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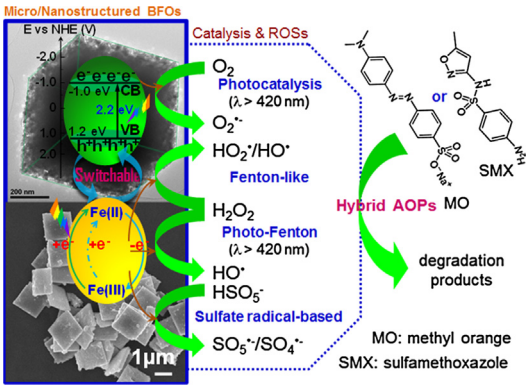
Controllable mullite bismuth ferrite micro/nanostructures with multifarious catalytic activities for switchable/hybrid catalytic degradation processes

Zhong-Ting Hu [a,b,*], Wen-Da Oh [c], Yiquan Liu [d], En-Hua Yang [b], Teik-Thye Lim [b,e,*]

[a] College of Environment, Zhejiang University of Technology, Hangzhou 310014, China
[b] School of Civil and Environmental Engineering, Nanyang Technological University (NTU), 50 Nanyang Avenue, Singapore 639798, Singapore
[c] Nanyang Environment and Water Research Institute (NEWRI), NTU, 1 Cleantech Loop, CleanTech One, Level 6, Singapore 637141, Singapore
[d] Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Avenue, Singapore 639798, Singapore
[e] Environmental Chemistry & Materials Centre, Nanyang Environment and Water Research Institute (NEWRI), NTU, 1 Cleantech Loop, CleanTech One, Level 6, Singapore 637141, Singapore

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, controllable preparation of micro/nanostructured bismuth ferrites (BFOs) were used to investigate multifarious heterogeneous catalyses, including Fenton/Fenton-like reaction, photocatalysis, photo-Fenton oxidation, and peroxymonosulfate (PMS) activation. Results showed that BFO can be used as a novel catalyst to activate switchable catalytic degradation of organic matters. Additionally, a novel catalytic system for degradation of organic pollutants, which integrating all-above heterogeneous catalyses is denoted as BFO/H_2O_2/PMS hybrid reaction, is introduced for the first time. BFO/H_2O_2/PMS system effectively degraded > 99% for both methyl orange (MO) and sulfamethoxazole (SMX) within 60 min, which shows better efficiency than above BFO-driven catalyses. The major SMX degradation pathway in BFO/H_2O_2/PMS system is proposed *via* detecting intermediates using LC/MS/MS. It was found that catalytic activities of BFOs are in the order of BFO-L (co-precipitation, micro/nanosize, single crystals exposing facet (0 0 1)) > BFO-H (hydrothermal, nanocluster with a higher surface area than other BFOs) > BFO-C (fabricated using calcination process, microsize), which demonstrated that crystallographic orientation is more significant in heterogeneous catalyses than specific surface area at

* Corresponding authors at: College of Environment, Zhejiang University of Technology, Hangzhou 310014, China (Z.-T. Hu). School of Civil and Environmental Engineering, Nanyang Technological University (NTU), 50 Nanyang Avenue, Singapore 639798, Singapore (T.-T. Lim).
E-mail addresses: zthu@ntu.edu.sg (Z.-T. Hu), cttlim@ntu.edu.sg (T.-T. Lim).

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micro/nanoscale. Besides, the required H_2O_2 consumption for achieving 99% TOC removal was identified in BFO-driven photo-Fenton oxidation. The other effects on degradation efficiency, such as H_2O_2 dosage and pH, were investigated as well. In Fenton/Fenton-like reaction, reaction conditions suggested are ~61.5 mM H_2O_2 dosage and pH ≥ 4.5 to avoid quenching of HO· into HO_2 by excessive H_2O_2 and Fe leaching.

1. Introduction

Advanced oxidation processes (AOPs) are one of the most effective remediation technologies for removing refractory organic pollutants in water/wastewater treatment. The key AOPs include UV photochemical oxidation, peroxone reaction (H_2O_2/O_3), ozonation, conventional Fenton oxidation, electrochemical oxidation, ultrasonication, supercritical water oxidation (SCWO), heterogeneous photo-Fenton oxidation, and photocatalysis [1–4]. The AOP based on heterogeneous catalysis has received increasing attention as a promising technology for the advantages of (1) eco-friendly, (2) cost-effective, (3) ease of catalyst recovery, (4) simpler post-treatment, and (5) energy efficient. From the viewpoint of environmental applications, it is critical to develop a solid catalyst with nontoxicity, good physiochemical stability, and high catalytic activity for effectively activating heterogeneous catalysis.

Over the past decades, metal oxides have attracted considerable attention as heterogeneous catalysts for various catalytic processes. For examples, TiO_2 has been extensively studied as an UV-driven heterogeneous catalyst for photocatalytic removal of recalcitrant pollutants [5,6]. The Fe_2O_3/Fe_3O_4 has been extensively developed as catalyst for Fenton/Fenton-like and photo-Fenton reaction [7]. As compared with the Fenton/Fenton-like reaction, photo-Fenton reaction by virtue of absorbing light energy can enhance the formation of radical species in the presence of illumination [8,9]. Moreover, Co_3O_4 is widely used to generate sulfate radical via catalytic activation of peroxymonosulfate (PMS, HSO_5^-) [10]. However, there are some disadvantages associated with the application of these metal oxides as heterogeneous catalyst for water treatment, such as low efficiency and poor stability of catalysts, strict conditions required for reaction systems (e.g., lower pH), or toxic metal leaching (e.g., Co^{2+}). As such, a robust catalyst without these disadvantages is desirable.

In ternary metal oxides, redox coupling effect between different polyvalent metal cations within a crystalline structure is beneficial to obtaining a robust catalyst with high activity (via strong electron-electron interactions) and chemical stability [11]. Recent studies revealed that ternary metal oxides can be utilized as heterogeneous catalysts for various applications including photocatalysis, photo-Fenton and Fenton/Fenton-like reactions, and PMS activation in water/wastewater treatment. In (photo-) catalytic oxidations, the mechanism of reaction can be ascribed to the redox reaction involving the interconversion of $M^{(n+1)+}/M^{n+}$ (M = metal element) state within the metal oxide catalyst along with the formation of various reactive oxygen species (e.g.·H_2O_2 converted to HO· or HO_2·, PMS to $SO_4^{\cdot-}$ or $SO_5^{\cdot-}$). The reported ternary metal oxides as catalysts for water treatment include $Bi_2Fe_4O_9$, $BiFeO_3$, $CuFeO_2$, $LaFeO_3$, MFe_2O_4 (M = Fe, Mn, Co, Ni, Cr, Cu, Mg, Zn, or Ti), and $M'_xM''_yO_z$ (M′ = Co, Cu, Mn, Zn, Ni, or Ru; M″ = Bi, Al, Ru, or Cr) [10,12–22]. It has been reported that nanostructured bismuth ferrite (e.g., $Bi_2Fe_4O_9$) exhibits remarkable visible-light-driven photo-Fenton and photocatalysis for the degradation of refractory organic pollutants in aqueous systems due to its narrow bandgap (~2.2 eV), iron-rich characteristics, distorted structure and spontaneous polarization [23,24]. In perspective, a catalyst possessing more than one desired catalytic abilities (or namely multifunctionalized catalysts) can be one of the most attractive candidates for degradation of organic matter in wet atmosphere. Moreover, the catalytic activity of metal oxides has a close relationship with material characteristics in terms of crystallographic orientation, crystallinity, nanostructure, morphology, particle size and surface property (namely structure-activity relationship) [25–29]. However, the daunting challenges in synthesis of $Bi_2Fe_4O_9$ are preventing formation of impurity phases and tuning its morphology, nanostructure or particle size simultaneously since $Bi_2Fe_4O_9$ is sensitive to synthesis parameters such as temperature and oxygen pressure [30].

In this study, different synthesis methods were used to successfully fabricate various bismuth ferrite (BFO)-based catalysts which possess different material characteristics such as single-crystalline or polycrystalline structures, particle sizes, nanostructures, or surface properties. For the first time, BFO was used to investigate the influences of material characteristics and different catalytic oxidation systems on the efficiency of heterogeneous catalyses in water treatment. The effects of pH value and type of chemical agents (H_2O_2, PMS) on the performance of the catalytic oxidation system were investigated. The required dosages of H_2O_2 in Fenton/Fenton-like and photo-Fenton reaction were determined. Besides methyl orange (MO) dye with the TOC removal, the degradation of organic matters were investigated using sulfamethoxazole (SMX) antibiotics. The SMX degradation pathway in BFO-L/H_2O_2/PMS hybrid reactions was proposed based on the detected reaction intermediates using LC/MS/MS. A plausible mechanism of BFO-driven switchable catalytic activity is proposed.

2. Experimental section

2.1. Chemicals and materials

All the chemicals were of analytical grade and used without further purification. The chemicals are bismuth(III) nitrate pentahydrate (≥98%, VWR), ferric(III) nitrate nonahydrate (≥99%, Merck), sodium hydroxide (pellet, Schedelco), nitric acid (1N, Merck), citric acid (≥99.5%, Merck), urea (99%, Sigma-Aldrich), methanol (LC grade, Merck), absolute ethanol (99.9%, Fisher chemical), methyl orange (85%, Sigma), PMS (in the form of Oxone®, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, Alfa Aesar), and hydrogen peroxide (35% w/w, Alfa Aesar). Milli-Q ultrapure water (18.2 MΩ cm) was used for all experiments.

2.2. Preparation of materials

The schematic illustration of the different synthesis methods is presented as shown in Scheme 1. Typically, $Bi(NO_3)_3{\cdot}5H_2O$ (1.21 g) and $Fe(NO_3)_3{\cdot}9H_2O$ (2.02 g) were dissolved in 2 ml of 2 M HNO_3 and citric acid (3.2 g) was dissolved in 5 mL of water, respectively. A transparent solution could be obtained after mixing the two solutions together in Teflon vessel. 33 mL of 12 M NaOH was then instantly added into the solution with vigorous stirring. After stirring for 1 h, the Teflon vessel containing the deep-brown slurry (Bi/