



High-performance porous spherical or octapod-like single-crystalline BiVO₄ photocatalysts for the removal of phenol and methylene blue under visible-light illumination

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ABSTRACT

Monoclinic BiVO₄ single-crystallites with a polyhedral, spherical or porous octapod-like morphology were selectively prepared using the triblock copolymer P123 (HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H)-assisted hydrothermal method with bismuth nitrate and ammonium metavanadate as metal source and various bases as pH adjustor. The BiVO₄ materials were well characterized and their photocatalytic activities were evaluated for the removal of methylene blue (MB) and phenol in the presence of a small amount of H₂O₂ under visible-light illumination. It is shown that the pH value of the precursor solution, surfactant, and hydrothermal temperature had an important impact on particle architecture of the BiVO₄ product. The introduction of P123 favored the generation of BiVO₄ with porous structures. The BiVO₄ derived hydrothermally with P123 at pH 3 or 6 possessed good optical absorption performance both in UV- and visible-light regions and hence showed excellent photocatalytic activities for the degradation of MB and phenol. It is concluded that the high visible-light-driven catalytic performance of the porous octapod-like BiVO₄ single-crystallites is associated with the higher surface area, porous structure, lower band gap energy, and unique particle morphology. Such porous BiVO₄ materials are useful in the solar-light-driven photocatalytic treatment of organic-containing wastewater.

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1. Introduction

BiVO₄ is an important material utilized in ferroelastics [1], conductors [2], and photocatalysis [3,4]. Its physicochemical properties are intimately associated with the crystalline structure, particle morphology, porous structure, and nano/microstructure. In the past years, BiVO₄-based materials have been investigated intensively and extensively due to their potential applications in the photocatalytic treatment of organic-containing wastewater.

Among the three crystalline structures (i.e., tetragonal zircon, monoclinic scheelite, and tetragonal scheelite) of BiVO₄, the monoclinic scheelite one exhibits the best photocatalytic activity under visible-light irradiation [3,4]. The crystal phase of BiVO₄ is strongly dependent on the preparation method employed. The tetragonal BiVO₄ is usually obtained by aqueous precipitation at low temperatures, whereas the monoclinic BiVO₄ can be generated via the solid-state reaction [5], hydrothermal treatment [6–11], organometallic decomposition [12,13], and sonochemical routes

[14]. Among these methods, the hydrothermal one attracts increasing attention due to its simplicity and effectiveness in generating monoclinically crystallized BiVO₄ with regular particle morphologies in an environmentally benign way [6,8,10]. Factors, such as precursor nature and concentration, surfactant, precursor solution pH value, hydrothermal temperature and time as well as subsequent thermal treatment, exert important impacts on the crystal structure and particle morphology of the product. A large number of BiVO₄ with different crystal phases and architectures have been reported in the literature. For instance, Xie and coworkers [15] obtained monoclinic BiVO₄ with hyperbranched structures by hydrothermally treating the Bi(NO₃)₃ and NaVO₄ mixture under an acidic condition at 200 °C; Yu and Kudo adopted a hydrothermal process to fabricate monoclinic scheelite BiVO₄ particles with polyhedral and rod-like shapes using Bi(NO₃)₃ and NH₄VO₃ as metal precursor and urea or ammonia as pH adjusting agent [6]. By employing a simple reflux procedure with Bi(NO₃)₃ and NH₄VO₃ as metal source and NaHCO₃ as pH adjustor, Wang and coworkers prepared single-crystalline monoclinic BiVO₄ microtubes [16]. In another work, Yu and Kudo [8] reported the preparation of BiVO₄ nanofibers via a cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal process, in which CTAB played a crucial role

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in controlling the phase structure and morphology of the product. With CTAB as surfactant and Bi_2O_3 and NH_4VO_3 as metal precursor, Li et al. hydrothermally prepared monoclinic BiVO_4 microparticles with cuboid-, square plate-, and flower-like shapes [11]. With the aid of a surfactant (e.g., CTAB, polyvinyl alcohol or polyvinyl pyrrolidone), BiVO_4 with rod-, slice-, flower-, and sphere-like morphologies could be obtained using the hydrothermal method with $\text{Bi}(\text{NO}_3)_3$ and NH_4VO_3 as the starting materials [17].

As an effective visible-light-responsive photocatalyst, BiVO_4 is highly required to possess a low band gap energy (favoring the absorption of visible light) and high surface area (facilitating the adsorption of reactant molecules). Up to now, however, only several works relevant to the preparation of high-surface-area porous monoclinic BiVO_4 crystals have been reported in the literature. For example, ordered mesoporous monoclinic BiVO_4 with a surface area of $59 \text{ m}^2/\text{g}$ was obtained through a nanocasting pathway with mesoporous silica (KIT-6) as template, and the mesoporous BiVO_4 performed well in catalyzing the degradation of methylene blue (MB) under visible-light irradiation [18]; using a hydrothermal method, Zhou et al. generated monoclinic BiVO_4 (surface area = $15.6 \text{ m}^2/\text{g}$) and observed a high activity for MB degradation under visible-light illumination [19]. Organics (such as phenol and MB) in wastewater originated from chemical industries are toxic, carcinogenic, teratogenic, and refractory in nature. It is highly desirable to develop a “green” and energy-saving strategy to remove these organic pollutants from wastewater. It was found that the B- TiO_2 [20], Bi_2WO_6 [21], and Bi_2MoO_6 [22] materials were photocatalytically active for the treatment of phenol-containing wastewater. Although monoclinic BiVO_4 possesses a narrow band gap, it displays a poor photocatalytic activity due to the difficulty in capturing the photoinduced electrons by oxygen [23]. In the presence of H_2O_2 (an electron scavenger), however, an enhancement in photocatalytic performance of BiVO_4 could be achieved for the removal of phenol under visible-light illumination [23–25].

Previously, our group investigated the preparation and physicochemical property characterization of a number of porous and/or nano/microstructured materials, such as mesoporous MgO [26] and CaO [27] single-crystallites and three-dimensionally (3D) ordered macroporous $\gamma\text{-Al}_2\text{O}_3$ and $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ with mesoporous walls [28], by means of the surfactant (e.g., triblock copolymers poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) Pluronic P123 ($\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$) and F127 ($\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{106}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{106}\text{H}$), CTAB or poly(ethylene glycol))-assisted hydrothermal strategies. Recently, we have extended our attention to the selective preparation of visible-light-responsive monoclinic bismuth vanadates with polyhedral, tubular, spherical, rod-like, leaf-like, flower-like, sheet-like, and olive-like morphologies via the hydrothermal or alcohol-hydrothermal routes with water, ethanol or ethylene glycol as solvent and/or dodecylamine, oleylamine, oleic acid or triblock copolymer as surfactant [29–31], in which a

morphology-dependent photocatalytic behavior was observed for the photodegradation of organic dyes and phenol. Compared to one of our previous works [31], our present work focuses on the P123-assisted preparation, characterization, and excellent photocatalytic performance of monoclinic BiVO_4 single-crystallites with multiple morphologies and/or porous structures for the removal of MB and phenol in the presence of a small amount of H_2O_2 under the visible-light illumination.

2. Experimental

2.1. Catalyst preparation

The BiVO_4 photocatalysts with different morphologies were prepared using the hydrothermal method with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 as metal source in the absence and presence of triblock copolymer surfactant P123. The detailed procedures were described in the [Supplementary data](#). For better presentation, we denoted the samples prepared under various conditions as BiVO_{4-x} ($x = \text{I, II, III, IV, and V}$), as shown in [Table 1](#).

2.2. Catalyst characterization

The samples were characterized by means of X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetric (DSC) analysis, laser Raman spectroscopy, N_2 adsorption–desorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy. The detailed procedures were described in the [Supplementary data](#).

2.3. Photocatalytic performance evaluation

Photocatalytic activities of the samples for the removal of MB or phenol were measured in a quartz reactor (QO250, Beijing Changtuo Sci. & Technol. Co. Ltd.) under visible light irradiation. A 300-W Xe lamp was employed as the light source and an optical cutoff filter was used to only permit the illumination of light with a wavelength of higher than 400 nm. (i) 0.01 g of the BiVO_4 or commercial TiO_2 (Degussa P25) sample was suspended in 100 mL of aqueous solution containing MB (initial MB concentration $C_0 = 0.01 \text{ mmol/L}$) or (ii) 0.2 g of the BiVO_4 or P25 sample and 0.6 mL of H_2O_2 solution (30 wt%) were added to 200 mL of the phenol-containing aqueous solution (initial phenol concentration $C_0 = 0.1, 0.2$ or 0.4 mmol/L). Before illumination, the mixed solution was ultrasonicated for 0.5 h and magnetically stirred for 3 h in the dark to ensure the establishment of the adsorption–desorption equilibrium. Then the suspension was magnetically stirred and exposed to the visible-light irradiation. The temperature of the reaction solution was kept at ca. 25°C using flowing cool water. 5 mL of the suspension was

Table 1

Preparation conditions, crystal structures, particle morphologies, BET surface areas, and band gap energies of the as-prepared BiVO_4 samples.

Sample code	Surfactant ^a	Alkaline source	pH	Hydrothermal condition ^b	Crystal structure	Particle morphology	Surface area (m^2/g)	Band gap energy (eV)
$\text{BiVO}_4\text{-I}$	P123	$\text{NH}_3 \cdot \text{H}_2\text{O}$	3	180°C , 6 h	Monoclinic	Polyhedral (major), porous octapod-like (minor)	0.7	2.43
$\text{BiVO}_4\text{-II}$	P123	NaHCO_3	6	180°C , 6 h	Monoclinic	Porous spherical (major), polyhedral (minor)	8.1	2.42
$\text{BiVO}_4\text{-III}$	P123	$\text{NH}_3 \cdot \text{H}_2\text{O}$	3	80°C , 6 h	Monoclinic	Porous octapod-like	11.8	2.38
$\text{BiVO}_4\text{-IV}$	P123	$\text{NH}_3 \cdot \text{H}_2\text{O}$	3	100°C , 6 h	Monoclinic	Porous octapod-like	8.6	2.41
$\text{BiVO}_4\text{-V}$	–	$\text{NH}_3 \cdot \text{H}_2\text{O}$	3	180°C , 6 h	Monoclinic	Hyperbranched	2.0	2.44

^a The BiVO_4 samples were prepared with a Bi/P123 molar ratio of 1:0.034.

^b After hydrothermal treatments, the obtained solids were calcined at 400°C for 4 h.

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