully fabricated.
- ✓ In-situs method is more effective at introducing the nickel into the GCN's structure.
- ✓ As the presence of nickel increases in the in-situs samples, the characteristic peak in the GCN FT-IR spectrum found at 810 nm shifts to the right. This suggests modification of the GCN structure.
- ✓ A band gap reduction of 0.9 eV in the doped sample confirms that the introduction of nickel enhances the electrical conductivity of GCN.

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