Hydrothermal Synthesis of Nanofibrous Bismuth Vanadate

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Bismuth vanadate ($BiVO_4$) nanofibrous arrays were synthesized by a hydrothermal route. Fibrous structure with the average diameter of 100 nm and length of up to several micrometers was fabricated by the hydrothermal process at 160 °C for 48 h under the assistance of a cationic surfactant, cetyltrimethylammonium bromide (CTAB). The $BiVO_4$ nanofibers possessed well-crystallized monoclinic scheelite structure.

One-dimensional (1-D) nanotubes, nanowires, and nanorods have raised widespread attention because of the enhanced properties, such as efficient transport of electrons and optical excitations.[1]

Metal vanadates have been used in high-energy density lithium batteries,[2,3] chemical sensors,[4] photocatalysis,[5] and so on owing to their unique physical and chemical properties. Recently, many reports have been published on the synthesis of nanoscaled vanadates.[4,6] Bismuth vanadate ($BiVO_4$) is a well-known compound as a pigment for the coloration of a high-molecular-weight organic material.[7] Considerable attentions have also been paid on $BiVO_4$ for its ferroelastic and/or paraelastic properties, acousto-optic and ion conductive properties.[8] Moreover, it was recently found that $BiVO_4$ is an excellent photocatalyst for O_2 evolution from an aqueous $AgNO_3$ solution under visible light irradiation.[5]

$BiVO_4$ may be prepared by several different processes and preparative conditions, such as a solid-state reaction,[9] an aqueous process,[5] a hydrothermal process,[10] and a metal organic decomposition method.[11] One of the authors explored an aqueous process using vanadate salts or a vanadium oxide as starting materials to synthesize $BiVO_4$ powder and applied the synthesized materials to the photocatalytic O_2 evolution reaction, where it was found that monoclinic scheelite $BiVO_4$ synthesized by this aqueous process exhibited much higher activity than that prepared by a solid-state reaction.[5] These facts suggest that the structure and the preparation process can greatly influence the properties of bismuth vanadate.

A sol–gel process is conventional route for the growth of low-dimensional materials including semiconductor. Recently, a general route for the growth of nanowires using CTAB micelles as microreactor was reported.[12] This process has been applied to the synthesis of phosphide, oxide, sulfide, and tungstate nanowires. In the present letter, we report the fabrication of nanofibrous arrays of $BiVO_4$ according to the similar approach.

All chemicals were analytical grades and were used as received without any purification. In a typical procedure, 50 mL of 0.12 $mol\,L^{-1}$ NH_4VO_3 in a 2.0 $mol\,L^{-1}$ HNO_3 solution was mixed with 2.19 g of CTAB and magnetically stirred for 10 min. Then, 20 mL of heptane and 6 mL of hexanol were added and continued to stirring for about 1 h until a yellow emulsion was formed. After that, 3.0 mL of 2.0 $mol\,L^{-1}$ $Bi(NO_3)_3$ in a 2.0 $mol\,L^{-1}$ HNO_3 solution was added dropwisely under stirring until a yellow-milky gel was formed. Followed by further stirring for half an hour, the mixture was transferred into a Teflon-lined stainless autoclave and heated to 160 °C stepwisely and then maintained at this temperature for 48 h. The products were filtered off, washed several times with distilled water and absolute ethanol, and finally dried at room temperature.

X-ray powder diffraction (XRD) patterns were measured using an X-ray diffractometer with Cu Kα radiation (Rigaku; MiniFlex). Field-emission scanning electron microscope (FE-SEM) images were obtained by a JEOL JSM-6700F electron microscope. Raman spectra were recorded on a JEOL made RS-RSU200 Raman spectrometer. A 1064 nm line from a Nd:YAG laser was used as the excitation source.

The typical SEM images of the synthesized $BiVO_4$ product are shown in Figure 1. A large number of nanofibrous arrays were observed. The high-magnified SEM image (Figure 1b) suggests that the products were composed of dense fiber-like struc-

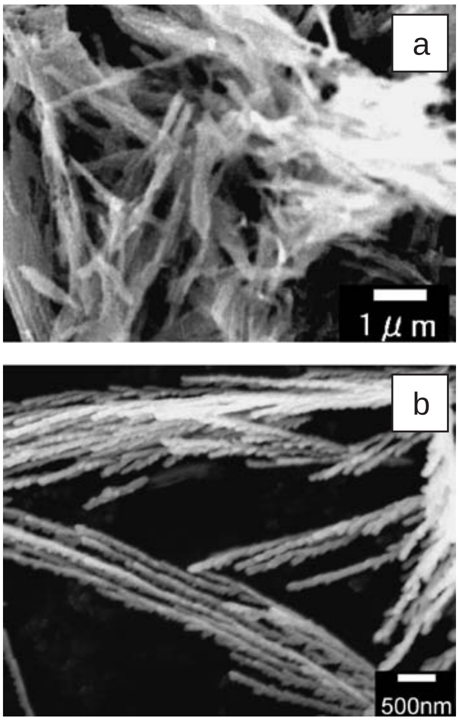

Figure 1. Typical FE-SEM images of $BiVO_4$ nanofibers synthesized hydrothermally.

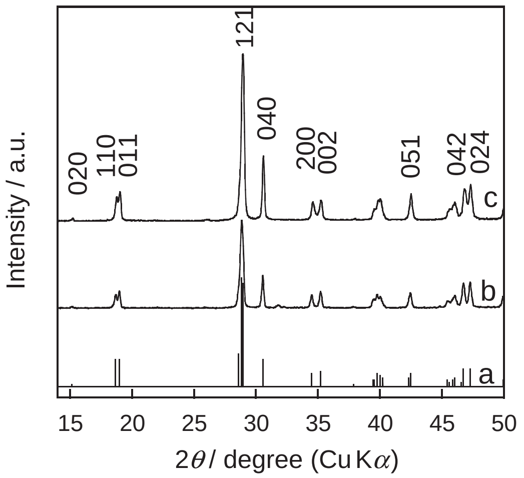

Figure 2. X-ray diffraction patterns of (a) JCPDS Card No. 14-0688, (b) prepared $BiVO_4$ nanofibers, (c) $BiVO_4$ prepared by an aqueous process.

tures with typical lengths in the range of several to several tens of micrometers. The average diameter of the nanofibers was about 100 nm, that was quite uniform. The BET surface area of nanofibrous $BiVO_4$ was 13 $m^2\,g^{-1}$, which was much larger than that of bulk $BiVO_4$ with a surface area of 0.5 $m^2\,g^{-1}$.

The XRD pattern of the synthesized product is shown in Figure 2. For comparison, the diffraction pattern of monoclinic scheelite $BiVO_4$ prepared by an aqueous process was also included. Characteristic reflection peaks at 15.2°, 18.7°, 28.6°, 30.5°, and so on were observed for both diffraction patterns. Three main crystal forms of $BiVO_4$, tetragonal zircon structure, monoclinic scheelite, and tetragonal scheelite structures, exist in nature. The cell parameters of a monoclinic scheelite crystal phase are different from that of a tetragonal scheelite one, because of the distortion of a Bi–O polyhedron by a $6s^2$ lone pair of Bi^{3+}, in which the angle of the monoclinic crystal is 90.4°, whereas that of the tetragonal crystal is 90°. In the XRD pattern of the monoclinic phase, a peak at $2\theta = 15.2°$ can be observed and peaks at $2\theta = 18.5°$, 35°, and 46° are split. These characters are the footprints to distinguish monoclinic from tetragonal structures and these values are also in good agreement with those reported in the literature.[14] All these characters have been unambiguously observed in the patterns of synthesized nanofibers. So, the synthesized nanofibers are of the monoclinic scheelite crystal.

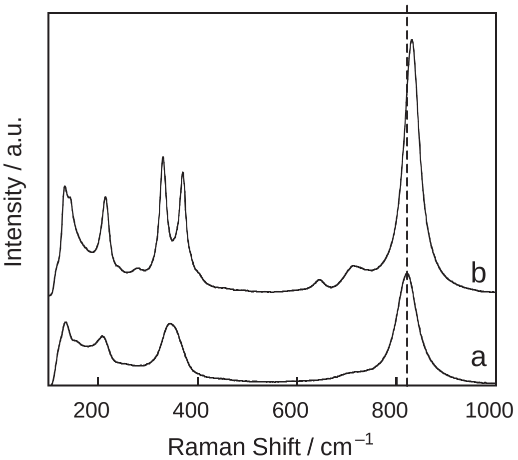

Figure 3. Raman spectra of (a) prepared $BiVO_4$ nanofibers and (b) $BiVO_4$ powder prepared by an aqueous process.

Raman scattering spectra have been used to characterize the nanofibrous material further as shown in Figure 3. Raman bands at 330, 373, 832 cm^{-1}, and so on were observed in the spectrum of the $BiVO_4$ powder. These Raman bands are the typical vibration bands of $BiVO_4$ and can be assigned to asymmetric and symmetric deformation modes of $VO_4{}^{3-}$, symmetric stretching mode of the V–O bond, respectively.[10,11,13] The Raman bands of $BiVO_4$ nanofibers were slightly different from those of the powder sample. The deformation mode of $VO_4{}^{3-}$ was merged and only one peak at 345 cm^{-1} was observed. The stretching mode of the V–O bond shifted from 832 cm^{-1} to 820 cm^{-1}, which may be attributed to the quantum size confinement effect in the nanofiber material or the changes in the local coordination environment of $BiVO_4$ nanofibers. Moreover, the asymmetric stretching mode at 700 cm^{-1} weakens greatly owing to the local structure of nanofibers. The absence of this band was also observed in $BiVO_4$ thin film.[11]

In summary, bismuth vanadate ($BiVO_4$) nanofiber arrays with monoclinic scheelite structure were fabricated via a hydrothermal process.

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