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Facile construction of the phase junction of BiOBr and $Bi_4O_5Br_2$ nanoplates for ciprofloxacin photodegradation

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ABSTRACT

The phase junction of BiOBr and $Bi_4O_5Br_2$ nanoplates is constructed by controlling the basicity in one-pot hydrothermal process. The crystalline phase, morphology, optical property, chemical state of surface elements and photocatalytic performance of the obtained samples are investigated in detail. Results display that the stacked BiOBr particles are gradually transformed to $Bi_4O_5Br_2$ with a multi-plate structure by increasing the pH value. The photocatalytic performance of the obtained samples is estimated by the degradation of ciprofloxacin solution under visible light. It is displayed that the photodegradation activity order is BiOBr/$Bi_4O_5Br_2$ (pH = 7) > $Bi_4O_5Br_2$ > BiOBr, which may be associated with the matching band structure and the efficient transfer and separation of charge. Moreover, a reasonable charge separation pathway is surveyed.

1. Introduction

Along with social development, water pollution has become a serious problem the world is facing today, which is not only caused by the dyes from textile, but also induced by the abuse of antibiotics in human and animal medication [1–3]. As a representative broad-spectrum antibiotic agent, ciprofloxacin (CIP) is widely used and difficultly degraded. Therefore, the removal of CIP from the natural water system and drinking water has urgently been needed for the friendly environment [4,5]. Among technologies dealing with antibiotic waste water, the technology of promising semiconductor photocatalysis has received a lot of attention due to its potential applications [6,7]. However, traditional semiconductor photocatalysts, such as TiO_2 and ZnO, generally have the wide band that can only absorb the ultraviolet part of the sunlight [8–10]. In order to overcome their shortcomings, all kinds of emerging visible light photocatalysts were explored to improve photocatalytic performance by the limit of recombination rate of charge carrier pairs [11].

In recent years, bismuth oxybromide photocatalysts have received much attention due to their unique layered structures, chemically stabilized, nontoxic and excellent photocatalytic performances [12]. To enhance the photocatalytic activity of bismuth oxybromide, many strategies have been developed, such as ion doping [13,14], crystal facets exposure [15,16], morphology modification [17] or construction of semiconductor compound [18]. In particular, phase junction construction of bismuth oxybromide and other semiconductors with matching band potentials is a practical way to enhance their photocatalytic activities.

Among various bismuth oxybromide materials with different Bi/O/Br elemental ratios [17-22], BiOBr has been widely concerned owing to the simplest atomic ratio , the preponderant structure and the suitable energy band (~2.6 eV) [19]. To further enhance the photocatalytic application of BiOBr, its phase junction construction, such as BiOBr/$BiVO_4$ [23], BiOBr/WO_3 [24], BiOBr/g-C_3N_4 [25], BiOBr/$NiFe_2O_4$ [26], and BiOBr/TiO_2 [27], has proven to be effective in improving the photocatalytic performance, which is attributed to the efficient transfer and separation of charge carrier pairs.

Moreover, compared to BiOBr, a Bi-rich bismuth oxybromide material, $Bi_4O_5Br_2$ displays more negative conduction band (CB) and valence band (VB), and more broadened visible light absorption edge, which is believed to be beneficial for improving photocatalytic activity. For example, Xiao et al. [28] reported that the I-doped $Bi_4O_5Br_2$ catalysts, synthesized via a convenient and rapid microwave method, were used to improve degradation of four parabens and mixture of parabens under visible light. Ji's group [29] fabricated 2D-2D g-C_3N_4/$Bi_4O_5Br_2$ composite material via a solvothermal process in the presence of hexadecyl-3-methylimidazolium bromide, which exhibited the enhanced photocatalytic degradation performance.

Furthermore, to the best of our knowledge, the pH value has a great effect on bismuth oxyhalide materials. By adjusting the pH value, a new layered phase gradually appears and combines well with the original phase, which is favorable to enhance the visible light absorbance and to improve the separation of charge carrier pairs [30]. Ning et al. [31] demonstrated that Bi_3O_4Cl/BiOCl plate-on-plate heterojunction

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photocatalyst was synthesized by controlling volume ratio of NaOH to improve the photocatalytic performance. Yu et al. [32] found that BiOI/Bi_5O_7I composite photocatalysts were successfully synthesized through hydrothermal method by adjusting the pH to enhance charge separation. Peng et al. [33] showed that one-dimensional $Bi_{12}O_{17}Br_2$/$Bi_{24}O_{31}Br_{10}$ heterostructures with high photocatalytic performance were prepared for the first time by calcination at 400 °C in air. However, phase junction of BiOBr and $Bi_4O_5Br_2$, which can provide a new possibility to improve the visible light photodegradation performance, has not been reported. Therefore, it is reasonable to suppose that transformation between BiOBr and $Bi_4O_5Br_2$ may also be observed by controlling the basicity.

In this work, a novel BiOBr/$Bi_4O_5Br_2$ phase junction was developed by simply controlling the basicity in one-pot hydrothermal preparation process. It was easy to obtain the well matched BiOBr/$Bi_4O_5Br_2$ composites. The photocatalysis properties of the catalyst samples were demonstrated by degradation of ciprofloxacin solution. BiOBr/$Bi_4O_5Br_2$ phase junction presents the excellent photocatalytic performance for degrading ciprofloxacin. The possible mechanism for the improvement of photocatalytic performance over the BiOBr/$Bi_4O_5Br_2$ composites was studied in detail. The high transfer and separation efficiency for charge carrier pairs contributes to the improvement of photocatalytic performance.

2. Experimental

2.1. Sample preparation

All chemicals used were of analytical grade and were without further purification. 3 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was added in 30 mL deionized water. Under stirring, a certain amount of 2.0 M NaOH was then added dropwise to adjust the pH value to a desired value (pH = 4, 5, 6, 7, or 8). 3 mmol CTAB was dissolved in 30 mL deionized water. Subsequently, the CTAB aqueous solution was transferred to the above prepared $Bi(NO_3)_3{\cdot}5H_2O$ suspension, and the obtained mixture was transferred into a 100 mL Teflon-lined stainless autoclave, which was heated at 180 °C, maintained for 12 h and then cooled down to room temperature naturally. The obtained products were gathered by centrifugation, washed six times and finally dried at 80 °C overnight.

Fig. 1 shows the proposed formation illustration of samples by controlling the pH values. According to experimental results, different color precipitates were obtained. The pale yellow precipitate (pure BiOBr sample) could be prepared without NaOH solution added, and the brilliant yellow precipitate (pure $Bi_4Br_5O_2$ sample) could be obtained at pH = 8. The yellow BiOBr/$Bi_4O_5Br_2$ composite samples named as Br/Br-4, Br/Br-5, Br/Br-6 and Br/Br-7 were synthesized at pH = 4, 5, 6 and 7, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were gained by a Rigaku D/Max 2500 power X-ray diffractometer using CuKα radiation (λ = 0.1542 nm). The scan range is from 5° to 70°. Scanning electron microscopy (SEM) was carried out on a FEI Inspect F50 microscope. Transmission electron microscopy (TEM) images were collected using a JEOL JEM-2100F field emission electron microscope at 200 kV. Diffuse reflectance spectra (DRS) were measured by a Shimadzu UV-3600 spectrophotometer with BaSO4 as a reference, and X-ray photoelectron spectroscopy (XPS) was achieved using an ESCALAB 250Xi X-ray photoelectron spectrometer with monochromated Al Ka radiation. Photoluminescence (PL) intensity was recorded with a wavelength range from 315 to 550 nm on a Fluoro Max-4 instrument.

2.3. Photocatalytic test

The CIP photodegradation was carried out in an improvised photocatalysis reactor under visible light. A 500 W Xe lamp (Shanghai Special Lighting Factory, China) was used to provide the visible-light. In the reactor, 0.1 g of catalyst sample and 100 mL of CIP solution (10 mg/L) were added. Prior to irradiation, the suspension was stirred in the dark for 1 h, which was allowed to obtain the equilibrium of absorption-desorption. After visible light irradiation, 3 mL of liquid was taken and centrifuged at every interval of 30 min. The obtained CIP solution was analyzed at 272 nm using a 752 UV–vis spectrophotometer (Shanghai Jinghua Science and Technology Instrument Co., Ltd., China).

3. Results and discussion

3.1. Crystalline phase

XRD analysis was carried out to identify the purity and phase structures of the catalyst samples synthesized at different pH values. Fig. 2 shows that the main diffraction peaks of pure BiOBr are detected at 2θ = 10.9°, 21.9°, 25.1°, 31.7°, 32.2° and 46.2°, which can be perfectly indexed as the tetragonal BiOBr phase [JCPDS 09-0393] and attributed to the (001), (002), (101), (102), (110), and (200) planes of BiOBr, respectively. With the increase of pH value (pH = 4, 5, 6, 7), the diffraction peaks of the $Bi_4O_5Br_2$ phase gradually appear and this phenomenon indicates coexistence of BiOBr and $Bi_4O_5Br_2$. Meanwhile,

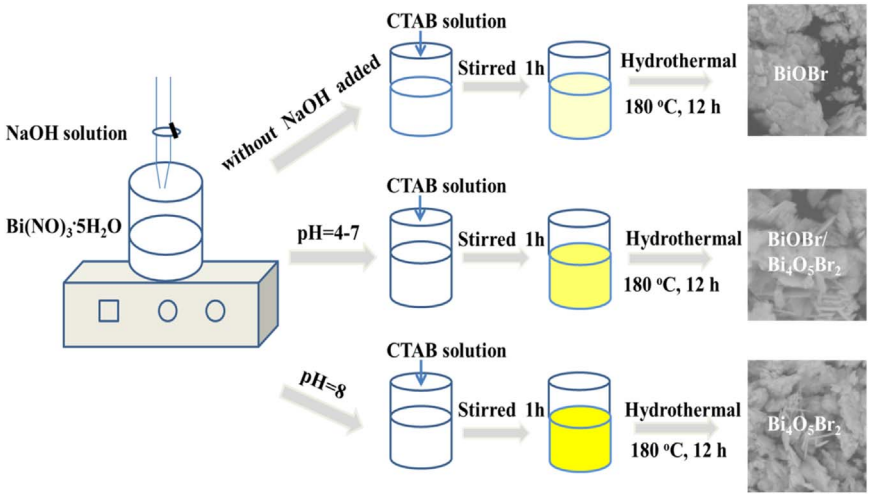

Fig. 1. The illustration of the synthesized process of samples with controlling the pH value.