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Article

Efficient removal of ammonia with a novel graphene-supported BiFeO₃ as a reusable photocatalyst under visible light

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ABSTRACT

Graphene-supported BiFeO₃ (rG-BiFeO₃) was synthesized by the hydrothermal method and used for the efficient removal of ammonia under visible light. X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, and ultraviolet-visible diffuse reflectance spectroscopy were conducted to characterize the rG-BiFeO₃. The specific surface area of the rG-BiFeO₃ catalyst was 48.6 m²/g, larger than that of BiFeO₃ (21.0 m²/g). When used as a heterogeneous photocatalyst, rG-BiFeO₃ achieved 91.20% degradation of a NH₃-N solution (50 mg/L) at pH = 11 under visible-light irradiation in the absence of hydrogen peroxide. The degradation of ammonia followed pseudo-first-order kinetics, and the catalyst retained high photocatalytic activity after seven reaction cycles. Study of the mechanism showed that the holes, superoxide anion radicals, and hydroxyl radicals, arising from the synergy between graphene and BiFeO₃, oxidized NH₃ directly to N₂.

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1. Introduction

Ammonia (NH₃) is the second largest product by volume of the Haber-Bosch process and is used for feedstock and fertilizers [1]. However, as a major nitrogen-containing pollutant, NH₃ is also a nutrient source that can promote eutrophication and algal growth in natural waters [2]. Excessive amounts of NH₃ in the environment can exert harmful effects on human health [3]. NH₃ attacks the human respiratory system, skin, and eyes, and exposure to high concentrations (>300 ppm) may cause death [4,5].

The discharge of NH₃ from wastewater has become an urgent challenge. Various conventional technologies, including biological processes, chemical precipitation, advanced oxida-

tion processes, ion exchange, air stripping, adsorption, and the use of membranes, are applied to remove NH₃ from industrial wastewater [6–11]. However, these treatment methods are generally focused on large chemical systems and are often energetically and operationally intensive.

Photocatalytic degradation of NH₃ [2,12–17] has been proposed as a practical method to decontaminate wastewater for renewable use because of its low cost and ability to rapidly disinfect and purify water. Many researchers have found that titanium dioxide (TiO₂) and TiO₂-based materials, which are the primary photocatalysts explored for NH₃ degradation, can completely destroy N–H bonds [18–23]. However, TiO₂-based materials can only utilize approximately 4% of the available solar energy, including 43% of visible light, because of the wide

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band gap of TiO_2 . Thus, the development of novel photocatalysts that can decompose NH_3 under visible-light irradiation is necessary.

BiFeO_3 , a perovskite-type photocatalyst, has attracted considerable attention because of its narrow band-gap energy (2.1 eV) [24], high chemical stability [25], and simultaneous presence of ferroelectric and magnetic order parameters [26]. In addition to potential electronic and magnetic applications, BiFeO_3 powders have been used as a new visible-light photocatalyst [27]. Many researchers have utilized BiFeO_3 as a high-efficiency photocatalyst to degrade various organic pollutants under ultraviolet (UV)-visible or visible-light irradiation [28–33].

Recently, we have fabricated photocatalysts based on graphene-manganese ferrite ($\text{rG-MnFe}_2\text{O}_4$) and activated carbon bonded to nickel ferrite ($\text{AC-NiFe}_2\text{O}_4$). These photocatalysts achieved high performance in the photocatalytic degradation of NH_3 in the presence of hydrogen peroxide under visible-light irradiation [16,17]. However, manufacturing hydrogen peroxide consumes energy and/or other chemical resources. Therefore, the development of magnetically separable graphene-based photocatalysts with high catalytic activity in the absence of hydrogen peroxide is warranted.

In this study, BiFeO_3 nanocrystals were deposited on graphene sheets via a one-step hydrothermal method. BiFeO_3 nanoparticles possess weak magnetic properties. This weak magnetism makes the rG-BiFeO_3 composite magnetically separable in a suspension system and thus conveniently renewable and reusable. The rG-BiFeO_3 composite material was tested for the first time as a highly active catalyst for NH_3 degradation under visible-light irradiation in the absence of hydrogen peroxide. The optimum operational parameters for NH_3 degradation were also determined.

2. Experimental

2.1. Chemicals

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were purchased from Tianjin Damao Chemical Factory. Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium chloride (NH_4Cl) were obtained from Nanjing Chemical Reagent Co., Ltd. Graphite powder with an average particle size of 30 μm was acquired from Shanghai Colloid Chemical Plant. All reagents used were of analytical grade and applied without further purification. All solutions were prepared with 18.2 M Ω cm deionized Milli-Q water.

2.2. Synthesis of rG-BiFeO_3

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.8507 g, 0.01 mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.7030 g, 0.01 mol) were separately dissolved in 15.0 mL of deionized water. The solutions were then stirred together to form Solution A. The final pH was adjusted to approximately 12 by adding NaOH . Graphene oxide (GO) was synthesized via a modified Hummers method as previously described [34]. The

as-synthesized GO (125.2 mg, ~4% of the BiFeO_3 mass) was dispersed in 10.0 mL of deionized water with an ultrasonic vibrator, and the resultant solution was denoted Solution B. Solution A was added dropwise to Solution B under stirring. NaOH (2.4 g, 0.06 mol) was dissolved in 10.0 mL of deionized water. This solution was added dropwise to the mixed suspension solution described above under continuous stirring. Deionized water was also added to the suspension to obtain a final volume of 60 mL. Afterward, the suspension solution was transferred to a 100-mL Teflon-lined stainless-steel autoclave, which was subsequently sealed and maintained at 180 $^\circ\text{C}$ for 10 h. The solution was cooled to room temperature and filtered to obtain rG-BiFeO_3 precipitates. The products were rinsed three times with water to remove excess NaOH and other electrolytes. A magnetic powder was obtained after sintering at 200 $^\circ\text{C}$ for 4 h. This weakly magnetic powder was used for the characterization and photocatalytic tests. Pure BiFeO_3 was similarly prepared for comparison.

2.3. Structural characterization of rG-BiFeO_3

X-ray diffraction (XRD) was performed with an X'Pert-Pro MPD X-ray diffractometer (Panalytical, Netherlands). The X-ray source emitted $\text{Cu K}\alpha$ radiation with a wavelength of 0.154 nm at a tube voltage of 40 kV and a tube current of 40 mA. Morphological observations were conducted with a transmission electron microscope (Tecnai G220; FEI, USA). The rG-BiFeO_3 and GO powders were dispersed in water by an ultrasonication device, placed on carbon-coated copper grids, and dried under ambient conditions prior to transmission electron microscopy (TEM). Brunauer-Emmett-Teller (BET) surface areas of the photocatalysts were measured by N_2 adsorption-desorption on a Micromeritics ASAP 2200. Prior to measurement, the samples were pretreated at 150 $^\circ\text{C}$ under vacuum (1.33 Pa) for 2 h. A Fourier transform infrared (FT-IR) spectrophotometer (Spectrum BX; PerkinElmer Ltd., USA) was used to characterize group vibrations at an optical resolution of 4 cm^{-1} . Raman spectrum measurements were performed on a Renishaw inVia Reflex Raman Microprobe. UV-vis diffuse reflectance spectroscopy was performed with a Hitachi U-3010 UV-vis spectrometer. The mulls of rG-BiFeO_3 were supported on KBr plates.

2.4. Degradation of NH_3

Photocatalytic experiments for NH_3 degradation were conducted under visible-light irradiation ($\lambda > 400$ nm). A 300-W UV-visible lamp (OSRAM, Germany) was used as a light source. Photocatalytic degradation of NH_3 solution (50.0 mg/L) was performed in a 100-mL beaker at room temperature (25 ± 2 $^\circ\text{C}$). The distance between the lamp and the test solution was approximately 10 cm, and the wall of the beaker was shielded from surrounding light by aluminum foil. Visible light was allowed to pass through a $\lambda > 400$ nm cut-off filter that covered the window of the beaker; this filter absorbed UV light and allowed visible light ($\lambda > 400$ nm) to pass through. About 50 mL of solution was used in a typical photocatalytic experiment. The NH_3 solutions were prepared according to the desired concen-

trations, and 0.20 g of the rG-BiFeO₃ catalyst was used for the photocatalytic experiments. NaHCO₃-Na₂CO₃ buffer (0.1 mol/L) was used to control the pH of the test solutions. At predetermined time intervals, approximately 3 mL of the sample was extracted with a 5-mL plastic syringe and then passed through a 0.45-μm membrane filter to a clean and dried glass tube for further analysis. All photocatalytic degradation experiments were performed in triplicate.

A double-beam TU-1901 spectrophotometer was used to determine the concentration of NH₃ by reaction with Nessler's reagent during the photocatalytic process [35]. Nessler's reagent is an alkaline solution of dipotassium tetraiodomercurate (II). This reagent was prepared by dissolving 10 g of HgI₂ and 7 g of KI in water, adding to NaOH solution (16 g of NaOH in 50 mL of water), and then diluting with deionized water to 100 mL. The reagent was stored in dark bottles and diluted appropriately before analysis. NH₃ reacts with this reagent to yield colored solutions via Reaction (1). As the absorbance of the solutions showed a maximum value at 392 nm, absorbance was measured at this wavelength for analysis.

In Reaction (1), [HgI₄]²⁻ was yellow, and HgO·Hg(NH₂)I was brown.

3. Results and discussion

3.1. XRD characterization

Fig. 1 presents the XRD patterns of BiFeO₃ and the 4% rG-BiFeO₃ hybrid catalyst (where 4% is the raw-material mass ratio of GO to BiFeO₃). The diffraction peaks obtained can be indexed as perovskite-type BiFeO₃ (JCPDS Card No. 20-0169). The peaks at 2θ values of 22.43°, 31.90°, 39.52°, 45.76°, 51.30°, and 57.07° can be indexed to the (012), (104), (202), (024), (116), and (300) crystal planes of spinel BiFeO₃, respectively. The diffraction peak of rG-BiFeO₃ was shifted toward a lower 2θ value, and the intensity of the diffraction peaks for the composites was reduced compared with pure BiFeO₃, which can be attributed to the intercalation of GO. No impurity peak was found in the rG-BiFeO₃ hybrid.

The average diameter (*D*) of the as-synthesized rG-BiFeO₃

Fig. 1. XRD patterns of BiFeO₃ (1) and rG-BiFeO₃ (2).

Fig. 2. FT-IR spectra of GO (1), BiFeO₃ (2), and rG-BiFeO₃ (3).

particles was calculated as 18.5 nm from the Debye-Scherrer equation, $D = K\lambda / (W \cos \theta)$, at a diffraction angle of 31.90° (2θ), where *W* is the breadth of the observed diffraction peak at its half height, *K* is the so-called shape factor (usually approximately 0.89), and λ is the wavelength of the X-ray source used (0.154 nm in our measurement). The *D* value derived from the Debye-Scherrer equation is consistent with that obtained from the TEM observations.

3.2. FT-IR characterization

FT-IR spectroscopy was conducted to characterize the chemical structures of GO, BiFeO₃, and rG-BiFeO₃, and hence the changes in the first two after the impregnation of GO with BiFeO₃ (Fig. 2). The various surface functional groups of GO are clearly evident in Fig. 2(1), including the C-O stretching vibration at 1051 cm⁻¹ and the C=O (carboxyl) stretching vibration at 1726 cm⁻¹, which were attributed to the typical functional groups of GO (e.g., -O-, -COOH, and -OH) [36–38]. The peak at 1618 cm⁻¹ can be assigned to the C=C skeletal vibration of unoxidized graphitic domains and/or the H-O-H bending band of the adsorbed H₂O [39,40].

Fig. 2(3) clearly shows that almost all the characteristic peaks of the oxygen-containing groups (C=O, O-H, C-OH, and C-O-C) disappeared for rG-BiFeO₃, suggesting that the GO in the composite was reduced to graphene. The adsorption by rG-BiFeO₃ around 1559 cm⁻¹ can be assigned to the stretching vibrations of the unoxidized carbon backbone [41]. The band at 634 cm⁻¹ can be attributed to the Bi-O vibration in the BiO₆ octahedra [42], and the band at around 811 cm⁻¹ was due to the presence of traces of trapped NO₃⁻ ions in the composite nanoparticle [43].

It exhibits characteristic peaks for BiFeO₃ at 441 cm⁻¹ (Fe-O stretching vibrations of the FeO₆ octahedra) and 548 cm⁻¹ (O-Fe-O bending vibrations of the FeO₄ tetrahedra) [44,45]. After being combined with rG, the peak positions of BiFeO₃ remained unchanged in the FT-IR spectrum of rG-BiFeO₃, but the corresponding intensities changed considerably, especially for rG-BiFeO₃ (Fig. 2). This is further evidence of the possible formation of chemical bonding between BiFeO₃ and rG [46].

Fig. 3. Raman spectra of BiFeO₃ (1) and rG-BiFeO₃ (2).

3.3. Raman characterization

The Raman spectra of BiFeO₃ and rG-BiFeO₃ are shown in Fig. 3. The G and D bands of rG-BiFeO₃ (4%) were observed at 1598 and 1361 cm⁻¹, respectively. In previous studies, Raman peaks at 1580 and 1350 cm⁻¹ were assigned to the G and D bands of GO [47]. Compared with GO, the blue shift in the G and D bands of rG-BiFeO₃ indicated that the GO was reduced to graphene during the hydrothermal process [48].

3.4. TEM observation

Fig. 4 shows the TEM images of GO, BiFeO₃, and rG-BiFeO₃. It reveals the wrinkled surface texture of the exfoliated GO sheets. BiFeO₃ nanoparticles were sparsely deposited on the two-dimensional rG. These nanoparticles evidently tended to accumulate along the edge of the rG (Fig. 4(c)), similarly to the previously reported BFO₂₄₉/rG (4.5) composites [46]. The diameter of the particles was about 18.5 nm.

3.5. Photocatalytic degradation of NH₃

Fig. 5 shows the degradation curves of NH₃-N without catalyst under visible-light irradiation; with rG-BiFeO₃ (4%) as the catalyst under visible-light irradiation, or in the dark; and with BiFeO₃ as the catalyst under visible-light irradiation. It shows that the photodegradation rate of NH₃-N after visible-light irradiation without catalyst for 8 h was 5.9%. The photodegradation rate after reaction with rG-BiFeO₃ (4%) as a catalyst for 8 h in the dark was 9.1%. This percentage corresponds to the

Fig. 5. Photocatalytic degradation of 50 mg/L NH₃-N in 50 mL solution. (1) 50.0 mg/L NH₃-N + visible light; (2) 50.0 mg/L NH₃-N + 0.20 g rG-BiFeO₃ in the dark; (3) 50.0 mg/L NH₃-N + 0.20 g BiFeO₃ + visible light; (4) 50.0 mg/L NH₃-N + 0.20 g rG-BiFeO₃ + visible light.

amount of NH₃ adsorbed on the rG-BiFeO₃ catalyst. After visible-light irradiation with pure BiFeO₃ as a catalyst, the degradation rate was 57.5%, indicating that pure BiFeO₃ is photocatalytically active and can be used as a photocatalyst under visible light. Notably, the rG-BiFeO₃ (4%) hybrid catalyst under the same conditions (visible-light irradiation for 8 h) achieved 91.2% degradation of NH₃. Therefore, the combination of BiFeO₃ and graphene resulted in exceptionally high catalytic activity for the degradation of the contaminant NH₃. A possible cause of this significant enhancement in photoactivity was a powerful synergistic effect of the combination of BiFeO₃ and the rG sheets, which promotes efficient separation of electrons (e⁻) and holes (h⁺). In this mechanism, the separated e⁻ migrated along the surface of the rG, and the e⁻ on the surfaces of both rG and BiFeO₃ were trapped by the adsorbed O₂ to form superoxide anion radicals (·O₂⁻) [46]. Meanwhile, the holes were scavenged by the adsorbed water to form hydroxyl radicals. Finally, the holes, superoxide anion radicals, and hydroxyl radical directly oxidized NH₃ adsorbed on the active sites of the rG-BiFeO₃.

3.6. Effects of operational parameters on NH₃ degradation

3.6.1. Effect of rG content

A series of rG-BiFeO₃ nanocomposite photocatalysts with different graphene contents were prepared, and their photocatalytic activities under visible light were evaluated by the

Fig. 4. TEM images of GO (a), BiFeO₃(b), and rG-BiFeO₃ (c).

Fig. 6. Effect of rG content on the NH_3 degradation ratio under visible-light irradiation. Reaction conditions: 50.0 mg/L $\text{NH}_3\text{-N}$ in 50.0 mL of solution + 0.20 g of the catalyst at pH = 11.

degradation of NH_3 in aqueous solutions. As shown in Fig. 6, the degradation ratios initially increased with increasing mass concentration of rG in the hybrid catalysts, reaching a maximum value of 91.2% with 4.0% rG. The significant enhancement in photo-activity under visible-light irradiation was connected with the reduction of graphene oxide. Therefore, increasing the content of rG facilitated the transfer of photo-generated electrons in BiFeO_3 from the conduction band to the reduced GO, effectively preventing the direct recombination of electrons and holes. In addition, the BET analysis revealed that while the specific surface area of BiFeO_3 was 21.0 m^2/g , that of the rG- BiFeO_3 (4%) composite was much higher, 48.6 m^2/g . The much greater BET surface area of the rG- BiFeO_3 is likely to have provided more active adsorption sites and photocatalytic reaction centers than BiFeO_3 .

However, when the rG contents were increased to 6.0% and 8.0%, the degradation ratios slightly decreased in comparison with the 4.0% composite, contrary to our expectations. This decrease may have been caused by a reduction in the quantity of NH_3 adsorbed on BiFeO_3 . Although increasing the rG content in the hybrid catalyst improved the absorption of visible light, an overload of rG may have inhibited the adsorption of NH_3 on the surface of the BiFeO_3 catalyst by decreasing the availability of active sites, i.e., transition metal atoms exposed on the surface of the hybrid catalyst. This phenomenon would have led to lower activity, which is consistent with a previous study of the rG- MnFe_2O_4 photocatalyst [16]. Therefore, 4% was the ideal mass ratio, and the 4% rG- BiFeO_3 catalyst was used in all subsequent tests.

3.6.2. Effect of solution pH value

The pH value of the solution plays an important role in the photocatalytic degradation of organic pollutants [50,51]. The effect of pH on the photodegradation of NH_3 was studied in the pH range of 6–11. As shown in Fig. 7, the degradation of NH_3 reached 2.99%, 3.57%, 14.81%, 73.62%, 82.11%, and 91.96% at pH = 6, 7, 8, 9, 10, and 11, respectively, after 8 h of irradiation. The degradation ratio of NH_3 therefore increased continually with increasing solution pH. This trend is ascribed to the protonation state of NH_3 [52]. As the pK_a of NH_4^+ is 9.3, this

Fig. 7. Photocatalytic degradation of 50.0 mg/L $\text{NH}_3\text{-N}$ using 0.20 g of the rG- BiFeO_3 catalyst in 50.0 mL of NH_4Cl solution at various pH levels under white-light irradiation.

species is predominantly protonated in solutions with pH < 9.3. The presence of NH_4^+ ions limits the adsorption of NH_3 on the BiFeO_3 surface. Hydroxyl radicals ($\cdot\text{OH}$) can oxidize NH_3 but not NH_4^+ [53]. Therefore, NH_3 is decomposed more rapidly in solutions with higher pH, as the fraction of NH_4^+ ions is smaller.

3.6.3. Effect of dosage of rG- BiFeO_3

The influence of the catalyst dosage on the heterogeneous photocatalytic degradation of NH_3 by rG- BiFeO_3 is illustrated in Fig. 8. Degradation ratios of 78.76%, 83.3%, 92.7%, and 86.0% were achieved when the dosages of the rG- BiFeO_3 catalyst were 0.1, 0.15, 0.2, and 0.25 g, respectively, after 8 h. A large enhancement in the degradation ratio of NH_3 was observed when the catalyst dosage was increased from 0.1 to 0.2 g, because the increase in the amount of the rG- BiFeO_3 catalyst increased the presence of active sites on the catalyst surface as well as the generation of free hydroxyl radicals [54]. However, when the dosage of the catalyst was increased from 0.20 g to 0.25 g, the decomposition rate of NH_3 decreased from 92.7% to 86.0%, because higher dosages of catalyst also increased the turbidity of the reaction solution, thus reducing the intensity of the visible-light irradiation available for the photocatalytic reaction [55].

Fig. 8. Effect of catalyst dosage on the degradation ratio. Initial conditions: $C_{\text{NH}_3\text{-N}} = 50.0$ mg/L, pH = 11.

Fig. 9. Kinetic analysis of NH_3 degradation at different concentrations of $\text{NH}_3\text{-N}$. Conditions: $\text{pH} = 11$, 0.2 g of rG-BiFeO₃ catalyst.

3.7. Reaction kinetics

Fig. 9 shows the effect of the NH_3 concentration on the degradation rate. Solutions of NH_3 at various concentrations, i.e., 25.0, 50.0, 75.0, and 100.0 mg/L $\text{NH}_3\text{-N}$, were degraded with 0.2 g of rG-BiFeO₃ catalyst at $\text{pH} = 11$, under visible-light irradiation. Study of the degradation kinetics showed that the photocatalytic degradation of $\text{NH}_3\text{-N}$ followed pseudo-first-order kinetic behavior. As shown in the inset of Fig. 9, the average reaction rate constant (k) was calculated to be 0.2949 min^{-1} and the average value of the linear correlation coefficient was 0.99381.

3.8. Stability of rG-BiFeO₃

The stability and reusability of a catalyst are key factors for its application, and must be investigated from the economic and environmental points of view. Fig. 10 shows that there was no obvious change in the photocatalytic activity of the recycled rG-BiFeO₃ catalyst after seven cycles under visible-light irradiation. Moreover, the catalyst could be easily separated from the reaction solution by simple precipitation to allow its reuse. This indicates that the catalyst is highly stable and is potentially suitable for practical applications.

Fig. 10. Stability of the rG-BiFeO₃ catalyst for the removal of $\text{NH}_3\text{-N}$ through multiple cycles.

3.9. Mechanistic discussion

3.9.1. Oxidation pathway of NH_3

Based on the literature, two different reaction pathways exist to oxidize the NH_3 adsorbed on the catalyst surface to form the final products [56,57]. The first pathway, in which N_2 is formed as the final product, produces a series of NH_2 , NH , and N_2H_{x+y} ($x + y = 0, 1, 2$) intermediates. The second pathway yields NO_2^- and NO_3^- ions as the final products through a HONH_2 intermediate. These two reaction pathways proceed as follows.

Reaction pathway 1:

Reaction pathway 2:

In UV-vis absorption spectrophotometry, the absorbance peaks of NO_2^- (nitrite) and NO_3^- (nitrate) ions appear at $\lambda = 206$ and 211 nm [58], respectively, if those ions are present. Therefore, the absorbance detected at those wavelengths reveals whether NO_2^- and NO_3^- ions formed during the reaction in our system. As illustrated in Fig. 11, consecutive measurements did not detect any absorbance in the wavelength range of 200–230 nm during the photocatalytic process, thereby excluding the possibility of the second reaction pathway, which yields these ions as the final products.

3.9.2. Photodegradation mechanism

As indicated earlier, rG-BiFeO₃ showed the highest photocatalytic activity for NH_3 degradation under visible light. Compared with that of the BiFeO₃ material, the diffuse reflectance spectrum of the rG-BiFeO₃ shows a red shift and an enhanced absorption of visible light, indicating that the rG-BiFeO₃ catalyst can utilize visible light more effectively than pure BiFeO₃ for the photocatalytic degradation of NH_3 (Fig. 12).

Fig. 11. UV-vis (full-wavelength scanning) recorded during degradation of NH_3 by rG-BiFeO₃. Conditions: 0.2 g of rG-BiFeO₃, 50 mL of solution, 50.0 mg/L $\text{NH}_3\text{-N}$, $\text{pH} = 11$.

Fig. 12. UV-visible diffuse reflectance spectra of BiFeO₃ (1) and rG-BiFeO₃ composite (2).

The transient photocurrent responses of BiFeO₃ and rG-BiFeO₃ electrodes were also recorded via several on-off cycles of irradiation. Fig. 13 shows the photocurrent transient responses under visible light and in the dark for these samples, where the photocurrent was measured at 0.8 V vs. SCE in Na₂SO₄ aqueous solution (0.1 mol/L). The photocurrent of the rG-BiFeO₃ was much higher than that of the BiFeO₃, indicating that the separation efficiency of photo-generated electrons and holes was much improved as a result of the electronic interaction between BiFeO₃ nanoparticles and graphene sheets.

Based on previous research [59], the most plausible mechanism for the degradation of NH₃ under visible-light irradiation is presented in Scheme 1. Photo-generated electrons and holes within the pure BiFeO₃ either took part in redox reactions at the surface or recombined. However, in rG-BiFeO₃, the photo-generated electrons transferred to graphene. Thus, the possibility of the recombination of electron-hole pairs decreased, enhancing NH₃ degradation. Meanwhile, O₂ molecules adsorbed on the surface of graphene and BiFeO₃ could capture e⁻ to form ·O₂⁻ radicals, while the holes reacted with the adsorbed water to form hydroxyl radicals. Finally, the holes, superoxide anion radicals, and hydroxyl radicals directly oxidized NH₃ adsorbed on the surface of the rG-BiFeO₃. This photocatalytic mechanism can be summarized as follows:

Fig. 13. Photocurrent transient responses of BiFeO₃ (1) and rG-BiFeO₃ (2).

Scheme 1. Reaction mechanism of the rG-BiFeO₃ photocatalyst for NH₃ degradation.

Active-species trapping experiments were carried out to identify the main oxidizing agent in the photocatalytic reaction process. Isopropanol (1.0 mL), disodium ethylenediamine tetraacetate (EDTA-2Na) (10 mg), and nitrogen gas were introduced as scavengers for the various reactive species, i.e., hydroxyl radicals (·OH), holes (h⁺), and superoxide anion radicals (·O₂⁻), respectively. As shown in Fig. 14, the addition of isopropanol greatly reduced the photodegradation rate of NH₃, whereas the addition of EDTA-2Na and purging with nitrogen gas had relatively weak effects on the photodegradation of NH₃. Therefore, we can conclude that hydroxyl radicals played the role of the main oxidant in the rG-BiFeO₃ system.

4. Conclusions

A novel heterogeneous photocatalyst consisting of graphene-supported BiFeO₃ was successfully prepared using a one-step hydrothermal method. The rG-BiFeO₃ hybrid photocatalyst effectively degraded NH₃ into N₂ under visible-light irradiation. Analysis of the reaction mechanism of the catalyst showed that its highly efficient photoactivity could be ascribed to the powerful synergistic effect of the combination of BiFeO₃

Fig. 14. Photocatalytic degradation of 50 mg/L NH₃-N in 50 mL solution (1) 50.0 mg/L NH₃-N + 0.20 g rG-BiFeO₃ + visible light; (2) 50.0 mg/L NH₃-N + 0.20 g rG-BiFeO₃ + isopropanol + visible light; (3) 50.0 mg/L NH₃-N + 0.20 g BiFeO₃ + EDTA-2Na + visible light; (4) 50.0 mg/L NH₃-N + 0.20 g rG-BiFeO₃ + N₂ + visible light.

and the rG sheets. Holes, superoxide anion radicals, and hydroxyl radicals, arising from the interaction between rG and BiFeO₃, oxidized NH₃ directly to N₂. It was found that the NH₃ removal efficiency increased with increasing pH. The optimal efficiency of the photocatalytic degradation process reached 91.2% at pH = 11 and a catalyst dosage of 0.2 g. Cycling and stability tests showed that the rG-BiFeO₃ catalyst was highly stable through multiple cycles, and easily separable after each cycle for subsequent reuse, suggesting its potential utility in the degradation of NH₃.

References

- [1] M. Cassidy, J. P. Ouweltjes, N. C. Dekker, in: R. Steinberger-Wilckens, W. Lehnert, eds., *Innovation in Fuel Cell Technologies*, RSC Press, London, **2010**, 169–171.
- [2] S. H. Xiao, J. H. Qu, X. Zhao, H. J. Liu, D. Wan, *Water Res.*, **2009**, 43, 1432–1440.
- [3] H. Yuzawa, T. Mori, H. Itoh, H. Yoshida, *J. Phys. Chem. C*, **2012**, 116, 4126–4136.
- [4] J. Netting, *Nature*, **2000**, 406, 928–928.
- [5] D. Saha, S. Deng, *J. Chem. Eng. Data*, **2010**, 55, 5587–5593.
- [6] H. M. Huang, Q. W. Song, W. J. Wang, S. W. Wu, J. K. Dai, *J. Environ. Manage.*, **2012**, 101, 68–74.
- [7] D. Yang, C. M. Ezyske, *Water Res.*, **2011**, 45, 6189–6194.
- [8] A. R. Ricardo, G. Carvalho, S. Velizarov, J. G. Crespo, M. A. Reis, *Water Res.*, **2012**, 46, 4556–4568.
- [9] N. Değermenci, O. N. Ata, E. Yıldız, *J. Ind. Eng. Chem.*, **2012**, 18, 399–404.
- [10] H. X. Huo, H. Lin, Y. B. Dong, H. Cheng, J. H. Wang, L. X. Cao, *Hazard. Mater.*, **2012**, 229, 292–297.
- [11] C. Stoquart, P. Servais, P. R. Bérubé, B. Barbeau, *J. Membr. Sci.*, **2012**, 411, 1–12.
- [12] M. Altomare, G. L. Chiarello, A. Costa, M. Guarino, E. Selli, *Chem. Eng. J.*, **2012**, 191, 394–401.
- [13] H. Kominami, H. Nishimune, Y. Ohta, Y. Arakawa, T. Inaba, *Appl. Catal. B*, **2012**, 111, 297–302.
- [14] M. Altomare, M. V. Dozzi, G. L. Chiarello, A. Di Paola, L. Palmisano, E. Selli, *Catal. Today*, **2014**, 252, 184–189.
- [15] Y. Shavisi, S. Sharifnia, S. N. Hosseini, M. A. Khadivi, *J. Ind. Eng. Chem.*, **2014**, 20, 278–283.
- [16] Y. Zhou, B. Xiao, S. Q. Liu, Z. D. Meng, Z. G. Chen, C. Y. Zou, C. B. Liu, F. Chen, X. Zhou, *Chem. Eng. J.*, **2016**, 283, 266–275.
- [17] B. Xiao, S. Q. Liu, *Acta Phys.-Chim. Sin.*, **2014**, 30, 1697–1705.
- [18] M. Altomare, G. L. Chiarello, A. Costa, M. Guarino, E. Selli, *Chem. Eng. J.*, **2012**, 191, 394–401.
- [19] H. Kominami, H. Nishimune, Y. Ohta, Y. Arakawa, T. Inaba, *Appl. Catal. B*, **2012**, 111, 297–302.
- [20] P. A. Kolinko, D. V. Kozlov, *Appl. Catal. B*, **2009**, 90, 126–131.
- [21] Y. C. Dong, Z. P. Bai, R. H. Liu, T. Zhu, *Atmos. Environ.*, **2007**, 41, 3182–3192.
- [22] Q. J. Geng, Q. J. Guo, C. Q. Cao, Y. C. Zhang, L. T. Wang, *Ind. Eng. Chem. Res.*, **2008**, 47, 4363–4368.
- [23] M. Altomare, E. Selli, *Catal. Today*, **2013**, 209, 127–133.
- [24] X. Y. Chen, T. Yu, F. Gao, H. T. Zhang, L. F. Liu, Y. M. Wang, Z. S. Li, Z. G. Zou, J. M. Liu, *Appl. Phys. Lett.*, **2007**, 91, 022114/1–022114/3.
- [25] Z. F. Bian, Y. N. Huo, Y. Zhang, J. Zhu, Y. F. Lu, H. X. Li, *Appl. Catal. B*, **2009**, 91, 247–253.
- [26] T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, S. W. Cheong, *Science*, **2009**, 324, 63–66.
- [27] J. H. Luo, P. A. Maggard, *Adv. Mater.*, **2006**, 18, 514–517.
- [28] T. Soltani, M. H. Entezari, *Ultrason. Sonochem.*, **2013**, 20, 1245–1253.
- [29] X. Wang, Y. Lin, X. F. Ding, J. G. Jiang, *J. Alloys Compd.*, **2011**, 509, 6585–6588.
- [30] F. Gao, X. Y. Chen, K. B. Yin, S. Dong, Z. F. Ren, F. Yuan, T. Yu, Z. G. Zou, J. M. Liu, *Adv. Mater.*, **2007**, 19, 2889–2892.
- [31] W. Wang, N. Li, Y. Chi, Y. J. Li, W. F. Yan, X. T. Li, C. L. Shao, *Ceram. Int.*, **2013**, 39, 3511–3518.
- [32] L. F. Fei, J. K. Yuan, Y. M. Hu, C. Z. Wu, J. L. Wang, Y. Wang, *Cryst. Growth. Des.*, **2011**, 11, 1049–1053.
- [33] S. Li, Y. H. Lin, B. P. Zhang, Y. Wang, C. W. Nan, *J. Phys. Chem. C*, **2010**, 114, 2903–2908.
- [34] S. Q. Liu, B. Xiao, L. R. Feng, S. S. Zhou, Z. G. Chen, C. B. Liu, F. Chen, Z. Y. Wu, N. Xu, W. C. Oh, Z. D. Meng, *Carbon*, **2013**, 64, 197–206.
- [35] P. Niedzielski, I. Kurzyca, J. Siepak, *Anal. Chim. Acta*, **2006**, 577, 220–224.
- [36] G. I. Titelman, V. Gelman, S. Bron, R. L. Khalfin, Y. Cohen, H. Bianco-Peled, *Carbon*, **2005**, 43, 641–649.
- [37] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.*, **2008**, 130, 5856–5857.
- [38] A. N. Cao, Z. Liu, S. S. Chu, M. H. Wu, Z. M. Ye, Z. W. Cai, Y. L. Chang, S. F. Wang, Q. H. Gong, Y. F. Liu, *Adv. Mater.*, **2010**, 22, 103–106.
- [39] J. C. Liu, H. S. Jeong, J. Z. Liu, K. M. Lee, J. Y. Park, Y. H. Ahn, S. N. Lee, *Carbon*, **2010**, 48, 2282–2289.
- [40] C. Nethravathi, T. Nisha, N. Ravishankar, C. Shivakumara, M. Rajamathi, *Carbon*, **2009**, 47, 2054–2059.

Graphical Abstract

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Efficient removal of ammonia with a novel graphene-supported BiFeO₃ as a reusable photocatalyst under visible light

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rG-BiFeO₃ showed a 91.20% degradation of 50 mg/L NH₃ under visible light at pH 11 in the absence of hydrogen peroxide. Holes, superoxide anion radical and hydroxyl radical oxidize NH₃ directly to N₂.

- [41] M. M. Murshed, G. Nénert, M. Burianek, L. Robben, M. Mühlberg, H. Schneider, R. X. Fischer, T. M. Gesing, *J. Solid State Chem.*, **2013**, 197, 370–378.
- [42] H. W. Zhang, X. Y. Fu, S. Y. Niu, Q. Xin, *J. Alloys Compd.*, **2008**, 457, 61–65.
- [43] M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, C. Capillas, A. Kirov, H. Wondratschek, *Z. Kristallogr.*, **2006**, 221(1), 15–27.
- [44] D. Voll, A. Beran, H. Schneider, *Phys. Chem. Miner.*, **2006**, 33, 623–628.
- [45] Z. T. Hu, J. C. Liu, X. L. Yan, W. D. Oh, T. T. Lim, *Chem. Eng. J.*, **2015**, 262, 1022–1032.
- [46] X. Q. Fu, F. L. Bei, X. Wang, S. O. Brien, J. R. Lombardi, *Nanoscale*, **2010**, 2, 1461–1466.
- [47] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Y. Jia, Y. Wu, S. T. Nuyen, R. S. Ruoff, *Carbon*, **2007**, 45, 1558–1565.
- [48] Y. S. Fu, P. Xiong, H. Q. Chen, X. Q. Sun, X. Wang, *Ind. Eng. Chem. Res.*, **2012**, 51, 725–731.
- [49] S. Balachandran, M. Swaminathan, *J. Phys. Chem. C*, **2012**, 116, 26306–26312.
- [50] S. Balachandran, M. Swaminathan, *Dalton Trans.*, **2013**, 42, 5338–5347.
- [51] E. M. Bensen, S. Schroeter, H. Jacobs, J. C. Broekaert, *Chemosphere*, **1997**, 35, 1431–1445.
- [52] M. Mouallem-Bahout, S. Bertrand, O. Peña, *J. Solid State Chem.*, **2005**, 178, 1080–1086.
- [53] S. Guo, G. K. Zhang, Y. D. Guo, J. C. Yu, *Carbon*, **2013**, 60, 437–444.
- [54] O. B. Ayodele, B. H. Hameed, *J. Ind. Eng. Chem.*, **2013**, 19, 966–974.
- [55] X. D. Zhu, S. R. Castleberry, M. A. Nanny, E. C. Butler, *Environ. Sci. Technol.*, **2005**, 39, 3784–3791.
- [56] J. Lee, H. Park, W. Choi, *Environ. Sci. Technol.*, **2002**, 36, 5462–5468.
- [57] D. L. Miles, C. Espejo, *Analyst*, **1977**, 102, 104–109.
- [58] A. W. Sun, H. Chen, C. Y. Song, F. Jiang, X. Wang, Y. S. Fu, *RSC Adv.*, **2013**, 3, 4332–4340.

可见光辐射下新型可循环石墨烯-铁酸铋杂化催化剂高效光催化降解氨氮

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摘要: 近年来, 本课题组利用简单的一步水热法, 将石墨烯和铁酸铋、铁酸镍进行掺杂, 先后制备出石墨烯铁酸铋和活性炭铁酸镍纳米光催化材料, 并发现在可见光辐射作用下, 这两种光催化剂均能利用可见光能量催化分解过氧化氢产生活性因子, 从而有效地降解氨。基于此, 本文采用简单的水热法成功制备出新型的高效多相石墨烯铁酸铋(rG-BiFeO₃)催化剂, 并尝试在不添加H₂O₂的条件下进行光降解氨氮实验。结果表明, 该复合光催化剂仍可接受可见光辐射, 在rG和BiFeO₃的协同作用下高效地光分解氨氮。

由X射线衍射结果计算出rG-BiFeO₃的平均粒径约为18.5 nm。通过清晰的rG-BiFeO₃的透射电镜图可以观察到, BiFeO₃纳米颗粒物较均匀地分散在rG的二维表面上。对比BiFeO₃和rG-BiFeO₃的傅里叶变换红外光谱可以发现, rG和BiFeO₃之间可能形成了化学键。拉曼光谱结果表明, 相对于纯的GO, rG-BiFeO₃拉曼谱线的D带和G带发生了蓝移, 表明石墨烯铁酸铋复合材料中的GO被充分还原成石墨烯。对比BiFeO₃和rG-BiFeO₃的紫外-可见漫反射光谱发现, rG-BiFeO₃的漫反射光谱发生了红移, 表明rG-BiFeO₃光催化材料对可见光的响应程度进一步提高。比表面积测定表明, BiFeO₃的比表面积为21.0 m²/g, 而rG-BiFeO₃催化剂的比表面积则增加到48.6 m²/g, 说明rG-BiFeO₃的吸附性能将得到很大提高。

可见光催化反应结果表明, 在不添加H₂O₂, pH = 11的条件下, 0.2 g rG-BiFeO₃对50 mg/L NH₃-N的降解率达到91.2%。动力学研究表明, BiFeO₃光催化剂氧化氨氮反应遵循一级反应动力学规律。另外, 由于BiFeO₃纳米材料本身具有一定的弱磁性, 所以BiFeO₃和rG的复合材料也具有一定的磁性, 较易回收。催化剂经过7次循环使用后, 仍然具有很高的光催化活性。根据已有文献报道, 吸附在催化剂表面的氨氮被氧化的路径有两条: (1)氨在被氧化为NH₂, NH和N₂H_{x+y} (x+y = 0, 1, 2)等一系列中间产物后, 最终被分解为氮气; (2)氨被氧化为中间产物HONH₂, 最终分解为硝酸盐和亚硝酸盐。本文利用紫外-可见分光光度计对rG-BiFeO₃光降解体系下的氨溶液进行了全波长扫描, 在206和211 nm处未检测到任何吸光度, 从而排除了氨氮最终分解产物为硝酸盐和亚硝酸盐的可能性。这意味着 rG-BiFeO₃可见光降解氨体系符合第一种氧化路径。进一步的机理研究表明, 反应过程中石墨烯与铁酸铋之间的协同作用所产生的空穴、超氧阴离子自由基和羟自由基共同将NH₃直接氧化成N₂, 其中羟基自由基在整个氧化分解过程中起着最主要的作用。

关键词: 石墨烯-铁酸铋; 光催化剂; 可见光; 氨去除

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