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Solvothermal synthesis of novel hierarchical $Bi_4O_5I_2$ nanoflakes with highly visible light photocatalytic performance for the degradation of 4-*tert*-butylphenol

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ABSTRACT

A facile solvothermal route is successfully developed to synthesize $Bi_4O_5I_2$, a novel I-poor bismuth oxyiodide, with hierarchical nanoflake structure. The composition, structure, morphology, formation mechanism, photoabsorption, energy band, and photocatalytic properties of this material are systematically investigated. The results reveal that highly pure $Bi_4O_5I_2$ can be easily obtained by reacting Bi^{3+}, I^-, and OH^- at pH values of 6 to 10 under solvothermal conditions, and the formation of such hierarchical structure can be explained by a dissolution–recrystallization mechanism. The as-synthesized $Bi_4O_5I_2$ nanoflakes show a favorable energy band structure (bandgap energy 2.17 eV, conduction band edge potential is more negative than the reduction potential of superoxide radicals), a high specific surface area ($38.6\ m^2\ g^{-1}$), and a hierarchical micro/nano structures. Thus, they exhibit superior photocatalytic and mineralization efficiency for the degradation of 4-*tert*-butylphenol (PTBP, a representative alkylphenol) under visible light irradiation, with a reaction rate is 6.8 and 57 times faster than that of BiOI microspheres and N-doped TiO_2, respectively. The photogenerated reactive species and degradation intermediates are identified, and possible photocatalytic mechanism is proposed. What's more, the as-synthesized $Bi_4O_5I_2$ nanoflakes remain stable during the photocatalytic reaction and can be used repeatedly, revealing their promising applications in the treatment of organic wastewaters.

1. Introduction

Environmental pollution and the energy crisis are two major problems in human society that seriously threaten the existence of terrestrial lives [1]. In the past two decades, numerous investigations have focused on semiconductor-based photocatalysts because they may be widely applied for solar energy conversion and environmental purification [2,3]. To date, many semiconductors have been extensively studied as photocatalysts for degrading pollutants or splitting water [4,5]. However, wide-bandgap semiconductors, such as TiO_2, ZnO, and SnO_2, are only able to absorb <5% of the solar radiation that reaches the earth's surface, while narrow-bandgap semiconductors, such as Fe_2O_3, CuO, and CdS, usually exhibit poor photocatalytic performance due to their high carrier recombination rate, low electronic conduction, low oxidation, or poor photo-stability, which greatly limits their practical applications [6]. Therefore, the development of novel, highly efficient, persistently stable, and visible light driven photocatalysts remains a major challenge.

Recently, as a new family of promising photocatalysts, the bismuth oxyhalides (BiO*X*, *X* = Cl [7], Br [8], and I [9]), have demonstrated remarkable photocatalytic activities because their uniquely layered structure features an internal static electric field perpendicular to each layer that may induce more effective separation of photogenerated charge carriers [10]. Thereinto, BiOI has the smallest band gap and a strong absorption in the visible light region, thus demonstrating excellent photocatalytic efficiency under sunlight irradiation [11]. Aside from BiOI (O:I = 1:1), other I-poor bismuth oxyiodides, including $Bi_4O_5I_2$ [12], $Bi_7O_9I_3$ [13], α-Bi_5O_7I [14], and β-Bi_5O_7I [15], have also been reported. Since the valence band for bismuth oxyiodides mostly contains O 2p and I 5p orbitals, while the conduction band is based the Bi 6p orbital [16], it can be predicted that the I-poor bismuth oxyiodides have bandgap energies that are higher than BiOI but lower than Bi_2O_3 [17,18]; therefore, these materials may be used as visible light induced photocatalysts. More importantly, the composition and structure of the bismuth oxyiodides strongly influences their optical, electronic, oxidizing ability, and other physicochemical properties, offering an

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opportunity to obtain novel photocatalysts that for effective degradation of environmental pollutants with various features. However, the information describing these bismuth oxyiodides' synthesis, characterization, and evaluated properties has remained scarce until recently, especially for $Bi_4O_5I_2$. Recently, Li and coworkers prepared plate-like $Bi_4O_5I_2$ using a precipitation–filtration process followed by hydrothermal treatment and studied its photocatalytic activity for decomposition of methyl orange [19]. To investigate the photocatalytic properties of oxygen-rich bismuth oxyhalides, we synthesized $Bi_4O_5I_2$ using commercial Bi_2O_3, HNO_3, and KI under hydrothermal conditions, and preliminary evaluated its photocatalytic activity for the degradation of bisphenol-A [17]. Nevertheless, due to the restricted crystal growth under the routine depositing conditions, synthesizing nanostructured $Bi_4O_5I_2$ via wet chemical processes remains a major challenge. What's more, the formation conditions, optical properties, electronic structure, photocatalytic activity, and visible light induced photocatalytic mechanism for $Bi_4O_5I_2$ also require further investigation.

As a representative alkylphenol, 4-*tert*-butylphenol (PTBP) is an important industrial chemical that is widely used to make phosphate esters, fragrances, oil field chemicals, detergents, and demulsifiers [20]. Owing to its widespread use, a considerable amount of PTBP has been released into aquatic environments, causing its frequent detection in river and seawaters [21], as well as in aquatic animals [22] and human urine [23]. PTBP is now recognized as a serious aquatic pollutant because it persists in the environment and demonstrates acute and chronic toxicities [24], in addition to estrogenic activity [25,26]. Therefore, removing PTBP from aquatic environments is crucial for environmental protection [27]. However, although heterogeneous photocatalysis are potentially advantageous for the degradation of organic contaminants in water, the photocatalytic decomposition of PTBP has hardly been investigated [28]. To the best of our knowledge, the degradation of PTBP over a non-titania photocatalyst utilizing visible light irradiation has not been reported. In this paper, novel hierarchical $Bi_4O_5I_2$ nanoflakes were synthesized using a solvothermal route; their structure, morphology, photoabsorption, band structure, and specific surface properties were characterized. And then, the $Bi_4O_5I_2$ nanoflakes' photocatalytic and mineralization efficiency for PTBP degradation was evaluated under visible light irradiation, the photogenerated reactive species and degradation intermediates were identified, and possible photocatalytic mechanism was proposed.

2. Experimental

2.1. Materials and methods

The PTBP was obtained from Aladdin Reagent Co., Ltd. The Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) and potassium iodide (KI) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Ethylene glycol (EG) was bought from Chinasun Specialty Products Co., Ltd. All of the chemicals were analytical grade and used as received.

The $Bi_4O_5I_2$ nanoflakes were synthesized using a solvothermal route. In a typical synthesis, 0.728 g $Bi(NO_3)_3{\cdot}5H_2O$ and 0.498 g KI were orderly dissolved in 35 mL EG with magnetic stirring at room temperature, and then the pH of the system was adjusted to 9 using 2 mol L^{-1} NaOH. Afterwards, the mixture was poured into a Teflon-lined stainless-steel autoclave (45 mL capacity) and incubated in an oven at 150 °C for 12 h. After completion of the reaction, the precipitates were collected by centrifugation, washed several times with distilled water and ethanol to remove any ionic residue, and finally dried in an oven at 60 °C.

For comparison, a BiOI sample was synthesized using the same process but without adding the NaOH solution. Additionally, an N-doped TiO_2 (N–TiO_2) sample was prepared by a solvothermal method using ethylenediamine as the nitrogen source, as described by Yang et al. [29] (Fig. S1, Supporting information).

2.2. Crystal structure and theoretical calculation

The crystal structure of $Bi_4O_5I_2$ was modified from that of $Bi_4O_5Br_2$ (ICSD-94498) with replacement of Br by I on the structure, and the details were refined according to previous reports [30]. Subsequently, the crystal structure of $Bi_4O_5I_2$ was used to calculate the theoretical powder diffraction pattern using the Diamond software. The band structure calculations were performed with the Cambridge Serial Total Energy Package (CASTEP) code within Materials Studio that was based on the density functional theory (DFT). Ultrasoft pseudopotentials were used for the geometric optimization to make the computations more tractable and efficient. The exchange and correlation interactions were modeled using the generalized gradient approximation (GGA), together with the Perdew–Burke–Ernzerhof (PBE). A plane-wave cutoff energy of 340 eV was employed. The energies and electronic structures were calculated based on the optimized geometric structures.

2.3. Catalyst characterization

The crystalline structures of the samples were determined using powder X-ray diffraction (XRD) with a Bruker D8 Advance (Bruker AXS, Germany) X-ray diffractometer with Cu $K\alpha$. The sample's surface composition was analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA) equipped with an Al $K\alpha$ source. And the valence band X-ray photoelectron spectroscopy (VB XPS) of as-prepared samples were acquired with an energy step of 0.100 eV. The morphology and structure were examined using scanning electron microscopy (SEM, JSM-6510, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2100HR, Japan).The iodide content in the sample was determined with an ion chromatograph (IC, Dionex ICS 900, USA) equipped with an anion exchange column and an electrical conductivity detector. The specific surface areas were measured using nitrogen adsorption–desorption isotherms at 77 K according to the Brunauer–Emmett–Teller analysis (BET, ASAP 2020, Micromeritics, USA). A desorption isotherm was used to determine the pore size distribution using the Barrett–Joyner–Halenda (BJH) method. The UV–vis diffuse reflection spectra (DRS) was recorded on a UV–vis spectrophotometer (UV-3010, Hitachi, Japan) by using $BaSO_4$ as a reference and was converted from reflection to absorbance by the Kubelka–Munk method.

2.4. Photocatalytic activity measurements

The photocatalytic degradation experiments were performed in a photochemical reactor (XPA-VII, Xujiang, China) equipped with a 1000 W Xe lamp combined with a 420 nm cutoff filter as the light source, and the system was cooled with a circulating water bath maintained at room temperature. All photocatalytic reactions were performed using the same initial conditions: 50 mL reaction solution containing PTBP at various initial concentrations (from 20 to 100 mg L^{-1}, typically 60 mg L^{-1}) was mixed with an *as*-synthesized photocatalyst (varying from 0.5 to 2.5 g L^{-1}, typically 1.0 g L^{-1}) with constant magnetic stirring. Before irradiation, the solution containing the catalyst was stirred for 1 h in the dark to allow the system to reach adsorption equilibrium. During the photocatalytic process, approximately 3 mL of the suspension was taken out at a specified time, and subsequently, the solids were removed from the solution using a 0.45 μm nitrocellulose filter and the filtrate was then