BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCES, PILANI

REPORT

SECOND SEMESTER 2021-22

Modification of g-C3N4 materials for use as catalyst

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SUPERVISOR:

Dr. Bibhas Ranjan Sir

Department of Chemistry

SUBMITTED BY:

Riddhi Arora

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ABSTRACT

By modifying the surface of graphite Carbon Nitride with Hydrazine, it allows connection of other function groups and ligands easily. The general method for noble-metal free h2 gas evolution Graphite carbon nitride catalyst with stable hydrogen evolution is also mentioned. With 0.2 wt% nickel on the modified Graphite carbon nitride leads to 40% hydrogen evolution and more efficiency of 3 wt% Pt deposited on the g-C3N4 surface.

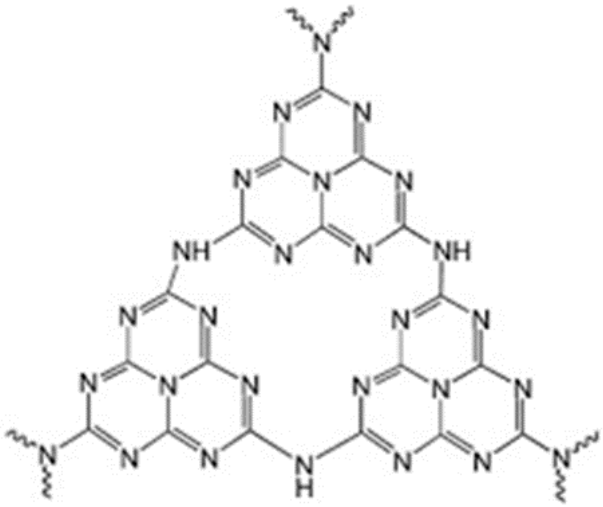
INTRODUCTION

The Polymeric carbon Nitride has gained much attention due to its application in Photocatalytic hydrogen evolution. The hydrogen evolution can be improved with modifying graphite carbon Nitrite's surface with noble metal or by doping the C3N4 with other building metals.

Few advantages are that the material can be produced using low cost starting materials, with that, it is non-toxic in nature, sustainable and eco-friendly.

The presence of strong C-N bonds, the material is ensured to have good thermal and chemical stability.

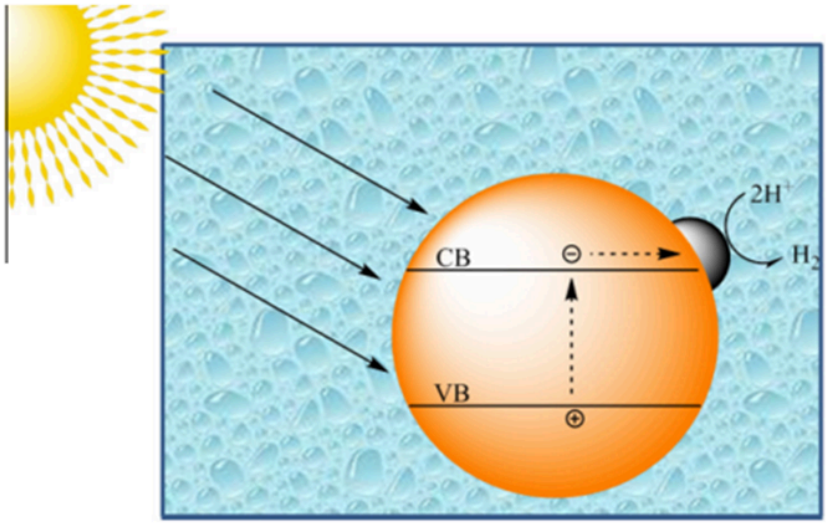
All these merits make it an ideal material for the application in hydrogen evolution as well as environmental pollutant degradation.



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SCHEMATIC REACTION MECHANISM OF CARBON NITRIDE PHOTO-CATALYSED HYDROGEN EVOLUTION



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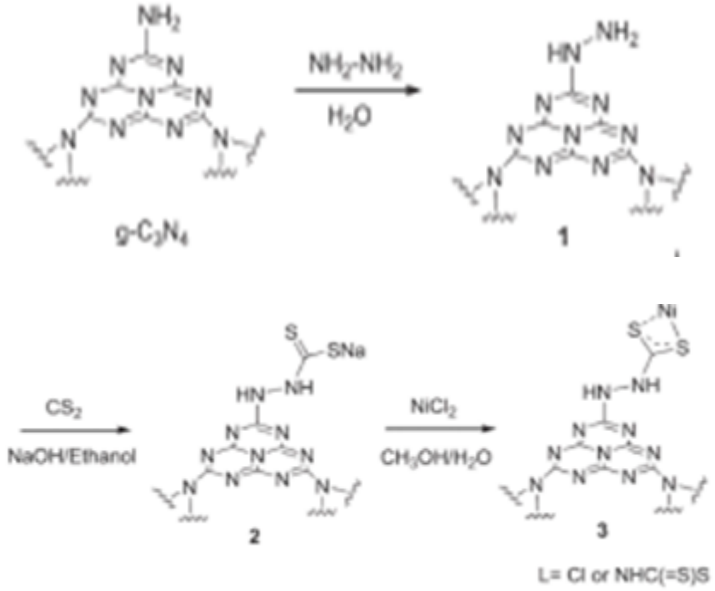
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Initiation: The g-C3N4 molecule absorbs photon energy equivalent to a minimum or more amount of band gap and thus produces an electron. The electron goes to the platinum nanoparticle trapped on the surface of the g-C3N4 molecule. This will initiate the charge separation due to lower work function which acts as a hydrogen electrolysis active centre.

The presence of heterogeneous catalyst gets the activity from the scarce locations on the surface; thus, it becomes difficult to regulate and understand how the active species like platinum nanoparticles react with the g-C3N4. Because of this it becomes difficult to improve the catalysis performance of g-3N4.

PREPARATION OF g-C3N4-NHNH(CS2Ni)

In this work, we have altered the surface of g-C3N4 with hydrazine and introduced the highly reactive $NHNH_2$ group; this later can be easily converted to CH2NS2- group after reacting with Carbon disulphide. Noble metal free hydrogen evolution catalysts can be obtained when the CH2NS2- group is coordinated to Ni2+.



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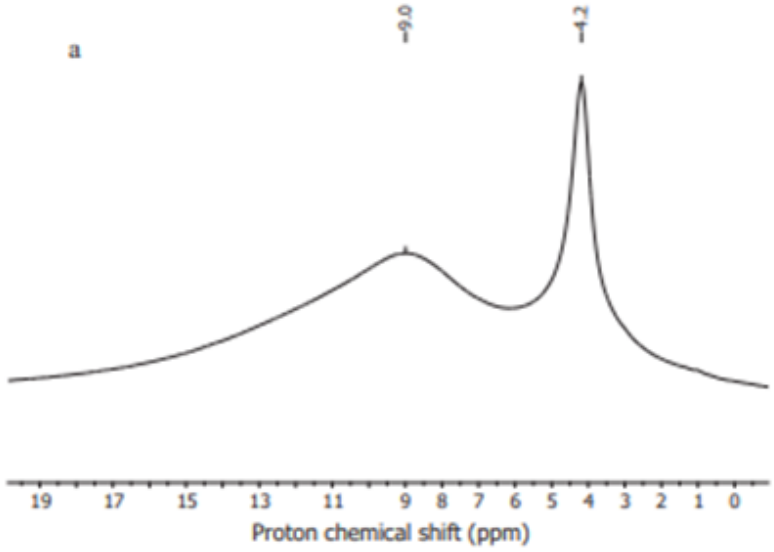
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Compound 1 g-C3N4-NHNH2

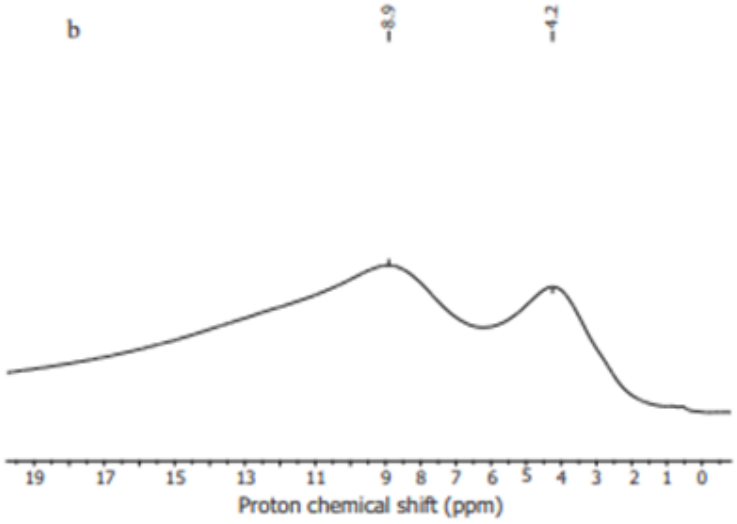
Compound 2 g-C3N4-NHNH(CS2Na)

Compound 3 g-C3N4-NHNH(CS2Ni)

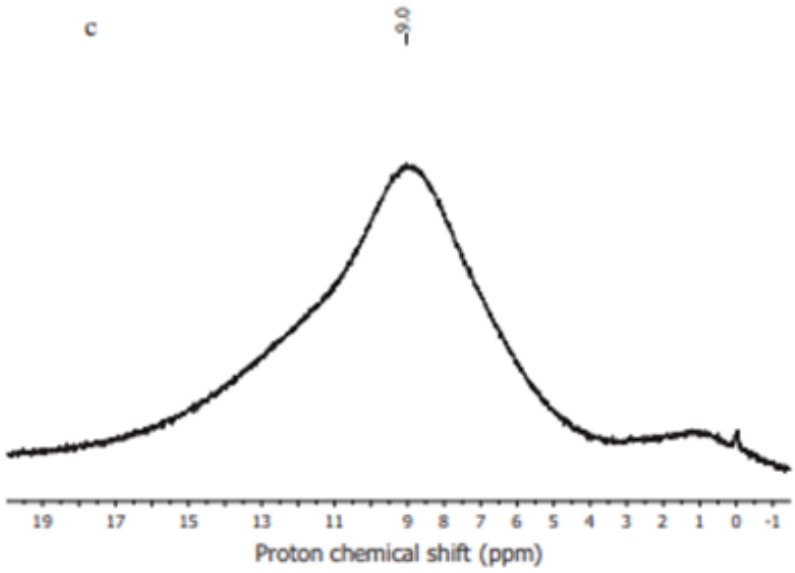
1 H MAS (magic angle spinning) NMR



For the raw g-C3N4, 1 H MAS NMR showed a peak around 9.0 ppm due to the presence of NH2 and NH groups.



After the reaction with CS2, the intensity of the peak for the NHNH2 group decreased indicating most of the diazinyl group were consumed in the making of g-C3N4-NHNH(CS2Na)



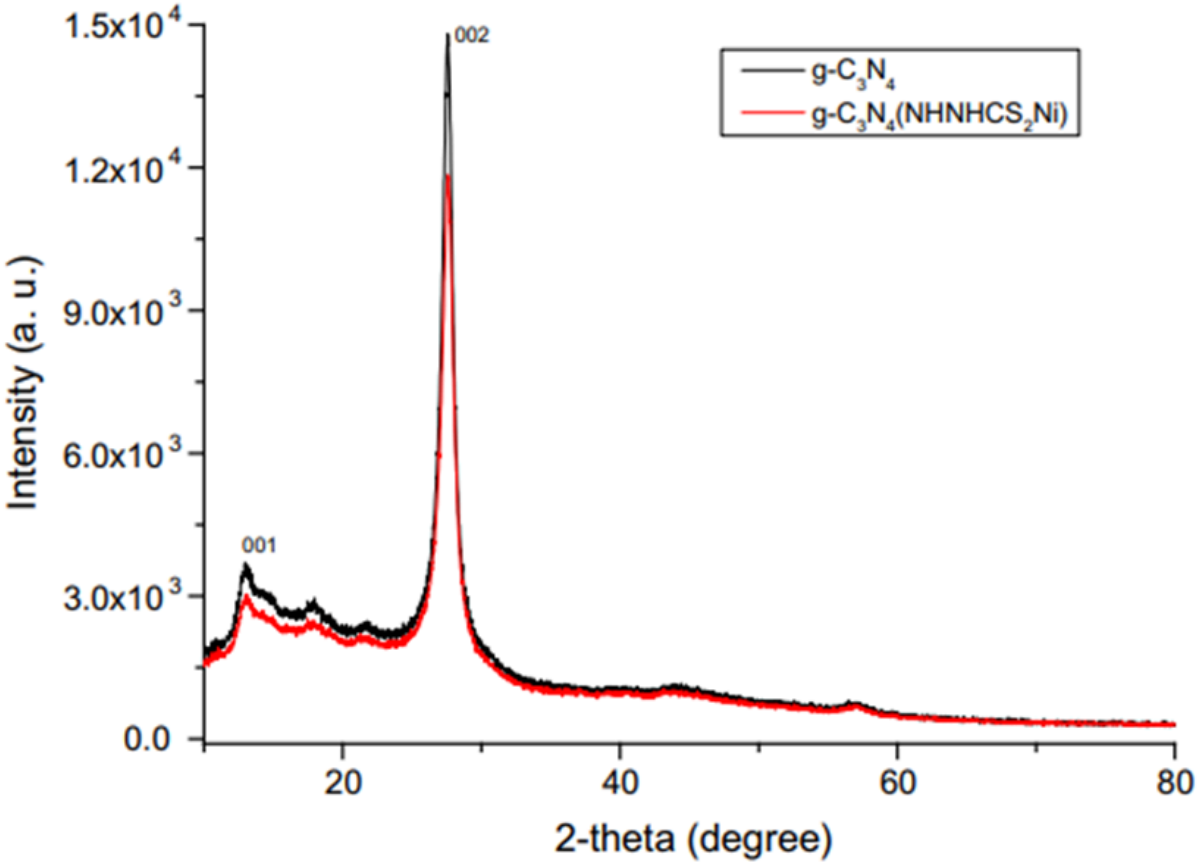
We know that the diazinyl group reacts with NaNO2 to make the Triazo group, we found the peak at 4.2 ppm for g-C3N4-NHNH2 **disappeared after reaction with excessive NaNO2** at room temperature in ethanol for 15 min.

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Powder-XRD of g-C3N4 and g-C3N4 (NHNHCS2Ni)



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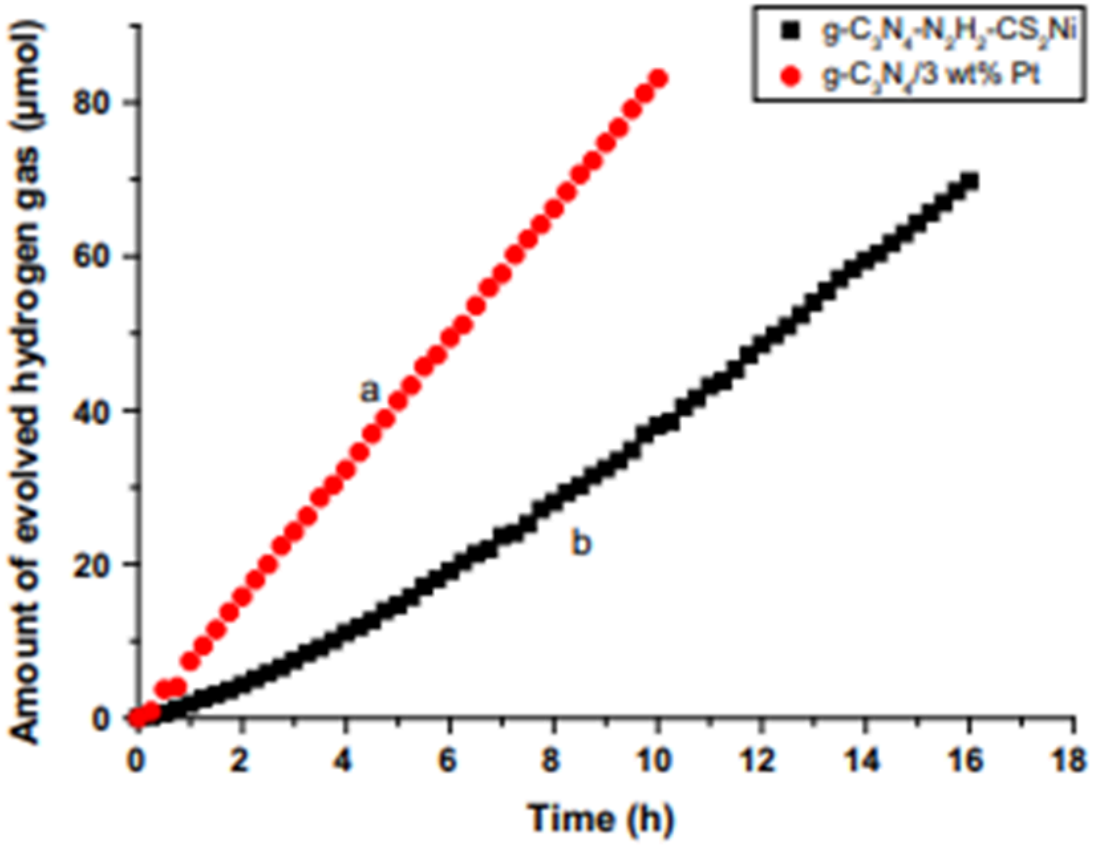
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- The above Powder-XRD of g-C3N4 and g-C3N4 (NHNHCS2Ni) showed that there is no difference between their patterns.

· This also proves that the structure of graphite carbon nitride didn't change after a three steps reaction.

TIME VS AMOUNT OF HYDROGEN GAS EVOLVED GRAPH



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Curve a) It is a curve of time required for the evolution of water using 3 wt.% Pt deposited g-C3N4

Curve b) the time required for hydrogen evolution with g-C3N4-NHNH(CS2Ni)

This proves that g-C3N4-NHNH(CS2Ni) functions as a stable photocatalyst for visible-light-driven H2 production.

Conclusions

In this project, we mentioned very simple ways of activating the surface of graphite carbon nitride which are comparatively cheap and easy g-C3N4 hydrogen evolution catalysts.

By treating the surface of g-C3N4 with noble metals. By adding diazinyl groups in g-C3N4, it becomes possible to introduce other functional groups or ligands to the compound. After reacting with carbon disulphide, the dithiocarbonate ligand is introduced into the graphite carbon nitride, which leads to the production of noble metal free hydrogen evolution catalyst after reacting with Nickel cation.

These results indicate that the molecular level catalyst designed strategy can work as H2 evolution based on Graphite Carbon nitride, the surface catalysis active molecule can successfully replace the traditional co-catalyst nanoparticle. Because of this higher molecular catalysis efficiency was achieved.

REFERENCES

- **High Efficiency Photocatalytic Water Splitting Using 2D α-Fe2O3/g-C3N4 Z-Scheme Catalysts by Xiaojie She et al First published: 08 May 2017**
- **Surface modification of g-C3N4 by hydrazine: Simple way for noble-metal free hydrogen evolution catalysts YinChen et al; Chemical Engineering Journal; Volume 286**

Thank you