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 50°C).

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

\[
2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (\text{E(}\text{H}_2\text{O}_2/\text{H}_2\text{O}) = +1.77 \text{ V vs. RHE})
\]

(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.

\[
\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (\text{E(}\text{O}_2/\text{H}_2\text{O}_2) = +0.68 \text{ V vs. RHE})
\]

(2)

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)). 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)).

\[
2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2 \quad (\text{two-photon process})
\]

(3)

\[
2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{H}_2\text{O}_2 \quad (\text{two-photon process})
\]

(4)

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

Here, we focused on a surface modification of the metal oxide (MeO$_x$) layers on the WO$_3$/BiVO$_4$ photoanode surface to achieve selective efficiency of generation and accumulation of H$_2$O$_2$ 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$_2$O$_3$ layer was found to specifically permit oxidative H$_2$O$_2$ generation and accumulation with exceptional selectivity in an aqueous KHCO$_3$ electrolyte because of the blocking effect of oxidative degradation of the generated H$_2$O$_2$ into O$_2$ on the photoanode.

Details regarding experimental procedures for preparation and photoelectrochemical reactions of photoanodes are provided in the ESI$^\dagger$.

The effects of MeO$_x$ layers, modified on the WO$_3$/BiVO$_4$ photoanode, for oxidative H$_2$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 KHCO$_3$ aqueous electrolyte. As shown in Fig. 2, all MeO$_x$-coated photoanodes, except CoO$_x$, enhanced the oxidative H$_2$O$_2$ generation compared to a bare WO$_3$/BiVO$_4$ photoanode, and the enhanced effect, ranked by the modified metal oxide, was Al$_2$O$_3$ > ZrO$_2$ > TiO$_2$ > SiO$_2$ > CoO$_x$. Little H$_2$O$_2$ was observed on the CoO$_x$ coated photoanode, because CoO$_x$ probably decomposed the generated H$_2$O$_2$ quickly, or O$_2$ may be evolved on CoO$_x$ directly. It should be noted that the Al$_2$O$_3$ modification on the WO$_3$/BiVO$_4$ photoanode achieved roughly twice the oxidative H$_2$O$_2$ generation compared to the bare WO$_3$/BiVO$_4$ photoanode. The Al$_2$O$_3$ uniformly, smoothly and flatly covered the entire area of the WO$_3$/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$^\dagger$). It was also confirmed, from XRD measurement (Fig. S2; ESI$^\dagger$), that no diffraction peaks derived from MeO$_x$ were observed in all WO$_3$/BiVO$_4$/MeO$_x$ photoanodes, suggesting that all tried MeO$_x$ modified on WO$_3$/BiVO$_4$ photoanode possess amorphous-like structure. As shown in Fig. S3; ESI$^\dagger$ little change of the light harvesting efficiency (LHE) was also confirmed in tried all photoanodes, suggesting that these MeO$_x$ introduced on the WO$_3$/BiVO$_4$ have little effect to light absorption efficiency on WO$_3$/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$_2$O$_2$ generation reaction were also confirmed (Fig. S4; ESI$^\dagger$). The voltages for applying steady photocurrent of 1 mA slightly increased by introducing MeO$_x$ on the WO$_3$/BiVO$_4$ photoanode. In particular, WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanode, coated uniformly, smoothly and flatly at Al$_2$O$_3$ compared to other MeO$_x$ required highest applied voltage. In order to confirm the effect introducing the Al$_2$O$_3$ on the photoanode in more detail, the photocurrent property of the WO$_3$/BiVO$_4$/Al$_2$O$_3$ photoanode was investigated in a 0.5 M KHCO$_3$ aqueous solution (Fig. S5; ESI$^\dagger$). The bare WO$_3$/BiVO$_4$ photoanode exhibited excellent photocurrent property in all applied voltage ranges as with our past reported example,\textsuperscript{11,12,28,29} and the photocurrent property slightly decreased by introducing the Al$_2$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 Al$_2$O$_3$, having an insulation property, covered the entire area of the WO$_3$/BiVO$_4$ photoanode. A similar
phenomenon has also been observed in O₂ and H₂ generation through water splitting on a photoanode coated with amorphous-like Ta2O₅.22 In addition, it was confirmed, from the N₂ absorption and desorption measurement of MeO₂ particles (Fig. S6; ESI†), that almost all MeO₂ possess mesoporous structure at a pore size of 4.2–20 nm. In particular, a pore size of the Al₂O₃ was ca. 4.7 nm. The thicknesses of Al₂O₃ calculated from the coating amount on the WO₃/BiVO₄ photoanode by XRF measurement were ca. 100 nm (0.055 mg cm⁻²). In order to also investigate the effects of dense Al₂O₃ on WO₃/BiVO₄ on the oxidative H₂O₂ generation, increasing Al₂O₃ amount on WO₃/BiVO₄ photoanode was performed by decreasing the spin coating number (500 rpm) of precursor solution of EMOD solved in butyl acetate containing ethylcellulose when introducing Al₂O₃ layers. The thickness of Al₂O₃ 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 H₂O₂ generation amounts was observed on these WO₃/BiVO₄/Al₂O₃ photoanodes prepared at 500 and 1000 rpm, indicating that increasing Al₂O₃ on WO₃/BiVO₄ photoanode has little effect on the oxidative H₂O₂ generation. In subsequent experiments, WO₃/BiVO₄/Al₂O₃ photoanode prepared at 1000 rpm was utilized as the photoanode. These results indicate that the specific effect enhancing oxidative H₂O₂ generation property was achieved on the WO₃/BiVO₄ though the mesoporous and amorphous Al₂O₃ layer covered uniformly, smoothly and flatly the entire area.

To track the specific performance enhancing effect of generating H₂O₂ by introducing the Al₂O₃ layer, the concentration dependency of KHCO₃ aqueous electrolytes on the oxidative H₂O₂ generation property was investigated at an applied electric charge of 0.9C (Fig. 4(A)). We have already reported that the oxidative H₂O₂ generation property on the WO₃/BiVO₄ photoanode was improved with increasing concentration of KHCO₃, which acts as an effective catalyst for H₂O₂ generation via the two-electron oxidation of H₂O.28 Even in the case of using the WO₃/BiVO₄/Al₂O₃ photoanode, the selectivity (η(H₂O₂)) for H₂O₂ generation was significantly enhanced with increasing concentration of KHCO₃, and the η(H₂O₂) in the 2.0 M KHCO₃ aqueous solution reached ca. 80% at 0.9C, whereas that using the bare WO₃/BiVO₄ photoanode was ca. 54%. It should be noted that the selectivity (η(H₂O₂) = ca. 53%) on the WO₃/BiVO₄/Al₂O₃ photoanode in lowly concentrated KHCO₃ (0.1 M) was comparable to that (ca. 54%) on the bare WO₃/BiVO₄ photoanode in highly concentrated KHCO₃ (2.0 M). This suggests that the Al₂O₃ could effectively be contributing to oxidative H₂O₂ generation from H₂O even in the lowly concentrated KHCO₃. Moreover, as shown in Fig. 4(B), the excellent H₂O₂ generation property on the WO₃/BiVO₄/Al₂O₃ photoanode compared to the WO₃/BiVO₄ photoanode was significantly maintained even at high electric charge up to 50C. As a result, the accumulation amount, using the WO₃/BiVO₄/Al₂O₃ photoanode, reached >2500 μM at 50C, while using the bare WO₃/BiVO₄ photoanode was >1300 μM at 50C. The dependency of the applied voltage on the oxidative H₂O₂ generation was investigated to confirm the effect of the Al₂O₃ coating in detail (Fig. S8; ESI†). A small change in H₂O₂ generation performance was observed in all ranges of applied voltages (0.8–1.8 V), suggesting that the enhanced effect of introducing an Al₂O₃ 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 KHCO₃.

Although little development with regards to highly selective H₂O₂ generation via two-photon oxidation of H₂O and accumulation using photoanodes has been reported, our method of Al₂O₃ coating on the WO₃/BiVO₄ photoanode produced tremendous improvement in selective H₂O₂ generation and accumulation from H₂O in a KHCO₃ aqueous electrolyte. It is speculated that the specific enhancement of selectivity for H₂O₂ generation on the WO₃/BiVO₄/Al₂O₃ photoanode may be caused by a blocking effect, on the mesoporous Al₂O₃ layer, that inhibits oxidative H₂O₂ degradation into O₂ on the BiVO₄. To investigate the blocking effect on the Al₂O₃ layer, a degradation property test of H₂O₂ was performed in a 2.0 M KHCO₃ aqueous solution containing H₂O₂ (550 μM) in the presence of the bare WO₃/BiVO₄ or WO₃/BiVO₄/Al₂O₃ 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 H₂O₂ was maintained in the dark condition, however, the H₂O₂ amount drastically decreased with irradiation by simulated solar light, suggesting that the H₂O₂ was decomposed by photocarriers (excited electrons and holes) produced on the BiVO₄. It should be noted that the H₂O₂ degradation in the presence of the WO₃/BiVO₄/Al₂O₃ photoanode was dramatically inhibited compared to the degradation in the presence of a bare WO₃/BiVO₄ photoanode. The oxidative H₂O₂ generation test was also confirmed in a 2.0 M KHCO₃ aqueous electrolyte, initially containing H₂O₂ (210 μM) on the bare WO₃/BiVO₄ and WO₃/BiVO₄/Al₂O₃ photoanodes, to track the generated H₂O₂ degradation behaviour in more detail (Fig. 6). The generated rates of H₂O₂ were reduced by the initial addition of H₂O₂ in both cases of presence or absence of Al₂O₃.

Fig. 4 (A) Oxidative H₂O₂ generation in KHCO₃ 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 H₂O₂ generation in a 2.0 M KHCO₃ aqueous solution (35 mL) under visible light irradiation (λ > 420 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 WO₃/BiVO₄ and (b) WO₃/BiVO₄/Al₂O₃ photoanodes.
However, the decreasing rate of \( \text{H}_2\text{O}_2 \) generation was significantly inhibited, from ca. 61% to ca. 39%, by introducing the \( \text{Al}_2\text{O}_3 \) layer on the \( \text{WO}_3/\text{BiVO}_4 \) photoanode. These results suggest that introducing the \( \text{Al}_2\text{O}_3 \) layer significantly contributed to the highly selective \( \text{H}_2\text{O}_2 \) generation and accumulation from \( \text{H}_2\text{O} \), with a high photocurrent property, by a blocking effect that inhibited the oxidative degradation of generated \( \text{H}_2\text{O}_2 \). The mechanism of blocking effect is proposed that the \( \text{H}_2\text{O}_2 \) generated on the \( \text{BiVO}_4 \) in the \( \text{WO}_3/\text{BiVO}_4/\text{Al}_2\text{O}_3 \) photoanode diffuses in electrolyte of \( \text{KHCO}_3 \) aqueous solution through mesoporous of the \( \text{Al}_2\text{O}_3 \), and contact of the \( \text{H}_2\text{O}_2 \) diffused in electrolyte with the \( \text{BiVO}_4 \) covered uniformly and smoothly \( \text{Al}_2\text{O}_3 \) may be significantly inhibited compared with that with bare \( \text{BiVO}_4 \), resulting in the formation of effective inhibition of oxidative \( \text{H}_2\text{O}_2 \) degradation. Furthermore, there may be other possible mechanisms such as a blocking effect of a direct \( \text{O}_2 \) evolution site via a 4-photon process covering by \( \text{Al}_2\text{O}_3 \), or an enrichment effect resulting from the increasing \( \text{KHCO}_3 \) concentration around the photoanode based on the acid-base adsorption between \( \text{HCO}_3^- \) (a weak base) and the weakly acidic sites on the \( \text{Al}_2\text{O}_3 \) surface, related to the good \( \eta (\text{H}_2\text{O}_2) \) in lower \( \text{KHCO}_3 \) concentration, as shown in Fig. 4(A). The tracking and contribution of these other mechanisms, on the \( \text{Al}_2\text{O}_3 \) layer, is currently under investigation.

### Conclusions

In summary, various metal oxides were coated onto a \( \text{WO}_3/\text{BiVO}_4 \) photoanode to enhance the selectivity (faradaic efficiency) of oxidative \( \text{H}_2\text{O}_2 \) generation, in an aqueous electrolyte of \( \text{KHCO}_3 \), from water under solar light irradiation. Among the various metal oxides, the \( \text{Al}_2\text{O}_3 \) coating, which produced a mesoporous and amorphous structure on the \( \text{WO}_3/\text{BiVO}_4 \) photoanode, achieved excellent oxidative \( \text{H}_2\text{O}_2 \) generation at a selectivity of ca. 80% and an accumulation of >2500 \( \mu \text{M} \) (50°C).

Interestingly, the \( \text{Al}_2\text{O}_3 \)-coated \( \text{WO}_3/\text{BiVO}_4 \) photoanode dramatically inhibited oxidative degradation of \( \text{H}_2\text{O}_2 \) generated on the \( \text{WO}_3/\text{BiVO}_4 \) photoanode after introducing the \( \text{Al}_2\text{O}_3 \) layer. This study contributes to developing a promising design for a clean \( \text{H}_2\text{O}_2 \) production system that uses only water as the raw material under solar light irradiation. More effective dreamy \( \text{H}_2\text{O}_2 \) 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