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

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Received: August 14, 2020; Revised: November 13, 2020; Accepted: December 5, 2020

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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 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 (25–65 °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 generation of the internal electric field which strengthens the separation of the positive and negative carriers and further accelerates their migrations. 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 material; 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 great source of the thermal energy, can change the

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internal polarization intensity of the pyroelectric materials so that a charge imbalance forms between the internal polarization charges and the external compensation charges, leading to the separation and migration of these pyroelectrically-induced positive and negative charges to the surface of catalyst. Then, the pyroelectrically-induced charges react with hydroxyl ions and the dissolved oxygens to form the active free radicals with the strong oxidizing properties to decompose dye molecules [7,8].

Recently, pyrocatalysis becomes increasingly popular in the dye decomposition [8–10]. Wu *et al.* [8] have reported that the BiFeO₃ nanoparticles can decompose ~99% Rhodamine B (RhB) dye after 85 cold-hot cycles. Xu *et al.* [9] 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. You *et al.* [10] have reported a decomposition ratio of RhB dye up to ~86.5% after 80 min with NaNbO₃ nanofibers in response to vibration together with cold-hot cycles. How to further enhance the pyrocatalytic performance of the pyroelectric materials is crucial to their practical application in dye decomposition.

The method of fabricating heterostructure with the narrow-gap semiconductors to enhance catalytic performance has been widely applied in photocatalysis [11–13]. Benefitting from the generation of internal electric field on the interface, the heterostructure can strengthen the separation of the positive and negative carriers and further accelerate their migrations [14–16]. Therefore, this method may be available to enhance the pyrocatalytic performance of the pyroelectric materials in theory, which is rarely reported.

Graphitic carbon nitride (g-C₃N₄), as an organic semiconductor material, can be regarded as an ideal narrow-gap semiconductor option in the heterostructure due to its narrow band gap ($E_g = 2.7$ eV), metal-free property, and great thermal and chemical stability [17–20]. Fabricating heterostructure with g-C₃N₄ has been widely used for improving the catalytic performance in the photocatalytic technology while its reports in pyrocatalysis field are rare up to now [21–23].

In our previous works, it has been reported that the pyroelectric materials of BaTiO₃ nanofibers [24], Pb(Zr_{0.52}Ti_{0.48})O₃ ceramics [7], ZnO nanorods [25], and NaNbO₃ nanorods [26] can respectively decompose ~99%, ~98%, ~98%, and ~96% of RhB dye under the cold-hot cycles. Besides dye decomposition, other application of pyrocatalysis such as H₂ evolution

[27,28] has been realized. Some methods to enhance the pyrocatalytic performance have been developed such as the noble metal loading [29], fabricating heterostructures [30], and the optimizing poling field treatment [31].

In this work, a significantly-enhanced pyrocatalytic performance is found in the pyroelectric BiFeO₃/g-C₃N₄ heterostructure catalysts, which are fabricated via a simple mixing-calcining method. With the growth of g-C₃N₄ content in the heterostructure pyrocatalysts from 0 to 25%, the decomposition ratio of Rhodamine B (RhB) dye after 18 cold-hot 25–65 °C temperature fluctuation 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 [32,33]. 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 centrifugalized 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 and heated 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 [17]. 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 mixture product was gained via centrifuge and dried at 70 °C for 12 h. Finally, it was placed into a muffle and calcined 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 microstructure characterizations of samples were conducted through a scanning electron microscopy (SEM; Phenom ProX, the Netherlands) and a transmission electron microscope (TEM; Tecnai G2 F20 S-Twin, USA) with a high resolution transmission electron microscope (HRTEM). 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 Pyrocatalytic dye decomposition

In this experiment, all the pyrocatalytic 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. A single cold-hot temperature fluctuation cycle was carried out between 25 and 65 °C with 10 min heating and 10 min cooling. The brown bottle with the RhB dye solution and the BiFeO₃/g-C₃N₄ heterostructure catalyst was placed in the middle of a water bath container (RCT-B-S25, IKA, Germany) to realize the cold-hot temperature fluctuation between 25 and 65 °C [6,34]. The temperature was monitored via a thermometer placed in the middle of the mechanically-stirred dye solution [9]. After every 3 cycles, 3 mL of the mixture solution was taken out and centrifugalized for the UV–vis spectrum measurements.

3 Results and discussion

Figure 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 [32]. Because of the low g-C₃N₄ content, there is no obvious difference of the XRD patterns between BiFeO₃/g-C₃N₄ heterostructures and the pure BiFeO₃ as shown in Fig. 1(a) [21,33,35].

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

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 [35,36]. With regard to g-C₃N₄, the peak at ~802 cm⁻¹ is ascribed to the out-of-plane bending modes of C–N heterocycles [37,38]. 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 [39,40]. 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 pyrocatalytic mechanism with 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.

Fig. 2 Schematic diagram of the pyrocatalytic reaction with BiFeO₃/g-C₃N₄ heterostructure catalyst.

Therefore, a charge imbalance forms between the internal polarization charges and the external compensation charges [8]. It has been reported that the BiFeO₃ is a kind of n-type semiconductor ($E_g = \sim 2.2$ eV) while g-C₃N₄ behaves as a p-type semiconductor ($E_g = \sim 2.7$ eV) [41–43]. On the interface of the heterostructure, both the conduction band (CB) potential difference and the valence band (VB) potential difference between BiFeO₃ and g-C₃N₄ drive the electrons to diffuse from the CB of n-type BiFeO₃ to that of p-type g-C₃N₄, while on the contrary, holes diffuse from the VB of p-type g-C₃N₄ to that of n-type BiFeO₃ [44–46]. The diffusion of these carriers generates the negative charge center on the interface of g-C₃N₄ and the positive charge center on the interface of BiFeO₃, leading to the formation of the internal electric field, which further accelerates the separation of pyroelectrically-induced positive and negative charges, and the migration of pyroelectrically-induced positive charges from BiFeO₃ to g-C₃N₄.

Then, these pyroelectrically-induced charges react with hydroxyl ions and the dissolved oxygen on the surface of catalyst. The specific chemical equations in the pyrocatalytic reaction for dye decomposition with BiFeO₃/g-C₃N₄ heterostructure catalysts can be expressed as Eqs. (1)–(4) [47]:

The dissolved oxygen (O₂) reacts with the pyroelectrically-induced negative charges (q^-) on the surface of BiFeO₃ to generate the superoxide radicals (O₂^{·-}) according to Eq. (2):

Similarly, the pyroelectrically-induced positive charges (q^+) react with the hydroxyl ions (OH⁻) on the surface of g-C₃N₄ to form the hydroxyl radicals (·OH) based on Eq. (3):

Both the ·OH and O₂^{·-} have the strong oxidizing properties to decompose dye molecules on the basis of Eq. (4):

The pure BiFeO₃ of a square nanosheet structure with an average width of ~ 600 nm and the g-C₃N₄ of a layer structure are clearly seen in the SEM images of Fig. 3(a) and Fig. 3(b). The small size of BiFeO₃ 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 [7,48]. BiFeO₃ presents the similar morphology in Fig. 3(a) and Fig. 3(b), indicating that the formation of heterostructure does not significantly affect the square nanosheet structure of BiFeO₃ [49]. Figure 3(c) exhibits the TEM image of the BiFeO₃/g-C₃N₄ heterostructure. The square nanosheet structure of BiFeO₃ shown in Fig. 3(c) is in keeping with the observed morphology in the SEM images in Fig. 3(a) and Fig. 3(b). As displayed in Fig. 3(d), the HRTEM is employed to further confirm the microstructure of BiFeO₃ and the combination between g-C₃N₄ and BiFeO₃. The lattice fringe in BiFeO₃ is ~ 0.433 nm, which is in line with the (0 1 2) crystal

Fig. 3 SEM images of (a) the pure BiFeO₃ and (b) BiFeO₃/g-C₃N₄ heterostructure. (c) TEM and (d) HRTEM images of BiFeO₃/g-C₃N₄ heterostructure.

plane of BiFeO₃. The interface between g-C₃N₄ and BiFeO₃ is presented clearly in the HRTEM image while its enlarged image inset shows the extremely close attachment of two materials as well.

The photocatalytic performances of BiFeO₃/g-C₃N₄ heterostructure catalysts are evaluated via the decomposition of RhB dye under cold-hot temperature fluctuation cycles. Figure 4 shows the UV-vis absorption spectra of RhB dye solution with BiFeO₃/g-C₃N₄ heterostructure catalysts at different temperature fluctuation (between 25 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 BiFeO₃/10%g-C₃N₄ heterostructure catalyst displays an extremely weak signal of the absorption peak at ~554 nm, suggesting a nearly complete decomposition of RhB dye.

As the BiFeO₃/g-C₃N₄ heterostructure catalysts have demonstrated a obvious decomposition of RhB dye, it is 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 *C*₀ and *C* are the initial concentration and the current concentration of RhB dye solution, respectively [50]. Figure 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%, ~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 and reduces the number of the BiFeO₃/g-C₃N₄ heterostructure unit on the other hand [51,52]. 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 Eq. (6) [53–55]:

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

where *t* and *K* are the cycle and the kinetic rate constant in the photocatalytic reaction, respectively. The

Fig. 4 UV-vis spectra of RhB dye solution after different numbers of cycles using BiFeO₃/g-C₃N₄ heterostructure catalysts. (a) 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) 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) Plot of the negative logarithm of C/C_0 versus cycle. The inset shows the dependence of the kinetic rate constant on the g-C₃N₄ content.

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 ~ 0.1513 cycle⁻¹ at 10%, which is about 3 times as high as the K value of the pure BiFeO₃ (~ 0.0686 cycle⁻¹). The larger K value means the better pyrocatalytic performance of the BiFeO₃/g-C₃N₄ heterostructure catalyst. All BiFeO₃/g-C₃N₄ heterostructure catalysts behave the better pyrocatalytic performance than the pure BiFeO₃, while the optimal performance appears at the g-C₃N₄ content of 10% in heterostructure catalyst.

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 presents 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/

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

10%g-C₃N₄ heterostructure catalyst, revealing the essential role of the temperature fluctuation in pyrocatalytic 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 almost the same as that of using the pure BiFeO₃, which further proves the formation of the heterostructure and its indispensable role played in the significantly-enhanced pyrocatalytic performance.

In order to detect the intermediate products that play an important role in the pyrocatalytic decomposition of RhB dye, the pyrocatalytic 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 pyrocatalytic performance. Ethylene diamine tetraacetic acid (EDTA), benzoquinone (BQ), and tert-butyl alcohol (TBA) are the scavenger of hole, O₂^{·-}, and ·OH, respectively [56]. Therefore, holes, ·OH, and O₂^{·-} are the main intermediate products in the pyrocatalytic 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 them.

The recycling utilization results of the BiFeO₃/g-C₃N₄ heterostructure catalyst for RhB dye decomposition can be seen from Fig. 7(b). After 18 cold-hot cycles, the BiFeO₃/10%g-C₃N₄ heterostructure catalyst was centrifugalized out from the dye solution and washed with the deionized water. Then, it was dried at 70 °C for 12 h in an air oven and added into 50 mL of 5 mg/L RhB dye solution for the next 18 cycles. There is a slight decrease of the decomposition ratio after recycling

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

the catalyst for 3 times, indicating the remarkable stability of its pyrocatalytic decomposition performance for RhB dye [57]. Furthermore, as a magnetic material, BiFeO₃ also has been reported with the excellent recyclable ability [58], 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 pyrocatalytic 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 pyrocatalytic reaction for RhB dye decomposition are detected and confirmed, among 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 (Nos. 51872264 and 51778391), Shaanxi Provincial National Science Foundation of China (No. 2020JM-579), Key Research and Development Program of Shaanxi Province, China (No. 2020GXLH-Z-032), and the Basic Public Welfare Research Program of Zhejiang Province, China (No. LGG18E020005).

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