Research Article

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Preparation and photocatalytic degradation of Sulfamethoxazole by g-C₃N₄ nano composite samples

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Abstract: Graphite-carbon nitride (g-C₃N₄) was prepared by thermocondensation, and g-C₃N₄/BiVO₄ material (GCB) and g-C₃N₄/CNTs composite material (GCC) were prepared by doping different contents of BiVO₄ and carbon nanotubes (CNTs) with g-C₃N₄ samples, respectively. Then, BiVO₄/CNTs, and g-C₃N₄ samples with different contents were doped to prepare ternary composite material (GCBC). In the performance experiment, Sulfamethoxazole (SMZ) was used as degradation material to evaluate the photocatalytic performance of the prepared samples, and the degradation reaction kinetics equation, quadric cycle stability experiment, free radical capture, and intermediates identification were studied. The intermediates of photocatalytic degradation of SMZ were analyzed by high-performance liquid chromatography-mass spectrometry. From the experimental data, it can be seen that for SMZ solution, when the reaction time \( T = 0 \) min and retention time \( r_t = 7.53 \) min, there is a peak corresponding to the substance with \( m/z [M + H]^+ \) of 254, which is judged as SMZ. At 20, 40, and 60 min, \( r_t \) was 2.00, 7.06, and 9.57 min, indicating the presence of intermediates in the photocatalytic process. Experimental analysis shows that there are three intermediates of SMZ degradation by composite sample GCBC. In this work, three kinds of composite materials were successfully prepared, and a variety of characterization, SMZ as pollutants, test the photocatalytic performance of composite materials (GCB, GCC, and GCBC) samples, and elucidated the cyclic stability of the material, active species capture, and photocatalytic degradation mechanism.

Keywords: BiVO₄, CNTs, sulfamethoxazole, high-performance liquid chromatography-mass spectrometry, photocatalytic activity

1 Introduction

With the development of global economy, environmental pollution, especially water pollution, has become increasingly serious, posing a serious threat to ecological security. Antibiotics refer to a class of drugs that can inhibit the growth of bacteria or kill bacteria, generally a class of secondary metabolites or fermented products produced by microorganisms in the process of life activities. After the use of antibiotics, antibiotics cannot be fully absorbed by the human body, and most antibiotics are excreted as metabolites through the body’s urine or feces and enter the water and soil. The removal method of antibiotics in water body cannot adopt the traditional treatment method, resulting in antibiotics entering the surface with water body. Investigations were conducted on the presence of more than 150 drugs and pharmaceutical and personal care products (PPCPs) in water [1, 2]. Sulfonamides (SNs) have the highest content of PPCPs, among which Sulfamethoxazole (SMZ) has a very high content, followed by silting density index (SDI) [3]. It can be seen that SNs is ubiquitous in our water environment.

SMZ, under the trade name of neomine, belongs to the SMZ class of antibiotics. SMZ is a commonly used antibiotic in daily life, and it has become a persistent pollutant which is difficult to deal with today [4]. In addition to the widespread presence of SMZ in water bodies, there is also a large amount of SMZ in the sediment below water bodies, which cannot be completely adsorbed by traditional wastewater treatment methods using the adsorption principle. But if humans drink water containing SMZ for a long time, they may develop allergic symptoms or drug...
resistance. When it accumulates in humans, it can cause serious damage to the human kidneys, urinary system, and nervous system. Therefore, using photocatalytic technology to completely remove SMZ has become a hot research topic in today’s society.

At present, the main methods of sewage treatment are physical method, chemical method, biological method, etc., but these methods generally have high cost and long cycle, and it is difficult to deal with the toxic and harmful substances of biodegradation, and the degradation efficiency is low, so they cannot completely solve the pollution problem. Photocatalytic oxidation technology has attracted the attention of researchers from all over the world because it directly uses sunlight, is simple, economical and practical, mild reaction conditions, and has no secondary pollution [5]. In the study of photocatalytic degradation of organic pollutants, it is urgent to develop efficient and stable photocatalysts. In recent years, the development and research on the basic theory and application technology of photocatalysis continue to deepen, and important research achievements have been made in developing new visible light induced photocatalysts, improving photocatalytic efficiency and developing photocatalytic functional materials.

In 1972, Fujishima and Honda [6] found that H2 could be prepared by photocatalytic decomposition of water on n-type TiO2 semiconductor electrode. Since then, the application of this technology has been widely concerned by human beings, and has been widely used in the actual life of human beings, for example, photocatalytic decomposition of H2O to produce H2, degradation of SNs, disinfection, waste gas purification, etc. Therefore, photocatalysis technology has become the focus of research. TiO2, with its advantages of non-toxic, stable properties, resistance to chemical and photocorrosion, complete mineralization of pollutants, and no secondary pollution, has become the most potential semiconductor photocatalytic material, and has attracted extensive attention from researchers at home and abroad [7]. However, in the actual application of TiO2 photocatalyst, there are problems such as easy deactivation, condensation, low utilization rate of solar energy, difficult recovery of suspended powder, and high cost, which limit the industrial application of TiO2 photocatalyst.

Normally, the semiconductor structure contains two parts, valence band (VB) and conduction band (CB), and the energy difference between them is called Eg. Different semiconductor materials have unique Eg ranges. The size of Eg range plays a decisive role in λg. According to theoretical analysis, the two are negatively correlated, and the smaller the value of Eg is, the larger the absorption range of λg is [8]. The basic principle of photocatalysis is: when the visible light is much larger than the Eg range, the e− on VB transitions to the corresponding CB, and because of the loss of e−, VB produces h+, thus forming e−−h+.

Under the effect of positive and negative charge on the space, the e−−h+ can be rapidly separated, and a single e− and h+ can be attached to the semiconductor surface, which has strong reductive property. The e− negative charge and h+ positive charge can undergo strong oxidation and REDOX reactions, and the combination can completely degrade organic pollutants into small molecules such as CO2 and H2O.

According to the photocatalytic principle of photocatalyst, the main reasons for limiting the activity of photocatalytic technology can be analyzed: (1) the Eg of semiconductor material itself is too wide, which leads to the reduction in the absorption range of visible light, and the limited range can only react under ultraviolet light, which does not make full use of sunlight. (2) e−−h+ is easy to compound, which leads to the reduction in the absorption range of visible light and the low utilization rate of solar energy conversion. According to the nature of the catalyst itself, the factors affecting the photocatalytic activity include internal and external factors, the external factors include: light intensity, T, pH, etc. Internal factors include Eg, crystal structure, particle size, and its specific surface area. This work studies the internal causes.

In 2009, the photocatalytic performance of an ancient composite graphite-carbon nitride (g-C3N4) was discovered and became a research hotspot. Naturally occurring g-C3N4 is a kind of non-metallic polymer organic semiconductor material with C and N elements as the main elements, slightly soluble in water, and with a molecular weight of 92 [9,10]. It has excellent thermal, electrical and optical properties. The high temperature stability makes g-C3N4 very suitable for preparation and modification under high temperature environment conditions, and can be synthesized by simple thermal polymerization process [11]. Therefore, g-C3N4, as a new semiconductor material, has attracted more and more attention and research because of its high chemical stability, non-toxic and pollution-free, simple synthesis method, and other advantages.

As a new photocatalyst, g-C3N4 has solved the problems of energy shortage and environmental pollution. It is favored by people because of its good thermal stability, acid and alkali resistance, and good visible light response. With the help of photocatalytic technology, g-C3N4 can successfully decompose H2O into H2 and O2, which makes g-C3N4 become a research hotspot as a photocatalyst. Although g-C3N4 has excellent electronic and optical properties, there are still some defects [12,13]. g-C3N4 photogenerated e−−h+ recombination rate is high,
resulting in the photocatalytic process, which cannot fully form free radicals. The low specific surface area of g-C$_3$N$_6$ limits the production of active sites and the capture of light sources. The band gap of g-C$_3$N$_6$ is about 450 nm, and the effective capture of visible light can still be further enhanced. Therefore, it is necessary to further explore ways to improve the photocatalytic activity of g-C$_3$N$_6$.

The low visible light catalytic activity of g-C$_3$N$_6$ is due to the low effective utilization of visible light and the low separation efficiency of e$^-$–h$^+$, resulting in frequent recombination.

To solve these problems, e$^-$–h$^+$ was modified to improve the photocatalytic performance. The modification methods are as follows:

1. Structural regulation: After morphology regulation, the specific surface area is larger and more active sites are provided, which is conducive to the transmission of e$^-$ and the recombination inhibition of e$^-$–h$^+$, so as to improve the catalytic performance and other advantages [16].

2. Metal doping: Doping metal in semiconductor materials can effectively narrow the band gap range and improve the photocatalytic activity. Metals can also be divided into alkali metals and transition metal doping [15]. After metal doping, the remaining metal is easy to discharge with water, causing secondary pollution to the environment [16].

3. Non-metallic doping: Compared with metal doping, non-metallic element doping does not contain electron transfer process and will not cause secondary pollution to the environment. Non-metallic doping mainly uses N, C, P, S, and other elements. In addition, the photocatalytic activity can be improved by doping halogen elements [17].

4. Noble metal deposition: Pt, Au, Ag, Pd, and other noble metal particles are used to deposit on the surface of g-C$_3$N$_6$, which effectively changes the electron classification and transmission in the system and improves the optical quantum efficiency of g-C$_3$N$_6$.

5. Semiconductor recombination: Two or more semiconductors are doped together to produce a new photocatalyst through the interaction between semiconductors [19].

In order to improve the separation of e$^-$–h$^+$ and effectively reduce the recombination probability, the energy range between the semiconductors can be realized.

Commonly used composite semiconductors are ZnO, Ag$_3$PO$_4$, graphene oxide (GO), Bi system, WO$_4^2$– class, PPy, and so on. In this work, g-C$_3$N$_6$ was modified by semiconductor recombination. Bismuth BiVO$_4$ with large specific surface area was used for recombination.

As a new generation of photocatalytic materials and environmental protection materials, BiVO$_4$ has the advantages of narrow Eg, high photocatalytic activity, and good stability [20,21]. BiVO$_4$ has monoclinic scheelite type (M-S), tetragonal scheelite type (T-S), and tetragonal zircon type (Z-T) crystal phase structures, which can be converted into each other under certain temperature conditions. BiVO$_4$ can effectively utilize visible light and expand the range of visible light response. The preparation method is simple, safe, non-toxic, and stable. BiVO$_4$ and g-C$_3$N$_6$ were used to prepare Z-type heterojunction composite photocatalyst to improve the separation rate of photogenerated carriers and achieve the desired purpose.

Carbon nanotubes (CNTs) are seamless hollow nanoscale cylinders wound by single or multiple layers of GO, which can be divided into single-walled carbon nanotubes and CNTs according to the different number of wound layers. CNTs are type II-conjugate structures with electron conduction, which have been widely used in environmental sciences in recent years [22]. Commonly prepared CNTs contain many impurities, such as amorphous carbon, carbon nanoparticles and carbon fibers. These impurities will reduce their specific surface area and even aggregate. Therefore, it is necessary to pretreat CNTs to remove surface impurities, effectively cut CNTs to expose more defect sites, and introduce active functional groups such as –COOH or –OH that are easy to bind to semiconductor materials [23].

Semiconductor photocatalytic technology has been widely concerned because of its advantages of environmental protection, high efficiency, and no pollution. Compared with other technologies, photocatalysis has more remarkable and excellent performance in dealing with environment and energy. In recent years, the non-metallic polymer g-C$_3$N$_6$ has made breakthrough progress in the research of photocatalysis by virtue of its unique photoelectric chemical properties, stability, non-toxic, visible light response, and other strong advantages. However, the photocatalytic performance of g-C$_3$N$_6$ cannot meet the practical requirements, which limits the application of g-C$_3$N$_6$. Therefore, this work will focus on improving the photocatalytic efficiency of g-C$_3$N$_6$ using composite semiconductor, and evaluate the performance of different composite catalysts through synthesis, so as to provide a theoretical basis for the efficient removal and mineralization of SNs in the application and design of photocatalytic technology in water treatment.
2 Experimental procedure

2.1 Instruments

Analytical balance (FA2004), Guangzhou Precision Scientific Instrument Factory; Digital acidity meter (DF-101S) sartorius, Germany; Electric Heating Constant Temperature Air Blowing Drying Oven (DZF-6020), Nanjing Gengchen; Centrifuge (LG10-2.4a), Beijing Jingli Centrifuge Co., Ltd; Ultrasonic Instrument (DS-2510 DT H) Kunshan Ultrasonic Instrument Co., Ltd; Muffle Furnace (KSY-6D-16) Shenyang Energy-saving Electric Furnace Factory; UV Spectrophotometer (UV-2550) Shimadzu Co., Japan; X-ray Diffractometer (3DMAX-iii C); Transmission electron microscope (TEM; Auriga) Zeiss, Germany; Fluorescence spectrometer (LS-55) Platinum Elmer Instrument Co., Ltd; Liquid chromatography mass spectrometry (700B) Waters Technology Co., Ltd.

2.2 Reagents

Concentrated sulfuric acid (AR), Beijing Double ring Chemical Reagent Factory; Anhydrous ethanol (AR) Tianjin Kemiou Chemical Reagent Co., Ltd; Deionized water laboratory homemade; Bismuth nitrate (AR) pentahydrate, Shanghai Adamas Reagent Co., Ltd; Ammonium metavanadate (AR), Shanghai Adamas Reagent Co., Ltd; Nitric acid (AR), Beijing Double ring Chemical Reagent Factory; SMZ (AR), Shanghai Aladdin Biochemical Technology Co., Ltd; Acetonitrile (GR), Merck Chemical Technology Co., Ltd; and Formic acid (AR) Merck Chemical Technology Co., Ltd.

3 Experimental methods

3.1 Sample preparation

3.1.1 g-C3N4 control standby

The above block g-C3N4 was ground into powder and put into a beaker, then 10 mL, 2 mol·L⁻¹ NH₃·H₂O was added, stirred for 30 min at room temperature, and the powder was dispersed evenly after 30 min of ultrasound. The mixture was transferred to the reaction kettle and stored in an air-dried box at 160°C for 4 h. After cooling to room temperature, g-C3N4 tubes were obtained by centrifugation at high speed, centrifuged with deionized water and absolute ethanol, washed several times, and dried at 60°C for 8 h.

3.1.2 Preparation of g-C3N4 composites

According to the previous papers of our research group [24], Z-type heterojunction g-C3N4/bismuth vanadate (BiVO₄) (GCB), g-C3N4/CNT composites (GCC), and g-C3N4/BiVO₄/CNT ternary composites (GCBC) were prepared. A series of samples are described in another English article.

3.2 Preparation of reserve liquid

Weigh SMZ powder of certain mass, dissolve by ultrasonic method. Put the solution in a brown volumetric bottle with deionized water and store it in the refrigerator at 4°C for later use.

3.3 Catalyst performance evaluation

Under visible light conditions, SMZ was used as the simulated target degradation substance to evaluate the catalytic activity of the photocatalyst, and its chemical structure formula is shown in Figure 1. The absorbance of SMZ under different photocatalytic reaction times was measured by UV-vis spectrophotometer, the degradation effect of the prepared photocatalyst was investigated, and the performance of the new photocatalyst was evaluated.

A certain concentration of SMZ solution was prepared and stored in the refrigerator. In the range λ = 200–800 nm, deionized water was used as the reference, and the solution was placed in a 1 cm colorimetric dish. The SMZ solution was measured and the UV-vis spectrum was obtained. The photocatalytic reaction device is shown in Figure 2.

The photocatalytic experiment is as follows. A certain concentration of SMZ solution was placed in a 100 mL
double beaker. After stable storage in a cool place for 1 day, appropriate amount of SMZ solution was put in a double beaker and appropriate amount of sample was added as well. The light source was fixed at 10 cm away from the liquid level. Before illumination, the stirring in dark for 60 min to ensure adsorption–desorption equilibrium to ensure that the adsorption–desorption balance was reached. After 300 min of light reaction, xenon lamp light source and condensing device were turned on for visible light catalytic degradation experiment. About 5 mL of reaction solution was extracted at regular intervals, and the supernatant was taken by high-speed centrifugation to determine the absorbance of SMZ at catalyst was investigated, on was poured back into the double beaker to continue the reaction.

\[ D = \frac{A_0 - A_t}{A_0} \times 100\% = \frac{C_0 - C_t}{C_0} \times 100\% \]

where \( D \) – decolorization rate (%); \( C_0 \) – the initial mass concentration of SMZ (mg·L\(^{-1}\)); \( C_t \) – mass concentration of SMZ after degradation time \( t \) (mg·L\(^{-1}\)); \( A_0 \) – the initial absorbance value of SMZ; \( A_t \) – absorbance value after time \( T \) of SMZ degradation.

At 25°C, \( C \) is directly proportional to \( A \) in a certain range. The decolorization rate of SMZ was calculated according to Lambert–Beer law.

### 3.4 Identification of intermediates

In order to study the changes of intermediates during the degradation of SMZ by composite samples at different times, and to clarify the transformation mode of SMZ, the active components generated in the photocatalytic reaction were correlated with the intermediates degraded by SMZ, and the relationship between them was clarified, so as to clarify the photocatalytic degradation path of SMZ. The intermediates were identified and analyzed by liquid chromatography-mass spectrometry.

Chromatographic conditions: ACQUITY UPLC BEH C18 column (2.1 mm × 50 mm, 1.7 μm), injection volume 10 μL, and flow rate 0.1 mL·min\(^{-1}\). The flow ratio was as follows: highly pure water (0.1% formic acid); acetonitrile = 70:30 (v/v).

Ms conditions: ESI+ was used to identify the intermediates. Voltage 30 V, dissolution temperature 900°C, collision voltage 2 kV, MS scanning range 50–600 m/z, and scanning time 0.3 s.

### 4 Results and discussion of SMZ degradation by catalyst

#### 4.1 Analysis of performance experiment results

Under visible light, SMZ was taken as the simulated target degradation material, and the degradation rate of SMZ was tested, respectively, as shown in Figure 3.

It can be seen from Figure 3 that after 60 min of dark reaction and 300 min of photocatalytic reaction, the \( D_{SMZ} \) of SMZ itself is 4.2%, which is basically negligible, and the \( D_{SMZ} \) of g-C\(_3\)N\(_4\) vs \( D_{SMZ} \) is 22.1%. GCB vs \( D_{SMZ} \) = 62.7%; GCC vs \( D_{SMZ} \) = 60.4%, while GCBC vs \( D_{SMZ} \) = 91.5%. Therefore, it can be concluded that the GCBC composite sample has the best degradation effect on SMZ.
4.2 Dynamic analysis

The photocatalytic reaction kinetics of each sample were analyzed. Each sample was subjected to dark reaction in SMZ solution for 60 min to reach adsorption–desorption equilibrium. The experimental results showed that LN \((C_0/C_t)\) of the sample was linearly correlated with the photocatalytic reaction time \(T\) (Figure 4) (Table 1).

It can be seen from Figure 4, that after 300 min of illumination, the GCBC-0.1% composite sample has a higher \(k\) value, \(k = 0.0046 \text{ min}^{-1}\), and its \(D_{SMZ}\) degree is the highest, about 6.7 times that of g-C\(_3\)N\(_4\) nanotubes. The correlation coefficient \(R^2\) of each sample is greater than 0.9, which indicates that the \(D_{SMZ}\) in each sample conforms to the first-order reaction kinetic equation, and the GCBC composite sample has a good degradation effect on SMZ.

4.3 Analysis of cyclic stability of catalyst

GCBC-0.1% was selected for recycling, as shown in Figure 5 and Table 2. The \(D_{SMZ}\) value of the GCBC-0.1% sample decreased to 80%, indicating that the structure of GCBC sample was not damaged and it had good activity. After four cycles, \(D_{SMZ}\) decreased by 7.6%, indicating that the GCBC composite sample had good reuse performance.

4.4 Identification of intermediate products

GCBC-0.1% mineralizes SMZ under visible light irradiation. This means that intermediates are produced during degradation. Experiments were performed to determine the intermediates that might be converted to SMZ during degradation. Figure 6 shows that for SMZ solution, when the reaction time \(t = 0\) min and the retention time \(RT = 7.53\) min, a peak appears. The corresponding \(m/z\) \([M + H]^+\) of this substance is 254, which is judged as SMZ. At 20, 40, and 60 min, when \(RT = 2.00, 7.06,\) and \(9.57\) min, respectively, the new chromatographic peaks appear, which proved the existence of intermediates in the photocatalytic process. The ion distribution of mass spectrometric fragments at different \(RT\) is shown in Table 3.

At 2.00 min, \(m/z\) is 99, and \(C_6H_4N_2O\) is formed due to S–N bond fracture, denoted as M100. At 7.06 min, \(m/z\) was 270, and \(C_{10}H_3N_4O_3\) formed after -OH was introduced into Ar, denoted as M271. At 9.89 min, \(m/z\) was 284, because \(-NH_2\) was oxidized to \(-NO_3\) in Ar to form

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Regression equation</th>
<th>(k)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C(_3)N(_4)</td>
<td>(y = 0.0007x + 0.0066)</td>
<td>0.0007</td>
<td>0.9276</td>
</tr>
<tr>
<td>GCB-1%</td>
<td>(y = 0.0028x - 0.0057)</td>
<td>0.0028</td>
<td>0.9920</td>
</tr>
<tr>
<td>GCC-0.1%</td>
<td>(y = 0.0022x + 0.0030)</td>
<td>0.0022</td>
<td>0.9898</td>
</tr>
<tr>
<td>GCBC-0.1%</td>
<td>(y = 0.0046x + 0.0392)</td>
<td>0.0046</td>
<td>0.9952</td>
</tr>
</tbody>
</table>

**Table 2: Photocatalytic degradation after catalyst reuse for four times**

<table>
<thead>
<tr>
<th>No. of uses</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decolorization rate (%)</td>
<td>91.5</td>
<td>88.3</td>
<td>86.4</td>
<td>83.9</td>
</tr>
</tbody>
</table>
Figure 6: Chromatogram of SMZ degradation at different reaction times.

Table 3: Molecular structure formula and mass spectrum fragment ion distribution of intermediates

<table>
<thead>
<tr>
<th>Material structure</th>
<th>Molecular formula</th>
<th>[M+H]⁺</th>
<th>MS2</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>C₁₀H₁₁N₃O₃S</td>
<td>254</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>C₄H₆N₂O</td>
<td>99</td>
<td>53, 79</td>
<td>M100</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>C₁₀H₉N₃O₅S</td>
<td>284</td>
<td>122, 43, 182, 189</td>
<td>M285</td>
</tr>
</tbody>
</table>
–NO₃–C₁₀H₉N₃O₅S, denoted as M285. The above analysis showed that there were three intermediates in the degradation of SMZ by GCBC composite samples.

4.5 Analysis of free radical capture experiment results

The photocatalytic degradation of SMZ was investigated by using the GCBC-0.1% composite sample to degrade SMZ. The active species of intermediates were studied as shown in Figure 7.

Figure 7 shows that the CBC-0.1% of D_{SMZ} is 91.5%. After adding three kinds of collectors, the photocatalytic degradation rate was observed. According to the analysis of M100 intermediates, h⁺ and ·O₂⁻ are the main active substances of SMZ degradation by M100. The analysis of M271 intermediates showed that ·OH was the main active substance of SMZ degrading by M271. The intermediates of M285 showed that h⁺ and ·O₂⁻ were the main active species of SMZ degradation by M285, and h⁺ played a greater role in SMZ degradation by M285.

Based on the combination of intermediates and active species, the degradation path of SMZ can be predicted by GCBC. As shown in Figure 8, first, SMZ produces M100 intermediate with simple structure and small molecular weight due to S–N bond fracture. The M271 intermediate is then catalyzed by OH⁻. Finally, SMZ is mineralized by ·NO₂ to generate a higher molecular weight M285 intermediate, which is finally decomposed into CO₂, H₂O, and other inorganic substances.
4.6 GCBC composite sample characterization

4.6.1 TEM

The prepared Z-type GCBC composite samples were characterized by TEM, and the results are shown in Figure 9.

It can be seen from Figure 9 that CNTs were wrapped by GCB composite sample and dispersed in GCB without obvious agglomeration. After doping CNTs, the particle size of GCB composite sample does not change much, but the specific surface area increases, and the surface distribution is uniform and there are some rough and small bumps which enhance the surface activity, provide more reaction sites, and improve the photocatalytic activity.
Figure 11: XPS diagram of spectrum analysis of GCBC composite samples: (a) full spectrum of all five elements, (b) spectrum of C, (c) spectrum of N, (d) spectrum of Bi, (e) spectrum of V, and (f) spectrum of O.
4.6.2 X-ray diffraction (XRD)

In order to study the preparation of Z-type GCBC composite, samples were characterized by XRD, the results are shown in Figure 10.

Figure 10 shows that the diffraction peak intensity of g-C3N4 at 27.4° is strong, corresponding to the crystal plane (002). BiVO4 has several distinct characteristic peaks with high intensity and sharp shape. The diffraction peaks of GCBC composite samples are similar to those of g-C3N4 and BiVO4, indicating that the crystal structure of the single component in the composite samples remains unchanged. In addition, no diffraction peak of CNTs was observed in all composite samples, suggesting that CNTs were fully integrated into the structure of GCB-1%, indicating successful combination of the three.

4.6.3 X-ray photoelectric spectrum (XPS)

The prepared Z-type GCBC composite samples were characterized by XPS, and the results are shown in Figure 11.

Figure 11(a) shows the full XPS spectrum of GCBC composites, in which the presence of C, N, Bi, V, and O elements can be detected. As shown in Figure 11(b), C1s has two characteristic peaks with binding energies of 284.6 and 288.2 eV. As shown in Figure 11(c), N1s has three characteristic peaks with binding energies of 397.4, 398.7, and 401.3 eV. As shown in Figure 11(d), Bi4f has two characteristic peaks, the binding energies of Bi4F7/2 and Bi4F5/2 are 159.2 and 164.5 eV. As shown in Figure 11(e), V2p has two characteristic peaks, and the binding energies of V2P1/2 and V2P3/2 are 516.8 and 523.7 eV. As shown in Figure 11(f), O1s has three characteristic peaks, 529.5, 530.2, and 532.3 eV. The results showed that GCBC composite photocatalyst was successfully prepared.

4.6.3.1 Photocurrent response

The prepared Z-type GCB, GCC, and GCBC composite samples were tested by transient photocurrent response and electrochemical impedance spectroscopy, and the results are shown in Figures 12 and 13.

As can be seen in Figure 12, all samples showed a significant photocurrent response to irradiation with visible light, with a strong increase in the photocurrent signal when illuminated with visible light and a strong decrease in the photocurrent response when trying to avoid light. However, the photocurrent intensity of GCBC (d) composites is significantly stronger than that of GCB (b) and GCC (c) materials. This phenomenon indicates that the GCBC composite is effective in separating and migrating photo-generated carriers.

4.7 Electrochemical impedance spectroscopy

Figure 13 shows the EIS response of Z-type GCB, GCC, and GCBC composite samples under UV irradiation. It is clear
that pure CNTs exhibit a significant high frequency arc whose diameter corresponds to the electron transfer resistance of the interfacial dynamics. GCB arc radius decreases gradually, GCC arc radius increases, and GCBC arc radius is the smallest. The size of the arc radius reflects the reaction rate occurring on the surface. With the prolongation of time, the photocurrent value of each sample changes little and is relatively stable. When the light source is turned off, the photocurrent drops rapidly, indicating that the photocurrent in the sample is generated by photoelectron–holes. Therefore, GCBC can achieve the maximum separation of electron–hole pairs and improve the charge transfer efficiency.

6 Conclusion

In this study, g-C$_3$N$_4$ prepared by thermal polymerization method was taken as the main research object. Binary and ternary composite samples were synthesized by hydrothermal method, and characterized by microscopic morphology, crystal structure, chemical element composition, degradation performance, and other aspects. According to the cycle stability test, the samples prepared are all reproducible. Photocatalytic reaction mechanism of the samples was investigated by UV-vis and UPLC-MS, and the z-type heterojunction system was confirmed. The main research conclusions of this study are as follows:

1) The g-C$_3$N$_4$ samples were synthesized by optimizing the experimental conditions, and the composite samples of GCB, GCC, and GCBC with excellent photocatalytic performance were successfully prepared. The photocatalytic activity of g-C$_3$N$_4$ was improved by morphology regulation, heterojunction construction, and semiconductor recombination. The DRhB rates of each sample were 33.4, 90.4, 91.7, and 92.6%. Among them, the $K$ value of GCBC sample is about 6 times that of g-C$_3$N$_4$.

2) The results of free radical capture were used to clarify the degradation mechanism of each sample. $h^+$ and O$_2$ are the main active species of GCB, O$_2^-$ is the main active species of GCC, and $h^+$, and O$_2$ are the main active species of GCBC. According to the cycle stability test, the prepared samples have good reusability.

3) In addition, all samples have strong degradation effect on SMZ. This study will improve the water environment, effectively remove and mineralize antibiotics, and lay a certain theoretical foundation for human development.

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