



# High performance of magnetic BiFeO<sub>3</sub> nanoparticle-mediated photocatalytic ozonation for wastewater decontamination



Jing Yin, Gaozu Liao<sup>\*</sup>, Jialu Zhou, Chumei Huang, Yu Ling, Ping Lu, Laisheng Li<sup>\*</sup>

Guangdong Provincial Engineering Research Center for Drinking Water Safety, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

## ARTICLE INFO

### Article history:

Received 20 January 2016

Received in revised form 5 May 2016

Accepted 28 May 2016

Available online 30 May 2016

### Keywords:

Bismuth ferrite

Photocatalytic ozonation

Norfloracin

Synergy

Hydroxyl radical

## ABSTRACT

In this paper, bismuth ferrite (BiFeO<sub>3</sub>) magnetic nanoparticles were used as visible light photocatalyst in the photocatalytic ozonation coupling system. It was successfully synthesized by thermal decomposition of a glyoxylate complex. The as-prepared photocatalyst was characterized by XRD, FT-IR, SEM, TEM, UV–Vis DRS and vibrating sample magnetometer. The magnetic hysteresis loop demonstrated that BiFeO<sub>3</sub> possessed certain magnetization. Oxalic acid (OA) and norfloracin (NFX) were selected as target pollutants for photocatalytic ozonation reactions to evaluate the catalytic ability of BiFeO<sub>3</sub>. The pseudo-first-order kinetic rate constants of degrading OA and NFX removal in O<sub>3</sub>/Vis/BiFeO<sub>3</sub> at given time are 5.48 and 1.65 times as great as the sum of that when using Vis/BiFeO<sub>3</sub> and O<sub>3</sub>, respectively. This enhancement was due to a synergy between photocatalysis and ozonation triggered by BiFeO<sub>3</sub>. In O<sub>3</sub>/Vis/BiFeO<sub>3</sub> process, the photo-generated electrons produced on BiFeO<sub>3</sub> could be trapped by ozone and reaction with them. Subsequently, the improved yield of hydroxyl radicals enhanced the degradation efficiency of organics. In addition, the stability and reusability of BiFeO<sub>3</sub> in photocatalytic ozonation process were examined in this work.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Recent years, it is well known that the combination of various advanced oxidation processes (AOPs) may result in an enhanced generation of oxidative species, and consequently accelerate the degradation and mineralization of refractory organic pollutants [1–3]. In this sense, an increasing number of worldwide researchers have paid attention to a new combined oxidation method called photocatalytic ozonation, which is coupling photoactivated semiconductors (as photocatalysts) with ozone [4–7]. This combination resulting in synergistic effects is thought to be a promising technique for wastewater decontamination [8]. On one hand, the synergistic effects between semiconductor-mediated photocatalysis and ozonation not only effectively improve the utilization of ozone but also decrease the recombination rate of photo-generated electrons and holes. On the other hand, the decomposition of dissolved ozone is primarily responsible for the formation of non-selective hydroxyl radicals ( $\cdot\text{OH}$ ), which react with almost all organic molecules at a rate of  $10^6$ – $10^9 \text{ M}^{-1} \text{ s}^{-1}$  [9].

In photocatalytic ozonation system, TiO<sub>2</sub> is one of the widely-investigated materials due to its nontoxicity, good stability and

excellent photocatalytic activity [10–13]. However, because of the band gap limitation (about 3.2 eV), TiO<sub>2</sub> can only absorb ultra-violet light which occupies about 4% of the total solar energy [14]. Therefore, in order to increase solar energy harvesting efficiency, researchers always seek for new catalysts that are photocatalytically active under visible light irradiation. It is essential for the practical applications of photocatalytic technique in wastewater decontamination.

Bismuth ferrite (BiFeO<sub>3</sub>) has attracted much attention as a well-known multiferric compound that displays the coexistence of ferroelectric and antiferromagnetic order above room temperature [15,16]. Recently, BiFeO<sub>3</sub> has been used for applications in photocatalysis [17,18] and photovoltaics [19] due to its narrow energy band gap (2.0–2.7 eV) and ferroelectric property. Additionally, BiFeO<sub>3</sub> was also used as nanocatalysts for contaminant degradation in heterogeneous Fenton-like reactions [20–22]. During heterogeneous Fenton-like process, BiFeO<sub>3</sub> could effectively catalyze the decomposition of H<sub>2</sub>O<sub>2</sub> into  $\cdot\text{OH}$  which was responsible for degrading organic pollutants. In conclusion, the properties of BiFeO<sub>3</sub> allow it to be one of the third-generation visible-light responsive photocatalysts [23].

To the best of our knowledge, there are no reports on application of BiFeO<sub>3</sub> nanoparticle-mediated photocatalytic ozonation (O<sub>3</sub>/Vis/BiFeO<sub>3</sub>) for wastewater decontamination. It is

<sup>\*</sup> Corresponding authors.

E-mail addresses: [liaogaozu@m.scnu.edu.cn](mailto:liaogaozu@m.scnu.edu.cn) (G. Liao), [llsh@scnu.edu.cn](mailto:llsh@scnu.edu.cn) (L. Li).

expected that BiFeO<sub>3</sub> nanoparticle is a powerful candidate for the catalytic activation of ozone due to the perovskite-type structure and Fe element of BiFeO<sub>3</sub>. Moreover, BiFeO<sub>3</sub> is also expected to exhibit behaviors of catalytic ozonation resulting in an enhanced synergy between photocatalysis and ozonation. In this study, BiFeO<sub>3</sub> nanoparticle was synthesized by thermal decomposition of a glyoxylate complex achieved by the redox reaction between ethylene glycol and nitrate anions. The resulting product as an active photocatalyst in the photocatalytic ozonation system is expected to achieve efficient removal of organics under visible light irradiation. The performance of magnetic BiFeO<sub>3</sub>-mediated photocatalytic ozonation for wastewater decontamination was investigated detailedly. Oxalic acid (OA) and norfloxacin (NFX) were selected as target pollutants in photocatalytic ozonation reactions to test the catalytic ability of BiFeO<sub>3</sub> under visible light irradiation.

## 2. Experimental section

### 2.1. Chemicals and reagents

Iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) were provided by MACKLIN (Shanghai, China). Ethylene glycol, nitric acid, phosphoric acid, oxalic acid and norfloxacin were purchased from Guangzhou Chemical Reagents Factory. The reagents were used without further purification. Deionized water was used to prepare aqueous solutions.

### 2.2. Synthesis of BiFeO<sub>3</sub>

The precursor of BiFeO<sub>3</sub> was synthesized by dissolving 16 mmol of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in 15 mL of 3 mol L<sup>-1</sup> nitric acid solution and then added into ethylene glycol containing 16 mmol Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O under magnetic stirring at 100 °C for 2 h. After drying at 130 °C, the synthesized precursor was decomposed at 500 °C for 2 h in ambient air. The resulting product was finally hand-grinded into fine powders.

### 2.3. Characterization of BiFeO<sub>3</sub>

The crystal structure of the sample was identified by X-ray diffraction (XRD, BRUKER D8 ADVANCE) employing Cu-Kα radiation. FT-IR spectra were recorded on a Nicolet 6700 spectrophotometer with KBr as the reference sample. The morphology of the sample was observed on a scanning electron microscopy (SEM, Hitachi SU8020). The sizes of the sample was measured by the transmission electron microscopic (TEM, FEI Tecnai G20, America) with an accelerating voltage of 200 kV. The XPS characterization was investigated by a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI, America). UV-Vis absorption spectra were characterized using a UV-Vis spectrophotometer (U-3010, HITACHI, Japan) with BaSO<sub>4</sub> pellet. The magnetic property (M - H curve) was measured at 300 K on a vibrating sample magnetometer (MPMS-XL-7, Quantum Design).

### 2.4. Photocatalytic ozonation experiments

1 L tubular photoreactor (h = 400 mm, Φ<sub>in</sub> = 85 mm) was used to perform the photocatalytic ozonation experiments. A high pressure xenon lamp (GXH500W, China) was used as the visible light source. The reaction used the flowing aqueous NaNO<sub>2</sub> solution (1 M) as a filter to eliminate UV light (λ < 400 nm) [24,25]. The reaction temperature was controlled by a thermostatic bath (SDC-6, Ningbo, China). Ozone was generated by an ozone generator (COM-A-D-01-OEM, Anseros, Germany). The ozonized oxygen

was continuously fed into the solution through a porous glass plate and flowed upward at the bottom of the reactor with a flow rate of 1.0 L min<sup>-1</sup>. The dosage of ozone was 75 mg h<sup>-1</sup>. 1 L simulated wastewater (the initial concentration of oxalic acid solution and norfloxacin solution were both 10 mg L<sup>-1</sup>) and 0.20 g catalyst powder were added into the reactor. The samples were filtered by 0.45 μm micro-filters. The continuous ozonation reaction was quenched in the samples by 300 mg L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

### 2.5. Analytical procedures

The concentration of OA was detected by high performance liquid chromatography (HPLC, LC10A, Shimadzu, Japan) using a UV detector (SPD-10AV) at 210 nm and a diamonsil 5U C18 column (5 L m, 250 × 4.6 mm, China). The analysis was measured using a mobile phase containing ultrapure water and phosphoric acid solution at about pH = 2.5 with the flow rate of 1.0 mL min<sup>-1</sup>. Total organic carbon (TOC) removal of NFX was analyzed by TOC 5000 analyzer (Shimadzu, Japan).

## 3. Results and discussion

### 3.1. Morphology and structural characterization

The morphology of BiFeO<sub>3</sub> was observed by scanning electron microscopy (SEM) as displayed in Fig. 1. As we can see from the image, the BiFeO<sub>3</sub> nanoparticles distributed averagely and present quasi spherical shapes with grain sizes range from 50 to 150 nm. The TEM image of BiFeO<sub>3</sub> shown in the inset of Fig. 1 revealed that the particles were observed roughly spherical.

### 3.2. Crystal structure of BiFeO<sub>3</sub>

The XRD pattern of BiFeO<sub>3</sub> nanoparticle was demonstrated in Fig. 2. According to JCPDS NO. 86-1518, the peaks in the XRD pattern were corresponded to a pure-phase BiFeO<sub>3</sub> with a rhombohedral perovskite structure, which is well consistent with the reported documents [26–28]. No additional peaks related to the impurity were observed in the highly crystalline and single phase BiFeO<sub>3</sub>.

Fig. 3 present FT-IR spectrum of BiFeO<sub>3</sub> nanoparticle, indicating its perovskite type vibrations. Three strong absorption peaks observed around 447 cm<sup>-1</sup>, 557 cm<sup>-1</sup> and 621 cm<sup>-1</sup> in the FT-IR spectrum were attributed to O–Fe–O bending vibrations, the

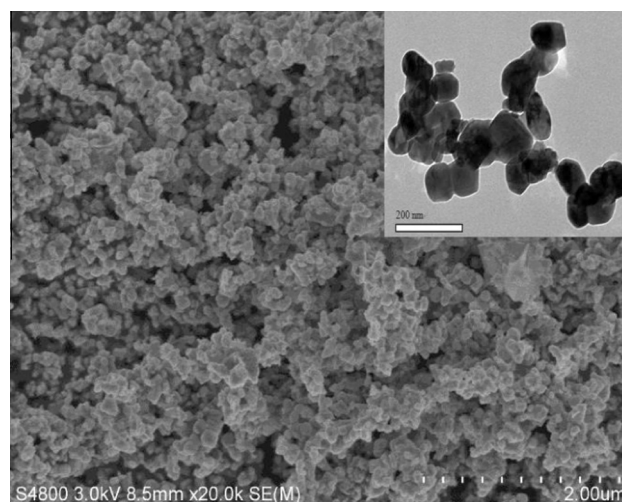


Fig. 1. SEM image of BiFeO<sub>3</sub> nanoparticle (the inset shows TEM of BiFeO<sub>3</sub>).

Download English Version:

<https://daneshyari.com/en/article/640051>

Download Persian Version:

<https://daneshyari.com/article/640051>

[Daneshyari.com](https://daneshyari.com)