CONTROLLING THE SELECTIVITY OF SOLAR O2/HClO PRODUCTION FROM SEAWATER BY SIMPLE SURFACE MODIFICATION OF VISIBLE-LIGHT RESPONSIBLE PHOTOELECTRODES

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Photoelectrochemical (PEC) production of H2 from saltwater over a semiconductor photoelectrode under solar-light irradiation is one of the effective technologies for developing a cost-effective sustainable energy conversion process. However, because saltwater such as seawater contains Cl−, O2 and HClO are produced competitively during oxidation reactions by photogenerated holes from electrolytes containing Cl− during the photocatalysis reaction. HClO is a high value-added chemical used for bleaching, etc., however, it is also an undesirable chemical that accelerates corrosion deterioration of large-scale water splitting systems. Therefore, it is necessary to control selectivity of oxidative O2/HClO production in electrolytes containing Cl− over photoelectrodes. In this review, we summarized our recent innovations in selective O2 or HClO production over visible-light driven BiVO4/WO3 photoanodes by simple modification of metal oxides. Modifications of metal oxides such as MnOx or CoOx via spin-coating onto a photoelectrode could control the selectivity on the O2/HClO production from an aqueous solution containing Cl− effectively. In addition, controlling loading conditions such as the loading amount of metal oxides, and calcination temperatures after coating a metal precursor solution enabled us to prepare photoelectrodes that produce O2 or HClO with selectivity of almost 100% using MnOx or CoOx, respectively, along with maintaining their PEC performance under solar-light irradiation.

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1. Introduction

Towards the establishment of a sustainable society, international efforts have been actively made to develop technologies that use renewable energy to mitigate global warming caused by CO2 emissions from fossil fuel consumption. Especially, hydrogen (H2) has been focused as clean energy that is expected to be used for power, transportation, and various industrial applications such as steelmaking.1–4 Over the past decade, several methods for producing H2 have been developed such as electrolysis, photocatalytic or photoelectrochemical (PEC) water splitting, and bio-reforming.5–12 Among them, photocatalytic and PEC solar water splitting using semiconductor photocatalysts and/or photoelectrodes have attracted considerable attention because of the potential application for clean H2 production from water utilizing renewable solar light.6–11 In particular, PEC systems have some advantages including achieving highly solar-to-hydrogen efficiency and the capability of separating H2 and O2 gases. Many visible-light responsible semiconductor photoelectrodes are used in PEC systems;13–18 one of the most attractive ones for producing O2 is BiVO4 because it has a narrow bandgap of approximately 2.4 eV, which can harvest visible light up to ca. 550 nm and favorable band edge positions for water oxidation, as well as having chemical stability.16–18 Furthermore, a BiVO4/WO3 multilayer photoanode, where BiVO4 is fabricated over a WO3 underlayer formed on a fluorine-doped SnO2 (FTO) conductive glass substrate, has been reported to provide relatively high PEC properties for water splitting under visible-light irradiation. In this multilayer photoanode, BiVO4 acts as a primary light absorber, and WO3 underlayer acts as an electron conductor which promote the separation of electron–hole pairs, allowing effective electron transfer from BiVO4 to the FTO glass substrate (as shown in Fig. 1).19,20

For future practical applications of PEC systems, the use of seawater as an electrolyte has an advantage over...
freshwater resources. However, when seawater, which contains Cl\textsuperscript{−}, is used as an electrolyte solution, the oxidation of H\textsubscript{2}O to O\textsubscript{2} and Cl\textsuperscript{−} ion to HClO compete at the anode. From an electrochemical perspective, this HClO are two-electron oxidation products of Cl\textsuperscript{−}; Cl\textsuperscript{−} is first oxidized to Cl\textsubscript{2} at the anode [Eq. (1), e is the charge on the electron], and then the produced Cl\textsubscript{2} disproportionates in the aqueous environment to form HClO [Eq. (2)]. Notably, the concentrations of Cl\textsubscript{2} and HClO in an aqueous solution are depending on the pH of the electrolyte, and the fraction of HClO is the largest at around neutral pH. Besides, the reduction reaction of H\textsuperscript{+} into H\textsubscript{2} are proceed at the cathode [Eq. (3)].

\[
\begin{align*}
\text{Anode:} & \quad 2\text{Cl}^{-} \rightarrow \text{Cl}_2 + 2e^{-}, \quad E = +1.48 \text{ V vs. RHE} \quad (1) \\
\text{Cathode:} & \quad 2\text{H}^+ + 2e^{-} \rightarrow \text{H}_2, \quad E = 0.0 \text{ V vs. RHE} \quad (3)
\end{align*}
\]

So far, there have been many reports about oxidative Cl\textsubscript{2} production over a metal electrode, such as Ru or Ir oxides coated on a Ti substrate, under applied bias in the dark. In these researches, improving the current density and selectivity for Cl\textsubscript{2} production are the major issues for the development of the electrodes. Dimensionally stable anodes (DSAs), which are generally composed of noble metal oxides (such as RuO\textsubscript{2} or IrO\textsubscript{2}), are known as the most advanced Cl\textsubscript{2} production catalysts. In particular, Ir, whether as a pure oxide or dopant, can maintain both low electrical resistance and a long-term stability, and therefore it is the most used electrode material for Cl\textsubscript{2} production. Subsequently, a series of iridium-based oxides (e.g., Ba\textsubscript{2}LaIrO\textsubscript{6} and Ba\textsubscript{2}YIrO\textsubscript{6}) has been synthesized and studied. However, high manufacturing cost of noble metal used in DSAs and requirement of a huge supply of electrical energy has been remaining as the issues for electrochemical Cl\textsubscript{2} production system. Alternatively, the application of a PEC system has environmental and economic benefits such as reduction of electrical energy consumption due to the utilization of light energy and cost reduction of electrode materials. So far, Cl\textsubscript{2} production on the TiO\textsubscript{2} photoelectrode from an aqueous NaCl solution under UV light irradiation have been reported by Anderson et al., and that on the WO\textsubscript{3} or BiVO\textsubscript{4} photoelectrode from an aqueous Cl\textsuperscript{−} containing solution under visible light irradiation have been reported by Grätzel or Zou et al.. However, there are still few reports on oxidative Cl\textsubscript{2} or HClO production over photoelectrode under UV or visible-light irradiation. Recently, our group has demonstrated PEC oxidative HClO and O\textsubscript{2} production from an aqueous NaCl solution over a BiVO\textsubscript{4}/WO\textsubscript{3} multilayer photoanode under visible light irradiation (Fig. 1). HClO is well-known agent used for bleaching, antibacterial treatment, and environmental purification, and therefore, effective production of HClO has been desired in the field of high value-added chemical production. On the other hand, in a large-scale water electrolysis system, suppression of HClO production is strongly desired because it is known as a chemical that accelerates corrosion deterioration of the system. Therefore, it is necessary to control the selectively of oxidative HClO or O\textsubscript{2} production from an aqueous solution containing Cl\textsuperscript{−} ions over a BiVO\textsubscript{4}/WO\textsubscript{3} photoanode under visible-light irradiation depending on the application. One of the potential approaches to controlling the selectivity of HClO or O\textsubscript{2} production is a surface modification with metal oxide layers on the surface of a BiVO\textsubscript{4}/WO\textsubscript{3} photoelectrode, as loading appropriate co-catalysts on a photoelectrode can promote photo-excited electrons and holes, which influences photocatalytic performance in the case of water splitting reaction. So far, there have been a few reports on the modification effect of metal electrodes used in electrolysis in the dark on catalytic performance for selective HClO or O\textsubscript{2} evolution from an electrolyte solution containing Cl\textsuperscript{−}. However, the modification effect of various metal oxides onto the photoelectrode on the selectivity of oxidative substance has not been fully investigated. In this review, we present our recent investigations about the effect of modification of metal oxides on the selective production of O\textsubscript{2} and HClO from an aqueous solution containing Cl\textsuperscript{−} over a BiVO\textsubscript{4}/WO\textsubscript{3} photoanode. It was found that manganese oxide (MnO\textsubscript{2}), or cobalt oxide (CoO\textsubscript{2}) loading by facile spin-coating could enable BiVO\textsubscript{4}/WO\textsubscript{3} photoelectrodes to selectively produce O\textsubscript{2} or HClO from an aqueous solution containing Cl\textsuperscript{−} under visible-light irradiation.

2. Preparation and characterization of MO\textsubscript{x} loaded BiVO\textsubscript{4}/WO\textsubscript{3} photoelectrodes

The preparation of BiVO\textsubscript{4}/WO\textsubscript{3} photoanodes has been previously described. Briefly, a WO\textsubscript{3} layer was fabricated on an FTO conductive glass substrate by spin-coating an aqueous peroxy-tungstic acid solution (1.4 M) containing W ions and then calcinated at 500 °C for 30 min in air. BiVO\textsubscript{4} was also fabricated on the obtained WO\textsubscript{3}/
FTO by spin-coating using a Bi and V precursor solution, which was mixed with 0.2 M Bi$^{3+}$ and V$^{5+}$ solutions in a 1:1 volume ratio diluted with butyl acetate and then calcined at 550 °C for 30 min in air. The modification of MO$_x$ (where M = Mn, Co, Fe, Ni, Pt, and Rh) layer on the BiVO$_4$/WO$_3$ photoanode was conducted by similar spin-coating using a metal–organic solution in butyl acetate and calcination at basically 400 °C for 1 h in air. The MO$_x$ modified photoelectrodes are denoted as MO$_x$/$\gamma$M, where $y$ is concentration of precursor metal–organic solution)/BiVO$_4$/WO$_3$. The presence of MO$_x$ loaded on the BiVO$_4$/WO$_3$ photoanodes was confirmed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM)/transmission electron microscopy (TEM) observations. The XPS spectra and top-view images of the pristine, and MnO$_x$ or CoO$_x$ loaded BiVO$_4$/WO$_3$ photoelectrodes are presented in Fig. 2 as representative samples. The XPS spectra of the MnO$_x$ or CoO$_x$ loaded BiVO$_4$/WO$_3$ photoelectrodes showed peaks attributed to MO$_x$ and BiVO$_4$/WO$_3$, respectively [Fig. 2(a)]. In addition, from SEM images of the MnO$_x$ or CoO$_x$ loaded BiVO$_4$/WO$_3$ photoelectrodes in Fig. 2(b), the edge of particles was unclear in the MnO$_x$ loaded photoelectrode, and many nanoparticles were dispersed on the surface of the CoO$_x$ loaded photoelectrode. Furthermore, cross-sectional TEM-energy dispersive X-ray (EDX) images of the MnO$_x$(0.1 M)/BiVO$_4$/WO$_3$ photoanode showed a thin MnO$_x$ layer with a thickness of ca. 10–30 nm was present on the surface of the BiVO$_4$/WO$_3$ photoanode [Fig. 2(c)]. Although the peaks attributed to MO$_x$ were undetectable by XRD because of their insufficient amount, no diffraction peak without attribution to BiVO$_4$, WO$_3$, and MO$_x$ originated after loading MO$_x$. These results indicate that MO$_x$ could be loaded on the surface of BiVO$_4$/WO$_3$ photoelectrodes by the simple spin-coating of an organic solution and calcination without producing any impurities.

3. Photoelectrochemical O$_2$ and/or HClO production over MO$_x$ loaded BiVO$_4$/WO$_3$ photoanode

Photo-oxidative O$_2$ and/or HClO production reactions on a BiVO$_4$/WO$_3$ photoanode loaded with/without MO$_x$ were performed using an aqueous NaCl solution with a concentration of basically 0.5 M, which is the same as seawater, as an electrolyte under simulated solar light. In experimental work, a two-compartment cell (Pyrex-made) with an ion-exchange membrane (SELEMION, AGC Engineering), and a photoanode, an Ag/AgCl electrode and a Pt wire were used as the working, reference, and counter electrodes, respectively. A solar simulator (SAN-EL ELECTRIC Co., XES-151S), which was calibrated to AM-1.5 with a spectroradiometer (SOMA Optics, Ltd., Model S-2440) was used as the light source. The quantities of O$_2$ and HClO produced by oxidation reactions were measured using an O$_2$ gas sensor and DPD reagent. The faradaic efficiency (FE) of O$_2$ or HClO production [denoted as FE(O$_2$) or FE(HClO), respectively] can be calculated as follows:

$$\text{FE(O}_2\text{)} = \left(\frac{\text{amount of generated O}_2}{\text{theoretical amount of O}_2}\right) \times 100$$

$$\text{FE(HClO)} = \left(\frac{\text{amount of generated HClO}}{\text{theoretical amount of HClO}}\right) \times 100$$

![Fig. 2. (a) XPS spectra and (b) Surface SEM images of the pristine BiVO$_4$/WO$_3$ photoanode and that with MnO$_x$ or CoO$_x$ loading. (c) Cross-sectional TEM image, and (ii–vi) EDX mapping images of each element of BiVO$_4$/WO$_3$ photoanodes with MnO$_x$. The concentration of the MnO$_x$ and CoO$_x$ precursor solution used for modification was 0.1 M. Reproduced from Refs. 57 and 58 with permission from the Royal Society of Chemistry and Elsevier.](image)
During the electrolysis reaction under solar-light irradiation, all the pristine and MOx coated BiVO4/WO3 photoanodes produced O2 and/or HClO from an aqueous NaCl solution [Fig. 3(a)]. FE(O2) and FE(HClO) during electrolysis depended on the loading MOx elements, however, the sum of FE(O2) and FE(HClO) became almost 100%. The result suggests that O2 and HClO are the main products, and other oxidative byproducts (Cl2, HClO2, HClO3, etc.) are not generated, as we have recently reported.25 Interestingly, HClO production was significantly suppressed by loading MnOx on the photoanode, and O2 was produced with an FE greater than 90%. In contrast, HClO production was improved markedly on the CoOx loaded photoanode compared to the pristine one. Similar trends of improved O2/HClO production on the MnOx or CoOx loaded photoanode from a pure NaCl solution were also observed from artificial seawater [Fig. 3(b)], implying that various ion species such as SO4²⁻ and Mg²⁺, which are contained in the artificial seawater, have little effect on selectivity due to their low concentrations compared to Na⁺ and Cl⁻.24,25 As mentioned above, the simple loading of MnOx or CoOx enabled the preparation of BiVO4/WO3 photoelectrodes capable of controlling the selectivity of photo-oxidative HClO/O2 production from an aqueous solution containing Cl⁻ under simulated solar-light.

4. Selective O2 production over MnOx loaded BiVO4/WO3 photoanode

As remarked above, selective O2 production from an aqueous solution containing Cl⁻ was successfully demonstrated on a MnOx loaded BiVO4/WO3 photoanode under solar-light irradiation. Therefore, such reactions under various conditions were investigated. For electrolysis conditions shown in Figs. 4(a) and 4(b), HClO production was suppressed in an aqueous NaCl solution of different concentrations (0.05–2 M) or pH levels (3–9) under solar-light irradiation. Furthermore, HClO production was effectively suppressed on all cases of electrolysis under simulated solar-light using the MnOx(0.01–0.1 M)/BiVO4/WO3 photoanodes, whose loading MnOx amounts were confirmed to increase as the Mn precursor concentration increases [Fig. 4(c)]. Notably, although the apparent surface coverage, which was calculated from XPS spectra, of the MnOx (0.01 M) loaded BiVO4/WO3/FTO photoanode was almost 30%, HClO production was sufficiently suppressed. The result indicates that the entire coverage of MnOx on the BiVO4/WO3/FTO surface was unnecessary to suppress HClO production. Similar suppression behaviors in HClO production were also observed in electrolysis reactions using MnOx loaded FTO electrodes in the dark.57 Alternatively, the PEC performance on the obtained MnOx loaded BiVO4/WO3 photoanode, calcined at 400 °C, was almost similar to that on the pristine one, indicating that undesired changes such as thermal doping or chemical changes during calcination after coating the Mn precursor solution.57 Thus, photoelectrodes capable of producing O2 selectively while retaining their PEC performance have successfully prepared by a simple surface MnOx modification.

Reasons for selective O2 production on MnOx loaded BiVO4/WO3 photoanodes or FTO electrodes are considered to be (i) direct O2 production on MnOx and (ii) indirect O2 production from the decomposition of HClO as an intermediate [Fig. 5(a)]. However, the latter (ii) was excluded because of the following HClO decomposition behaviors; HClO initially added to an aqueous NaCl solution did not decompose on a MnOx/WO3 photoanode under dark conditions. The result suggests that O2 was directly produced on MnOx loaded photoanode in the NaCl aqueous solution. For the former (i), selective O2 production from an aqueous Cl⁻ containing solution was demonstrated using anodes with Mn species coating in electrolysis in the dark. As shown in Table 1, several Mn species-coated electrodes that can produce O2 selectively have been developed in the field of seawater electrolysis.46–56 After H. Tamura et al. and J. E. Bennett reported special anodic characteristics of Mn-coated electrodes for evolution of O2.
in an aqueous Cl\(^-\) containing solution.\(^{46,59}\) In this field, mechanisms of selective O\(_2\) production have been discussed; selective O\(_2\) production has been assumed to proceed via a “Cl\(^-\)-impermeable mechanism” where Cl\(^-\) ions cannot pass through the MnO\(_x\) layer and a “catalytic mechanism” where MnO\(_x\) functions as a O\(_2\) evolution catalyst [Fig. 5(b)].\(^{56}\) The precious mechanism of whether the selective O\(_2\) production proceeds is still unclear though. The former “Cl\(^-\)-impermeable mechanism” has been supported for a long time in the field of seawater electrolysis using noble metal anodes such as IrO\(_2\)/Ti. For example, Koper et al. reported that a MnO\(_x\) layer can function as a diffusion barrier preventing Cl\(^-\) from reacting on the IrO\(_2\) catalyst underneath, and O\(_2\) production can occur on the surface of the IrO\(_2\) catalyst.\(^{56}\) However, the above-mentioned selective O\(_2\) production on partially MnO\(_x\) loaded (photo)electrodes cannot be explained by this mechanism. Therefore, a reasonable explanation on the

![Fig. 4](image)

**Table 1.** Mn-based electrodes that can produce O\(_2\) selectively from an aqueous solution containing Cl\(^-\) under the electrolysis reaction

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>conditions</th>
<th>FE(O(_2))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MnO(_2)/IrO(_2)/Ti</td>
<td>seawater, dark</td>
<td>99 %</td>
<td>46</td>
</tr>
<tr>
<td>2 MnO(_2)/IrO(_2)/Ti and (Mn-W)O(_x)/IrO(_2)/Ti</td>
<td>0.5 M NaCl (pH 8), dark</td>
<td>&gt;99 %</td>
<td>47</td>
</tr>
<tr>
<td>3 (Mn(_{1-x}),Mo(<em>x))O(</em>{2+x})/IrO(_2)/Ti</td>
<td>0.5 M NaCl (pH 12), dark</td>
<td>100 % (initial)</td>
<td>48</td>
</tr>
<tr>
<td>4 Mn(_{1-x}),Mo(<em>x),O(</em>{2+x})/IrO(_2)/Ti</td>
<td>0.5 M NaCl (pH 12), dark</td>
<td>100 % (initial)</td>
<td>49</td>
</tr>
<tr>
<td>5 Mn-Mo-Sn oxide/IrO(_2)/Ti</td>
<td>0.5 M NaCl (pH 8.7), dark</td>
<td>100 % (initial)</td>
<td>50</td>
</tr>
<tr>
<td>6 Mn-Mo-W oxide/IrO(_2)/Ti</td>
<td>0.5 M NaCl (pH &lt;0.5), dark</td>
<td>&gt;94 %</td>
<td>51</td>
</tr>
<tr>
<td>7 Mn-Mo-W oxide/IrO(_2)/Ti</td>
<td>0.5 NaCl (pH &lt;0.5), dark</td>
<td>&gt;94 %</td>
<td>52</td>
</tr>
<tr>
<td>8 Mn(<em>{1-x}),Mo(<em>x),Sn(</em>{0.5}),O(</em>{2+x})/IrO(_2)/Ti</td>
<td>0.5 M NaCl (pH 2), dark</td>
<td>100 % (initial)</td>
<td>53</td>
</tr>
<tr>
<td>9 Mn-Mo-W oxide/IrO(_2)/Ti</td>
<td>0.5 M NaCl (pH 8.7), dark</td>
<td>&gt;94 %</td>
<td>54</td>
</tr>
<tr>
<td>10 Mn-Fe-V oxide/IrO(_2)/Ti</td>
<td>3.5 wt % NaCl (pH 12), dark</td>
<td>100 % (initial)</td>
<td>55</td>
</tr>
<tr>
<td>11 MnO(_2)/IrO(_2)/GC</td>
<td>0.03–0.08 M KCl, dark</td>
<td>—</td>
<td>56</td>
</tr>
<tr>
<td>12 MnO(_2)/FTO</td>
<td>0.5 M NaCl (pH 3–9), dark</td>
<td>&gt;90 %</td>
<td>57 (This work)</td>
</tr>
</tbody>
</table>
mechanism of selective \( \text{O}_2 \) production on MnO\(_2\) loaded (photo)electrodes in an aqueous solution containing \( \text{Cl}^- \) should be the catalytic mechanism. The catalytic mechanism can be supported by the relatively high turnover number (ca. 154) of the loading MnO\(_2\), and lower onset potential for \( \text{O}_2 \) production in aqueous NaCl solutions on the MnO\(_2\) loaded FTO electrode compared to that on the pristine one.\(^{57}\)

Based on the results that the catalytic specificity of Mn enabled selective \( \text{O}_2 \) production on the MnO\(_2\) loaded photoelectrode, we focus on the \( \text{O}_2 \) evolution catalyst of natural photosynthesis; the Mn\(_4\)CaO\(_5\) oxygen-evolving complex in photosystem II (PSII). To date, \( \text{O}_2 \) evolution centers containing elements other than Mn have been unknown; moreover, reasons for selecting Mn as \( \text{O}_2 \) evolution centers in PSII have been unknown. Judging from the results of above-mentioned behaviors on selective \( \text{O}_2 \) production from an aqueous solution containing \( \text{Cl}^- \) over MnO\(_2\) loaded photoanode, one of the possible reasons for selecting Mn is “Mn is the only element that can produce only \( \text{O}_2 \) in aqueous solutions containing \( \text{Cl}^- \) under various conditions in vivo, without generating HClO which is toxic to organisms”.\(^{58}\)

Considering the specific nature of MnO\(_2\) produces \( \text{O}_2 \) selectively in an aqueous solution containing \( \text{Cl}^- \) under various conditions, it is reasonable to propose a new hypothesis as to why MnO\(_2\) was selected as \( \text{O}_2 \) evolution centers of PSII that appeared on the ancient earth. Thus, we have proposed a new hypothesis of manganese’s significant role as the element for \( \text{O}_2 \) evolution centers in natural photosynthesis and contribute to the practical application of artificial photosynthesis using seawater (Fig. 6).

5. Efficient HClO production over CoO\(_x\) loaded BiVO\(_4\)/WO\(_3\) photoanode

As mentioned before, higher FE for oxidative HClO production from an aqueous solution containing \( \text{Cl}^- \) under visible-light irradiation was obtained on a CoO\(_x\)-loaded photoanode than on the bare one. Such a high FE(HClO) in an aqueous solution containing \( \text{Cl}^- \), especially with a dilute chloride ion concentration such as seawater (ca. 0.5 M), is desired to realize the practical application of low-cost PEC systems. Therefore, to achieve efficient HClO production, we examined the effect of CoO\(_x\) loading onto the BiVO\(_4\)/WO\(_3\) photoelectrode on oxidative HClO production under visible-light irradiation in detail.

Similar to MnO\(_2\) loaded photoelectrodes, the CoO\(_x\) loaded BiVO\(_4\)/WO\(_3\) photoanode, which was prepared by calcination at 400 °C, was confirmed to maintain its PEC performance sufficiently [Fig. 7(a)]. HClO production was also produced selectively with the FE of ca. 100 % in all cases of the photo-electrolysis using the BiVO\(_4\)/WO\(_3\) photoanodes loaded with different amounts of CoO\(_x\)(0.001–0.1 M). The result indicates that HClO production from an aqueous NaCl solution could be improved by partially CoO\(_x\) loading a photoanode surface. For photo-electrolysis at a fixed potential of 1 V vs. RHE, the activities of HClO production over the CoO\(_x\)(0.001–0.1 M)/BiVO\(_4\)/WO\(_3\) photoelectrodes increased with the amount of coated CoO\(_x\) up to 0.03 M, after which the activities decreased [Fig. 7(b)]. The excess loading of CoO\(_x\) (>0.05 M) was confirmed to inhibit light absorption by UV–vis spectra, which decreased the activity. Therefore, the loading amount of CoO\(_x\) that can maintain light absorption is one of the key factors in obtaining the photoanodes for efficient HClO production. The possibility of efficient charge separation in CoO\(_x\) can be excluded as one of the reasons for increased oxidative HClO production on CoO\(_x\) loaded photoanodes; the photocurrents observed in \( i-V \) curves on the CoO\(_x\) loaded photoanodes were comparable to that on the pristine one, indicating that the charge separation on both bare and CoO\(_x\) loaded photoanodes occur comparably in an aqueous NaCl solution. Because of cobalt’s ability to interact with \( \text{Cl}^- \) easily, the interaction between Co and Cl on the CoO\(_x\) surface can improve the HClO production in an aqueous NaCl solution.\(^{60}\) The results of HClO production on the BiVO\(_4\)/WO\(_3\) photoanodes loaded with/without CoO\(_x\) in an aqueous NaCl solution with different concentrations also support the specific ability of the loaded CoO\(_x\); higher FE of HClO were obtained on photoanodes loaded with CoO\(_x\) than on bare ones in particular aqueous NaCl solutions of low concentration (<0.5 M, as the same level as seawater), suggesting that CoO\(_x\) can capture photogenerated holes effectively, even in dilute NaCl aqueous solutions. Along with the above-mentioned mechanistic insights on selective HClO production, the possibility of using seawater whose Cl concentration is known to be approximately 0.5 M was also suggested from the basis of the result of high FE of HClO production using CoO\(_x\) loaded photoelectrodes.

6. Summary and outlook

We attempted to prepare visible-light responsible photoanodes that can selectively produce \( \text{O}_2 \) or HClO from an
Moreover, photoelectrodes capable of producing O\textsubscript{2} or HClO and CoO\textsubscript{2} can improve the selectivity of HClO up to almost 100\%.

Based on results, loading metal oxide types over the BiVO\textsubscript{4}/WO\textsubscript{3} photoelectrodes influenced the selectivity of oxidative O\textsubscript{2}/HClO production from an aqueous solution containing Cl\textsuperscript{-} significantly. MnO\textsubscript{2} modification onto the BiVO\textsubscript{4}/WO\textsubscript{3} photoanodes specifically catalyzed selective O\textsubscript{2} production under various conditions. In addition, CoO\textsubscript{2} modification not only promotes HClO production but also improves the selectivity of HClO up to almost 100\%. Moreover, photoelectrodes capable of producing O\textsubscript{2} or HClO without significantly degrading their PEC performance have been successfully prepared by controlling preparation conditions. Although some mechanistic studies on selective O\textsubscript{2}/HClO production over the photoelectrodes by in-situ characterizations and theoretical calculations will be required, these findings will not only provide some insight into practical applications of artificial photosynthesis using seawater, but also facilitate the elucidation of the role of Mn\textsubscript{4}O\textsubscript{5} core clusters in natural photosynthesis.

For practical applications of solar H\textsubscript{2} and/or HClO production using seawater, it is essential to develop PEC systems capable of producing them efficiently under solar-light irradiation. Therefore, developing photoelectrodes with a high solar-to-chemical conversion is necessary. Such developments will be vital to upgrade photocatalytic materials to improve photocurrent and onset potentials, along with fine-tuning of their preparation processes. For example, some oxides, (oxy)nitrides and oxysulfides, which can absorb light up to ca. 600–700\,nm, should be applied to improve the PEC performance. The long-term stability of the developed photoelectrodes is also an important factor, because photo-corrosion often occurs on the surface of electrodes. Loading co-catalyst or surface modification have been reported to inhibit such the photo-corrosion, so Mo\textsubscript{2} modification presented in this review can also contribute to PEC stability in the future.

Designing scalable PEC systems is another important point that needs to be addressed. A photoactive area has a significant and negative effect on photocurrent density, because of the increased resistive of substrates. Hence, it is necessary to develop a strategy for scaling up photoelectrodes while maintaining their high PEC performance, along with developing large-scale devices. We hope this review can motivate the development of solar energy conversion systems and seawater electrolysis systems for future sustainable energy applications.

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