Preparation of Graphite Phase Bismuth Carbon Nitride Vanadate Composites and Experimental Analysis of Free Radical Capture

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Abstract. Photocatalysts are mainly divided into two categories: one is that they have good response to sunlight and visible light, such as BiVO₄ and Fe₂O₃; One is that it has its own defects and can not make full use of the energy converted by visible light. In recent years, a class of oxides have attracted much attention because of their good performance of visible light photocatalytic degradation of pollutants. People also have a strong interest in the research of compound oxides in pollutant degradation. In order to further clarify the photocatalytic mechanism of GCB composite samples, different capture agents were added to determine the main active species in the photocatalytic process. Only through the method of modification, the synergistic effect can enhance its photocatalytic activity. 1% g-C₃N₄/BiVO₄(GCB) sample, dhrb = 90.4%, the photocatalytic activity did not change significantly after adding IPA. After adding EDTA and VC, the photocatalytic activity decreased, dhrb = 32.6% and dhrb = 51%. Therefore, the experiments show that h+ and ·O₂⁻ are active species of GCB catalytic system, O²⁻ is more important for RHB degradation.

1. Introduction

At present, photocatalytic productivity technology is mainly used to prepare H₂ and CH₄. As a clean energy, H₂ has been widely used in recent years. Wang Sheng synthesized Z-ZnO/CdS composite catalyst by hydrothermal method to improve the performance of H₂ production. In Muhammad's research, GO/ZnO heterostructure composite catalyst was prepared by in-situ hydrothermal method. The photocatalyst can generate CH₄ under visible light by catalyzing CO₂ and adding H₂ in situ. As the main component of natural gas, the preparation of CH₄ by photocatalytic technology will replace the traditional method of preparing CH₄ and become a new pollution-free and efficient best method[1-6]. Photocatalysts are mainly divided into two categories: one is that they have good response to sunlight and visible light, such as BiVO₄ and Fe₂O₃; One is that it has its own defects and can not make full use of the energy converted by visible light. Only through the method of modification, the synergistic effect can be used to enhance its photocatalytic activity. According to the statistics of experimental data, heterostructure construction is a common improvement method. The common heterostructures are Z-type, I-type, II type and so on.

At present, Z-type hetero junction has strong oxygen reduction potential, which can prolong the lifetime of light e⁻·h⁺ and reduce the recombination probability. According to the difference between the two semiconductors, CB and VB construct Z-type structure, which has low cost and does not need to use noble metal composite, so it is widely used. Huo successfully prepared Z-type-g-C₃N₄/PDA
hetero structure by ultrasonic dispersion method. The -NH\textsubscript{2} in PDA has strong irreversibility, which can more effectively improve the photocatalytic efficiency of g-C\textsubscript{3}N\textsubscript{4}. Singh et al. Prepared and synthesized type I BiVO\textsubscript{4}/TiO\textsubscript{2} composites, which were successfully transformed into type II hetero structures by hydrogen treatment with TiO\textsubscript{2}. Semiconductor recombination is essentially the modification of one particle to another. Recombination can improve the charge separation effect of the system and expand its spectral response range. It is an effective way to expand the absorption spectrum of the catalyst and improve the photocatalytic efficiency[7-8]. In this paper, g-C\textsubscript{3}N\textsubscript{4} was modified by semiconductor composite method, and BiVO\textsubscript{4} with large specific surface area was selected for composite. The experiments show that h\textsuperscript{+} and \cdotO\textsubscript{2} are the main active species of GCB catalytic system, and \cdotO\textsubscript{2} is more important for RHB degradation.

2. Experiment
Analytical Balances (FA2004); Constant temperature heating magnetic stirrer (DF-101S); Digital acidity meter (pHS-3C); Vacuum drying oven; Centrifuge; Ultrasound system (DS-2510DTH); UV spectrophotometer (UV-2550); X-ray diffractometer (3DMAX-IIIC); Scanning electron microscope (HITA CHI S-4800); Fourier transform infrared spectrometer (NEXUS-670); Fluorescence photometer (970);

2.1. BiVO\textsubscript{4} Preparation
Dissolve 0.25g Bi(NO\textsubscript{3})\textsubscript{3}•5H\textsubscript{2}O in 10ml 2mol/L H\textsubscript{3}PO\textsubscript{4} solution, and then take 0.12g NH\textsubscript{4}VO\textsubscript{3} in 10ml 2mol/L NH\textsubscript{3}•H\textsubscript{2}O solution, mix them slowly to make them stir evenly, and adjust the pH to 7. After the above process, a uniform clear yellow suspension is formed. Transfer the suspension to the reactor and keep it at 160\textdegree C for 8h in a constant temperature blast drying oven. Cool to room temperature, carry out high-speed centrifugation, centrifuge and wash with deionized water to obtain yellow powder BiVO\textsubscript{4}.

2.2. Preparation of Z-type Heterojunction g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4}
Dissolve g-C\textsubscript{3}N\textsubscript{4} in deionized water, conduct ultrasonic treatment to disperse g-C\textsubscript{3}N\textsubscript{4} nanotubes evenly, add BiVO\textsubscript{4} with different mass fractions, adjust the pH of the solution to 7, 160\textdegree C and keep it for 8h. That is, GCB with different mass fraction.

2.3. Transmission Electron Microscope TEM
TEM reflects the bulk phase information of the catalyst, and can directly visualize the shape, distribution, particle size, thickness, lattice and other information of the sample at the micro level, so as to provide a reasonable basis for the performance of the catalyst. The sample was observed after ethanol volatilization.

2.4. Study on Influencing Factors of Photocatalysis
The structure of g-C\textsubscript{3}N\textsubscript{4} is complex. In the preparation process, subtle changes in conditions will have a great impact on the structure and morphology of the sample, and even change the properties of the sample.

2.5. Catalyst Cycle Stability Test
After photocatalytic degradation of the catalyst, the suspension in the quartz tube is transferred to the centrifugal tube, and the final solid is collected by filtration and centrifugation. Wash and dry repeatedly with deionized water and absolute ethanol for standby. Repeat the above visible light catalytic degradation experiment for the collected samples, keep the control conditions unchanged, and repeat the experiment for 6 times. The stability and reusability of the catalyst were evaluated according to the four decolorization rates.

2.6. Free Radical Capture Experiment
In order to further understand photocatalytic degradation mechanism and the degradation process, the free radical trapping experiment was carried out. Generally, ROS includes: h\textsuperscript{+}, \cdotO\textsubscript{2} and \cdotOH. The
capture experiment repeats the above visible light catalytic degradation experiment, measures the concentration after the reaction, and calculates the degradation rate.

3. Transmission Electron Microscope
The block g-C$_3$N$_4$ and BiVO$_4$ sample was characterized by TEM, and the results are shown in Fig. 1, Fig. 2.

It can be seen from figure 1 that figure shows massive g-C$_3$N$_4$ with many layers, serious agglomeration and small specific surface area, which is not conducive to the photocatalytic reaction.

It can be seen from figure 3 shows the GCB composite sample. It can be seen that BiVO$_4$ surface contains g-C$_3$N$_4$ nanotubes to form an enclosing structure and increase its contact area, which is conducive to better absorption of visible light and separation of photogenerated charges, so as to improve the photocatalytic efficiency.

![Figure 1. TEM diagram of g-C$_3$N$_4$](image1)
![Figure 2. TEM diagram of BiVO$_4$](image2)
![Figure 3. TEM diagram of GCB composite sample](image3)

3.1. Photoluminescence Spectrum
Generally speaking, the fluorescence intensity has a negative correlation with the photocatalytic activity of photocatalysts, and lower fluorescence intensity has higher photocatalytic activity. It can be seen from Fig. 4 that the sample has strong fluorescence emission peaks at 547nm, the fluorescence intensity of block g-C$_3$N$_4$ is high and that of tube is low. The results show that the position of the emission peak remains unchanged after morphology regulation, but the fluorescence intensity is relatively reduced. Therefore, the tubular fluorescence intensity of g-C$_3$N$_4$ is the lowest.

![Figure 4. Block hotoluminescence 4 pl diagram](image4)

3.2. Analysis of Experimental Results of Free Radical Capture
Different capture agents were added to determine the main active species in the photocatalytic process. After adding capture agent, the photocatalytic activity decreased significantly. Select gcb-1% as the control for RHB degradation, and the changes of RHB photocatalytic degradation after adding three capture agents are shown in Figure 5 below.

It can be seen from figure that drhb of gcb-1% sample is 90.4%, and the change of photocatalytic activity is not obvious after adding IPA. After adding EDTA and VC, the photocatalytic activity is reduced, drhb = 32.6% and drhb = 51%. Therefore, the experiments show that h$^+$, O$_2^-$ are the main active species of GCB catalytic system, O$_2^-$ is more important for RHB degradation.
4. Conclusions
In this paper, g-C₃N₄ was modified by semiconductor composite method, and BiVO₄ with large specific surface area was selected for composite. The experiments show that h⁺ and O₂⁻ are the main active species of GCB catalytic system, and O₂⁻ is more important for RHB degradation.

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References
[1] Liang can. Study on photocatalytic remediation of arsenic contaminated soil with ZnO nano sheets [J]. Design of chemical fertilizer, 2018, 56(5): 11 - 14.
[2] Zheng Rui, Li Chunhu, Zhang Chengzhen. G-C₃N₄/ceramic foam photocatalytic flue gas desulfurization performance [J]. industrial catalysis, 2018, 26(11): 122-126.
[3] Xin X, Li S, Zhang N, et al. 3D graphene/AgBr/Ag cascade aerogel for efficient photocatalytic disinfection[J]. Applied Catalysis B: Environmental, 2019, 245: 343-350.
[4] Liu Xiangyue, Zhang Yu, Wang Chen. Preparation of high crystallinity mil-100 (FE) nano materials from ferrous salts and their photodegradation properties of organic dyes [J]. Materials engineering, 2018, 46(10): 127-134.
[5] Zhang Wei, Wang Jue, Wang Aihe. Study on influencing factors and kinetics of photocatalytic degradation of Omethoate pesticide by MWNTs/TiO₂ [J]. Journal of water ecology,
[6] Jiang Caiyun, Yan Weidong, Li Guoyu. Preparation of spherical TiO₂ by alcohol thermal method and its photocatalytic activity [J]. New chemical materials, 2019, 47(01): 194-197.
[7] Zhang Zhongjie, Du Yajie, Huang Xiaojun. Preparation of octahedral bipo₄ and its degradation of tetracycline [J]. Applied Chemical Engineering, 2018, 47(09): 1903-1906.
[8] Ren Yanan. Study on photodegradation of tetracycline antibiotics by uranyl complexes [D]. Ningbo University, 2018: 121.

Figure 5. Effect of Different capture agents on the photocatalytic activity of RhB
(a GCB-1% b IPA c EDTA d VC)