Photocatalytic and photoelectrochemical properties of zirconium-doped bismuth vanadate

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Abstract: Impacts of zirconium (Zr) doping into the $BiVO_4$ powder on its photocatalytic and photo electrochemical (PEC) properties for O_2 evolution were examined. In the powder photocatalytic system, formation of the $BiVO_4$ powder crystallized in the monoclinic scheelite structure (ms-$BiVO_4$) was achieved when the sample doped with relatively small amount of Zr; the Zr-doped ms-$BiVO_4$ powder showed relatively high photocatalytic activity when compared to that of non-doped ms-$BiVO_4$. Similar effects of Zr doping were also confirmed by the PEC system based on the $BiVO_4$ thin film doped with Zr. The Zr doping would induce increase in carrier (electron) density by the selective replacement of the Bi site of $BiVO_4$ samples.

Keywords: Zr-doping, photocatalytic water oxidation, crystalline structure.

1. Introduction

Bismuth vanadate ($BiVO_4$) has been studied extensively as a potential photocatalyst and/or photoanode for oxygen (O_2) production through water-splitting using sunlight.[1] Especially, the compound has been employed for a two-step photoexcitation system, called a Z-scheme water splitting.[2,3] The $BiVO_4$ compound exists in three crystalline phases, namely monoclinic scheelite (ms-$BiVO_4$), tetragonal scheelite (ts-$BiVO_4$), and tetragonal zircon (tz-$BiVO_4$) structures. For the water oxidation, the ms-$BiVO_4$ compound is known to be the most active of all. Therefore, several approaches were examined for selective production of ms-$BiVO_4$ with high crystallinity.[4] As another strategy for the improvement of photocatalytic or PEC function, doping with a secondary element is also examined. In accordance with the study of density functional theory (DFT) reported by Yin et al., group IVB elements such as Zr and Hf can substitute the Bi site in $BiVO_4$ because of its low formation energy.[5] Since replacements of trivalent Bi with tetravalent Zr and Hf should induce increments of n-type conductivity, these electrostructural changes would be beneficial for the improvement of photocatalytic water oxidation. In this study, therefore. we investigated fabrication of $BiVO_4$ powders and films doped with Zr; their photocatalytic and PEC properties for water oxidation were discussed in relation to their structural characteristics.

2. Experimental

$BiVO_4$ powders were prepared in an aqueous nitric acid solution containing Bi^{3+} ions and V_2O_5 powders, as reported in the literature.[3] For the doping with Zr, the reaction was performed in the same procedure with an addition of a Zr source. Amounts of doped Zr were varied from 0.1 to 3.0%. Thus-obtained samples were labelled Z(x)BVO, where x denotes molar content of doped Zr, i.e., Z(0.5)BVO represents 0.5 mol% of Zr-doped $BiVO_4$.

$BiVO_4$ thin film electrodes were prepared on fluorine-doped tin-oxide-coated glass slide (FTO/glass, Aldrich) by spin coating in accordance with the literature procedure using commercial binary oxide precursor solutions.[6] A ZrO_2 soliton precursor was also used for the Zr-doping. In the same manner as the above powder system, thus-obtained non-doped $BiVO_4$ and Zr-doped $BiVO_4$ powders were labeled BVO*f* and Z(x)BVO*f* (x: molar amount of doped Zr).

Photocatalytic O_2 evolution were performed in a borosilicate-glass test tube containing 50 mg of BVO or Z(x)BVO powders suspended in 5 cm^3 of aqueous $AgNO_3$ solution (0.05 M). After replacement of air to Ar in the test tube, and the suspension was photoirradiated by a Xe lamp. The amount of evolved O_2 was analyzed every 0.5 h. The PEC water oxidation was performed by using a three-electrode system consisting of the thin-film sample as a working electrode, a Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. These electrodes were immersed in a phosphate buffer with pH 6.86. The above-mentioned Xe lamp was used as a light source.

3. Results and discussion

The XRD patterns of BVO, Z(x)BVO showed diffractions assignable to scheelite $BiVO_4$, and there was no diffraction derived from any other impurities. As observed by SEM, BVO and Z(x)BVO samples consisted of aggregates of angular shaped crystals with submicron sizes; there is almost no structural and morphological differences between these samples.

Figure 1 shows typical time course curves of O_2 evolution over the BVO and Z(0.5)BVO powders. Compared to the BVO sample, Z(0.5)BVO showed higher activity: this would be the first demonstration to achieve a significant enhancement of photocatalytic activity of ms-$BiVO_4$ by the Zr doping. We also examined effects of amounts of the Zr doping in the $BiVO_4$ lattice on photocatalytic properties. As a result, further increment of the content of doped Zr was found to be detrimental due to the induction of structural transition from ms-$BiVO_4$ to ts-$BiVO_4$.

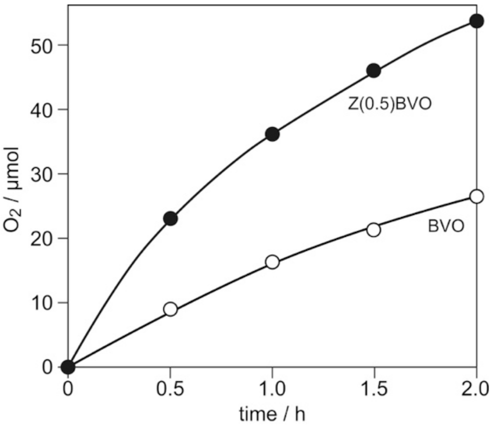

Figure 1. Time course curves of O_2 evolution over BVO and Z(0.5)BVO powders.

Figure 2 shows typical current density-voltage scans of BVO_f, Z(0.5)BVO_f, Z(1.0)BVO_f, and Z(3.0)BVO_f under photoirradiation. All the film did not provide appreciable anodic photocurrents when the current density-voltage scan was performed under dark, indicating that observed currents showed derived from PEC water oxidation. Similar to the above results on photocatalytic O_2 evolution, the significant improvement of PEC water oxidation was achieved for the Zr doping with relatively low content (Z(0.5)BVO_f).

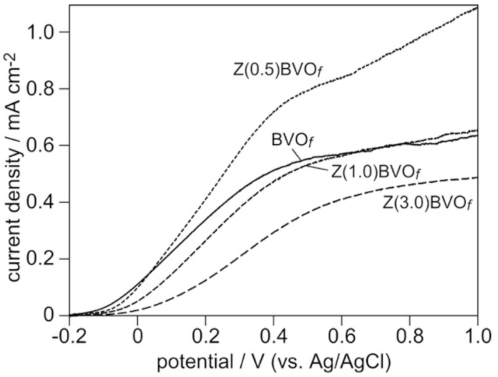

Figure 2. LSV scans of BVO_f, Z(0.5)BVO_f, Z(1.0)BVO_f, and Z(3.0)BVO_f films under photoirradiation.

4. Conclusions

In this study, we have proved effectiveness of Zr doping into the ms-$BiVO_4$ crystal for improvements of its photocatalytic and PEC functions for water oxidation to produce O_2. The doped Zr was assumed to be replaced with the Bi site: due to the replacement of electron-rich Zr, the n-type doping would occur. However, details in crystallographic and electric structures, e.g., the actual doping site(s) of Zr in the crystalline lattice of ms-$BiVO_4$, the quantitative evaluation of carrier densities of the sample with or without doped Zr …etc., are not clarified. Further studies along these lines are now in progress.

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