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Sodium citrate-assisted anion exchange strategy for construction of $Bi_2O_2CO_3$/BiOI photocatalysts

Peng-Yuan Song, Ming Xu, Wei-De Zhang *

School of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510640, PR China

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ABSTRACT

$Bi_2O_2CO_3$/BiOI heterojuncted photocatalysts were constructed through a facile partial anion exchange strategy starting from BiOI microspheres and urea with the assistance of sodium citrate. The content of $Bi_2O_2CO_3$ in the catalysts was regulated by modulating the amount of urea as a precursor, which was decomposed to generate CO_3^{2-} in the hydrothermal process. Citrate anion plays a key role in controlling the morphology and composition of the products. The $Bi_2O_2CO_3$/BiOI catalysts display much higher photocatalytic activity than pure BiOI and $Bi_2O_2CO_3$ towards the degradation of rhodamine B (RhB) and bisphenol A (BPA). The enhancement of photocatalytic activity of the heterojuncted catalysts is attributed to the formation of p–n junction between *p*-BiOI and *n*-$Bi_2O_2CO_3$, which is favorable for retarding the recombination of photoinduced electron-hole pairs. Moreover, the holes are demonstrated to be the main active species for the degradation of RhB and BPA.

1. Introduction

Novel visible light-driven photocatalysis has been regarded as one of the most promising solutions for energy and environmental issues since visible light accounts for 43% of solar spectrum [1–3]. However, the photocatalytic activity of many photocatalysts is limited by the light response range and the quantum efficiency of photons [4]. It has been reported that constructing heterostructured photocatalysts can significantly combine the advantages of two or more semiconductive materials with matched band structures both for light absorption and charge separation [5], for example, BiOI/TiO_2 [6], $Bi_2O_2CO_3$/BiOCl [7], $Bi_2O_2CO_3$/Bi_2MoO_6 [8], Bi_2WO_6/TiO_2 [9], ZnO/In_2O_3 [10] and $ZnFe_2O_4$/MWCNTs [11].

Recently, bismuth-containing semiconductors have stood out from other novel efficient visible light photocatalysts because of the hybridized valence band by O 2p and Bi 6s [12]. Among various Bi-based photocatalysts, BiOI is one of the members of the Sillén family with a layer structure characterized by $[Bi_2O_2]^{2+}$ slabs interleaved by double slabs of iodine atoms, and has attracted much attention because of its narrow bandgap (1.73–1.92 eV) [13–15]. However, its photocatalytic activity still needs to be improved for practical applications. Meanwhile, $Bi_2O_2CO_3$ is another typical "Sillén" phase constructed by $[Bi_2O_2]^{2+}$ layers interleaved by slabs comprising CO_3^{2-} with a wide bandgap (2.87–3.58 eV) [16–18]. It only functions well under UV light or artificial sun light. In view of the similar crystal structure and different solubility of BiOI and $Bi_2O_2CO_3$, it is envisaged that BiOI can be partially or completely converted to $Bi_2O_2CO_3$ upon partial or total replacement of I^- by CO_3^{2-}. In such a way, heterojuncted photocatalysts consisting of *p*-BiOI and *n*-$Bi_2O_2CO_3$ could be created. In fact, heterojuncted $Bi_2O_2CO_3$/BiOI composites have been prepared with the assistance of surfactant and their photocatalytic activity towards degradation of RhB as a dye representative under visible light was reported [19]. However, the possible sensitizing effect of the dye on the photocatalytic activity of the catalysts was not discussed and the photocatalytic degradation of colorless organic compounds was not studied.

It is well-known that citrate anion possesses three carboxylic groups and one hydroxyl group. Thus, it can provide coordinating sites to form stable complexes with metal ions, such as Bi^{3+}, Al^{3+}, Fe^{3+}, Zn^{2+} and Mg^{2+}, and can selectively bind to specific crystallographic facets for controlling crystal growth [20–24]. A lot of bismuth-containing compounds with diverse morphologies, such as flower-like BiOI [25], nest-like or flower-like BiOCl [23], pinecone-like or flower-like $Bi_2O_2CO_3$ [18] and 3D hierarchical umbilicate Bi_2WO_6 microspheres [26] have been synthesized with the assistance of citrate anion.

Herein, we report the preparation of $Bi_2O_2CO_3$/BiOI microspheres through a facile partial anion exchange process with the assistance of sodium citrate. The content of $Bi_2O_2CO_3$ in the composites can be tuned by altering the amount of urea as a

* Corresponding author. Tel.: +86 20 8711 4099; fax: +86 20 8711 4099.
E-mail address: zhangwd@scut.edu.cn (W.-D. Zhang).

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precursor. In addition, control experiments were conducted to observe the evolution of the structure and the effect of citrate anion on the formation of $Bi_2O_2CO_3$/BiOI microspheres. The photocatalytic activity of the obtained $Bi_2O_2CO_3$/BiOI microspheres toward degradation of RhB and BPA was evaluated under visible light irradiation. Furthermore, a possible photocatalytic mechanism was proposed based on the experimental results.

2. Experimental

2.1. Chemicals

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) was purchased from Shanghai Chemical Reagent Co., Ltd. Potassium iodide (KI), sodium citrate and urea were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents used in this study were of analytical grade and were directly used as received. Deionized water was employed in all experiments.

2.2. Preparation of flower-like BiOI microspheres

Flower-like BiOI microspheres were prepared according to our previous report [27]. In brief, 0.728 g $Bi(NO_3)_3{\cdot}5H_2O$ was added into 20 mL absolute ethanol in a 150 mL flask, and stirred for 30 min; then 40 mL KI solution (0.249 g KI dissolved in deionized water) was added drop by drop. Subsequently, the pH was adjusted to 7 by dropwise adding 1.5 M $NH_3{\cdot}H_2O$ prior to stirring for 3 h at 80 °C. The resulting brick red products were centrifuged and rinsed with deionized water and ethanol, and finally dried at 60 °C overnight.

2.3. Preparation of the $Bi_2O_2CO_3$/BiOI photocatalysts

For the preparation of $Bi_2O_2CO_3$/BiOI composites, 0.1759 g BiOI, 0.20 mmol sodium citrate, 0.010–0.10 g urea and 40 mL deionized water were put into a 50 mL Teflon-lined autoclave and stirred for 30 min. Then, the autoclave was sealed and heated at 150 °C for 12 h. After cooling down to room temperature naturally, the resulting products were collected by centrifugation and washed with deionized water and ethanol several times, and finally dried at 60 °C overnight for further characterization and photocatalytic reactions. The obtained samples were denoted as S01, S02, S04, S06, S08 and S10, respectively.

Additionally, pure $Bi_2O_2CO_3$ microspheres were prepared by adding 1.0 g urea, 0.20 mmol sodium citrate to 40 mL $Bi(NO_3)_3$ solution and a white precipitate was obtained through a hydrothermal process at 150 °C for 12 h. The sample was thoroughly washed with deionized water and ethanol, and finally dried at 60 °C overnight.

For comparison, two types of $Bi_2O_2CO_3$/BiOI composites were prepared in different conditions: (1) $Bi_2O_2CO_3$/BiOI synthesized using $Bi(NO_3)_3$ and KI as raw materials instead of the prepared BiOI, (2) $Bi_2O_2CO_3$/BiOI synthesized using Na_2CO_3 instead of urea, while other synthesis conditions were kept unchanged. The products were coded as BS04 and NS04, respectively.

2.4. Characterization

The products were characterized by various physical techniques. X-ray diffraction (XRD) patterns were recorded with an X′Pert PRO MRD diffractometer with Cu Kα (0.154 nm) in 2θ range of 10–70°. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken on JEOL JSM-6380-LA and Tecnai G220 FEI microscopes, respectively. UV–vis diffuse reflection spectra (DRS) were obtained over a UV-3010 spectrophotometer with $BaSO_4$ as a reference.

2.5. Photocatalytic activity of the $Bi_2O_2CO_3$/BiOI catalysts

The photocatalytic activity of the as-prepared samples was evaluated toward degradation of RhB under visible light irradiation using a 300 W tungsten halide lamp (Foshan Electric Light Ltd., Foshan, China) combined with a 400 nm cut-off filter. In a typical photocatalytic experiment, 0.10 g photocatalyst was dispersed in 100 mL RhB solution (5.0 mg/L). Before illumination, the suspension was magnetically stirred in the dark for 1 h to establish the adsorption/desorption equilibrium. At given time intervals, 4 mL of the suspension was taken for analysis after centrifugation. For the degradation of BPA, a 500 W Xe lamp (Xujiang Electromechanical Plant, Nanjing, China) was used as light source, with a thin layer of 2.0 M $NaNO_2$ solution as a filter to eliminate UV light (cut-off $\lambda < 400$ nm) [28]. 0.40 g photocatalyst was dispersed in 400 mL BPA solution (20.0 mg/L), while other conditions were kept unchanged. The schemes of photocatalytic experiments under visible light are schematically illustrated in Fig. S1, Electronic Supplementary Information (ESI). The concentrations of RhB and BPA in the sample solutions were determined by a UV-3010 spectrophotometer at 553 and 276 nm, respectively. Chemical oxygen demand (COD) of the sample solutions was determined using a XJ-III Analytical Instrument (Taihong Medical Instrument Ltd., Shaoguan, China).

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1 shows the XRD patterns of the as-prepared samples. All the peaks of the pure BiOI can be clearly indexed to the tetragonal phase (JCPDS No. 73-2062) and those of pure $Bi_2O_2CO_3$ were also perfectly coincident with the tetragonal phase (JCPDS No. 41-1488). The $Bi_2O_2CO_3$/BiOI composites were prepared through a partial anion exchange reaction starting from BiOI microspheres, in which CO_3^{2-} was generated from the decomposition of urea at 150 °C. The XRD result clearly reveals the coexistence of both BiOI and $Bi_2O_2CO_3$ in the samples, without any other impurity (Fig. 1). Upon increasing urea amount, the intensities of diffraction peaks of $Bi_2O_2CO_3$ strengthened continuously whereas those of BiOI decreased simultaneously, indicating that BiOI transformed gradually to $Bi_2O_2CO_3$. It is also noted that, these composites showed a gradient evolution in color from brick red to gray (inset in

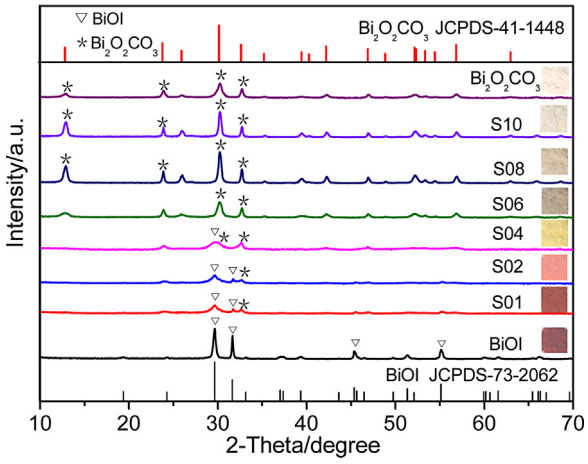

Fig. 1. XRD patterns of BiOI, $Bi_2O_2CO_3$ and $Bi_2O_2CO_3$/BiOI starting with different urea contents. The inset shows color variations of the samples. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)