Journal of Power Sources 293 (2015) 409–415

Contents lists available at ScienceDirect

Journal of Power Sources

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

Synthesis of black ultrathin BiOCl nanosheets for efficient photocatalytic H_2 production under visible light irradiation

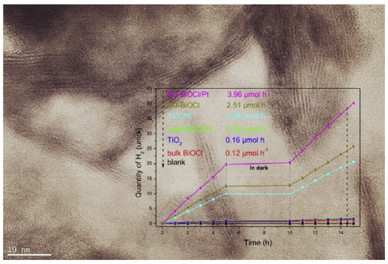
Liqun Ye [a], [*], Xiaoli Jin [a], Yumin Leng [b], Yurong Su [a], Haiquan Xie [a], [*], Chao Liu [a]

[a] College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, People's Republic of China
[b] College of Physics and Electronic Engineering, Nanyang Normal University, Nanyang 473061, People's Republic of China

HIGHLIGHTS

- Black ultrathin BiOCl nanosheet (BU–BiOCl) was synthesized.
- BU-BiOCl have expanded spacing of the (001) crystal plane and oxygen vacancy.
- BU-BiOCl showed very high activity for H_2 production under visible light irradiation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form
7 May 2015
Accepted 23 May 2015
Available online

Keywords:
BOCl
Ultrathin nanosheets
Photocatalysis
Visible light
H_2 production

ABSTRACT

The thickness of 2D BiOCl nanosheets along [001] direction control the internal electric fields intensity. In order to enhance the photocatalytic properties of BiOCl, decreasing the thickness is the best choice. In this paper, black ultrathin BiOCl nanosheet (BU–BiOCl) with expanded spacing of the (001) crystal plane and oxygen vacancy was synthesized in high viscosity and alcohol group concentration glycerol system. It was characterized by X-ray diffraction patterns (XRD), X-ray photoelectron spectroscopy (XPS), X-ray photoelectron scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM), electron spin resonance (ESR), UV–vis diffuse reflectance spectra (DRS) and photoluminescence (PL) spectra. The experimental characterization and theoretical calculation results also indicated that expanded facets spacing and oxygen vacancy of as-synthesized BU-BiOCl enhanced separation efficiency of photoinduced carriers and photon absorption efficiency. Therefore, BU-BiOCl showed higher activity than bulk BiOCl for H_2 production under visible light irradiation.

1. Introduction

Photocatalytic technology have gained increasing attention for solar-to-hydrogen/hydrocarbons conversion [1–3]. The traditional photocatalysts (such as TiO_2 and ZnO) have wide band gap. The high position of conduction band (CB) and low position of valence band (VB) can result in high photocatalytic reduction and oxidation ability, respectively. Unfortunately, they can not be excited by visible light. In order to enhance the utilization efficiency of full sunlight spectrum, many attempts have been dedicated and more new visible-light-driven (VLD) photocatalysts were developed to overcome this drawback [4,5].

Recent years, layered nanomaterials, such as atomically-thick graphene, MoS_2 and graphitic carbon nitrides, have been used in

---

[*] Corresponding authors.
E-mail addresses: yeliquny@163.com (L. Ye), Xie-hq@163.com (H. Xie).

http://dx.doi.org/10.1016/j.jpowsour.2015.05.101
0378-7753/© 2015 Elsevier B.V. All rights reserved.

photocatalysis [6–10]. As alternative photocatalysts, bismuth oxyhalides BiOX (X = Cl, Br, and I) also belong to a new class of promising layered semiconductor photocatalysts for environment remediation and energy conversion [11–13]. The layered structures of BiOX consisting of [X-Bi-O-Bi-X] slices stacked together by the van der Waals interaction through the halogen atoms along the [001] direction [14–16]. In the past five years, based on the layered structures of BiOX, many scientific workers have bend themselves to research them. They have reported many exciting achievements which include synthesis of 2D BiOX nanosheets and 3D BiOX structure assembled with 2D nanoplates [17,18], modification of BiOX to improve their visible-light-driven photocatalytic activity, and study on facet effect [19,20]. They also consider that the self-built internal electric field of BiOX can promote the effective separation of the photoinduced electron–hole pairs. More importantly, it was found that the thickness of 2D BiOX nanosheets along [001] direction control the internal electric fields intensity [21–23]. Therefore the photocatalytic properties of BiOX can be enhanced by decreasing the thickness of 2D BiOX nanosheets.

Among layered BiOX photocatalysts, BiOCl show the widest band gap and the highest photocatalytic reduction and oxidation ability [13,18]. But, the pure BiOCl can not display VLD photocatalytic activity [17,18]. At present, cocatalyst utilization, element doping, VLD photocatalysts coupling, surface plasmon resonance and dye sensitization were employed to improve its VLD photocatalytic activity [19,20,24]. However, it can be found that those modifications all needed other materials assisting. We all know that appropriate amount defect is propitious to enhance the visible light absorption and VLD photocatalytic activity [21,25]. So, making defect is a suitable way to modify BiOCl without materials assisting. For examples, black BiOCl with oxygen vacancy has been obtained by UV light irradiation or Fe reduction [25–27].

In this paper, we attempt enhance the internal electric fields intensity and visible light absorption simultaneously. It means that ultrathin thickness and oxygen vacancies all are necessary for BiOCl. Recently, *Zhang* found that the alcohol groups of ethylene glycol can reacts with the oxygen exposed on the (001) surfaces of BiOCl to remove some surface oxygen atoms, resulting in the formation of oxygen vacancies [22]. On the other hand, the viscosity of solvent influences the ion diffraction efficiency, which can regulate the thickness of 2D BiOX nanosheets along [001] direction [28]. Therefore, the ultrathin BiOCl nanosheets with oxygen vacancies may be synthesized in a high viscosity and alcohol group concentration solvent. Comparing with ethylene glycol, glycerol has higher viscosity and more alcohol group. Here, it was used as solvent to prepare BiOCl nanosheets. And TEM images and ESR spectrum showed that the thickness of as-synthesized BU-BiOCl was about 3 nm. The oxygen vacancies and expanded spacing of the (001) crystal plane also were found, which resulted in very high photocatalytic activity of as-synthesized black ultrathin BiOCl (BU–BiOCl) nanosheets for H_2 production.

2. Experimental

2.1. Synthesis

2.1.1. Black ultrathin BiOCl nanosheets

0.002 mol KCl was dissolved into 20 mL glycerol and 0.002 mol $Bi(NO_3)_3 \cdot 5H_2O$ also dissolved into 20 mL glycerol. Then, KCl solution was added into the $Bi(NO_3)_3 \cdot 5H_2O$ solution drop by drop with continuously stirring. The suspension was transferred into Teflon-lined stainless steel autoclaves (50 mL), and then the autoclaves were kept at 160 °C for 16 h. After reaction, the black BiOCl precipitate was obtained by centrifugation, and then washed with ethanol. Finally, it was dried at 60 °C in air.

2.1.2. Bulk BiOCl

The synthesis process is same with that of black ultrathin BiOCl nanosheets except for ethanol as solvent.

2.2. Characterization

X-ray diffraction patterns (XRD) of the samples recorded at room temperature, by a Bruker D8 advance X-ray diffractometer using Cu Kα radiation and 2θ scan rate of 6 min^{-1}. Diffraction patterns were taken over the 2θ range 20–80°. VG Multilab 2000 spectrometer (Thermo Electron Corporation) was used to obtain X-ray photoelectron spectroscopy (XPS, the spectra calibrated to the C 1s peak at 284.6 eV). FESEM images of BU-BiOCl were obtained by a JEOL JEM-7600F Field Emission Scanning Electron Microscope. Their size and morphology of bulk BiOCl were inspected with scanning electron microscope (SEM, FEI, QUANTA 200). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL JEM-2100 (RH) Field Emission Electron Microscope. UV–vis diffuse reflectance spectra (DRS) were obtained using a Shimadzu UV-3600 spectrometer by using BaSO4 as a reference. Photoluminescence (PL) spectra of samples were obtained by a cary eclipse spectro-uorophotometer with $\lambda_{exc} = 310$ nm. The Brunauer–Emmett–Teller (BET) surface areas of samples were measured using quantachrome autosorb-1 automated gas sorption systems at 77 K.

2.3. Photocatalytic experiments

The photocatalytic H_2 production experiments were performed in Labsolar-IIIAG closed gas system (Beijing Perfectlight Technology Co., Ltd China) at ambient temperature. Typically, the photoreaction system contains 50 mg of BU-BiOCl or bulk BiOCl as a photocatalyst, 50 mL of water containing 10 vol% triethanolamine (TEOA) as an electron donor. Long-wavelength pass filter ($\lambda \geq 420$ nm) was equipped with a 300 W xenon lamp to get visible light irradiation. During the whole reaction process, the aqueous solution with photocatalyst was continuously stirred by a magnetic stirrer. The generated hydrogen gas was sampled by a syringe and measured by a gas chromatography (GC9790II, Zhejiang Fuli Analytical Instrument Co., Ltd China) equipped with a thermal conductivity detector (TCD), where Ar was used as a carrier gas.

2.4. Theoretical calculation method

Both the ultrathin and bulk BiOCl (001) nanosheets were studied by the supercell model combined a plane-wave method as implemented in the Vienna ab initio simulation package (VASP) [29,30]. The ion–electron interaction was described by the Perdew-Burke-Ernzerhof (PBE) function [31] with the generalized gradient approximation (GGA) and the core electrons were described by the full-potential projector augmented wave (PAW) method [32,33] with an energy cutoff of 520 eV for the plane-wave expansion. The geometry optimization ended until the force on the relax atoms less than -0.02 eV/Å and all calculations utilized the spin-polarization. Integrations in the Brillouin zone were performed using k-point grid generated with the Monkhorst–Pack grid.

The BiOCl (001) surface was modeled by a periodic slab and the (1 × 1) surface was applied. The thin one was modeled by 11 atom layers with O atoms exposed on the top and bottom; the thick one was modeled by 16 atom layers with the bottom 5 atom layers fixed [14]. The slabs were separated by a vacuum region of 20 Å. The k-point grid $4 \times 4 \times 4$ was used for the BiOI bulk, and $4 \times 4 \times 1$ for the 001 surface.