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Preparation of Mo- and W-doped $BiVO_4$ fine particles prepared by an aqueous route for photocatalytic and photoelectrochemical O_2 evolution

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ABSTRACT

Mo- and W-doped $BiVO_4$ fine particles with a diameter of 50–200 nm were prepared from Bi_2O_3 and, Mo- and W-doped V_2O_5 by an aqueous route using an aqueous acetic acid solution. The Mo- and W-doped $BiVO_4$ calcined at 673 K was elongate polyhedral particles grown along with the b-axis, while the non-doped $BiVO_4$ prepared by the same method was featureless particles. X-ray absorption near edge structure (XANES) and electron spin resonance (ESR) measurements revealed that the Mo^{6+} and W^{6+} ions were doped at V sites, resulting in the formation of V^{4+} in $BiVO_4$. The Mo- and W-doped $BiVO_4$ powders showed lower activity for photocatalytic O_2 evolution than the non-doped $BiVO_4$. In contrast, the Mo- and W-doped $BiVO_4$ photoelectrodes fabricated by an electrophoresis method using these fine particles gave higher photoelectrochemical performance due to a positive effect of the increase in the n-type character by Mo- and W-doping.

1. Introduction

Photocatalytic water splitting of artificial photosynthesis is an attractive reaction to convert solar energy to chemical energy. The systems for water splitting can be divided into a powdered system with one-step or two-step (Z-scheme system) photoexcitation and a photoelectrode system [1–5]. The powdered Z-scheme and photoelectrode systems can employ photocatalysts that have only H_2- or O_2-evolution ability, and hence various photocatalyst materials can be applicable for the systems. In such water splitting systems, $BiVO_4$ has been widely used as an O_2-evolving photocatalyst and photoanode [6–18].

$BiVO_4$ has three typical phases including scheelite monoclinic, scheelite tetragonal, and zircon tetragonal phases [19–21]. Among them, the scheelite monoclinic phase is a highly active for photocatalytic and photoelectrochemical water oxidation to O_2 using visible light. Moreover, Mo- and/or W-doping drastically improves the photocatalytic and photoelectrochemical performances of $BiVO_4$ [22–31].

In terms of sacrificial O_2 evolution using $AgNO_3$ as an electron scavenger, relatively large $BiVO_4$ particles with clear facets usually show high activity [32–34]. In contrast, fine particles are favorable for a powder-based photoelectrode to improve the contact between particles and a conductive substrate [35]. In the Z-scheme systems driven by inter particle electron transfer [7], fine particles would be favorable to increase possibility of collision between H_2-evolving and O_2-evolving photocatalyst particles. Thus, formation of Mo- and W-doped $BiVO_4$ fine particles has significance.

We previously reported the synthesis of $BiVO_4$ fine particles with a particle size of 100–200 nm by stirring Bi_2O_3 and V_2O_5 starting materials in an acetic acid solution at room temperature [35]. In the present study, we prepared either Mo- or W-doped $BiVO_4$ fine particles by the modified process using an acetic acid solution. The states of the Mo and W doped in $BiVO_4$ were characterized with X-ray absorption near edge structure (XANES) and electron spin resonance (ESR). Their photocatalytic and photoelectrochemical properties were also investigated.

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2. Material and methods

M-doped $BiVO_4$ (M = Mo and W) fine particles were synthesized by stirring Bi_2O_3 and M-doped V_2O_5 powders of starting materials in an acetic acid solution (Fig. S1). M(x at %)-doped V_2O_5 (M = Mo and W) was prepared from V_2O_5 and either MoO_3 or WO_3 by a solid-state reaction at 973 K for 5 h. One gram of M-doped V_2O_5 (M = Mo and W) powder was pulverized by a planetary ball mill (Fritsch Japan; Pulverisette) at 800 rpm for 5 min with zirconium balls (10 g, Φ1 mm) in pure water (6 mL). Bi_2O_3 (5 mmol) and pulverized Mo- and W-doped V_2O_5 (5 mmol) powders were stirred in 2 mol L^{-1} of an aqueous acetic acid solution at 343 K for 24 h. The 343 K was applied to shorten the synthesis time because more than 1 week was necessary to obtain single phase of $BiVO_4$ at room temperature [35]. The obtained powder was carefully washed with water using a centrifuge (3000 rpm for 15 min, 3–4 times), and was subsequently calcined at 673 K or 873 K for 5 h in air for photocatalytic O_2 evolution. The M-doped $BiVO_4$ powder without calcination was loaded on a tin-doped indium oxide (ITO) transparent conductive substrate (GEOMATEC, HD-TCO) by an electrophoresis method (50 V, 30 s) and subsequent calcination at 673 K or 873 K for 1 h in air for photoelectrochemical measurements.

The crystal phase of the prepared powder was analyzed on an X-ray diffractometer (Rigaku, MiniFlex). Diffuse reflectance spectra were obtained using a UV-vis-NIR spectrometer (JASCO; Ubest-570) equipped with an integrating sphere, and were converted from reflection to absorbance by the Kubelka-Munk method. The specific surface area of the sample was determined by N_2 adsorption using the Brunauer-Emmett-Teller (BET) method (Coulter; SA3100). Morphology of the photocatalyst powder was observed using a scanning electron microscope (Jeol; JSM-6700F). Electron spin resonance (ESR) spectra were recorded at room temperature on an ESR spectrometer (ADANI; SPINSCAN) with a microwave frequency of 9.4 GHz.

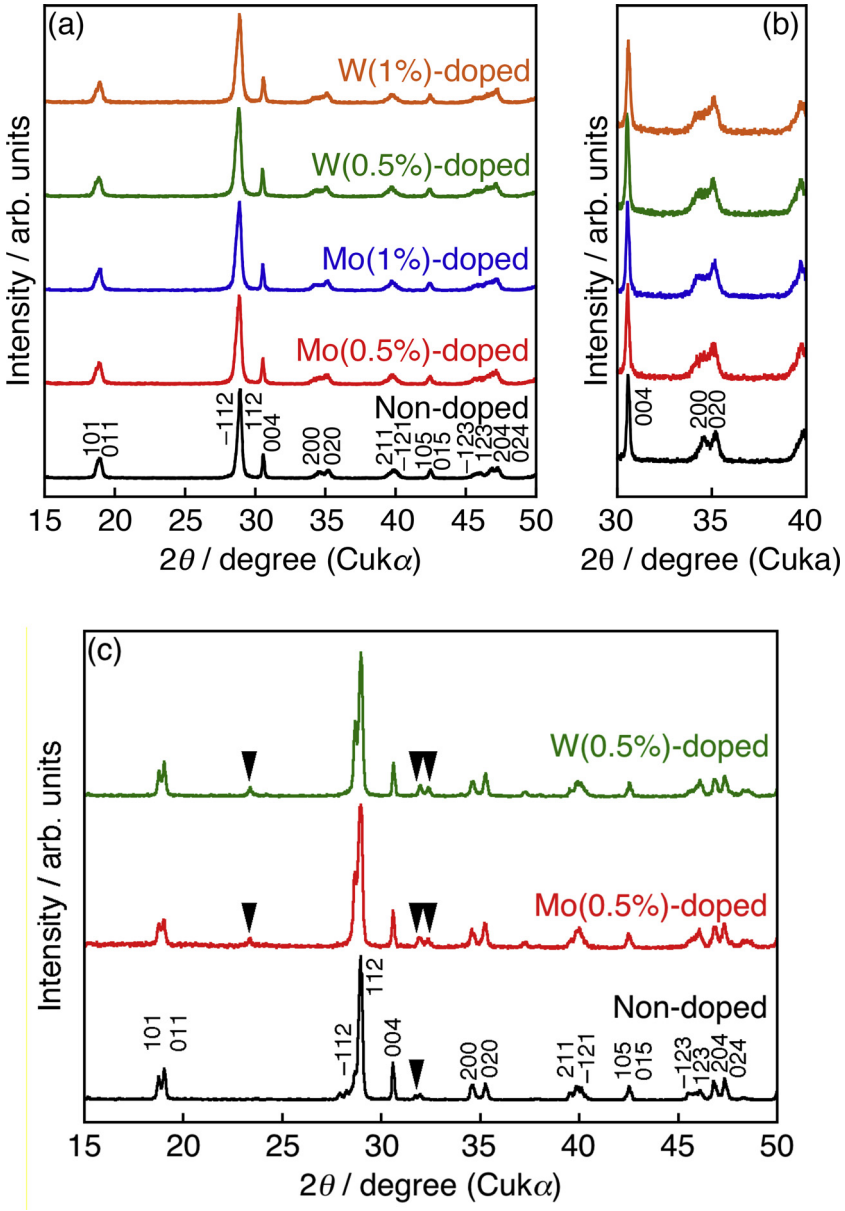

Fig. 1. XRD patterns of non-, Mo-, and W-doped $BiVO_4$ prepared by stirring starting materials of Bi_2O_3 and, non-, Mo-, and W-doped V_2O_5 in an aqueous acetic acid solution at 343 K for 24 h and subsequent calcination at (a,b) 673 K and (c) 873Kfor 5 h in air. Triangles represent peaks from impurities.