Preparation of g-C₃N₄/BiOBr Composites and Their Enhanced Visible-Light Photocatalytic Performance

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Abstract. Novel g-C₃N₄/BiOBr composites were prepared successfully by a simple liquid-phase precipitation method. The morphologies and microstructures of the photocatalysts were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). With dye Rhodamine B as a model pollutant, the photocatalytic activities of the g-C₃N₄/BiOBr composites with various mass ratio was explored, and the possible photocatalytic mechanism was investigated briefly. The results showed that g-C₃N₄/BiOBr composites were formed successfully, and some fine flakes of g-C₃N₄ embedded in the staggered spaces and surface of BiOBr nanosheets with thickness of 50-80 nm. Compared with pure g-C₃N₄ and pure BiOBr, g-C₃N₄/BiOBr composites showed enhanced activities for both adsorption and photocatalytic decoloration of RhB. The optimum mass ratio was found to be 1:4 (g-C₃N₄:BiOBr) exhibiting the highest photocatalytic activity. The combination between g-C₃N₄ and BiOBr in composites could increase the surface area, so then improve the adsorption properties, moreover, it could contribute to separation and migration for the charge carriers. The effects of various scavengers on photocatalytic efficiency revealed that h⁺ played predominant role for the photo-decoloration of RhB on g-C₃N₄/BiOBr composites.

1. Introduction
The heterostructured semiconductor photocatalyst has been proved to be an effective material for the degradation of organic pollutants in water treatment because of their appropriate band structures to increase separation efficiency of photo-generated charges [1-4]. BiOBr and g-C₃N₄ are p-type and n-type semiconductors with appropriate band gap, respectively. Due to their special electronic structure, excellent chemical properties, environmental friendliness and low preparation cost, BiOBr and g-C₃N₄ have attracted increasing interest in heterogeneous photocatalysis for photocatalytic degradation of dye wastewater [5-8]. However, some researchers have found that both pure BiOBr and pure g-C₃N₄ has some defects, such as low quantum efficiency, low utilization rate of light energy, and unsatisfactory recycling rate, which limits their practical application in photocatalytic degradation of dye wastewater. Many literatures have reported that the composite photocatalyst with p-n heterojunction structure can better promote the separation of photo-generated charge, improve the quantum efficiency and improve its stability [9-10]. Herein, we prepared g-C₃N₄/BiOBr composites by simple liquid-phase precipitation method with g-C₃N₄ as precursor at room temperature. The microstructure characteristics of the as-synthesized composites were determined. The visible-light photocatalytic performance of the as-synthesized composites was explored via the photocatalytic decolorization of Rhodamine B (RhB) dye.
2. Experimental

2.1. Preparation of Photocatalysts
The dye, Rhodamine B (C_{31}H_{31}CIN_{2}O_{3}, RhB) was purchased from YiEn Chemical Technology Co., Ltd. (Shanghai, China), and used as received. Other chemical reagents were analytical grade and used without further purification.

g-C_{3}N_{4} was synthesized by thermal polycondensation of melamine[11], and then treated in concentrated nitric acid. The g-C_{3}N_{4}/BiOBr heterojunction composites were synthesized as follows: 1.0mmol Bi(NO_{3})_{3}·5H_{2}O was added into 100 mL 1mol/L nitric acid aqueous solution under magnetic stirring until a clear solution was obtained. A certain amount of as-prepared g-C_{3}N_{4} powders were dispersed into 100 mL the above clear solution with vigorous stirring for more than 5 h. Then 40 mL 1.0mmol KBr solution was introduced slowly into the above g-C_{3}N_{4} dispersion, and the obtained mixture was kept with stirring at 80°C for 2 h. The formed precipitate was collected, then washed several times with deionized water and ethanol. Finally, the obtained powders were dried at 60°C in vacuum. Using this method, the g-C_{3}N_{4}/BiOBr composites with various mass ratios of g-C_{3}N_{4} and BiOBr were prepared, and marked as α-g-C_{3}N_{4}/β-BiOBr, where α and β refer to the calculated stoichiometric mass ratio coefficient for g-C_{3}N_{4} and BiOBr, respectively. For control experiment, pure BiOBr was synthesized with the same method and conditions mentioned above without adding g-C_{3}N_{4}.

2.2. Characterization of Photocatalysts
The SEM images were recorded on a SU8010 high resolution field emission scanning electron microscopy (Hitachi, Japan). The crystalline phases of the samples were determined by X-ray diffraction analysis (X’Pert Pro, PANalytical, Holland) using Cu Kα radiation (λ=0.15406 nm) in the range of 2θ=10° to 80° with a step scan of 0.026°/s.

2.3. Photocatalytic Activity Measurements
The photocatalytic performance of samples was evaluated using RhB decoloration in aqueous solution under visible-light irradiation. Experiments were performed in a quartz reactor, which was placed in a circulating cold water bath to keep dye solution at constant room temperature during irradiation. Typically, 30 mg of as-prepared photocatalyst was dispersed in 100 mL of 10 mg/L dye RhB solution with gently stirring for 0.5h in dark to ensure adsorption/desorption equilibrium, and then the above reactor was exposed to a tungsten-halogen lamp (500 W, λ_{d}=584 nm) which was fixed at a distance of 150 mm above the surface of the suspension. Then about 3–5mL supernatant was extracted and centrifuged to remove the photocatalyst at given irradiation time intervals. The absorbance of the supernatant was determined using a TU-1810 UV–vis spectrophotometer at 554 nm.

To evaluate the effects of related reactive species, various scavengers were added respectively into the RhB solution before introducing the photocatalyst in the photocatalytic experiment process. The introduced scavengers were 6mmol ammonium oxalate (AO), 6mmol tert-butanol (t-BuOH) and 6mmol silver nitrate (AgNO_{3}).

3. Results and Discussion

3.1. Characterization Analysis
Figure 1 shows the XRD patterns of as-prepared pure g-C_{3}N_{4} and 1g-C_{3}N_{4}/4BiOBr composites (the mass ratios of g-C_{3}N_{4} and BiOBr is 1:4). It could be seen from the XRD pattern of 1g-C_{3}N_{4}/4BiOBr that all the diffraction peaks of BiOBr labelled as crystal face number could be well corresponded to the tetragonal structure of BiOBr according to the JCPDS file No. 09-0393 [12]. The five main diffraction peak of 1g-C_{3}N_{4}/4BiOBr at 2θ of 10.91°, 25.14°, 31.67°, 32.20° and 57.19° were indexed as the (001), (101), (102), (110) and (212) crystal faces of BiOBr, respectively. In addition to peaks of BiOBr, there was one clear peak with 2θ = 27.88°, which was indexed for interlayer stacking of aromatic segments of (002) crystal plane for graphitic materials [13]. The (002) peak position of g-C_{3}N_{4} in 1g-C_{3}N_{4}/4BiOBr was the same as that of pure g-C_{3}N_{4} in curve b (Figure 1), but the intensity of (002) peak in the composites became much lower owing to the lower amount of g-C_{3}N_{4}. These
results demonstrated that the crystalline phases of both g-C$_3$N$_4$ and BiOBr were maintained in the composites. Furthermore, The sharp typical diffraction peak for 1g-C$_3$N$_4$/4BiOBr composites indicated that both g-C$_3$N$_4$ and BiOBr in the composite photocatalyst possessed good crystallinity, and no other diffractions peak were detected, indicating that the as-prepared composites had high purity.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of 1g-C$_3$N$_4$/4BiOBr (a) and pure g-C$_3$N$_4$ (b).

The morphology and surface of g-C$_3$N$_4$ and 1g-C$_3$N$_4$/4BiOBr were studied by SEM, as shown in Figure 2. It could be found from Figure 2a that pure g-C$_3$N$_4$, treated with concentrated nitric acid had a loose and fine lamellar structure and relatively rough surface. Figure 2b shows the SEM image of 1g-C$_3$N$_4$/4BiOBr. As shown in Figure 2b, the morphology of BiOBr exhibited sheet-like nanostructures with the thickness in the range of 50-80 nm. The lamellar BiOBr were approximately parallel or staggered to form a better intercalation structure, and some fine flakes of g-C$_3$N$_4$ were embedded in the staggered spaces and surface of BiOBr nanosheets. Due to the rough surface of g-C$_3$N$_4$, g-C$_3$N$_4$ could combine well with BiOBr nanosheets, indicating the successful formation 1g-C$_3$N$_4$/4BiOBr composites.

![Figure 2](image2.png)

**Figure 2.** SEM images of pure g-C$_3$N$_4$ (a) and 1g-C$_3$N$_4$/4BiOBr (b).

### 3.2. Photocatalytic Activity for RhB Decoloration

The photocatalytic activities of all samples including pure g-C$_3$N$_4$, pure BiOBr and the as-prepared g-C$_3$N$_4$/BiOBr composites with different mass ratio were investigated through RhB decoloration under visible light illumination. In order to achieve an adsorption–desorption equilibrium between the photocatalysts and the dye RhB, the reaction suspension system was magnetically stirred in the dark for 0.5h before irradiation. As seen in Figure 3, the adsorption performance for RhB in dark over pure g-C$_3$N$_4$, pure BiOBr, 4g-C$_3$N$_4$/1BiOBr, 3g-C$_3$N$_4$/2BiOBr, 1g-C$_3$N$_4$/1BiOBr, 2g-C$_3$N$_4$/3BiOBr, and 1g-
C$_{3}$N$_{4}$/4BiOBr was 12.3%, 10.9%, 19.5%, 17.4%, 23.0%, 20.9%, and 22.1%, respectively. The absorptivity of all g-C$_{3}$N$_{4}$/BiOBr composites were higher than both pure g-C$_{3}$N$_{4}$ and pure BiOBr, implying that the surface area and porous structure of the composites were improved compared to those of single component. Also, the photo decoloration rates of RhB over all the g-C$_{3}$N$_{4}$/BiOBr composite photocatalysts could all reach above 50% within 60 min visible-light illumination, which were much higher than that over pure BiOBr and pure g-C$_{3}$N$_{4}$. And the 1g-C$_{3}$N$_{4}$/4BiOBr photocatalyst exhibited the maximum decoloration rate of 86.4% after 60min irradiation. Moreover, the kinetic analysis of photocatalytic reaction could obtain the same results. The pseudo-first-order kinetic model is usually used to describe the photocatalytic reaction, expressed as the following equation [14]:

$$\ln \frac{C_0}{C_i} = k_{app}t$$  \hspace{1cm} (1)

\[Figure 3.\] Photocatalytic activities of g-C$_{3}$N$_{4}$, BiOBr, ag-C$_{3}$N$_{4}$/BiOBr on the decoloration of RhB under visible light irradiation.

\[Figure 4.\] The kinetic linear fitting curves of RhB decoloration over various samples.

\[Table 1.\] Photocatalytic kinetic parameters for the decoloration of RhB over various samples

| Photocatalysts       | $k_{app}$ (min$^{-1}$) | $R^2$ |
|----------------------|------------------------|-------|
| pure g-C$_{3}$N$_{4}$| 0.0057                 | 0.9981|
| pure BiOBr           | 0.00677                | 0.9801|
| 4g-C$_{3}$N$_{4}$/1BiOBr | 0.00802               | 0.9978|
| 3g-C$_{3}$N$_{4}$/2BiOBr | 0.01194               | 0.9940|
| 1g-C$_{3}$N$_{4}$/1BiOBr | 0.01517               | 0.9941|
| 2g-C$_{3}$N$_{4}$/3BiOBr | 0.02183               | 0.9961|
| 1g-C$_{3}$N$_{4}$/4BiOBr | 0.028                 | 0.9965|

Where $C_i$ and $C_t$ are the reactant concentrations at times $t = 0$ and $t = t$, respectively, and $k_{app}$ (min$^{-1}$) is the apparent reaction rate constant determined by plotting $\ln(C/C_0)$ versus $t$ (min). Figure 4 shows the linear plots of the photocatalytic decoloration data applied to the equation (1), and the obtained photocatalytic kinetic parameters of the as-prepared samples is shown in Table 1. We could see that 1g-C$_{3}$N$_{4}$/4BiOBr composites provided the highest $k_{app}$ value which was approximately 4.9 and 4.1 times than that of pure g-C$_{3}$N$_{4}$ and BiOBr respectively. All the results showed that the photocatalytic performance of the g-C$_{3}$N$_{4}$/BiOBr composites with appropriate component proportion were much better than that of their individual photocatalyst, suggesting the combination of BiOBr with moderate
g-C₃N₄ could effectively induced positive synergies and enhance their photocatalytic activities. The main reason might be that efficient heterojunction interface formed between two components, which led to greatly increase the surface area of the composites and reduce the recombination rate of photo-generated hole-electron pair, thus the photocatalytic performance of the g-C₃N₄/BiOBr composites was effectively improved [15].

3.3. Possible Photocatalysis Mechanism of g-C₃N₄/BiOBr Composites

To investigate the possible photocatalytic mechanism of g-C₃N₄/BiOBr composites, the effects of the main reactive species for the photocatalytic decoloration of RhB under visible light were explored. It is known that the main reactive species in photocatalytic reactions usually include hydroxyl radicals (•OH), active holes (h⁺) and active electrons (e⁻). The predominant reactive oxygen species trapping experiments were carried out in the photocatalytic reactor mentioned before by using three different radical scavengers, which were tert-butanol(t-BuOH), ammonium oxalate(AO) and silver nitrate(AgNO₃) for capturing •OH, h⁺ and e⁻, respectively[4, 16]. It is clear from Figure 5 that the introduction of 6mmol t-BuOH and 6mmol AgNO₃ possessed a weak effect in this photocatalytic process, in comparison with no scavenger under the same conditions, while the adding of 6mmol AO caused obvious suppression on the photocatalytic decoloration for RhB. The result implied that •OH radicals and active electrons were not the predominant reactive species on the decoloration rate of RhB over g-C₃N₄/BiOBr, but active hole (h⁺) played a very vital role for the photo-decoloration of RhB on g-C₃N₄/BiOBr composites.

![Figure 5. Effects of various scavengers on the decoloration of RhB over 1g-C₃N₄/4BiOBr under visible light irradiation.](image)

4. Conclusions

g-C₃N₄/BiOBr composite photocatalysts with unique microstructure and improved visible-light photocatalytic performance were prepared through a simple liquid-phase precipitation method. The mass ratio of the g-C₃N₄/BiOBr composites at 1:4 showed the highest visible-light photocatalytic activity on RhB decoloration. The introducing of a few g-C₃N₄ to BiOBr could increase the pore volume, surface area and the heterojunction structure, thereby further improve the adsorption and photocatalytic performance of g-C₃N₄/BiOBr. The investigation of possible photocatalytic mechanism demonstrated that the active h⁺ played more important roles on g-C₃N₄/BiOBr composites in the RhB decoloration process. In summary, the visible-light photocatalytic activity of g-C₃N₄/BiOBr were enhanced obviously after the formation of the heterojunctions between g-C₃N₄ and BiOBr, owing to the increased separation efficiency of photo-generated electron–hole pairs. Therefore, g-C₃N₄/BiOBr
composites hold significant promise as a visible-light photocatalyst for dye removal in wastewater treatment.

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6. References
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