Controlling crystallization and morphologies of monoclinic bismuth vanadate (BiVO₄) dendrite with enhanced photocatalytic activities

Haoyong Yin¹, Yongfei Sun¹, Dejun Shi¹, Xiaoxi Wang¹ and Ling Wang²*

¹College of Materials and Environmental Engineering, Hangzhou Dianzi university, Hangzhou, 310018, P. R. China. ²Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, P. R. China.

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The monoclinic BiVO₄ dendrites constructed by Bismuth vanadate (BiVO₄) branches with average diameters of about 100 nm have been successfully fabricated by Sodium dodecyl sulfate (SDS) assistant hydrothermal process. The monoclinic BiVO₄ dendrites were characterized by X-ray diffraction, scanning electron microscopy, Raman spectroscopy and transmission electron microscopy. The monoclinic BiVO₄ dendrites have uniform branches and the branches were transformed from the aggregated monoclinic BiVO₄ nanoparticles through the Ostwald ripening process. The monoclinic BiVO₄ dendrites show high efficient photocatalytic activities in decomposition of methyl orange.

Key words: Controlling crystallization, hierarchical structures, bismuth vanadate dendrites.

INTRODUCTION

Nowadays, the controllable synthesis of micro- and nanoscale materials with unique morphology and hierarchy has stimulated intensive interest due to their importance in basic scientific research and technological applications (Wang et al., 2006; Xia et al., 2003; Huang et al., 2006). Many efforts have been focused on the assembly of lower dimensional nanostructures into three-dimensional ordered superstructures, such as multipods, snowflakes and dendritic structures (Toprak et al., 2007; Ding et al., 2006; Wu et al., 2006). However, due to the difficulties in controlling the nucleation and growth processes, the construction of well-defined three-dimensional architectures with lower dimensional components is still a great challenge (Whitesides et al., 2002; Park et al., 2004; Xu et al., 2008). These hierarchical structures may endow them with morphology-dependant properties and imply their potential application in various fields. Therefore, further research is warranted to realize the advantages of them. Bismuth vanadate (BiVO₄), known for its ferroelasticity (Baker et al., 1991) ionic conductivity (Abraham et al., 1988) and pigmentation (Wood et al., 2004) has been extensively investigated recently. It has been used for a wide range of applications including gas sensors, posistors, solid-state electrolytes, positive electrode materials for lithium rechargeable batteries, and nontoxic yellow pigment for high-performance lead-free paints (Zhao et al., 2008) and recently proved to be a good photocatalyst for water splitting and pollutant decomposing under visible light irradiation (Ke et al., 2009; Shang et al., 2009). In the three structure types of bismuth vanadate–zircon tetragonal, scheelite monoclinic, and scheelite tetragonal, only the monoclinic scheelite BiVO₄ exhibits much higher visible-light photocatalytic activity over the other forms, giving rise to more attentions and wider researches (Zhang et al., 2006; Su et al., 2010, 2009). Besides crystalline form, the photocatalytic property of BiVO₄ also depends strongly on its microstructure, which is related to the synthesis method. To further improve the visible-light photocatalytic activity, a few submicron- or nanometer-sized BiVO₄ with various morphologies have been prepared. Spindle-like BiVO₄ modified by polyaniline (PANI) (Shang et al., 2009) was synthesized via a sonochemical approach which shows efficient photocatalytic activity in the degradation of rhodamine (RhB) and phenol. Hydrothermal method was used to synthesize the bismuth vanadate (BiVO₄) nanosheets with good visible photocatalytic activities.

*Corresponding author. E-mail: yhy@hdu.edu.cn. Tel: +86-591-87441126.
Pyramidal-shaped BiVO₄ nanowire arrays (Su et al., 2010) were vertically oriented to a fluorine doped tin oxide coated glass substrate by seed-mediated growth approach and show higher photocurrents in photoelectrochemical water splitting. The starlike BiVO₄ was also prepared using water/ethanol mixture as the solvent which exhibited high visible-light-driven photocatalytic efficiency (Sun et al., 2009). Considering the properties and applications are closely related to the microstructure and corresponding synthetic techniques and processes, it is of great importance to study the controllable synthesis of BiVO₄ with the desired crystalline phase and morphology.

Herein, we reported the preparation of monoclinic BiVO₄ dendrite by a simple hydrothermal method using SDS (Sodium dodecyl sulfate) to control its crystallization and morphologies. In this method SDS can both determine the crystalline phase and morphology of BiVO₄. Encouragingly, the as-prepared monoclinic BiVO₄ dendrites exhibit high photocatalytic efficiency.

**RESULTS AND DISCUSSION**

The phase and composition of the as-prepared products were investigated using XRD measurement (Figure 1). In Figure 1a, all diffraction peaks can be assigned to the monoclinic structure of BiVO₄ (JCPDS No. 14-0688) with space Group I2/a and no other peaks for impurities were detected. This observation is further confirmed by the splitting of the peaks at 2θ = 18.5, 35 and 46°, which is characteristic of the monoclinic structure of BiVO₄ (Tokunaga et al., 2001). The results show that the monoclinic scheelite BiVO₄ could be successfully synthesized by this simple hydrothermal method. Comparatively, for the samples synthesized without adding SDS in the mixed solution, the peaks were more complicated than that of the one with SDS at the same temperature (Figure 1b). There are tetragonal BiOCl phase coexisting with monoclinic BiVO₄ in the No SDS samples. The peaks in Figure 1b (marked with stars) fit well with the tetragonal BiOCl (JCPDS No. 85-0861). It suggested that the SDS did improve the crystallization of the BiVO₄. It is very helpful to the photocatalytic activity of BiVO₄. The morphologies of the monoclinic BiVO₄ dendrites prepared by SDS controlling procedures were revealed by SEM (Figure 2). The panoramic view in Figure 2a clearly demonstrates that the as-prepared products are almost entirely dendrite-like crystals with a length of 1 to 2 µm. As shown in Figure 2b, the individual dendrite has well defined branches with uniform diameters of about 100 nm and length of 100 to 500 nm, which demonstrates that the well-defined three-dimensional dendrites are successfully constructed with one dimensional branch components. The morphology and microstructure of monoclinic BiVO₄ dendrites were also investigated by transmission electron microscopy (Figure 3). Figure 3a shows a TEM image of part of monoclinic BiVO₄ dendrites. It also displays that the dendrites are comprised of 100 nm diameter branches which is consistent with the results of SEM images. Close observation of the samples revealed by HRTEM image (Figure 3b) shows that the surface of the monoclinic BiVO₄ dendrites branches is composed of a lot of BiVO₄ nano particles with the average diameter of about 8 nm. The clear lattice fringe (Figure 3c) indicates the high-crystallinity and single-crystalline nature of the branches. It can be measured that the d spacing is 0.468 nm, which agrees well with the lattice spacing (011) of monoclinic BiVO₄.

In order to investigate the effect of SDS on the morphology of BiVO₄ crystals, the samples prepared with the same procedure with different concentration of SDS were obtained. The SEM images (Figure 4) show that the morphologies can be greatly affected by the addition of SDS. Without SDS, the experimental system can only get the rod-like crystals with the diameter of about 100 nm (Figure 4a). After addition of 0.01 M SDS, the nanorods changed into shorter rods (Figure 4b). With 0.02 M SDS, the shorter rods began to aggregate (Figure 4c).

**MATERIALS AND METHODS**

All chemicals were analytical grade and were used as received without further purification. In a typical synthesis, 50 ml 0.13 M NH₄VO₃ solution was prepared by dissolving 6.5 mmol NH₄VO₃ into 50 ml NH₄H₂O solution (2 M). Meanwhile, 6.5 mmol BiCl₃ was dissolved in 50 ml of HNO₃ (4 M) which was added 5 mmol SDS in advance. Then NH₄VO₃ solution was slightly added into BiCl₃ solution under magnetic stirring. At last, the pH was adjusted by NH₃•H₂O solution. This precursor solution was poured into a Teflon-lined stainless steel autoclave until 80% of the volume of the autoclave was occupied. The autoclave was heated at 160°C for 10 h at autogenous pressure. After the autoclave was cooled to room temperature, the precipitate was separated by filtration, washed with distilled water and absolute alcohol several times, and then dried at 60°C for 4 h. For comparison, another BiVO₄ sample was also prepared by the same procedure without adding SDS. The powder X-ray diffraction (XRD) patterns of as-synthesized samples were measured on a X-ray diffractometer (Bruker D8 ADVANCE) using monochromatized Cu Kα (λ = 0.15418 nm) radiation under 40 kV and 100 mA. The morphologies and microstructures of as-prepared samples were examined with scanning electron microscopy (SEM, JSM-6700F). Transmission electron microscopy (TEM) observations were carried out on a JEOL JEM-2100 instrument with accelerating voltage 200 kV in bright-field. The specimens used for TEM studies were dispersed in absolute ethanol by ultrasonic treatment. The sample was then dropped onto a copper grid coated with a holey carbon film and dried in air. The Raman spectra were analyzed using a German Bruker RFS 100/S Raman spectrometer. Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen adsorption using a Micromeritics ASAP 2000 system.

Photocatalytic activities of the monoclinic BiVO₄ dendrites were evaluated by degradation of methyl orange under visible-light irradiation of a 500 W Xe lamp with a 420 nm cutoff filter. An aqueous BiVO₄ dispersion was prepared by adding 0.2 g of BiVO₄ powder into 100 ml of methyl orange solution (1 mg/L). The solution was magnetically stirred and irradiated by visible-light. After irradiation for a designated time, the dispersion was filtered to separate the BiVO₄ particles, and the methyl orange concentration of the filtrate was determined using the Lambda-35 UV-Vis spectrometer.
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Continuously increasing the concentration of SDS to 0.03 M resulted in the appearing of small BiVO₄ dendrites (Figure 4d). When the concentration was increased into 0.05 M, the products are almost all dendrites BiVO₄ (Figure 4e). However, the over high concentration of SDS (0.07 M) can lead to the formation of BiVO₄ nanoparticles (Figure 4f). It can be drown from the results that SDS actually play an important role in controlling the morphologies of BiVO₄ dendrites. Combined with the results of XRD measurement (Figure 1b) the rod-like crystals mainly consist of monoclinic BiVO₄ and tetragonal BiOCl. This may be due to the formation process.
Figure 3. TEM image (a), HRTEM image (b) and enlarged HRTEM image (c) of monoclinic BiVO₄ dendrites.

Figure 4. SEM image of BiVO₄ prepared with different concentration of SDS ((a) 0 M; (b) 0.01 M; (c) 0.02 M; (d) 0.03 M; (e) 0.05 M, and (f) 0.07 M).
process of the monoclinic BiVO$_4$ during which some of BiCl$_3$ can hydrolyze fast to BiOCl when dissolving in the solvent. Then BiOCl reacts with NH$_4$VO$_3$ to form monoclinic BiVO$_4$. In the SDS absent system, BiOCl can not entirely react with NH$_4$VO$_3$, therefore results in the mixed monoclinic BiVO$_4$ and tetragonal BiOCl phase nanorods. However, when adding SDS into the reaction system, the hydrolyzation of BiCl$_3$ may be inhibited, resulting in the direct reaction of Bi$^{3+}$ with NH$_4$VO$_3$ to form pure monoclinic BiVO$_4$ dendrites. The XRD pattern in Figure 1a with pure monoclinic BiVO$_4$ peaks approved this reaction. Raman spectra also verified the improved crystallization of monoclinic BiVO$_4$ dendrites. The Raman scattering spectra of the crystalline BiVO$_4$ samples were obtained in different experimental conditions (Figure 5). Raman bands at 330, 365 and 827 cm$^{-1}$ were observed in both monoclinic BiVO$_4$ dendrites and BiVO$_4$ nanorods. These Raman bands represented the typical vibration bands of monoclinic scheelite BiVO$_4$ and could be assigned to the asymmetric and symmetric deformation modes of VO$_4^{3-}$ and the symmetric stretching mode of the V-O bond, respectively (Li et al., 2008). The Raman band at 210 cm$^{-1}$ relates to the external mode of BiVO$_4$, which gives little structural information of the sample (Guo et al., 2010). However, the Raman bands of monoclinic BiVO$_4$ dendrites were slightly different from the BiVO$_4$ nanorods. The peaks of 710 and 640 cm$^{-1}$ in Figure 5a, assigned to the asymmetric V-O$_1$ stretch (as1) and asymmetric V-O$_2$ stretch (as2) disappeared in Figure 5b which hints that the SDS does improve the crystallization of monoclinic BiVO$_4$ dendrites. The aforementioned results suggested that SDS played a vital role in the formation of monoclinic BiVO$_4$ dendrites. The whole process of SDS affecting the morphology of monoclinic BiVO$_4$ dendrites can be illustrated in Scheme 1. As an anionic surfactant, SDS can form pillar micelles in aqueous solution when the concentration is higher than its critical micelle concentration (CMC) (Step 1). Bi$^{3+}$ will produce when BiCl$_3$ dissolve in the solution and each Bi$^{3+}$ ion interacts electrostatically with sodium dodecyl sulfate ions to form bi-sodium dodecyl sulfate complexes, which then result in an ordered pillar mesostructure (Step 2). After addition of NH$_4$VO$_3$ the VO$_3^-$ can react with Bi$^{3+}$ on the pillar mesostructure surface which then forms the monoclinic BiVO$_4$ nucleus on the surface (Step 3). Continuously reaction of Bi$^{3+}$ and VO$_3^-$ will result in more monoclinic BiVO$_4$ nucleus and the congregation of the nucleus along energetically favorable directions on the pillar mesostructure surface (Step 4). These nucleus may eventually developed into the branches of the monoclinic BiVO$_4$ dendrites which can get a hint from the HRTEM of Figure 3b where there are still some undeveloped nucleus on the branch surface. During the hydrothermal process, the aggregated nucleus may undergo an Ostwald ripening process to form larger crystals, that is, the branches of the monoclinic BiVO$_4$ dendrites. Therefore, the well-defined monoclinic BiVO$_4$ dendrites with uniform branch components were successfully obtained by this simple hydrothermal SDS assistant method (Step 5). In order to investigate the effect of SDS on the photocatalytic activities of the as prepared products, the photocatalytic
CH₃(CH₂)₇SO₃

pillar micelles

ordered pillar mesostructure

Bi³⁺

BiVO₄ nucleus

Step 1

Step 2

Electrostatic interaction

Step 3

Nucleation

Step 4

Aggregation

Step 5

Oswald ripening

monoclinic BiVO₄ dendrites

Scheme 1. Mechanism of the monoclinic BiVO₄ dendrites growth affected by SDS.

Figure 6. Degradation rates of MO on monoclinic BiVO₄ dendrites (a) and BiVO₄ nanorods (b) catalysts.

activities of monoclinic BiVO₄ dendrites and BiVO₄ nanorods were measured in liquid phase reactions. The decomposition of methyl orange in an aqueous solution was chosen as the photoreaction probe. The result shows that the degradation rates of monoclinic BiVO₄ dendrites is much higher than that of BiVO₄ nanorods (Figure 6) under the irradiation of visible light (400 nm < λ < 660 nm). Actually, there is almost no reaction when BiVO₄
nanorod was used as photocatalyst. This may be due to the fact that the hydrolyzation of BiCl$_3$ into BiOCl decreases the crystallization performance of BiVO$_4$ (Liu et al., 2010). Generally, the particles with well crystallinity can decrease the defects inside the crystals, which allows for the more efficient transfer of electron–hole pairs, generated inside the crystal, to the surface. Therefore, it is not surprising that the well-crystallized monoclinic BiVO$_4$ dendrites show the higher photocatalytic activity than that of BiVO$_4$ nanorod which might also be due to its unique morphologies and higher surface area (the surface area of BiVO$_4$ dendrites is 3.12 m$^2$/g which is higher than 1.26 m$^2$/g of BiVO$_4$ nanorods). It was reported that the photocatalytic property of monoclinic BiVO$_4$ is related to the distortion of the bi-O polyhedron (Zhang et al., 2006). The monoclinic BiVO$_4$ dendrites products are composed of branches with relatively large distortion of the unit cell due to the large surface strain which may be beneficial to its high photocatalytic activities.

**Conclusion**

In summary, the monoclinic BiVO$_4$ crystals with dendritic morphology have been synthesized by a facile hydrothermal process. SDS plays a decisive role in the formation of the monoclinic BiVO$_4$ dendrites. It can both enhance the crystallization and determine the morphology of the monoclinic BiVO$_4$ dendrites. In addition, the photocatalytic activities of monoclinic BiVO$_4$ dendrites are also much higher than that of BiVO$_4$ nanorods. These results may not only enrich the dendrite structures of inorganic compounds but also can provide a new surfactant assistant strategy to synthesize hierarchical structures materials.

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