

The enhanced pyrocatalysis of the pyroelectric BiFeO₃/g-C₃N₄ heterostructure for dye decomposition driven by cold-hot temperature alternation

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Abstract: The BiFeO₃/g-C₃N₄ heterostructure, which is fabricated via a simple mixing-calcining method, benefits the significant enhancement of the pyrocatalytic performance. With the growth of the g-C₃N₄ content in the heterostructure pyrocatalysts from 0 to 25 %, the decomposition ratio of Rhodamine B (RhB) dye after 18 cold-hot temperature fluctuation (25 °C - 65 °C) cycles increases at first and then decreases, reaching a maximum value of ~ 94.2 % at 10 % while that of the pure BiFeO₃ is ~ 67.7 %. The enhanced dye decomposition may be due to the fabrication of the heterostructure which strengthens the separation of the positive and negative carriers and further accelerates their migration. The intermediate products in the pyrocatalytic reaction also have been detected and confirmed, which proves the key role of the pyroelectric effect in realizing the dye decomposition using BiFeO₃/g-C₃N₄ heterostructure catalyst. The pyroelectric BiFeO₃/g-C₃N₄ heterostructure shows the potential application in pyrocatalytically degrading dye wastewater.

Keywords: Pyroelectric materials; BiFeO₃; g-C₃N₄; Heterostructure; Pyrocatalysis.

1 Introduction

The limited clean water has been seriously polluted by a large number of the chemical dyes discharged from the textile and printing industries, which results in a heavy environmental crisis [1, 2]. Photocatalysis, as an advanced oxidation technology, in which the clean solar energy can drive photocatalyst to generate free radicals in the end to degrade pollutants, has been widely reported for wastewater treatment [3-5]. However, the disadvantages of no response in darkness and the high requirements on the light's transmission condition limit the practical application of photocatalysis in the dye decomposition [6]. Temperature fluctuation, as a common natural phenomenon that behaves day and night in surroundings, can be considered as a great source of the thermal energy [7]. The pyroelectric materials behaves a strong ability to transfer the thermal energy into the electrical energy, which has been reported to further generate the active free radicals with a strong oxidizing property to decompose pollutants, named pyrocatalysis [8].

Recently, pyrocatalysis becomes increasingly popular in the dye decomposition [9-11]. Wu *et al.* have reported that the BiFeO₃ nanoparticles can decompose ~ 99 % Rhodamine B (RhB) dye after 85 cold-hot cycles [9]. Xu *et al.* have realized the decomposition ratio of ~ 99 % for RhB dye after 50 cold-hot cycles with Ba_{0.7}Sr_{0.3}TiO₃@1.5%Ag nanoparticles [10]. You *et al.* have reported a decomposition ratio of RhB dye up to ~ 86.5 % after 80 mins with NaNbO₃ nanofibers in response to vibration together with cold-hot cycles [11]. How to further enhance the pyrocatalytic performance of the pyroelectric materials is crucial to their practical application in dye decomposition.

Fabricating heterostructure with the narrow-gap semiconductors to enhance catalytic performance has been widely applied in photocatalysis [12-14]. Benefitting from the energy gradient

which is originated from the energy band alignment on the interface, the heterostructure can strengthen the separation of the positive and negative carriers and further accelerate the migration of carriers [15-17]. Therefore, this method may be available to enhance the photocatalytic performance of the pyroelectric materials in theory, which is rarely reported.

g-C₃N₄, as an organic semiconductor material, can be regarded as the ideal narrow-gap semiconductor option in the heterostructure due to its narrow band gap ($E_g = 2.7$ eV), metal-free property, great thermal and chemical stability [18-21]. Fabricating heterostructure with g-C₃N₄ has been widely used for improving the catalysts' activity in the photocatalytic technology while its report in photocatalysis field is rare up to now [22-24].

In this work, a significantly-enhanced photocatalytic performance is found in the pyroelectric BiFeO₃/g-C₃N₄ heterostructure catalysts, which is fabricated via a simple mixing-calcining method. With the growth of the g-C₃N₄ content in the heterostructure photocatalysts from 0 to 25 %, the decomposition ratio of Rhodamine B (RhB) dye after 18 cold-hot temperature fluctuation (25 °C - 65 °C) cycles increases at first and then decreases, reaching a maximum value of ~ 94.2 % at 10 % while that of the pure BiFeO₃ is ~ 67.7 %.

2 Materials and method

2.1 Synthesis of BiFeO₃

All the raw materials were analytical reagents in this experiment. BiFeO₃ was synthesized through a hydrothermal method [25, 26]. 2.425 g of Bi(NO₃)₃·5H₂O was dissolved in 50 mL of ethylene glycol. After the continuous magnetic stirring for 0.5 h, 1.352 g of FeCl₃·6H₂O and 200 mL of deionized water were added into the mixed solution. Then, NH₃·H₂O was added dropwise until the pH value of

the solution up to ~ 11. The product in the solution was centrifuged out and then washed with the deionized water until its pH value fell to ~ 7. Thereafter, the washed product was put into 40 mL of 5 M NaOH with the continuous magnetic stirring for 0.5 h. Finally, the mixture solution was put into a teflon-lined stainless steel autoclave at 140 °C for 72 h to obtain BiFeO₃.

2.2 Fabrication of BiFeO₃/g-C₃N₄ heterostructure

To obtain g-C₃N₄, 10 g of melamine was calcined in a muffle at 550 °C for 4 h with a heating rate of 5 °C/min [18]. To fabricate the BiFeO₃/g-C₃N₄ heterostructure, a certain amount of the prepared g-C₃N₄ and BiFeO₃ were dispersed in the absolute ethanol with the magnetic stirring for 0.5 h. Then, the product in the mixture solution was gained via centrifugation and dried at 70 °C for 12 h. Finally, it was placed into a muffle and calcining at 400 °C for 4 h. Based on this method, BiFeO₃/g-C₃N₄ heterostructures with different g-C₃N₄ weight fractions of 0 %, 5 %, 10 %, 15 %, 20 %, 25 % were obtained.

2.3 Characterization

An X-ray diffractometer (XRD, Rigaku MiniFlex/600 powder, Japan) was employed to characterize the crystal structures of samples. The infrared spectra of samples were recorded on a fourier transform infrared spectrometer (FTIR, Nicolet iS5, USA). The morphology observations of samples were conducted through a scanning electron microscopy (SEM, Phenom ProX, the Netherlands). The photocatalytic decomposition performances of BiFeO₃/g-C₃N₄ heterostructure catalysts for RhB dye were measured via a UV-vis spectrophotometer (Ocean Optics QE65Pro, USA).

2.4 Photocatalytic dye decomposition

In this experiment, all the photocatalytic reactions were carried out in darkness to avoid the influence of photocatalysis on the RhB dye decomposition. 50 mg of BiFeO₃/g-C₃N₄ heterostructure catalyst

and 50 mL of RhB aqueous solution (5 mg/L) were added into a brown bottle with the magnetic stirring for 1 h to achieve an absorption equilibrium. After every 3 cycles, 3 mL of the mixture solution was taken out and centrifugalized for the UV-vis spectra measurements.

3 Results and discussion

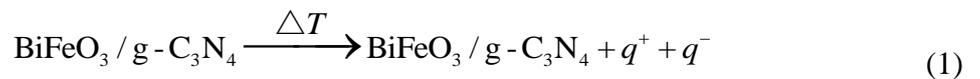
Fig. 1 (a) shows the XRD patterns of BiFeO₃/g-C₃N₄ heterostructures as well as the pure BiFeO₃. The diffraction peaks of the pure BiFeO₃ accord well with the rhombohedral phase based on the JCPDS Card No. 86-1518 [25]. Because of the low g-C₃N₄ content, there is no obvious difference of the XRD patterns between BiFeO₃/g-C₃N₄ heterostructures and pure BiFeO₃ can be seen in Fig. 1 (a) [22, 26, 27].

The FTIR spectra of the pure BiFeO₃, BiFeO₃/10%g-C₃N₄ heterostructure and g-C₃N₄ are employed to confirm the existence of g-C₃N₄ in BiFeO₃/g-C₃N₄ heterostructure, as shown in Fig. 1 (b). The pure BiFeO₃ displays two obvious infrared signal peaks at ~ 484 and ~ 592 cm⁻¹, attributing to the O-Fe-O bending vibrations and the Fe-O stretching of FeO₆ groups in BiFeO₃ [28, 29]. With regard to g-C₃N₄, the peak at ~ 802 cm⁻¹ is ascribed to the out-of-plane bending modes of C-N heterocycles [30, 31]. In the range of 1200 - 1600 cm⁻¹, several strong infrared signal peaks are seen clearly from the curve of g-C₃N₄, corresponding to the C=N and the aromatic C-N stretching vibration modes [32, 33]. The characteristic infrared signal peaks of g-C₃N₄ and the pure BiFeO₃ also exhibit in the infrared spectrum of BiFeO₃/10%g-C₃N₄ heterostructure, revealing the great combination between g-C₃N₄ and the pure BiFeO₃.

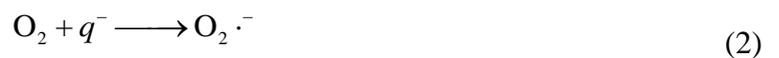
The photocatalytic mechanism of BiFeO₃/g-C₃N₄ heterostructure catalyst is proposed in Fig. 2. BiFeO₃ is a kind of crystal that possesses a spontaneous polarization property. While it keeps a

thermal equilibrium with the external medium, its internal polarization charges are shielded by the external compensation charges so that BiFeO₃ shows the electroneutrality. Once the thermal equilibrium is broken, temperature fluctuation changes the electric dipole moment of BiFeO₃, which leads to the variation of the intensity of internal polarization. Therefore, a charge imbalance forms between the internal polarization charges and the external compensation charges [9]. These pyroelectrically-induced positive and negative charges separate and start to transfer via the heterostructure. The negative charges move from the conduction band (CB) of BiFeO₃ to the CB of g-C₃N₄ while the positive charges move from the valence band (VB) of g-C₃N₄ to the VB of BiFeO₃. Then, these pyroelectrically-induced charges react with hydroxyl ions and the dissolved oxygens on the surface of catalyst. Benefitting from the energy gradient which is originated from the energy band alignment on the interface, the heterostructure in catalyst can strengthen the separation of the pyroelectrically-induced charges and further accelerate the migration of carriers, which contributes to the significantly-enhanced photocatalytic performance for dye decomposition.

The specific chemical equations in the photocatalytic reaction for dye decomposition with BiFeO₃/g-C₃N₄ heterostructure catalysts can be expressed as Eqs. (1) - (4) [34]:



The dissolved oxygens (O₂) react with the pyroelectrically-induced negative charges (q⁻) on the surface of g-C₃N₄ to generate the superoxide radicals (O₂^{·-}) according to the Eq. (2):



Similarly, the pyroelectrically-induced positive charges (q⁺) react with the hydroxyl ions (OH⁻) on the surface of BiFeO₃ to form the hydroxyl radicals (·OH) based on Eq. (3):



Both the $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ have the strong oxidizing properties to decompose dye molecules on the basis of Eq. (4):

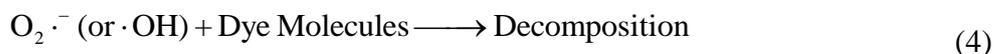


Fig. 3 shows the SEM images of the pure BiFeO_3 , $\text{g-C}_3\text{N}_4$ and $\text{BiFeO}_3/\text{g-C}_3\text{N}_4$ heterostructure. The pure BiFeO_3 of a square nanosheet structure with an average width of ~ 600 nm and the $\text{g-C}_3\text{N}_4$ of a layer structure are clearly seen in Fig. 3 (a) and Fig. 3 (b). The small size of BiFeO_3 is beneficial for enlarging the surface area for reaction and shortening the migration distance for the pyroelectrically-induced charges to reach the surface of catalyst [8, 35]. BiFeO_3 presents the similar morphologies in Fig.3 (a) and Fig.3 (b), indicating that the formation of heterostructure do not significantly affect the square nanosheet structure of BiFeO_3 [36]. As shown in Fig.3 (b), the attachment between $\text{g-C}_3\text{N}_4$ and BiFeO_3 square nanosheets is fairly close, which serves to form the heterostructure.

The photocatalytic performances of $\text{BiFeO}_3/\text{g-C}_3\text{N}_4$ heterostructure catalysts are evaluated via the decomposition of RhB dye under cold-hot temperature fluctuation cycles. Fig. 4 shows the UV-vis absorption spectra of RhB dye solution with $\text{BiFeO}_3/\text{g-C}_3\text{N}_4$ heterostructure catalysts at different temperature fluctuation (between 25°C and 65°C) cycles shown in the inset of Fig. 4 (a). The absorption peak locating at ~ 554 nm decreases obviously with the increase of the cycle, indicating a rapid decomposition of RhB dye. After undergoing 18 cycles, the $\text{BiFeO}_3/10\%\text{g-C}_3\text{N}_4$ heterostructure catalyst displays an extremely weak signal of the absorption peak at ~ 554 nm, suggesting a nearly complete decomposition of RhB dye.

As the $\text{BiFeO}_3/\text{g-C}_3\text{N}_4$ heterostructure catalysts have demonstrated a obvious decomposition of RhB dye, it's necessary to further estimate their photocatalytic decomposition performances. The

corresponding degradation ratios (D) of RhB dye over BiFeO₃/g-C₃N₄ heterostructure catalysts are calculated via Eq. (5):

$$D = (1 - C / C_0) \times 100 \% \quad (5)$$

Where the C_0 and C are the initial concentration and the current concentration of RhB dye solution, respectively [37]. Fig. 5 (a) exhibits the decomposition ratios of RhB dye at different cycles with BiFeO₃/g-C₃N₄ heterostructure catalysts. After 18 cycles, the BiFeO₃/g-C₃N₄ heterostructure catalysts with different g-C₃N₄ contents of 0 %, 5 %, 10 %, 15 %, 20 %, 25 % can respectively decompose ~ 67.7 %, ~ 76.7 %, ~ 94.2 %, ~ 91.7 %, ~ 87.4 % of RhB dye. The dependence of decomposition ratio on the g-C₃N₄ content of BiFeO₃/g-C₃N₄ heterostructure catalysts is shown in the inset of Fig.5 (a). The decomposition ratio of RhB dye increases significantly with the heterostructure and as high as ~ 94.2 %, which is the highest decomposition ratio of RhB dye among the BiFeO₃/g-C₃N₄ heterostructure catalysts, can be achieved via BiFeO₃/10%g-C₃N₄ heterostructure catalyst. As the g-C₃N₄ content of BiFeO₃/g-C₃N₄ heterostructure catalysts increases from 0 to 10 %, the increasing g-C₃N₄ content leads to a growing number of the BiFeO₃/g-C₃N₄ heterostructure unit so that the decomposition ratio of RhB dye increases at the beginning. When the content of g-C₃N₄ exceeds 10 %, the g-C₃N₄ of a layer structure stacks with itself, which becomes a new recombination center on the one hand. On the other hand, reduces the number of the BiFeO₃/g-C₃N₄ heterostructure unit. Both the increasing recombination ratio and the decreasing heterostructure unit number eventually result in the decrease of the RhB dye decomposition ratio.

A kinetic analysis of the photocatalytic reaction for RhB dye decomposition with BiFeO₃/g-C₃N₄ heterostructure catalysts is exhibited in Fig. 5 (b). The results accord well with the pseudo first order kinetic function based on the Eq. (6) [38]:

$$\ln(C / C_0) = -K \cdot t \quad (6)$$

Where t and K are the cycle and the kinetic rate constant in the photocatalytic reaction, respectively. The dependence of K on the g-C₃N₄ content of BiFeO₃/g-C₃N₄ heterostructure catalysts can be found in the inset of Fig. 5 (b). As the g-C₃N₄ content of BiFeO₃/g-C₃N₄ heterostructure catalysts grows from 0 to 25 %, the value of K increases at first and then decreases, giving a maximum value of $\sim 0.1513 \text{ cycle}^{-1}$ at 10 %, which is about 3 times as high as the K value of the pure BiFeO₃ ($\sim 0.0686 \text{ cycle}^{-1}$). The larger K value means the better photocatalytic performance of the BiFeO₃/g-C₃N₄ heterostructure catalyst. All BiFeO₃/g-C₃N₄ heterostructure catalysts behave the better photocatalytic performance than the pure BiFeO₃, while the optimal ratio of g-C₃N₄ content is obtained at 10 %.

The decomposition ratios of RhB dye with different catalysts and under various experimental conditions are shown in Fig.6. In the absence of BiFeO₃/10%g-C₃N₄ heterostructure catalyst, RhB dye solution shows almost no decomposition, which shows the excellent stability of RhB dye and excludes the influence of temperature fluctuation on RhB dye decomposition. Without temperature fluctuation, no obvious decomposition of RhB dye can be observed with BiFeO₃/10%g-C₃N₄ heterostructure catalyst, indicating the essential role of the temperature fluctuation in photocatalytic reaction. When BiFeO₃/10%g-C₃N₄ heterostructure catalyst is replaced with the corresponding masses of BiFeO₃ and g-C₃N₄, the decomposition ratio of RhB dye becomes about half what it is before, which further proves the formation of the heterostructure and the indispensable role played via the heterostructure in the significantly-enhanced photocatalytic performance.

In order to detect the intermediate products that play an important role in the photocatalytic decomposition of RhB dye, the photocatalytic experiments are carried out through adding different kinds of scavengers respectively. As shown in Fig. 7 (a), the decomposition ratios of RhB using

BiFeO₃/10%g-C₃N₄ heterostructure catalyst with different kinds of scavengers decrease in different degrees. The lower decomposition ratio of RhB dye means the stronger inhibition effect of scavenger to the catalyst's photocatalytic performance. Ethylene diamine tetraacetic acid (EDTA), benzoquinone (BQ) and tert-butyl alcohol (TBA) are the scavenger of hole, O₂^{·-} and ·OH, respectively [39]. Therefore, holes, ·OH and O₂^{·-} are the main intermediate products in the photocatalytic reaction, while the lowest decomposition ratio of RhB dye using BiFeO₃/10%g-C₃N₄ heterostructure catalyst with BQ suggests that the O₂^{·-} is the most crucial active substance among these intermediate products.

The recycling utilization results of the BiFeO₃/g-C₃N₄ heterostructure catalyst for RhB dye decomposition can be seen from Fig. 7 (b). There is a slight decrease of the decomposition ratio after recycling the catalyst for 3 times, indicating the remarkable stability of its photocatalytic decomposition performance for RhB dye [40]. Furthermore, as a magnetic material, BiFeO₃ also has been reported with the excellent recyclable ability [41], which makes the recycling process of the catalyst convenient. Both the remarkable stability and the excellent recyclability of BiFeO₃/g-C₃N₄ heterostructure catalyst are helpful to its practical application in dye decomposition.

4 Conclusions

The significantly-enhanced photocatalytic performance is realized via the BiFeO₃/g-C₃N₄ heterostructure, which is fabricated through a simple mixing-calcining method. The decomposition ratio of RhB dye using the BiFeO₃/10%g-C₃N₄ heterostructure catalyst is about 30 % higher than that using the pure BiFeO₃. The main intermediate products in the photocatalytic reaction for RhB dye decomposition are detected and confirmed, in which the O₂^{·-} shows the most crucial influence. No

obvious loss of the pyrocatalytic performance can be observed after recycling the catalyst for 3 times. The significantly-enhanced pyrocatalytic performance makes BiFeO₃/g-C₃N₄ heterostructure catalysts to have the potential in dealing with wastewater through utilizing the thermal energy of temperature fluctuation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51872264), Shaanxi National Science Foundation of China (2020JM-579), Key Research and Development Program of Shaanxi Province, China (Program No. 2020GXLH-Z-032), and the Public Welfare Technology Application Research Project of Zhejiang Province, China (LGG18E020005).

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Figure Captions:

Fig. 1 (a) The XRD patterns of the pure BiFeO₃ and BiFeO₃/g-C₃N₄ heterostructures. (b) The FTIR spectra of the pure BiFeO₃, BiFeO₃/10%g-C₃N₄ heterostructure and g-C₃N₄.

Fig. 2 The schematic diagram of the photocatalytic reaction with BiFeO₃/g-C₃N₄ heterostructure catalyst.

Fig. 3 The SEM images of (a) the pure BiFeO₃ and (b) BiFeO₃/g-C₃N₄ heterostructure.

Fig. 4 The UV-vis spectra of RhB dye solution after different numbers of cycles using BiFeO₃/g-C₃N₄ heterostructure catalysts. (a) The pure BiFeO₃. The inset is the ideal temperature fluctuation curve in the photocatalytic experiment. (b) BiFeO₃/5%g-C₃N₄. (c) BiFeO₃/10%g-C₃N₄. (d) BiFeO₃/15%g-C₃N₄. (e) BiFeO₃/20%g-C₃N₄. (f) BiFeO₃/25% g-C₃N₄.

Fig. 5 (a) The decomposition ratios of RhB dye after different numbers of cycles using BiFeO₃/g-C₃N₄ heterostructure catalysts. The inset shows the dependence of decomposition ratio on the g-C₃N₄ content after 18 cycles. (b) The plot of the negative logarithm of C/C_0 versus cycles. The inset shows the dependence of the kinetic rate constant on the g-C₃N₄ content.

Fig. 6 The comparison of the decomposition ratios of RhB dye with different catalysts and under different reaction conditions.

Fig. 7 (a) The detection of intermediate products in the photocatalytic reaction using BiFeO₃/10%g-C₃N₄ heterostructure catalyst with different scavengers. (b) The recycling utilization of BiFeO₃/10%g-C₃N₄ heterostructure catalyst for RhB dye decomposition.