Research on Photodegradation of Norfloxacin by Modified Carbon Nitrogen Compounds

ZHAI ENZI
Beijing University of Chemical Technology, College of Materials Science and Engineering, Beijing, China, 100029
Author’s e-mail address: zhaienzi@163.com

Abstract. Photocatalysis is an economical and reliable method for degradation of pharmaceutical pollutants. Under mild conditions, the photocatalyst can absorb optical energy and accelerate the photo degradation of pollutants. As a new type of non-metallic semiconductor catalyst, graphite phase carbon nitride (g-C3N4) has many excellent properties such as low band gap, large specific surface area and so on. Norfloxacin (NOR) is a synthetic antibiotic with many good properties such as high antibacterial activity and low toxicity. Because of its wide application in medical treatment and animal breeding, it has caused great pollution to the environment. In this paper, the performance of g-C3N4 and the mechanism of photocatalytic degradation of NOR are analyzed. Several effective modification methods are described, and several problems that need to be solved in current research are put forward.

1. Introduction
Nowadays, with the rapid development of antibiotics, people are getting used to fighting against bacterial infections with antibiotics. This has greatly improved the average life span and the quality of life of human beings. Among them, norfloxacin, as a kind of quinolones which are synthetic antibiotics, have been widely used in human medical treatment and breeding industries because of their highly effective antibacterial activity, low cross resistance with other antibiotics and little side effects.[1]

However, with the overusing, antibiotics has caused serious water pollution. For example, studies have shown that in the Yangtze River Delta Basin, the highest concentration of norfloxacin (NOR) in natural waters has reached 134.2ng/L. [2] Therefore, it is necessary to develop an efficient and reliable method to degrade the antibiotics.

Photocatalytic degradation under visible light of has long been regarded as an economic and effective means to degrade pharmaceutical pollutants. Among many photocatalyst, semiconductor photocatalyst has been widely used in photocatalytic degradation of pollutants due to its low cost and high catalytic efficiency. However, because of the low photoelectric efficiency of traditional semiconductor catalysts, the utilization efficiency of solar energy is insufficient, which limits its further application.

In recent years, graphite phase carbon nitride has attracted wide attention due to its special electronic structure and low band gap.[1] However, because of its small specific surface area and low photoelectron separation efficiency, the actual utilization of light energy is very low. In order to improve the photocatalytic efficiency of carbon nitride, many modification methods, such as
morphology control, element doping and heterostructure construction deposition, have been proposed to improve the degradation efficiency of NOR.

2. g-C3N4 and its photocatalytic degradation mechanism
g-C3N4 is a semiconductor photocatalyst with excellent performance. The graphite like structure and van der Waals force between the two-dimensional lamellae give g-C3N4 good chemical and thermal stability.[3] In addition, g-C3N4 is easy to prepare. Urea, cyanamide, dicyandiamide and melamine are rich in carbon and nitrogen and are usually selected as precursors.[4] Its common preparation methods such as solid-state method, electrochemical deposition method and solvothermal method have the advantages of simple equipment, short process flow and short preparation time.

The band gap of g-C3N4 is 2.7eV, which makes it a good photocatalyst for visible light response. Because g-C3N4 is a kind of polymer semiconductor, its unique properties lead to multiple excitation after single photon absorption, which can produce a large number of active substances (such as •O2, •OH) and degrade organic pollutants such as NOR.[5]

The mechanism of g-C3N4 photocatalytic degradation of organic compounds has been clearly discussed by predecessors, and its degradation mechanism is shown in the figure1.

![Figure 1: Mechanism of NOR degradation by g-C3N4][6]

Under visible light irradiation, g-C3N4 can absorb photons and excite the electrons in the valence band into the conduction band to produce an electron-hole pair. The electrons in the conduction band can be captured by molecules to produce an O2•−, which reacts with H+ to form •OH. Nor can be degraded by the effect of •OH.[6][7]

\[
g - C_3N_4 + h\nu \rightarrow h^+ + e^- \\
e^- + O_2 \rightarrow O_2^{•−} \\
O_2^{•−} + 2H^+ + 2e^- \rightarrow •OH + OH^- \\
•OH + NOR \rightarrow degradation
\]

3. Modification of g-C3N4

3.1. Element doping
The g-C3N4 synthesized by traditional method has the disadvantages of small specific surface area and narrow absorption spectrum range, and the quantum efficiency will be reduced for the rapid recombination of photogenerated electrons and holes. Element doping can effectively change the electronic structure of g-C3N4, so as to increase the absorption range of visible light, and finally improve the photocatalytic performance of g-C3N4. There are many methods of doping such as nonmetal element doping, metal element doping and element co-doping.
Yang et al. synthesized P-Cl co-doped with g-C3N4 photocatalyst by thermal condensation.[8] The degradation efficiency of the catalyst for NOR was 2 times higher than that of pure g-C3N4, and it showed very good cycle stability. Subsequent experiments showed that more defects in the tri-s-triazine units of g-C3N4 have been produced, exposing more active centers and eventually improved the photoexcited charge carrier separation. Yang et al. speculated that the reason for the improvement of catalytic ability of the element doped catalyst may be that the addition of P atoms and Cl atoms changes the electronic structure of g-C3N4, and nitrogen vacancies in g-C3N4 can make photogenerated electrons easier to be captured, thus improving the separation efficiency of photogenerated electrons. Figure 2 shows the degradation mechanism of the modified catalyst.

![Degradation mechanism of modified catalyst under visible light](image)

Dai et al. synthesized Interlayer and intralayer Cu doped g-C3N4 photocatalyst using calcination method. [9]The catalyst can degrade 90.5% NOR in 120 minutes. Dai's team used electrical and theoretical calculation to prove that copper doping can increase reactive sites, induce more superoxide radicals and improve catalytic activity. This work provides a possible solution for improving the photocatalytic activity of metal doped g-C3N4 in the degradation of NOR.

### 3.2. Z-scheme

Compared with pure g-C3N4, Z-scheme photocatalysts have narrower band gap and stronger light absorption, which can significantly improve the photocatalytic activity comparing with pure g-C3N4. In Z-scheme, the lower energy conductive electrons and valence band holes of the two semiconductors are combined to retain the higher valence band holes and conductive electrons, which maintain the higher oxidation and reduction ability of the composite photocatalyst.

The LaNiO3 nanospheres and Ag-Br nanoparticles were successfully grown on g-C3N4 by Jiang et al. [10]As an active electron transfer center, Ag enhances the separation of charge pairs. The catalytic degradation rate of NOR by modified g-C3N4 reached 92% within 120 minutes and the reaction rate reached 0.0179 min⁻¹, which was 4.39 times of that of pure g-C3N4. Through the cycle test, it was found that the catalyst 3-ALG had good stability whose catalytic rate did not change significantly after four cycles. It was found that O₂⁻, H⁺ and •OH were the main active substances in the photodegradation of NOR.

Jiang et al. Grown LeFeO3 nanospheres in the heterojunction composed of g-C3N4 nanosheets and AgI by ultrasonic assisted hydrothermal method. By this synthesis process, electron transfer medium of dual-Z scheme is finally formed.[11] In this catalyst, AgI / LaFeO3 / g-C3N4 enhanced the efficiency of electron migration and separation, and eventually enhanced the photodegradation efficiency. In the degradation test which came later, it was found that AgI / LaFeO3 / g-C3N4 could degrade more than 98% NOR in 120 minutes. Moreover, after six cycles, the catalytic performance can still maintain more than 95% of efficiency.

Zhu et al. synthesized the lanthanide series perovskite structure nano sheet – sphere – sheet photocatalysts by ultrasonic assisted hydrothermal method.[12] In this work, MFeO3 (M =Y, Gd, La) nanospheres and AgI nanosheets were uniformly dispersed on the surface of g-C3N4 nanosheets, which formed dual-Z-scheme. LaFeO3 nanospheres were acting as the electron transmission media...
after assembled with AgI and g-C3N4 nanosheets, promoting the separations and migrations while weakening recombination of photogenerated electron–hole pairs. In the test, Zhu et al. found that the catalyst can degrade NOF more than 95% within 180 minutes, and the cycle stability is also very good. After six cycles, the catalytic performance still remains above 92%.

3.3. Composite modification

Compared with pure g-C3N4, the combination of g-C3N4 and some other materials can improve the separation and transmission of photogenerated carriers, promote the structural stability, and adjust the energy band structure. In addition, the high specific surface area of g-C3N4 can expose more active sites and increase the active sites of the reaction. Therefore, composite modification is an effective method to obtain high efficiency and stable composite photocatalyst. Shut like CeO2 modified with g-C3N4 composites combined with persulfate(PS) were synthesized by Liu et al.[13] The catalyst can degrade 88.6% NOR in 60 minutes, and the cycle stability is high. The subsequent active spectra trapping experiments showed that PS addition could produce additional sulfate radicals and singlet oxygen, which promoted the degradation of NOR.

Prabavathi et al. prepared cowo4 and g-C3N4 composite catalyst by ultrasonic method and hydrothermal method.[14] Subsequent experiments confirmed that the synergistic effect of CoWO4 and g-C3N4 inhibited the fast recombination of photogenerated e–h+ pairs. They found that CoWO4 / g-C3N4 catalyst can degrade 80% of NOF in 80 minutes. They proposed a possible mechanism of photodegradation (Figure 3).

![Figure 3. Schematic illustration of possible Z-Scheme photocatalytic mechanism[14]](image)

3.4. Heterostructure construction

When g-C3N4 is combined with other semiconductors which have suitable band structure, heterojunction structure can be formed. This structure can increase the separation rate of photogenerated electron hole pairs, thus increasing the utilization of light energy and improving the catalytic activity.

Prabavathi et al. Synthesized heterojunction nanocomposite NiWO4@g-C3N4 photocatalyst by hydrothermal method followed by acoustic method.[15] The degradation rate of NOR by synthetic nanocomposite was 3.59 times higher than that of pure g-C3N4, and 97% NOR could be degraded in 60 minutes. The results show that the visible light absorbitivity and specific surface area of g-C3N4 are improved, and retard charge carriers separation. The results of trapping experiments showed that the
hydroxyl radical and hole formed during the photodegradation process and played an important role in improving the degradation rate.

Liu et al. Synthesized the catalyst of graphene like carbon plane grafted g-C3N4 coupling with TiO2 by calcination method.[16] The catalyst exhibited excellent NOR degradation rate. It could degrade 93.5% NOR in 90 min, which was 9.4 times of that of pure g-C3N4. The catalyst also showed very good recycling ability. After four cycles, the catalytic performance did not decrease significantly. This work opens up a new idea for the design of Novel Ternary heterostructures. It is proved that this kind of heterostructure can improve the efficiency of charge separation and inhibit the photocatalysis of electron hole pair recombination.

4. Conclusion
As a non-metallic semiconductor catalyst with visible light response, g-C3N4 has many excellent properties, which gives it a broad application prospect in the field of photocatalytic degradation of pharmaceutical pollutants such as NOR. However, g-C3N4 has been restricted in practical application because of its small surface area, poor visible light absorption capacity and high composite efficiency of photogenerated electrons and cavities. In recent years, many modification methods have been developed to improve the photocatalytic performance of g-C3N4, such as element doping, composite modification, heterostructure construction, etc.

At present, the modification of g-C3N4 for NOR degradation mainly focuses on the following aspects: (1) Providing more active centers for photocatalytic reaction. (2) Enhancing the efficiency of electron separation and inhibit the recombination of electron hole pairs. (3) Increasing the specific surface area by controlling the morphology of g-C3N4.

However, the combination of g-C3N4 with other materials still has a lot of scientific and technical problems. The future research work can be carried out from the following aspects to fully tap its application potential: (1) The prediction of the catalytic activity of g-C3N4 by existing theoretical models is not accurate enough, so the reaction mechanism should be further studied. (2) Because the composition of natural water is relatively complex and there are some unknown reactions, it is necessary to further simulate the catalytic efficiency of NOR under natural water and natural light conditions to study the catalytic effect of catalyst in the actual environment. (3) At present, g-C3N4 is mainly modified by a single method in the field of NOR degradation, so it is necessary to further study the combination of various modification methods to improve the catalytic performance.

References
[1] ZHANG Q, ZHANG H, ZHANG Q. Degradation of norfloxacin in aqueous solution by atmospheric-pressure non-thermal plasma: Mechanism and degradation pathways[J]. Chemosphere, Elsevier Ltd, 2018, 210: 433–439.
[2] LIU X, WANG Z, WANG X L. Status of Antibiotic Contamination and Ecological Risks Assessment of Several Typical Chinese Surface-Water Environments [J]. Huanjing Kexue/Environmental Science, 2019, 40(5): 2094–2100.
[3] QIANJING F A N, JIANJUN L I U, YINGCHUN Y U. Research progress in a new metal-free photocatalyst——graphitic carbon [J]. 2014.
[4] ONG W-J, TAN L-L, YUN HAU NG,§ SIEK-TING YONG and S-P C. Graphitic Carbon Nitride (g-C3N4)-Based Photocatalysts for Artificial[J].
[5] TEGZE A, SÁGI G, KOVÁCS K. Radiation induced degradation of ciprofloxacin and norfloxacin: Kinetics and product analysis[J]. Radiation Physics and Chemistry, 2019, 158(February): 68–75.
[6] WANG Ying-fei, WANG Feng-liang, LI Jie-hua. Photocatalytic degradation kinetics and mechanism of norfloxacin using mesoporous g-C3N4 under visible-light irradiation. [J]. 2018, 38(4): 1346–1355.
[7] WANG Y, WANG F, FENG Y. Facile synthesis of carbon quantum dots loaded with mesoporous g-C3N4 for synergistic absorption and visible light photodegradation of fluoroquinolone
antibiotics[J]. Royal Society of Chemistry, 2018: 1284–1293.

[8] YANG Y, JIN H, ZHANG C. Nitrogen-deicient modified P and Cl co-doped graphitic carbon nitride with enhanced photocatalytic performance[J]. Journal of Alloys and Compounds, Elsevier B.V., 2020, 821: 153439.

[9] DAI Y, GU Y, BU Y. Modulation of the photocatalytic performance of g-C3N4 by two-sites co-doping using variable valence metal[J]. Applied Surface Science, Elsevier, 2020, 500(September 2019): 144036.

[10] LANIO A, COMPOSITE N, NORFLOXACIN V P. Synthesis of Novel Ternary Dual Z-scheme[J]. 2020.

[11] ZHANG J, ZHU Z, JIANG J. Fabrication of a novel AgI / LaFeO 3 / g-C 3 N 4 dual Z-scheme photocatalyst with enhanced photocatalytic performance[J]. Materials Letters, Elsevier B.V., 2020, 262: 127029.

[12] Y A M N M, NANO L, ACTIVITIES P. Ultrasound-Assisted Hydrothermal Fabrication of Sheet – Sphere – Sheet Photocatalysts with Enhanced[J]. 2020, 4.

[13] LIU W, ZHOU J, YAO J. Shuttle-like CeO 2 / g-C 3 N 4 composite combined with persulfate for the enhanced photocatalytic degradation of norfloxacin under visible light[J]. Ecotoxicology and Environmental Safety, Elsevier Inc., 2020, 190(October 2019): 110062.

[14] PRABAVATHI S L, GOVINDAN K, SARAVANAKUMAR K. Construction of heterostructure CoWO 4 / g-C 3 N 4 nanocomposite as an efficient visible-light photocatalyst for NOR floxacin degradation[J]. 2019, 80: 558–567.

[15] PRABAVATHI S L, MUTHURAJ V. Superior visible light driven photocatalytic degradation of fluoroquinolone drug norfloxacin over novel NiWO 4 nanorods anchored on g-C 3 N 4 nanosheets[J]. Colloids and Surfaces A, Elsevier, 2019, 567(January): 43–54.

[16] LIU C, DONG S, CHEN Y. Enhancement of visible-light-driven photocatalytic activity of carbon plane / g-C 3 N 4 / TiO 2 nanocomposite by improving heterojunction contact[J]. Chemical Engineering Journal, Elsevier, 2019, 371(January): 706–718.