https://chemclassjournal.com/
ChemClass Journal Vol. 9 Issue 4 (2025); 330 - 339
e-ISSN:3092-8214 p-ISSN:3092-8206
doi.org/10.33003/chemclass-2025-0904/25

Synthesis and Characterization of Modified Graphitic Carbon Nitride for Hydrogen Fuel Generation

Salihu Suleiman[1], Hafeez Yusuf Hafeez[2] Hadiza Abdullahi[3] and Mohammed Zaharraddeen[4]

[1, 3 and 4] Department of Chemistry, Federal University Dutse, Dutse, Jigawa State.
[2]Department of Physics, Federal University Dutse, Dutse, Jigawa State.

***Corresponding author:** Email: salibinsulei@gmail.com & 08060032934

Abstract

A graphitic carbon-nitrate (g-C_3N_4) has gained tremendous interest and attracted the attention of many scholars in environmental photocatalysis, due to its outstanding properties such as low toxicity, easy synthesis, good thermal and electronic properties, suitable energy band gap. Despite all these unique properties, there are still some drawbacks that affect its photocatalytic performance for hydrogen generation through photocatalytic water-splitting processes like massive charge carriers' recombination, low surface area and low visible light absorption. A lot of attempts have been made to address these drawbacks for better performance of g–C_3N_4–based material. In spite of all the attempts, there is still little research work that discusses more on the recent synthesis method and strategies to enhance the performance of g–C_3N_4–based photocatalyst. The study also centers on synthesis and characterization of the structure and properties of g-C_3N_4, and hydrogen generation using water splitting method and modified elemental doping for hydrogen generation of g–C_3N_4–based materials. The defect-rich and N-bridged tri–s–triazine g–C_3N_4–based material has been confirmed to be energetically favored relative to other phases, exhibiting extraordinary thermal stability at 700 °C. The doping and composite formation and the most common results of g-C_3N_4 characterization, regarding structural and morphological analysis, with better properties such as film's surface appearing wrinkled with the lighter spots confirming the presence of nitrogen, graphitic-like structure with characteristic peaks signifying crystalline lattice. The result reveals the presence of a hexagonal unit cell, which provides information on structural parameters such as the interlayer spacing and crystallite size. It also verifies the formation of g-C_3N_4 especially the quality, when used as a catalyst. XRD pattern in-plane heptazine units has a repeating unit of 0.6917 nm for the packing period and 0.319 nm as the interlayer stacking distance. The networks and functional groups, C–N, are confirmed by FTIR spectra measurements. Defect-rich and N-bridged tri-s-- triazine g–C_3N_4–based has revealed energetically favored relative to the other phases, which tend to exhibit thermal stability at 700 °C with triazine ring vibration at a wavenumber of 807 cm^{-1}.

Keywords: Elemental doping, graphite carbon nitrate, photocatalysis, morphological, fuel, charge carriers, hydrogen generation.

© CSN Zaria Chapter

Introduction

The rapid growth and industrial development in the global population have become one of the most critical aspects for meeting energy demands [1]. Renewable energy is highly essential to address the energy crisis and protect the Earth from global warming [2]. Renewable energy sources, such as wind, heat, biomass, water, and sunlight, have gained tremendous interest as abundant, unlimited, and eco-friendly options [3]. One of the most abundant renewable energies is solar energy due to its tremendous usage, such as inexhaustible, economical, and clean source of energy during the daytime [4]. Solar energy is the most significant source, having excellent energy [5]. Its abundance and potentiality in respect of sustainability due to its peculiar properties, such as non-poisonous gas emitter, availability, and eco-friendliness [6]. Although it has some disadvantages hindering its application, such as non-availability during the rainy season and at night [7].

In the past years, energy change from sunlight to chemical energy, that is, solar fuel through photocatalytic water splitting has gained attention due to the abundance of water and sunlight, including the surface of the earth covering nearly 75% water, which makes it inexhaustible, renewable, and economical to solve the rapidly increasing demand of solar energy ([8]. Hydrogen is promising and environmentally friendly, better than conventional fuel due to its higher energy density and free carbon emissions [9]. It can easily be processed by cracking and reforming methods of natural gas, oil, coal gasification, electrolysis, photolysis, thermolysis, etc. [10].

Among various techniques for hydrogen production, more attention has been focused on water splitting, which is one of the most promising clean and green technologies for hydrogen production and splits the earth's most abundant resources into hydrogen and oxygen with nearly no carbon emissions [11]. Hydrogen production from solar energy has a central role to play in combating this menace against the global energy crisis [12]. Utilization of photocatalytic splitting of water to produce hydrogen is still insufficient because of its low efficiency to utilize all the generated electrons for hydrogen reduction, and the use of expensive materials as photocatalysts [13].

In an attempt to find strong and fixed visible-light-driven semiconductor photocatalysts, graphitic carbon nitride (g-C_3N_4) has gained immense attention due to its high condensation degree [14] and heptazine ring structure, which enables it to possess many benefits like less cost, ecologically friendly, good stability of physicochemical properties free from toxins, as well as appealing electronic structure with relative low-band gap [15]. These beneficial properties make g-C_3N_4 a promising candidate for photocatalytic activity under visible light irradiation [16]. Furthermore, g-C_3N_4 is abundant and can be easily produced by thermal polymerization or thermal condensation as the

most used technique with nitrogen-rich precursors such as melamine, dicyandiamide, cyanamide, thiourea, and urea [17]. Nevertheless, even though g-C_3N_4 has these advantages, pure g-C_3N_4 has some drawbacks, such as a small specific surface area, poor visible light utilization efficiency, and high recombination of charge carriers [18]. To address these challenges, various techniques have been applied to improve g-C_3N_4 potentiality, including elemental doping, defect engineering, formation of heterojunctions, construction of nanostructures in morphologies, and formation of g-C_3N_4-based heterostructures [19].

[20] reported elemental doping of g-C_3N_4 as an enhancement strategy for the production of hydrogen. [21], discussed the synthesis and preparation of g-C_3N_4 based on heterocatalysts for photocatalytic hydrogen production. [22], as well discussed the effect of synthesis and structural modification on g–C_3N_4–based materials and the investigation of the material [23]. However, despite all these published paper and research articles, few of these articles has discussed more on recent synthesis method and progress of photocatalytic hydrogen performance of g–C_3N_4–based photocatalyst.

Delocalized π conjugated layers are formed when carbon and nitrogen hybridize in sp^2 at a highly stable state built up by van der Waals forces of layers [10, 24]. There are numerous synthetic routes to control the structure of g-C_3N_4, such as exfoliation and doping, porosity induced by template strategies, dissimilar ratios of precursors, and different condensation temperatures [25]. As compared to other allotropes, g-C_3N_4 is regarded as a common stable semiconductor under resistant alkaline and acidic conditions, eco-friendly, and ambient conditions. The visible solar spectrum of g-C_3N_4 is situated around 460 nm, having an Eg edge of approximately 2.7 eV, which meets the thermodynamic requirement for photocatalytic hydrogen production [18].

Several procedures can be used to prepare g-C_3N_4, including thermal polymerization, hydrothermal synthesis, solvothermal synthesis, microwave-assisted synthesis, and physical vapor deposition. Among various methods, thermal polymerization is considered the most widely used method due to its cost-effectiveness, efficiency, and simplicity, as well as the abundance of nitrogen precursors such as urea, melamine, thiourea, and cyanamide [13, 26].

Thus, each layer of g-C_3N_4 in the perfect periodic units could be easily identified by the XRD peak together with the packing structure in-plane. The defect-rich and N-bridged tri-s-- triazine g–C_3N_4–based has been discovered to be energetically favored relative to the other phases, which exhibits extraordinary thermal stability from 550 to 600 ^oC [27].

This research article focuses on recent developments and prospects for improving the photocatalytic hydrogen generation of g–C_3N_4–based materials for photocatalytic water splitting.

Materials and Methods

The materials used include a crucible, a muffle furnace, urea (Sigma-Aldrich), and glucose (Sigma-Aldrich).

Synthesis of Graphitic Carbon Nitride (g-C_3N_4)

Graphitic carbon nitride (g-C_3N_4) was synthesized via a one-step pyrolysis method using urea and glucose as precursor materials. Three different samples were prepared by varying the precursor composition to investigate the effect of glucose incorporation on the physicochemical properties of the resulting materials.

For the first sample, urea was used as the sole precursor. A predetermined amount of urea was placed directly into an alumina crucible without further pretreatment. For the second sample, urea and glucose were mixed in a 2:1 mass ratio (urea: glucose). The precursors were thoroughly ground using an agate mortar and pestle to ensure homogeneous mixing before transferring them into an alumina crucible. For the third sample, urea and glucose were mixed in a 1:1 mass ratio following the same grinding and homogenization procedure.

Each prepared precursor mixture was placed in a covered alumina crucible and introduced into a tubular furnace. The furnace was heated to 700 °C at a controlled heating rate (typically 5 °C min^{-1}) under a nitrogen atmosphere to prevent unwanted oxidation. The samples were maintained at the target temperature of 700 °C for 1 h to promote thermal polymerization and condensation of the precursors into graphitic carbon nitride. After calcination, the furnace was allowed to cool naturally to room temperature.

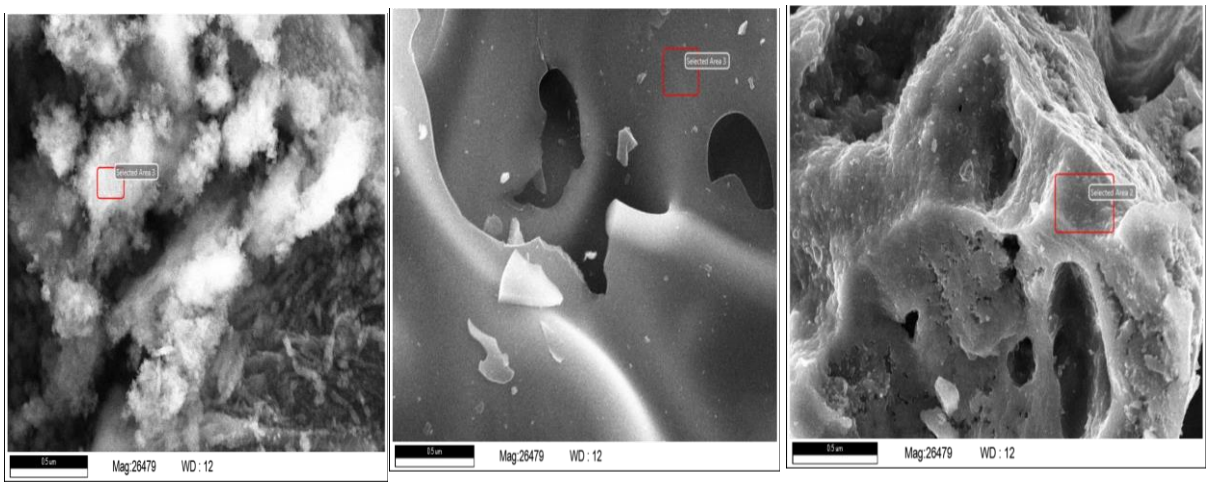
The obtained solid products were collected and washed repeatedly with deionized water through vacuum filtration to remove residual impurities and unreacted species. The filtered samples were then dried in an oven at 80 °C for 12 hours until a constant weight was achieved. The final dried powders were denoted as g-C_3N_4-1, g-C_3N_4-2, and g-C_3N_4-3 with slight modification.

Characterization

The morphology was studied using a scanning electron microscope (Model Vega3 Tescan). X-ray diffraction (Aeris instrument by Malvern Panalytical, Ronnebug, Thuringia Germany was carried out to determine the crystalline structure and an FTIR (Model Nicolet iS5 Spectrometer, PerkinElmer, USA.

Results and Discussion

The results of the research work are presented and discussed below:



(a) (g-C_3N_4-1) (b) (g-C_3N_4-2) (c) (g-C_3N_4-3)

Figure 1: Scanning Electron Microscopy of g-C_3N_4-1, g-C_3N_4-2, g-C_3N_4-3

The SEM pictures of the samples prepared by g-C_3N_4-1, g-C_3N_4-2, and g-C_3N_4-3 are presented in Fig 1, a, b, and c, respectively. SEM analyses using different magnifications are presented in Fig 1, with clear differences in the structures of the different modifications

The size of lighter spots is up to 10 µm. The higher magnification at 25 ^oC shows that the

closest neighborhood of spots is semi-disturbed. The film's surface appears to be wrinkled, similar to refined waves. Based on the recorded maps, it could be seen that the lighter spots have nitrogen. In our investigation, the nitrogen (M = 14 g/mol) is slightly heavier than carbon (M = 12 g/mol). Thus, based on the EDS maps and the SEM imaging performances, the lighter spots are quite certain to be connected to g-C_3N_4 particles similar to the work reported by [28].

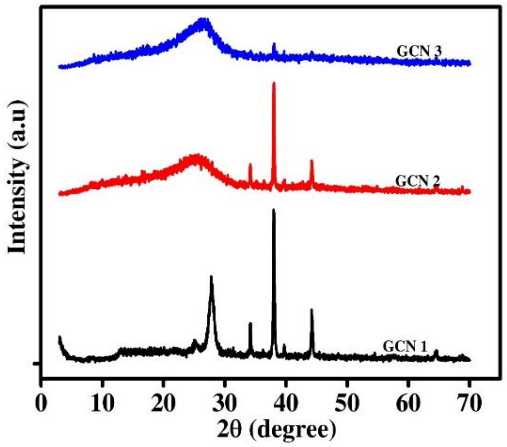


Figure 2: Combined XRD spectra of all the samples

The crystalline structure of the sample was studied by powder XRD as a suitable characterization technique, as reported by [29]. The modifications of g-C_3N_4 with doping, heterojunction formation, and co-catalyst present small differences between modified CN and pristine CN XRD, two distinct peaks: (a) A sharp

peak located close to 28◦, which can be attributed to (002) planes, indicative of interlayer stacking of aromatic systems and (b) a lower peak near 14◦, attributable to (100) planes, characteristic of the periodic in-plane conjugated tri-s-triazine (heptazine) rings similar to the work reported by [30]. In the case of lattice modification, such as doping, crystal lattice deformation leads to small alterations in peak intensity, width, and diffraction angles, pointing to the preservation of basic g-C_3N_4 [12, 31]. In spite of their minute scale, the small shifts can be quite beneficial as indicators for the successful integration of dopants into g-C_3N_4 [32].

XRD investigation of graphite-carbon nitride (g-C_3N_4) reveals a layered, graphitic-like structure with characteristic peaks signifying a crystalline lattice. The analysis confirms the presence of a hexagonal or orthorhombic unit cell, which provides information on structural parameters such as interlayer spacing and crystallite size. The resulting XRD pattern is used to verify the formation of g-C_3N_4 and its quality, especially when used in composites or as a catalyst.

The pristine g-C_3N_4 provides two characteristic diffraction peaks at 19.2◦ and 26.9◦ in a typical XRD pattern (XRD pattern, by inputting to in-plane heptazine units with a repeating of 0.6917 nm for the packing period as well as 0.319 nm for the interlayer stacking distance. Furthermore, 26.9◦ is shown more distinct peak for the g-C_3N_4 component. Thus, each layer of g-C_3N_4 can be easily identified by the XRD peak, along with the in-plane packing structure. These networks and functional groups (C–N) are promoted to determine FTIR spectra measurements.

However, the defect-rich and N-bridged tri–s–triazine g–C3N4–based material has been discovered to be energetically favored relative to the other phases, which exhibits extraordinary thermal stability from 550 to 600 °C [6].

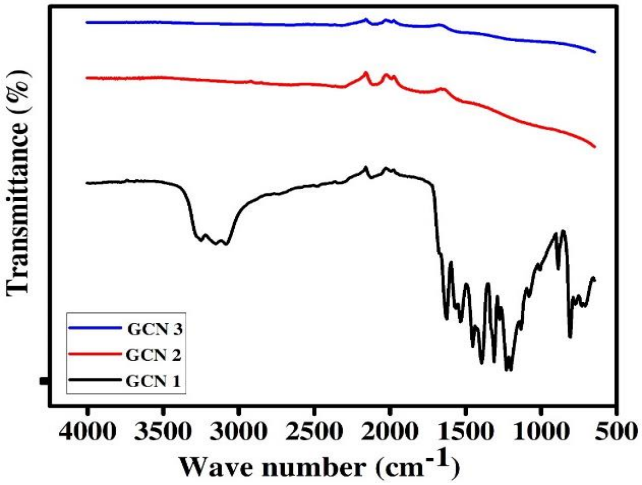


Figure 3: Combined FTIR spectra of all the samples

The doping of g-C_3N_4 was carried out at room temperature. Iron oxide powder in microscale, CN of FTIR presented in Fig 3. The products with CN show a characteristic peak C= O 1638 cm^{-1}. FTIR investigation was carried out for initial graphitic carbon g-C_3N_4 to determine the characteristic bands and then compared with the bands of g-C_3N_4 + Fe_2O_3 and g-C_3N_4 +Fe_2O_3 + CN, respectively.

Preparation of g-C_3N_4, and the melting of melamine in an electric furnace, was tested along with Fe_2O_3 and CN at the same temperature. In

the event of melting with Fe_2O_3, the reaction that occurred in thermal analysis was confirmed, while g-C_3N_4 reduces in the presence of Fe_2O_3. In the case of CN, the melting temperature is approximately identical to the temperature at which the second exothermic reaction takes place for CN. The obtained product visually resembles a mixture of carbon black and C_3N_4, and subsequent identification by FTIR, as seen in Fig 3. The reaction temperature was slightly increased during the reaction of CN in a hydrogen peroxide environment to modify CN during the reaction of g-C_3N_4 (FTIR presented in Fig 3).

FTIR analysis was carried out on selected products of the g-C_3N_4 reaction, and SEM images were taken at different resolutions of 500 µm, 50 µm, and 5 µm. Thermal analysis was carried out and evaluated on the products from the reaction.

All acquired spectra are characterized by two regions, namely at 2800 cm^{-1} and then a forest of peaks in the range 1600-500 cm^{-1}, where there are vibrations of CN – heterocycles. In all the prepared products, a wavenumber of 807 cm^{-1} is identified, which is interpreted as a triazine ring vibration in accordance with the reference [12, 33].

Conclusion

In conclusion, we can infer that possible routes for efficiently improving g-C_3N_4 have been achieved, demonstrating its incredible versatility as a photocatalytic material for hydrogen production. The thermal calcination treatment appears to be the most efficient method for the synthesis and modification of g-C_3N_4. The exposure of amino groups on the surface of g-C_3N_4 provides minor charges in hydrogen production but creates suitable bonding positions for non-metal and plasmonic metal decoration, and hydrogen production. Increased specific surface area has been achieved in many ways, including higher temperature treatment, increased heating rates, the doping process, and co-catalyst integration. More notably, the addition of a co-catalyst, especially plasmonic metals, results in the immediate and significant increase in the production of hydrogen. We can conclude that further research into the efficient combination of different types of modification is needed for significant advancement.

Acknowledgements

This work was supported by the Institutional-Based Research of the 2025 intervention. We acknowledge the support of the TETFund intervention for encouraging research and innovation in tertiary institutions.

References

1. Reddy, S. N., Nanda, S., Vo, D. V. N., Nguyen, T. D., Nguyen, V. H., Abdullah, B., & Nguyen-Tri, P. (2020). Hydrogen: fuel of the near future. In *New dimensions in production and utilization of hydrogen* (pp. 1-20). Elsevier.
2. Vetter, S., Nayak, D., McBey, D., Dondini, M., Kuhnert, M., & Oyesiku-Blakemore, J. (2023). Environmental issues: greenhouse gas emissions. In *Sustainable food science: A*

comprehensive approach (pp. 216-248). Elsevier.

3. Overland, I., Juraev, J., & Vakulchuk, R. (2022). Are renewable energy sources more evenly distributed than fossil fuels? *Renewable Energy*, *200*, 379-386.
4. Siddik, M. A. B., Grubert, E., Caldwell, P., & Marston, L. T. (2023). Retirement of US fossil fuel-fired power plants will increase water availability. *Journal of Hydrology*, *617*, 128984.
5. Nazir, H., Louis, C., Jose, S., Prakash, J., Muthuswamy, N., Buan, M. E., ... & Kannan, A. M. (2020). Is the H_2 economy realizable in the foreseeable future? Part I: H2 production methods. *International Journal of Hydrogen Energy*, *45*(27), 13777-13788.
6. Prasad, C., Tang, H., Liu, Q., Bahadur, I., Karlapudi, S., & Jiang, Y. (2020). A latest overview on photocatalytic application of g-C_3N_4 based nanostructured materials for hydrogen production. *International Journal of Hydrogen Energy*, *45*(1), 337-379.
7. Hussain, A., Ali, N., Ali, S. S., Hou, J., Aslam, I., Naeem, H., ... & Wang, X. (2022). Diverse morphological study for nonmetal-doped g-C_3N_4 composites with narrow bandgap for improved photocatalytic activity. *Research on Chemical Intermediates*, *48*(7), 2857-2870.
8. Yapicioglu, A., & Dincer, I. (2023). A newly developed renewable energy driven multigeneration system with hot silica sand storage for power, hydrogen, freshwater and cooling production. *Sustainable Energy Technologies and Assessments*, *55*, 102938.
9. Ahmed, A., Al-Amin, A. Q., Ambrose, A. F., & Saidur, R. (2016). Hydrogen fuel and transport system: A sustainable and environmental future. *International journal of hydrogen energy*, *41*(3), 1369-1380.
10. Diboma, B. S., Atiotsia, V. H., Che, L. C., Essomba, P. B., Bot, B. V., & Tamba, J. G. (2023). Gasification of charcoal derived from tropical wood residues in an updraft fixed bed reactor. *Bioresource Technology Reports*, *21*, 101308.
11. Zhou, H., Tian, J., Wang, R., Zhan, D., Liu, P., Chen, R., ... & Han, C. (2023). Lewis acid molten salts prepared Ti3C2Cl2 MXenes assembling with g-C_3N_4 nanosheets for enhanced photocatalytic H_2 evolution. *Ceramics International*, *49*(8), 13042-13049.
12. Hafeez, H. Y., Mohammed, J., Suleiman, A. B., Ndikilar, C. E., Sa'id, R. S., & Muhammad, I. (2023). Insights into hybrid TiO_2-g-C_3N_4 heterostructure composite decorated with rGO sheet: A highly efficient photocatalyst for boosted solar fuel (hydrogen) generation. *Chemical Physics Impact*, *6*, 100157.
13. Bhosale, R., Kim, D. J., Gosavi, S., & Tonda, S. (2023). 2D Nanomaterials-based Heterostructures for H_2O Splitting and CO_2 Reduction.
14. Rouzkhosh, M., Jaafarzadeh, N., Varshosaz, K., Orak, N., & Dashti, S. (2023). Neural network to quantify the amount of greenhouse gases produced by flue gases affecting climatic conditions in Iran's southern areas. *Geoenergy Science and Engineering*, *221*, 111224.
15. Xu, D., Cai, H., Li, D., Chen, F., Han, S., Chen, X., ... & Feng, Y. (2025). Recent Advances in Graphitic Carbon Nitride-Based Materials in the Photocatalytic Degradation of Emerging Contaminants. *Inorganics*, *13*(10), 319.
16. Alaghmandfard, A., & Ghandi, K. (2022). A comprehensive review of

graphitic carbon nitride (g-C_3N_4)–metal oxide-based nanocomposites: potential for photocatalysis and sensing. *Nanomaterials*, *12*(2), 294.

17. Bhanderi, D., Lakhani, P., & Modi, C. K. (2024). Graphitic carbon nitride (g-C_3N_4) as an emerging photocatalyst for sustainable environmental applications: A comprehensive review. *RSC sustainability*, *2*(2), 265-287.
18. Qian, A., Han, X., Liu, Q., Ye, L., Pu, X., Chen, Y., ... & Jia, X. (2023). Ultrathin Pd metallenes as novel co-catalysts for efficient photocatalytic hydrogen production. *Applied Surface Science*, *618*, 156597.
19. Liu, X., Ma, R., Zhuang, L., Hu, B., Chen, J., Liu, X., & Wang, X. (2021). Recent developments of doped g-C_3N_4 photocatalysts for the degradation of organic pollutants. *Critical Reviews in Environmental Science and Technology*, *51*(8), 751-790.
20. Vasilchenko, D., Zhurenok, A., Saraev, A., Gerasimov, E., Cherepanova, S., Tkachev, S., ... & Kozlova, E. (2022). Highly efficient hydrogen production under visible light over g-C_3N_4-based photocatalysts with low platinum content. *Chemical Engineering Journal*, *445*, 136721.
21. Cao, J., Fan, H., Wang, C., Ma, J., Dong, G., & Zhang, M. (2020). Facile synthesis of carbon self-doped g-C_3N_4 for enhanced photocatalytic hydrogen evolution. *Ceramics International*, *46*(6), 7888-7895.
22. Ismael, M., & Wu, Y. (2019). A mini-review on the synthesis and structural modification of gC_3 N_4-based materials, and their applications in solar energy conversion and environmental remediation. *Sustainable Energy & Fuels*, *3*(11), 2907-2925.
23. Tang, R., Gong, D., Deng, Y., Xiong, S., Zheng, J., Li, L., ... & Zhao, J. (2022). π-π stacking derived from graphene-like biochar/g-C_3N_4 with tunable band structure for photocatalytic antibiotics degradation via peroxymonosulfate activation. *Journal of Hazardous Materials*, *423*, 126944.
24. Li, Y., Liu, Y., Xing, D., Wang, J., Zheng, L., Wang, Z., ... & Huang, B. (2021). 2D/2D heterostructure of ultrathin $BiVO_4/Ti_3C_2$ nanosheets for photocatalytic overall Water splitting. *Applied Catalysis B: Environmental*, *285*, 119855.
25. Guo, R. T., Wang, J., Bi, Z. X., Chen, X., Hu, X., & Pan, W. G. (2022). Recent advances and perspectives of g–C_3N_4–based materials for photocatalytic dyes degradation. *Chemosphere*, *295*, 133834.
26. Gao, Z., Wang, Y., Xu, L., Tao, Q., Wang, X., Zhou, Z., ... & Huang, Y. (2022). Optimizing local charge distribution of metal nodes in bimetallic metal–organic frameworks for efficient urea oxidation reaction. *Chemical Engineering Journal*, *433*, 133515.
27. Zeng, Y., Lu, S., Wang, H., Khalil, M. N., Hua, Q., & Qi, X. (2025). In Situ Electrodeposition Self-Supported Bimetallic Sulfides for Urea Electrooxidation. *ChemCatChem*, *17*(9), e202500298.
28. Bhunia, M. K., Melissen, S., Parida, M. R., Sarawade, P., Basset, J. M., Anjum, D. H., ... & Takanabe, K. (2015). Dendritic tip-on polytriazine-based carbon nitride photocatalyst with high hydrogen evolution activity. *Chemistry of Materials*, *27*(24), 8237-8247.
29. Wang, K., Huang, W., Cao, Q., Zhao, Y., Sun, X., Ding, R., ... & Gao, P. (2022). Engineering NiF_3/Ni_2P heterojunction as efficient

electrocatalysts for urea oxidation and splitting. *Chemical Engineering Journal*, *427*, 130865.

30. Hwang, S. W., Noh, T. H., & Cho, I. S. (2019). Optical properties, electronic structures, and photocatalytic performances of bandgap-tailored $SrBi_2Nb_2{-}xVxO_9$ compounds. *Catalysts*, *9*(5), 393.
31. Lu, Y., Wang, W., Cheng, H., Qiu, H., Sun, W., Fang, X., ... & Zheng, Y. (2022). Bamboo-charcoal-loaded graphitic carbon nitride for photocatalytic hydrogen evolution. *International Journal of Hydrogen Energy*, *47*(6), 3733-3740.
32. Feng, S., Luo, J., Li, J., Yu, Y., Kang, Z., Huang, W., ... & Tian, X. (2022). Heterogeneous structured Ni_3Se_2/MoO_2@ $Ni1_2P_5$ catalyst for durable urea oxidation reaction. *Materials Today Physics*, *23*, 100646.
33. Darkwah, W. K., & Oswald, K. A. (2019). Photocatalytic applications of heterostructure graphitic carbon nitride: pollutant degradation, hydrogen gas production (water splitting), and CO_2 reduction. *Nanoscale Research Letters*, *14*(1), 234.