A Comprehensive Experiment on the Synthesis and Performance of Carbon Nitride Photocatalyst Modified by Copolymerization

Dandan Zheng¹, a, Yixin Li¹

¹School of Environmental and Safety Engineering, Fuzhou University, Fuzhou, Fujian, China

aE-mail: ddzheng@fzu.edu.cn

Abstract: Based on cutting-edge topics and research foundation, a comprehensive experiment on the preparation and performance of a copolymerization modified carbon nitride (g-CN) photocatalyst was designed. This experiment involved the preparation of g-CN photocatalytic materials, the basic experimental operation of photocatalytic water decomposition, the use of material characterization instruments such as FT-IR, DRS and PL, as well as the processing and analysis of origin data. It covers knowledge of physical chemistry, analytical chemistry, instrumental analysis and materials chemistry. The comprehensive innovation experiment is beneficial to expand students’ knowledge and cultivate students’ innovation consciousness, exploration spirit, and scientific literacy.

1. Introduction

Due to the curriculum setting, the domestic colleges and universities lack the connection with the frontiers of science and technology and production practice, resulting in insufficient training and improvement of students’ scientific research and innovation ability and comprehensive quality. This is a realistic and urgent problem faced by higher education at present. In recent years, the construction of the first-class undergraduate education in China has put forward the integration of teaching and scientific research, and the transformation of new scientific research results into teaching content, which is an effective way to keep the frontier, scientific and practical nature of university classroom. Based on the characteristics of Fuzhou University, the research platform and achievements of the State Key Laboratory of Energy and environmental photocatalysis of Fuzhou University are used, the comprehensive chemical innovation experiments are carried out, and the achievements of semiconductor photocatalysis technology are introduced into undergraduate teaching, which is one of the effective ways to realize the integration of science and education.

Carbon nitride (g-CN), as a kind of visible light photocatalyst without metal component, is a hot material in the field of photocatalysis due to its low cost, stability and easy modification[4,5]. However, due to structural defects such as poor degree of polymerization and low crystallinity, there are problems such as low utilization of visible light in the solar spectrum, slow migration of photogenerated carriers, and high recombination rate, resulting in low quantum efficiency of g-CN in the process of photocatalytic reaction. Therefore, how to effectively extend the π-conjugated system of g-CN and optimize its electronic band structure is a key factor to improve its photocatalytic performance. Copolymerization is an effective method to control the structure of conjugated polymer semiconductors. By incorporating aromatic functional groups into the g-CN system, the π-conjugated
system is extended and the visible light absorption range is greatly expanded, thereby enhancing the photocatalytic performance and achieving effective control of the chemical composition and molecular structure of polymers at the molecular level and microcosmic scale. Our research group has carried out a long-term systematic study on the modification of g-CN through copolymerization. A series of copolymerization modified g-CN nano-photocatalysts were prepared using thiophene, diaminobenzonitrile, and barbituric acid as monomers \cite{8-10}. On the basis of the previous research, the effect of copolymerization modification on the photocatalytic performance of carbon nitride was investigated and the comprehensive innovation experiment for undergraduates was carried out accordingly. The experiment includes the preparation, characterization, and photocatalytic performance testing of the g-CN photocatalyst modified by copolymerization of different monomers. It integrates physical chemistry, analytical chemistry, organic polymer chemistry, structural chemistry, instrumental analysis, spectroscopy, and other courses. The knowledge points of the course involve the preparation of g-CN materials, photocatalytic decomposition of water, and other basic chemical operations and the use of modern instruments such as Fourier transform infrared spectroscopy (FT-IR), diffuse reflectance spectroscopy (DRS), and fluorescence spectroscopy (PL).

The content of this experiment is comprehensive and innovative. Through this experiment, students can deepen their understanding of professional knowledge, broaden their knowledge fields, cultivate their experimental operation skills, and improve their literature research and reading ability, as well as scientific research and innovation ability. It is especially suitable as a comprehensive innovation experiment for students majoring in chemistry or environmental engineering.

2. Experimental Design

2.1 Purpose of the Experiment

(1) Cultivate students' ability to flexibly use professional theoretical knowledge, comprehensively review the physical chemistry, analytical chemistry, environmental chemistry, spectroscopy they have learned, and deeply understand the principles of semiconductor photocatalytic technology; (2) Master the preparation method of copolymerization modified g-CN, be familiar with the experimental operation of photocatalytic dye degradation, and understand the characterization methods of material structure and optical properties; (3) Master the operation of muffle furnace, magnetic stirrer, photocatalytic dye degradation device and other experimental equipment, be familiar with the principle and operation process of characterization instruments such as infrared spectrometer, diffuse reflection spectrometer, and fluorescence spectrometer, and learn the methods of experimental data processing and experimental spectrum analysis; (4) Cultivate students' scientific research thinking ability, comprehensive experimental skills and the ability to analyze and solve problems independently by means of data searching and investigation, experimental design and implementation, result analysis and discussion.

2.2 Experimental Principle

g-CN was prepared by high temperature thermal polymerization of N-rich organic compounds (such as cyanamide, melamine, melamine, etc.). In this experiment, two monomers, thiophene and barbituric acid were used to prepare different copolymerization-modified g-CN photocatalysts, and the effect of copolymerization modification on the photocatalytic performance was discussed. The precursor dimer cyanamide was prepared through “electrophilic/nucleophilic” attack of benzene ring molecules functionalized with amino or cyano groups. Through the copolymerization of monomer 2-aminobenzonitrile or thiophene with the precursor dimer cyanamide, the benzene ring was incorporated into the structure of g-CN, effectively prolonging its π-conjugated system, so as to enhance the light absorption and photocatalytic performance of g-CN.

g-CN has strong visible light response (band gap width of 2.7 eV) and suitable energy band position. The process of photocatalytic degradation of dyes includes the following steps: (1) The generation of photogenerated carriers: the semiconductor absorbs solar photons whose energy is
greater than or equal to its forbidden band width ($E_g$), the electrons in the valence band ($e^-$) are excited to the conduction band, at the same time, holes ($h^+$) are generated in the valence band. (2) The migration of photo-generated carriers: After the electrons and holes are generated, they need to migrate to the surface of the photocatalyst to participate in the photocatalytic reaction. In this process, the bulk-phase recombination of photo-generated electrons and holes is likely to occur. (3) Redox reaction: photogenerated electrons have strong reducibility, and photogenerated holes have strong oxidizing properties. The photogenerated electrons and holes that successfully migrate to the photocatalyst surface are transferred at the interface, captured by the reaction substrate, and then redox reaction occurs, which can directly oxidize various pollutants such as methyl blue (MB) dyes into inorganic small molecules such as CO$_2$ and H$_2$O$^{[11]}$. 

2.3 Experimental Reagents and Instruments

2.3.1 Reagents
Dicyandiamide, thiophene, barbituric acid, methyl blue (MB), deionized water, and ethanol.

2.3.2 Instruments
Analytical balance, mortar, crucible with cover, high temperature muffle furnace, blast drying oven, ultrasonic machine, photocatalytic dye degradation device, centrifuge, centrifuge tube, volumetric flask, measuring cylinder, dropper, UV-visible spectrophotometer, Fourier Infrared Spectrometer (FT-IR), Diffuse Reflectance Spectrometer (DRS), and Fluorescence Spectrometer (PL).

2.4 Experimental Content

2.4.1 Preparation of g-CN Photocatalyst
Synthesis of bulk phase g-CN:
Urea (1 g) was put into a 100 mL crucible with cover and then put into a muffle furnace, the temperature was raised to 550 °C at the rate of 5 °C/min and maintained for 4 h. The sample obtained after firing was the bulk phase g-CN.

Synthesis of bulk phase CN-BA:
Dimeric cyanamide (DCDA, 3g) was pre-dissolved in 15 mL of H$_2$O (100 °C) and 0.3 g of barbituric acid (BA) was added to completely dissolve it. The solution was stirred and evaporated at 100 °C. The obtained solid was ground, placed in a crucible (20 mL) with cover, and calcinated at 550 °C for 4 h (heating rate: 2.3 °C/min). After cooling naturally to room temperature, the sample was taken out and marked as CN-BA.

Synthesis of bulk phase CN-T:
DCDA (3 g) was pre-dissolved in 15 mL of H$_2$O (100 °C) and 0.3 g of thiophene was added to completely dissolve it. The solution was stirred and evaporated at 100 °C. The obtained solid was ground, placed in a crucible (20 mL) with cover, and calcinated at 550 °C for 4 h (heating rate: 2.3 °C/min). After cooling naturally to room temperature, the sample was taken out and marked as CN-T.

2.4.2 Characterization of the chemical structure and optical properties of g-CN
The chemical structure of the sample was determined by AVATAR360 Fourier Transform Infrared Spectrometer: under continuous irradiation of infrared lamp, the sample and KBr solid were ground and mixed at a mass ratio of 1:100, and then prepared into thin slices, which were put into the instrument for testing. Test conditions: the scanning range was 4000-400 cm$^{-1}$ and the number of cyclic scanning was 32 times.

The optical properties of the samples were characterized by Varian Cary 500 scan UV-Vis diffuse reflectance spectroscopy: BaSO$_4$ was used as the reference sample, and the scanning range was 200-800 nm. The diffuse reflectance measured in the experiment was transformed into absorbance by using Kubelka-Munk equation: $F(R) = (1-R_\infty)^2/(2R_\infty) = K/S$, where $R_\infty$ denotes the limit value of
reflection coefficient $R$ of infinite thickness sample, K represents the absorption coefficient, and refers to the scattering coefficient, so as to obtain the UV-vis diffuse reflectance spectrum.

The steady-state fluorescence spectra of the sample were measured at room temperature by FL/FS920 fluorescence spectrometer from Edinburgh, UK: the light source was xenon lamp and the photomultiplier tube was used as the detector. Catalyst powder (30 mg) was pressed into tablets, adhered to the slide, and then fixed in the sample tank. The scanning wavelength range was 400-800 nm, the scanning times were 3, and the resolution was 1 nm.

2.4.3 Performance Test of Photocatalytic Degradation of Methyl blue
Methyl blue solution (10 ppm, 100 mL) and photocatalyst (0.05 g) were added into the photocatalytic reactor respectively, and stirred for 30 min before the experiment to ensure the adsorption-desorption equilibrium of g-CN photocatalyst in methyl blue solution. Then the reactor was placed under the irradiation of xenon lamp, and the photocatalytic reaction was carried out while stirring under the visible light with wavelength greater than 420 nm. The duration of the photocatalytic degradation experiment was 40 min and 2 mL of the reaction solution was taken every 10 min. The absorbance at 600 nm was measured by an ultraviolet spectrophotometer. According to the formula of absorbance-concentration of methyl blue, the concentration of reaction solution under different illumination time was calculated and the C/C$_0$ curve was drawn.

2.5 Results and Discussion

2.5.1 Characterization of Structure and Morphology
The chemical structure of the sample was analyzed according to the spectrum of FT-IR and the course content of spectroscopy. As shown in Figure 1a, the FT-IR spectra of all copolymerized g-CN materials and bulk phase g-CN show three groups of characteristic infrared absorption peaks, which are located at 3500-3000 cm$^{-1}$, 1600-1200 cm$^{-1}$, and 810 cm$^{-1}$ respectively. The absorption peak in the range of 3500-3000 cm$^{-1}$ is large and wide, mainly due to the stretching vibration of N-H bond and O-H bond, which belongs to the incompletely polymerized amino groups on the surface of g-CN and the water molecules adsorbed by the material; the absorption peak within 1600-1200 cm$^{-1}$ is caused by the stretching vibration of C=N bond and C-N bond; the peak at 810 cm$^{-1}$ is the respiratory vibration of heptazine ring, indicating that the synthesized g-CN has the molecular structure of heptazine ring. The results show that the main structure of g-CN has not been destroyed by copolymerization.

The effect of copolymerization modification on the optical properties of g-CN was investigated by UV-Vis and PL spectra. As can be seen from the photos of the copolymerized modified g-CN samples in Figure 1b, the semiconductor absorption band edge also had an obvious red shift, in which the absorption band edge of CN-ABN was red-shifted from 460 nm to 700 nm. This result shows that copolymerization modification can effectively narrow the semiconductor band gap of the material, expand the absorption range of visible light, and significantly enhance its absorption and utilization of sunlight.
Figure 1. (a) FT-IR and (b) UV-Vis spectra of g-CN, CN-BA and CN-T photocatalysts.

Figure 2a is the fluorescence emission spectrum of the copolymer modified g-CN sample. It can be seen from the figure that the PL luminescence properties of the g-CN sample modified by copolymerization also changed significantly. Under 400 nm excitation light, g-CN has a strong fluorescence emission peak at 520 nm, indicating serious photo-generated electron-hole recombination in g-CN. In contrast, the fluorescence peak intensity of g-CN samples modified by copolymerization decreased in varying degrees, suggesting that copolymerization modification can significantly inhibit the recombination of photogenerated carriers.

Figure 2. (a) PL spectra and (b) comparison diagram of photocatalytic degradation rate of methyl blue for g-CN, CN-BA and CN-T photocatalysts.

2.5.2 Photocatalytic Degradation of Dyes
From the curve of dark adsorption and photocatalytic degradation of methyl blue in Figure 2b, it can be seen that the degradation ability of g-CN modified by different copolymerization is better than that of bulk phase g-CN, and the photodegradation performance of CN-T is the best. When the photocatalytic degradation reaction was carried out for 110 min, the degradation rate of methyl blue of CN-T was 94.5%, which was 36.8% higher than that of bulk g-CN.

2.5.3 “Structure-effect” Relationship Analysis
The copolymerization modification can not only effectively expand the π-conjugated system of g-CN, narrow the semiconductor energy band structure, make the absorption band edge of the catalyst significantly red shift, and significantly improve the light absorption capacity of g-CN, but also reduce the exciton binding energy, promote the generation and rapid separation of photogenerated carriers,
and significantly inhibit their recombination. As a result, the activity of photocatalytic reaction and the photocatalytic degradation of methyl blue were significantly improved compared with that of bulk phase g-CN.

3. Teaching Design

3.1 Teaching Objects and Pre-class Preparation
This comprehensive experiment mainly includes four parts: preparation of catalyst, characterization of structure and morphology, testing of photocatalytic performance and exploration of experimental mechanism. Students are required to master the relevant theoretical knowledge of four basic chemistry and instrumental analysis, and have certain chemical experiment operation skills. It is suitable for senior undergraduates in junior and senior years.

Before the experiment, students should carry out the corresponding independent preview work: by consulting related literature or experimental courseware, they should understand the concepts and principles of photocatalyst, photocatalytic reaction and semiconductor photocatalytic technology. Furthermore, they should be familiar with the common synthesis methods of copolymerization modified g-CN, and learn the basic working principles of FT-IR, DRS, PL and UV-Vis spectrophotometers, as well as experimental data processing methods.

3.2 Schedule
This experiment is planned to set up 24 class hours, including 4 class hours for the explanation of experimental background and principle, 4 class hours for the preparation of catalyst, 6 class hours for the characterization of catalyst, 4 class hours for the performance test of catalyst, and 6 class hours for data analysis and discussion of experimental results.

3.3 Evaluation of the Completion of the Experiment
After the completion of the experiment, students should use Origin, Excel and other software to analyze and process the experimental data, draw corresponding experimental charts, write experimental reports, and discuss and summarize the experimental results by means of classroom PPT presentation. The score assessment is divided into 4 parts: 40 points for experiment operation, 20 points for data processing, 20 points for experiment report, and 20 points for classroom presentation.

4. Conclusion
In this comprehensive experiment, combined with professional theoretical knowledge and cutting-edge scientific research achievements, different copolymerization modified g-CN photocatalysts were prepared and their effects on photocatalytic performance were explored. The introduction of this experimental subject into the comprehensive chemistry experiment teaching of senior undergraduates can not only enable students to understand the cutting-edge technology in the field of photocatalysis and stimulate their interest and enthusiasm in scientific research and study, but also review and test the learning achievements of related subjects, strengthen their comprehensive ability to apply professional theoretical knowledge, and improve their experimental operation skills and scientific research literacy. It will lay a solid foundation for students to carry out scientific research in the field of photocatalysis in the future.

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