



Nano Layered Corrosion Resistance Powder with Graphitic Carbon Nitride by Hydrothermal Method

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ABSTRACT :

The heterogeneous compound of graphitic carbon nitride is based on the development of a photoactive semiconductor Aluminum nitride of mesoporous structure and high surface area, constructed via a hydrothermal route in a single pot in situ as the electron acceptor zone. found the structure modification function of graphitic carbonitride on aluminum nitride during the hydrothermal process, which can be attributed to the coordination between the empty orbital of the ion Aluminum and the lone electron pair of the Nitride atom. The as-synthesized heterojunction exhibited much higher photocatalytic activity than pure graphitic carbon nitride. The hydrogen generation rate and degradation reaction rate constants of methyl orange on 50% graphitic carbonitride under visible light irradiation were 2.5 and 7.3 times respectively, higher than those over pristine graphitic carbon nitride. The enhanced activity of the heterojunctions is attributed to their large specific surface areas between the components as well as their excellent adsorption performance and efficient charge transferability.

Keywords: Aluminum; graphitic carbon nitride; catalysis; ceramics; photochemistr

CHAPTER-1

INTRODUCTION :

Introduction

Corrosion is when a material gets damaged by its surroundings. This can cause big problems like shutting down factories, wasting resources, making products less effective, and being dangerous. It happens often and can be expensive to fix or prevent.

Reaction steps for the formation of rust:

Step 1: iron + oxygen \rightleftharpoons iron oxide

Step 2: iron oxide + water hydrated \rightleftharpoons iron oxide (rust)

Metals like aluminum, chromium, and zinc may erode more swiftly than iron, but their oxides form a sub cast that protects them from farther damage. Rust is brittle and can flake off the surface of iron, exposing a new surface to more damage. Therefore, metals like aluminum, chromium, and zinc may be a better choice for products exposed to rusting conditions, such as air and water.



Understanding the behavior and mechanism of a corrosion problem is crucial in finding an effective solution. There are five methods of corrosion control:

- Barrier protection: This involves physically separating the metal from the environment with a barrier coating, such as paint, plastic, or enamel.
- Cathodic protection: This involves making the metal a cathode in a galvanic cell, where it is connected to a sacrificial anode. The anode corrodes preferentially, protecting the metal.
- Material selection: Choosing the right material for the environment can prevent corrosion. For example, using stainless steel instead of regular steel in a corrosive environment.
- Modification of the environment: Changing the environment in which the metal is exposed can prevent corrosion. For example, reducing the moisture content or acidity of the environment.
- Inhibitors: Adding chemical inhibitors to the environment can slow down the corrosion process. Inhibitors work by reacting with the metal surface to form a protective layer that prevents further corrosion.

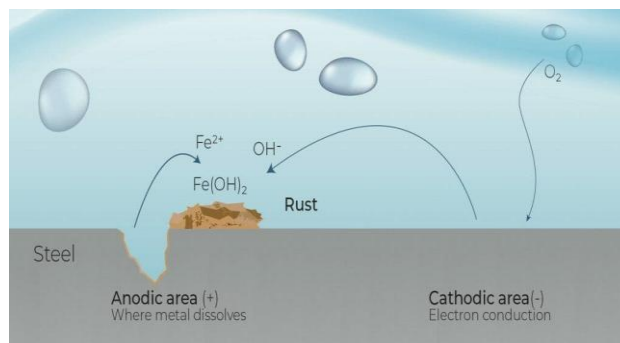


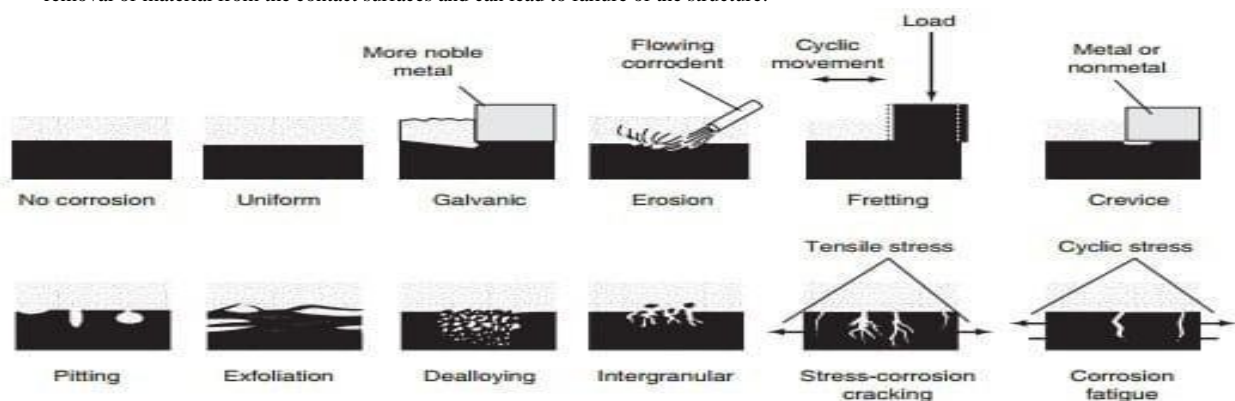
Fig.2. corrosion reaction

1.0.1 The Effects of Corrosion

Corrosion has direct as well as indirect effects on our entire lives. Directly, corrosion affects the lifespan and usefulness of our possessions, such as cars, outdoor furniture, and tools. Preventative measures such as painting or using corrosion inhibitors can help protect against corrosion. Corrosion protection is also built into household appliances like water heaters, furnaces, and washers.

dangerous. Plant closures due to corrosion can cause large financial losses and endanger public safety. In some cases, such as in power plants or chemical processing plants, the consequences of corrosion can be catastrophic, leading to large-scale damage, injuries, and even loss of life. Therefore, it is crucial for industries to take preventive measures and regularly inspect and maintain their equipment to avoid corrosion-related failures. There are several forms of corrosion that can be classified based on appearance, including:

1. **Uniform corrosion:** This is the most common form of Corrosion and occurs when entire face of the metal corrodes slightly. It often results in a loss of metal thickness and can eventually lead to failure of the structure.
2. **Galvanic corrosion:** when two alike metals get in touch with each other in the non-absence of an electrolyte, like saltwater. One metal act as an anode and corrodes rapidly than the other one, which acts as a cathode.
3. **Pitting corrosion:** This form of corrosion creates small pits or holes on the surface of the metal. It often occurs in areas where the metal is exposed to a corrosive environment, such as saltwater or acidic solutions.
4. **Crevice corrosion:** This occurs in crevices or tight spaces where the metal is exposed to a corrosive environment. It can occur in areas such as welds, gaskets, and fasteners.
5. **Intergranular corrosion:** This occurs along the grain boundaries of the metal and can result in cracking and failure of the structure. It often occurs in alloys that are sensitive to intergranular corrosion, such as stainless steel.
6. **Stress corrosion cracking:** This occurs when a metal is exposed to a corrosive environment while under stress, such as tension or compression. It can result in cracking and failure of the structure.
7. **Erosion corrosion:** This occurs when a metal is exposed to a high-velocity fluid or gas, which causes both mechanical erosion and chemical corrosion of the metal surface. It often occurs in pipes, valves, and other equipment used in fluid or gas handling.
8. **Fretting corrosion:** This occurs when two surfaces are in contact and undergo repeated small motions, such as vibration. It can result in the removal of material from the contact surfaces and can lead to failure of the structure.



Schematics of the common forms of corrosion

Fig .3. Schematics of Common forms of corrosion

1.0.2 Methods to Control Corrosion

Corrosion is when metals break down and become damaged because of chemical reactions with the things around them, like air or water. Corrosion can have significant economic and safety implications, particularly in industries such as oil and gas, transportation, and infrastructure. Here are some methods to control corrosion:

1. **Protective coatings:** Applying a protective coating such as paint or varnish can prevent direct contact between the metal surface and the environment. The coating acts as a barrier and reduces the rate of corrosion.
2. **Cathodic protection:** This method involves connecting a more reactive metal, such as zinc or magnesium, to the metal that needs protection. The more reactive metal acts as a sacrificial anode and corrodes instead of the protected metal.
3. **Inhibitors:** Inhibitors are chemicals that can be added to the environment or applied to the metal surface to reduce the rate of corrosion.

These substances or treatments create a thin layer of protection on the surface of the metal that prevents or slows down the corrosion process. This It

1.0.3 The Economic Impact of Corrosion

Corrosion is a natural process that occurs when metals or other materials are exposed to the environment. It is a costly problem that affects various industries around the world, leading to economic losses. Here are some examples of how corrosion impacts the economy:

Table .1 Table showing the cost corrosion globally in different sector

Economic Regions	Agriculture CoC US\$ billion	Industry CoC US\$ billion	Services CoC US\$ billion	Total CoC US\$ billion	Total GDP US\$ billion	CoC % GDP
United States	2.0	303.2	146.0	451.3	16,720	2.7%
India	17.7	20.3	32.3	70.3	1,670	4.2%
European Region	3.5	401	297	701.5	18,331	3.8%
Arab World	13.3	34.2	92.6	140.1	2,789	5.0%
China	56.2	192.5	146.2	394.9	9,330	4.2%
Russia	5.4	37.2	41.9	84.5	2,113	4.0%
Japan	0.6	45.9	5.1	51.6	5,002	1.0%
Four Asian Tigers + Macau	1.5	29.9	27.3	58.6	2,302	2.5%
Rest of the World	52.4	382.5	117.6	552.5	16,057	3.4%
Global	152.7	1446.7	906.0	2505.4	74,314	3.4%

1. Transportation: Corrosion of vehicles such as cars, ships, and airplanes can lead to increased maintenance costs and decreased safety. In 2013, Boeing estimated that corrosion-related issues cost the aviation industry \$3 billion annually.
2. Oil and Gas: Corrosion in the oil and gas industry can lead to equipment failures, production downtime, and environmental damage. According to NACE International, a corrosion engineering society, corrosion in the oil and gas industry costs an estimated \$1.372 billion annually in the US alone. Water Systems: Corrosion of water systems such as pipes and tanks can lead to water quality issues, reduced capacity, and leaks. In the UK, the cost of repairing and replacing corroded water pipes is estimated to be around £1.2 billion annually.
3. Manufacturing: Corrosion in manufacturing can lead to decreased productivity and increased maintenance costs. For example, a study by NACE International found that the annual cost of corrosion in the US manufacturing sector is around \$17.6 billion.

1.0.5 Experimental introduction

Graphitic carbon nitride (g-C₃N₄) has attracted increasing interest in the fields of photocatalysis, electrochemistry, and photo electrochemistry ever since Wang et al. [1] reported its capacity to produce hydrogen in 2009 due to its intriguing two-dimensional (2D) structure and notable characteristics,.

On the other hand, for realistic large-scale application in industry, the quest for suitable earth-abundant, affordable, and nontoxic semiconductors is essential. Based on its capacity to respond to UV light and its active function as an electron acceptor, Al₂N₃ can fulfil the requirements. structural modification role for Al₂N₃ in the hydrothermal process, and the resulting hybrid with the proper g-C₃N₄ratio has about the same SBET value as pure g-C₃N₄. The combination has a significantly better photocatalytic capacity for hydrogen generation and methyl orange (MO) breakdown under visible light as compared to bare g-C₃N₄. In addition, unlike other g-C₃N₄-based composites, the hybrids exhibit decreased photo-luminescence intensity when compared to pristine g-C₃N₄ [6]. In addition to discovering a structure adjustment effect of g-C₃N₄in designing heterojunctions [7] and providing a new method for producing inexpensive photoactive mesoporous Al₂N₃, this research also provides a new insight into defect chemistry with regards to the photoluminescence behavior of heterojunctions composed of g-C₃N₄and semiconductors with plenty of defect sites.

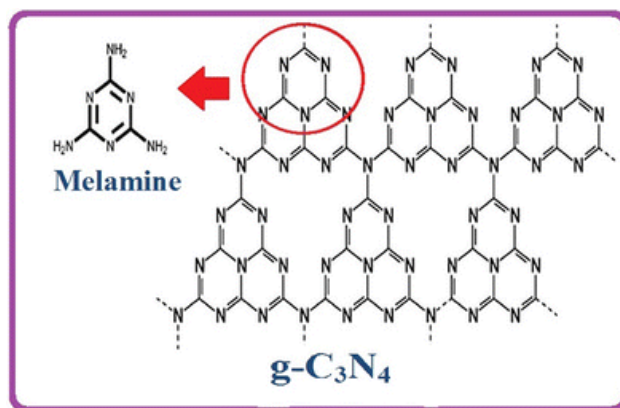


Fig.4. Structure of graphitic carbon nitride

<https://www.researchgate.net/publication/316968099/figure/fig1/AS:779394238930956@1562833475471/Structures-of-the-graphitic-carbon-nitride-g-C3N4.gif>

CHAPTER-3

MATERIALS AND METHODS :

Materials

3.1.1 Melamine

Melamine ($C_3H_6N_6$)

Properties: form: powder
 Color: White
 Odor: Inodorous
 Molecular weight: 126.12
 Formula: $C_3H_6N_6$
 Melting point: $345^{\circ}C$
 Boiling point: sublime

3.1.2 Aluminum nitride

Aluminum nitride (Al_2N_3)

Properties: form: crystal
 Color: White
 Molecular weight: 375.13
 Formula: (Al_2N_3)
 Melting point: $72.8^{\circ}C$
 Boiling point: $135^{\circ}C$

3.1.3 Sodium hydroxide

Sodium hydroxide (NaOH)

Properties: form: white solid ionic compound
 Color: white
 Molecular weight: 39.997
 Melting point: $318^{\circ}C$
 Boiling point: $1388^{\circ}C$

3.1.4 Distilled water

Prepared in laboratory by using ion exchange equipment.

3.1.5 Graphitic carbon nitride

Graphitic carbon nitride(g-C₃N₄)

Properties: form: pale yellow colored powder

Color: pale yellow

Molecular weight:92.06

Melting point:600-700°C

solubility: Insoluble in water.

Experimental procedure

gC₃N₄ was prepared through the thermal condensation of melamine. Melamine (5.0g) was added in a semi covered crucible and heated to 550°C for 2 h at a rate of 10⁰ Cmin⁻¹. g-C₃N₄/Al₂N₃.9H₂O hybrids were synthesized through a hydrothermal route and a following calcination. The designed total weight of the one part hetero junction was 0.30 g. In a typical procedure for 50% gC₃N₄/Al₂N₃.9H₂O (1.103 g) was dissolved in distilled water (30mL) and then as-prepared g-C₃N₄ (0.150g) was dispersed in the solution under ultrasonication for 20 min. Afterwards, 1m NaOH solution was added drop wise to the mixture till the pH reached 8–9. After being magnetically stirred for 2h, the mixed suspension was transferred into a 50 mL Teflon-lined stainless autoclave and heated at 140°C for 24 h. Then the obtained product was collected, thoroughly washed with deionized water for three times and air dried at 80°C for 3h. Finally, the resultant solid particles were calcined at 400°C for 2 h to obtain g-C₃N₄/ Al₂N₃.9H₂O composites, which are labeled as x% g-C₃N₄/ Al₂N₃.9H₂O (x=mass fraction of g-C₃N₄ in the hybrids). By using the aforementioned process, pristine Al₂N₃.9H₂O was synthesized without the addition of g-C₃N₄. For comparison, g-C₃N₄/ Al₂N₃.9H₂O (2:1) was prepared through chemisorption according to reference [14], in which Al₂N₃.9H₂O was obtained by precipitation synthesis.

3.2.1 Hydrothermal Method

50 ml of alumini graphitic carbon nitride solution was kept in a teflon-lined stainless autoclave.

After that its was kept in a Owen at a temperature of 140°C for 24hours. When the solution gets cooled. Then the obtained product was collected, thoroughly washed with deionized water for three times. Crucible with product kept in a muffle furnace at a temperature of 400°C for 2hours.



Fig.5. Hydrothermal method

3.2.2 Ultra sonication

- The designed total weight of the one-part hetero junction was 0.30 g. In a typical procedure for 50% gC₃N₄/ Al₂N₃.9H₂O (1.103 g) was dissolved in distilled water (30 mL) and then as-prepared g-C₃N₄ (0.150 g) was dispersed in the solution under ultra sonication for 20 min.
- Afterwards, 1m NaOH solution was added drop wise to the mixture till the pH reached 8– 9.



Fig.6. ultrasonication method

CHAPTER-4

RESULTS & DISCUSSION :

4.0. Results and Discussion

In pure $g\text{-C}_3\text{N}_4$ obtained through melamine pyrolysis without hydrothermal processing, distinct peaks at 27.48 and a faint peak at 13.18 are indexed as (002) and (100) planes of $g\text{-C}_3\text{N}_4$, respectively. The XRD pattern of hydrothermally treated $g\text{-C}_3\text{N}_4$ in the absence of Al_2N_3 shows no change compared to untreated $g\text{-C}_3\text{N}_4$.

However, for $g\text{-C}_3\text{N}_4 / \text{Al}_2\text{N}_3$ hybrids, two changes are observed compared to pure $g\text{-C}_3\text{N}_4$: the peaks at 13.1 and 27.48 shift to 14.2 and 27.68, respectively. This shift indicates narrower interlamellar spacings in the presence of Al ions, possibly due to coordination between the unoccupied 3p or 3d orbitals of Al ions and lone-pair electrons on the N atoms. Scheme 1 visually represents this interaction, depicting how Al can shorten the (100) spacing in $g\text{-C}_3\text{N}_4$.

In summary, the XRD patterns provide insights into the structural characteristics and interactions between $g\text{-C}_3\text{N}_4$, Al_2N_3 , and their composites, shedding light on their potential applications.

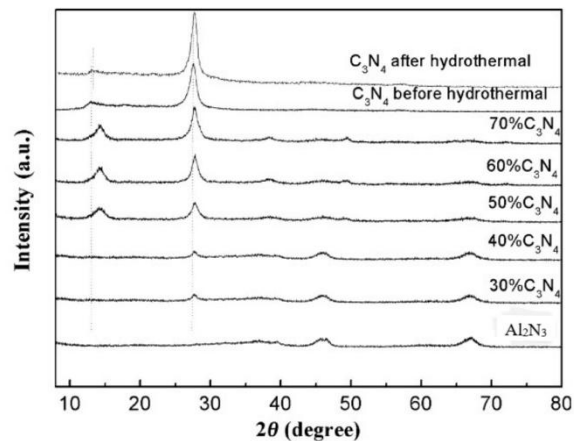


Fig.7. XRD Analysis of $g\text{-C}_3\text{N}_4$

Figure 7 illustrates X-ray diffraction (XRD) patterns of three materials: pure $g\text{-C}_3\text{N}_4$, pure Al_2N_3 , and various $g\text{-C}_3\text{N}_4 / \text{Al}_2\text{N}_3$ composites with different mass ratios. The XRD pattern of Al_2N_3 reveals peaks at 45.7 and 67.18, corresponding to the (400) and (440) diffraction planes of cubic $g\text{-Al}_2\text{N}_3$, respectively, indicating low crystallinity and the presence of defects. The absence of peaks related to the raw material (Al_2N_3) suggests complete transformation to Al_2N_3 through hydrothermal and calcination processes.

CHAPTER-5

CONCLUSION :**Conclusion**

Mesoporous g-C₃N₄/Al₂N₃ heterojunctions and photoactive g-Al₂N₃ have been synthesized in situ one-pot hydrothermal process, followed by a calcination process. It is advantageous to add that g-C₃N₄, which plays a vital function in the hydrothermal process that adjusts the structure of Al₂N₃ with a large specific surface area. In contrast to other g-C₃N₄-based heterojunctions, the photoluminescence behavior of pure g-C₃N₄ and g-C₃N₄/Al₂N₃ composites demonstrated the importance of defects, this work exhibits the structure modification function of g-C₃N₄ for Al₂N₃ in addition to hydrothermally producing a defect photoactive Al₂N₃ with a large surface area.

REFERENCES:

- [1] H. Li, J. Liu, W. Hou, N. Du, R. Zhang, X. Tao, Synthesis and characterization of g-C₃N₄/Bi₂MoO₆ heterojunctions with enhanced visible light photocatalytic activity, *Appl Catal B*. 160–161 (2014) 89–97. <https://doi.org/10.1016/j.apcatb.2014.05.019>.
- [2] C. Chang, Y. Fu, M. Hu, C. Wang, G. Shan, L. Zhu, Photodegradation of bisphenol A by highly stable palladium-doped mesoporous graphite carbon nitride (Pd/mpg-C₃N₄) under simulated solar light irradiation, *Appl Catal B*. 142–143 (2013) 553–560. <https://doi.org/10.1016/J.APCATB.2013.05.044>.
- [3] D. Wang, H. Sun, Q. Luo, X. Yang, R. Yin, An efficient visible-light photocatalyst prepared from g-C₃N₄ and polyvinyl chloride, *Appl Catal B*. 156–157 (2014) 323–330. <https://doi.org/10.1016/J.APCATB.2014.03.034>.
- [4] F. Tzompantzi, Y. Piña, A. Mantilla, O. Aguilar-Martínez, F. Galindo-Hernández, X. Bokhimi, A. Barrera, Hydroxylated sol-gel Al₂O₃ as photocatalyst for the degradation of phenolic compounds in presence of UV light, *Catal Today*. 220–222 (2014) 49–55. <https://doi.org/10.1016/J.CATTOD.2013.10.027>.
- [5] F.T. Li, Y. Zhao, Y.J. Hao, X.J. Wang, R.H. Liu, D.S. Zhao, D.M. Chen, N-doped P25 TiO₂-amorphous Al₂O₃ composites: One-step solution combustion preparation and enhanced visible-light photocatalytic activity, *J Hazard Mater*. 239–240 (2012) 118–127. <https://doi.org/10.1016/J.JHAZMAT.2012.08.016>.
- [6] F.T. Li, Y. Zhao, Q. Wang, X.J. Wang, Y.J. Hao, R.H. Liu, D. Zhao, Enhanced visible-light photocatalytic activity of active Al₂O₃/g-C₃N₄ heterojunctions synthesized via surface hydroxyl modification, *J Hazard Mater*. 283 (2015) 371–381. <https://doi.org/10.1016/J.JHAZMAT.2014.09.035>.
- [7] X. Zou, R. Silva, A. Goswami, T. Asefa, Cu-doped carbon nitride: Bio-inspired synthesis of H₂-evolving electrocatalysts using graphitic carbon nitride (g-C₃N₄) as a host material, *Appl Surf Sci*. 357 (2015) 221–228. <https://doi.org/10.1016/J.APSUSC.2015.08.197>.
- [8] V.C. Anadebe, V.I. Chukwuike, V. Selvaraj, A. Pandikumar, R.C. Barik, Sulfur-doped graphitic carbon nitride (S-g-C₃N₄) as an efficient corrosion inhibitor for X65 pipeline steel in CO₂-saturated 3.5% NaCl solution: Electrochemical, XPS and Nanoindentation Studies, *Process Safety and Environmental Protection*. 164 (2022) 715–728. <https://doi.org/10.1016/J.PSEP.2022.06.055>.
- [9] B. Cai, J. Feng, D. Guo, S. Wang, T. Ma, T.L. Eberhardt, H. Pan, Highly efficient isomerization of glucose to fructose over a novel aluminum doped graphitic carbon nitride bifunctional catalyst, *J Clean Prod*. 346 (2022) 131144. <https://doi.org/10.1016/J.JCLEPRO.2022.131144>.
- [10] A. Bahadoran, M. Najafizadeh, Q. Liu, J.R. De Lile, D. Zhang, S. Masudy-Panah, S. Ramakrishna, A. Fakhri, V.K. Gupta, Co-doping silver and iron on graphitic carbon nitride-carrageenan nanocomposite for the photocatalytic process, rapidly colorimetric detection and antibacterial properties, *Surfaces and Interfaces*. 26 (2021) 101279. <https://doi.org/10.1016/J.SURFIN.2021.101279>.
- [11] J. Liu, H. Liang, C. Li, J. Bai, Construction of V-doped graphitic carbon nitride with nanotube structure for sustainable photodegradation of tetracycline, *Vacuum*. 204 (2022) 111342. <https://doi.org/10.1016/J.VACUUM.2022.111342>.
- [12] R. Škuta, V. Matějka, K. Foniok, A. Smýkalová, D. Cvejn, R. Gabor, M. Kormunda, B. Smetana, V. Novák, P. Praus, On P-doping of graphitic carbon nitride with hexachlorotriphosphazene as a source of phosphorus, *Appl Surf Sci*. 552 (2021) 149490. <https://doi.org/10.1016/J.APSUSC.2021.149490>.
- [13] X. Zhao, Y. Zhang, F. Li, Y. Wang, W. Pan, D.Y.C. Leung, Salt-air template synthesis of Na and O doped porous graphitic carbon nitride nanorods with exceptional photocatalytic H₂ evolution activity, *Carbon N Y*. 179 (2021) 42–52. <https://doi.org/10.1016/J.CARBON.2021.04.030>.
- [14] K. Qi, N. Cui, M. Zhang, Y. Ma, G. Wang, Z. Zhao, A. Khataee, Ionic liquid-assisted synthesis of porous boron-doped graphitic carbon nitride for photocatalytic hydrogen production, *Chemosphere*. 272 (2021) 129953. <https://doi.org/10.1016/J.CHEMOSPHERE.2021.129953>.
- [15] A. Irshad, H.H. Smaili, S. Zulfiqar, M.F. Warsi, M.I. Din, K. Chaudhary, M. Shahid, Silver doped NiAl₂O₄ nanoplates anchored onto the 2D graphitic carbon nitride sheets for high-performance supercapacitor applications, *J Alloys Compd*. 934 (2023) 167705. <https://doi.org/10.1016/J.JALLCOM.2022.167705>.
- [16] H.S. Zhai, L. Cao, X.H. Xia, Synthesis of graphitic carbon nitride through pyrolysis of melamine and its electrocatalysis for oxygen reduction reaction, *Chinese Chemical Letters*. 24 (2013) 103–106. <https://doi.org/10.1016/J.CCLET.2013.01.030>.
- [17] Z. Zhou, X. Ji, S. Pourhashem, J. Duan, B. Hou, Investigating the effects of g-C₃N₄/Graphene oxide nanohybrids on corrosion resistance of waterborne epoxy coatings, *Compos Part A Appl Sci Manuf*. 149 (2021) 106568. <https://doi.org/10.1016/J.COMPOSITESA.2021.106568>.
- [18] M. Pourmadadi, E. Rahmani, M.M. Eshaghi, A. Shamsabadipour, S. Ghotekar, A. Rahdar, L.F. Romanholo Ferreira, Graphitic carbon nitride (g-C₃N₄) synthesis methods, surface functionalization, and drug delivery applications: A review, *J Drug Deliv Sci Technol*. 79 (2023)