Materials Research Bulletin xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Materials Research Bulletin

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

# Oxygen-deficient bismuth oxychloride nanosheets: Superior photocatalytic performance

Peng Zhang[a,b,*], Yongfu Qiu[b], Shuyan Yang[a], Yuanqi Jiao[a], Chuanwei Ji[a], Yangping Li[a], Baiman Chen[c], Hongbo Fan[a,b,*]

[a] Dongguan Cleaner Production Center, School of Environment and Civil Engineering, Dongguan University of Technology, Guangdong 523808, PR China
[b] Guangdong Engineering and Technology Research Center for Advanced Nanomaterials, Dongguan University of Technology, Guangdong 523808, PR China
[c] School of Energy and Chemical Engineering, Dongguan University of Technology, Guangdong 523808, PR China

ARTICLE INFO

*Article history:*
Received 21 February 2017
Received in revised form 17 March 2017
Accepted 29 March 2017
Available online xxx

*Keywords:*
Oxygen-deficient
Nanosheets
Photocatalytic
BiOCl

ABSTRACT

It is demonstrated an effective to significantly improve the photocatalytic acitivity of BiOCl hierichial nanosheets by creating oxygen vacancies. These oxygen-deficient BiOCl nanosheets prepared via a two-step process exhibit substantially enhanced photocatalytic performance toward dye degradation when compared to the pristine BiOCl nanosheets. Such the superior photocatalytic performance is owing to the improved light-harvesting ability and increased doner density as a result of the induced oxygen vacancies.



## 1. Introduction

With the ever-increasing concerns on environmental pollution problems, semiconductor oxides photocatalysis has drawn considerable attention as a promising environmental technology for air purification and wastewater remediation [1–3]. Over the past few years, substantial efforts have been put in exploring high-efficient photocatalysts, and various semiconductor oxides including $CeO_2$ [8],$TiO_2$ [4,5], ZnO [6], and $BiVO_4$ [7] have been widely investigated as photocatalysts for wastewater treatment. Among these semiconductors, bismuth oxychloride (BiOCl) is of great interest for its attractive photocatalytic activity that shows better performance than commercial $TiO_2$ in photocatalytic degradation of organic wastewater contaminants under UV light irradiation [9–13]. And it is well known that BiOCl is an indirect band gap semiconductor with a lamellar-structure composing of $[Bi_2O_2]^{2+}$ layers sandwiched between two slabs of halogen ions [9,14]. Such these features allow the spontaneous formation of internal static electric fields within BiOCl, which favors the separation of photogenerated electron−hole pairs and promotes its photocatalytic activity [15]. However, the current photocatalytic performance of BiOCl is still not satisfactory for practical application owing to its wide band gap (~3.5 eV) and fast recombination of photo-generated charge carriers.

In order to overcome these drawbacks, considerable attentions have been directed toward minimizing the band gap and promoting the separation of the photo-generated charge carriers of the BiOCl photocatalysts [12,15,16]. In recent years, great achievements have been made, and two effective strategies have been developed to improve the photocatalytic activity of BiOCl [15,17]. The first strategy is to design nanostructured BiOCl photocatalysts with high surface area and desirable architecture [18–22]. The photocatalytic activity of nanostructures is known to greatly depend on their morphology, structure, component and exposed planes [18,23–25]. It has proven that the nanostructures with a well-defined shape and dimension can not only provide a high interface area for photocatalytic reaction, but also can effectively suppress the recombination rate of photoexcited carriers [26]. In this regard, multifarious BiOCl nanostructures, including nanoparticles [18], nanodisks [19], nanoplates [20], and nanoflowers [21] have been successfully synthesized, and their enhanced photocatalytic activities have been reported. The second one is to construct BiOCl-based heterostructures with reasonable band edge alignment [11,27–29]. For instance, numerous BiOCl heterostructures such as BiOCl/BiOBr [30], BiOCl/BiOI [27], $Bi_2S_3$/BiOCl [31,32] and $Bi_2MoO_6$/BiOCl [33] have been developed and proven to be exhibited much higher photocatalytic performances

* Corresponding authors at: Dongguan Cleaner Production Center, School of Environment and Civil Engineering, Dongguan University of Technology, Guangdong 523808, PR China
*E-mail addresses:* ZhangPeng@dgut.edu.cn (P. Zhang), fhb666666@126.com (H. Fan).

http://dx.doi.org/10.1016/j.materresbull.2017.03.071
0025-5408/

than the pristine BiOCl. Despite these achievements, there is still plenty of room to further improve the photocatalytic activity of BiOCl.

In this work, we reported a facile and effective strategy for significantly improving the photocatalytic activity of the BiOCl hierarchical nanosheets by inducing oxygen vacancies. As a fundamental and intrinsic defect, oxygen vacancy have proven to play a great role in determining the electronic and physico-chemical properties of the BiOX (X = Cl, Br, I) photocatalysts [9,10,34]. Recent reports have shown that oxygen vacancies servers as shallow donors for BiOX (X = Cl, Br, I), and their donor density (electrical conductivity) as well as charge transportation will substantially enhanced with the increase the density of oxygen vacancies [8,35,36].On the other hand, hierarchical nanostructures not only offer a high surface area for photocatalytic reaction, but also can shorten the diffusion pathway of species and facilitate the separation of the photogenerated carriers [37,38]. Benefiting from these advantages above, the BiOCl hierarchical nanosheets with oxygen vacancies that obtained through a facile cost-effective electrochemical reduce method yielded a substantially higher photocatalytic activity than the pristine BiOCl hierarchical nanosheets for methyl orange (MO) degradation under light irradiation. Further, the as-prepared oxygen-deficient BiOCl hierarchical nanosheets also have excellent photocatalytic stability with no any decay in photocatalytic activity after 5 cycles.

## 2. Experimental section

### 2.1. Preparation of oxygen-deficient BiOCl nanosheets

All the reagents were of analytical grade and used without any purification. Hierarchical BiOCl nanosheets arrays were synthesized via a modified solvothermal method according to the previous literature [39]. In a typical process, 1 mmol $Bi(NO_3)_3$ and 1 mmol KCl were dissolved in 20 mL of methanol at room temperature, and the solution was kept with continuous stirring for 2 h. Then, a cleaned F doped $SnO_2$ (FTO) glass substrate with a size of $2 \times 3$ cm was placed in a 50 mL Teflon lined stainless autoclave with the aforementioned solution. The autoclave was allowed to be heated up to 160 °C and kept at 160 °C for 8 h under spontaneous pressure. After cooled to room temperature, the final FTO substrate coated with a layer of BiOCl hierarchical nanosheets was washed anhydrous ethanol several times. To introduce oxygen vacancies into the BiOCl nanosheets, the as-prepared BiOCl hierarchical nanosheets were electro-reduced with −1.1 V vs Ag/AgCl for 30 s in a three-electrode cell with a platinum counter electrode, and follow calcined at 400 °C in $N_2$ atmosphere for 1 h (denoted as N-BiOCl). The electrolyte is 1 M $Na_2SO_4$. For comparison, the as-prepared BiOCl nanosheets were also annealed at 400 °C for 1 h in air (denoted as A-BiOCl).

### 2.2. Characterizations

The morphology, composition and crystal phase structures of products were investigated by field-emission SEM(FE-SEM, JSM-6330F), TEM(TEM, JEM2010-HR, 200 kV), X-ray diffractometry (XRD, D8 ADVANCE) and XPS(XPS, ESCALab250, Thermo VG). EPR spectra were recorded on a Bruker, A300-10-12 Bruker EPRspectrometer at 77 K with 5.00 G modulation amplitude and a magnetic field modulation of 100 kHz.The optical absorption properties of the samples were measured with an UV–vis–NIR spectrophotometer(UV–vis–NIR, Shimadzu UV-2450). All the electrochemical measurements were performed on a CHI 760D electrochemical

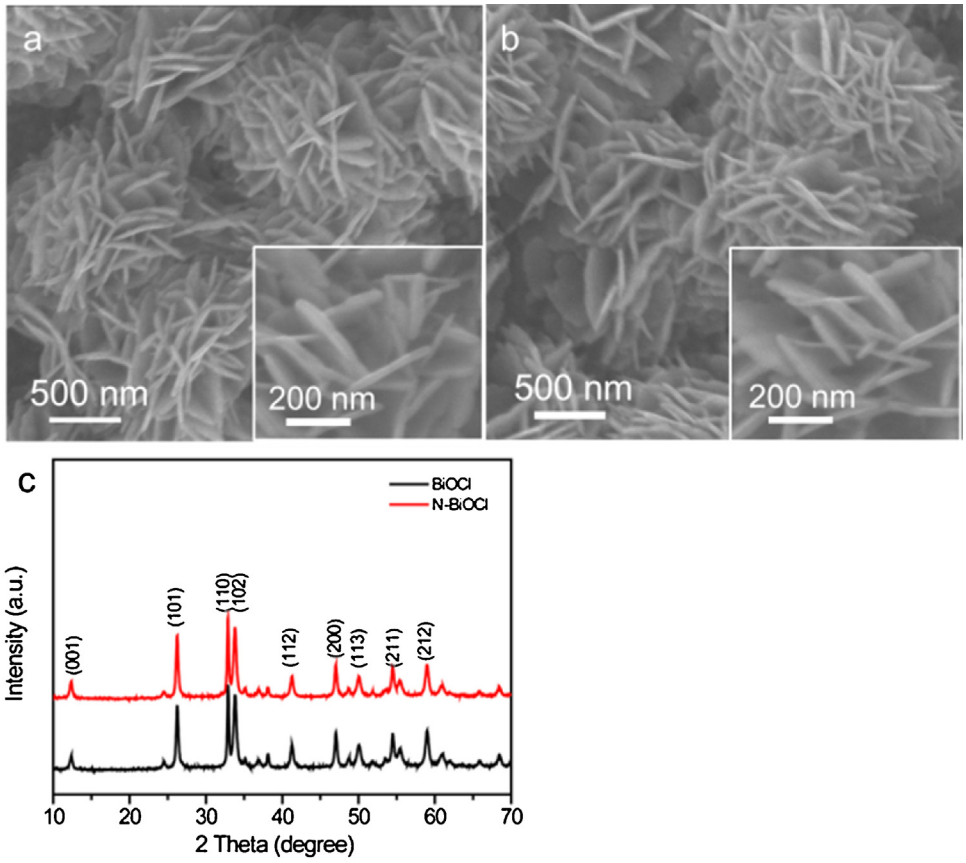


**Fig. 1.** SEM images of the as-prepared (a) BiOCl and (b) N-BiOCl hierarchical nanosheets. (c) XRD patterns of the BiOCl and N-BiOCl hierarchical nanosheets.

Please cite this article in press as: P. Zhang, et al., Oxygen-deficient bismuth oxychloride nanosheets: Superior photocatalytic performance, Mater. Res. Bull. (2017), http://dx.doi.org/10.1016/j.materresbull.2017.03.071