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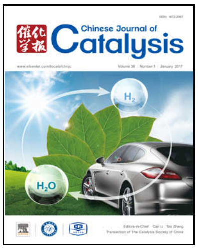

Article

Efficient removal of ammonia with a novel graphene-supported $BiFeO_3$ as a reusable photocatalyst under visible light

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ABSTRACT

Graphene-supported $BiFeO_3$ (rG-$BiFeO_3$) 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-$BiFeO_3$. The specific surface area of the rG-$BiFeO_3$ catalyst was 48.6 m^2/g, larger than that of $BiFeO_3$ (21.0 m^2/g). When used as a heterogeneous photocatalyst, rG-$BiFeO_3$ achieved 91.20% degradation of a NH_3-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 $BiFeO_3$, oxidized NH_3 directly to N_2.

1. Introduction

Ammonia (NH_3) 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, NH_3 is also a nutrient source that can promote eutrophication and algal growth in natural waters [2]. Excessive amounts of NH_3 in the environment can exert harmful effects on human health [3]. NH_3 attacks the human respiratory system, skin, and eyes, and exposure to high concentrations (>300 ppm) may cause death [4,5].

The discharge of NH_3 from wastewater has become an urgent challenge. Various conventional technologies, including biological processes, chemical precipitation, advanced oxidation processes, ion exchange, air stripping, adsorption, and the use of membranes, are applied to remove NH_3 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 NH_3 [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 (TiO_2) and TiO_2-based materials, which are the primary photocatalysts explored for NH_3 degradation, can completely destroy N–H bonds [18–23]. However, TiO_2-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 (rG-$MnFe_2O_4$) and activated carbon bonded to nickel ferrite (AC-$NiFe_2O_4$). 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 ($FeCl_3\cdot6H_2O$) and sodium hydroxide (NaOH) were purchased from Tianjin Damao Chemical Factory. Bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot5H_2O$), ammonium sulfate ($(NH_4)_2SO_4$) 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 MΩ cm deionized Milli-Q water.

2.2. Synthesis of rG-$BiFeO_3$

$Bi(NO_3)_3\cdot5H_2O$ (4.8507 g, 0.01 mol) and $FeCl_3\cdot6H_2O$ (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 °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 °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 Cu K_α 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 °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 °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-