## Preparation of BiVO<sub>4</sub> Typed Photoanode for Photoelectrochemical Water Splitting

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## 1 Introduction

The H<sub>2</sub> production by water splitting using photoelectrode has attracted attention as promising energy conversion system. In particular, numerous efforts have been focused on various BiVO<sub>4</sub> typed photoanodes capable of utilizing a wide range of light energy (~520 nm) and achieving efficient O<sub>2</sub> generation through water splitting. [1] Recently, photoelectrode system capable of producing and accumulating high-value-added oxidation reagents (*e.g.* oxidative H<sub>2</sub>O<sub>2</sub> production from H<sub>2</sub>O) using the BiVO<sub>4</sub> typed photoanode has been also focused as effective utilization technique of oxidation (anode) reaction. [2-3]

The photocurrent properties (photocurrent and onset potential) in almost of  $BiVO_4$  typed photoanodes significantly depend on the presence or absence of interlayer (underlayer) and the species. For example, a  $WO_3/BiVO_4$  photoanode combining  $BiVO_4$  with a  $WO_3$  underlayer shows exceptional photoelectrochemical performance for water splitting. [1] However, detail mechanism on the photocurrent properties of  $BiVO_4$  is still unclear about effects of underlayer.

At the beginning, we focused on the  $BiVO_4$  on various substrates, *i.e.*, the change and difference of supported condition of  $BiVO_4$  supported on various substrates were investigated using the X-ray absorbance fine structure (XAFS) spectra.

## 2 Experiment

The WO<sub>3</sub>/BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub> and BiVO<sub>4</sub> on F-doped SnO<sub>2</sub> conductive glass (FTO) substrate prepared using metal organic decomposition (MOD) method were used as photoanode samples. The WO<sub>3</sub> and SnO<sub>2</sub> underlayer were prepared on the FTO substrate by calcination after spin coating of solution of tungsten hexachloride and tin chloride as precursors. The mixed solution (Bi:V=1:1) of commercial Bi and V solutions was coated on WO<sub>3</sub> and SnO<sub>2</sub> underlayers and the FTO substrate by same spin coating, and then the film was calcined, resulting in the formation of WO<sub>3</sub>/BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub> and BiVO<sub>4</sub> photoanode. These photoanodes were characterized using XRD and the Bi  $L_{III}$ -edge XAFS (fluorescence mode).

## 3 Results and Discussion

 $BiVO_4$  on these photoanodes exhibited similar diffraction patterns derived from monoclinic type  $BiVO_4$  from result of the XRD measurement. Fig. 1 shows Bi L<sub>III</sub>-edge XANES spectra of these  $BiVO_4$  typed photoanodes. For comparison, 5 wt%  $BiVO_4$  powder was also measured as reference sample. The XANES spectra



Fig. 1: Bi  $L_{III}$ -edge XANES spectra of (a) 5 wt% BiVO<sub>4</sub> powder (reference), (b) BiVO<sub>4</sub>, (c) WO<sub>3</sub>/BiVO<sub>4</sub> and (d) SnO<sub>2</sub>/BiVO<sub>4</sub>.

of all samples were similar to that of the reference BiVO<sub>4</sub> powder, and few energy shift was also observed. Interestingly, although the WO<sub>3</sub>/BiVO<sub>4</sub> photoanode exhibited particularly-excellent photocurrent and onset potential in electrolyte of KHCO3 aqueous solution compared to BiVO<sub>4</sub> photoanode without underlayer, little change of selectivity (Faraday efficiency) of oxidative H<sub>2</sub>O<sub>2</sub> production using H<sub>2</sub>O as raw materilal was also confirmed in the BiVO<sub>4</sub> and WO<sub>3</sub>/BiVO<sub>4</sub> photoanodes [3]. These results indicate that these BiVO<sub>4</sub> particles prepared using the MOD method possess similar valence and coordination structure despite different substrates, and these specific phenomena on photocurent properties and product selectivity by species of substrates may derive from interface between the BiVO<sub>4</sub> and underlayer or FTO substrate. More detail tracking for mechanism elucidation are currently under investigation.

References

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