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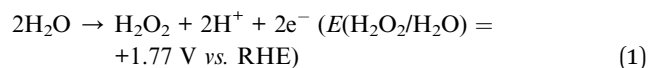
# WO<sub>3</sub>/BiVO<sub>4</sub> photoanode coated with mesoporous Al<sub>2</sub>O<sub>3</sub> layer for oxidative production of hydrogen peroxide from water with high selectivity†

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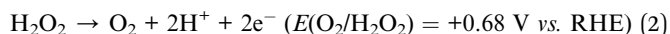
A WO<sub>3</sub>/BiVO<sub>4</sub> photoanode coated with various metal oxides demonstrated high selectivity (faradaic efficiency) for hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) generation from water (H<sub>2</sub>O) under irradiation of simulated solar light in a highly concentrated hydrogen carbonate (KHCO<sub>3</sub>) aqueous solution. A mesoporous and amorphous aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) layer significantly facilitated inhibition of the oxidative degradation of generated H<sub>2</sub>O<sub>2</sub> into oxygen (O<sub>2</sub>) on the photoanode, resulting in unprecedented H<sub>2</sub>O<sub>2</sub> selectivity (ca. 80%) and the accumulation (>2500 μM at 50°C).

Chemical conversions using light energy have been performed in various fields since the discovery of the Honda–Fujishima effect.<sup>1–25</sup> Significant efforts have recently been devoted to H<sub>2</sub> production by water splitting using inexhaustible light for clean energy conversion processes.<sup>1–4,8–29</sup> Photoelectrode systems are widely recognised as a promising technology for H<sub>2</sub> production because they operate at an electrolysis voltage lower than the theoretical electrolysis voltage of water (<1.23 V).<sup>1,8–29</sup> Visible light-responsive oxide photoanodes with a narrow bandgap energy, such as WO<sub>3</sub>, BiVO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, are desirable for the efficient utilisation of solar light and economical synthetic processes.<sup>8–29</sup> Most importantly, numerous efforts have been focused on BiVO<sub>4</sub> photoanodes capable of utilising a wide range of light energy (~520 nm) and achieving efficient O<sub>2</sub> generation by water splitting.<sup>9–21,28,29,32</sup> A WO<sub>3</sub>/BiVO<sub>4</sub> photoanode that combines BiVO<sub>4</sub> with a WO<sub>3</sub> underlayer for the efficient transfer of excited electrons on BiVO<sub>4</sub> to the F-doped SnO<sub>2</sub> conductive glass (FTO) substrate shows exceptional photoelectrochemical performance for water splitting into H<sub>2</sub> and O<sub>2</sub>.<sup>10–13,17–20,28,29,32</sup> However, most previous investigations, containing electrochemical reactions, focused solely on the recovery of H<sub>2</sub> energy generated on the cathode and little attention was paid to the recovery of the oxidation products simultaneously evolved during water splitting.<sup>24–31</sup>

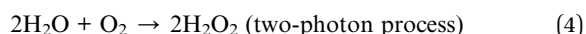
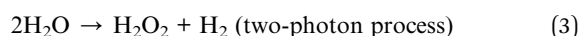
H<sub>2</sub>O<sub>2</sub> is an especially versatile and clean oxidation product having the potential to generate instead of O<sub>2</sub> from H<sub>2</sub>O (eqn (1)).



However, the accumulation of H<sub>2</sub>O<sub>2</sub>, generated oxidatively is extremely difficult because degradation of H<sub>2</sub>O<sub>2</sub> into O<sub>2</sub> also occurs easily and oxidatively in a conventional photoelectrochemical system *i.e.* the redox potential of H<sub>2</sub>O<sub>2</sub> degradation is more negative than the redox potential of H<sub>2</sub>O<sub>2</sub> production from H<sub>2</sub>O (eqn (1) and (2)), resulting in low selectivity for oxidative H<sub>2</sub>O<sub>2</sub> generation.



Recently, we reported that a photoelectrochemical system combining the WO<sub>3</sub>/BiVO<sub>4</sub> photoanode and aqueous electrolyte of KHCO<sub>3</sub> under CO<sub>2</sub> bubbling could achieve simultaneous generation and accumulation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> from H<sub>2</sub>O (eqn (3)).<sup>28,29</sup> In this system, the aqueous electrolyte of KHCO<sub>3</sub> acts as an excellent oxidative catalyst for generating H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub>O. Moreover, H<sub>2</sub>O<sub>2</sub> could be produced at no external bias on both a WO<sub>3</sub>/BiVO<sub>4</sub> photoanode (from H<sub>2</sub>O) and an Au cathode (from O<sub>2</sub>) *via* a two-photon process (eqn (4)).<sup>29</sup>



Although the selectivity (faradaic efficiency:  $\eta(\text{H}_2\text{O}_2)$ ) of reductive H<sub>2</sub>O<sub>2</sub> production from O<sub>2</sub> on cathodes such as Au was very high, almost 100%, the maximum selectivity ( $\eta(\text{H}_2\text{O}_2)$ ) for oxidative H<sub>2</sub>O<sub>2</sub> production on WO<sub>3</sub>/BiVO<sub>4</sub> photoanodes was still

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† Electronic supplementary information (ESI) available: Experimental section, SEM images, XRD spectra, LHE spectra, applied voltage properties, *I*–*V* characteristic of photoanodes, pore size distribution of the MeO<sub>x</sub> particles, effect of Al<sub>2</sub>O<sub>3</sub> amount on WO<sub>3</sub>/BiVO<sub>4</sub> and dependence of applied voltage. See DOI: 10.1039/c7ra09693c



low, only *ca.* 54%. The design of novel photoanodes capable of achieving efficient  $\text{H}_2\text{O}_2$  generation and inhibiting oxidative degradation of generated  $\text{H}_2\text{O}_2$  is absolutely imperative for building a clean and breakthrough technology, by accumulating  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  with unprecedented  $\text{H}_2\text{O}_2$  selectivity using only  $\text{H}_2\text{O}$  as the raw material.

Here, we focused on a surface modification of the metal oxide ( $\text{MeO}_x$ ) layers on the  $\text{WO}_3/\text{BiVO}_4$  photoanode surface to achieve excellent selectivity of generation and accumulation of  $\text{H}_2\text{O}_2$  in the  $\text{KHCO}_3$  aqueous solution under simulated solar light irradiation (Fig. 1). The  $\text{MeO}_x$  layers were prepared by spin-coating of metal organic solutions and calcination. Introducing a porous  $\text{Al}_2\text{O}_3$  layer was found to specifically permit oxidative  $\text{H}_2\text{O}_2$  generation and accumulation with exceptional selectivity in an aqueous  $\text{KHCO}_3$  electrolyte because of the blocking effect of oxidative degradation of the generated  $\text{H}_2\text{O}_2$  into  $\text{O}_2$  on the photoanode.

Details regarding experimental procedures for preparation and photoelectrochemical reactions of photoanodes are provided in the ESI†.

The effects of  $\text{MeO}_x$  layers, modified on the  $\text{WO}_3/\text{BiVO}_4$  photoanode, for oxidative  $\text{H}_2\text{O}_2$  generation properties were investigated at an applied electric charge of 0.9C (900 s at steady photocurrent of 1 mA) in a 0.5 M  $\text{KHCO}_3$  aqueous electrolyte. As shown in Fig. 2, all  $\text{MeO}_x$ -coated photoanodes, except  $\text{CoO}_x$ , enhanced the oxidative  $\text{H}_2\text{O}_2$  generation compared to a bare  $\text{WO}_3/\text{BiVO}_4$  photoanode, and the enhanced effect, ranked by the modified metal oxide, was  $\text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{TiO}_2 > \text{SiO}_2 \gg \text{CoO}_x$ . Little  $\text{H}_2\text{O}_2$  was observed on the  $\text{CoO}_x$  coated photoanode, because  $\text{CoO}_x$  probably decomposed the generated  $\text{H}_2\text{O}_2$  quickly, or  $\text{O}_2$  may be evolved on  $\text{CoO}_x$  directly. It should be noted that the  $\text{Al}_2\text{O}_3$  modification on the  $\text{WO}_3/\text{BiVO}_4$  photoanode achieved roughly twice the oxidative  $\text{H}_2\text{O}_2$  generation compared to the bare  $\text{WO}_3/\text{BiVO}_4$  photoanode. The  $\text{Al}_2\text{O}_3$  uniformly, smoothly and flatly covered the entire area of the  $\text{WO}_3/\text{BiVO}_4$  photoanode as shown in the SEM images (Fig. 3), whereas other  $\text{MeO}_x$  were granularly and uniformly supported on that and possessed any crack holes (Fig. S1; ESI†). It was also confirmed, from XRD measurement (Fig. S2; ESI†), that no

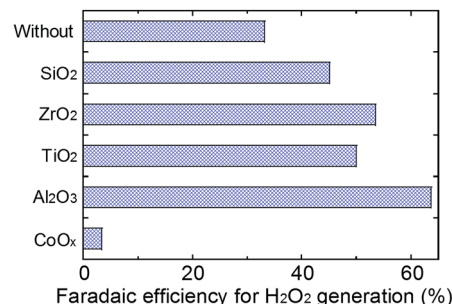


Fig. 2 Oxidative  $\text{H}_2\text{O}_2$  generation on photoanodes ( $\text{WO}_3/\text{BiVO}_4/\text{MeO}_x$ ) modified various metal oxides on a  $\text{WO}_3/\text{BiVO}_4$  at an electric charge of 0.9C (900 s at steady photocurrent of 1 mA) in a 0.5 M  $\text{KHCO}_3$  aqueous electrolyte (35 mL) in an ice bath (below  $5^\circ\text{C}$ ) under simulated solar light.

diffraction peaks derived from  $\text{MeO}_x$  were observed in all  $\text{WO}_3/\text{BiVO}_4/\text{MeO}_x$  photoanodes, suggesting that all tried  $\text{MeO}_x$  modified on  $\text{WO}_3/\text{BiVO}_4$  photoanode possess amorphous-like structure. As shown in Fig. S3; ESI†, little change of the light harvesting efficiency (LHE) was also confirmed in tried all photoanodes, suggesting that these  $\text{MeO}_x$  introduced on the  $\text{WO}_3/\text{BiVO}_4$  have little effect to light absorption efficiency on  $\text{WO}_3/\text{BiVO}_4$  photoanode. The time courses of voltages applied between photoanode and a counter electrode of Pt mesh at steady photocurrent of 1 mA (Fig. 2) in oxidative  $\text{H}_2\text{O}_2$  generation reaction were also confirmed (Fig. S4; ESI†). The voltages for applying steady photocurrent of 1 mA slightly increased by introducing  $\text{MeO}_x$  on the  $\text{WO}_3/\text{BiVO}_4$  photoanode. In particular,  $\text{WO}_3/\text{BiVO}_4/\text{Al}_2\text{O}_3$  photoanode, coated uniformly, smoothly and flatly at  $\text{Al}_2\text{O}_3$  compared to other  $\text{MeO}_x$ , required highest applied voltage. In order to confirm the effect introducing the  $\text{Al}_2\text{O}_3$  on the photoanode in more detail, the photocurrent property of the  $\text{WO}_3/\text{BiVO}_4/\text{Al}_2\text{O}_3$  photoanode was investigated in a 0.5 M  $\text{KHCO}_3$  aqueous solution (Fig. S5; ESI†). The bare  $\text{WO}_3/\text{BiVO}_4$  photoanode exhibited excellent photocurrent property in all applied voltage ranges as with our past reported example,<sup>11,12,28,29</sup> and the photocurrent property slightly decreased by introducing the  $\text{Al}_2\text{O}_3$  layer. However, it should be noted that the decreasing degree of the photocurrent property was slight, only *ca.* 9% and 5% at +1.23 V and +1.77 V vs. RHE, respectively, although the  $\text{Al}_2\text{O}_3$ , having an insulation property, covered the entire area of the  $\text{WO}_3/\text{BiVO}_4$  photoanode. A similar

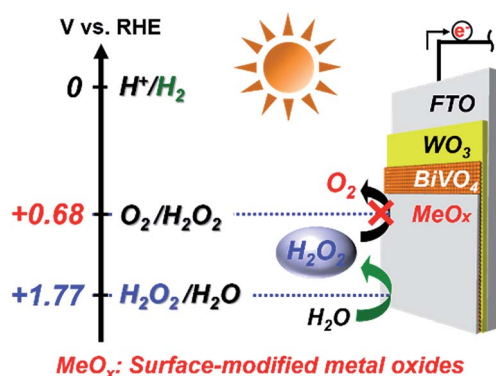


Fig. 1 Pattern and energy diagrams for photoelectrochemical  $\text{H}_2\text{O}_2$  generation from  $\text{H}_2\text{O}$  on  $\text{WO}_3/\text{BiVO}_4/\text{MeO}_x$  photoanodes under solar light irradiation.

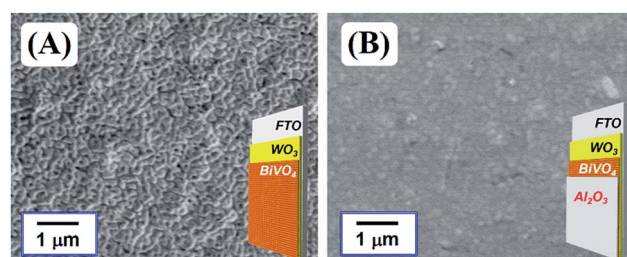


Fig. 3 SEM images of (A)  $\text{WO}_3/\text{BiVO}_4$  and (B)  $\text{WO}_3/\text{BiVO}_4/\text{Al}_2\text{O}_3$  photoanodes.



phenomenon has also been observed in  $O_2$  and  $H_2$  generation through water splitting on a photoanode coated with amorphous-like  $Ta_2O_5$ .<sup>32</sup> In addition, it was confirmed, from the  $N_2$  absorption and desorption measurement of  $MeO_x$  particles (Fig. S6; ESI†), that almost all  $MeO_x$  possess mesoporous structure at a pore size of *ca.* 4–20 nm. In particular, a pore size of the  $Al_2O_3$  was *ca.* 4.7 nm. The thicknesses of  $Al_2O_3$  calculated from the coating amount on the  $WO_3/BiVO_4$  photoanode by XRF measurement were *ca.* 100 nm ( $0.055 \text{ mg cm}^{-2}$ ). In order to also investigate the effects of dense  $Al_2O_3$  on  $WO_3/BiVO_4$  on the oxidative  $H_2O_2$  generation, increasing  $Al_2O_3$  amount on  $WO_3/BiVO_4$  photoanode was performed by decreasing the spin coating number (500 rpm) of precursor solution of EMOD solved in butyl acetate containing ethylcellulose when introducing  $Al_2O_3$  layers. The thickness of  $Al_2O_3$  introduced at 500 rpm calculated from the XRF measurement was *ca.* 127 nm ( $0.070 \text{ mg cm}^{-2}$ ), suggested that the thickness increases with decreasing the spin coating number. As shown in Fig. S7; ESI†, little change of the  $H_2O_2$  generation amounts was observed on these  $WO_3/BiVO_4/Al_2O_3$  photoanodes prepared at 500 and 1000 rpm, indicating that increasing  $Al_2O_3$  on  $WO_3/BiVO_4$  photoanode has little effect on the oxidative  $H_2O_2$  generation. In subsequent experiments,  $WO_3/BiVO_4/Al_2O_3$  photoanode prepared at 1000 rpm was utilized as the photoanode. These results indicate that the specific effect enhancing oxidative  $H_2O_2$  generation property was achieved on the  $WO_3/BiVO_4$  though the mesoporous and amorphous  $Al_2O_3$  layer covered uniformly, smoothly and flatly the entire area.

To track the specific performance enhancing effect of generating  $H_2O_2$  by introducing the  $Al_2O_3$  layer, the concentration dependency of  $KHCO_3$  aqueous electrolytes on the oxidative  $H_2O_2$  generation property was investigated at an applied electric charge of 0.9C (Fig. 4(A)). We have already reported that the oxidative  $H_2O_2$  generation property on the  $WO_3/BiVO_4$  photoanode was improved with increasing concentration of  $KHCO_3$ , which acts as an effective catalyst for  $H_2O_2$

generation *via* the two-electron oxidation of  $H_2O$ .<sup>28</sup> Even in the case of using the  $WO_3/BiVO_4/Al_2O_3$  photoanode, the selectivity ( $\eta(H_2O_2)$ ) for  $H_2O_2$  generation was significantly enhanced with increasing concentration of  $KHCO_3$ , and the  $\eta(H_2O_2)$  in the 2.0 M  $KHCO_3$  aqueous solution reached *ca.* 80% at 0.9C, whereas that using the bare  $WO_3/BiVO_4$  photoanode was *ca.* 54%. It should be noted that the selectivity ( $\eta(H_2O_2) = \text{ca. } 53\%$ ) on the  $WO_3/BiVO_4/Al_2O_3$  photoanode in lowly concentrated  $KHCO_3$  (0.1 M) was comparable to that (*ca.* 54%) on the bare  $WO_3/BiVO_4$  photoanode in highly concentrated  $KHCO_3$  (2.0 M). This suggests that the  $Al_2O_3$  could effectively be contributing to oxidative  $H_2O_2$  generation from  $H_2O$  even in the lowly concentrated  $KHCO_3$ . Moreover, as shown in Fig. 4(B), the excellent  $H_2O_2$  generation property on the  $WO_3/BiVO_4/Al_2O_3$  photoanode compared to the  $WO_3/BiVO_4$  photoanode was significantly maintained even at high electric charge up to 50C. As a result, the accumulation amount, using the  $WO_3/BiVO_4/Al_2O_3$  photoanode, reached  $>2500 \mu\text{M}$  at 50C, while that using the bare  $WO_3/BiVO_4$  photoanode was  $>1300 \mu\text{M}$  at 50C. The dependency of the applied voltage on the oxidative  $H_2O_2$  generation was investigated to confirm the effect of the  $Al_2O_3$  coating in detail (Fig. S8; ESI†). A small change in  $H_2O_2$  generation performance was observed in all ranges of applied voltages (0.8–1.8 V), suggesting that the enhanced effect of introducing an  $Al_2O_3$  layer is independent of the voltages applied between a photoanode as the working electrode and a Pt mesh as counter electrode using the aqueous electrolyte of the  $KHCO_3$ .

Although little development with regards to highly selective  $H_2O_2$  generation *via* two-photon oxidation of  $H_2O$  and accumulation using photoanodes has been reported, our method of  $Al_2O_3$  coating on the  $WO_3/BiVO_4$  photoanode produced tremendous improvement in selective  $H_2O_2$  generation and accumulation from  $H_2O$  in a  $KHCO_3$  aqueous electrolyte. It is speculated that the specific enhancement of selectivity for  $H_2O_2$  generation on the  $WO_3/BiVO_4/Al_2O_3$  photoanode may be caused by a blocking effect, on the mesoporous  $Al_2O_3$  layer, that inhibits oxidative  $H_2O_2$  degradation into  $O_2$  on the  $BiVO_4$ . To investigate the blocking effect on the  $Al_2O_3$  layer, a degradation property test of  $H_2O_2$  was performed in a 2.0 M  $KHCO_3$  aqueous solution containing  $H_2O_2$  ( $550 \mu\text{M}$ ) in the presence of the bare  $WO_3/BiVO_4$  or  $WO_3/BiVO_4/Al_2O_3$  photoanodes in presence or absence of simulated solar light irradiation in an ice bath (below  $5^\circ\text{C}$ ). In both cases, as shown in Fig. 5, almost all the initial amount of  $H_2O_2$  was maintained in the dark condition, however, the  $H_2O_2$  amount drastically decreased with irradiation by simulated solar light, suggesting that the  $H_2O_2$  was decomposed by photocarriers (excited electrons and holes) produced on the  $BiVO_4$ . It should be noted that the  $H_2O_2$  degradation in the presence of the  $WO_3/BiVO_4/Al_2O_3$  photoanode was dramatically inhibited compared to the degradation in the presence of a bare  $WO_3/BiVO_4$  photoanode. The oxidative  $H_2O_2$  generation test was also confirmed in a 2.0 M  $KHCO_3$  aqueous electrolyte, initially containing  $H_2O_2$  ( $210 \mu\text{M}$ ) on the bare  $WO_3/BiVO_4$  and  $WO_3/BiVO_4/Al_2O_3$  photoanodes, to track the generated  $H_2O_2$  degradation behaviour in more detail (Fig. 6). The generated rates of  $H_2O_2$  were reduced by the initial addition of  $H_2O_2$  in both cases of presence or absence of  $Al_2O_3$ .

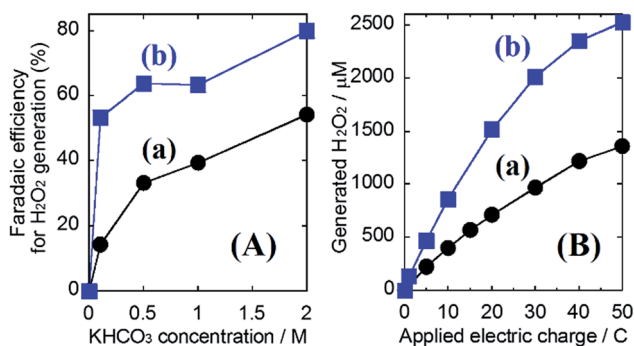


Fig. 4 (A) Oxidative  $H_2O_2$  generation in  $KHCO_3$  aqueous electrolytes (35 mL) of different concentrations at applied electric charges of 0.9C (900 s at steady photocurrent of 1 mA) under simulated solar light and (B) accumulation of oxidative  $H_2O_2$  generation in a 2.0 M  $KHCO_3$  aqueous solution (35 mL) under visible light irradiation ( $\lambda > 420 \text{ nm}$ ) using an intense Xe lamp at an applied voltage of 1.5 V in an ice bath (below  $5^\circ\text{C}$ ) on a (a) bare  $WO_3/BiVO_4$  and (b)  $WO_3/BiVO_4/Al_2O_3$  photoanodes.





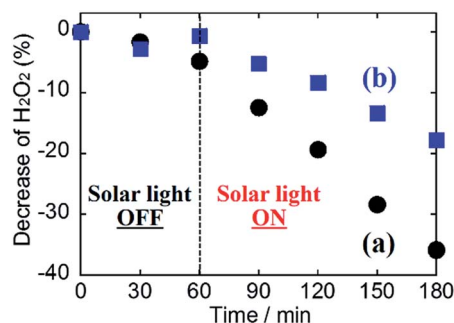


Fig. 5 Degradation properties of H<sub>2</sub>O<sub>2</sub> (550 μM) initially added in a 2.0 M KHCO<sub>3</sub> aqueous solution in an ice bath (below 5 °C) under CO<sub>2</sub> bubbling and simulated solar light irradiation in the presence of a (a) WO<sub>3</sub>/BiVO<sub>4</sub> and (b) WO<sub>3</sub>/BiVO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> photoanodes at no applied voltage.

However, the decreasing rate of H<sub>2</sub>O<sub>2</sub> generation was significantly inhibited, from ca. 61% to ca. 39%, by introducing the Al<sub>2</sub>O<sub>3</sub> layer on the WO<sub>3</sub>/BiVO<sub>4</sub> photoanode. These results suggest that introducing the Al<sub>2</sub>O<sub>3</sub> layer significantly contributed to the highly selective H<sub>2</sub>O<sub>2</sub> generation and accumulation from H<sub>2</sub>O, with a high photocurrent property, by a blocking effect that inhibited the oxidative degradation of generated H<sub>2</sub>O<sub>2</sub>. The mechanism of blocking effect is proposed that the H<sub>2</sub>O<sub>2</sub> generated on the BiVO<sub>4</sub> in the WO<sub>3</sub>/BiVO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> photoanode diffuses in electrolyte of KHCO<sub>3</sub> aqueous solution through mesoporous of the Al<sub>2</sub>O<sub>3</sub>, and contact of the H<sub>2</sub>O<sub>2</sub> diffused in electrolyte with the BiVO<sub>4</sub> covered uniformly and smoothly Al<sub>2</sub>O<sub>3</sub> may be significantly inhibited compared with that with bare BiVO<sub>4</sub>, resulting in the formation of effective inhibition of oxidative H<sub>2</sub>O<sub>2</sub> degradation. Furthermore, there may be other possible mechanisms such as a blocking effect of a direct O<sub>2</sub> evolution site *via* a 4-photon process covering by Al<sub>2</sub>O<sub>3</sub>, or an enrichment effect resulting from the increasing KHCO<sub>3</sub> concentration around the photoanode based on the acid-base adsorption between HCO<sub>3</sub><sup>−</sup> (a weak base) and the weakly acidic sites on the Al<sub>2</sub>O<sub>3</sub> surface, related to the good

$\eta(\text{H}_2\text{O}_2)$  in lower KHCO<sub>3</sub> concentration, as shown in Fig. 4(A). The tracking and contribution of these other mechanisms, on the Al<sub>2</sub>O<sub>3</sub> layer, is currently under investigation.

## Conclusions

In summary, various metal oxides were coated onto a WO<sub>3</sub>/BiVO<sub>4</sub> photoanode to enhance the selectivity (faradaic efficiency) of oxidative H<sub>2</sub>O<sub>2</sub> generation, in an aqueous electrolyte of KHCO<sub>3</sub>, from water under solar light irradiation. Among the various metal oxides, the Al<sub>2</sub>O<sub>3</sub> coating, which produced a mesoporous and amorphous structure on the WO<sub>3</sub>/BiVO<sub>4</sub> photoanode, achieved excellent oxidative H<sub>2</sub>O<sub>2</sub> generation at a selectivity of ca. 80% and an accumulation of >2500 μM (50C). Interestingly, the Al<sub>2</sub>O<sub>3</sub>-coated WO<sub>3</sub>/BiVO<sub>4</sub> photoanode dramatically inhibited oxidative degradation of H<sub>2</sub>O<sub>2</sub> generated on the WO<sub>3</sub>/BiVO<sub>4</sub> photoanode after introducing the Al<sub>2</sub>O<sub>3</sub> layer. This study contributes to developing a promising design for a clean H<sub>2</sub>O<sub>2</sub> production system that uses only water as the raw material under solar light irradiation. More effective dreamy H<sub>2</sub>O<sub>2</sub> generation, at an excellent selectivity close to 100%, can be expected by modifying the surface-treatment technology, and it is currently under investigation.

## Conflicts of interest

There are no conflicts to declare.

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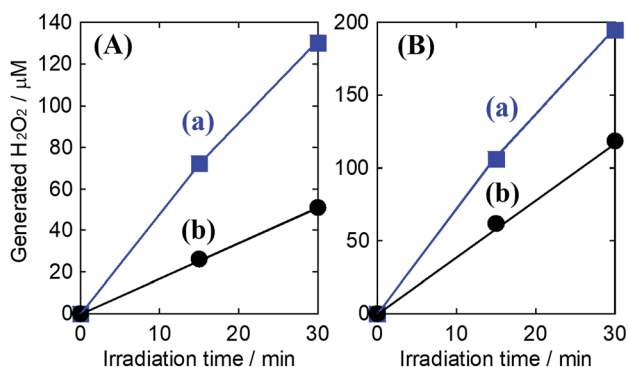


Fig. 6 Comparison of oxidative H<sub>2</sub>O<sub>2</sub> generation in a 2.0 M KHCO<sub>3</sub> aqueous electrolyte (a) in the absence of or (b) containing initially-added H<sub>2</sub>O<sub>2</sub> (210 μM) in an ice bath (below 5 °C) on a (A) WO<sub>3</sub>/BiVO<sub>4</sub> and (B) WO<sub>3</sub>/BiVO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> photoanodes under simulated solar light irradiation at steady photocurrent of 1 mA.



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