



Novel urea assisted hydrothermal synthesis of hierarchical BiVO₄/Bi₂O₂CO₃ nanocomposites with enhanced visible-light photocatalytic activity

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ABSTRACT

A novel hydrothermal approach is developed for the first time to synthesize hierarchical BiVO₄/Bi₂O₂CO₃ nanocomposites with reactive crystalline facets using urea as a morphology mediator. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, N₂ absorption–desorption isotherms and UV–visible diffuse reflectance spectroscopy. The photocatalytic activity of the as-prepared samples was evaluated towards degradation of Rhodamine B (RhB) by visible-light. Our results indicate that both physical parameters and associated photocatalytic activity of BiVO₄/Bi₂O₂CO₃ nanocomposites can be tuned by urea concentration and reaction time in the synthesis process. With increasing urea concentration, the specific surface area, pore volume and average pore size increase. Compared to BiVO₄ and Bi₂O₂CO₃ bulk counterpart, BiVO₄/Bi₂O₂CO₃ nanocomposites show enhanced photocatalytic degradation activity of RhB. The mechanisms for the formation of BiVO₄/Bi₂O₂CO₃ nanocomposites and enhanced photoreactivity are discussed.

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1. Introduction

Over the past decades, considerable efforts have been made to design and synthesize nanostructures for water-splitting and organic pollutant degradation under UV and visible-light irradiation [1–6]. Ever since Fujishima and Honda reported water-splitting by TiO₂, there has been significant attention towards the preparation of low-dimensional nanomaterials (e.g., nanosheets) in micro- and nano-regime with well-defined reactive facets, which could be useful in splitting water and decomposition of organic pollutants [7]. For example, theoretical and experimental studies on the photocatalytic activity of anatase TiO₂ showed that the {001} facets are much more reactive than {101} facets [8–10]. Very recently, TiO₂ nanomaterials with highly reactive {001} facets and excellent photoreactivity were successfully prepared in our laboratory [11–14]. Nevertheless, TiO₂ is only active under UV excitation due to its large band gap. Therefore, developing novel solar-driven photocatalysts is highly desirable [15–18]. Indeed, there are a lot of visible-light responsive photocatalysts such as CdS, CdSe, Bi₂WO₆, BiVO₄, Bi₂S₃, CdIn₂S₄, Fe₂O₃, etc. have been reported in literatures [19,20].

In recent years, bismuth-based nanostructured materials are receiving great attention due to their potential applications in semiconductors, catalysts and biomedicine. As an important multicomponent semiconductor, bismuth vanadate (BiVO₄) has relatively narrow bandgap with a wide range of applications in ferroelectrics, photochemical solar cells, ionic conductivity, photocatalytic evolution of O₂, and photodegradation of organic pollutants [21]. Since crystalline bismuth vanadates were reported [22], many synthesis approaches have been developed for the fabrication of monoclinic BiVO₄ crystals, such as solid state reaction, co-precipitation, hydrothermal treatment, aqueous process, sonochemistry and metalorganic decomposition [23–27]. Among these approaches, hydrothermal methods show great promises due to its simplicity in preparing monoclinic BiVO₄ with perfect crystallinity and controllable morphologies in an environmental benign way. Given that the size, shape and phase of BiVO₄ are crucial in determining the photocatalytic properties, a variety of crystal architectures has been fabricated. For example, Xie and co-workers [28] reported synthesis of ellipsoidal m-BiVO₄ nanostructures by oleic acid assisted solvothermal process. Zhang et al. [29] synthesized monoclinic BiVO₄ nanosheets using SDBS surfactant as a morphology-directing template. Kudo and Yu [30] prepared highly crystalline monoclinic BiVO₄ with polyhedral and rod-like morphologies via a hydrothermal process. Zhou et al. prepared single-crystalline monoclinic BiVO₄ microtubes by employing a reflux method [31]. Meng et al. reported monoclinic BiVO₄

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single-crystallites with different morphologies using a triblock copolymer P123 assisted hydrothermal method [32]. Very recently, Ye and Xi reported synthesis of monoclinic BiVO_4 nanoplates with exposed $\{001\}$ facets and remarkable visible-light photocatalytic activity [33]. However, most architectures were synthesized in the presence of surfactants, which not only add the costs but make it difficult to scale up production. Therefore, it is of great significance to synthesize BiVO_4 nanostructure with desirable morphology in the absence of surfactants.

In addition, bismuth-containing materials with particular layered structures could present unique photocatalytic properties under visible-light. For instance, aurivillius structured $\text{Bi}_2\text{O}_2\text{CO}_3$ constitutes of layered structure with alternative stacking of $(\text{Bi}_2\text{O}_2)^{2+}$ sheets interleaved by CO_3^{2-} groups. Furthermore, the internal layered structure of aurivillius structured $\text{Bi}_2\text{O}_2\text{CO}_3$ could guide the lower growth rate along (001) axis compared to that along other axes, and thus form 2D morphologies like nanosheets. The highly anisotropic internal structure of $\text{Bi}_2\text{O}_2\text{CO}_3$ could facilitate the formation of sheet-like morphology with particular exposed facets potentially unique and useful in photocatalysis. To the best of our knowledge, $\text{Bi}_2\text{O}_2\text{CO}_3$ is primarily used in medicine and microelectrode [34–37], and less attention has been directed towards its photocatalytic applications [38,39].

In this study, we report for the first time the synthesis of hierarchical $\text{BiVO}_4/\text{Bi}_2\text{O}_2\text{CO}_3$ nanocomposites by a novel low-temperature template-free hydrothermal approach. Compared to BiVO_4 bulk counterparts, the as-synthesized hierarchical $\text{BiVO}_4/\text{Bi}_2\text{O}_2\text{CO}_3$ nanocomposites with exposed high reactive facets display enhanced photodegradation towards Rhodamine B (RhB) by visible-light.

2. Experimental details

2.1. Sample preparation

All the chemicals are of analytical reagent grade and were used as received from Shanghai Chemical Reagent Factory of China without further purification. Distilled water was used in all our experiments. In a typical synthesis, 2.33 g of Bi_2O_3 and 0.58 g of NH_4VO_3 were dissolved in 15 ml of 4.0 M HNO_3 aqueous solution separately and stirred for 30 min at room temperature to form a clear solution. Then these two solutions were mixed together to obtain stable yellow clear solution. A certain amount of urea was added to the above solution and further stirred for 30 min. The amount of urea added was from 0, 6, 12 to 20 g and the corresponding samples were labeled as U0, U6, U12 and U20, respectively. The resulting precursor suspension was loaded into a Teflon-lined stainless steel autoclave with a capacity of 50 ml and maintained at 180 °C for 24 h, and subsequently cooled to room temperature naturally. The precipitate was then collected by centrifugation, washed with distilled water and ethanol for several times to remove ions and un-reacted urea and then dried in a vacuum oven at 60 °C for 10 h. For comparison, pure $\text{Bi}_2\text{O}_2\text{CO}_3$ nanosheets were also prepared according to the method reported by Huang and co-workers [38].

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of as-prepared samples were obtained on an X-ray diffractometer (type HZG41B-PC) using monochromatized $\text{Cu K}\alpha$ (0.15418 nm) at a scan rate (2θ) of $0.05^\circ \text{ s}^{-1}$. The accelerating voltage and the applied current were 40 kV and 80 mA, respectively. The average crystallite sizes were calculated according to Scherrer formula ($d = 0.89\lambda / \beta \cos \theta$, where d , λ , β and θ are crystallite size, $\text{Cu K}\alpha$ wavelength,

full width at half maximum intensity and Bragg's diffraction angle, respectively). Scanning electron microscopy (SEM) images were recorded by a field emission scanning electron microscopy (JEOL, Japan) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses were conducted using JEM-2100F electron microscopy (JEOL, Japan) operating at 200 kV. The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) of the powders was analysed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All the as-prepared samples were degassed at 180 °C prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. A desorption isotherm was used to determine the pore size distribution via the Barret–Joyner–Halender (BJH) method, assuming a cylindrical pore model [40]. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.994 was used to determine the pore volume and average pore size. The X-ray photoelectron spectroscopy (XPS) measurement was performed in an ultrahigh vacuum VG ESCALAB 210 electron spectrometer using $\text{Mg K}\alpha$ (1253.6 eV) radiation source (operating at 200 W) of a twin anode in the constant analyzer energy mode with a pass energy of 30 eV. All the binding energies were referenced to the adventitious C1s line at 284.8 eV as the internal standard. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Renishaw InVia) in the back-scattering geometry with a 514.5 nm Ar^+ laser as an excitation source. The Fourier transform infrared spectroscopy (FTIR) of the samples was recorded on IRAffinity-1 FTIR spectrometer (Shimadzu, Japan) at a resolution of 4 cm^{-1} . UV–visible absorbance spectra of composite powders were obtained for the dry-pressed disk samples with a UV–visible spectrophotometer (UV-2550, Shimadzu, Japan) using BaSO_4 as a standard.

2.3. Photocatalytic activity

The photocatalytic activity of the as-prepared samples was evaluated towards photodegradation of RhB aqueous solutions at ambient temperature. In details, 0.1 g of the as-prepared catalyst powders was dispersed in a 20 ml of RhB ($2 \times 10^{-5} \text{ mol L}^{-1}$) aqueous solutions in a 90 mm culture dish. Prior to irradiation, the suspensions were kept in the dark for 30 min to reach an adsorption–desorption equilibrium. A 350 W Xenon lamp (Shanghai Lansheng Electronic Co., China) with a 420 nm cutoff filter positioned 25 cm above the dish was used as a visible light source to trigger the photocatalytic reaction. The integrated visible-light intensity on the surface of the reaction solution was measured with a visible-light radiometer (Model: FZ-A, made in Photoelectric Instrument Factory of Beijing Normal University, China). The concentration of pollutant was determined by an UV–visible spectrophotometer (UV-2550, Shimadzu, Japan). At an interval of 15 min, the reaction solution was sampled to record the intensity change of absorption peak at 553 nm.

3. Results and discussion

3.1. Phase structures and morphology

The crystalline structures of the as-prepared samples were examined by X-ray diffraction. Fig. 1 shows the XRD patterns of the as-prepared samples obtained under various conditions. As shown in Fig. 1, $\text{BiVO}_4/\text{Bi}_2\text{O}_2\text{CO}_3$ nanocomposite photocatalysts are well crystallized. The diffraction pattern of sample U0 is indexed with standard data of monoclinic scheelite BiVO_4 structure (JCPDS card No. 14-0688) and no other impurities were detected, indicating

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