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WO₃/BiVO₄ photoanode coated with mesoporous Al₂O₃ layer for oxidative production of hydrogen peroxide from water with high selectivity†

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A WO₃/BiVO₄ photoanode coated with various metal oxides demonstrated high selectivity (faradaic efficiency) for hydrogen peroxide (H₂O₂) generation from water (H₂O) under irradiation of simulated solar light in a highly concentrated hydrogen carbonate (KHCO₃) aqueous solution. A mesoporous and amorphous aluminium oxide (Al₂O₃) layer significantly facilitated inhibition of the oxidative degradation of generated H₂O₂ into oxygen (O₂) on the photoanode, resulting in unprecedented H₂O₂ selectivity (ca. 80%) and the accumulation (>2500 μM at 50C).

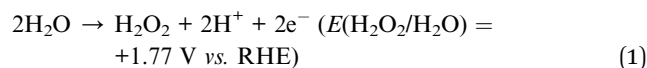
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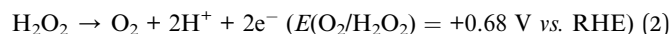
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Chemical conversions using light energy have been performed in various fields since the discovery of the Honda–Fujishima effect.^{1–25} Significant efforts have recently been devoted to H₂ production by water splitting using inexhaustible light for clean energy conversion processes.^{1–4,8–29} Photoelectrode systems are widely recognised as a promising technology for H₂ production because they operate at an electrolysis voltage lower than the theoretical electrolysis voltage of water (<1.23 V).^{1,8–29} Visible light-responsive oxide photoanodes with a narrow bandgap energy, such as WO₃, BiVO₄ and Fe₂O₃, are desirable for the efficient utilisation of solar light and economical synthetic processes.^{8–29} Most importantly, numerous efforts have been focused on BiVO₄ photoanodes capable of utilising a wide range of light energy (~520 nm) and achieving efficient O₂ generation by water splitting.^{9–21,28,29,32} A WO₃/BiVO₄ photoanode that combines BiVO₄ with a WO₃ underlayer for the efficient transfer of excited electrons on BiVO₄ to the F-doped SnO₂ conductive glass (FTO) substrate shows exceptional photoelectrochemical performance for water splitting into H₂ and O₂.^{10–13,17–20,28,29,32} However, most previous investigations, containing electrochemical reactions, focused solely on the recovery of H₂ energy generated on the cathode and little attention was paid to the recovery of the oxidation products simultaneously evolved during water splitting.^{24–31}

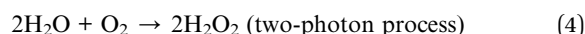
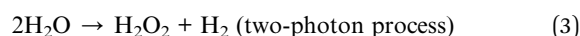
H₂O₂ is an especially versatile and clean oxidation product having the potential to generate instead of O₂ from H₂O (eqn (1)).



However, the accumulation of H₂O₂, generated oxidatively is extremely difficult because degradation of H₂O₂ into O₂ also occurs easily and oxidatively in a conventional photoelectrochemical system *i.e.* the redox potential of H₂O₂ degradation is more negative than the redox potential of H₂O₂ production from H₂O (eqn (1) and (2)), resulting in low selectivity for oxidative H₂O₂ generation.



Recently, we reported that a photoelectrochemical system combining the WO₃/BiVO₄ photoanode and aqueous electrolyte of KHCO₃ under CO₂ bubbling could achieve simultaneous generation and accumulation of H₂O₂ and H₂ from H₂O (eqn (3)).^{28,29} In this system, the aqueous electrolyte of KHCO₃ acts as an excellent oxidative catalyst for generating H₂O₂ from H₂O. Moreover, H₂O₂ could be produced at no external bias on both a WO₃/BiVO₄ photoanode (from H₂O) and an Au cathode (from O₂) *via* a two-photon process (eqn (4)).²⁹



Although the selectivity (faradaic efficiency: $\eta(\text{H}_2\text{O}_2)$) of reductive H₂O₂ production from O₂ on cathodes such as Au was very high, almost 100%, the maximum selectivity ($\eta(\text{H}_2\text{O}_2)$) for oxidative H₂O₂ production on WO₃/BiVO₄ 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_x particles, effect of Al₂O₃ amount on WO₃/BiVO₄ and dependence of applied voltage. See DOI: 10.1039/c7ra09693c



low, only *ca.* 54%. The design of novel photoanodes capable of achieving efficient H_2O_2 generation and inhibiting oxidative degradation of generated H_2O_2 is absolutely imperative for building a clean and breakthrough technology, by accumulating H_2O_2 and H_2 with unprecedented H_2O_2 selectivity using only H_2O as the raw material.

Here, we focused on a surface modification of the metal oxide (MeO_x) layers on the $\text{WO}_3/\text{BiVO}_4$ photoanode surface to achieve excellent selectivity of generation and accumulation of H_2O_2 in the KHCO_3 aqueous solution under simulated solar light irradiation (Fig. 1). The MeO_x layers were prepared by spin-coating of metal organic solutions and calcination. Introducing a porous Al_2O_3 layer was found to specifically permit oxidative H_2O_2 generation and accumulation with exceptional selectivity in an aqueous KHCO_3 electrolyte because of the blocking effect of oxidative degradation of the generated H_2O_2 into O_2 on the photoanode.

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

The effects of MeO_x layers, modified on the $\text{WO}_3/\text{BiVO}_4$ photoanode, for oxidative H_2O_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 KHCO_3 aqueous electrolyte. As shown in Fig. 2, all MeO_x -coated photoanodes, except CoO_x , enhanced the oxidative H_2O_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 H_2O_2 was observed on the CoO_x coated photoanode, because CoO_x probably decomposed the generated H_2O_2 quickly, or O_2 may be evolved on CoO_x directly. It should be noted that the Al_2O_3 modification on the $\text{WO}_3/\text{BiVO}_4$ photoanode achieved roughly twice the oxidative H_2O_2 generation compared to the bare $\text{WO}_3/\text{BiVO}_4$ photoanode. The Al_2O_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 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

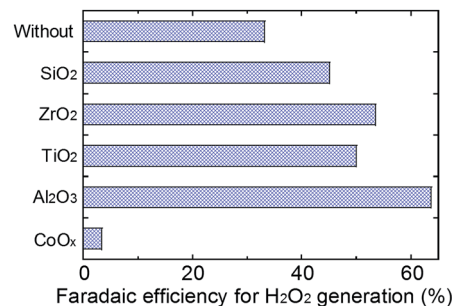


Fig. 2 Oxidative H_2O_2 generation on photoanodes ($\text{WO}_3/\text{BiVO}_4/\text{MeO}_x$) modified various metal oxides on a $\text{WO}_3/\text{BiVO}_4$ at an electric charge of 0.9C (900 s at steady photocurrent of 1 mA) in a 0.5 M KHCO_3 aqueous electrolyte (35 mL) in an ice bath (below 5°C) under simulated solar light.

diffraction peaks derived from MeO_x were observed in all $\text{WO}_3/\text{BiVO}_4/\text{MeO}_x$ photoanodes, suggesting that all tried 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 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 H_2O_2 generation reaction were also confirmed (Fig. S4; ESI†). The voltages for applying steady photocurrent of 1 mA slightly increased by introducing 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 Al_2O_3 compared to other MeO_x , required highest applied voltage. In order to confirm the effect introducing the Al_2O_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 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,^{11,12,28,29} and the photocurrent property slightly decreased by introducing the Al_2O_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 Al_2O_3 , having an insulation property, covered the entire area of the $\text{WO}_3/\text{BiVO}_4$ photoanode. A similar

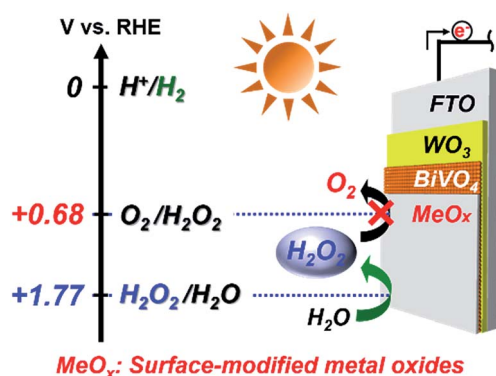


Fig. 1 Pattern and energy diagrams for photoelectrochemical H_2O_2 generation from H_2O on $\text{WO}_3/\text{BiVO}_4/\text{MeO}_x$ photoanodes under solar light irradiation.

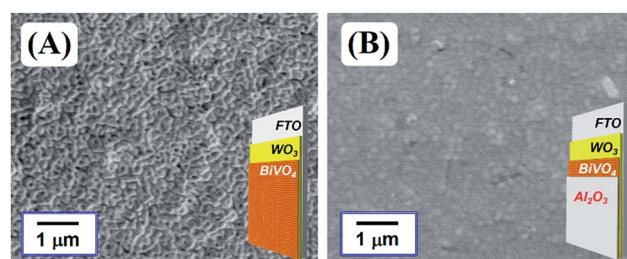


Fig. 3 SEM images of (A) $\text{WO}_3/\text{BiVO}_4$ and (B) $\text{WO}_3/\text{BiVO}_4/\text{Al}_2\text{O}_3$ photoanodes.



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 .³² 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 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 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 .²⁸ 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 ($\eta(H_2O_2) = ca. 53%$) 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 μM at 50C, while that using the bare $WO_3/BiVO_4$ photoanode was >1300 μM 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 μM) 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 °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 μM) 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 .

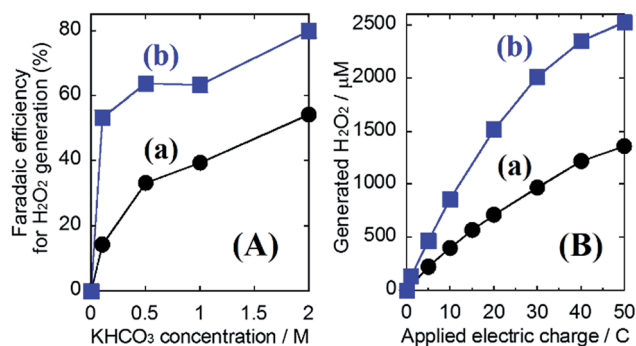


Fig. 4 (A) Oxidative H_2O_2 generation in $KHCO_3$ aqueous electrolytes (35 mL) of different concentrations at applied electric charges of 0.9C (900 s at steady photocurrent of 1 mA) under simulated solar light and (B) accumulation of oxidative H_2O_2 generation in a 2.0 M $KHCO_3$ aqueous solution (35 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 °C) on a (a) bare $WO_3/BiVO_4$ and (b) $WO_3/BiVO_4/Al_2O_3$ photoanodes.



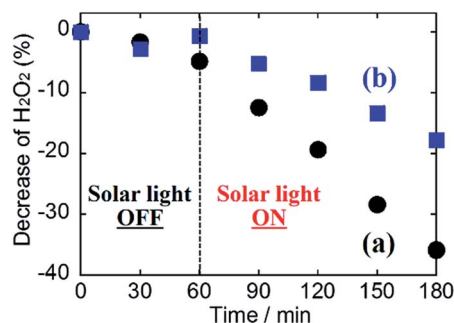


Fig. 5 Degradation properties of H₂O₂ (550 μM) initially added in a 2.0 M KHCO₃ aqueous solution in an ice bath (below 5 °C) under CO₂ bubbling and simulated solar light irradiation in the presence of a (a) WO₃/BiVO₄ and (b) WO₃/BiVO₄/Al₂O₃ photoanodes at no applied voltage.

However, the decreasing rate of H₂O₂ generation was significantly inhibited, from *ca.* 61% to *ca.* 39%, by introducing the Al₂O₃ layer on the WO₃/BiVO₄ photoanode. These results suggest that introducing the Al₂O₃ layer significantly contributed to the highly selective H₂O₂ generation and accumulation from H₂O, with a high photocurrent property, by a blocking effect that inhibited the oxidative degradation of generated H₂O₂. The mechanism of blocking effect is proposed that the H₂O₂ generated on the BiVO₄ in the WO₃/BiVO₄/Al₂O₃ photoanode diffuses in electrolyte of KHCO₃ aqueous solution through mesoporous of the Al₂O₃, and contact of the H₂O₂ diffused in electrolyte with the BiVO₄ covered uniformly and smoothly Al₂O₃ may be significantly inhibited compared with that with bare BiVO₄, resulting in the formation of effective inhibition of oxidative H₂O₂ degradation. Furthermore, there may be other possible mechanisms such as a blocking effect of a direct O₂ evolution site *via* a 4-photon process covering by Al₂O₃, or an enrichment effect resulting from the increasing KHCO₃ concentration around the photoanode based on the acid–base adsorption between HCO₃[−] (a weak base) and the weakly acidic sites on the Al₂O₃ surface, related to the good

$\eta(\text{H}_2\text{O}_2)$ in lower KHCO₃ concentration, as shown in Fig. 4(A). The tracking and contribution of these other mechanisms, on the Al₂O₃ layer, is currently under investigation.

Conclusions

In summary, various metal oxides were coated onto a WO₃/BiVO₄ photoanode to enhance the selectivity (faradaic efficiency) of oxidative H₂O₂ generation, in an aqueous electrolyte of KHCO₃, from water under solar light irradiation. Among the various metal oxides, the Al₂O₃ coating, which produced a mesoporous and amorphous structure on the WO₃/BiVO₄ photoanode, achieved excellent oxidative H₂O₂ generation at a selectivity of *ca.* 80% and an accumulation of >2500 μM (50C). Interestingly, the Al₂O₃-coated WO₃/BiVO₄ photoanode dramatically inhibited oxidative degradation of H₂O₂ generated on the WO₃/BiVO₄ photoanode after introducing the Al₂O₃ layer. This study contributes to developing a promising design for a clean H₂O₂ production system that uses only water as the raw material under solar light irradiation. More effective dreamy H₂O₂ 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.

Acknowledgements

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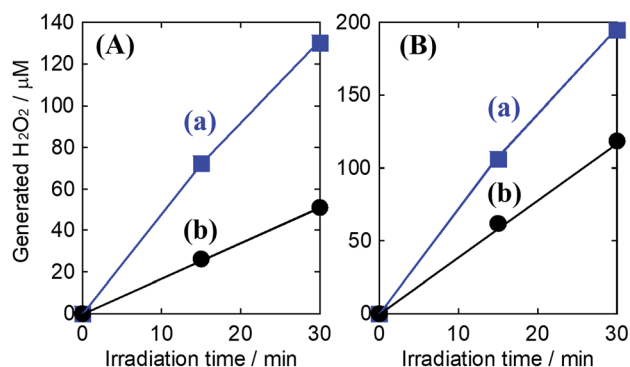


Fig. 6 Comparison of oxidative H₂O₂ generation in a 2.0 M KHCO₃ aqueous electrolyte (a) in the absence of or (b) containing initially-added H₂O₂ (210 μM) in an ice bath (below 5 °C) on a (A) WO₃/BiVO₄ and (B) WO₃/BiVO₄/Al₂O₃ photoanodes under simulated solar light irradiation at steady photocurrent of 1 mA.



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