Functions of MnO$_x$ in NaCl Aqueous Solution for Artificial Photosynthesis

“Why the manganese oxide is used for the O$_2$ evolution reaction?”

MnO$_x$ loaded photoanode in NaCl aq.

HIGHLIGHTS

- Selectivity of O$_2$/HClO production in NaCl aq. sol. on photoanodes was investigated
- MnO$_x$ modification promoted O$_2$ evolution specifically without HClO production
- The results are useful for practical application of artificial photosynthesis
- A hypothesis about the evolution in natural photosynthesis was proposed

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SUMMARY
Photoelectrochemical water splitting has been intensively investigated as artificial photosynthesis technology to convert solar energy into chemical energy. The use of seawater and salted water has advantages for minimum environmental burden; however, the oxidation of Cl\textsuperscript{-}/C\textsubscript{0} ion to hypochlorous acid (HClO), which has toxicity and heavy corrosiveness, should occur at the anode, along with the oxygen evolution. Here, O\textsubscript{2} and HClO production in aqueous solution containing Cl\textsuperscript{-} on photoanodes modified with various metal oxides was investigated. The modification of MnO\textsubscript{x} resulted in the promotion of the O\textsubscript{2} evolution reaction (OER) specifically without HClO production over a wide range of conditions. The results will contribute not only to the practical application of artificial photosynthesis using salted water but also to the elucidation of substantial function of manganese as the element for OER center in natural photosynthesis.

INTRODUCTION
Various photoanodes composed of oxide semiconductors on conducting glass substrate have been widely studied for artificial photosynthesis technology with water oxidation into O\textsubscript{2} under simulated solar light and low applied bias in aqueous electrolyte solution (Fujishima and Honda, 1972; Hisatomi et al., 2014; Kang et al., 2015; Sivula and van de Krol, 2016; Roger et al., 2017), whereby the efficiency was determined to be improved by loading with metal oxides (MO\textsubscript{x}) such as FeO\textsubscript{x}, NiO\textsubscript{x}, and CoO\textsubscript{x} (Zhong et al., 2015; Chemelewski et al., 2014). The ability of O\textsubscript{2} evolution reaction (OER) of MO\textsubscript{x} has been further improved by modification with phosphate, borate, and carbonate ions (Kim and Choi, 2014; Bediako et al., 2012; Li et al., 2016). Moreover, the use of seawater and salted water for electrolyte solution has been investigated because of some significant advantages to minimize the environmental burden and provide cost reduction on electrochemical systems using photoanodes (Desilvestro and Gra¨etzel, 1987; Luo et al., 2011; Barczuk et al., 2013; Fukuzumi et al., 2017; Iguchi et al., 2018) as well as metal anodes (Bennet., 1980; El-Moneim et al., 2009; Vos et al., 2018; Ibrahim and Canan, 2015; Gidon et al., 2018). However, in seawater containing Cl\textsuperscript{-}/C\textsubscript{0} anions, hypochlorous acid (HClO, neutral form of Cl\textsubscript{2}) production reaction (abbreviated as CPR) by Cl\textsuperscript{-} oxidation proceeds concurrently with the OER by water oxidation (Figure 1). Although HClO is a valuable chemical for disinfection and bleaching to some extent (Sayama, 2018), control of the selectivity and the suppression of CPR on photoanodes are important requirements for H\textsubscript{2} production in large-scale water-splitting systems because of the toxicity and corrosiveness of HClO (Fujimura et al., 1999). The CPR via 2-electron reaction proceeds easily compared with the OER via 4-electron reaction, whereas the OER is more preferable to the CPR with respect to the redox potential (HClO/Cl\textsuperscript{-} = ca. +1.28 V and O\textsubscript{2}/H\textsubscript{2}O = +0.83 V versus SHE, pH = 7). There have been some reports that the CPR on metal anodes is effectively suppressed by the use of cation-exchange membranes or entirely coating the anode with MnO\textsubscript{x}, as Cl\textsuperscript{-}-impermeable layers (El-Moneim et al., 2009; Vos et al., 2018; Balaji et al., 2009), and by buffered conditions to maintain an alkaline pH (Dionigi et al., 2016). However, it is more difficult to suppress the CPR in buffered NaCl solution because the anode is subjected to partially acidic conditions. Here, we systematically investigated the effect of loading various simple metal oxide species (MO\textsubscript{x}) including precious metals, on the selectivity toward HClO/O\textsubscript{2} production from buffered NaCl aqueous solution over a BiVO\textsubscript{4} photoanode, which is one of the most popular visible-light responsive photoanodes for efficient water splitting (Hong et al., 2011; Saito et al., 2012; Fuku et al., 2017), and found that MnO\textsubscript{x} loading could specifically suppress the CPR on the photoanode under a wide range of conditions. Finally, we could advocate a new hypothesis why manganese is selected as the element for OER center of natural photosynthesis (Barber., 1998; Yano et al., 2006; Umema et al., 2011). (Figure 1)
RESULTS AND DISCUSSION

Properties of MOx/BiVO4/WO3/FTO under Simulated Solar Light

A multilayer photoanode of BiVO4/WO3/FTO (FTO = F-doped SnO2 conducting glass), which has excellent performance for water splitting into H2 and O2 under low applied bias (Hong et al., 2011; Saito et al., 2012; Fukuzumi et al., 2017), was used in this work. Figure 2A shows the faradaic efficiencies (FE) for O2 and HClO generation (FE(O2) and FE(HClO)) from aqueous NaCl solution on a BiVO4/WO3/FTO photoanode loaded with/without MOx under simulated solar light (AM 1.5, 1 SUN). The potential required for the photo-electrolysis for steady current (2 mA) using these photoelectrodes was listed in Table S1. The bare photoanode produced both HClO and O2, and other oxidative by-products (Cl2, HClO2, HClO3 etc.) were not generated, as we recently reported (Iguchi et al., 2018). For all photoanodes, the sum of FE for the oxidative products (O2 and HClO) became around 100% considering the measurement error (ca. 15%), which suggested the main products were O2 and HClO. O2 production with a high FE(O2) of >90% was observed on the MnOx/BiVO4/WO3/FTO photoanode, and no significant amount of HClO was detected with MnOx loading. FE(HClO) with a CoOx-loaded photoanode was increased to ca. 88%. The dependence of FE(HClO) on the concentration of the Mn precursor solution and the concentration or pH of aqueous NaCl electrolyte solution were also investigated (Figures 2B–2D), and the CPR was effectively suppressed when the Mn precursor concentration was ≤0.01 M, the NaCl concentration was between 0.05 M–2 M, or the pH was between 3 and 9, respectively. Figure S1A shows current-potential (I-V) curves for the MnOx/BiVO4/WO3/FTO photoanodes under simulated solar light though a light chopper. The photocurrent could be observed on the photoanodes with or without MnOx at much less than +0.88 V versus SHE, pH = 7. The optimum preparation temperature for MnOx loading was 400°C for the best photocurrent among all MnOx-loaded photoanodes (Figure S1B). The photocurrent could be kept at almost 80% after MnOx loading compared with that of the bare photoanode, because the color of the photoanode became brown and the photoabsorption might be inhibited by MnOx loading (Figure S1C). Another possibility of decreased photocurrent could be considered to be producing some doped layers to accelerate charge recombination at the interface of MnOx/BiVO4 during the calcination process. We also examined the photoelectrochemical CPR in artificial seawater rather than in pure NaCl solution (Figure S2). The behavior of HClO selectivity in artificial seawater was very similar to that in pure NaCl solution (Figure 2A), and only the MnOx-loaded photoanode suppressed the CPR efficiently. The results suggest no significant effect of various anions and cations contained in the artificial seawater, such as SO4²⁻ and Mg²⁺, on the selectivity due to the low concentrations of these ions compared with Na⁺ and Cl⁻ (Desilvestro and Graetzel, 1987; Luo et al., 2011; Barczuk et al., 2013; Fukuzumi et al., 2017; Iguchi et al., 2018). It was also confirmed that H2 was produced on a Pt cathode in artificial seawater with a high FE(H2) (ca. 100%).

Characterizations of MOx/BiVO4/WO3/FTO

The amounts of MOx loading on the BiVO4/WO3/FTO photoanodes calculated from X-ray fluorescence (XRF) measurements are summarized in Table S2. The amount of MnOx was 0.02 μmol/cm², and those of other MOx were in a similar range between 0.01 and 0.024 μmol/cm². Surface scanning electron microscopic (SEM) observations of bare BiVO4/WO3/FTO (Figure 3A-(i)) confirmed a nanostructure with particle networks that consist of primary particles with diameters of ca. 100 nm. In contrast, the edge of the particles on the photoelectrode was not clear for MnOx(0.1 M)/BiVO4/WO3/FTO (Figure 3A-(ii)), which suggests the loaded MnOx covered the entire surface.
surface of the photoanode. Transmission electron microscopic-energy dispersive X-ray spectroscopic (TEM-EDX) cross-sectional images of the photoanode loaded with MnOx (0.1 M, Figure 3B) showed that a thin layer (ca. 10–30 nm thick) of MnOx was present over the surface of the BiVO₄/WO₃/FTO photoanode. No electron diffraction pattern was obtained at the MnOx part, which indicates that MnOx was not crystalline. The apparent surface coverage of MnOx layers calculated from the peak area of X-ray photoelectron spectroscopy (XPS; Figure 3C) measurements are summarized in Table S3. In the case of the MnOx (0.1 M)-coated sample, the peaks attributed to Bi, V, W, and Sn of the photoanode were not observed, whereas the peak attributed to Mn 2p₃ was clear, which suggested the surface coverage of MnOx was almost 100%. In contrast, for the MnOx (0.03 M)-coated sample, the peaks attributed to Mn 2p₃ decreased and peaks attributed to V 2p₃, Bi 4f, W 4f, and Sn 3d were observed, which indicates that MnOₓ(0.03 M) was not completely covering the photoanode surface, unlike that prepared with 0.1 M precursor solution. The dependence of the apparent surface coverage of MnOx on the concentration of manganese precursor solution is shown by the right-hand axis in Figure 2B. The coverage of MnOx decreased on decreasing the concentration of the manganese precursor solution. Although the apparent surface coverage of MnOx (0.01 M)-loaded BiVO₄/WO₃/FTO photoanode was only 30%, the selectivity toward the CPR was very low. Therefore, it is concluded that entire coverage of MnOx on the BiVO₄/WO₃/FTO surface was not necessary to suppress the CPR. The results indicate that the selectivity toward HClO/O₂ production could be controlled by this simple coating method using metal precursor solutions, and the CPR could be suppressed in aqueous solution containing Cl⁻ ions with a photoanode surface partially loaded with MnOx.

Properties of MOₓ/FTO under Dark Conditions

The electrochemical properties of the simple structured-MOₓ/FTO anodes without semiconductor layers were also evaluated under dark conditions (Figure S3). We checked the product amount of HClO/O₂...
and calculated the values of $\text{FE(HClO)}$, $\text{FE(O}_2\text{)}$, and $\text{MO}_x/\text{FTO}$, confirming that the sum of the $\text{FE(HClO)}$ and $\text{FE(O}_2\text{)}$ became almost 100% within variation of measurement errors in each electrode. $\text{FE(H-ClO)}$ for various $\text{MO}_x/\text{FTO}$ anodes (Figure S3A) had a similar tendency to that for the $\text{MO}_x/\text{BiVO}_4/\text{WO}_3/\text{FTO}$ photoanodes (Figure 2A). It was also confirmed that $\text{MnO}_x$ loading of the anodes effectively suppressed the CPR in aqueous NaCl solution under a wide range of conditions, regardless of the Mn precursor solution concentration (0.01–0.1 M), the NaCl concentration (0.005–2 M), pH (3–9), applied bias (1.5–1.8 V versus SHE, $\text{pH} = 7$), the valence or structure of $\text{MnO}_x$ (amorphous, $\text{Mn}_2\text{O}_3$ and $\text{Mn}_3\text{O}_4$), preparation methods of $\text{MnO}_x$ such as calcination temperature (300–550°C), and the kinds of manganese salt dissolving the precursor solution, as shown in Figures S3B–S3I. SEM images, $\text{MnO}_x$ coverages, and $\text{FE(HClO)}$ of $\text{MnO}_x/\text{FTO}$ anodes are shown in Figure S4. In the case of the $\text{MnO}_x$ (0.03 M)/FTO with very low $\text{FE(HClO)}$, SEM observations indicated that $\text{MnO}_x$ did not entirely coat the surface of FTO, and the apparent coverage of $\text{MnO}_x$ (0.03 M) calculated from the XPS spectrum was only 65%. It is suggested that complete coating of $\text{MnO}_x$ on FTO anodes was not needed to suppress the CPR, as well as photoanodes.

**Mechanism of Selective $O_2$ Production on $\text{MnO}_x$-Loaded Photoanode**

There are two possibilities why the $\text{MnO}_x$ loaded on the photoanodes or anodes could suppress the CPR; direct $O_2$ production on $\text{MnO}_x$ and indirect $O_2$ production through the decomposition of HClO as an intermediate. The HClO initially added to the NaCl aqueous solution was not decomposed on a $\text{MnO}_x/\text{FTO}$ anode under dark conditions (Figure S5). This suggests that indirect $O_2$ production on $\text{MnO}_x/\text{FTO}$ by HClO decomposition on the $\text{MnO}_x$ surface can be denied and that $O_2$ was directly produced on $\text{MnO}_x/\text{FTO}$ in NaCl aqueous solution.

In the case of noble metal anodes such as IrO$_2$, selective OER from an aqueous solution containing Cl$^-$ ions can be realized by coating an $\text{MnO}_x$ layer on the entire surface of the anode (Bennet, 1980; El-Moneim et al., 2009; Vos et al., 2018; Ibrahim and Canan, 2015; Gidon et al., 2018). In the field of water electrolysis, this selective OER has been explained by a “Cl$^-$-impermeable mechanism,” where Cl$^-$ ions cannot reach the surface of the noble metal through the $\text{MnO}_x$ layer, rather than by a “catalytic mechanism” where $\text{MnO}_x$ itself functions as an electrocatalyst for $O_2$ production (Vos et al., 2018). In this Cl$^-$-impermeable mechanism, the $\text{MnO}_x$ layer must completely cover the entire surface of the noble metal, and no oxidation reaction should occur on the $\text{MnO}_x$ but rather on the noble metal catalyst, which indicates that the reaction sites are completely different with each mechanism. However, in this study, much data that cannot be explained by the Cl$^-$-impermeable mechanism was obtained. First, current-voltage (I-V) curves for the $\text{MnO}_x/\text{FTO}$ anode showed that the onset potential was significantly shifted to lower potential compared with that for bare FTO (Figures 4A and 4B). Second, complete coating of $\text{MnO}_x$ on FTO anode was not necessary.
to suppress the CPR (Figures S3B and S4). Third, it was confirmed whether or not the oxidation reaction occurred on MnOx (Figures 4C and 4D). A thick MnOx (0.1 M) layer that covered the entire FTO surface was prepared, and then it was coated with Pt by vapor deposition method (Pt (VD)/MnOx/FTO). The I-V properties and Tafel slope were improved by Pt (VD) loading (Figure 4B-(ii)). The FE (HClO) on the Pt (VD)/MnOx/FTO anode (65.2%) was almost same as that on the Pt (VD)/FTO anode (66.9%) and was completely different from that on MnOx/FTO (<1.6%), as shown in Figure 4C, which indicates that the selectivity and I-V properties could be controlled by modification of the top surface. These results suggest that the oxidation reaction occurred on the top surface of MnOx on the MnOx (0.1 M)/FTO anode, and not on the surface of FTO (Figure 4D). Furthermore, the Cl\(^-\) adsorption characteristics of MOx were compared using XPS, and Cl\(^-\) ions were found not to be adsorbed by CoOx, FeOx, NiOx, or MnOx (Table S4, Cl coverage <1%). Therefore, it was difficult to explain MnOx peculiarity by the difference of the adsorption characteristics of Cl\(^-\). From all these results, we can conclude that the mechanism for the selectivity toward the OER/CPR on MnOx/FTO from an aqueous solution containing Cl\(^-\) ions can be explained not by the Cl\(^-\)-impermeable mechanism but rather by the catalytic mechanism (Figure 4D-(iii and iv)).

The special OER selectivity on the MnOx catalyst-loaded anodes might be explained by the difference or the ratio of the overpotential with the OER and CPR reactions in each electrolyte solution. The potentials required for steady current electrolysis on various MOx/FTO were listed in Table S5. The behaviors of potential on each anode were similar in NaCl and NaH2PO4 aqueous solutions except for unstable anodes; the precious metals showed the lowest potential level, and CoOx, FeOx, NiOx, and MnOx showed the second lowest level. On the other hand, the evaluation of each specific overpotential in NaCl aqueous solution is difficult because both the OER and CPR occur. It should be emphasized again that the FE (HClO) was very low even when MnOx was not fully coated on FTO; therefore, it is surmised that the overpotential for the
OER on MnOx was much lower than those of the other reactions such as the CPR on MnOx, and the OER and CPR on FTO relatively in NaCl solution (Figure 5A). As for the photoanode reactions using MOx/BiVO4/WO3/FTO, the specificity of MnOx could not be explained by the decomposition of HClO produced into O2 by UV light excitation from solar light as reported (Fukuzumi et al., 2017), because the results in Figure 2A were compared under the same irradiation conditions. It was confirmed that the HClO selectivity was very low, even when the apparent coverage of MnOx was only 30%, as shown in Figure 2B. Considering the analogy with the results for the MnOx/FTO anode, the Cl\(^-\)/Co\(^-\)-impermeable mechanism for MnOx loaded on a photoanode can also be excluded. The turnover number (ca. 154) of e\(^-\) to Mn on the MnOx-loaded photoanode was much more than 1. Therefore, it is reasonable to explain the results by the catalytic mechanism, where photoexcited h\(^+\) on BiVO4 immediately moves to MnOx and the preferential oxidation of water on the MnOx surface into O2 occurs without the CPR (Figure 5B). It should be noted that various MnOx catalysts such as amorphous MnO2, Mn3O4, and Ca-MnOx could suppress the CPR (Figure S3G), which indicates that manganese oxides themselves may have specificity with a large overpotential ratio for the CPR to the OER in NaCl solution. This catalytic mechanism of MnOx is generally that for the OER on Mn4O5 core cluster with Ca in the photosystem II (PSII) of natural photosynthesis (Suga et al., 2017; Zhang et al., 2018; Zaharueva et al., 2011; Najafpour et al., 2010); therefore, it can also be a common mechanism in the fields of electrolysis and artificial photosynthesis using photoanodes. Currently, the intrinsic reason for the specific dependence of the overpotentials on these elements including manganese is not clear, and the comparison of energy barriers of transition state between CPR and OER on a certain model structure of each MOx through computational chemistry is under investigation.

Evolutional Hypothesis for the Mn4O5 Core of Natural Photosynthesis

Natural OER metal centers of cyanobacteria, algae, or plants containing elements other than Mn have not been found to date. Mn has many advantages such as a low overpotential for OER and earth-abundant transition metal element with various valence states (Zhang et al., 2018; Armstrong., 2008; Sauer and Yachandra, 2002; Raveau and Seikh, 2012; Bryan et al., 2016). On the other hand, some metal oxides such as Fe, Ni, and Co also basically satisfy all these requirements (Zaharueva et al., 2011; Raveau and Shiek, 2012; Bryan et al., 2016). Therefore, there is no hypothesis to explain why Fe, Ni, or Co is not used as the OER center in PSII so far. Based on our specific results that MnOx catalyzes the OER selectively from NaCl aqueous solution under a wide range of conditions, even at low pH and low Cl\(^-\) concentration compared with those for natural photosynthesis in vivo (ca. 100 mM of Cl\(^-\) in chloroplasts) (Robinson and Downton, 1984; Baranov and Haddy, 2017; Jagendorf and Urbe, 1966; Beebo et al., 2013), it is possible to advocate a new hypothesis as to why MnOx is selected as the OER center in PSII that appeared on the ancient earth. It is because HClO is significantly toxic to organisms, and Mn is the only element that can produce only O2 without the generation of HClO in aqueous solution containing Cl\(^-\) ions under various conditions in vivo. Considering that HClO has extremely strong bactericidal properties compared with H2O2 (McKenna and Davies, 1988), and that it should be necessary to avoid the generation of even a small amount of HClO in vivo, the specialty of natural Mn4O5 can be comprehensively explained by the results of this study.

Limitation of the Study

We investigated the O2/HClO production in aqueous solution containing Cl\(^-\) on BiVO4/WO3/FTO photoanodes and FTO anodes modified with various MOx. It is emphasized that the modification of partially
loaded MnOx resulted in specifically catalyzing the OER without HClO production over a wide range of conditions. These results will not only provide some insight into the practical application of artificial photosynthesis technologies using salted water and solar energy but also facilitate the elucidation of the function of Mn4O5 core cluster with Ca in natural photosynthesis. Considering our results, one hypothesis about the evolutional process of Mn4O5 core cluster in natural PSII can be proposed; HClO is toxic to bacteria, so that manganese element might be selected by nature due to the unique catalysis on MnOx, where HClO production is fully suppressed. Complete elucidation of evolutional hypothesis is difficult generally; however, our hypothesis will be elucidated by various ways. For example, we have some plans about the investigation on the effect of coordination of organic compounds with carboxyl and amino groups, mimicking the atmosphere in the protein of PSII, on various nano-size MOx and multinuclear metal complexes as electrocatalysts systematically, as well as investigation through computational chemistry in the future.

Resource Availability

Lead Contact
Further information and requests for resources should be directed to the Lead Contact, Kazuhiro Sayama (k.sayama@aist.go.jp).

Materials Availability
This study did not generate new unique reagents.

Data and Code Availability
This study did not generate/analyze datasets/code.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101540.

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AUTHOR CONTRIBUTIONS
S.O. and K.S. designed the experiments. S.O. performed all sample preparation, characterization, and (photo)electrochemical property experiments. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Functions of MnO_x in NaCl Aqueous Solution for Artificial Photosynthesis

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Supplemental Information

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Transparent Methods

Materials

Metal organic solutions of Mn, Co, Fe, Ni were purchased from Symetrix Co., USA (purchased from Koujundo Chemical Co., Japan). H₂PtCl₆·6H₂O and Rh(NO₃)₃, IrCl₃, AgNO₃, NaCl, NaH₂PO₄ were purchased from Wako Pure Chemical, Japan. Pd(NO₃)₂, RuCl were purchased from Nakalai Tesque. All reagents were used as received, and all the experiments were carried out under ambient condition without eliminating the moisture from the atmosphere.

Preparation of BiVO₄/WO₃/FTO photoanode

BiVO₄/WO₃/FTO photoanodes were prepared as follows. Precursor solutions of each oxide semiconductor were coated on F-doped SnO₂ conductive glass substrate (FTO; 10 Ω sq⁻¹, Nippon Sheet Glass Co.) by spin-coating and then calcination for each coating. A WO₃ underlayer was coated on the FTO substrate by spin-coating (1500 rpm, 15 s) aqueous peroxo-tungstic acid solution (1.4 M) containing W ions, followed by calcination at 500 °C for 30 min in air. The BiVO₄ layer on WO₃/FTO was also fabricated by spin-coating (1000 rpm, 15 s) using a Bi and V precursor solution, followed by calcination at 550 °C for 30 min in air. The BiVO₄ precursor solutions was a mixed solution of 0.2 M Bi³⁺ and 0.2 M V⁵⁺ in a 1:1 volume ratio diluted with butyl acetate.

Preparation of MOₓ/BiVO₄/WO₃/FTO photoanodes and MOₓ/FTO anodes

The MOₓ (where M = Mn, Co, Fe, Ni, Pt, Rh) layers on the BiVO₄/WO₃/FTO photoanodes (denoted as MOₓ/BiVO₄/WO₃/FTO) or FTO anodes (denoted as MOₓ/FTO) were prepared by spin-coating (1500 rpm, 15 s) metal organic solutions in butyl acetate on the BiVO₄/WO₃/FTO and calcination at 400 °C in air for 1 h. In the case of loading the non-noble metals, metal organic solutions (Symetrix Co., USA, purchased from Koujundo Chemical Co., Japan) in butyl acetate (0.1 M) were used. In the cases of loading with noble metals, aqueous solutions of H₂PtCl₆·6H₂O (Wako), Rh(NO₃)₃ (Wako) were prepared. It is difficult to prepare high concentration solutions of these noble metal precursor salts; therefore, the concentration of these solutions was adjusted to 0.03 M. The MOₓ layers on the FTO electrodes (denoted as MOₓ/FTO) were prepared by spin-coating (1500 rpm, 15 s) metal organic solutions in butyl acetate on the FTO and calcination at 400 °C in air for 1 h.

To examine the effect of manganese species on FE (HClO), Mn₂O₃/FTO, Mn₃O₄/FTO,
and Ca-MnOₓ/FTO anodes were prepared as follows. A Mn₂O₃/FTO anode was prepared by electrochemical deposition (ED-S) in a solution of 0.25 M MnSO₄ and 0.25 M Na₂SO₄ (1:1 v/v) for 10 min. The films were rinsed with water and dried, followed by calcination at 400 °C for 1 h in air (Ramírez. et al. 2014). The Mn₃O₄/FTO anode was prepared by electrochemical deposition (ED-N) in a solution of 0.25 M Mn(NO₃)₂ and 0.25 M Na₂SO₄ (1:1 v/v) for 10 min at 70 °C. (Qi. et al. 2016) The films were rinsed with water and dried at 80 °C for 1 h in air. A Ca-MnOₓ(Mn/Ca=4) anode was prepared by spin-coating (1500 rpm, 15 s) metal organic solutions (0.1 M, Ca:Mn = 1:4 molar ratio, Symetrix Co., USA, purchased from Koujundo Chemical. Co., Japan) in butyl acetate on the FTO and calcination at 400 °C in air for 1 h.

**Characterization**

The anode samples obtained were characterized using X-ray diffraction (XRD; PANalytical, EMPYREAN, rotating anode diffractometer, 40 kV, 10 mA) with Cu Kα radiation (λₖα = 1.5406Å), X-ray fluorescence (XRF; Rigaku, Supermini200), X-ray photoelectron spectroscopy (XPS; Ulvac Co., XPS-1800), scanning electron microscopy (SEM; HITACHI, S-4100), and transmission electron microscopy (TEM; Hitachi High-Technologies Co., Ltd., HD2700) with energy dispersive X-ray spectroscopy (EDX) mapping. The MnOₓ coverage was calculated using the spectrum area obtained from XPS spectrum and intensity factor of Mn to the sum of those of Mn, Bi, V, W and Sn.

**Photoelectrochemical and electrochemical production of HClO and O₂**

**Photoelectrochemical properties**

The photoelectrochemical performance of the photoanodes was measured using an electrochemical analyzer (BAS. Inc., ALS 760E) and a solar simulator (SAN-EI ELECTRIC Co., XES-151S) calibrated to AM-1.5 (1 SUN, 100 mW cm⁻²) with a spectroradiometer (SOMA Optics, Ltd., Model S-2440). The irradiation area (0.28 cm²) was defined using a black mask. The simulated solar light was irradiated from the semiconductor side. The current–voltage (I–V) characteristics were measured using a two-compartment cell (Pyrex-made) with an ion-exchange membrane (SELEMION, AGC Engineering), and a photoanode equipped with a back-reflection plate as the working electrode, an Ag/AgCl electrode as the reference electrode, and a Pt wire as the counter electrode The scan rate was 50 mV s⁻¹. The measured potentials vs. Ag/AgCl were converted to the standard hydrogen electrode (SHE) and the reversible hydrogen electrode (RHE) scale according to:

\[ E_{SHE} = E_{Ag/AgCl} + 0.206 \]  \hspace{1cm} (S1)

\[ E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^0_{Ag/AgCl} \]  \hspace{1cm} (S2)

where \( E_{SHE} \) and \( E_{RHE} \) are the converted potential vs. SHE or RHE, \( E^0_{Ag/AgCl} = 0.1976 \) at 25 °C, and \( E_{Ag/AgCl} \) is the experimentally measured potential against the Ag/AgCl reference. An aqueous solution of 0.5 M NaCl (35 mL, pH = 5.9) was used as the electrolyte.
Electrochemical properties

The current–voltage ($I$–$V$) characteristics on the FTO and $MO_x$/FTO anodes were measured using a two-compartment cell (Pyrex-made) with an ion-exchange membrane (SELEMION, AGC Engineering), and an anode as the working electrode, an Ag/AgCl electrode as the reference electrode, and a Pt wire as the counter electrode. The scan rate was 50 mV s$^{-1}$. The measured potentials vs. Ag/AgCl were converted to the SHE and the RHE. An aqueous solution of 0.5 M NaCl (35 mL, pH = 5.9) was used as the electrolyte.

Simultaneous production of HClO and O$_2$

The simultaneous production of HClO and O$_2$ on the photoanodes was measured using an electrochemical analyzer (BAS. Inc., ALS 760E) and a solar simulator (SAN-EI ELECTRIC Co., XES-151S) calibrated to AM-1.5 (1 SUN, 100 mW cm$^{-2}$) with a spectroradiometer (SOMA Optics, Ltd., Model S-2440). The simulated solar light was irradiated from the semiconductor side. The reaction on the obtained photoanodes was performed under solar light irradiation using a two-compartment cell, equipped with an ion-exchange membrane (SELEMION, AGC Engineering) between the anode and cathode. Pt wire was used as a counter electrode to effectively reduce water to H$_2$. An aqueous solution (anode: 35 mL; cathode: 35 mL) of NaCl (0.5 M) was used as the electrolyte. In the photoelectrochemical reaction, photoanodes (1.5×5 cm) were used. Each solution was stirred by magnetic stirring at ca. 400 rpm. In the case of the FTO and $MO_x$/FTO anodes, the production of HClO in the dark was conducted by the same method.

The concentration of HClO produced was measured with a UV-vis spectrometer (JASCO, Y-730) using the $N,N$-diethyl-$p$-phenylenediamine (DPD) method. The faradaic efficiencies (FEs) of HClO (FE (HClO)) can be calculated as:

$$FE(HClO) = \frac{\text{amount of generated HClO}}{\text{theoretical amount of HClO}} \times 100 = \frac{\text{amount of generated HClO}}{\text{amount of generated electrons}/2} \times 100 \quad \text{(S3)}$$

The amount of O$_2$ evolved in both the liquid and gas phases were determined using an O$_2$ sensor (Optical Oxygen Meter, Pyro Science and FireStingO$_2$) and combining each value. These HClO/O$_2$ production reactions of the main part were measured 3 times, and the reproducibility of the data was confirmed with the variation of experimental errors within 10%. The amount of hydrogen evolved from Pt electrode was determined with a gas chromatograph equipped with a TCD detector. The faradaic efficiency of H$_2$ (FE (H$_2$)) can be calculated as:

$$FE(HClO) = \frac{\text{amount of generated H}_2}{\text{theoretical amount of H}_2} \times 100 = \frac{\text{amount of generated H}_2}{\text{amount of generated electrons}/2} \times 100 \quad \text{(S4)}$$
Results

Table S1. Potential required for photo-electrolysis for steady current (2 mA) using various $MO_x$/BiVO$_4$/WO$_3$/FTO photoelectrodes. Related to Figure 2.

| $MO_x$/BiVO$_4$/WO$_3$/FTO | Potential (V vs. SHE, pH=7) |
|---------------------------|----------------------------|
| None                      | 0.74                       |
| Mn                        | 0.83                       |
| Co                        | 0.68                       |
| Ni                        | 0.70                       |
| Fe                        | 0.78                       |
| Pt                        | 0.65                       |
| Rh                        | 0.80                       |

Potential required for electrolysis with an electric charge of 2 C in 0.5 M aqueous NaCl solution using various $MO_x$/BiVO$_4$/WO$_3$/FTO electrodes (1.5 cm x 5 cm). The concentration of loaded metal precursor solution was 0.03 M.

Table S2. Amount of $MO_x$ loading on the BiVO$_4$/WO$_3$/FTO photoanodes. Related to Figure 2.

| $MO_x$ | $MO_x$ loading (μmol/cm$^2$) |
|--------|-------------------------------|
| None   | 0                             |
| Mn     | 0.20                          |
| Co     | 0.014                         |
| Fe     | 0.017                         |
| Ni     | 0.024                         |
| Rh     | 0.016                         |
| Pt     | 0.010                         |

Amount of $MO_x$ loading on the BiVO$_4$/WO$_3$/FTO photoanodes was calculated using XRF spectra. The concentrations of loaded metal precursor solutions were (a) 0.1 M for Mn, Co, Ni, and Fe, and (b) 0.03 M for Rh and Pt.

Table S3. Apparent $MO_x$-coverage (%) for the BiVO$_4$/WO$_3$/FTO photoanodes. Related to Figure 2.

| $MO_x$ | Coverage (%) |
|--------|--------------|
|        | (A) 0.03 M   | (B) 0.1 M   |
| Mn     | 54.0         | 100.0       |
| Co     | 51.6         | 79.9        |
| Ni     | 77.6         | 91.9        |
| Fe     | 79.3         | 87.4        |
| Rh     | 32.1         | -           |
| Pt     | 38.5         | -           |

Apparent $MO_x$-coverage (%) calculated from XPS spectra for BiVO$_4$/WO$_3$/FTO photoanodes modified with various metal oxides ($MO_x$). The concentrations of the coated metal precursor solutions were (A) 0.03 M for Mn, Co, Ni, Fe, Rh and Pt, and (B) 0.1 M for Mn, Co, Ni, and Fe. The MnO$_x$ coverage was calculated using the spectrum area and intensity factor of Mn to
the sum of those of Mn, Bi, V, W and Sn.

**Table S4.** Amounts of adsorbed Cl\(^-\) ions on the MO\(_x\)/FTO after dipped in NaCl aq. Related to Figure 4.

| MO\(_x\)     | Amount of Cl (%) after immersion in NaCl aq. |
|--------------|---------------------------------------------|
| None         | 0.2                                         |
| Mn           | 0.2                                         |
| Co           | < 0.1                                       |
| Ni           | 0.5                                         |
| Fe           | 0.6                                         |
| Pt           | 3.2                                         |
| Rh           | 3.5                                         |

Amounts of adsorbed Cl\(^-\) ions on the MO\(_x\)/FTO anode after immersion in 10 mL of 0.5 M aqueous NaCl solution for 3 h, determined from XPS measurements. Although the amount of Cl\(^-\) adsorption on Pt and RhO\(_x\) on the FTO was slightly larger than that of other typical metals, this is because the precursor solutions of Pt and Rh contain Cl\(^-\) ions.

**Table S5.** Potential required for electrolysis for steady current (2 mA) using various MO\(_x\)/FTO electrodes. Related to Figure 4.

| MO\(_x\)/FTO | (A) Potential (V vs. SHE) in NaCl aq. | (B) Potential (V vs. SHE) in NaH\(_2\)PO\(_4\) aq. |
|--------------|----------------------------------------|-----------------------------------------------|
| None         | 2.43                                   | 2.45                                          |
| Mn           | 1.62                                   | 1.40                                          |
| Co           | 1.50                                   | 1.38                                          |
| Ni           | 1.61                                   | 1.50*                                         |
| Fe           | 1.67                                   | 1.44                                          |
| Cu           | 1.95*                                  | 2.23*                                         |
| Cr           | 1.95*                                  | 2.19*                                         |
| Ag           | 1.74                                   | 1.86                                          |
| Pt           | 1.23                                   | 1.34                                          |
| Pd           | 2.04*                                  | 1.50                                          |
| Rh           | 1.38                                   | 1.37                                          |
| Ru           | 1.35                                   | 1.36                                          |
| Ir           | 1.30                                   | 1.36                                          |

Potential after the electrolysis with an electric charge of 2 C (1000 s, in a steady current of 2 mA) in (A) 0.5 M aqueous NaCl solution (pH 5.9) and (B) 0.5 M aqueous NaH\(_2\)PO\(_4\) solution (pH 4.3) using various MO\(_x\)/FTO electrodes (1.5 cm x 4 cm). The concentration of loaded metal precursor solution was 0.03 M. *Elution was observed during the reaction.
Figure S1. Photoelectrochemical performance and optical property of photoanode. Related to Figure 2.
(A) I-V characteristics for bare BiVO₄/WO₃/FTO and MnOₓ(0.1M)/BiVO₄/WO₃/FTO photoanodes measured in 0.5 M NaCl aqueous solution under simulated solar light (AM-1.5, 1 SUN, irradiation area: 0.28 cm², irradiated from the semiconductor side) with a light chopper. MnOₓ was prepared using 0.1 M-Mn precursor solution and by calcination at 400 °C. (B) Photocurrent at + 0.88 V vs. SHE at pH=7 of the bare BiVO₄/WO₃/FTO and MnOₓ(0.1M)/BiVO₄/WO₃/FTO photoanodes, which were calcined at different temperatures (300 – 500 °C) after coating of the manganese precursor solution, measured in 0.5 M NaCl aqueous solution under simulated solar light. (C) Light harvesting efficiency (LHE) spectra for the bare BiVO₄/WO₃/FTO and MnOₓ(0.1M)/BiVO₄/WO₃/FTO photoanodes calcined at 400 °C after coating with the manganese precursor solution. LHE was calculated from transmittance (T, %) and reflectance (R, %) using the following formula:

\[\text{LHE (\%) } = 100 - T - R\]  (S5)
Figure S2. FE(HClO) on photoanodes in 0.5 M of NaCl aq. and artificial seawater. Related to Figure 2.
FEs for oxidative HClO generation on photoanodes (MO\textsubscript{x}/BiVO\textsubscript{4}/WO\textsubscript{3}/FTO) modified with and without various metal oxides at an electric charge of 2 C (1000 s at steady photocurrent of 2 mA) in 0.5 M of NaCl aq. and artificial seawater (35 mL) under simulated solar light (AM-1.5, 1 SUN). The concentrations of coated metal precursor solutions were 0.1 M for Mn, Co, Ni, and Fe, and 0.03 M for Rh and Pt. The artificial seawater (MARINE ART SF-1) was purchased from Osaka Yakken. Co. Ltd., Japan (Iguchi. et al. 2018).
Figure S3. FEs for HClO generation on MOₓ/FTO under dark conditions. Related to Figure 2.
The electric charge was 2 C (1000 s at a steady photocurrent of 2 mA) under various conditions.
(A) FE (HClO) and FE(O₂) on MOₓ (0.03 M)/FTO in 0.5 M aqueous NaCl solution. (B) FE
(HClO) and apparent MnOₓ-coverage calculated from XPS results for bare FTO and
MnOₓ/FTO photoanodes, which were prepared by coating the manganese precursor solution
with different concentrations (0.01–0.1 M) to change the MnOₓ loading amount. (C) FE
(HClO) on MnOₓ (0.1 M)/FTO in aqueous NaCl solution with various concentrations (0.005–
2 M). (E) FE (HClO) on MnOₓ (0.1 M)/FTO anode in 0.5 M aqueous NaCl solution with
various pH (pH 3–9). (F) FE (HClO) on various MOₓ/FTO anode at steady potentials (1.5–1.8
V vs. SHE, pH=7) in 0.5 M aqueous NaCl solution. pH was adjusted by using NaOH and HCl.
For the MOₓ/FTO electrodes (1.5 cm x 4 cm) used in the experiments of (B), (C) and (D),
the concentrations of the coated metal precursor solution were 0.1 M for Mn, Co, Ni, and Fe,
and 0.03 M for Rh. (G-i) XRD patterns of the various MnOₓ/FTO anodes prepared by
electrochemical deposition and followed by calcination at various temperatures. In the XRD
pattern of MnOₓ(ED-S(100 °C)/FTO anode, no diffraction peak originated from the coating
metal oxide, indicative of their amorpicity. (G-ii) FE (HClO) for MnOₓ/FTO anodes
prepared by electrochemical deposition followed by calcination at various temperatures, and
that for the Ca-MnOₓ anode in a 0.5 M aqueous NaCl solution. (H) FE (HClO) on MnOₓ/FTO
electrodes prepared by changing different calcination temperatures (300-550°C) in 0.5 M
aqueous NaCl solution. (I) FE (HClO) on MnOₓ/FTO electrodes prepared by using different
manganese precursor salt (Mn(NO₃)₂•6H₂O and manganese bis(2-ethylhexanoate)) The
obtained electrodes are denoted that Mn-N, Mn-H, respectively.

![SEM images and MnOₓ coverages](image)

| Apparent MnOₓ coverage | 0% | 65% | 99% |
|------------------------|----|-----|-----|
| FE(HClO)               | 41.3% | < 2.4% | < 1.6% |

Figure S4. SEM images and MnOₓ coverages of (A) FTO substrate and (B)(C) MnOₓ/FTO
anodes. Related to Figure 3.
Manganese precursor solutions with different concentrations ((B) 0.03 M and (C) 0.1 M) were
spin-coated on FTO, and calcined at 400 °C. The apparent MnOₓ coverage was evaluated
by using XPS spectra of Mn 2p to Sn 3d and these counts per seconds (cps) coefficients.
Figure S5. HClO degradation behavior for MnOₓ (0.1 M)/FTO under dark conditions. Related to Figure 4, 5.
HClO degradation reactions were performed by using MnOₓ (0.1 M)/FTO under dark conditions in 0.5 M aqueous NaCl solution (35 mL) with initial addition of 200 μM of NaClO; (i) without current flow (-), and (ii) at a steady current of 2 mA (○).

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