



Selective photocatalytic oxidation of benzyl alcohol into benzaldehyde with high selectivity and conversion ratio over Bi₄O₅Br₂ nanoflakes under blue LED irradiation



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ABSTRACT

Novel Bi₄O₅Br₂ nanoflakes with a thickness of approximately 5 nm and a band gap energy of 2.54 eV were synthesized by a rapid and energy-saving microwave route. Under blue light emitting diode (LED) irradiation and using the Bi₄O₅Br₂ nanoflakes as a photocatalyst, selective catalytic oxidation of benzyl alcohol (BA) into benzaldehyde (BAD) was successfully achieved with a high selectivity and conversion ratio. Compared to Bi₁₂O₁₇Cl₂, which has a similar blue LED light absorption capability and a band gap energy of 2.37 eV, these Bi₄O₅Br₂ nanoflakes exhibit superb conversion efficiency (>99%) and selectivity (>99%) toward the photocatalytic oxidation of BA into BAD. Based on the structural characterization of the as-synthesized photocatalyst, comparison of photocatalytic performances, investigation of active radicals, and quantum chemical calculations, a possible photoreaction pathway is explored and proposed. It is revealed that the high selectivity of the system comes from direct hole oxidation of alkoxide anions (BA⁻) and the appropriate valence band potential (+2.41 V vs. NHE) of Bi₄O₅Br₂. And the high conversion ratio is attributed to the positively charged surface, large specific surface area with micro-nano structures, and effective separation of photogenerated carriers of the as-synthesized photocatalyst. In addition, the as-synthesized Bi₄O₅Br₂ catalyst remains stable during the photocatalytic conversion process and can be utilized repeatedly, suggesting its potential for practical applications.

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1. Introduction

Benzaldehyde (BAD), the simplest aromatic aldehyde with an active carbonyl group, is widely used in dyestuff, perfumery, and pharmaceutical industries and is also an important organic reaction intermediate [1,2]. Besides, the selective oxidation of aromatic alcohols into corresponding aromatic aldehydes is generally identified as a fundamental reaction for direct synthesis of carbonylation compounds [3]. However, traditional synthesis of BAD through oxidation of liquid toluene or hydrolysis of benzal chloride not only forms the co-product bromobenzene since it uses sodium bromide to accelerate the reaction but also involves toxic or corrosive reagents such as chromate, hypochlorite, peroxy acids, and other chemicals [4]. And the alternative method for oxidizing benzyl

alcohol (BA) into BAD, based on metal complex compounds as the catalyst and molecular oxygen as the oxidant, also requires costly reactants such as noble metals and is a difficult way to produce BAD on a large scale [5]. Therefore, it is necessary and beneficial to develop a green, highly selective, and environmentally friendly approach to produce BAD under moderate conditions.

In past decades, semiconductor-based photocatalysis has been considered as an environmentally friendly and energy-efficient technology in the field of contamination elimination and energy conversion [6–9]. Recently, the photocatalytic partial oxidation of BA into BAD has attracted increasing attention due to its fundamental interest and potential applications. Titanium dioxide (TiO₂) was first used to convert aromatic alcohols to aldehydes under UV light, and approximately 50% conversion and 60% selectivity were achieved [10]. The low selectivity in this case can be ascribed to the fact that the hydroxyl radical formed in the UV-TiO₂ photocatalytic process is a non-selective oxidative species with strong oxidizing ability, resulting in a wide variety of reaction products. To improve

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the reaction selectivity, different types and modifications of TiO₂, such as diverse crystal phases [11], metal ion modifications [12,13], composites [14,15], and noble-metal-loaded TiO₂ [16], have been examined. In one of the most important results, Higashimoto et al. found that BA can be adsorbed on the surface of titanium dioxide to form a special complex that becomes an active center under visible light, resulting in high selectivity and conversion from BA into BAD [17,18]. In addition to TiO₂, CdS-based materials, such as CdS@SnO₂ nanorods [19], CdS-MOFs [20], and graphene-CdS nanocomposites [21], have also attracted attention for showing high selectivity and efficiency of BA conversion under visible light irradiation. Typically, a 60% conversion ratio and more than 80% selectivity can be gained [19]. The higher reaction selectivity over CdS under visible light than that of the UV-TiO₂ process can be attributed to the fact that there are •O₂⁻ and holes, instead of non-selective •OH⁻, acting as the main reactive species in the former.

Bismuth oxyhalides (BiOX, X = Cl, Br, and I), a type of V-VI-VII ternary semiconductor, have demonstrated outstanding photocatalytic performances owing to their unique layered structures, excellent stability, and broad tunable band gaps [22]. Recently, Zhang's group reported that BiOX materials, including Bi₁₂O₁₇Cl₂, Bi₃O₄Br, and BiOBr, can be used as visible-light-driven photocatalysts for the oxidation of BA into BAD with >99% selectivity and up to 44% conversion [23]. The authors believed that the high selectivity comes from the direct hole oxidative mechanism and appropriate band potentials of these catalysts. Very recently, Ding et al. described porous BiOCl hexagonal prisms that exhibited photocatalytic aerobic oxidation of BA to BAD with high activity and chemoselectivity under both UV and visible light [24]. According to their results, a calculated conversion of approximately 21% is obtained after visible light irradiation for 8 h. Moreover, Liu et al. reported a Bi₂₄O₃₁Cl₁₀/BiOCl heterojunction photocatalyst that displayed enhanced photocatalytic activity for BA conversion with >99% selectivity and more than 40% conversion [25]. These results reveal that BiOX-based catalysts are potential candidates for the photocatalytic BA/BAD transformation.

To date, although some studies have presented good selectivity for the BA/BAD conversion, cases reporting a high conversion ratio from BA into BAD are still very limited. Lower conversion implies that additional, complicated separation processes are required to obtain pure BAD, and it may also hinder a true understanding of the photocatalytic conversion pathway of the reaction. Particular attention should be paid to developing a system that can convert BA into BAD with high selectivity as well as a high conversion ratio and to understanding its mechanism. Herein, we demonstrate a Bi₄O₅Br₂ nanomaterial synthesized by a facile microwave route, which could be an exceptional catalyst for photocatalytic oxidation of BA into BAD, with high selectivity (>99%) and a high conversion ratio (>99%). In particular, the reaction conditions are very mild, i.e., under blue light emitting diode (LED) illumination, at ambient temperature and pressure, without additional air/oxygen purging, and without the need for other additives. A possible conversion mechanism for the partial oxidation of BA into BAD is proposed and discussed in detail, based on the experimental results and DFT calculations.

2. Experimental

2.1. Chemicals

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), potassium bromide (KBr), and acetonitrile were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. Ethylene glycol (EG) was obtained from Chinasun Specialty Products Co. Ltd. Benzyl alcohol (BA) and benzaldehyde (BAD) were bought from J&K Chemical Ltd. All chemicals

were analytical grade and used as received without further purification.

2.2. Preparation of photocatalysts

In a typical synthesis of Bi₄O₅Br₂ nanoflakes, 1.0 mmol of Bi(NO₃)₃·5H₂O was dissolved in 50 mL EG under magnetic stirring. Next, 0.5 mmol KBr was added into the solution. After complete dissolution, the solution was transferred into a 150 mL flat-bottom flask and then heated for 4 min at 400 W under atmospheric pressure in a microwave chemical reactor (MCR-3, at a fixed frequency of 2.45 GHz, Beijing Rui Chengwei Industry Equipment Co., Ltd., China). After the reaction, the suspension was cooled down to room temperature. The resulting light yellow precipitate was collected by centrifugation and washed with deionized water and ethanol, and then dried at 60 °C in an oven. Lastly, the product was calcined at 200 °C for 2 h to obtain the final sample.

For comparison, a Bi₁₂O₁₇Cl₂ sample was prepared by a hydrothermal route, according to the method described by Zhang et al. [23]. And three other Bi₄O₅Br₂ samples were respectively synthesized using a molecular precursor hydrolysis route [26], a direct hydrolysis process [27], and a reactable ionic liquids-assisted solvothermal method [28].

2.3. Catalyst characterization

Crystal phase composition and the crystallite size of samples were analyzed by a Bruker D8 Advance X-ray diffractometer (Bruker AXS, Germany) operating with Cu K α radiation at a scanning speed of 6° min⁻¹. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA) measurements were used to determine the surface composition of samples. The morphology and microstructure were observed using a scanning electron microscope (SEM, JSM-6510, JEOL, Japan). UV-vis diffuse reflection spectra (DRS) was acquired on a UV-vis spectrophotometer (UV-3100, Hitachi, Japan) using BaSO₄ as a reference standard. Nitrogen adsorption-desorption isotherms and Brunauer-Emmett-Teller (BET) surface areas were analyzed using an automatic specific surface area analyzer (Micromeritics ASAP 2020, USA). Photocurrent measurements were carried out on a CHI 660C electrochemical station (Shanghai Chenhua Apparatus Corporation, China) using as-prepared samples as the working electrodes with an active area of 1.0 cm², a platinum plate as the counter electrode, a commercial Ag/AgCl electrode as the reference electrode, and 0.5 mol L⁻¹ Na₂SO₄ aqueous solution as the electrolyte. A 300 W xenon lamp (PLS-SXE300/300UV, Beijing Trusttech Co. Ltd., China) assembled with a UV-cut filter to remove all wavelengths lower than 420 nm was used as the light source. Electron paramagnetic resonance (EPR, JES FA-200, JEOL, Japan) was applied to detect free radicals produced in the catalytic process, using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trap under the irradiation in three wavelength ranges ($\lambda > 420$ nm, >450 nm, and >480 nm).

2.4. Computational methods

The frontier electron density (FED) of BA and BA⁻ (alkoxide anion), including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were calculated using density functional theory (DFT) using the Gaussian 09 program. The optimized geometries and vibrational frequencies were obtained by the density functional B3LYP method with 6-311++G(d,p) as the basis set. All optimizations were carried out without any symmetry restrictions and were followed by harmonic frequency analyses to ensure that the optimized conformation was the true global minimum.

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