One-step hydrothermal synthesis of g-C₃N₄/TiO₂/BiOBr layered hybrid photocatalyst with enhanced visible light degradation of tetracycline

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Abstract. In this work, a ternary composite photocatalyst with layer structure was synthesized by a one-step hydrothermal method. The visible-light-driven layered ternary photocatalyst exhibited excellent photocatalytic performance for the degradation of tetracycline (TC). The degradation rate of TC reached 88.78% within 60 min under visible light exposure in presence of optimum ratio G-T-B-0.2, which is higher than pure g-C₃N₄, TiO₂ and BiOBr. Scanning electron microscope (SEM), Transmission electron microscope (TEM), X-ray diffractometer (XRD), Fourier transform infrared spectra (FTIR), spectrometer and X-ray photoelectron spectroscopy (XPS) were used to character the physicochemical properties of the synthesized samples. Photoelectrochemical measurements and radical trapping experiments revealed that the improvement of photocatalytic performance was mainly attributed to the rapid charge transfer at the interface of g-C₃N₄/TiO₂/BiOBr, which was benefit to the separation of photogenerated carriers and visible light absorption. This work provides a facile method for the synthesis of ternary heterojunctions, which has potential applications in environmental remediation.

1 Introduction

Antibiotic has been widely used in Medical institutions. 10, 000-20, 000 tons of antibiotic has been discharged into environment. Due to its molecular structure, it is difficult to handle by traditional water treatment. Tetracycline (TC) has been widely used in the world due to its low price and high activity[1]. It is released from different water sources and is harmful to humans and ecosystems[2]. Hence, it is necessary to find a way with low-cost, high-efficiency and environmental-friendly to eliminate TC. Photocatalysis has been recognized as a promising technology due to its low cost, time saving and high efficiency .

Many semiconductor materials have been used to remove TC from wastewater, such as TiO₂, Al₂O₃, ZnO, CdS, etc[3]. TiO₂ has received more and more attention for its high chemical stability, economic efficiency and durability[4]. Unfortunately, the drawback of the slow transfer of photogenerated electron-hole pairs and the high compliance rate have limited their wider application. Hence, it is a significant necessary to develop a semiconductor composite material which could make full use of visible light.

Graphitic carbon nitride (g-C₃N₄) with good visible light response and high chemical stability is a typical two-dimensional metal-free polymeric photocatalyst. However, the photocatalytic efficiency of g-C₃N₄ is limited due to its rapid complexation of electron-hole pairs and low charge mobility. One possible improvement is to construct a

heterojunction by combining with suitable band heterojunction. It is worth noting that several heterogeneous structures based on the formation of g-C₃N₄ and TiO₂ have been developed to enhance photocatalytic performance. Hao et al. prepared g-C₃N₄/TiO₂ heterojunctions with large specific surface area and excellent non-homogeneous structure, which could significantly improved the photocatalytic performance. Sheng et al. have also successfully prepared g-C₃N₄/TiO₂ heterojunction photocatalysts which could facilitate the separation and migration of photo-induced electron-hole pairs. Tang et al. have successfully fabricated TiO₂/g-C₃N₄ composite nanofibres with high porosity and large specific surface area, which can improve the photoresponse performance[5].

It is well known that bismuth bromide is consider to be a promising photocatalyst with the special layered halogen interlayer structure, which can further promote charge transfer due to its induced internal electrostatic field[6]. It has been reported that the heterojunction constructed by BiOBr and TiO₂ can both extend the photoresponse to the visible region and effectively separate the photogenerated electron-hole pairs[7]. Previously, the exfoliated g-C₃N₄-BiOBr hybridization products prepared by Chang et al, have improved photocatalytic performance due to the large specific surface area, unique optical properties and matched energy band structure. However, owing to the low ability of transport electrons, the binary heterojunction still has limitations for inhibiting the recombination of photogenerated carriers. As a result,

ternary heterojunctions can greatly promote charge separation and improve photocatalytic activity. Due to the insufficient research on the photocatalysis of organic pollutants degradation by $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{BiOBr}$ ternary system, constructing a layered $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{BiOBr}$ composite with high photocatalytic activity is essential. In this work, layered $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{BiOBr}$ ternary photocatalysts were prepared by a one-step hydrothermal method. The structure and morphology of the obtained sample composites were characterized by SEM, TEM, XRD, XPS and FT-IR, which showed that the prepared composites were layered and TiO_2 was uniformly loaded on the surface of $g\text{-C}_3\text{N}_4\text{-BiOBr}$. In addition, the photocatalytic mechanism of G-T-B-0.2 was explained by light experiments and photovoltaic performance analysis (UV-DRS). Comparing with the pure BiOBr , TiO_2 or $g\text{-C}_3\text{N}_4$ materials, the photocatalytic performance of composite material has been greatly improved. Finally, a possible photocatalytic mechanism is proposed by active species capture experiment.

2 Experimental

2.1 Materials

Sodium dodecyl sulfate (SDS, AR, 92.5-100.5%), Titanium butoxide (AR), Zinc chloride (ZnCl_2 , AR, 98%), Melamine (99%), Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AR, 99.0%), Hexadecyl trimethyl ammonium bromide (CTAB, 99%), chlorhydric acid (HCl , GR, 36%~38%), ethyl alcohol (AR, 99.7%), Isopropyl alcohol (IPA, AR, $\geq 99.5\%$), P-Benzoquinone (99%), EDTA disodium salt dihydrate (AR, 98%), potassium dichromate (AR, $\geq 99.8\%$) were purchased without any further purification. Ultrapure water was used throughout this study.

2.2 Preparation of photocatalysts

2.2.1 Preparation of TiO_2

Firstly, SDS (0.6g) was dissolved in 36.8ml ultrapure water with stirring for 10 min at 40°C , after that tetrabutyl titanate (3.36ml), ZnCl_2 (0.8g) and HCl (2.56ml) were slowly added into mixed solution. The obtained solution was stirred for 5min and quickly transfer to a petri dish with a diameter of 90 mm and a depth of 10 mm then store at room temperature for 24h. The white powder was dried in an oven at 60°C .

2.2.2 Preparation of layered $g\text{-C}_3\text{N}_4$

In a typical method, melamine (30.0g) was placed in a 200ml crucible and calcined at 550°C at a rate of $2.5^\circ\text{C}/\text{min}$ in a temperatures-programmed muffle furnace for 4 hours. The obtained yellow powder was placed in a temperature-programmed muffle furnace and calcined at 500°C at a rate of $5^\circ\text{C}/\text{min}$ for 2 hours to form sheet $g\text{-C}_3\text{N}_4$.

2.2.3 Preparation of $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{BiOBr}$

$g\text{-C}_3\text{N}_4$ (0.1g) and TiO_2 (1.0g) were dissolved into 40ml ultrapure water with sonicate for 30 minutes. Subsequently, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.0g) and CTAB (1.0g) were added into mixed solution with stirring for 15 minutes. Moreover, the mixed solution was adjusted to pH 11.5 by use of 1mol/L NaOH solution and transferred into a 200ml Teflon autoclave at 160°C for 18 hours. After the temperature is decreased to room temperature, the obtained powder was washed by ethanol and ultrapure water for several times and placed in a vacuum drying oven at 80°C for 12 hours.

2.3 Characterization

Morphology and microstructure were achieved using a scanning electron microscope (SEM, JSM7800F) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM 2100). Crystal phase of catalysts was identified by an X-ray diffractometer (D8 Advance, Germany). X-ray photoelectron spectroscopy (XPS) was performed on a ESCALABXi+ XPS System (Thermo Fisher Scientific). FTIR spectrometer (IR Affinity-1s, Shimadzu Corporation, Japan) provide FT-IR spectrum. Optical property was analyzed by UV-Vis spectrophotometer (UV-2600 Shimadzu). The light source for the photocatalytic reaction consists of a 300 W xenon lamp (CEL-LAM500) with a filter. The wavelength range of 350 ~ 780 nm.

2.4 Photocatalytic performance

Before each experiment, 10mg of the catalyst was taken and immersed in a re-prepared 30mL TC (20mg/L) solution, sonicate the catalyst for 30 minutes in the dark to fill the entire solution and then stir to reach the adsorption-desorption equilibrium. After that, using a 300 W Xe lamp (Beijing Zhongjiao Jinyuan Technology Co., Ltd., Beijing), during the photocatalysis process, 1mL of the solution was collected every 10 minutes and the concentration of remaining TC in the solution was analyzed by liquid injection. In addition, a free radical capture experiment was conducted. In the experiment, the concentration of TC was $45\mu\text{M}$, and isopropanol (IPA, $0.75\mu\text{L}$) and potassium dichromate (7.65mM) were used as hydroxyl radicals ($\bullet\text{OH}$) and Electron (e^-) scavengers, p-benzoquinone (PBQ, 9.25mM) and EDTA disodium salt dihydrate (8.06mM) are used as superoxide radicals ($\bullet\text{O}_2^-$) and pore scavengers, respectively.

3 Results and discussion

3.1 Morphology and structure of catalysts

3.1.1 SEM

Fig. 1 exhibit the microscopic morphology and elemental composition of the prepared sample. From Fig. 1a and 1b, it can be found that the flower-like layered structure of BiOBr , along with uniformly grown TiO_2 nanoparticles

and a small amount of TiO_2 nanorods. The lamellar structure of $\text{g-C}_3\text{N}_4$ was found in Fig.1c. Fig. 1(d-i) EDS results prove that C, N, Ti, O, Bi and Br are uniformly distributed in G-T-B, indicating that the combination of these three materials is successful.

3.1.2 TEM

In order to further observe the morphology and structure of the ternary composite material, as shown in Fig.2(a) and

(b), the clear and regular lattice stripes with a width of 0.33 nm are belong to the anatase $\text{TiO}_2(101)$ crystal plane. We can also faintly see the curved lattice stripe of $\text{g-C}_3\text{N}_4$ [8]. It is clearly shown in Fig. 2(c) that the interconnection of the two lamellar structures of $\text{g-C}_3\text{N}_4$ and BiOBr provides a larger specific surface area for the formation of heterojunctions[9]. In Fig.2(d), the black TiO_2 grains are uniformly distributed on the lamellar surface of the $\text{g-C}_3\text{N}_4$ and BiOBr composites, indicating the successful formation of the ternary system.

Fig. 1.(a-c). SEM image of G-T-B-0.2. (d-i). EDS element mapping for the corresponding regions of C, N, O,Ti,Bi and Br.

Fig. 2. TEM analysis of the G-T-B-0.2 nanocomposite.

3.1.3 XRD

Crystal structure of the g-C₃N₄, TiO₂, BiOBr, G-T-B-0.1, G-T-B-0.15, G-T-B-0.2, G-T-B-0.5 and G-T-B-0.8 corresponding ternary composite nanomaterials were confirmed by XRD (Fig.1). There are two characteristic diffraction peaks at 12.8°(1 0 0) and 27.6°(0 0 2) for g-C₃N₄(JCPDS No. 87-1526). The diffraction peaks of 26.9°, 38.18° and 45.6°, which is corresponded to the (101), (004) and (200) planes of anatase TiO₂ (JCPDS, No.21-1272). While the peak at 29.3° was consistent with (211) crystal plane of Brookite TiO₂ (JCPDS, No. 76-1934). All diffraction peaks of the pure BiOBr material at 12.9°, 26.1°, 30.2°, and 39.5°, which can be well matched to the four crystal planes (0 0 1), (1 0 1) (1 1 0) and (1 1 2) respectively.

All of the five composites possess peaks of pure g-C₃N₄ and BiOBr materials. When g-C₃N₄ was added at 0.5 g and 0.8 g, a new peak appeared which coincided with g-C₃N₄ (JCPDS No. 87-1526) at 27.6°(0 0 2) [10]. However, the intensity of the four single peaks at 12.9°(0 0 1), 26.1°(1 0 1), 30.2°(1 1 0) and 39.5°(1 1 2) showed a decreasing trend with the increase of g-C₃N₄ addition (0.1 ~ 0.2 g). These results suggest that the weakening of the characteristic peak of g-C₃N₄ is due to the low content and high dispersion in the composite, or may be the result of disruption of the crystal order of the carbon-nitrogen material during the one-step hydrothermal synthesis. In addition, the characteristic peaks of the TiO₂ composites are obscure, which may be due to their poor crystallinity or the formation of a new substance by combining g-C₃N₄ during the one-step hydrothermal process, resulting in crystal changes and obscure characteristic peaks.

Fig. 3. XRD patterns of the corresponding nanomaterials.

3.1.4 XPS

The chemical composition and chemical valence of g-C₃N₄/TiO₂/BiOBr were analyzed by x-ray photoelectron spectroscopy (XPS). In Fig.4 (a), the peaks of C1s, N1s, O1s, Ti2p and Bi4f are detected in G-T-B-0.2 sample. There are three peaks located at 284.16, 285.5 and 287.9 eV for C1s spectrum(Fig.4 (b)). The peak at 284.16 eV can be assigned to the sp² C-C bonds of graphitic or amorphous carbon adsorbed on the surface of composite. The peak at 287.8 eV can be identified as the sp²-hybridized carbon atoms in aromatic rings (N-C=N) and 285.3 eV is related to C-N[11]. A new peak is observed compared to pure g-C₃N₄. The N 1s spectra (Fig. 4(c)) exhibits three peaks at 404.31, 399.9 and 398.36 eV, where 398.36 eV corresponded to the nitrogen atoms in the triazine rings (C-N=C), peaks at 399.9 eV and 404.31 eV are related to N-(C)₃ and (C)₂-N-H, respectively[12]. In Figure 4(d), the O1s spectrum is located on two peaks at

529.5 eV and 531.1 eV. The higher energy peak at 529.5eV corresponds to O1s in Ti—O bond of brookite and lower energy peak at 531.1 eV corresponds to Ti—OH bonding. In Fig.4(e), for G-T-B-0.2, the characteristic peak at 457.9 eV was attributed to Ti 2p_{3/2}, whereas that at 464.44 eV was corresponding to the superposition of two peaks at 464.09 eV (Ti 2p_{1/2}) and 466.48 eV (Bi 4d). The binding energy of the Ti2p_{3/2} and Ti2p_{1/2} peaks of G-T-B-0.2 is higher than that of pure TiO₂, which may be ascribed to the stronger chemical bond between BiOBr and TiO₂(formation of Bi-O-Ti or Br-O-Ti bonded compounds)[13]. As seen in Fig. 4(f), binding energies of 164.48 eV and 159.18 eV two strong peaks corresponding to the two spin-orbit components of Bi 4f_{5/2} and Bi 4f_{7/2}, which ascribes to the lattice oxygen (Bi—O) formed in the BiOBr lattice and also determine the valence state of Bi³⁺ in the composite materia[14]. A slight shift in binding energy could be attributed to the possible interaction between g-C₃N₄, TiO₂ and BiOBr. Hence, G-T-B composites were successfully prepared.

Figure 4. XPS survey spectra of the G-T-B-0.2 composite

(a) survey spectrum, (b) C 1s, (c) N 1s, (d) O 1s, (e) Ti 2p and (f) Bi 4f.

Fig.5 (a). Photocatalytic degradation curves of TC by different samples.

(b). The pseudo-first-order kinetic plots for TC degradation.

3.2 Photocatalytic performance of the properties of composite materials

We conducted photocatalytic experiments on the composites with different $g\text{-C}_3\text{N}_4$ additions in order to investigate the effect of different $g\text{-C}_3\text{N}_4$ contents on the visible light photocatalytic activity of the composites.

Fig.5 (a) shows that the activity of photocatalytic composite was evaluated by TC degradation under visible light irradiation. The materials were saturated with adsorption by immersing them in TC solution for 30 min in a dark environment before illumination. The experimental results showed that the degradation rates of TC by BiOBr and $g\text{-C}_3\text{N}_4$ within 60 min under visible light irradiation were only 9.7% and 12.86%, while the degradation rate of TiO_2 was 82.4%. It has been proved that the addition of SDS can improve photoelectric

conversion efficiency[15]. It may be due to the fact that surfactants play an important role in the formation of TiO_2 films. At the same time, the degradation rate of composite materials is much higher than BiOBr and $g\text{-C}_3\text{N}_4$. Consequently, this phenomenon is probably due to the TiO_2 playing an important role in the composite. From figure, it can be found that the degradability of the composites increases first and then decreases, and the degradation rates of the composites for G-T-B-0.1, G-T-B-0.15, G-T-B-0.2, G-T-B-0.5 and G-T-B-0.8 are 86.1%, 82.6%, 88.78%, 77.48% and 75.03%, respectively. The photocatalytic performance of the composites is reduced by the addition of a few and an overdose amounts of $g\text{-C}_3\text{N}_4$. Which could be caused by a small amount and an excessive amount of $g\text{-C}_3\text{N}_4$ on the formation (morphology, structure) of the ternary system heterojunction. In order to investigate the photocatalytic performance of different samples, the degradation kinetics

of TC were performed.

$$\ln(C_0 / C) = K_a t \quad (1)$$

where C_0 is the initial concentration of TC, K_a is the pseudo-first order rate constant, C is the concentration of the TC and t is the illumination time. From Fig.5(b), it is evidently found that pseudo-first order kinetics could well described all the photocatalytic data. The G-T-B-0.2 (0.03711min⁻¹) has the highest first-order rate constant, which was about 14.3, 22.77, 1.43, 1.21, 1.33, 1.69 and 1.67 times larger compared to that of g-C₃N₄ (0.0026min⁻¹), BiOBr (0.00163min⁻¹), TiO₂ (0.02596min⁻¹), G-T-B-0.1 (0.03075min⁻¹), G-T-B-0.15 (0.02782min⁻¹), G-T-B-0.5 (0.02199min⁻¹) and G-T-B-0.8 (0.02234min⁻¹), respectively. It is suggested that G-T-B-0.2 has the best photocatalytic performance. This may be due to the fact that the photoexcited electrons in the TiO₂-BiOBr heterostructure can be rapidly accepted by the appropriate number of g-C₃N₄ layers, which effectively suppresses the electron-hole complexation. Prolongate carrier lifetime in the G-T-B nanoheterojunction leads to the production of more active oxide species[16].

In order to probe the optical performance of the composite material, the optical activity of the synthesized sample was measured by ultraviolet-visible diffuse reflectance spectroscopy. It can be seen that the absorption thresholds of BiOBr and TiO₂ are 403nm and 436nm, respectively, while the absorption threshold of the composite at around 450 nm is lower than that of g-C₃N₄ (550 nm), which may be related to the amount of g-C₃N₄ added[17]. Furthermore, E_g can be calculated by formula $\alpha h\nu = A(h\nu - E_g)^{n/2}$ [18]. Owing to the g-C₃N₄, TiO₂, and BiOBr are all indirect bandgap semiconductors($n=4$). Extrapolate the linear part of $(\alpha h\nu)^{1/2}$ and $h\nu$ to the energy axis to determine the energy band gap. Fig.6(a) shows that the band gap of the G-T-B-0.1, G-T-B-0.15, G-T-B-0.2, G-T-B-0.5, and G-T-B-0.8 are 2.951eV, 3.002eV, 2.987eV, 3.005eV, and 3.025eV, respectively. These results indicated that the composite material produced more electron-hole pairs under visible light irradiation, which improves the photocatalytic activity[19]. In the process of degradation of TC by g-C₃N₄/TiO₂/BiOBr, free radical trapping experiments were carried out to further detect the mechanism of photocatalytic degradation of TC. Superoxide radicals ($\cdot O_2^-$), hydroxyl radicals ($\cdot OH$), and holes (h^+) And electronics (e^-) were detected by using p-benzoquinone (PBQ), isopropanol (IPA), EDTA-2Na and potassium dichromate as scavengers. It can be seen from the figure that the degradation rate of the TC solution with PBQ added is 58%, which has a remarkable negative effect on the removal rate of TC under visible light and indicating that superoxide radical ($\cdot O_2^-$) is the chief active substance. Besides, the other three quenchers had no inhibitory effect on the degradation rate of TC and there was no significant divergence between the degradation rate and the blank experiment without quenching agent.

4 Conclusion

In summary, g-C₃N₄/TiO₂/BiOBr photocatalysts were

successfully synthesized by a one-step hydrothermal method. A high visible light absorption capacity of the g-C₃N₄/TiO₂/BiOBr photocatalyst and the double interface contact increase the fast transport of photogenerated electron-hole pairs and reduce recombination. The morphology and functional group structure were characterized by SEM, TEM, XRD, FT-IR and XPS, which further confirmed that the combination of g-C₃N₄, TiO₂ and BiOBr was successful. The as prepared G-T-B photodegradation was well fitted by pseudo-first order kinetics for photodegradation of TC. Approximately 89% of the TC was removed during the 60 min photodegradation process by G-T-B-0.2. The results of radicals trapping experiments suggested that $\cdot O_2^-$ was the main active species during the photocatalytic process. This study shows that the ternary heterojunction material has great potential to degrade persistent organic pollutants from wastewater.

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