Chemical conversions using light energy have been performed in various fields since the discovery of the Honda–Fujishima effect. Significant efforts have recently been devoted to H₂ production by water splitting using inexhaustible light for clean energy conversion processes. 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). Visible light-responsive oxide photoanodes with a narrow bandgap are desirable for the efficient utilisation of solar light and economical synthetic processes. 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. 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. 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.

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

\[ 2H_2O \rightarrow H_2O_2 + H_2 (two-photon process) \] (3)

\[ 2H_2O + O_2 \rightarrow 2H_2O_2 (two-photon process) \] (4)

Although the selectivity (faradaic efficiency: \( \eta(H_2O_2) \)) of reductive H₂O₂ production from O₂ on cathodes such as Au was very high, almost 100%, the maximum selectivity (\( \eta(H_2O_2) \)) for oxidative H₂O₂ production on WO₃/BiVO₄ photoanodes was still unknown.

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 50°C).
low, only ca. 54%. The design of novel photoanodes capable of achieving efficient H₂O₂ generation and inhibiting oxidative degradation of generated H₂O₂ is absolutely imperative for building a clean and breakthrough technology, by accumulating H₂O₂ and H₂ with unprecedented H₂O₂ selectivity using only H₂O as the raw material.

Here, we focused on a surface modification of the metal oxide (MeOₓ) layers on the WO₃/BiVO₄ photoanode surface to achieve excellent selectivity of generation and accumulation of H₂O₂ in the KHCO₃ aqueous solution under simulated solar light irradiation (Fig. 1). The MeOₓ layers were prepared by spin-coating of metal organic solutions and calcination. Introducing a porous Al₂O₃ layer was found to specifically permit oxidative H₂O₂ generation and accumulation with exceptional selectivity in an aqueous KHCO₃ electrolyte because of the blocking effect of oxidative degradation of the generated H₂O₂ into O₂ on the photoanode.

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

The effects of MeOₓ layers, modified on the WO₃/BiVO₄ photoanode, for oxidative H₂O₂ 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 KHCO₃ aqueous electrolyte. As shown in Fig. 2, all MeOₓ-coated photoanodes, except CoOₓ, enhanced the oxidative H₂O₂ generation compared to a bare WO₃/BiVO₄ photoanode, and the enhanced effect, ranked by the modified metal oxide, was Al₂O₃ > ZrO₂ > TiO₂ > SiO₂ > CoOₓ. Little H₂O₂ was observed on the CoOₓ coated photoanode, because CoOₓ probably decomposed the generated H₂O₂ quickly, or O₂ may be evolved on CoOₓ directly. It should be noted that the Al₂O₃ modification on the WO₃/BiVO₄ photoanode achieved roughly twice the oxidative H₂O₂ generation compared to the bare WO₃/BiVO₄ photoanode. The Al₂O₃ uniformly, smoothly and flatly covered the entire area of the WO₃/BiVO₄ photoanode as shown in the SEM images (Fig. 3), whereas other MeOₓ 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 diffraction peaks derived from MeOₓ were observed in all WO₃/BiVO₄/MeOₓ photoanodes, suggesting that all tried MeOₓ modified on WO₃/BiVO₄ 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 MeOₓ introduced on the WO₃/BiVO₄ have little effect to light absorption efficiency on WO₃/BiVO₄ 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 H₂O₂ generation reaction were also confirmed (Fig. S4; ESI†). The voltages for applying steady photocurrent of 1 mA slightly increased by introducing MeOₓ on the WO₃/BiVO₄ photoanode. In particular, WO₃/BiVO₄/Al₂O₃ photoanode, coated uniformly, smoothly and flatly at Al₂O₃ compared to other MeOₓ required highest applied voltage. In order to confirm the effect introducing the Al₂O₃ on the photoanode in more detail, the photocurrent property of the WO₃/BiVO₄/Al₂O₃ photoanode was investigated in a 0.5 M KHCO₃ aqueous solution (Fig. S5; ESI†). The bare WO₃/BiVO₄ photoanode exhibited excellent photocurrent property in all applied voltage ranges as with our past reported example,₁,₁₂,₂₈,₂₉ and the photocurrent property slightly decreased by introducing the Al₂O₃ 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 Al₂O₃, having an insulation property, covered the entire area of the WO₃/BiVO₄ photoanode. A similar

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**Fig. 1** Pattern and energy diagrams for photoelectrochemical H₂O₂ generation from H₂O on WO₃/BiVO₄/MeOₓ photoanodes under solar light irradiation.

**Fig. 3** SEM images of (A) WO₃/BiVO₄ and (B) WO₃/BiVO₄/Al₂O₃ photoanodes.
phenomenon has also been observed in O$_2$ and H$_2$ generation through water splitting on a photoanode coated with amorphous-like Ta$_2$O$_5$.\cite{22} In addition, it was confirmed that 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$_2$O$_3$ was ca. 4.7 nm. The thicknesses of Al$_2$O$_3$ 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$_2$O$_3$ on WO$_3$/BiVO$_4$ on the oxidative H$_2$O$_2$ generation, increasing Al$_2$O$_3$ 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$_2$O$_3$ layers. The thickness of Al$_2$O$_3$ 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$_2$O$_2$ generation amounts was observed on these WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanodes prepared at 500 and 1000 rpm, indicating that increasing Al$_2$O$_3$ on WO$_3$/BiVO$_4$ photoanode has little effect on the oxidative H$_2$O$_2$ generation. In subsequent experiments, WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanode prepared at 1000 rpm was utilized as the photoanode. These results indicate that the specific effect enhancing oxidative H$_2$O$_2$ generation property was achieved on the WO$_3$/BiVO$_4$ though the mesoporous and amorphous Al$_2$O$_3$ layer covered uniformly, smoothly and flatly the entire area.

To track the specific performance enhancing effect of generating H$_2$O$_2$ by introducing the Al$_2$O$_3$ layer, the concentration dependency of KHCO$_3$ aqueous electrolytes on the oxidative H$_2$O$_2$ generation property was investigated at an applied electric charge of 0.9C (Fig. 4(A)). We have already reported that the oxidative H$_2$O$_2$ 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$_2$O$_2$ generation via the two-electron oxidation of H$_2$O.\cite{28} Even in the case of using the WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanode, the selectivity ($\eta$[H$_2$O$_2$]) for H$_2$O$_2$ generation was significantly enhanced with increasing concentration of KHCO$_3$, and the $\eta$[H$_2$O$_2$] 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$_2$O$_2$] = ca. 53%) on the WO$_3$/BiVO$_4$/Al$_2$O$_3$ 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$_2$O$_3$ could effectively be contributing to oxidative H$_2$O$_2$ generation from H$_2$O even in the lowly concentrated KHCO$_3$. Moreover, as shown in Fig. 4(B), the excellent H$_2$O$_2$ generation property on the WO$_3$/BiVO$_4$/Al$_2$O$_3$ 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$_2$O$_3$ photoanode, reached >2500 $\mu$M at 50C, while that using the bare WO$_3$/BiVO$_4$ photoanode was >1300 $\mu$M at 50C. The dependency of the applied voltage on the oxidative H$_2$O$_2$ generation was investigated to confirm the effect of the Al$_2$O$_3$ coating in detail (Fig. S8; ESI†). A small change in H$_2$O$_2$ generation performance was observed in all ranges of applied voltages (0.8–1.8 V), suggesting that the enhanced effect of introducing an Al$_2$O$_3$ 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$_2$O$_2$ generation via two-photon oxidation of H$_2$O and accumulation using photoanodes has been reported, our method of Al$_2$O$_3$ coating on the WO$_3$/BiVO$_4$ photoanode produced tremendous improvement in selective H$_2$O$_2$ generation and accumulation from H$_2$O in a KHCO$_3$ aqueous electrolyte. It is speculated that the specific enhancement of selectivity for H$_2$O$_2$ generation on the WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanode may be caused by a blocking effect, on the mesoporous Al$_2$O$_3$ layer, that inhibits oxidative H$_2$O$_2$ degradation into O$_2$ on the BiVO$_4$. To investigate the blocking effect on the Al$_2$O$_3$ layer, a degradation property test of H$_2$O$_2$ was performed in a 2.0 M KHCO$_3$ aqueous solution containing H$_2$O$_2$ (550 $\mu$M) in the presence of the bare WO$_3$/BiVO$_4$ or WO$_3$/BiVO$_4$/Al$_2$O$_3$ 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$_2$O$_2$ was maintained in the dark condition, however, the H$_2$O$_2$ amount drastically decreased with irradiation by simulated solar light, suggesting that the H$_2$O$_2$ was decomposed by photocarriers (excited electrons and holes) produced on the BiVO$_4$. It should be noted that the H$_2$O$_2$ degradation in the presence of the WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanode was dramatically inhibited compared to the degradation in the presence of a bare WO$_3$/BiVO$_4$ photoanode. The oxidative H$_2$O$_2$ generation test was also confirmed in a 2.0 M KHCO$_3$ aqueous electrolyte, initially containing H$_2$O$_2$ (210 $\mu$M) on the bare WO$_3$/BiVO$_4$ and WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanodes, to track the generated H$_2$O$_2$ degradation behaviour in more detail (Fig. 6). The generated rates of H$_2$O$_2$ were reduced by the initial addition of H$_2$O$_2$ in both cases of presence or absence of Al$_2$O$_3$.
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 η(H2O2) 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 (50°C). 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.

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Notes and references