Journal of Research and Development on Nanotechnology **Review**

Hierarchical Porous g-C_3N_4 as a Photocatalyst Nanomaterial

Adhe Aryswan[a*]

Heterogeneous photocatalysts are in the spotlight recently due to the rise in environmental pollution and energy crisis. Graphitic carbon nitride (g-C_3N_4) material shows a potential photocatalyst with attractive properties such as metal-free, low bandgap, and high stability. However, the bulk g-C_3N_4 photocatalytic performance is insufficient to be work properly in practical applications. The hierarchical porous nanostructure is one modification that could be applied to improve photocatalytic activity. This review discusses the g-C_3N_4 material as a promising photocatalyst, including other potential modifications to improve its photocatalytic performance

Received
13 June 2021
Accepted
17 July 2021
Published
21 July 2021

DOI: 10.5614/jrdn.2021.1.1.16534

Keywords: g-C_3N_4; Hierarchical; Photocatalyst; Nanomaterial

Introduction

The advancement of technology adoption in industry has led to an uplift in the standard of living. However, this cannot be secluded from environmental pollution. Hazardous chemicals used in the textile industry require its wastewater to be treated more sophisticatedly (Kiani *et al.*, 2020; Kuleyin, Gök, and Akbal, 2021). Likewise, the handling of hospital wastewater (Top et al., 2020) and the coal chemical industry (Shi et al., 2020). On the other hand, the environmental impact of mounting fossil fuel consumption has raised awareness to replace it with renewable and eco-friendly energy sources.

Photocatalysts emerge as a great approach to tackle those problems. The material can degrade the organic pollutants in the wastewater and produce hydrogen through light-induced water splitting (Chen *et al.*, 2014). Nevertheless, the performance of heterogeneous photocatalysts needs to be improved due to their shortcomings, e.g., low efficiency, stability, and selectivity. One of the optimizations is a fabrication of a hierarchical nanostructure (Li, Yu, and Jaroniec, 2020). Graphitic carbon nitride (g-C_3N_4) is a potential hierarchical photocatalyst due to its appealing properties such as stability, hardness, biocompatibility, and ease of modifying the surface (Dong *et al.*, 2014).

This mini-review describes the g-C_3N_4 material as a promising photocatalyst, including other potential modifications to improve its photocatalytic performance.

Graphitic Carbon Nitride g-C_3N_4

Atomic and electronic structure

Graphitic carbon nitride is a carbon-based layered polymer resembling graphene, which also consists of nitrogen. The material is a *p*-type semiconductor, having high chemical stability, high photostability, and high activity under visible light irradiation (Masih, Ma, and Rohani, 2017). Among the seven known graphitic carbon nitride phases, g-C_3N_4 is considered suitable for visible sunlight activation due to its relatively low bandgap at 2.7 eV (Ajiboye, Kuvarega, and Onwudiwe, 2020).

The g-C_3N_4 structure consists of only carbon and nitrogen, which form the basic units, i.e., triazine (C_3N_3) and heptazine or tri-s-triazine (C_6N_7). Compared to triazine, the heptazine system exhibits lower energy; hence it is known as the most stable phase. Therefore, the g-C_3N_4 is mainly considered a conjugated π system linking a large number of tri-s-triazine rings based on van der Waals forces between layers (Zhang and Sun, 2018). The structure is shown in the following **Figure 1**.

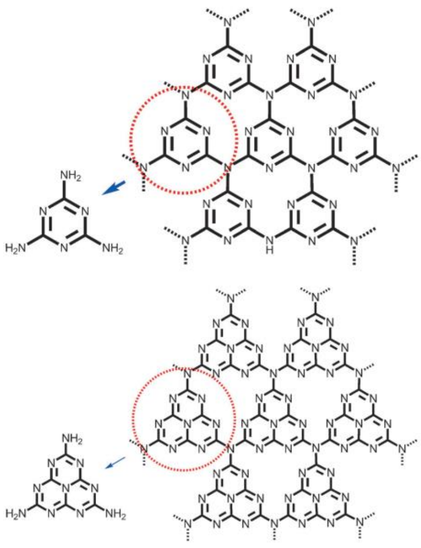

Figure 1. g-C_3N_4 structures: s-Triazine (top) and heptazine (bottom) (Wang, Wang and Antonietti, 2012).

---

[a] *Mechanical Engineering Department, Politeknik Negeri Batam Indonesia*
* Corresponding author: adhearyswan@polibatam.ac.id

An ab initio study conducted by Wang *et al.* (2017) presumes that the heptazine-based g-C_3N_4 has two possible, stable arrangements, as shown in **Figure 2**.

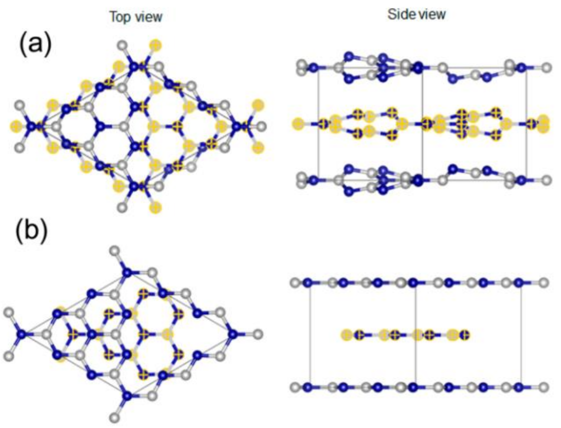

Figure 2. Predicted configuration of heptazine-based g-C_3N_4 (a) buckled; (b) planar (Wang *et al.*, 2017).

Their calculations showed that the buckled configuration has a direct bandgap of 2.87 eV. Meanwhile, the planar one has two bandgaps, direct 2.66 eV and indirect 2.27 eV. The experimental data reveal that the prepared material has a bandgap of 2.86 eV. This fact confirms that the heptazine g-C_3N_4 structure is likely to be in buckled configuration.

However, Jeong *et al.* (2019) found that g-C_3N_4 nanosheets have two distinct band gaps of 2.20 eV and 2.79 eV. These results correspond to planar heptazine g-C_3N_4 electronic structures. We may conclude that the bandgaps are tunable through morphology engineering.

Photocatalytic activity

In comparison to the conventional TiO_2 photocatalyst, g-C_3N_4 exhibits different photocatalytic behavior. While TiO_2 activity was enhanced by Pt addition, the graphitic carbon nitride showed an opposite effect, as shown in **Figure 3**.

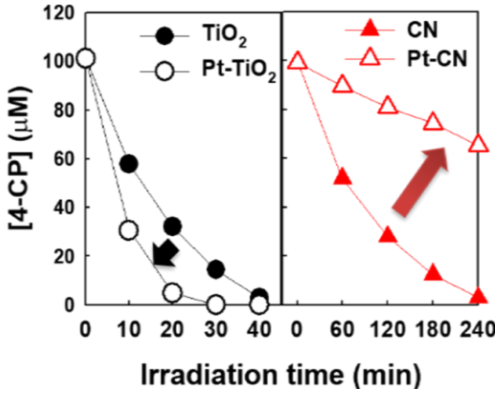

Figure 3. Photocatalytic degradation of organic substrate 4-chlorophenol (4-CP) by bare TiO_2, bare g-C_3N_4 (CN), and their Pt-loaded counterpart (Lim *et al.*, 2020).

Lim *et al.* (2020) reveal that the contrary effects are due to hydroxyl radical formation in both photocatalytic systems. The adverse outcome of Pt on g-C_3N_4 is attributed to the fact that Pt breaks down the in situ generated H_2O_2, which takes place as an intermediate of hydroxyl radical formation. Consequently, the hydroxyl radical formation is inhibited so that the photocatalytic activity decreased. The following Table 1 shows a brief comparison between g-C_3N_4 photocatalyst and TiO_2.

Table 1. Comparisons between g-C_3N_4 and TiO_2

Properties	**g-C_3N_4**	**TiO_2**
Band-gap (eV)	2.7	3.2 (Dar *et al.*, 2014)
Working range	Visible light	Ultraviolet
Semiconductor type	*p*	*n*
Pore size (nm)	5 – 50 (Zhang *et al.*, 2018)	2 – 20, 25 – 150 (Tao *et al.*, 2011)

Synthesis and modifications

Bulk g-C_3N_4 can be synthesized by thermal condensation of assorted precursors with R-C-NH_2 units, as shown in **Figure 4**.

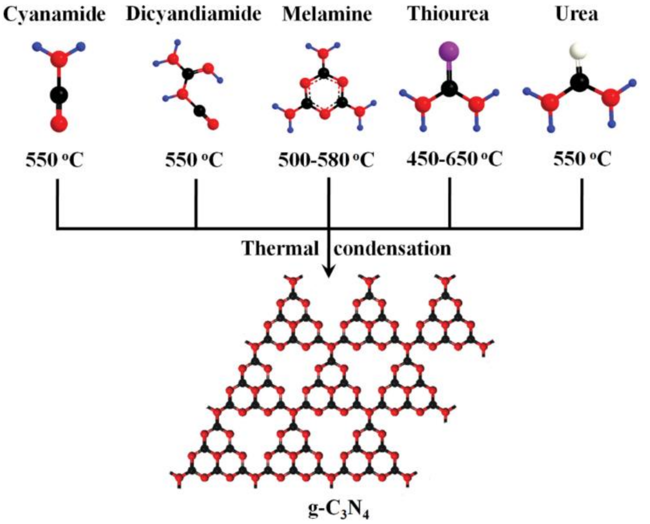

Figure 4. Preparations of g-C_3N_4 of various nitrogen-rich precursors (Cao *et al.*, 2015).

Nonetheless, the material prepared by this method has many defects, which led to a short visible light utilization range, low specific surface area, limited active site, and rapid recombination of the photoinduced carrier (Antil *et al.*, 2020; Zheng *et al.*, 2020). Hence, various efforts have been made in favor of improving the g-C_3N_4 photocatalytic performance.

Superstructure TiO_2/SiO_2/g-C_3N_4 hybrid has been reported to have an excellent performance to degrade berberine in seawater (Yu *et al.*, 2020). Azami *et al.* (2020) has successfully synthesized a g-C_3N_4/fibrous titania silica photocatalyst. Oxygen doping has enhanced g-C_3N_4 for visible-light photodegradation of Rhodamin B (Tran *et al.*, 2021).

Hierarchical Porous g-C_3N_4

Hierarchical porous structure

Today, the fabrication of 3D hierarchical nanostructures has drawn significant attention due to their promising applications as photocatalysts (Liu *et al.*, 2015). The hierarchical structure comprises low-dimensional nanocrystal, e.g., nanosheets, nanowires, and nanorods, thus improving the material properties (Yang *et al.*, 2013). It is renowned that the hierarchical photocatalyst could present more porous sites as scattering the light to increase its absorption, a superior steric hindrance to inhibit the agglomeration of catalyst, and greater specific surface area to present more active sites (Li *et al.*, 2018; Wang *et al.*, 2019).

Synthesis of hierarchical porous g-C_3N_4

Hierarchical Sr-ZnO/g-C_3N_4 composite was prepared by diluting g-C_3N_4 powder via ultrasonic assistance. Then the solution was stirred in addition to $Zn(NO_3)_2$ hydrate, $Sr(NO_3)_2$, $C_6H_9Na_3O_9$, and NaOH solution. The obtained precipitate was rinsed with water and absolute ethanol consecutively and dried at 65°C for 15 h (D *et al.*, 2020).

On the other hand, (Liu *et al.*, 2020) successfully built the 3D hierarchical CdS/g-C_3N_4 two-dimensional heterojunction structure through facile hydrothermal method only with g-C_3N_4 powder, $CdSO_4$, and thiourea as precursors without any surfactants as assisting template. Lin, Yu, and Huang (2020) have successfully fabricated a cellulose-derived hierarchical g-C_3N_4/TiO_2 nanotube heterostructured nanocomposite by in situ coating thin g-C_3N_4 layers onto the surfaces of the TiO_2 nanotubes. The fabricated material is shown in **Figure 5**.

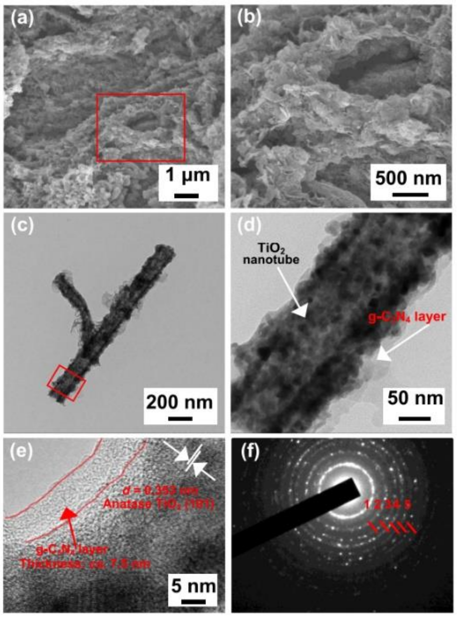

Figure 5. Electron microscopy images of the g-C_3N_4/TiO_2: (a, b) FE-SEM micrograph of the material, showing the hierarchical assemblies of the nanotubes. (c, d) TEM images of a single composite nanotube isolated from the assemblies. (e) HR-TEM micrograph of a part of the nanocomposite tube surface. (f) SAED pattern of the nanocomposite (Lin, Yu, and Huang, 2020).

Photocatalytic activities

The hierarchical Sr-ZnO/g-C_3N_4 and CdS/g-C_3N_4 show superior photocatalytic degradation towards organic pollutants than pristine g-C_3N_4. These findings are consistent with the previous discussion and prove that the modification is compatible with photocatalytic activity. While Lin, Yu, and Huang (2020) vary the g-C_3N_4 contents of 15%, 46%, and 66%. The comparison of g-C_3N_4/TiO_2 nanocomposite photocatalytic activity in visible light is shown in **Figure 6**.

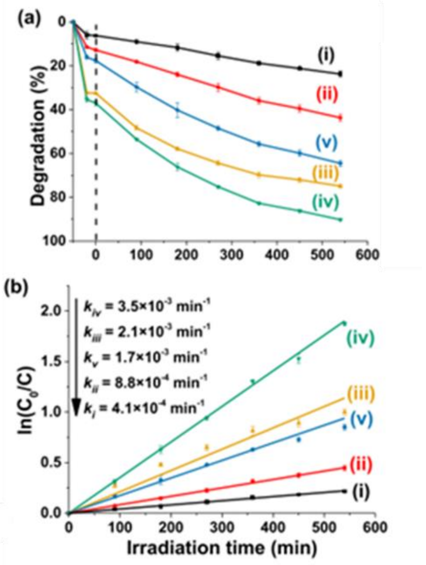

Figure 6. (a) Photocatalytic activity of g-C_3N_4/TiO_2 nanocomposite. (b) Respective pseudo-first-order simulations of the photocatalytic results by the referential TiO_2 nanotubes (i), referential g-C_3N_4 powder (ii), cellulose-derived 15% g-C_3N_4/TiO_2 (iii), cellulose-derived 46% g-C_3N_4/TiO_2 (iv), and cellulose-derived 66% g-C_3N_4/TiO_2 (v) nanocomposites (Lin, Yu, and Huang, 2020).

Summary

The g-C_3N_4 material is a promising photocatalyst due to its stability, environmentally friendly, low cost, and able to be activated by visible light. Despite the material yet having some shortcomings, a comprehensive option of modifications is available to be applied. The Hierarchical porous nanostructure is one of the modifications that has been proved to have more excellent photocatalytic activity than bare g-C_3N_4. Indeed, the material properties would improve if coupled with other modifications, such as being a composite or being doped with a particular element. The graphitic carbon nitride material commercial applications in the near future would create more exciting results.

Conflict of Interest

I have no conflict to declare.

References

Ajiboye, T. O., Kuvarega, A. T. and Onwudiwe, D. C. (2020) ‘Graphitic carbon nitride-based catalysts and their applications: A review’, *Nano-Structures and Nano-Objects*. Elsevier B.V., 24, p. 100577. doi: 10.1016/j.nanoso.2020.100577.

Antil, B. *et al.* (2020) ‘Directed holey and ordered g-C3N4.5nanosheets by a hard template nanocasting approach for sustainable visible-light hydrogen evolution with prominent quantum efficiency’, *Journal of Materials Chemistry A*, 8(26), pp. 13328–13339. doi: 10.1039/d0ta02734k.

Azami, M. S. *et al.* (2020) ‘Tuning of the electronic band structure of fibrous silica titania with g-C3N4 for efficient Z-scheme photocatalytic activity’, *Applied Surface Science*. Elsevier, 512(December 2019), p. 145744. doi: 10.1016/j.apsusc.2020.145744.

Cao, S. *et al.* (2015) ‘Polymeric Photocatalysts Based on Graphitic Carbon Nitride’, *Advanced Materials*, 27(13), pp. 2150–2176. doi: 10.1002/adma.201500033.

Chen, D. *et al.* (2014) ‘Synthesis and characterization of the ZnO/mpg-C3N4 heterojunction photocatalyst with enhanced visible light photoactivity’, *Dalton Transactions*. Royal Society of Chemistry, 43(34), pp. 13105–13114. doi: 10.1039/c4dt01347f.

D, N. *et al.* (2020) ‘Hierarchical Sr-ZnO/g-C3N4 heterojunction with enhanced photocatalytic activities’, *Journal of Photochemistry and Photobiology A: Chemistry*. Elsevier, 396(August 2019), p. 112515. doi: 10.1016/j.jphotochem.2020.112515.

Dar, M. I. *et al.* (2014) ‘Controlled synthesis of TiO2 nanoparticles and nanospheres using a microwave assisted approach for their application in dye-sensitized solar cells’, *Journal of Materials Chemistry A*, 2(6), pp. 1662–1667. doi: 10.1039/c3ta14130f.

Dong, G. *et al.* (2014) ‘A fantastic graphitic carbon nitride (g-C3N4) material: Electronic structure, photocatalytic and photoelectronic properties’, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. Elsevier B.V., 20(1), pp. 33–50. doi: 10.1016/j.jphotochemrev.2014.04.002.

Jeong, T. *et al.* (2019) ‘Atomic and electronic structures of graphene-decorated graphitic carbon nitride (g-C3N4) as a metal-free photocatalyst under visible-light’, *Applied Catalysis B: Environmental*. Elsevier, 256(March), p. 117850. doi: 10.1016/j.apcatb.2019.117850.

Kiani, R. *et al.* (2020) ‘Real textile wastewater treatment by a sulfate radicals-Advanced Oxidation Process: Peroxydisulfate decomposition using copper oxide (CuO) supported onto activated carbon’, *Journal of Water Process Engineering*. Elsevier Ltd, 38(September), p. 101623. doi: 10.1016/j.jwpe.2020.101623.

Kuleyin, A., Gök, A. and Akbal, F. (2021) ‘Treatment of textile industry wastewater by electro-Fenton process using graphite electrodes in batch and continuous mode’, *Journal of Environmental Chemical Engineering*, 9(1). doi: 10.1016/j.jece.2020.104782.

Li, X., Yu, J. and Jaroniec, M. (2020) *Hierarchical porous photocatalysts*, *Interface Science and Technology*. doi: 10.1016/B978-0-08-102890-2.00003-8.

Li, Z. *et al.* (2018) ‘Hierarchical photocatalyst of In2S3 on exfoliated MoS2 nanosheets for enhanced visible-light-driven Aza-Henry reaction’, *Applied Catalysis B: Environmental*. Elsevier B.V., 237, pp. 288–294. doi: 10.1016/j.apcatb.2018.05.087.

Lim, J. *et al.* (2020) ‘How g-C3N4 Works and Is Different from TiO2 as an Environmental Photocatalyst: Mechanistic View’, *Environmental science & technology*, 54(1), pp. 497–506. doi: 10.1021/acs.est.9b05044.

Lin, Z., Yu, B. and Huang, J. (2020) ‘Cellulose-Derived Hierarchical g-C3N4/TiO2-Nanotube Heterostructured Composites with Enhanced Visible-Light Photocatalytic Performance’, *Langmuir*, 36(21), pp. 5967–5978. doi: 10.1021/acs.langmuir.0c00847.

Liu, X. *et al.* (2015) ‘Synthesis of bilayer ZnO nanowire arrays: Morphology evolution, optical properties and photocatalytic performance’, *Ceramics International*. Elsevier, 41(9), pp. 11710–11718. doi: 10.1016/j.ceramint.2015.05.135.

Liu, X. *et al.* (2020) ‘In situ self-assembly of 3D hierarchical 2D/2D CdS/g-C3N4 hereojunction with excellent photocatalytic performance’, *Materials Science in Semiconductor Processing*. Elsevier Ltd, 105(August 2019), p. 104734. doi: 10.1016/j.mssp.2019.104734.

Masih, D., Ma, Y. and Rohani, S. (2017) ‘Graphitic C3N4 based noble-metal-free photocatalyst systems: A review’, *Applied Catalysis B: Environmental*. Elsevier B.V., 206, pp. 556–588. doi: 10.1016/j.apcatb.2017.01.061.

Tao, T. *et al.* (2011) ‘Porous TiO2 with a controllable bimodal pore size distribution from natural ilmenite’, *CrystEngComm*, 13(5), pp. 1322–1327. doi: 10.1039/c0ce00533a.

Tran, D. A. *et al.* (2021) ‘One-step synthesis of oxygen doped g-C3N4 for enhanced visible-light photodegradation of Rhodamine B’, *Journal of Physics and Chemistry of Solids*. Elsevier Ltd, 151, p. 109900. doi: 10.1016/j.jpcs.2020.109900.

Wang, J. *et al.* (2017) ‘Determination of Crystal Structure of Graphitic Carbon Nitride: Ab Initio Evolutionary Search and Experimental Validation’, *Chemistry of Materials*, 29(7), pp. 2694–2707. doi: 10.1021/acs.chemmater.6b02969.

Wang, S. *et al.* (2019) ‘Direct Z-scheme ZnO/CdS hierarchical photocatalyst for enhanced photocatalytic H2-production activity’, *Applied Catalysis B: Environmental*. Elsevier B.V., 243, pp. 19–26. doi: 10.1016/j.apcatb.2018.10.019.

Wang, Y., Wang, X. and Antonietti, M. (2012) ‘Polymeric graphitic carbon nitride as a heterogeneous organocatalyst: From photochemistry to multipurpose catalysis to sustainable chemistry’, *Angewandte Chemie - International Edition*, 51(1), pp. 68–89. doi: 10.1002/anie.201101182.

Yang, C. *et al.* (2013) ‘Controlled growth, properties, and application of CdS branched nanorod arrays on transparent conducting oxide substrate’, *Solar Energy Materials and Solar Cells*. Elsevier, 115, pp. 100–107. doi: 10.1016/j.solmat.2013.03.023.

Yu, Y. *et al.* (2020) ‘Soft-template assisted construction of superstructure TiO2/SiO2/g-C3N4 hybrid as efficient visible-light photocatalysts to degrade berberine in seawater via an adsorption-photocatalysis synergy and mechanism insight’, *Applied Catalysis B:*

Environmental. Elsevier, 268(February), p. 118751. doi: 10.1016/j.apcatb.2020.118751.

Zhang, B. *et al.* (2018) 'Pompon-like structured g-C3N4/ZnO composites and their application in visible light photocatalysis', *Research on Chemical Intermediates*. Springer Netherlands, 44(11), pp. 6895–6906. doi: 10.1007/s11164-018-3528-4.

Zhang, J. and Sun, H. (2018) *Carbon nitride photocatalysts*, *Multifunctional Photocatalytic Materials for Energy*. Elsevier Ltd. doi: 10.1016/B978-0-08-101977-1.00007-7.

Zheng, Y. *et al.* (2020) 'Integrating CuInSe2nanocrystals with polymeric carbon nitride nanorods for photocatalytic water splitting', *Dalton Transactions*, 49(22), pp. 7598–7604. doi: 10.1039/d0dt00865f.