Separation and Purification Technology 202 (2018) 242–247

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Fabrication of magnetic Co/$BiFeO_3$ composite and its advanced treatment of pharmaceutical waste water by activation of peroxysulphate

Huixuan Zhang[a], Shi Cheng[a], Bo Li[a,c], Xiuwen Cheng[a,c,*], Qingfeng Cheng[b]

[a] Key Laboratory of Western China's Environmental Systems (Ministry of Education), College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, PR China
[b] College of Resources and Environment, Chengdu University of Information Technology, Chengdu 610225, PR China
[c] Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xinning Road 18, Chengxi District, Xining 810008, PR China

ARTICLE INFO

Keywords:
Co/$BiFeO_3$
Persulfate
Tetracycline
Sulfate radicals

ABSTRACT

In the present study, cobalt-doped bismuth ferrite (Co/$BiFeO_3$) composite was fabricated by sol-gel method, followed by annealing treatment. Afterwards, physicochemical properties of the resulting composite were systematically studied by scanning electron microscope, X-ray diffraction, transmission electron microscope, N_2 physical adsorption/desorption and vibration magnetometer measurements. Results indicated that after doping with Co species, average diameter of $BiFeO_3$ distinctly reduced, accordingly, specific surface area increased, in which Co element existed in the form of Co_3O_4. In addition, Co/$BiFeO_3$ displayed superior magnetic recovery characteristics. Furthermore, Co/$BiFeO_3$ composite was applied to decompose tetracycline in water by activation of persulfate (PS, $S_2O_8{}^{2-}$) via the formation of sulfate radicals. It was found that Co/$BiFeO_3$ exhibited high efficiency for removal of tetracycline, in which 81.09% of tetracycline could be decomposed. This study provides a versatile strategy to fabricate high-efficient recyclable catalysts which would be applied in advanced pharmaceutical waste water treatment.

1. Introduction

In recent years, the production and use of pharmaceutical and personal care products (PPCPs) as un-biodegradable substances have grown rapidly, causing them to remain in the water body, soil and atmospheric environments. Until the late of 1990s, they were demonstrated as environmental pollutants and were widely concerned. Up to date, PPCPs have been potentially harmful to human beings, animals, plants and microbes [1–3].

Antibiotics are one of the most widely used PPCPs in the treatment of infected humans and animals. However, these antibiotics are difficult to completely metabolize, and their residues are discharged into the environment through urine and feces [4–6]. Tetracyclines as a typical antibiotic, due to its cheapness, easy to utilization and side effects, in the low dose can increase the growth of livestock and poultry, and high doses can be used to treat diseases and other reasons, is widely used in livestock production [7]. In many countries such as China, India and USA, tetracycline was reported as the most widely used antibiotic in animal feed [8,9]. Hamscher et al. [10] indicated that the content of tetracycline and chlorotetracycline was 4.0 mg·kg^{-1} and 0.1 mg·kg^{-1} in liquid manure, respectively. Hirsch et al. [11] systematically analyzed the effluent and surface water in a German wastewater treatment plants (WWTPs) and detected the presence of antibiotics such as tetracyclines, sulfonamides, etc., with a concentration of tetracycline of 20 ng·L^{-1}. Sarmah et al. [12] analyzed four groundwater samples from Iowa, USA, and found that there are a variety of antibiotic substances such as oxytetracycline, chlorotetracycline and lincomycin. Jiang et al. [13] studied water samples from 19 sampling sites along the Huangpu River in June and December 2009, the results showed that all 19 sampling sites were contaminated by antibiotic substances, with the highest content of sulfonamides and tetracycline.

In the past decades, removal of tetracycline has been widely studied by other researchers, various technologies have been employed to remove and degrade tetracycline, such as ion exchange method [14], membrane technology [15,16], adsorption [4,17,18], wet oxidation method [19,20] and photocatalysis. Among them, advanced oxidation processes have been recognized as a promising technology due to its low cost, high efficiency, and non-selectivity [21,22]. Therefore, exploiting the novel, high-efficient and eco-friendly nano-materials for wastewater treatment are necessary. The use of transition metal cobalt activated persulfate (PMS) to produce sulfate radicals is one of the most effective means of activation. Homogeneous Co/PMS system has many

* Corresponding author at: College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, PR China.
E-mail address: chengxw@lzu.edu.cn (X. Cheng).

https://doi.org/10.1016/j.seppur.2018.03.072
Received 28 January 2018; Received in revised form 25 March 2018; Accepted 30 March 2018
Available online 31 March 2018
1383-5866/

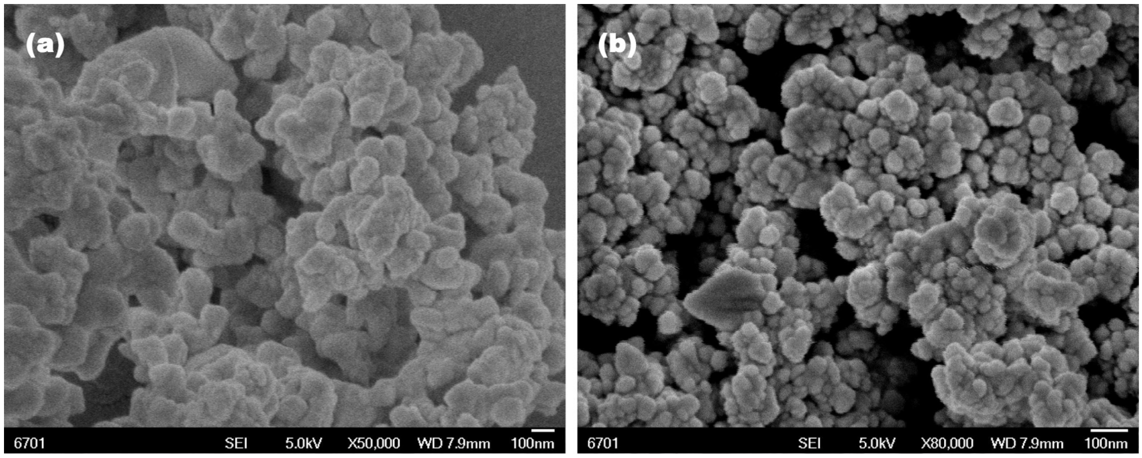

Fig. 1. SEM image of $BiFeO_3$ (a) and $Co/BiFeO_3$ (b) nanoparticles.

advantages such as high catalytic efficiency and strong oxidation ability. But at the same time, it has many limitations, such as difficult to recover the catalyst from the slurry system, and cobalt may be dissolved in water, which could induce health problems [23–25]. If the Co^{2+} can be fixed, then the above bottlenecks can be overcome. As a typical perovskite type oxide (ABO_3) and a good heterogeneous catalyst, $BiFeO_3$ material has good magnetic properties, strong acid and alkali resistance, can effectively activate hydrogen peroxide and other oxidants. Luo et al. found that $BiFeO_3$ can activate H_2O_2 to produce hydroxyl radicals, which can efficiently degrade RhB [26]. As reported, Co possessed higher results than Fe by activating persulfate due to the similarity and chemical properties of atomic radius. Thus, Co-doped $BiFeO_3$ can be formed, allowing Co and Fe to act synergistically to activate PMS. As a result of the formation of $Co/BiFeO_3$ structure, to avoid the dissolution of Co, reducing the pollution; the catalyst has a magnetic, easy recycling, so that the catalyst can be reused, economic and environmental protection.

In this study, cobalt-doped bismuth ferrite ($Co/BiFeO_3$) nano-particle was prepared by sol-gel process, and its physicochemical properties were analyzed. Meanwhile, the catalytic activity of $Co/BiFeO_3$ was evaluated by degradation of tetracycline via the formation of sulfate radicals and hydroxyl radicals by catalyzing PS.

2. Materials and methods

2.1. Materials

Ferric nitrate, cobalt nitrate, bismuth nitrate and potassium persulfate were purchased from Tianjin Kemiou Chemical Reagent Co. LTD. Ethylene glycol monomethyl ether and citric acid, nitric acid and ethylene glycol were from Lianlongbohua (Tianjin) Pharmaceutical Chemical Co. LTD. Methylene blue was purchased from Tianjin Institute of Chemical Reagents, and tetracycline was from Tokyo Chemical Industry Co. Ltd. All chemicals were of analytical reagent grade and used without any further purification. Ultra-pure water was used throughout this experiment.

2.2. Fabrication of $Co/BiFeO_3$ composite

Co-doped $BiFeO_3$ ($Co/BiFeO_3$) composite was fabricated through sol-gel method, followed by annealing treatment. In detail, 8.0 mmol of bismuth nitrate, 72 mmol of ferric nitrate and 8.0 mmol of cobalt nitrate were uniformly mixed in a beaker under stirring at 333 K. Then, 20 mL of ethylene glycol methyl ether and 100 μL of 0.1 $mol·L^{-1}$ nitric acid were added. Afterwards, 8.0 mmol citric acid and 10 mL ethylene glycol were also added into the aforementioned mixture. Noted, dark brown sol was promptly formed. Next, the dark brown sol was heated and evaporated to form a tan gel in an oil bath at 373 K for 1 h. Subsequently, the gel was transferred to a crucible for carbonization of 30 min. Finally, the composite was dried at 773 K for 2 h in an oven.

2.3. Characterization

Surface morphology of $Co/BiFeO_3$ composite was observed by scanning electron microscopy (SEM) at 20 kV. The crystal structure, composition and lattice constant of samples were measured on a Rigaku D/MAX III-3B X-ray diffractometer (XRD) with Cu kα (λ = 0.15418 nm) radiation. The accelerating voltage and applied current were held at 40 kV and 200 mA, respectively. TECNAI G2 transmission electron microscope (TEM) was applied to record the morphology and particle size of $Co/BiFeO_3$. The specific surface area and pore size distribution of samples were measured on a AUTOSORB-1 (Quantachrome Instruments) at 77 K. It should be pointed that the as-fabricated samples had been vacuum-dried at 573 K overnight before measurements. Lakershore Model 7304 instrument was used to measure the magnetic properties of samples.

2.4. Performance of $Co/BiFeO_3$ composite

In this study, tetracycline was selected and served as probing molecule to evaluate the activity of $Co/BiFeO_3$ composite. In each run, 30 mg of $Co/BiFeO_3$ sample was added into 60 mL of tetracycline solution (10 $mg·L^{-1}$) under stirring. Prior to reaction, the suspension was kept in dark for 20 min to ensure the establishment of adsorption/desorption equilibrium. Afterwards, 0.2 g PS was dropwise added into the system. At given time intervals, the collected samples after centrifugation and filtration (through a 0.22 μm membrane) were measured at the characteristic peak of 356 nm by using a T6 ultraviolet-visible spectrophotometer. Also, several individual experiments were carried out to distinguish the contribution of hydroxyl radicals and sulfate radicals. Noted, triplicate analyses were performed for each sample.

3. Results and discussion

Fig. 1 showed the top-view SEM image of $BiFeO_3$ and $Co/BiFeO_3$ samples. Clearly, both of samples exhibited an irregular shape with a relatively narrow size distribution. By comparison, the particle size of $BiFeO_3$ became smaller after decoration with Co species, which could be ascribed to the following aspects. Firstly, participation of cobalt made the crystallization more difficult and inhibited the grains growth of $BiFeO_3$, resulting in the decrease of particle size. Secondly, the addition of cobalt increased the rate of nucleation and consequently resulted in a smaller particle size. In addition, there was a certain degree