

## Short Communication

## 3D nano-scale perovskite-based composite as Fenton-like system for efficient oxidative degradation of ketoprofen

Hongying Zhao<sup>a,b</sup>, Jinlei Cao<sup>a</sup>, Huanli Lv<sup>a</sup>, Yanbin Wang<sup>a</sup>, Guohua Zhao<sup>a,b,\*</sup><sup>a</sup> Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai 200092, PR China<sup>b</sup> Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, 1239 Siping Road, Shanghai 200092, PR China

## ARTICLE INFO

## Article history:

Received 4 May 2013

Received in revised form 23 June 2013

Accepted 9 July 2013

Available online 16 July 2013

## Keywords:

Perovskite

Heterogeneous

Fenton-like

Stability

Pharmaceutical wastewater

## ABSTRACT

Novel perovskite-based composite BiFeO<sub>3</sub>/carbon aerogel (BFO/CA) as heterogeneous Fenton-like catalyst with three-dimensional (3D) structure, nano-scaled size and high surface area was fabricated by a sol-gel method. Catalyst characterization showed nano BFO active sites were not simply placed on the surface of support CA, but grown along with the 3D structure of CA. The reactivity of catalyst was investigated by the oxidation of ketoprofen as a model pollutant, which exhibited efficient catalytic activity. Moreover, nano BFO/CA retained almost its high catalytic activity in wide pH range of 3–7, and had a very low iron leaching even in acidic condition.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Advanced oxidation process (AOPs) involving the production of highly reactive hydroxyl radicals ( $\text{OH}^\bullet$ ) has shown great potential for destroying various organic pollutants [1,2]. Especially, Fenton's reagent (i.e.,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ) included in AOPs is very attractive since its low cost, wide application range, and mild operating conditions. However, the main shortcomings of the homogeneous Fenton process are the necessity of working at low pH (~3) and the formation of iron oxide sludge [3]. Meanwhile, iron ions ( $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$ ) could not be recycled, generating a new contamination. Therefore, replacing dissolved iron with solid catalysts in so-called heterogeneous Fenton-like reaction is greatly developed to overcome these drawbacks. The general requirements for heterogeneous catalysts in Fenton-like system are: high catalytic oxidation efficiency and  $\text{H}_2\text{O}_2$  utilization, minimum metal leaching, and effectiveness at extended pH range. Lots of studies about exploring heterogeneous catalysts suitable for Fenton process have been previously reported, such as iron oxides [4], and iron-immobilized zeolites, clays and carbon materials [5]. However, many of them do not show favorable catalytic activity [6]. Apart from this, care should be taken to minimize the possibility of Fe leakage from catalysts and supports which often results new pollution for the treated water.

Perovskite-style oxide ( $\text{ABO}_3$ ) was reported as important heterogeneous catalysts in industrial reactions: the decomposing of nitrogen

oxides, and the oxidation of hydrocarbon, CO and  $\text{NH}_3$  [7,8]. BiFeO<sub>3</sub> (BFO), as a typical  $\text{ABO}_3$  compound, has stable perovskite-type structure in liquid phase and Fe element, which is a powerful candidate for catalytic activation of  $\text{H}_2\text{O}_2$  with high stability [9]. Whereas, since the catalytic ability of typical BFO was not so strong especially in pure Fenton process to degrade more persistent and complex pollutants, such as pharmaceutical wastewater [9,10], it is necessary to develop the catalytic activity of BFO in Fenton oxidation reaction.

As an extension of this direction, we fabricated a novel BFO-based catalyst with nano-scale and three-dimensional (3D) network structure to improve its catalytic performance. Here, ketoprofen (KP,  $\text{C}_{16}\text{H}_{14}\text{O}_3$ ), recognized as a refractory and hazardous component in pharmaceutical wastewater, was selected as a target pollutant to be removed. Moreover, this coupled system, not only offers a new idea to improve the activity of catalysts, but also inspires us to design new advanced oxidation system for practical refractory treatment.

## 2. Experimental

All chemicals were of analytic grade and used without further purification. For bulk BiFeO<sub>3</sub>, 0.01 mol  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.01 mol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were dissolved in diluted  $\text{HNO}_3$  solution ( $2 \text{ mol L}^{-1}$ ), forming a mixture solution (denoted as S1). S1 was slowly dropped into KOH solution ( $40 \text{ mL}$ ,  $4 \text{ mol L}^{-1}$ ) to form precipitates. The obtained precipitates were washed with distilled water and ethanol to remove  $\text{K}^+$  and  $\text{NO}_3^-$ , and then added to  $12 \text{ mol L}^{-1}$  KOH solution to form muddy mixture. Finally, the mixture was transferred to a stainless steel Teflon-lined autoclave, which was sealed and heated at  $200 \text{ }^\circ\text{C}$  for 24 h and then naturally cooled to room temperature. The final products

\* Corresponding author at: Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai 200092, PR China. Tel.: +86 21 65981180; fax: +86 21 65982287.

E-mail address: [g.zhao@tongji.edu.cn](mailto:g.zhao@tongji.edu.cn) (G. Zhao).

were collected and washed with distilled water and ethanol, dried at 70 °C for 4 h before further characterization. While for nano BFO, to S1 solution were added 0.02 mol tartaric acid as a complexant. The mixture was stirred around 65 °C for 1 h and then evaporated at 150 °C until to obtain dark viscous resin. The resin was finally calcined at 400 °C in N<sub>2</sub> at 5 °C min<sup>-1</sup> for 2 h. Specially, for nano BFO/carbon aerogel (CA), all preparation procedures were same as nano BFO except another 70wt.% CA (0.7 g) was added into the mixture after tartaric acid.

### 3. Results and discussion

The morphology of as-prepared products was investigated by SEM. The morphological and dimensional of different BFO strongly depend on preparation method. When using hydrothermal process, the bulk BFO showed uniform spherical microstructure (Fig. 1A) with a diameter of about 20 μm. Part of spherical BFO exhibited cracked-structure consisting of small fragmental particles (Fig. 1A, inset). Interestingly, while using sol-gel process, well-defined BFO nanoparticles can be obtained in a large scale with average size of ~60 nm (Fig. 1B). It is well known that the catalytic performance of BFO is closely related with its particle size and structure [11]. Note that, novel BFO nanoparticles with 3D network structure were observed for nano BFO/CA system after using CA as substrate (Fig. 1C). Although CA presents 3D network structure and high surface area (Fig. S1A), BFO active sites were not simply placed on the surface of CA, but were grown along with the 3D structure of CA. In order to clarify this investigation, nano BFO/CA catalyst was recalcined in air at 400 °C for 4 h to remove substrate CA and then examined the structure of pure BFO by SEM (Fig. S1B). It indicated that pure BFO possessed obviously 3D structure and with larger particles than CA.

The phase composition and structure of prepared catalysts were examined by XRD. As shown in Fig. 2., all the reflection peaks can be indexed to perovskite BiFeO<sub>3</sub> (JCPDS card No. 86–1518) and no peaks from other single phase were detected except for nano BFO/CA, which contained one small impurity peak belonged to Bi<sub>24</sub>Fe<sub>2</sub>O<sub>39</sub>. Table 1 shows the BET surface area and bulk Fe composition of catalysts. The specific surface area of bulk BFO was only 1 m<sup>2</sup> g<sup>-1</sup>, while for nano BFO was 14 m<sup>2</sup> g<sup>-1</sup>. When using CA as support, the surface area of nano BFO/CA was increased to 403 m<sup>2</sup> g<sup>-1</sup>. The concentration of Fe for bulk BFO and nano BFO was both around 13.7%, corresponding to 100% BiFeO<sub>3</sub>. While for nano BFO/CA, the Fe% was 6.2%, corresponding to 33% BiFeO<sub>3</sub>.

To get further insight on the structural variations of different BiFeO<sub>3</sub> samples, a Raman study was also carried out, as shown in Fig. 3A. The peaks of bulk BFO catalyst at 136, 166, 216 cm<sup>-1</sup> can be assigned to A<sub>1</sub>(1TO), A<sub>1</sub>(2TO), A<sub>1</sub>(3TO) mode for rhombohedral BiFeO<sub>3</sub> system, respectively, while the peak at 281 cm<sup>-1</sup> was the E mode of BiFeO<sub>3</sub> [12]. It can be clear to see that obtained peaks shift to lower frequencies and the intensity of peaks become weaker for nano BFO and nano BFO/CA catalysts. The difference between the spectra is attributed to the grain size and the morphology. The Raman peaks would become weaker when morphological changes from regular cube (bulk BFO) to irregular aggregation (nano BFO) and dispersion (nano BFO/CA) and the particles size increases [13].

TPR profile in Fig. 3B was used to study the redox properties of obtained catalysts, which may affect its catalytic activity [14]. It is possible to correlate redox properties with the presence of different Fe(III) and Bi(III) surface species. Bulk BFO presented a peak centered at 514 °C with a right-shoulder maximized at 694 °C typically due to the reduction of BiFeO<sub>3</sub> to Bi and Fe(II) and/or even to Fe [15]. All two peak maxima were significantly shifted to a lower temperature for sample nano BFO, i.e., 376 and 484 °C. Hence, it indicated the high reducibility of catalysts. It is interesting to note that nano BFO/CA exhibited a broad peak from 300 to 600 °C, suggesting the high dispersion of BFO active sites. The integrated area of TPR peak, shown in Fig. S2, varied in the

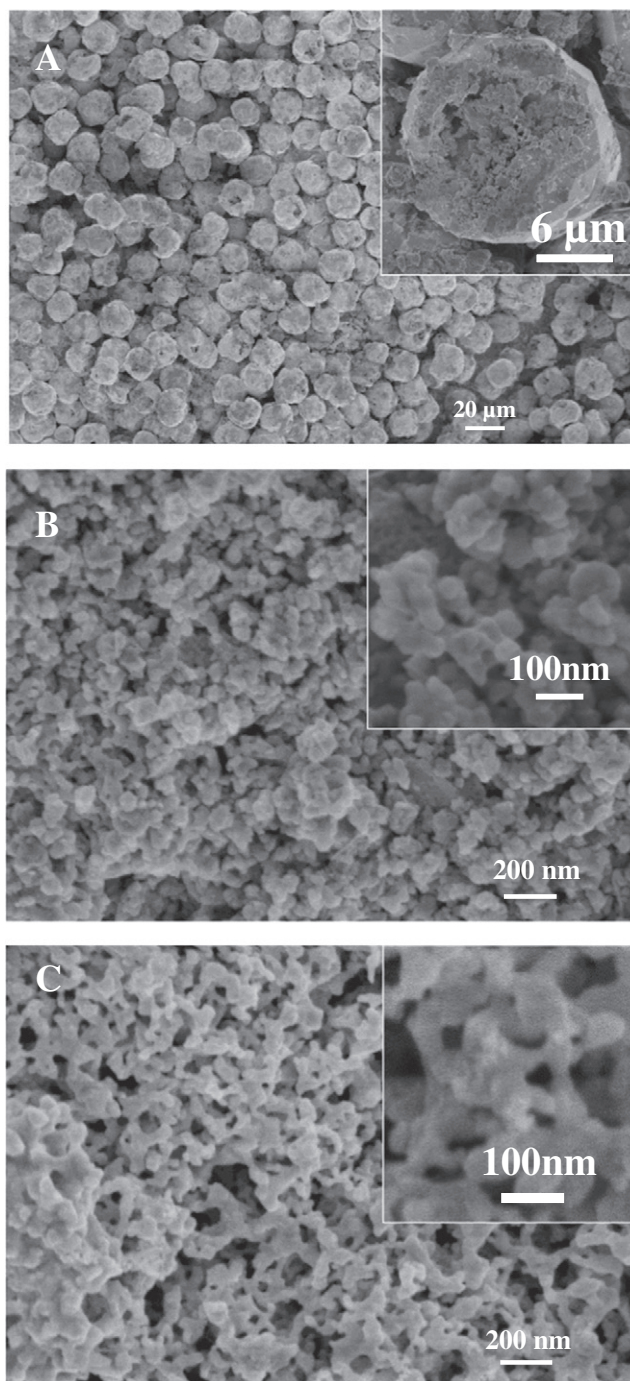


Fig. 1. SEM images of (A) bulk BFO, (B) nano BFO, (C) nano BFO/CA catalysts.

order of bulk BFO < nano BFO < nano BFO/CA, indicating that nano BFO/CA possessed more efficient active sites during the reaction.

The hydroxyl radical ( $\cdot\text{OH}$ ), generated through the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> with active sites, is the crucial parameters for understanding the efficiency of Fenton reaction. Thus we measure the concentration of  $\cdot\text{OH}$  (C<sub>OH</sub>) for different catalysts (see Fig. 4A). It depicted that the  $\cdot\text{OH}$  radical was hard to be produced if only with solo CA. Whereas, the C<sub>OH</sub> for other catalysts was increased with increasing the reaction time. The C<sub>OH</sub> of nano BFO/CA catalyst remained highest during the whole reaction. For example, at 150 min, C<sub>OH</sub> of nano BFO/CA was 24.2 μM, which was 134% and 333% higher than that of pure nano BFO (10.3 μM) and bulk BFO (5.6 μM) catalysts,

Download English Version:

<https://daneshyari.com/en/article/6503542>

Download Persian Version:

<https://daneshyari.com/article/6503542>

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