Recent Developments in Visible-Light-Absorbing Semitransparent Photoanodes for Tandem Cells Driving Solar Water Splitting

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The development of an efficient conversion system to transform solar energy into chemical energy, such as renewable hydrogen, is a promising way to overcome energy problems. Photoelectrochemical (PEC) water splitting is a promising means of obtaining renewable hydrogen directly from water utilizing sunlight. Recent reports have demonstrated that a PEC cell with a tandem configuration (tandem cell) has the potential to realize a high solar-to-hydrogen (STH) energy conversion efficiency by solar water splitting. However, there are still many obstacles to the development of practical and cost-effective tandem cells. In particular, development of efficient photoanodes for the oxygen evolution reaction (OER) is a prerequisite for improving the STH efficiency. Herein, recent progress in developing (semi)transparent photoanodes for the OER, such as Fe$_2$O$_3$, BiVO$_4$, and Ta$_2$N$_5$, is described based on the topics of preparation methods, semiconductor properties, and PEC performance. In addition, the strategies for enhancing the STH efficiency of tandem cells consisting of (semi) transparent photoanodes conjugated with photovoltaic (PV)-based cathodes are summarized. This Review is expected to provide guidelines for the future development of tandem cells capable of highly efficient and stable water splitting.

1. Introduction

The development of an efficient solar energy conversion system into transportable and storable chemical energy, in particular for hydrogen, is a promising method to overcome energy problems and establish a carbon-neutral society.[1–6] Hydrogen production from water using semiconductor materials and sunlight would be preferable for environmentally friendly energy conversion systems.[7] As the water-splitting reaction to produce hydrogen is an uphill reaction that requires a Gibbs free energy of 237 kJ mol$^{-1}$, additional input of external energy is necessary to drive the reaction. Photoelectrochemical (PEC) cells consist of semiconductor photoelectrodes that can split water into hydrogen and oxygen via two-step photo-excitation without the application of further input of external energy.[2,8] A typical PEC cell is composed of photoanodes for oxygen evolution reaction (OER) and photovoltaic (PV) modules connected to the electrocatalysts for hydrogen evolution reaction (HER). These photoelectrodes are electrically connected with each other and immersed in an electrolyte. This combination of photoelectrodes on the PEC cell can relax the strict requirement for each photoelectrode, such as the positions of the conduction band minimum (CBM) and valence band maximum (VBM). Moreover, water splitting by the PEC cells would be expected to be simple and cost-effective because both light absorption and reaction take place on a single component utilizing the semiconductor/liquid interfaces.

To accomplish efficient and cost-effective solar water splitting will require economically viable PEC cells designed to split water. Figure 1a shows a schematic illustration of a tandem cell having a stacked structure incorporating a first (semi)transparent photoanode for the OER along with a PV-based cathode for the HER that responds to the light transmitted through the front-side photoanode, which could potentially achieve a sufficiently high level of solar-to-hydrogen (STH) energy conversion efficiency on water splitting.[9–11] In this Review, we delineate the (semi)transparent photoanodes that have high transmittance in the wavelength region longer than the absorption edge wavelength of the semiconductor materials. A first transparent photoanode absorbs a part of the sunlight, and electrons and holes are generated in the photoanode. The potential of photogenerated holes must
be more positive than the standard redox potential of water oxidation to drive the OER. The first photoanode is fabricated on transparent conductive layer–coated substrates, such as indium tin oxides (ITO) and fluorine-doped tin oxides (FTO). Sunlight with a longer wavelength than the absorption edge wavelength of the photoanode is transmitted to the back side of the photoanode. A second PV-based cathode absorbs the transmitted light from the first transparent photoanode, and then the photogenerated electrons are used to drive the HER. Unused electrons and holes in each electrode are recombined to close the circuit in the tandem cell.

The electric and optical coupling between the transparent photoanode and PV module on the back side must be carefully optimized to maximize the STH conversion efficiency. As the photocurrent values generated by PV-based cathodes placed on the back side are determined by the intensity and wavelength of transmitted light from the front-side photoanode, the optical characteristics of the photoanodes need to be tuned. Figure 1b shows photocurrent density–potential (j–E) curves for photoanodes and PV-based cathodes. The STH energy conversion efficiency of the PEC cell, including tandem cells, is determined by the current matching of both electrodes denoted as the operating current density ($j_{op}$) corresponding to the intersection of the j–E curves in Figure 1b. In addition, the Faradaic efficiency for O$_2$ (H$_2$) evolution should be confirmed by gas quantification to obtain the STH efficiency accurately. Ideally, the operating potential of the photoanodes should be the potential that generates saturated photocurrent like the intersection of the j–E curves of the “ideal photoanode” and “PV module,” in Figure 1b. However, in the case of recent studies, the operating point of the tandem cell has been far from the saturated photocurrent as the intersection point of j–E curves for a “non-ideal photoanode” and “PV modules,” as shown in Figure 1b. To maximize the STH efficiency of the tandem cell, high transmittance and a sufficiently narrow bandgap of the front transparent photoanodes are prerequisites. Recently, many studies have attempted to develop efficient transparent photoanodes. This Review focuses on (semi)transparent Fe$_2$O$_3$, BiVO$_4$, and Ta$_3$N$_5$ photoanodes with yellow (BiVO$_4$) or red (Fe$_2$O$_3$ and Ta$_3$N$_5$) coloration, which can absorb visible light up to 520 nm (BiVO$_4$) or 600 nm (Fe$_2$O$_3$ and Ta$_3$N$_5$) and potentially achieve a high level of STH energy conversion efficiency. Fe$_2$O$_3$ has attracted much attention as a transparent photoanode.$^{[11–23]}$ In 2020, Park et al. achieved the highest reported STH of 4.49% in Fe$_2$O$_3$-based tandem cells with a PV-based cathode by using a tandem cell composed of a Ti- and Si-codoped Fe$_2$O$_3$ transparent photoanode modified with a NiFeO$_x$ electrocatalyst and a perovskite solar cell (PSC).$^{[11]}$ Many researchers also have devoted much effort to developing efficient BiVO$_4$ transparent photoanodes.$^{[10,24–36]}$ In 2018, Wang et al. developed a tandem cell consisting of dual NiOOH/FeOOH-modified BiVO$_4$ and a PSC exhibiting the highest STH efficiency of 6.5% in a BiVO$_4$-based tandem cell with PV modules.$^{[10]}$ In addition to oxide materials, Ta$_3$N$_5$-based photoanodes with an absorption edge wavelength of 600 nm and a suitable band-edge position for water splitting have been considered as one of the leading candidates to realize highly efficient PEC water splitting.$^{[9,37–50]}$ Ta$_3$N$_5$ thin-film photoanodes fabricated on transparent conductive substrates are found to be potentially applicable to the front-side photodelectrode in a tandem cell.$^{[9,38,48]}$ In 2019, Higashi et al. reported a tandem cell composed of a NiFeO$_x$ electrocatalyst–modified Ta$_3$N$_5$ transparent photoanode fabricated on n-type GaN-coated sapphire (Ta$_3$N$_5$/GaN/Al$_2$O$_3$) on the front side and two-series-connected CuInSe$_2$ elements terminated with a Pt electrode on the back side, which achieved overall water splitting with an STH efficiency of 7.0% in the initial stage of the reaction.$^{[9]}$

However, there are still problems associated with PEC cells with tandem configuration, which will need to be overcome for the tandem cell to become a practical solution to energy problems. A technoeconomic analysis has suggested that an STH efficiency of at least 10% is required to meet the cost of $2.00–4.00 per kg H$_2$ for dispersed hydrogen.$^{[51]}$ The main reason for limiting the efficiency of the PEC device is the positive onset potential of photoanodes, which allows the operation point of the tandem cell to be far from the saturated photocurrent as shown in Figure 1b. The most negative onset potential for the OER is $\approx0.3$ V versus reversible hydrogen electrode (RHE) when transparent BiVO$_4$ is used$^{[25,28,29]}$ and 0.5–0.7 V versus RHE when transparent Fe$_2$O$_3$ or Ta$_3$N$_5$ is used.$^{[9,14,38]}$ In particular, the values of the onset potential for Ta$_3$N$_5$ are far from the expected

Figure 1. a) Schematic illustration of the PEC water splitting reaction using a tandem cell composed of a modified transparent photoanode for the OER and a PV-based cathode for the HER responding to the light transmitted from the transparent photoanode. b) A typical j–E curve for ideal (solid line) and recent (dashed line) photoanodes, and a PV-based cathode. $j_{op}$ expresses the expected photocurrent values generated by PEC cells.
value. In addition, the long-term stability of photoanodes during the water-splitting reaction is also an important issue for efficient, durable water splitting by a tandem cell. Although nonoxide materials, including Ta$_3$N$_5$, have fascinating characteristics, they also suffer from deterioration due to photocorrosion or self-photooxidation, unlike oxide photoanodes. For instance, in the present stage, the stability of the Ta$_3$N$_5$-based tandem cell during the water-splitting reaction was found to be insufficient for practical application, with STH dropping from 7.0% to 5.5% after 15 min of the reaction.\[^{9}\] This deterioration in performance of the tandem cell is thought to be mainly due to the self-photooxidation of Ta$_3$N$_5$ during water splitting.\[^{46, 47, 52}\]

This Review will focus on the recent efforts to develop efficient and transparent photoanodes applicable to the tandem cell for water splitting, and summarize the STH energy conversion efficiency of PEC tandem cells without the application of an external bias voltage. In addition, the problems limiting the efficiency of the tandem cell are discussed. To overcome the problems, various modifications, such as other element doping\[^{53–58}\] electrocatalyst coating\[^{14, 31, 59–61}\] and function layer inserting\[^{62–67}\] have been demonstrated. Finally, this Review will introduce some efforts and the future perspective to allow PEC devices, such as tandem cells, to be one of the practical and efficient systems to obtain renewable energy resources.

### 2. Recent Progress of Transparent Photoanode–Based Tandem Cells

To achieve the required STH energy conversion efficiency of 10% by tandem cells, transparent photoanodes should utilize visible light, which occupies a large portion of sunlight. This section focuses on promising candidates as high-performance transparent photoanodes for tandem cells, such as Fe$_2$O$_3$, BiVO$_4$, and Ta$_3$N$_5$, and introduces preparation methods, unique properties, and performance of the transparent photoanodes. The properties and STH efficiency of tandem cells based on the photoanodes are summarized in Table 1. To accurately measure the STH efficiency, it is necessary to consider the Faradaic efficiency of the water-splitting reaction by the tandem cell. Lower than 100% Faradaic efficiency indicates that oxidation reaction takes place other than O$_2$ evolution, such as material self-oxidation, which is closely related to the durability of the samples. The Faradaic efficiencies for the reported systems are also shown in Table 1.

#### 2.1. Fe$_2$O$_3$

Fe$_2$O$_3$ has a narrow bandgap of 2.0–2.2 eV, which could potentially achieve STH values as high as 13–16%\[^{6}^{6}\] and it has a suitable VBM position to drive the OER. Fe$_2$O$_3$-based photoanodes on conductive transparent substrates have been fabricated through a variety of methods, including spray pyrolysis\[^{14, 18}\] electrodeposition,\[^{18}\] chemical vapor deposition,\[^{21, 24, 25}\] hydrothermal synthesis,\[^{13, 15}\] and calcination of precursors.\[^{11, 14, 21}\] In 2010, Brillet et al. compared the STH energy conversion efficiency generated by three different types of tandem cells consisting of a Fe$_2$O$_3$ photoanode and two dye-sensitized solar cells (DSCs).\[^{19}\] The transparent Si-doped Fe$_2$O$_3$ photoanode on FTO was prepared by atmospheric pressure chemical vapor deposition (APCVD) from Fe(CO)$_5$ and tetraethoxysilane at 693 K. A proposed “trilevel” tandem cell, i.e., Fe$_2$O$_3$/DSC–squaraine dye/DSC–panchromatic dye, achieved the highest STH efficiency of 6.3%.

#### Table 1. The properties and performance of tandem cells based on transparent Fe$_2$O$_3$, BiVO$_4$, or Ta$_3$N$_5$ and PV-based cathodes.

| Transparent photoanode material | Year | Preparation method | Surface modification | PV-based cathode material | Faradaic efficiency | The STH efficiency of the tandem cell |
|---------------------------------|------|--------------------|----------------------|--------------------------|---------------------|-------------------------------------|
| Si-doped Fe$_2$O$_3$\[^{19}\]   | 2010 | APCVD              | –                    | DSC                      | –                   | 1.36%\[^{6}\]                        |
| Si-doped Fe$_2$O$_3$\[^{22}\]   | 2012 | APCVD              | Co cat. and Al$_2$O$_3$ | DSC                      | ≈100%               | 1.17%                               |
| Fe$_2$O$_3$\[^{4}\]            | 2015 | Hydrothermal       | NiFe$_2$O$_4$         | Si                       | ≈100%               | 0.91%                               |
| Si-doped Fe$_2$O$_3$\[^{23}\]   | 2015 | APCVD              | FeNiO$_2$             | PSC                      | ≈100%               | 1.9%                                |
| Mn-doped Fe$_2$O$_3$ nanoparticle\[^{11}\] | 2015 | Hydrothermal       | CoP$_i$               | PSC                      | 95% (O$_3$)         | 2.4%\[^{6}\]                        |
| Sn-doped Fe$_2$O$_3$ nanoparticle\[^{15}\] | 2017 | Hydrothermal       | CoP$_i$ and SnO$_2$   | PSC                      | –                   | 3.4%\[^{6}\]                        |
| Dual Ti-, Si-codoped Fe$_2$O$_3$\[^{11}\] | 2020 | Hydrothermal       | NiFe$_2$O$_4$         | PSC                      | 90–92%              | 4.49%\[^{6}\]                      |
| W-doped BiVO$_4$\[^{21}\]      | 2013 | Spray pyrolysis    | CoP$_i$               | Si                       | 100%                | 4.9%                                |
| W-doped BiVO$_4$\[^{21}\]      | 2014 | Spray pyrolysis    | CoP$_i$               | Si                       | 100%                | 5.2%                                |
| BiVO$_4$\[^{27}\]              | 2015 | Metal–organic      | CoP$_i$               | PSC                      | 50–75% (H$_2$)      | 2.5%\[^{6}\]                       |
| H$_2$-treated Mo-doped BiVO$_4$\[^{20}\] | 2015 | Metal–organic      | CoCl$_2$              | PSC                      | ≈100%               | 4.3%                                |
| BiVO$_4$\[^{23}\]              | 2018 | Electrodeposition  | CoB$_2$ and TiO$_2$   | Si                       | ≈100%               | 3%                                  |
| Dual BiVO$_4$\[^{10}\]         | 2018 | Electrodeposition  | NiOOH/FeOOH           | PSC                      | 95%                 | 6.5%\[^{6}\]                       |
| Dual W-doped BiVO$_4$ (50 cm$^2$)\[^{24}\] | 2019 | Spray pyrolysis    | CoP$_i$               | Si                       | >99%                | 2.1%                                |
| Mo-doped BiVO$_4$ nanoparticle\[^{28}\] | 2020 | Metal–organic      | CoP$_i$               | PSC                      | –                   | 2.43%\[^{6}\]                      |
| Mg-doped Ta$_3$N$_5$\[^{7}\]    | 2019 | Nitridation of Ta  | NiFe$_2$O$_4$         | ZnSe/CIGS                | ≈100%               | Photocurrent: 46 μA                 |
| Ta$_3$N$_5$\[^{8}\]            | 2019 | Nitridation of Ta  | NiFe$_2$O$_4$         | CIS                      | 96% (O$_3$)         | 7.0%\[^{6}\]                       |

\[^{6}\]The marked STH efficiencies do not consider the Faradaic efficiency.
of 1.36% among the three types of tandem cells, including Fe₂O₃/connected DSCs abreast and two-abreast DSCS/Fe₂O₃. The authors intended to maximize the utilization ratio of sunlight by using two kinds of dyes that absorb different wavelength regions. The same group has also demonstrated overall water splitting using a tandem cell employing Fe₂O₃ modified by a Co catalyst and Al₂O₃.⁴⁴ Although the tandem cell had an STH efficiency of 1.17%, their WO₃/DSC tandem cell achieved a relatively high STH of 3.10%. In 2015, Jang et al. reported a different type of Fe₂O₃-based tandem cell.⁴⁴ FeOOH was grown on FTO in a solution containing iron (III) chloride hexahydrate and sodium nitrate at 373 K for 1 h. Next, the film was calcined at 1073 K for 5 min to form Fe₂O₃ from FeOOH. The obtained transparent Fe₂O₃ photoanode via two cycles of this regrowth treatment was named “rgH II.” This new synthesis method improved the onset potential of the OER and enhanced the photocurrent values compared to the hematite prepared by atomic layer deposition (ALD) (Figure 2a) by expanding the photovoltage, but the reason for the improvement remains unclear. Furthermore, the authors successfully improved the onset potential and photocurrent values using NiFeOₓ as the electrocatalyst for the OER (see Figure 2a). The tandem cell consisted of the NiFeOₓ-modified transparent rgH II photoanode and a TiO₂/PTx-loaded amorphous Si (a-Si) photocathode achieved an STH efficiency of 0.91% with no externally applied bias.

Doping for Fe₂O₃ is an effective strategy for improving the onset potential of the OER. Gurudayal et al. developed a Fe₂O₃-based tandem cell in 2015.⁴⁵ Figure 2b shows the schematic of a tandem cell composed of the Mn-doped Fe₂O₃ photoanode and Pt-connected PSC. The Mn-doped Fe₂O₃ nanorod was prepared on an FTO substrate through the hydrothermal method, as follows. An aqueous solution containing FeCl₃-6H₂O, urea, and MnCl₂·4H₂O was heated at 373 K for 6 h. The sample was splayed with iron acetylacetone at 798 K and annealed at 823 K for 2 h in air and at 1023 K over 20 min in argon. Mn doping for Fe₂O₃ enhances the photocurrent significantly, which is attributable to suppression of electron–hole recombination and a reduction in the energy barrier for hole transport.⁶⁸ Finally, the tandem cell composed of cobalt phosphate (CoPi)-modified Mn-Fe₂O₃ and a single PSC achieved an STH efficiency of nearly 2.4%.

Morales-Guio et al. focused on a transparent NiFeOₓ electrocatalyst that boosts the photocurrent density of cauliflower-type Fe₂O₃ prepared through APCVD.⁶² These authors demonstrated unassisted overall water splitting with an STH efficiency of 1.9% using a tandem cell composed of NiFeOₓ-modified Fe₂O₃ (NiFeOₓ/Fe₂O₃) and a PSC, as shown in Figure 3a.⁶² Gurudayal et al. treated a Fe₂O₃ nanorod photoanode by a SnOₓ layer and improved the STH efficiency in 2017.⁶³ These authors coated the FeOOH nanorod prepared by the hydrothermal method with a SnOₓ layer by ALD of a Sn precursor, tetrakis(dimethylamido)tin (IV), and an oxidant, H₂O. The Sn-doped Fe₂O₃ was formed by calcination of SnOₓ-coated FeOOH at 923 K for 2 h, as shown in Figure 3b. The SnOₓ modification significantly improved the charge transfer efficiency and photocurrent value compared with the unmodified one. Furthermore, the tandem cell composed of a CoPi/SnOₓ-coated Fe₂O₃ nanorod and a CH₃NH₃PbI₃ PSC shows a great deal of progress, achieving a high STH of 3.4%.

Park et al. recently reported a Fe₂O₃-based tandem cell, as shown in Figure 3c, that achieved further progress, an STH efficiency of 4.49%.⁶¹ This is one of the highest reported STH values for tandem cells based on Fe₂O₃-based transparent photoanodes and PV modules. These authors developed a Ti- and Si-codoped transparent Fe₂O₃ photoanode (Ti:Si-Fe₂O₃) as follows. First, Ti-doped Fe₂O₃ was prepared by the hydrothermal method followed by heat treatment at 373 K for 3 h using an aqueous solution containing FeCl₃-6H₂O and TiCl₃, followed by calcination at 1073 K for 20 min. Next, Si doping was conducted by dip coating of a mixed solution of H₂O and 3-(aminopropyl) trimethoxysilane followed by annealing. The film thickness was optimized to 70 nm to allow Fe₂O₃ to be highly transparent. Thus, dual NiFeOₓ-modified Ti:Si-Fe₂O₃ was used for a tandem cell with a PSC. As shown in Figure 3d, the STH energy conversion efficiency with the dual NiFeOₓ-modified Ti:Si-Fe₂O₃ photoanode was significantly increased compared to that with the single NiFeOₓ-modified Ti:Si-Fe₂O₃ photoanode. The modifications of transparent Fe₂O₃ improved bulk and surface carrier transport properties, resulting in increasing photocurrent.

![Figure 2](image-url)
density. Such reported unique morphologies and surface modifications of Fe$_2$O$_3$ improved the photocurrent density and performance of the tandem cell.

### 2.2. BiVO$_4$

BiVO$_4$ has also attracted much attention as an oxide material for efficient water oxidation due to its CBM position close to the potential for the HER, resulting in a negative onset potential as well as its relatively narrow bandgap (~2.4 eV). In addition, the relatively long carrier diffusion length of BiVO$_4$, ~70 nm compared to other photoanode materials (Fe$_2$O$_3$: ~2–4 nm; Ta$_2$N$_5$: 3–9 nm), potentially achieved high photocurrent due to the induced long carrier lifetime.$^{[60]}$ Assuming the quantum efficiency of the OER is 100% under 1 sun illumination, the maximum photocurrent density can be estimated to be 7.5 mA cm$^{-2}$, corresponding to an STH energy conversion efficiency of 9.2%.

Interestingly, most studies have focused on modifications of BiVO$_4$ or the development of efficient photocathodes of tandem cells instead of preparation methods for BiVO$_4$. This is because of the superior characteristics of BiVO$_4$. In 2013, Abdi et al. developed the first BiVO$_4$-based tandem cell.$^{[29]}$ The authors maximized the performance by gradient W doping that can improve the charge separation efficiency. The gradient W-doped BiVO$_4$ was synthesized by 200 cycles of spray pyrolysis of the BiVO$_4$ precursor solution containing different W concentrations every 20 cycles, followed by annealing at 723 K for 2 h in air. The tandem cell with the CoPi-modified gradient W-doped BiVO$_4$ and a double-junction a-Si showed a high STH efficiency of 4.9%, which is slightly higher than that generated by the tandem cells based on Fe$_2$O$_3$. The same group developed a tandem cell based on a transparent W-doped BiVO$_4$ photoanode (Figure 3a), which achieved a high STH efficiency of 5.2% by the absorption enhancement effect of textured FTO as a substrate for the BiVO$_4$ photoanode.$^{[71]}$ Figure 4b shows the characteristics of two types of FTO substrates. The top-left and
using a Mo precursor solution in BiVO$_4$/FTO prepared by the metal–organic decomposition method using dissolved Bi(NO$_3$)$_3$·5H$_2$O in acetic acid and VO(acac)$_2$ in acetylacetonite. The enhanced bulk charge separation efficiency and extended hole diffusion length by such dual doping were confirmed by the ratio of photocurrent derived from the oxidation of SO$_4^{2-}$ to that generated by absorbed light ($J(500)/J_{shunt}$) and the result of incident photon-to-current efficiency (IPCE), respectively. Eventually, the proposed method produces an improvement in STH efficiency of up to 4.3% on BiVO$_4$-PSC tandem cells.

In 2018, Xue et al. attempted to improve the efficiency and stability of non-doped BiVO$_4$ by surface modification with a TiO$_2$ function layer and a cobalt borate (CoB) electrocatalyst. The authors claimed that the passivation effect of the TiO$_2$ layer extended the carrier lifetime, and the CoB electrocatalyst enhanced the charge separation and transportation of carriers. TiO$_2$/CoB/TiO$_2$/BiVO$_4$ generated 3.0 mA cm$^{-2}$ at 1.23 V versus RHE with a relatively negative onset potential of ~0.3 V versus RHE. TiO$_2$ also worked as a protection layer for BiVO$_4$, and it significantly improved the stability of the BiVO$_4$ photoanode. Although the non-doped BiVO$_4$ was used, the tandem cell composed of the TiO$_2$/CoB-modified BiVO$_4$ and amorphous Si (Figure 5a) achieved an STH efficiency of ~3%. In the same year, Wang et al. developed an innovative electrodeposition and subsequent calcination process as follows to produce a highly efficient transparent photoanode. First, a bismuth precursor film was electrodeposited on FTO at 2.82 V versus RHE for 0.5–2.0 h in an aqueous solution containing Bi(NO$_3$)$_3$·5H$_2$O, acetic acid, and HNO$_3$. Next, vanadyl acetylacetonate solution was dropped on the films; then, the films were annealed at 773 K for 2 h in air. The synthesized BiVO$_4$ has many more oxygen vacancies compared to another one prepared by spin coating. The authors suggested that the oxygen vacancies on BiVO$_4$ increased the electronic conductivity, resulting in enhancement of the photocurrent density up to 6.22 mA cm$^{-2}$ at 1.23 V versus RHE. Among the transparent BiVO$_4$/PV tandem cells, the tandem cell (Figure 5b) composed of dual NiOHH/FeOHH/BiVO$_4$ and PSC demonstrated the highest STH efficiency (of 6.5%).

Some authors have reported technologies for scaling up PEC water-splitting devices. In 2019, Ahmet and co-workers developed a PEC–PV cell consisting of a dual CoPi-modified W-doped BiVO$_4$ with an electrode area of 50 cm$^2$, and a two-series-connected Si heterojunction solar cell. Spray pyrolysis was applied to fabricate the large-scale W-doped BiVO$_4$ photoanode. Figure 5c shows a photograph of the BiVO$_4$ photoanode with a geometric area of 50 cm$^2$. While the PEC–PV device with a small area of 0.24 cm$^2$ showed an STH efficiency of 5.5%, the large-scale device exhibited an STH efficiency of 2.1%. As the size of the electrode becomes larger, it becomes more difficult to collect the carriers. Therefore, effective carrier collection was attempted by inserting nickel-metal lines at ~8 cm intervals (Figure 5c, right). In contrast, Wang et al. developed a tandem cell based on BiVO$_4$ nanofibers in 2020 for large-scale systems. A mixture of Bi(NO$_3$)$_3$·5H$_2$O, 1-octadecene, oleylamine, and oleic acid was heated at 448 K under a N$_2$ atmosphere, and then NH$_4$VO$_3$ dissolved in boiling water and molybdenum solution was added and maintained at 373 K for 5 min to synthesize the Mo-doped BiVO$_4$ nanoparticle. The photoanode on FTO was prepared by spin coating of the nanoparticle solution at 2000 rpm.

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Figure 4. a) Cross-sectional sketch of a tandem cell composed of a CoPi-modified W-doped BiVO$_4$ and a Si solar cell. b) AFM images of a flat TEC-15 FTO surface (top left) and a textured Asahi VU-type FTO glass substrate (top right), and the cross-sectional profile of the flat surface (blue curve) and textured substrate (red curve) (bottom left). Absorption of 250 nm W-doped BiVO$_4$ films on flat TEC-15 FTO (blue curve) and textured (Asahi VU-type) FTO-glass substrates (red curve) (bottom right). Adapted with permission. Copyright 2014, Wiley-VCH GmbH.
In addition to oxide semiconductors, metal (oxy)nitride materials are widely seen as promising candidates for efficient solar water splitting. The VBM consisting of N 2p orbitals has more negative potential than that of oxides consisting of O 2p orbitals. Therefore, the bandgap is narrowed with a suitable band position for overall water splitting. Among them, the Ta3N5-based photoelectrode has been extensively examined because it has a suitable bandgap energy of 2.1 eV. Ta3N5 is expected to generate an upper limit photocurrent of 12.9 mA cm−2, corresponding to an STH energy conversion efficiency of 15.9% under 1 sun illumination. Moreover, the Fermi level of Ta3N5 was estimated at −0.2 V versus standard hydrogen electrode (SHE), which was determined by the results of ultraviolet photoelectron spectroscopy. Ta3N5 potentially generated anodic photocurrent at an even more negative potential than 0.0 V versus SHE.

However, this material required nitridation at high temperature (>1073 K), which prevented the use of transparent conductive oxide (TCO)-coated substrates, such as FTO and ITO, because these TCO-coated substrates deteriorated under harsh nitridation conditions giving rise to bad conductivity of the substrates. Hajibabaei et al. used the ALD method followed by moderate ammonolysis at 1023 K to synthesize Ta3N5 on Ta-doped TiO2 (TTO). First, they deposited TaOxNy on TTO by ALD of a tantalum precursor, Ta[N(CH3)2]5, under N2 flow with coreactants CH3NHNH2 and water. Nitridation was conducted at the optimized condition to form pure crystalline Ta3N5. The synthesized CoPi-modified Ta3N5/TTO containing 1.6% Ta with a thickness of 75 nm generated a photocurrent of ~0.77 mA cm−2 at 1.23 V versus RHE with an onset potential of ~0.8 V versus RHE under simulated sunlight (100 mW cm−2) in a 0.5 M K2HPO4 aqueous solution containing KOH. This CoPi/Ta3N5/TTO reported in 2016 was the first report of transparent Ta3N5 photoanodes for PEC water oxidation. In 2019, Hajibabaei et al. also reported direct deposition of crystalline Ta3N5 on FTO via the ALD system (Figure 6). The Ta3N5 films were deposited by sequential pulses of TaCl5 and anhydrous ammonia with N2 carrier gas flow. The authors evaluated the thickness dependence and illumination direction dependence by measuring the IPCE. The measurement was conducted at 1.0 V versus RHE in an aqueous solution containing 0.1 M K4[Fe(CN)6] as a hole scavenger with a pH of 7. The IPCE increased to 25% at the wavelength of ~450 nm with film thickness up to 103 nm. However, when Ta3N5 with a thickness of 230 nm was used, the efficiency decreased. This was due to a
trade-off relationship between absorptance and carrier diffusion length. In addition, the authors claimed that the difference of IPCEs by illumination direction originated from the difference of diffusion length of holes. When the short wavelength light was illuminated from the FTO side, the holes generated in Ta3N5 near the FTO substrate needed to transfer into the Ta3N5 surface. The diffusion length of holes increases with increasing of the Ta3N5 thickness, resulting decrease of IPCEs and current density (Figure 6, right). In the PEC measurements, the Ta3N5/FTO generated photocurrent density of 2.4 mA cm⁻² at 1.23 V versus RHE ascribable to oxidation of K₂[Fe(CN)]₆ with an onset potential of 0.3 V versus RHE (Figure 6, right).

In 2019, Akagi et al. made use of carbon nanotube (CNT)-coated quartz substrates because of their high thermal and chemical stability as well as conductivity and transparency. Ta metal containing a minute amount of oxygen (TaO₃) was sputtered on CNT substrates, then heated under NH₃ flow to obtain transparent Ta3N5 thin films. The OER performance of the Ta3N5 thin films on CNT-coated quartz (Ta3N5/CNT) showed dependence of the amount of CNT. It indicated that the efficiency of carrier transport from Ta3N5 to the CNT layer as the back contact impacted the OER performance. The NiFeO₃-modified Ta3N5/CNT of 0.6 μg cm⁻² clearly demonstrated photocurrent in aqueous 0.5 M K₃PO₄ solution adjusted to pH 13 with KOH under simulated sunlight without losing transparency. The authors also evaluated Mg modification by spin coating of ethanol containing tantalum ethoxide and MgCl₂. The NiFeO₃/Mg-modified Ta3N5/CNT improved the photocurrent, 0.41 mA cm⁻² at 0.8 V versus RHE, being three times higher than that generated by NiFeO₃/Ta3N5/CNT. Eventually, the authors constructed a tandem cell composed of NiFeO₃/Mg-modified Ta3N5/CNT and a photocathode, a solid solution of ZnSe and Cu(In,Ga)Se₂ (ZnSe:CIGS). The tandem cell generated 46 μA with an operating point of ≈0.7 V versus RHE.

Higashi et al. used n-type GaN-coated sapphire (GaN/Al₂O₃) substrates to produce a transparent Ta3N5 photoanode to survive the harsh nitridation condition. The conjugation of Ta3N5 and n-type GaN forms an energy barrier to suppress the carrier recombination of generated holes at the Ta3N5/GaN interface, producing a hole-blocking effect. The concept of the hole blocking layer has been used for other semiconductor material-based photoanodes, such as BiVO₄ and particulate Ta3N5. They sputtered Ta metal by radio frequency magnetron sputtering in an Ar atmosphere with a thickness of 500 nm. Then, the films were annealed at 1098 K for 1 h under the mixed flow of NH₃ and N₂ to transform from Ta to Ta3N5. The synthesized Ta3N5/GaN/Al₂O₃ has a red color with high transparency, as high as 60–70% at a wavelength over 600 nm, and demonstrated a current density of 6.3 mA cm⁻² at 1.23 V versus RHE under simulated sunlight (AM 1.5G, 100 mW cm⁻²) in 0.2 M potassium phosphate aqueous solution with pH of 13 (Figure 7a). It is the highest value

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**Figure 7.** a) j–E curve obtained from NiFeO₃/Ta3N5/GaN/Al₂O₃ photoanode in 0.2 M aqueous potassium phosphate solution with pH adjusted to 13 under simulated sunlight (1 sun, AM 1.5G). b) Schematic illustration of overall water splitting by a tandem PEC cell composed of a transparent Ta3N5 photoanode on the front side and a Pt/Ni/dual CIS electrode on the back side. c) STH values as a function of reaction time for a tandem PEC cell under simulated sunlight in a 0.2 M aqueous potassium phosphate solution with pH adjusted to 13. Adapted with permission. Copyright 2019, Wiley-VCH GmbH.
in photocurrent generated by transparent Ta$_3$N$_5$ photoanodes. The authors also constructed a tandem cell composed of NiFeO$_x$/Ta$_3$N$_5$/GaN/Al$_2$O$_3$ and two-series-connected CuInSe$_2$ (CIS) elements terminated with a Pt electrode (Figure 7b). Figure 7c shows the j–v curve of the tandem cell. Although the tandem cell achieved the highest STH energy conversion efficiency in this Review, 7% at the initial stage of the reaction, the efficiency gradually decreased with time and dropped to 5.5% after 15 min.

The properties of the transparent substrates used for Ta$_3$N$_5$ photoanodes are summarized in Table 2. The properties of three substrates in Table 2 were considered suitable for transparent photoanode applications. In the case of the TTO substrate, Ta doping increased the transmittance and decreased the resistivity of TiO$_2$. The properties were measured after annealing in ammonia. In the case of CNT/quartz, although the photocurrent was improved with the CNT amount increasing, the transmittance decreased with the CNT amount. GaN/Al$_2$O$_3$ has high transmittance of above 70% in the range above 400 nm. In contrast, the transmittance loss of the quartz (SiO$_2$) substrate was negligible. In 2020, Higashi and colleagues reported a transparent Ta$_3$N$_5$ photoanode prepared directly on SiO$_2$ insulating substrates. Generally, semiconductor-based photoelectrodes have been fixed on an appropriate metal or TCO layer as the back contact to collect the electrons or holes. However, the reported transparent Ta$_3$N$_5$/SiO$_2$ photoanode exhibited OER without the introduction of a TCO layer. The authors used the modified methods producing Ta$_3$N$_5$/GaN/Al$_2$O$_3$ to obtain Ta$_3$N$_5$/SiO$_2$. They sputtered Ta with a thickness of 750 nm and conducted nitridation at 1048 K for 1 h in a NH$_3$/N$_2$ mixed gas flow, and finally obtained a Ta$_3$N$_5$ thin film with a thickness of 1000 nm on SiO$_2$. The Ta$_3$N$_5$/SiO$_2$ also has a high transparency (≈70%) above 600 nm. The semiconductor properties were measured by Hall effect measurement using the van der Pauw method. The Hall (electron) mobility, carrier density, and resistivity of Ta$_3$N$_5$/SiO$_2$ were 1.6 cm$^2$ V$^{-1}$ s$^{-1}$, 5.8 $\times$ 10$^{19}$ cm$^{-3}$, and 6.8 $\times$ 10$^{-2}$ $\Omega$ cm, respectively. Compared to the carrier concentration of another opaque Ta$_3$N$_5$ photoelectrode with a thickness of 960 nm (4.7 $\times$ 10$^{18}$ cm$^{-3}$), this higher carrier concentration is consistent with the fact that Ta$_3$N$_5$ has a lower resistivity. This low resistivity allows this self-standing photoelectrode on the insulator to drive the OER efficiently. Intriguingly, the NiFeO$_x$/Ta$_3$N$_5$/SiO$_2$ generated a photocurrent density of 6.0 mA cm$^{-2}$ at 1.23 V versus RHE under AM 1.5G simulated sunlight in a 0.2 M potassium phosphate aqueous solution with pH of 13. This photocurrent density is comparable to that of a Ta$_3$N$_5$-based photoanode fabricated on GaN/Al$_2$O$_3$ with a hole-blocking layer. However, the onset potential on the OER was pinned at 0.65 V versus RHE regardless of with or without the TCO layer. Nevertheless, efficient OER by Ta$_3$N$_5$/SiO$_2$ photoanodes can be achieved due to the optimized film preparation conditions such as nitridation temperature and sputtering condition as a function of time, radiofrequency power, and working pressure during sputtering. As mentioned earlier, the STH value obtained using tandem cells was not sufficient for practical application. Further improvement of transparent photoelectrodes with a narrow bandgap is now needed.

### 2.4. Other Photon Absorbers

In addition to the three transparent photoanodes described earlier, the development of transparent photoanodes using other oxide and oxynitride semiconductors has been extensively examined. Although TiO$_2$ and ZnO photoanode layers have been studied for a long time, these photoanodes can absorb only ultraviolet light. WO$_3$ is one of the most studied transparent photoanodes responding to visible light due to its bandgap (2.6–2.8 eV). Brillet et al. fabricated a transparent WO$_3$ photoanode by an aqueous sol–gel method on an FTO substrate. The authors constructed a tandem cell composed of a WO$_3$ photoanode and a DSC-based cathode. The cell achieved an STH efficiency of 3.1%. In addition to these oxide-based photoanodes, MFe$_2$O$_4$ (M = Ca, Mg, Zn, Co, Ni, Mn, and so on) and MTiO$_3$ (M = Mn, Fe, Co, Ni) has been reported. For example, a transparent Zr-doped ZnFe$_2$O$_4$ photoanode was reported.

The ferrite has a suitable band position for water splitting as well as a relatively narrow bandgap, 1.9–2.1 eV, despite the oxide-based photoanode. Zr-doped FeOOH was prepared by a hydrothermal method with FeCl$_3$, NaNO$_3$, and ZrO(NO$_3$)$_2$, and then a Zr-doped ZnFe$_2$O$_4$ photoanode was synthesized by quenching after adding Zn(NO$_3$)$_2$. The photoanode exhibited photocurrent of 0.49 mA cm$^{-2}$ at 1.23 V versus RHE with transparency. MTiO$_3$ photoanodes have attracted attention due to the high stability originating from TiO$_2$ and the bandgap responding to visible light (2.7–2.9 eV) originating from Fe$_2$O$_4$. Yoshimatsu et al. have reported ilmenite-like MTiO$_3$ (M = Mn, Fe, Co, and Ni) thin films on Ta-doped SnO$_2$/Al$_2$O$_3$ prepared by pulsed-laser deposition. NiTiO$_3$ exhibited the highest IPCE in these photoanodes. The authors suggested that the degree of hybridization between M 3d and O 2p states caused the difference of photoanodic properties.

Transparent oxynitrides, such as LaTiO$_3$N and SrTa$_2$O$_7$N, have been also reported by Ma et al. in 2020. The oxynitrides prepared by spin coating of precursors followed by nitridation had high transparency (60–70%). The photocurrent values generated by LaTiO$_3$N and SrTa$_2$O$_7$N on GaN/Al$_2$O$_3$ at 1.23 V versus RHE under simulated sunlight were found to be 20 and 7 $\mu$A cm$^{-2}$, respectively. It is noteworthy that these photoanodes showed photosresponse at about 0.0 V versus RHE. Therefore, oxynitride films are expected to produce photocurrent with a more negative onset potential compared to Ta$_3$N$_5$, resulting in improvement of STH efficiency. Through further optimization of film preparation, including surface modifications for these oxynitride-based transparent photoanodes, the materials will be promising candidates for front-side photoanodes on tandem cells.

### Table 2. The properties of substrates for transparent Ta$_3$N$_5$ photoanode applications.

| Substrate | Variable | Transmittance at 600 nm | Resistivity [$\Omega$ cm] |
|-----------|----------|-------------------------|-------------------------|
| Ta-doped TiO$_2$ (TTO) | 1.1–5.0% Ta | 60–70% | 2 $\times$ 10$^{-3}$ to 6 $\times$ 10$^{-1}$ |
| CNT/quartz | 0.6–1.2 $\mu$g cm$^{-2}$ CNT | 30–60% | 80–350 $\Omega$ sq$^{-1}$ (sheet resistance) |
| GaN/Al$_2$O$_3$ | | ≈70% | 5 $\times$ 10$^{-2}$ |
3. Problems Limiting STH Efficiency of Tandem Cells

The development of an efficient tandem cell is currently underway, but the highest STH efficiency on tandem cells is 6–7%, which is still below the target of 10% STH efficiency. The candidates for transparent photoanodes, such as Fe₂O₃, BiVO₄, and Ta₃N₅, have attractive properties for the OER. However, there is a strong demand for both higher OER performance and higher durability on water splitting. This section focuses on the semiconductor properties of these materials and the two main problems that limit their performance: onset potential and stability.

3.1. Onset Potential

In case of Fe₂O₃, the flat band potential of Fe₂O₃ was placed at ≈0.5 V versus RHE.[83] However, the onset potential of the most recent transparent Fe₂O₃ photoanodes was found to be 0.7–0.9 V versus RHE mainly due to the short hole diffusion length and carrier trapping.[11,13,15,23] Kennedy and Frese Jr. reported a diffusion length of 2–4 nm revealed by electrochemical measurements,[86] this being shorter than that of other semiconductor materials: BiVO₄ ≈ 70 nm[70] and Ta₃N₅, 3–9 nm.[84] The authors used Equation (1) derived from the Gärtner equation[84] to obtain the hole diffusion length of Fe₂O₃ by fitting the $i–E$ curve.

\[
\eta_p = 1 - e^{-\alpha W} \left/ \left( 1 + a L_p \right) \right.
\]

where $\eta_p$, $\alpha$, $W$, $L_p$, and $q \Phi$ are photocurrent efficiency, absorption coefficient, depletion layer thickness, hole diffusion length, photocurrent density, elementary charge, and photon flux density, respectively. As shown in Equation (2), the photocurrent efficiency $\eta_p$ means the absolute value of $j$ divided by the product of $q$ and $\Phi$. Such a short hole diffusion length means a short lifetime, requiring large external voltage to promote charge separation and hole transport toward the electrode/electrolyte interfaces.

In addition, mid-bandgap energy states have been considered to trap the photogenerated carriers and induce recombination of carriers, resulting in a positive onset potential. Klahr et al. suggested that photogenerated holes in Fe₂O₃ were transported to the interface via surface trapped states as shown in Figure 8a by the results of impedance spectroscopy.[85] Figure 8b shows the equivalent circuit corresponding to the model for the charge carrier dynamics in the Fe₂O₃ photoanode. The resistance of trapping electrons and holes ($R_{\text{trapping}}$), the resistance of hole transfer affected by surface states ($R_{\text{ct,trap}}$), and the capacitance of trap states ($C_{\text{trap}}$) were arranged in parallel with the resistance of charge transfer from the semiconductor band directly. Figure 8c shows the current density generated by the Fe₂O₃ photoanode, $R_{\text{ct,trap}}$, and $C_{\text{trap}}$ as a function of electrode potential. At a more negative potential than the onset potential (<0.7 V vs RHE), decreasing $R_{\text{ct,trap}}$ and increasing $C_{\text{trap}}$ with applied potential was observed. This indicated the charging of the trap states. In addition, the peak top of the curves of $R_{\text{ct,trap}}$ and $C_{\text{trap}}$ coincided with the onset potential (Figure 8c). These results strongly indicate that the hole transport took place via surface states (Figure 8a).

Furthermore, Barroso et al. reported carrier trapping in Fe₂O₃ using transient absorption spectroscopy (TAS).[86] Figure 9a shows the scheme of the nature of electronic transitions, and Figure 9b shows the results. The behavior of a broad peak centered at 650 nm assigned to the photogenerated holes in Figure 9b indicated that the hole lifetime was extended with applied voltage. Therefore, the authors proposed that the sufficient electric field induced by the large external voltage efficiently separated electrons and holes, and residual holes that did not recombine with electrons accumulated at the surface and drove...
the OER. Figure 9c shows a scheme of the carrier transport process at each electrode potential. Under biases close to the flat band potential, the photogenerated electrons and holes were rapidly trapped in the intraband states and recombined (Figure 9c(i)). When a positive bias relative to the flat band potential producing a partial depletion layer is applied, the insufficient electric field cannot separate the photogenerated carriers (Figure 9c(ii)). When a sufficient depletion layer is induced by the significant anodic bias voltage, the photoexcited carriers are separated efficiently, and the holes are transported to the electrode/electrolyte interface to drive the OER (Figure 9c(iii)).

The onset potential for the OER using Ta$_3$N$_5$ is pinned at ~0.6 V versus RHE regardless of the preparation methods. According to a report by Chun et al., the Fermi level of Ta$_3$N$_5$ was estimated at ~4.21 eV (corresponding to ~0.23 vs SHE) using ultraviolet photoelectron spectroscopy.[37] Thus, the photocurrent should be observed at a more negative potential than 0 V versus SHE ideally. He and colleagues estimated that the pseudo-flat-band potential was placed at ~−0.2 V versus SHE by open circuit potential measurements in a non-aqueous solution.[50] The authors suggested contact with water shifted the surface Fermi level, resulting in such a positive onset potential, as shown in Figure 10a. Surface N atoms are displaced by O atoms during the OER in an aqueous solution, leading to the Fermi level change toward 0.6 V versus SHE corresponding to the recent onset potential using Ta$_3$N$_5$. Fan et al. also evaluated the band-edge behavior in an aqueous environment using theoretical methods.[87] The band-edge potential of Ta$_3$N$_5$ was found to shift to a positive potential in an aqueous solution. These reports suggest that contact of Ta$_3$N$_5$ with water shifted the band-edge potential or the Fermi level toward positive potential, resulting in a positive onset potential on the OER.

In addition to Fermi level/band-edge potential shift, defects and surface states have been considered one of the main causes of a positive onset potential. Murthy et al. were engaged in the investigation of ultrafast dynamics of electrons and holes in Ta$_3$N$_5$ by TAS.[88] By detecting a positive signal from 650 to 750 nm produced by trapped electrons and a negative signal at 590 nm originating from deep-level trap sites in TA spectra, these authors concluded that an electron trap at reduced tantalum...
species and a hole trap at nitrogen vacancies ($V_N$) limited the performance of Ta$_3$N$_5$ for water splitting (Figure 10b). Khan et al. investigated the semiconductor-electrolyte interfacial properties of pristine Ta$_3$N$_5$ nanorods in Na$_2$SO$_4$ aqueous electrolyte. The reduced tantalum, Ta$^{4+}$, and oxygen species were detected by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction. The peaks being distinctive under illumination in cyclic voltammetry were assigned to filling and depopulation of charge at trap states. It implied the trapping of photoinduced charge carriers at trap sites, such as reduced tantalum species and substitutional oxygen impurities (O$_N$). Other reports also mentioned the trapping of charge carriers at oxygen defects causing the low performance of Ta$_3$N$_5$.

As described previously, carrier trapping has been found to require high external voltage. However, the most detrimental trapping sites in O$_N$, V$_N$, and reduced tantalum remain unclear. Fu et al. proposed that Ta$^{4+}$ was the most detrimental to the water-splitting performance of Ta$_3$N$_5$. The authors used low-temperature photoluminescence (PL) spectroscopy to evaluate the effect of deep trap states. They assigned a peak in PL spectra at 730 nm to V$_N$ and the other peak at 830 nm to Ta$^{4+}$ by the difference of NH$_3$ flow rate dependence. Furthermore, they confirmed the deep trap states derived from N vacancies or Ta$^{4+}$ were placed $\approx$0.43 or $\approx$0.64 eV below the conduction band.

In the case of BiVO$_4$, although a relatively negative onset potential 0.17 V versus RHE has been achieved, application of large external bias voltage is still required to generate the saturated photocurrent. The main causes are charge separation efficiency in the bulk and carrier transport efficiency at the photoanode/electrolyte interface. The reported charge separation efficiency was below 30% at negative potential (\textlessthan;0.6 V vs RHE) when W-doped BiVO$_4$ was used. To improve the separation efficiency, enhancement of the carrier lifetime and carrier mobility is needed. Moreover, the kinetics of the extraction of holes from the photoelectrode surface at the semiconductor/water interface for the OER seem to be sluggish, which requires a large external voltage. Dotan et al. expressed the sluggish kinetics as “high injection barriers.” Such problems should be considered in the case of not only BiVO$_4$ but also Fe$_2$O$_3$ and Ta$_3$N$_5$ even after achievement of negative onset potential.

### 3.2. Stability

The poor stability of transparent photoanodes is one of the problems for practical use of tandem cells. In the case of BiVO$_4$, photocorrosion caused the instability of BiVO$_4$. Berglund et al. investigated the cause of the poor stability by XPS and inductively coupled plasma mass spectrometry (ICP-MS). After long-term PEC measurements, the locations of peaks of XPS spectra remained, but the intensities changed; i.e., the ratio of V/Bi was changed from 1.54 to 0.51 during the reaction. Furthermore, according to the ICP-MS, the V concentration in the electrolyte went from below the detection limits to 247 ppb during the PEC test, although the Bi concentration remained below the detection limits after the test. Based on these results, the authors concluded that photocurrent drop should be derived from vanadium dissolution into the electrolyte. In contrast, the dissolution of Bi species during water splitting was also reported. The dissolved Bi species were adsorbed at the Pt electrocatalyst on photocathodes, a similar case to Bi...
underpotential deposition (UPD). It is well known that Bi UPD on Pt strongly prevents the HER. Kim and Choi suggested that the problem was due to PEC instability, as well as the chemical instability of BiVO$_4$.[96] In other words, the slow interfacial hole transfer kinetics of BiVO$_4$ for the OER leads to accumulation of holes at the interface of BiVO$_4$/the electrolyte, resulting in anodic photocorrosion of BiVO$_4$. These reports claim the necessity of prohibition of the dissolution of Bi and V from BiVO$_4$ for the development of highly durable transparent BiVO$_4$ photoanodes.

In the case of Ta$_3$N$_5$, the self-photooxidation reaction to produce the TaO$_x$ layer at the Ta$_3$N$_5$ surface is expected to worsen the water splitting efficiency. Hara et al. used XPS and reported that Ta$_3$N$_5$ contained larger amounts of O species in water, implying a partially hydrolyzed surface.[98] However, the authors did not mention the impact of the surface containing the O species on the instability of Ta$_3$N$_5$. In subsequent work by Higashi et al., the photocurrent was generated by Ta$_3$N$_5$ under light illumination. However, a drastic decrease of the photocurrent over time was observed.[99] The authors suggested the self-oxidative decomposition of Ta$_3$N$_5$ by oxidation of nitrogen anions (2N$_3^-$ + 6h$^+$ → N$_2$). In the case of tantalum oxynitride (TaON), self-oxidative decomposition was considered to decrease the photocurrent by an obvious decrease in nitrogen content in the XPS spectrum after 1 h of illumination.[100] He et al. confirmed that the self-photooxidation of Ta$_3$N$_5$ caused the low stability.[50]

4. Solution

There have been attempts to use several modification methods to overcome problems and achieve highly efficient PEC water splitting using tandem cells. This section focuses on these approaches, such as doping, electrocatalyst coating, and additional functional layer inserting at the solid/liquid interface.

4.1. Doping

Various kinds of doping (Si, Ti, and Mn) have been examined in attempts to improve the onset potential of transparent Fe$_2$O$_3$ photoanodes.[13,17,21] Cesar et al. conducted Si doping via ultrasonic spray pyrolysis.[17] The doping reduced the grain size to a

![Figure 11](image-url)
level of hole diffusion length, and improved the electrical conductivity of Fe$_2$O$_3$ by increasing the carrier concentration. Ti doping by Wang et al. also increased the carrier density, and reduced electron–hole recombination according to the Mott–Schottky plots and TAS.\cite{JCP122,11} These effects by cation doping resulted in a 100–200 mV cathodic onset potential shift. W doping and Mo doping were attempted for transparent BiVO$_4$ photoanodes.\cite{JPSJ87,92–99,110} Although a few kinds of cations were applied, the doping effects, such as band structure control, provided an internal electric field in the BiVO$_4$ bulk by increasing the carrier concentration. The cation doping enhanced the entire performance of the tandem cell, e.g., a Fe$_2$O$_3$-based tandem cell.\cite{JAP118} The photocurrent density at the intersection of $j-E$ curves of the photoanode and the cathode was shifted from 1.21 to 1.93 mA cm$^{-2}$ by Mn doping for a transparent Fe$_2$O$_3$ photoanode.

Cation doping (B, Mg, Sc, and Zr) has also been conducted for opaque Ta$_2$N$_5$ photoanodes to shift the onset potential.\cite{JPSJ87,92–99,110} Seo et al. developed Mg–Zr co-substituted Ta$_3$N$_5$ (Ta$_3$N$_5$:Mg+Zr) by using the precursor containing Ta$_2$O$_5$, Mg(NO$_3$)$_2$•6H$_2$O, and ZrO(NO$_3$)$_2$•2H$_2$O.\cite{JPSJ87} The Ta$_3$N$_5$:Mg+Zr photoanode demonstrated a lower onset potential of 0.55 V versus RHE compared to that of Ta$_3$N$_5$: 0.8 V versus RHE with a photocurrent of 2.3 mA cm$^{-2}$ at 1.23 V versus RHE (Figure 12a). Because the onset potentials of Ta$_3$N$_5$:Mg and Ta$_3$N$_5$:Zr were 0.70 and 0.57 V versus RHE, respectively, the authors concluded that Zr caused a negative shift in the onset potential (Figure 12a). The negative shift in band-edge potential as shown in Figure 12b was considered to result in a negative onset potential. The shift of the band-edge potential was confirmed by Tauc plots, photoemission yield spectroscopy in air, and Mott–Schottky plots. This was presumably due to the incorporation of more cationic ions (Mg$^{2+}$ and Zr$^{4+}$) than Ta$^{5+}$. Kim et al. reported a B-doped Ta$_3$N$_5$ photoanode prepared by nitridation of B$_2$O$_3$ on Ta$_2$O$_5$.\cite{JPSJ87} The modified Ta$_3$N$_5$ exhibited an onset potential shift from 0.45 V (pure Ta$_3$N$_5$) to 0.25 V (10% B-doped Ta$_3$N$_5$) versus RHE. The authors attributed the shift to the change of the flat-band position correlated with the higher electron concentration. In contrast, Pei et al. reported the onset potential shift using Sc-doped Ta$_3$N$_5$ by reducing trap states and increasing conductivity.\cite{JPSJ87} The synthesized Sc-doped Ta$_3$N$_5$ by Na$_2$CO$_3$ flux-assisted nitridation using ScCl$_3$ and Ta$_2$O$_5$ as precursors exhibited a 220 mV cathodic potential shift using Sc-doped Ta$_3$N$_5$. The authors confirmed the reduction of surface recombination by PL spectra and the increase of carrier concentration, probably due to substituted oxygen. Xiao et al. reported another doping method: gradient doping of Mg.\cite{JPSJ87} The authors confirmed the band-edge shift by Mg doping, and they produced a band slope in Ta$_3$N$_5$ bulk by making a gradient concentration of Mg. The gradient Mg-doped Ta$_3$N$_5$ showed a high photocurrent density of 8.5 mA cm$^{-2}$ at 1.23 V versus RHE with a low onset potential of ≈0.4 V versus RHE, probably due to the internal electric field and reduced defect-related recombination. Although cation doping has been conducted for many opaque Ta$_3$N$_5$ photoanodes, there have been few reports addressing the doping for transparent Ta$_3$N$_5$. One of the few reports is Mg-doped Ta$_3$N$_5$/CNT by Akagi et al.\cite{JPSJ87} The transparent photoanode demonstrated a three times larger photocurrent than pristine Ta$_3$N$_5$ with a slightly negative shift of the onset potential.

The onset potential shift by cation doping reported by recent studies was mainly due to the negative shift of the band-edge or flat-band potential by increasing carrier concentration. Consequently, the reported onset potential was still far from the flat-band potential, especially in the case of Ta$_3$N$_5$, although the onset potential shift was observed. In other words, other methods to reduce trap states are required to overcome the problem of such a positive onset potential (e.g., the modification of the calcination method to synthesize transparent photoanodes). Wang et al. were the first to demonstrate overall water splitting by particulate Ta$_3$N$_5$.\cite{JAP118} Although conventional Ta$_3$N$_5$ has been synthesized via nitridation for 1 h or more, the reported Ta$_3$N$_5$ particle was fabricated by nitridation of KTaO$_3$ at a high temperature (1173 K) for a short time (0.25 h). This heating for a short time at a high temperature can allow Ta$_3$N$_5$ to be a single crystal on the edge of the KTaO$_3$ particle, and the structure allowed Ta$_3$N$_5$ to achieve overall water splitting. The same group concluded that nitridation for a long time produced some defect states, Ta$^{5+}$ and V$_{Ta}$, in Ta$_3$N$_5$ bulk, resulting in the prohibition...
of overall water splitting (Figure 10b). The results indicated that the modification of the calcination method is a promising approach to overcome the problems of onset potential. This approach has succeeded in the case of transparent Fe$_2$O$_3$. The optimized calcination method evidently changed the surface structure and shifted the onset potential of Fe$_2$O$_3$.

4.2. Electrocatalyst Coating

4.2.1. Accelerating the Reaction Kinetics toward Negative Onset Potential

Electrocatalysts are usually employed to boost the performance of photoelectrodes (see Table 1). Zhong et al. suggested that CoPi addition almost completely eliminated losses due to surface recombination, resulting in a cathodic shift of ≈440 mV in the onset potential of W-doped BiVO$_4$. The $j–E$ curve for W-doped BiVO$_4$ in H$_2$O$_2$ (sacrificial electron donor)/potassium phosphate (KPi) solution was matched with that for CoPi/W-doped BiVO$_4$ in a KPi solution, especially in the low potential range. As a result, modification with the CoPi electrocatalyst can provide a facile route for efficient charge transfer at the photoanode/electrolyte interface by suppression of surface electron–hole recombination (Figure 13).

Although electrocatalyst coating potentially improves the onset potential of transparent photoanodes, the large amount of electrocatalyst induces useless light absorption and loss of transparency of the photoanodes. Therefore, electrocatalyst coating of photoanodes without losing transparency has been studied for the development of efficient transparent photoanodes applicable to tandem cells. A transparent NiFeO$_x$ was synthesized by reactive magnetron cosputtering of Ni and Fe in Ar and O$_2$ mixed gas. The authors tuned the concentration of Fe and synthesized a transparent NiFeO$_x$ electrocatalyst transmitting over 50% of light in the range of over 500 nm wavelength with a thickness of 200 nm. Pilli et al. modified a semitransparent BiVO$_4$-based photoanode with a CoPi electrocatalyst. The CoPi-modified photoanode exhibited a ≈420 mV cathodic shift in the onset potential. Ziani et al. fabricated a transparent Co oxide electrocatalyst via thermal evaporation of cobalt phthalocyanine (CoPc) at room temperature followed by heat treatment for 30 min under air. The CoPc structure can provide highly ordered molecular assembly without a complicated synthesis protocol, resulting in the deposition of amount-tunable, ultrathin, regularly ordered, and transparent OER catalysts. The optimized CoPc electrocatalyst not only enhanced the photocurrent, but also shifted the onset potential of BiVO$_4$/WO$_3$ from 0.5 to 0.1 V versus RHE. Morales-Guido et al. developed a transparent amorphous FeNiO$_x$ (Fe:Ni = 80:20) OER electrocatalyst. The electrocatalyst fabricated by oxidative electrodeposition in a solution containing nickel (II) acetate and iron (III) sulfate demonstrated higher turnover frequency (TOF) than NiO$_x$, CoO$_x$, and IrO$_x$ with a small loading amount, microgram per centimeter square. This small amount allowed the FeNiO$_x$ electrocatalyst to have high transparency. The photoelectrodeposition of the FeNiO$_x$ on Fe$_2$O$_3$ shifted the intersection of $j–E$ curves of the photoanode and the cathode, resulting in enhancement of the STH efficiency up to 1.9%. Jang et al. reported that NiFeO$_x$ electrocatalyst coating by photochemical metal–organic deposition shifted the onset potential from 0.67 to 0.45 V versus RHE, and the photocurrent generated by the tandem cell also increased up to 0.91%.

4.2.2. Accelerating Carrier Transport toward High Stability

Laskowski et al. confirmed that electrocatalysts on the photoelectrode acted as both hole collectors and OER catalysts by PEC measurements with a dual-working-electrode system. The potential of the electrocatalyst layer was changed into a similar potential by holes to generate a given current density regardless of the origin of holes (i.e., holes originating from ITO or photogenerated holes in photoelectrodes). The result indicated that electrocatalysts captured photogenerated holes from photoelectrodes, and electrocatalysts were oxidized to a potential sufficient to drive the OER. The promotion of carrier transport from the photoanode to the electrocatalyst layer can suppress photocorrosion and self-photooxidation, resulting in stability enhancement of the electrocatalyst-coated photoanode. In other words, electrocatalysts also work as a protective layer on photoanodes. The effect...
of electrocatalysts on opaque photoanodes has been reported previously. For example, although the photocurrent density generated by a bare BiVO₄ photoanode decreased within a few minutes due to photocorrosion of BiVO₄ by accumulated photogenerated holes at the surface, the FeOOH layer–covered BiVO₄ generated stable photocurrent for 6 h by suppression of the photocorrosion.⁵⁹ In addition, a Co₃O₄ electrocatalyst expanded the lifetime of a Ta₃N₅ photoanode. Although the photocurrent generated by the bare Ta₃N₅ diminished for seconds, 75% of the initial photocurrent generated by Co₃O₄/Ta₃N₅ remained after 2 h by suppression of self-photooxidation of Ta₃N₅⁶⁷. This approach can be applied to many transparent photoanodes.

Surface modification with electrocatalysts has improved both the onset potential and stability of opaque/transparent photoanodes. The complete covering of transparent photoanodes’ surface with an electrocatalyst layer can achieve significant onset potential shift by providing a facile route for efficient charge transport and passivating the surface trap states, and the electrocatalyst layer can solve the stability problem by prevention of photocorrosion of BiVO₄ or suppression of self-photooxidation of Ta₃N₅. A uniform and thin electrocatalyst layer is required to achieve complete covering of transparent photoanodes without losing transparency.

4.3. Functional Layer Inserting

4.3.1. Passivating Surface States toward Negative Onset Potential

The insertion of functional layers has been attempted for opaque photoanodes to passivate the trap states and shift the onset potential cathodically. Formal et al. proposed Al₂O₃ coating via ALD on a Fe₂O₃ photoanode.⁶⁶ The onset potential of Al₂O₃-coated Fe₂O₃ was shifted cathodically by as much as 100 mV. The authors conducted electrochemical impedance spectroscopy and confirmed the decrease of the Helmholtz capacitance after the ALD treatment. In addition, they observed a broad peak assigned to radiative recombination between the CBM and VBM in the PL spectra. From these results, it was concluded that cathodic shift of the onset potential by the ALD treatment was due to the passivation of surface trap states. The same group demonstrated the same effect, a 100–200 mV cathodic shift, by surface modification with a Ga₂O₃ or In₁₂O₃ layer.⁶⁶ This approach can be applied to transparent photoanodes if the over-layers have high transparency. A similar treatment has been conducted for transparent Fe₂O₃ and BiVO₄ photoanodes. A SnO₂ layer was used as a functional layer for a transparent Fe₂O₃ photoanode.⁵⁵ The layer was deposited by ALD of tetrakis(dimethylamido)tin (IV) followed by calcination at 923 K for 2 h. The authors mentioned that the ALD treatment helped to passivate the surface states, resulting in a negative onset potential. In addition, TiO₂ layers were applied to a transparent BiVO₄ photoanode by ALD.²³ Based on the results of intensity-modulated photocurrent spectroscopy, insertion of the TiO₂ layer extended the carrier lifetime of BiVO₄, probably due to the passivation effect. Because the effect shifted the onset potential toward a negative potential, the intersection of the j–E curves of the photoanode and the cathode was also shifted toward higher photocurrent density. TiO₂/Co₃O₄/TiO₂/BiVO₄ is a good example of entire efficiency enhancement by functional layer insertion.

4.3.2. Protecting Photoelectrodes toward High Stability

In addition, functional/protective layers have been conducted for the prevention of self-photooxidation and enhancement of stability of Ta₃N₅ by extraction of photogenerated holes from Ta₃N₅ or protection of Ta₃N₅ from water. Liu et al. inserted a ferricyanide (Fh) layer between a Co₃O₄ electrocatalyst and a Ta₃N₅ photoanode.⁶⁵ The deposition of Fh on Ta₃N₅ was conducted by immersion in an aqueous solution containing ferric nitrate and sodium nitrate followed by heating at 373 K for ≥30 min. Although only 30% of the initial photocurrent remained after 2 h illumination using Co₃O₄/Ta₃N₅, the Co₃O₄/Fh/Ta₃N₅ photoanode kept 94% of the initial photocurrent after 6 h. The authors mentioned that the Fh layer worked as a hole storage layer, capturing photogenerated holes from Ta₃N₅ and preventing the self-photooxidation of Ta₃N₅.

Zhong et al. used a GaN layer as a protection layer.⁶² The GaN layer was fabricated on Ta₃N₅/Ta by electron beam evaporation of GaOₓ followed by nitridation at 1273 K for 0.5 h in NH₃ flow. The authors confirmed that crystalline GaN/Ta₃N₅ was synthesized, and a 50 nm thick GaN layer covered the surface of Ta₃N₅. The CoPi/GaN/Ta₃N₅ photoanode exhibited a stable photocurrent for over 10 h, as shown in Figure 14a. The GaN layer also shifted the onset potential of the CoPi/Ta₃N₅ photoanode cathodically. Figure 14b shows the corresponding j–E curves. The authors attributed the phenomenon to the passivation of surface states by the GaN layer. Functional layers potentially work to suppress the surface states and to enhance stability. Therefore, the layers can shift the onset potential and improve the stability of photovoltaic electrodes simultaneously. Thin, uniform, and transparent functional/protective layers are needed for achieving efficient, durable transparent photoanodes.

5. Conclusion

PEC water splitting by a tandem cell composed of a first transparent photoanode and a PV-based cathode placed behind the photoanode is a promising way to achieve a high level of STH energy conversion efficiency. However, the highest reported efficiency using tandem cells is 6–7%, far from the expected level. The main reason limiting the efficiency of the PEC device is the positive onset potential of the front photoanodes. The operation potential of the tandem cell is far from the potential generating saturated photocurrent due to the positive onset potential. According to recent studies, unfavorable phenomena, such as carrier trapping at the surface states, short hole lifetime, and direct contact with water, contribute to the positive onset potential of the OER. The stability of photoanodes during the OER is also one of the issues to be solved. In the case of BiVO₄, the dissolution of Bi and V is the main reason for the poor stability of BiVO₄, and in the case of Ta₃N₅, self-photooxidation is the main cause.

The energy conversion efficiency of a PEC tandem cell is determined by current matching of the photoanode and photocathode used. The overall performance of the cell reflects the performance not only of the photoanodes for the OER but also of the photocathodes, including the PV-based cathode, for the HER. To accomplish efficient overall water splitting, series-connected PV
modules have frequently been used. From the viewpoint of cost effectiveness and structure simplicity of the system, using a single photocathode as the back-side electrode is expected to be preferable for the tandem system. Although various photocathode materials have been investigated to date, the STH energy conversion efficiency of tandem cells composed of a photocathode/single-photocathode combination is still lower than that of photoanode/PV-based multijunction cathodes. To enhance the STH energy conversion efficiency, narrow-bandgap materials responding to transmitted light through the front photocathode and high stability during the reaction in the aqueous solution are required. Furthermore, optimization of cell design is also beneficial to improving the overall efficiency of the tandem cell. Brillet et al. compared the STH energy conversion efficiency of three different types of tandem cells composed of a Fe$_2$O$_3$ photoanode and two DSCs. A proposed tandem cell structure, Fe$_2$O$_3$/DSC–squaraine dye/DSC–panchromatic dye, exhibited a higher STH efficiency of 1.36% compared to other types of tandem cells, i.e., Fe$_2$O$_3$/connected DSCs abreast (1.16%) and two-abreast DSCs/Fe$_2$O$_3$ (0.76%). The results suggested the importance of maximizing the utilization ratio of sunlight for enhancement of the STH energy conversion efficiency. Overall water splitting by tandem cells composed of transparent dual photoanodes for the OER and a PV module with an HER electrocatalyst has been investigated. Kim et al. obtained an STH efficiency of 7.7% using state-of-art tandem cells composed of transparent BiVO$_4$/Fe$_2$O$_3$ dual photoanodes and a back-side Si-based multijunction cathode. Designs to extend light harvesting should be worthy of consideration, such as thickness of photoanodes and light transmittance to the back side cathodes.

There are still numerous obstacles to achieve a high level of STH and to realize a practical PEC water-splitting device. Even though photoanodes were coupled with PV-based cathodes, the STH efficiency was below 10%. Therefore, this Review focuses on transparent semiconductor photoanodes. We hope this Review will allow researchers in many fields to gain a deeper understanding of the potential impact of PEC water splitting, such as the use of tandem cells, and thus contribute to the development of innovative concepts and advanced technologies to overcome the current problems related to the limitation of the STH efficiency on water splitting. Based on the previous discussion, the future research direction can be divided as follows.

The first strategy is to improve the bulk property of the photoelectrodes themselves. As described previously, cation doping has been considered to be effective for opaque/transparent Fe$_2$O$_3$, BiVO$_4$, and Ta$_5$N$_5$. Novel preparation procedures to suppress the number of trap states are required for improved performance of transparent photoanodes. For practical use, low cost and simple materials for photocathodes are needed to realize the large-scale application of solar energy conversion. Seeking for more appropriate synthesis methods should be established for better efficiency that meets demand.

The second direction is to establish the surface modification of the photoanodes. Surface modifications for the transparent photoanodes are expected to shift the onset potential and improve the stability drastically. For the development of highly durable transparent photoanodes, surface modification with an electrocatalyst as the catalyst/protective layer covering the whole part of the photoanode surface uniformly is expected to be effective. Surface modification should be developed without losing transparency, losing photocurrent density, or complicating the preparation method. Introduced electrocatalyst layers accelerate the reaction kinetics and charge separation by capturing carriers from photoelectrodes. In contrast, the functional layers passivate the surface states and protect the photoelectrodes from self-oxidation. These functions are expected to work not only on photoanodes, but also on photocathodes.

The third strategy is to assemble the components to effectively develop the entire system. When the efficiency becomes higher, the potential losses related to the mass transfer of reactants and products cause a pH gradient. The design of the gas collection system is also important to separate evolved gases safely. For practical application, reduction of all related costs for fabrication should be considered. Further investigations addressing these issues are expected to be future tasks in this study field.

For example, the electrolyte composition significantly affects the performance of photoelectrodes. In the case of BiVO$_4$, for example, the material is expected to be stable in 4 < pH < 11. Therefore, a BiVO$_4$ photocathode has been utilized in near-neutral pH solution. Furthermore, the photostability depends on the identity of the buffer species in the solution. In contrast, Fe$_2$O$_3$ and Ta$_5$N$_5$ are usually used in alkaline solution. Because pH affects the performance of electrocatalysts, the dependence of the photocatalytic performance on pH is of great importance. The deconvolution of electrocatalysts and photoanodes, such as Fe$_2$O$_3$/Ta$_5$N$_5$, has been considered to be effective for opaque/transparent Fe$_2$O$_3$, BiVO$_4$, and Ta$_5$N$_5$. Novel preparation procedures to suppress the number of trap states are required for improved performance of transparent photoanodes. For practical use, low cost and simple materials for photocathodes are needed to realize the large-scale application of solar energy conversion. Seeking for more appropriate synthesis methods should be established for better efficiency that meets demand.
as NiFeO$_2$/Ta$_3$N$_5$, is effective for detailed investigation.\cite{113} The influence of pH and solution composition on the PEC performance remains nonstraightforward. Continuous efforts and knowledge gains need to be devoted to rationally design the entire system.

The development of a scalable PEC system is thought to be of great interest. The collective efforts of the three aforementioned directions will achieve high STH efficiency of over 10% with high durability in the future, and the system is expected to play an important role in the achievement of a sustainable society.

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**Conflict of Interest**

The authors declare no conflict of interest.

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\cite{1} K. Takanabe, ACS Catal. 2017, 7, 8006.
\cite{2} M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, Chem. Rev. 2010, 110, 6446.
\cite{3} J. R. McKone, N. S. Lewis, H. B. Gray, Chem. Mater. 2014, 26, 407.
\cite{4} J. Jia, L. C. Seitz, J. D. Benck, Y. Huo, Y. Chen, J. W. D. Ng, T. Bilir, J. S. Harris, T. F. Jaramillo, Nat. Commun. 2016, 7, 13237.
\cite{5} C. R. Cox, J. Z. Lee, D. G. Nocera, T. Buonassisi, Proc. Natl. Acad. Sci. USA 2014, 111, 14057.
\cite{6} J. Luo, J. H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. G. Park, S. D. Tilley, H. J. Fan, M. Grätzel, Science 2014, 345, 1593.
\cite{7} A. Fujishima, K. Honda, Nature 1972, 238, 37.
\cite{8} M. Grätzel, Nature 2001, 414, 338.
\cite{9} T. Higashi, H. Nishiyama, Y. Suzuki, Y. Sasaki, T. Hisatomi, M. Katayama, T. Minegishi, K. Seki, T. Yamada, K. Domen, Angew. Chem., Int. Ed. 2019, 58, 2300.
\cite{10} S. Wang, P. Chen, Y. Bai, J. H. Yun, G. Liu, L. Wang, Adv. Mater. 2018, 30, 1800485.
\cite{11} J. Park, K. Y. Yoon, T. Kim, H. Jang, M. J. Kwak, J. Y. Kim, J. H. Jang, Nano Energy 2020, 76, 105089.
\cite{12} A. Duret, M. Grätzel, J. Phys. Chem. B 2005, 109, 17184.
\cite{13} Gurudayal, D. Sabba, M. H. Kumar, L. H. Wong, J. Barber, M. Grätzel, N. Mathews, Nano Lett. 2020, 15, 3833.
\cite{14} J. W. Jiang, C. Du, Y. Ye, Y. Lin, X. Yao, J. Thorne, E. Liu, G. McMahon, J. Zhu, A. Javey, J. Guo, D. Wang, Nat. Commun. 2015, 7, 6447.
\cite{15} Gurudayal, R. A. John, P. P. Boix, C. Yi, C. Shi, M. C. Scott, S. A. Veldhuis, A. M. Minor, S. M. Zakeeruddin, L. H. Wong, M. Grätzel, N. Mathews, ChemSusChem 2017, 10, 2449.
\cite{16} A. B. Murphy, P. R. F. Barnes, L. K. Randeniya, I. C. Plumb, I. E. Grey, M. D. Horne, J. A. Glasscock, Int. J. Hydrogen Energy 2006, 31, 1999.
\cite{17} I. Cesar, A. Kay, J. A. G. Martinez, M. Grätzel, J. Am. Chem. Soc. 2006, 128, 4582.
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