Degradation of antibiotics in water by salicylic acid modified carbon nitride photocatalytic material

Hao Wang1*

1Environmental Protection Technology R&D Institute, Angel Yeast Co., LTD., Hubei 443003, China

*Corresponding Author: Hao Wang, Email: newbee0551@foxmail.com

Abstract. The misuse and abuse of antibiotics lead to water environment problems in many countries including China all over the world. There are many deficiencies in traditional ways of antibiotics degradation such as high cost, low removal efficiency, low degradation rate etc. In this paper, the modified carbon nitride was synthesized from urea and salicylic acid with thermal copolymerization. The XRD, FT-IR and TEM were used to characterize the structure and optical properties of the material. From the radical sacrificial test, the super oxide radicals were examined as the major radicals in the degradation process. The material provides a good application prospect for the photocatalyst treatment of antibiotic wastewater.

1. Introduction

Antibiotics are chemicals produced by microorganisms or higher plants and animals that selectively inhibit certain life activities at low concentrations.[1] It utilizes four mechanisms, which interfere with the synthesis of cell walls by target microorganisms, interact with the cell membrane of the target microorganism, hinder the target microorganism from synthesizing proteins, interfere with the transcription and replication of nucleic acids of the target microorganism, and inhibit the growth of pathogenic microorganisms, or even completely eliminate them.[2] In 1877, Pasteur and Joubert discovered that some common microorganisms can inhibit the growth of Bacillus anthracis in the urine and make a hypothesis that microorganisms can be used as medicines for treating diseases. In 1928, Alexander Fleming of the United Kingdom observed that the chemicals produced by Penicillium killed many deadly bacteria, the first antibiotic known in the past, penicillin. In the following ninety years, humans have discovered less than 10,000 known antibiotics. Most of them are not suitable for human or animal treatment of diseases because of their high toxicity. Therefore, there are only a few antibiotics that can be used as medical treatment.[3]

Antibiotics can be used not only for the treatment of human diseases, but also for the treatment of animal and plant diseases and infection prevention, reducing the mortality of cultured animals and plants and improving the survival rate. In addition to medical and aquaculture, antibiotics are used in industries such as food processing. The consumption of antibiotics worldwide can reach up to 200,000 tons per year,[4] while the country with the most production and consumption of antibiotics is China. In the early 20th century, the production of penicillin accounted for 60% of the world, about 28,000 tons; Oxytetracycline production accounts for 65% of the world.[5]

The large use of antibiotics will inevitably lead to excessive antibiotics entering the environment. Water is one of the most important media for antibiotics. Antibiotics can be detected in sewage, surface and groundwater in China. In the fast-growing and densely populated large cities, the antibiotics of chloramphenicol and sulfonamides in the above seawater are the main antibiotics detected in the Yangtze...
River estuary. The antibiotics of tetracycline and sulfonamides are serious antibiotics that pollute the Huangpu River. At the same time, the type, concentration and detection frequency of antibiotics are higher in summer than in summer; in aquaculture wastewater, the content of antibiotics is very high, such as the high detection rate of fluoroquinolone antibiotics in some farms in Guangzhou and Fujian. As the main residual antibiotics; in the sewage treatment plants, antibiotics mainly based on fluoroquinolones and macrolides were detected in most sewage treatment plants in Guangzhou, Shatian, Beijing and Dalian; in natural surface water, Antibiotics of quinolones and macrolides are mainly in the waters of the Pearl River, Haihe River and Yellow River; in the groundwater, four sulfa antibiotics were detected in Chongming Island, Shanghai.

2. Overview of carbon nitride

2.1 Research progress in carbon nitride
Carbon nitride is a kind of organic semiconductor that does not contain metal. It has chemical and thermal stability. At present, its excellent visible light absorption performance has attracted the attention of many researchers. CN's research began with the formula for calculating the solid elastic modulus of sphalerite more than 30 years ago. [6] It has been found that there are five stable carbon nitride structures, namely g-C$_3$N$_4$, p-C$_3$N$_4$, α- C$_3$N$_4$, β-C$_3$N$_4$ and c-C$_3$N$_4$.[7] as shown in Fig.1. Under natural conditions, g-C$_3$N$_4$ is the most stable phase and has good photocatalytic performance. It is the main research object of carbon nitride.

![Figure 1. Five crystal forms of carbon nitride [8](a: α- C$_3$N$_4$; b: β- C$_3$N$_4$; c: c- C$_3$N$_4$; d: p- C$_3$N$_4$; e: g- C$_3$N$_4$)](image)

2.2 Carbon nitride application
Graphite phase carbon nitride is non-toxic and harmless, acid and alkali resistant and has high stability in aqueous solution. It has the characteristics of typical semiconductor, can absorb visible light, has simple preparation method and no metal element, so it is in catalytic reaction. Has a wide range of applications, such as photolysis of water to produce hydrogen, degradation of organic pollutants, etc..

In the graphite phase carbonitride polymer, the nitrogen atom provides an oxidation site for water to form O$_2$, which provides a reduction site for water to form H$_2$. The potential of the conduction band is
more negative than the potential of the hydrogen electrode, and the potential of the valence band is more positive than the potential of the oxygen electrode, which satisfies the requirement of hydrogen and oxygen generated by hydrolysis in thermodynamics. Wang Xinchen et al. obtained g-CN by pyrolysis of NH₂CN, using triethanolamine as a sacrificial agent and Pt as a cocatalyst to carry out an experiment of photocatalytic decomposition of water to produce hydrogen.[9] Zou Zhigang et al. calcined melamine in stages to obtain g-C₃N₄, and carried out photocatalytic degradation of methyl orange dye.[10] Three active substances of hydroxyl radical, photogenerated cavity and superoxide radical are generated in the photocatalytic process. Hydroxyl radicals are the main photocatalytically degrading oxidizing substances, which can degrade dyes by means of electron transfer and hydrogen atom separation.

3. Method for preparing catalyst
The synthesis of graphite phase carbon nitride (CN) is as follows: 15 g of melamine is weighed into a ceramic crucible, covered, and placed in the center of the muffle furnace. It was first heated to 550 °C at a heating rate of 12 °C per minute, then calcined at 550 °C for 2 hours, and finally cooled naturally. After cooling to room temperature, the resulting yellow cake (CN) was ground to a powder and weighed in a bag, about 1.3 g.

The synthesis method of salicylic acid modified carbon nitride (SA-CN) is as follows: prepared from urea and salicylic acid raw materials. First, different quality (25 mg, 50 mg, 100 mg) of salicylic acid and 10 g of urea were dispersed in 10 mL of ultrapure water, and then 1-2 ml of ethanol was added dropwise to form a suspension. The suspension was sonicated for 1 hour at room temperature and then stirred at room temperature for 1 hour. After stirring, the suspension was dried in a drying oven at 80 °C for 12 hours. After calcination, the calcination process is consistent with the synthesis method of CN. SA-CN (SA-CN-1, SA-CN-2, SA-CN-3) was obtained, which was ground into a powder and weighed in a bag. Their weight is about 0.45 g.

4. Catalyst characterization method
The crystal phases of CN and SA-CN were measured by a D/max-2500 X-ray diffractometer (XRD; Nippon Science) using Cu-Kα radiation (λ = 0.15406 nm) in the range of 2θ (10°-80°). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker spectrometer (spectrum 2000) with a scan range between 2000–450 cm⁻¹. The X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) of the sample was measured by X-ray photoelectron spectroscopy with Al-Kα radiation (hv = 1486.6 eV). The morphology of the sample was observed by transmission electron microscopy (TEM, JEOL JEM-2100F). Ultraviolet-visible diffuse reflectance spectroscopy (DRS) was obtained using an ultraviolet-visible spectrophotometer (Cary 300, USA) with an integrating sphere. The light source is a 300 W xenon arc lamp (PLS-SXE300, Beijing). The visible light used in this study was achieved by a cut-off UV filter (λ > 420 nm) (Beijing Perfect Light Co., Ltd.).

5. Characterization result

5.1 XRD analysis
The XRD models of CN and SA-CN-1, SA-CN-2, and SA-CN-3 were studied. The results are shown in Fig.2. All samples have similar XRD patterns, which can be attributed to having a typical graphite-like structure. The peak corresponding to the position of CN at 13.1° is due to the (100) crystal plane of the tris-triazine. The peak corresponding to the position of 27.2° is the (002) crystal plane of carbon nitride. The peak (100) of SA-CN is slightly enhanced compared to CN due to the characteristics of SA-CN and mesoporous structure. In addition, the (002) peak of SA-CN is significantly stronger and wider, which may be due to the addition of salicylic acid to affect some of the structure.
5.2 FT-IR analysis
The FT-IR spectra of CN and SA-CN-1, SA-CN-2, and SA-CN-3 are shown in Fig.3. According to the Fourier transform infrared spectrum of CN, the vibration in the section of 1200–1700 cm\(^{-1}\) is caused by the typical tensile vibration of the C-N heterocyclic compound. The peak at 805 cm\(^{-1}\) belongs to the triazine. These results are highly consistent with previous literature.

5.3 TEM analysis
Morphological images of CN and SA-CN can be characterized using transmission electron microscopy. As shown in Fig.4, the original CN exhibits a laminated structure and a relatively smooth surface. After the addition of salicylic acid, SA-CN clearly showed nanosheet structure and randomly distributed interstitial pores, which were significantly different from the original dense stacked sheets of the original CN. As shown in Fig.4d, there are many wells of approximately 30-40 nm in the SA-CN image. These surface pores are present on the SA-CN and can provide a large number of active sites, which further facilitates photocatalytic degradation.
6. Conclusion

Based on the above results, a possible mechanism is proposed to explain the high photocatalytic activity of the prepared SA-CN. SA-CN has a high specific surface area and numerous active sites for the reaction process. Under visible light illumination, SA-CN can generate electrons and holes. Taking SA-CN-2 as an example, the electrons on the CB (-0.98 eV) of SA-CN-2 are lower than E (O$_2^-$/O$_2$) (-0.33 eV) and are a good reducing agent. It can effectively reduce the oxygen molecules adsorbed on the surface of the photoanode to ·O$^-$ and then cause degradation of antibiotics. The standard redox potential of OH/OH$^-$ is +2.38 eV, which is higher than the VB position of SA-CN-2 (+1.42 eV). Therefore, the photogenerated hole (h$^+$) cannot react with H$_2$O to generate ·OH on the SA-CN nanosheet. The resulting ·OH may be due to the conversion of ·O$^-$.

The authors gratefully acknowledge the support provided by the Shanghai Science and Technology Support Program (09231202702) in China.

References

[1] Jonathan, W.P., Gu, B.H., Michael, D.S. (2015) Surface interactions and degradation of a fluoroquinolone antibiotic in the dark in aqueous TiO$_2$ suspensions. Science of the Total Environment, 532.

[2] Vera Homem, Lúcia Santos. (2011) Degradation and removal methods of antibiotics from aqueous
matrices – A review. Journal of Environmental Management, 92(10).

[3] B.M. Duggar. (2011) Aureomycin: A product of the continuing search for new antibiotics. Annals of the New York Academy of Sciences, 1241(1).

[4] Klaus Kümmerer. (2008) Antibiotics in the aquatic environment – A review – Part I. Chemosphere, 75(4).

[5] Bruce, J.R., Paul, K.S.L., Michael, M. (2005) Emerging chemicals of concern: Pharmaceuticals and personal care products (PPCPs) in Asia, with particular reference to Southern China. Marine Pollution Bulletin, 50(9).

[6] Liu, A.Y., Cohen, M.L. (1989) Prediction of new low compressibility solids. Science (New York, N.Y.), 245(4920).

[7] Ren, Z., Du, Y., Ying, Z., et al. (1994) Electronic and mechanical properties of carbon nitride films prepared by laser ablation graphite under nitrogen ion beam bombardment. Applied Physics Letters, 65(11): 1361-1363.

[8] Fellinger, T.P., Su, D.S., Engenhorst, M., et al. (2012) Thermolytic synthesis of graphitic boron carbon nitride from an ionic liquid precursor: mechanism, structure analysis and electronic properties. Journal of Materials Chemistry, 22(45):23996-24005.

[9] Wang, X., Maeda, K., Thomas, A., et al. (2009) A metal-free polymeric photocatalyst for hydrogen production from water under visible light. Nature Materials, 8(1):76-80.

[10] Jin, R.R., You, J.G., Zhang, Q., et al. (2010) Preparation of Fe-Doped Graphitic Carbon Nitride with Enhanced Visible-Light Photocatalytic Activity. ACTA PHYSICO-CHIMICA SINICA, 30(9):1706-1712.