Graphitic Carbon Nitride Photocatalysts for Degradation of Organic Pollutants

Huimin Li^a, Huixian Zhang^b, Keming Fang^c, Lining Yang^d, Jianrong Chen^{e*}

College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua, 321004, China.

^a lihimin2008@qq.com, ^b 953878987@qq.com, ^c sky65@zjnu.cn, ^d yln@zjnu.cn, ^e cjr@zjnu.cn

*Corresponding author: Tel: +86 579 82291275; Fax: +86 579 82282273

Keywords: Graphitic carbon nitride, Photodegradation, Organic pollutants.

Abstract: Organic pollutants have posed threat to human health and other creature. Photocatalytic technology arises, because it can use solar energy to degrade pollutants. Hence, graphitic carbon nitride (g-C₃N₄) with excellent photocatalytic performance has attracted global attention. This paper presents the introduction of g-C₃N₄ and recent achievements of g-C₃N₄ composites in the photodegradation of organic pollutants.

1. Introduction

Graphitic carbon nitride (g-C₃N₄) as one of the representative and promising photocatalysts, which is composed of two earth-abundant elements: carbon and nitrogen, has become a very hot research topic due to its excellent photocatalysis property with the bandgap 2.7 eV, outstanding chemical stability, fascinating optical and electrical properties[1]. These unique characteristics make g-C₃N₄ be widely applied in various photocatalytic fields, such as pollutant degradation[2], hydrogen production from water splitting[3], CO₂ reduction[4], and bacterial disinfection[4].

Many strategies have been reported for the synthesis of g-C₃N₄, and different methods could prepare different materials with specific topography and electronic properties. Such methods include solvothermal[5,6], thermal polymerization[7], electrochemical deposition[8], solid state[9], etc. Thermal polymerization has been the most commonly used synthetic method owing to its simple operation steps and short synthetic cycle. The precursors derive from a variety of carbon/nitrogen-rich molecules, such as urea, melamine, cyanate, thiourea, cyanamide, thiocyanate, guanidine hydrochloride and so on. In a typical synthesis, melamine was put into an alumina crucible which was heated to 550 °C in a muffle furnace with a heating rate of 2 °C/min. After calcination for 2 h, the alumina crucible was cooled naturally to room temperature. The sample was collected and ground into powder[10].

2. Applications of g-C₃N₄ in the photodegradation of organic pollutants

Nowadays, people are faced with environment problem, which promotes the development of semiconductor photocatalysis. G-C₃N₄ is one of non-metal photocatalysts, and has been widely used to photodegrade a variety of organic pollutants, including rhodamine B (RhB), methylene blue (MB), methyl orange (MO) and so on[11]. Table 1 shows the invention of a wide variety of g-C₃N₄ nanocomposites for the photodegradation of organic pollutants. Additionally, their photocatalytic performance is also displayed in the table. It is well known that photogenerated electrons (e⁻) and holes (h⁺) could generate radicals, such as hydroxyl radicals (•OH) and superoxide anion radicals (•O₂⁻) which have strong redox property[12]. Once reactive species are produced, they will oxidize organic pollutants during photocatalytic reactions.

Table 1 Recent achievements of g-C₃N₄ composites in the photodegradation of pollutants.

Catalyst	Pollutant	Catalyst dose (g/L)	Pollutant concentration	Degradation efficiency	Reference
BiOBr/g-C ₃ N ₄	RhB	0.5	20 mg/L	100 % in 40 min	[13]
Bi ₂ O ₃ /g-C ₃ N ₄	RhB	1.0	1.0×10 ⁻⁵ M	95% in 120 min	[14]
In ₂ VO ₄ /g-C ₃ N ₄	RhB	0.3	0.002 M	100 % in 20 min	[15]
NaTaO ₃ /g-C ₃ N ₄	RhB	0.25	5 mg/L	100 % in 90 min	[16]
SnO ₂ /g-C ₃ N ₄	RhB	2.0	10 mg/L	100 % in 120 min	[17]
ZnO/g-C ₃ N ₄	MO	3.0	5 mg/L	95 % in 100 min	[18]
BiOCl/g-C ₃ N ₄	MO	1.0	10 mg/L	100 % in 80 min	[19]
Ag ₃ PO ₄ /g-C ₃ N ₄	MO	0.25	10 mg/L	100 % in 20 min	[20]
ZnFe ₂ O ₄ /g-C ₃ N ₄	MO	0.25	10 mg/L	100 % in 180 min	[21]
Co ₃ O ₄ /g-C ₃ N ₄	MO	1.0	10 mg/L	100 % in 180 min	[22]
MoO ₃ /g-C ₃ N ₄	MB	1.0	10 mg/L	95 % in 180 min	[23]
Zn _{0.8} Cd _{0.2} S/g-C ₃ N ₄	MB	1.0	10 mg/L	100 % in 180 min	[24]
Ag ₃ VO ₄ /g-C ₃ N ₄	MB	0.5	10 mg/L	95 % in 30 min	[25]
N-doped TiO ₂ /g-C ₃ N ₄	MB	1.0	10 mg/L	100 % in 60 min	[26]
α-Fe ₂ O ₃ /g-C ₃ N ₄	Directred81	1.0	5.0×10 ⁻⁵ M	70 % in 120 min	[27]
BiOCl _x Br _{1-x} /g-C ₃ N ₄	Rhodamine 640	0.25	9 mg/L	55 % in 90 min	[28]
Ag/AgVO ₃ /g-C ₃ N ₄	Basic fuchsin	1.0	20 mg/L	99.3 % in 70 min	[29]
WO ₃ /g-C ₃ N ₄	Basic fuchsin	2.0	1.0×10 ⁻⁵ M	75 % in 60 min	[30]
Cu ₂ O/g-C ₃ N ₄	Acid Orange-II	0.1	40 mg/L	95 % in 180 min	[31]
g-C ₃ N ₄ /CdS/RGO	Congo red	0.4	20 mg/L	100 % in 20 min	[32]
CuFe ₂ O ₄ /g-C ₃ N ₄	Orange II	0.1	0.028 mM	90 % in 180 min	[33]
P-g-C ₃ N ₄ /ZnIn ₂ S ₄	4-nitroaniline	1.0	10 mg/L	99.4 % in 90 min	[34]
g-C ₃ N ₄ /TiO ₂ (TCN)	ciprofloxacin	0.5	20 mg/L	97.3% in 150 min	[35]
g-C ₃ N ₄ /WO ₃	acetaldehyde	0.1	11.2 μmol/L	100 % in 24 h	[35]
mpg-C ₃ N ₄ /Co ₃ O ₄	bisphenol	0.4	15 mg/L	93.6% in 180 min	[36]
g-C ₃ N ₄ /ZnIn ₂ S ₄	phenol	0.4	10 mg/L	73.2 % in 4 h	[37]
Bi ₅ Nb ₃ O ₁₅ /g-C ₃ N ₄	4-chlorophenol	1.0	10 mg/L	100 % in 60 min	[38]
Pd/mpg-C ₃ N ₄	bisphenol A	0.5	20 mg/L	93.9% in 180 min	[39]
Ag/AgBr/g-C ₃ N ₄	2-chlorophenol	1.0	20 mg/L	70.51 % in 4 h	[40]

3. Summary

In the view of the scientific reports, great efforts have been devoted to prepare g-C₃N₄ composites. It is delightful that remarkable achievements have been made on the field of photodegradation of pollutants. However, the mechanism of photocatalysis is not clear. More importantly, these materials still have long way to achieve practical application.

Acknowledgment

This research was supported by National Natural Science Foundation of China (No. 21275131).

References

- [1] Cao, S., Low J., Yu J., Jaroniec, M. (2015) Polymeric Photocatalysts based on Graphitic Carbon Nitride. *Advanced materials*, 27, 2150-2176.
- [2] Yan, S.C., Li, Z.S., Zou, Z.G. (2010) Photodegradation of Rhodamine B and Methyl Orange over Boron-doped G-C₃N₄ under Visible Light Irradiation. *Langmuir the Acs Journal of Surfaces & Colloids*, 26, 3894-3901.
- [3] Kohl, S.W., Weiner, L., Schwartzburd, L. (2009) Consecutive Thermal H₂ and Light-induced O₂ Evolution from Water Promoted by A Metal Complex. *Science*, 324, 74-77.

- [4] Roy, S.C., Varghese, O.K., Paulose, M. (2010) Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. *Acs Nano*, 4, 1259-1278.
- [5] Guo, Q., Xie, Y., Wang, X. (2003) Characterization of Well-crystallized Graphitic Carbon Nitride Nanocrystallites via A Benzene-thermal Route at Low Temperatures. *Chemical Physics Letters*, 380, 84-87.
- [6] Cui, Y., Ding, Z., Fu, X. (2012) Construction of Conjugated Carbon Nitride Nanoarchitectures in Solution at Low Temperatures for Photoredox Catalysis. *Angewandte Chemie*, 124, 11814-11818.
- [7] Groenewolt, M., Antonietti, M. (2005) Synthesis of G-C₃N₄ Nanoparticles in Mesoporous Silica Host Matrices, 17, 1789-1792.
- [8] Lv, Q., Cao, C., Zhang, Y. (2004) The Preparation of Insoluble Fibroin Films Induced by Degummed Fibroin or Fibroin Microspheres. *Journal of Materials Science Materials in Medicine*, 15, 1193-1197.
- [9] Fu, M., Pi, J., Dong, F. (2013) A Cost-effective Solid-state Approach to Synthesize G-C₃N₄ Coated TiO₂ Nanocomposites with Enhanced Visible Light Photocatalytic Activity. *International Journal of Photoenergy*, 2013, 10196-10202.
- [10] Zhang, X., Xie, X., Wang, H. (2013) ChemInform Abstract: Enhanced Photo Responsive Ultrathin Graphitic-phase C₃N₄ Nanosheets for Bioimaging. *Cheminform*, 135, 18.
- [11] Mamba, G., Mishra, A.K. (2016) Graphitic Carbon Nitride (g-C₃N₄) Nanocomposites: A New and Exciting Generation of Visible Light Driven Photocatalysts for Environmental Pollution Remediation. *Applied Catalysis B: Environmental*, 198, 347-377.
- [12] Lam, S.M., Sin, J.C., Mohamed, A.R. (2016) A Review on Photocatalytic Application of G-C₃N₄/Semiconductor (CNS) Nanocomposites towards the Erasure of Dyeing Wastewater. *Materials Science in Semiconductor Processing*, 47, 62-84.
- [13] Fu J., Tian, Y., Chang, B. (2012) BiOBr–Carbon Nitride Heterojunctions: Synthesis, Enhanced Activity and Photocatalytic Mechanism. *Journal of Materials Chemistry*, 22, 21159.
- [14] Zhang, J., Hu, Y., Jiang, X. (2014) Design of A Direct Z-scheme Photocatalyst: Preparation and Characterization of Bi₂O₃/g-C₃N₄ with High Visible Light Activity. *J Hazard Mater*, 280, 713-722.
- [15] Shi, W., Guo, F., Chen, J. (2014) Hydrothermal Synthesis of InVO₄/Graphitic Carbon Nitride Heterojunctions and Excellent Visible-light-driven Photocatalytic Performance for Rhodamine B. *Journal of Alloys and Compounds*, 612, 143-148.
- [16] Kumar, S., Kumar, B., Surendar, T. (2014) G-C₃N₄/NaTaO₃ Organic–inorganic Hybrid Nanocomposite: High-performance and Recyclable Visible Light Driven Photocatalyst. *Materials Research Bulletin*, 49, 310-318.
- [17] Zang, Y., Li, L., Li X. (2014) Synergistic Collaboration of G-C₃N₄/SnO₂ Composites for Enhanced Visible-light Photocatalytic Activity. *Chemical Engineering Journal*, 246, 277-286.
- [18] Sun, J.X., Yuan, Y.P., Qiu, L.G. (2012) Fabrication of Composite Photocatalyst G-C₃N₄-ZnO and Enhancement of Photocatalytic Activity under Visible Light. *Dalton Transactions*, 41, 6756.
- [19] Wang, X.J., Wang, Q., Li, F.T. (2013) Novel BiOCl–C₃N₄ Heterojunction Photocatalysts: In Situ Preparation via An Ionic-liquid-assisted Solvent-thermal Route and Their Visible-light Photocatalytic Activities. *Chemical Engineering Journal*, 234, 361-371.
- [20] Kumar, S., Surendar, T., Baruah, A. (2013) Synthesis of A Novel and Stable G-C₃N₄–Ag₃PO₄ Hybrid Nanocomposite Photocatalyst and Study of The Photocatalytic Activity under Visible Light Irradiation. *Journal of Materials Chemistry A*, 1, 5333.
- [21] Zhang, S., Li, J., Zeng, M. (2013) In Situ Synthesis of Water-soluble Magnetic Graphitic

Carbon Nitride Photocatalyst and Its Synergistic Catalytic Performance. *ACS applied materials & interfaces*, 5, 12735-12743.

[22] Han, C., Ge, L., Chen, C. (2014) Novel Visible Light Induced Co_3O_4 -g- C_3N_4 Heterojunction Photocatalysts for Efficient Degradation of Methyl Orange. *Applied Catalysis B: Environmental*, 147, 546-553.

[23] Huang, L., Xu, H., Zhang, R. (2013) Synthesis and Characterization of G- C_3N_4 / MoO_3 Photocatalyst with Improved Visible-light Photoactivity. *Applied Surface Science*, 283, 25-32.

[24] Li, D., Wu, Z., Xing, C. Novel $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$ /g- C_3N_4 Heterojunctions with Superior Visible-light Photocatalytic Activity: Hydrothermal Synthesis and Mechanism Study. *Journal of Molecular Catalysis A Chemical*, 395, 261-268.

[25] Zhu, T., Song, Y., Ji, H. (2015) Synthesis of G- C_3N_4 / Ag_3VO_4 Composites with Enhanced Photocatalytic Activity under Visible Light Irradiation. *Chemical Engineering Journal*, 271, 96-105.

[26] Wang, X.J., Yang, W.Y., Li, F.T. (2013) In Situ Microwave-assisted Synthesis of Porous N- TiO_2 /g- C_3N_4 Heterojunctions with Enhanced Visible-light Photocatalytic Properties. *Industrial & Engineering Chemistry Research*, 52, 17140-17150.

[27] Theerthagiri, J., Senthil, R.A., Priya, A. (2014) Photocatalytic and Photoelectrochemical Studies of Visible-light Active α - Fe_2O_3 -g- C_3N_4 Nanocomposites. *Rsc Advances*, 4, 38222-38229.

[28] Shi, S., Gondal, M.A., Rashid, S.G. (2014) Synthesis of g- C_3N_4 / $\text{BiOCl}_x\text{Br}_{1-x}$ Hybrid Photocatalysts and The Photoactivity Enhancement Driven by Visible Light. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 461, 202-211.

[29] Zhao, W., Guo, Y., Wang, S. (2015) A Novel Ternary Plasmonic Photocatalyst: Ultrathin G- C_3N_4 Nanosheet Hybridized by Ag/ AgVO_3 Nanoribbons with Enhanced Visible-light Photocatalytic Performance. *Applied Catalysis B: Environmental*, 165, 335-343.

[30] Chen, S., Hu, Y., Jiang, X. (2015) Fabrication and Characterization of Novel Z-scheme Photocatalyst WO_3 /g- C_3N_4 with High Efficient Visible Light Photocatalytic Activity. *Materials Chemistry and Physics*, 149-150, 512-521.

[31] Peng, B., Zhang, S., Yang, S. (2014) Synthesis and Characterization of G- C_3N_4 / Cu_2O Composite Catalyst with Enhanced Photocatalytic Activity under Visible Light Irradiation. *Materials Research Bulletin*, 56, 19-24.

[32] Pawar, R.C., Khare, V., Lee, C.S. (2014) Hybrid Photocatalysts Using Graphitic Carbon Nitride/Cadmium Sulfide/Reduced Graphene Oxide (g- C_3N_4 / CdS /RGO) for Superior Photodegradation of Organic Pollutants under UV and Visible Light. *Dalton Transactions*, 43, 12514-12527.

[33] Yao, Y., Lu, F., Zhu, Y. (2015) Magnetic Core-shell CuFe_2O_4 @ C_3N_4 Hybrids for Visible Light Photocatalysis of Orange II. *J Hazard Mater*, 297, 224-233.

[34] Chen, W., Liu, T.Y., Huang, T. (2016) Novel Mesoporous P-doped Graphitic Carbon Nitride Nanosheets Coupled with ZnIn_2S_4 Nanosheets as Efficient Visible Light Driven Heterostructures with Remarkably Enhanced Photo-reduction Activity. *Nanoscale*, 8, 3711-3719.

[35] Jiang, Z., Zhu, C., Wan, W. (2016) Constructing Graphite-like Carbon Nitride Modified Hierarchical Yolk-shell TiO_2 Spheres for Water Pollution Treatment and Hydrogen Production. *Journal of Materials Chemistry A*, 4, 1806-1818.

[36] Qiu, P., Chen, H., Jiang, F. (2014) Cobalt Modified Mesoporous Graphitic Carbon Nitride with Enhanced Visible-light Photocatalytic Activity. *RSC Adv*, 4, 39969-39977.

[37] Liu, H., Jin, Z., Xu Z. Fabrication of ZnIn_2S_4 -g- C_3N_4 Sheet-on-sheet Nanocomposites for Efficient Visible-light Photocatalytic H_2 -evolution and Degradation of Organic Pollutants. *RSC*

Advances, 5, 97951-97961.

[38] Zhang, S., Yang, Y., Guo, Y. (2013) Preparation and Enhanced Visible-light Photocatalytic Activity of Graphitic Carbon Nitride/Bismuth Niobate Heterojunctions. *J Hazard Mater*, 261, 235-245.

[39] Chang, C., Fu, Y., Hu, M. (2013) Photodegradation of Bisphenol A by Highly Stable Palladium-doped Mesoporous Graphite Carbon Nitride (Pd/mpg-C₃N₄) under Simulated Solar Light Irradiation. *Applied Catalysis B: Environmental*, 142-143.

[40] Cao J., Zhao, Y., Lin, H. (2013) Ag/AgBr/g-C₃N₄: A Highly Efficient and Stable Composite Photocatalyst for Degradation of Organic Contaminants under Visible Light. *Materials Research Bulletin*, 48, 3873-3880.