Tandem photoelectrochemical cells for solar water splitting

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ABSTRACT

Photoelectrochemical (PEC) water splitting without an external bias is a potential solution to the growing energy crisis because this method can directly convert solar energy into chemical energy. A tandem cell is a frequently used configuration for unassisted overall water splitting because of the advantages that each component are tied together to form a highly efficient integration. A tandem PEC water splitting device is based on different photoelectrode absorbers, and there are two main models including photoanode/photo-cathode (PEC/PEC) and photoelectrode/photovoltaic (PEC/PV) tandem cells. In this review, we will focus on the concepts, configurations and recent progress of PEC/PEC and PEC/PV cells. Light absorption and energy band matching are the key points to enhance the solar-to-hydrogen (STH) efficiency. Promoting the performance of a standalone semiconductor material and finding new materials, coupled with an optimized configuration, are future steps for the practical application of tandem PEC cells.

Abbreviations: PEC: Photoelectrochemical; STH: Solar-to-hydrogen; PV: Photovoltaic; PV-EL: Photovoltaic-electrolysis; CIGS: Cu(In,Ga)Se2; CGS: CuGa3Se5; ACGSe: (Ag,Cu)GaSe2 ; Co-Ci: Cobalt carbonate; Co-Pi: Cobalt phosphate; cDBR: conductive distributed Bragg reflector; DSC: Dye-sensitized solar cell; IMM: Inverted metamorphic multi-junction; PED: Photoelectrodeposition; S-P: Sputtering + Photoelectrodeposition.

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1. Introduction

Photoelectrochemical (PEC) water splitting is an important strategy for converting sunlight into a chemical fuel in the form of hydrogen, and has been widely studied for decades [1–5]. Many p-type semiconductors, such as GaP [6], InP [7], GaInP₂ [8–10], Si [11–14], SiC [15], WS₂ [16], Cu(In,Ga)Se₂ [17], Cu₂O [18], CuYO₂ [19], CaFe₂O₄ [20], and Mg-doped Fe₂O₃ [21], have been reported as photocathode materials for water reduction. Some of these photocathodes exhibit considerable solar-to-hydrogen (STH) efficiency. Compared to the two-electron reaction of water reduction, water oxidation involves a four-electron reaction, which makes it the rate-determining step for water splitting. The lack of efficient and stable photoelectrode materials for water oxidation has restricted the application of solar water splitting. Many efforts have been devoted to the investigation of photoelectrode materials. In addition to TiO₂ [22–24], WO₃ [25] and α-Fe₂O₃ [26], other oxides, such as BiVO₄ [27], ZnFe₂O₄ [28], β-Fe₂O₃ [29], and YFeO₃ [30], have been found to act as photoanode materials for water oxidation. Recently, (oxy)nitride photoanode materials with a visible-light response, such as Ta₃N₅ [31–35], TaON [32,36,37], LaTaON₂ [38], LaTiO₂N [39,40], and SrTaO₂N [40,42], have also attracted much attention due to their theoretical STH efficiency, although they exhibit poorer durability than many oxide photoanode materials.

However, a single photoelectrode (whether a photoanode or a photocathode) has exhibited many elusive problems for efficient overall water splitting, due to the challenge of driving this multi-electron process with a high yield at low overpotentials [43]. From the point of view of thermodynamics, the band gap of a single photoelectrode should straddle the O₂/H₂O and H⁺/H₂ standard electrode potential for overall water splitting, and the band gap of semiconductor materials should reach 1.23 eV. Considering ohmic losses and a kinetic loss due to the overpotentials for oxygen or hydrogen production, the band gap of a semiconductor photoelectrode should be larger than 2.03 eV, corresponding to the light absorption edge of 610 nm [44]. This large gap means that photons with long wavelengths cannot be absorbed and wide band gap semiconductor materials are required. Nevertheless, narrow band-gap semiconductor materials are indispensable to improve the utilization of the solar spectrum. In addition, an STH efficiency above 10% is needed for reaching a viable level for commercialization, which is a fundamental requirement [45,46]. Therefore, achieving this efficiency is very critical for individual photoelectrode materials.

To overcome the issue of a large external bias for the overall water splitting of a traditional single photoelectrode, some practical approaches to achieve efficient PEC water splitting without an external bias have been developed. The configuration of dual-absorber tandem systems has been increasingly more attractive for unassisted overall water splitting [47]. Dual-absorber PEC tandem devices can be accomplished by photoanode/photocathode (PEC/PEC) systems
or photoelectrode/photovoltaic (PEC/PV) coupled devices [47–49]. Therefore, dual-absorber tandem devices can generate a sufficient driving force for self-driven solar water splitting while simultaneously maximizing the fraction of solar energy collected.

Very recently, a photovoltaic-electrolysis (PV-EL) system, which is another type of cell devices for solar water splitting, has attracted much attention [50]. The water oxidation and water reduction reactions at the electrodes are driven by the electric energy, which is supported by solar cells. Only a p/n junction, instead of the semiconductor-electrolyte junction, is required in PV/EL cells. This type of cell is different from the PEC-based cells, which have a semiconductor–electrolyte junction.

Here, tandem PEC cells for water splitting are discussed including PEC/PEC and PEC/PV systems.

2. Concept of tandem PEC water splitting cells

2.1 Concept of the PEC/PEC cells

One approach for overall water splitting is to use a photocathode and a photoanode connected in series to form a PEC/PEC tandem cell, in which the sunlight can pass through the n-type semiconductor and then the p-type semiconductor. On the surface of the n-type semiconductor, water is oxidized to produce oxygen, and reduction reactions on the surface of the p-type semiconductor produce hydrogen.

More specifically, in this configuration, photons with the shorter wavelengths of the solar spectrum are absorbed by the top electrode (the photoanode). The remaining photons with longer wavelengths are transmitted and

![Figure 1. Simplified illustration of the PEC/PEC tandem cell configuration.](image-url)
captured by the bottom electrode (the photocathode). Thus, after two or more steps of sunlight absorption, more solar photons can be utilized. From the point of view of thermodynamics, the two semiconductors with smaller band gaps can be chosen compared with the single photoelectrode, because each photoelectrode only needs to provide part of the potential for overall water splitting. As shown in Figure 1, the band gap of each photoelectrode should cover the $\text{O}_2/\text{H}_2\text{O}$ or the $\text{H}^+/\text{H}_2$ standard electrode potential, and the conduction band of the photoanode is more negative than valence band of the photocathode. The smaller the band gap in the semiconductor material, the more photons can be absorbed, and the larger STH efficiency may be achieved [51].

In summary, when choosing semiconductor materials, it should be guaranteed that the energy necessary for water splitting is gathered entirely from the light source. In this system, the water splitting potential is generated directly at the semiconductor–electrolyte interfaces for water redox.

### 2.2 Concept of the PEC/PV cells

Another feasible pathway for unassisted overall water splitting is to combine the photoelectrodes with the photovoltaic cells to form a PEC/PV tandem cell. This tandem cell is a PEC device that is voltage-biased with an integrated PV device [9]. For the part of the PEC photoelectrodes in this configuration, it is invariable that the minority carriers of the semiconductor material participate in the water redox reaction and the reaction occurs at

![Figure 2](image-url). Simplified illustration of the PEC/PV tandem cell configuration (taking the photoanode/PV as an example).
the semiconductor–electrolyte junction. Taking the n-type semiconductor materials as an example, the majority carriers (electrons) generated in the photoanode are recombined in the PV cell through the external circuit. Hydrogen is generated at the metal counter electrode, which is connected with the PV cell, as shown in Figure 2.

Solar cells can support an operation when the power generated by the minority carriers is not enough. With the help of the bias generated by the solar cell, it is more flexible when choosing the photoelectrode materials and the PV cells because there is no request for the matching energy levels. For the whole system, light is also the only energy input, which is the same as in the PEC/PEC configuration.

3. PEC/PEC tandem cells

In 1975, Yoneyama and coworkers presented a PEC cell, which consisted of a TiO$_2$ photoanode and a p-GaP photocathode [52]. The n-TiO$_2$/p-GaP tandem cell was found to generate both hydrogen and oxygen with no external bias. According to the previous work, Nozik presented an energy analysis in 1976 and established the general theory for connecting photoanodes and photocathodes to form tandem cells [53]. Only a 0.25% of energy conversion efficiency for water splitting was achieved, partly due to the high internal resistance of the n-TiO$_2$/p-GaP cell [52].

After Yoneyama’s pioneering demonstration, very little attention has been paid to constructing photoanode/photocathode tandem cells, due to the difficulty in improving the PEC performance of the oxide photoanodes and developing inexpensive and stable photocathodes. There are many problems for reaching a high STH efficiency, such as lower saturation photocurrents and less overlap area between two photoelectrodes. If the onset potential of the photoanode negatively shifts enough to overlap the onset potential of the photocathode in a wider range, then the tandem cell will be more efficient. In addition, the long-term durability of the photoelectrodes should be considered.

3.1 BiVO$_4$-based PEC/PEC tandem cells

With the development of BiVO$_4$ semiconductor materials, BiVO$_4$ has frequently been utilized in PEC/PEC tandem cells because BiVO$_4$ (band gap, ~2.4 eV) absorbs a substantial portion of the visible spectrum and has a well-suited band structure for potential use in solar water splitting [54–56]. A tandem cell connecting the NiO photocathode with the BiVO$_4$ photoanode was fabricated by Mozer’s group. The BiVO$_4$/NiO tandem cell was stable over several hours, and the corresponding faradaic efficiency of hydrogen generation was 80% [57]. As a photocathode, NiO has a wide band gap of 3.6–4.0 eV;
therefore, NiO may not be a perfect photocathode for a PEC tandem cell. Therefore, the STH efficiency of such a BiVO$_4$/NiO tandem cell is very low.

Compared to NiO, Cu$_2$O as a photocathode has a much smaller band gap (2.0 eV), which can absorb wavelengths <600 nm. In 2014, Sivula’s group presented a BiVO$_4$/Cu$_2$O tandem cell for overall unassisted solar water splitting, and the corresponding STH efficiency was ca. 0.5%. In Sivula’s report, the expected tandem cell operating point was estimated by the individual J–V curves of the respective photoelectrodes (3-electrode). The operating point is where the J–V curves for the photoanode and photocathode intersect, as shown in Figure 3. Nevertheless, the performance was found to decay during the operation because of the detachment of the Co–Pi catalyst [58].

As the Si photocathode exhibits a band gap of 1.1 eV, it acts as an important candidate for the tandem PEC cells for solar water splitting. However, this photocathode exhibits a poor onset potential for water reduction. Compared with a planar Si photocathode film, p-type Si nanoarrays often have a larger onset potential for water reduction due to the decrease in the transfer distance of the photoinduced electrons from the bulk to the surface. The p-type Si nanoarrays with a preferred geometry then were chosen to construct the tandem cell. Xu et al. designed a PEC tandem cell consisting of a BiVO$_4$ photoanode and Si nanoarray photocathode, and an STH efficiency of 0.57% (corresponding photocurrent
density of 0.46 mA cm$^{-2}$) was achieved in this system. As shown in Figure 4(b), according to the operating point, an unassisted photocurrent of 0.6 mA cm$^{-2}$ is possible to achieve. The two-electrode system connecting Co-Pi/Mo:BiVO$_4$ with the Pt/p-Si nanoarray reached a stable photocurrent density of 0.12 mA cm$^{-2}$ after 3.5 h, which is slightly lower than the expected operating point. This density suggests that a noticeable loss occurs or an instability exists. A series resistance of the whole circuit may lead to the decline. The pH gradient that developed near the electrodes may cause extra loss, and the dissolution of the Co–Pi catalyst decreased the actual conversion efficiency of the device [59].

Composited photocathodes have also been used in constructing the tandem cells. In 2016, Lee’s group demonstrated a tandem device of a Pt/CdS/CuGa$_3$Se$_5$/(Ag,Cu)GaSe$_2$ photocathode and a NiOOH/FeOOH/Mo:BiVO$_4$ photoanode, which achieved an STH efficiency of 0.67% over 2 h without degradation. The Pt/CdS/CGS/ACGSe photocathode exhibited an onset potential of 0.9 V$_{RHE}$ and a 4.6 mA cm$^{-2}$ photocurrent filtered by the BiVO$_4$ photoanode. The excellent properties of the photocathode enhanced the tandem cell efficiency with a NiOOH/FeOOH/Mo:BiVO$_4$ photoanode with a 3.4 mA cm$^{-2}$ photocurrent at 1.23 V$_{RHE}$. The preferable performance of the Pt/CdS/CGS/ACGSe photocathode may be attributed to the proper contacts between similar crystal structures [60]. Although the limitation still lies in the photocurrent of the photoanode, utilizing a photocathode with preferable properties is equally important. In 2018, new strategies for a surface reaction and interface optimization were employed to improve the performance of the Cu(In,Ga)Se$_2$ (CIGS) photocathode by Gong’s group. The spatial dispersion and particle size of the Pt catalyst can be controlled by a two-step platinization strategy (sputtering + PED, S-P), while the defects at the Cds/TiO$_2$ interface can be passivated by an Al$_2$O$_3$ insertion layer. Then, the improved CIGS/CdS/Al$_2$O$_3$/TiO$_2$/S-P-

**Figure 4.** (a) Simplified energy diagram of the BiVO$_4$/Si nanoarray tandem cell. (b) Intersection point of the J–V curves of the BiVO$_4$ and Si nanoarray photoelectrodes [59].
Pt photocathode was connected with BiVO$_4$ to construct a tandem cell, which reached an STH efficiency of 1.01% [61]. The fabrication strategy requires an upgrade to obtain higher performance of the photoelectrodes, not only n-type but also p-type semiconductors, and then the tandem cells can be advanced.

3.2 Other PEC/PEC tandem cells

Hematite (α-Fe$_2$O$_3$) is also a prototypical material as a photoanode for tandem cells because of its potential performance [62,63]. A Mg- and Si-doped Fe$_2$O$_3$ tandem device was demonstrated in 1982, and the power conversion efficiency was approximately 0.05% in a 0.1 M Na$_2$SO$_4$ solution (pH 6) [64]. With an enhancement in the preparation technology, a self-driven tandem p/n-Fe$_2$O$_3$ device for photoelectrochemical water splitting was fabricated by Khan’s group in 2006, and the STH efficiency was calculated to be 0.11%. The p-type Fe$_2$O$_3$ material favours H$_2$ generation because of the band-edge modification by zinc [65]. However, there are still many problems to solve to improve the magnitude of the photocurrent and the stability in aqueous solutions.

Following the advances in oxide photoanode performance, increasingly more demonstrations of p/n tandem cells have appeared. In 2008, Turner’s group reported two p/n combinations. The n-Fe$_2$O$_3$ nanorod thin films and a WO$_3$ film were both connected with p-GaInP$_2$. For the case of WO$_3$/GaInP$_2$, the photocurrent of water splitting can achieve 20 μA cm$^{-2}$ under an illumination of 1 W cm$^{-2}$. The device did not work at below 0.2 W cm$^{-2}$ illumination intensities because of an insufficient potential difference. For the case of the Fe$_2$O$_3$/GaInP$_2$ tandem device, a very low current density was observed, even at 10 sun illumination (1 W cm$^{-2}$). The low photocurrent of Fe$_2$O$_3$ is the limiting photoelectrode for the two-photoelectrode combination system due to the low electron mobility, high recombination losses and short hole diffusion lengths of Fe$_2$O$_3$ [66]. Two years later, Turner’s group found that the mismatch of the conduction band minimum of the hematite film with the valence band maximum of p-GaInP$_2$ was the main reason for the low performance [67]. In 2015, Jang et al. reported a device that can achieve an STH efficiency of 0.91%. The Si photocathode was used to connect with a hematite photoanode in this device. The turn-on photovoltages of the Fe$_2$O$_3$ photoanode was improved, and finally 0.45 V was obtained due to the improved preparation strategy, which reduced the surface disorders [68]. The onset potential of the photoanode is the main challenge to improve the final efficiency of the whole system at all times. To achieve a standout performance, how to achieve higher photovoltages generated by the photoanodes may be the primary focus.
### 3.3 Current situation of the PEC/PEC cells

Some typical examples of the PEC/PEC cells are shown in Table 1. Fe$_2$O$_3$ and BiVO$_4$ are widely applied in PEC/PEC system. For the PEC/PEC system, the band gap of each photoelectrode should cover the O$_2$/H$_2$O or H$^+$/H$_2$ standard electrode potential and demonstrate an overlay region.

Actually, the PEC/PEC tandem device could theoretically achieve a maximum STH efficiency of approximately 29.7% [72]. However, in practical applications, there are many problems that may cause the low efficiency of the whole system. The more the region of the onset potential of the two photoelectrodes overlap, the higher efficiency could be achieved. One of the photoelectrodes with a lower photocurrent may limit the performance of the whole tandem device. The high internal resistance loss of the PEC/PEC configuration should also be considered as the reason for the low efficiency. In addition, the electrolyte is difficult to choose when considering the corrosion and stability problem of both photoelectrodes. Although the PEC/PEC system has a high theoretical STH efficiency, realizing large-scale utilization may still be a long way off.

### 4. PEC/PV tandem cells

There are two main kinds of PEC/PV tandem cells: one is an external device and the other is an immersed device. One alternative approach is that the solid-state PV is not directly in contact with the electrolyte but is connected to the electrolyser through external wiring. This configuration is the external device. As the PEC absorbers need to be immersed in the electrolyte to form the semiconductor–electrolyte junction, another alternative configuration employs a PV cell that is immersed and connected to the photoelectrodes without external wiring. The immersed device may decrease the cost of the whole system, but electrolyte stability and light scattering through bubbles need to be considered [73]. The two kinds of devices have their own advantages and disadvantages, which need further research.

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**Table 1.** Obtained impressed examples of the PEC/PEC tandem water splitting cells.

| Main photoelectrodes (n-type materials) | Connected p-type materials | STH efficiency | Year | References |
|----------------------------------------|----------------------------|----------------|------|------------|
| BiVO$_4$                               | Cu(In,Ga)Se$_2$            | 1.01%          | 2018 | [61]       |
| Fe$_2$O$_3$                            | Si                         | 0.91%          | 2015 | [66]       |
| BiVO$_4$                               | (Ag,Cu)GaSe$_2$            | 0.67%          | 2016 | [60]       |
| BiVO$_4$                               | Si                         | 0.57%          | 2016 | [59]       |
| BiVO$_4$                               | Cu$_2$O                    | 0.5%           | 2014 | [58]       |
| Fe$_2$O$_3$                            | Fe$_2$O$_4$                | 0.11%          | 2006 | [65]       |
| BiVO$_4$                               | SrTiO$_3$                  | <0.1%          | 2012 | [69]       |
| BiVO$_4$                               | Si                         | <0.1%          | 2014 | [70]       |
| BiVO$_4$                               | (CuGa)$_{1-x}$Zn$_x$S$_2$  | <0.1%          | 2015 | [71]       |
To establish a photoanode/PV tandem cell, a stable transition metal oxide is a frequently used material for the photoanode; this photoanode is accompanied by an excellent PV device. These materials have enticed many research groups to investigate various systems, such as TiO$_2$ photoanodes in tandem with a thin film PV device based on Cu(In,Ga)Se$_2$/CdS [74] and Fe$_2$O$_3$ photoanodes in tandem with a-Si:Ge PV [75].

4.1 BiVO$_4$-based PEC/PV tandem cells

With the development of BiVO$_4$ semiconductor materials, BiVO$_4$ has also frequently been utilized in PEC/PV tandem cells because it has relatively smaller band gap energy and strong light absorption properties [56,76–78]. In 2013, Krol’s group made a great progress in PEC/PV tandem cell development for water splitting. A gradient-doped BiVO$_4$ was combined with a 1-junction (1-jn) or 2-junction (2-jn) Si solar cell, as shown in Figure 5a. The use of a gradient dopant concentration in the metal oxide film could solve the problem of poor charge carrier separation. Consequently, a photocurrent of 4 mA cm$^{-2}$ was obtained by the tandem cell using a double-junction Si solar cell, corresponding to an STH efficiency of 4.9%. The expected operation point of the cell, $J_{\text{op}}$, was estimated by means of the intersection method, as shown in Figure 5(b) [79]. The intersection method was put forward in 1984 by Weber and coworkers. They predicted the operation conditions by overlapping the current-voltage curves of the photoelectrode and PV cell under actual illumination conditions, as the quantity obtained by the intersection point must be equal at both interfaces [80]. The point can reveal the ideal photocurrent ($J_{\text{op}}$), and the STH efficiency is given by the $J_{\text{op}}$.

Notably, the curve of the photoanode should be measured by the two-electrode system to match the practical operation situation, and the solar
cell should be placed behind the photoanode to obtain the curve when overlapping the J–V curves. In 2014, Kamat’s group and Smets’ group reported BiVO$_4$-based PEC/PV tandem cells with an STH efficiency of 2.5% and 5.2%, respectively [81,82]. A CoPi/BiVO$_4$ photoanode and a CH$_3$NH$_3$PbI$_3$ solar cell were chosen to constitute an all solution-processed tandem cell in Kamat’s research, while Smets presented a cell consisting of a gradient-doped BiVO$_4$ photoanode and a silicon solar cell. Kamat’s work established a foundation for exploring available photoanode–perovskite PV combinations. However, a slight decline in photocurrent appeared following the initial response, which is attributed to the partial dissolution of the CoPi catalyst [81,83]. The enhanced performance showed in Smets’ research could be attributed to the increased performance of the BiVO$_4$ photoanode, as well as better spectral matching between the BiVO$_4$ photoanode and the silicon solar cell [82].

In 2015 and 2016, Kim et al. reported two studies regarding tandem cells based on the BiVO$_4$ photoanode and different PV materials, and two different architectures were presented [84,85]. A CH$_3$NH$_3$PbI$_3$ perovskite single junction solar cell and parallel-connected Si solar cells were applied into the tandem system. In the former work, dual-doped BiVO$_4$ with a cobalt carbonate (Co–Ci) catalyst was fabricated as the photoanode material. The Co–Ci catalysts were compared with the frequently used cobalt phosphate (Co–Pi) catalysts; similar photocurrents were obtained but the Co–Ci catalysts realized an increase in the stability. This research provided a solution for the previously mentioned Co–Pi catalysts dissolution problem. BiVO$_4$ was combined with the perovskite solar cell in a well-designed tandem artificial-leaf-type device, and eventually an STH efficiency of 4.3% was produced [84]. In 2016, Kim et al. designed an unassisted solar water splitting system consisting of hetero-type dual photoanodes and parallel-connected Si solar cells, as shown in Figure 6. The modified BiVO$_4$ and

![Figure 6](image_url)

**Figure 6.** (a) Scheme of an unassisted solar water splitting tandem cell with a hetero-type dual photoelectrode (BiVO$_4$||Fe$_2$O$_3$) and parallel-positioned Si solar cells. (b) Practical picture of the monolithic tandem cell in operation under the illumination of real sunlight [85].
α-Fe$_2$O$_3$ electrodes were chosen to consist of dual photoelectrodes, which were connected in parallel for extended light harvesting, and visible light up to 610 nm can be utilized.

The tandem cell showed an excellent STH efficiency of 7.7%. The hetero-type dual photoanodes were regarded as a new strategy for unassisted water splitting and supported the blueprint of the tandem cells composed of the dual photoanodes. This work could facilitate the process of reaching an STH efficiency of above 10% for practical applications by further reducing the onset potential of the hetero-type dual photoanodes because the saturated photocurrent is already over 8.3 mA cm$^{-2}$. For portion of Fe$_2$O$_3$, increasing the bulk charge separation efficiency could be eventually beneficial for the performance of the whole tandem cell [85].

Park’s group also published an article regarding progress in WO$_3$/BiVO$_4$ heterojunction-based tandem devices in 2015. After coating the mesoporous WO$_3$ nanoparticle network with a thin BiVO$_4$ layer, a larger contact area between the two components were provided and the electron transport ability was well maintained. This kind of structure is called a core/shell structure and can be applied to other photoelectrode systems. Combined with a single dye-sensitized solar cell (DSSC), as shown in Figure 7, the WO$_3$/BiVO$_4$ heterojunction-based tandem devices showed an extraordinarily STH efficiency of 5.7% [86].

Based on former work, Park’s group increased the STH efficiency to 7.1%, as shown in Figure 8. To overcome the contradiction between high transparency and high photocurrent density of the front photoelectrode in a tandem device, a photon-recycling hybrid conductive distributed Bragg reflector
(cDBR) on the back side of the transparent conducting substrate was incorporated. The cDBR structure reflects short wavelength light ($\lambda < 500$ nm) for enhancing photocurrent generation of the front photoelectrochemical electrode, while transmitting longer-wavelength light ($\lambda > 500$ nm) for the rear solar cell. The hybrid cDBR can serve as not only as an optical filter but also as a counter electrode for the solar cell. The eventually an STH efficiency of 7.1% with no external potential reveals a great step towards an STH efficiency above 10% for commercialization [87].

### 4.2 Cu$_2$O-based PEC/PV tandem cells

A variety of studies regarding other photoanode or photocathode materials with various photovoltaic cells have been applied in tandem devices. For example, in 2015, Dias et al. turned their attention to a photocathode/PV system. A tandem cell for water splitting was constructed using a Cu$_2$O photocathode and a hybrid perovskite photovoltaic, as shown in Figure 9. In this tandem configuration, the flat anode electrode was positioned parallel to the path of light. The problem of the counter electrode areas was mentioned, which may be increased, as long as its placement is out of the illumination path in the tandem configuration. In addition, the increased area means more abundant and desirable employed catalyst materials. The final
tandem cell using a Cu$_2$O photocathode with a hybrid perovskite photovoltaic achieved an STH efficiency of 2.5%. The performance could be enhanced in the future by the development of the Cu$_2$O materials [88].

4.3 Fe$_2$O$_3$-based PEC/PV tandem cells

In addition to BiVO$_4$, another popular photoanode material used in tandem cells is hematite due to its favourable band gap (~2.1 eV), good stability, abundance, nontoxicity and economic viability [89,90]. In 2010, Brillet et al. combined a Fe$_2$O$_3$ photoanode with dye-sensitized solar cells. Three possible architectures for constructing the tandem cell were demonstrated: two side-by-side dye cells behind a Fe$_2$O$_3$ photoanode, two side-by-side dye-sensitized solar cells (DSCs) in front of the Fe$_2$O$_3$, and a trilevel Fe$_2$O$_3$/DSC/DSC/DSC architecture. The highest expected STH efficiency of 1.36% was obtained by the trilevel tandem architecture. The trilevel architectures can harvest more photons and decrease the photon energy loss [91]. This architecture of the photovoltaic cell behind the photoanode has been commonly adopted by researchers as the prepositive photoelectrode can capture more photons to reach higher photocurrents.

In 2015, Gurudayal et al. demonstrated a stable and simple water splitting tandem cell by combining a Mn-doped Fe$_2$O$_3$ photoanode with a single perovskite solar cell, and finally realized an overall unassisted water splitting with an STH efficiency of 2.4%. The performance of the tandem system could be limited by the low photocurrents generated by the photoanode
thin Fe$_2$O$_3$); thus, the indicated operating situation of the system is far below the maximum performance of the solar cell [92].

In 2017, Gurudayal et al. improved the fabrication of hematite, and then combined it with a CH$_3$NH$_3$PbI$_3$ perovskite solar cell to form a tandem cell. The STH efficiency of the device was 3.4% for overall unassisted water splitting. The preparation of Fe$_2$O$_3$ was based on an atomic layer deposition treatment approach. Because of an enhancement in the technology, the performance of the photoanode was also enhanced, which brings the increased STH efficiency of the whole tandem device [93].

4.4 Immersed configuration for the PEC/PV tandem cells

In addition to the aforementioned external device, there are other examples of the immersed device. The most impressive photoelectrode/PV device is an integrated design developed by Turner in 1998 with a GaAs p–n junction connected to a GaInP$_2$ photocathode [9]. Even though the hydrogen production efficiency of this system could reach 12.4%, the GaInP$_2$ photocathode quickly corroded when in contact with the aqueous electrolyte [10]. In addition, the chosen materials are expensive and poisonous and are not suitable for large-scale applications.

Another immersed configuration was demonstrated by Deutsch’s group in 2017 by using a buried p–n junction. With GaInP/GaInAs tandem absorbers, an STH efficiency of over 16% was obtained. Photons with energies higher than 1.8 eV are absorbed by GaInP, while those less than
1.8 eV pass through to the bottom GaInAs junction, as shown in Figure 10. When the device is illuminated, photogenerated electron and hole pairs appear. Then, electrons in the conduction band of GaInP are transferred to the electrolyte to produce H₂, while the holes in the GaInAs valence band are transferred through the Au back contact and a wire to a metal counter electrode to produce O₂. The GaInP and GaInAs are connected in series through the transparent tunnel junction where holes in the valence band of GaInP can recombine with electrons in the conduction band of GaInAs. The immersed devices could minimize external wiring, which may lead to lower-cost tandem device, because other solid-state solar cells are not immersed and must be connected to the electrolyser through external wiring. The device with GaInP/GaInAs tandem absorbers is called an inverted metamorphic multi-junction (IMM) device. A flexible platform then can be provided for realizing tandem band gap combinations to reach higher a STH efficiency [73].

### 4.4 Current situation of the PEC/PV tandem cells

Table 2 shows several typical examples of PEC/PV tandem cells. Compared to the PEC/PEC system, the choices of the photoelectrode materials and the PV cells are more flexible. Although the best design for unassisted solar water splitting is uncertain, the potential space for the development of PEC/PV tandem cells is wide, and to date a fairish efficiency for unassisted solar water splitting is easier to reach. The limitation lies in the photocurrent of the sand-alone semiconductor material, and the cost for the large-scale application of the PV cells should also be considered. In summary, this system has relatively vast potential for future development.

| Main PV cells | Connected photoelectrodes | STH efficiency | Year | References |
|---------------|--------------------------|----------------|------|------------|
| GaInAs        | GaInP                    | 16.2%          | 2017 | [73]       |
| Si Cell       | BiVO₄/Fe₂O₃*             | 7.7%           | 2016 | [85]       |
| DSSC          | WO₃/BiVO₄#               | 7.1%           | 2016 | [87]       |
| DSSC          | WO₃/BiVO₄#               | 5.7%           | 2015 | [86]       |
| Si Cell       | BiVO₄                    | 5.2%           | 2014 | [82]       |
| Si Cell       | BiVO₄                    | 4.9%           | 2013 | [79]       |
| CH₃NH₂PbI₃    | BiVO₄                    | 4.3%           | 2015 | [84]       |
| CH₃NH₂PbI₃    | Fe₂O₃                    | 3.4%           | 2017 | [93]       |
| Hybrid Perovskite | Cu₂O                | 2.5%           | 2015 | [88]       |
| CH₃NH₂PbI₃    | BiVO₄                    | 2.5%           | 2015 | [81]       |
| CH₃NH₂PbI₃    | Fe₂O₃                    | 2.4%           | 2015 | [92]       |
| DSSC          | Fe₂O₃                    | 1.36%          | 2010 | [91]       |

* Hetero-type dual photoelectrode BiVO₄/Fe₂O₃
# Heterojunction WO₃/BiVO₄
5. Conclusion and outlook

Here, the motivation and practical applied examples for the PEC water-splitting tandem cell were illustrated. Using a single semiconductor material, it is difficult to realize highly efficient unassisted overall water splitting. Researchers must turn their attention to PEC-based tandem cells. The high conversion efficiency for water splitting is proportional to the photocurrent of the whole system, and the photocurrent can be optimized by the appropriate selection of semiconductor materials and optimized configuration.

For the PEC/PEC tandem system, the fabrication cost is relatively low, while the poor energy conversion efficiency restrains the commercial application of the PEC/PEC tandem system. Compared to the PEC/PV system, the PEC/PEC configuration does not have complex electrical connections. However, the limit of the tandem PEC system is the restrictive matching of the band gap between two semiconductors. The stable and large photocurrents of the photoelectrode materials are urgent needs for the future. In addition, the onset potentials of the two photoelectrodes should have more overlay areas, and enhancing the onset potentials of photoanodes is more urgent at present.

On one hand, to increase the efficiency of the PEC/PEC system, more studies should be carried out to improve the existing photoanode performance, and we should pay more attention to the onset potential and improving the photocurrent at a low external bias. On the other hand, new photoanodes with suitable band gaps and band edge potentials are required. With the rapid development of computational capabilities and theoretical methods, computational screening of possible photoanodes is a promising solution towards finding new materials [94].

For the PEC/PV system, the efficiency is relatively high, but the drawback of PEC/PV system is the high cost. However, this system is more flexible when choosing the photoelectrode materials and the PV cells. However, with the rapid declining costs of the PV cells, the PEC/PV system is a competitive candidate for the future commercial application of water splitting. Specifically, the recent organic–inorganic perovskite solar cell offers low-cost, easy-fabrication solar energy utilization solutions. In addition, the replacement of noble metals with earth abundant elements in the PEC/PV system is another important issue, and many strategies, such as the alloys of noble metals, are promising solutions for reducing noble metal consumption. Up to now, it is easier to obtain a higher efficiency using the PEC/PV system.

Long-term durability, low cost and high performance are prerequisites for a practical water-splitting tandem cell. The durability of PEC cells may be prompted by the conformal coating of protective layers, which can isolate the photoelectrodes from the electrolytes [3,95]. From the viewpoint of cost, perovskite solar cells may be a candidate PV for tandem cells because of their high
performance and low cost. From the viewpoint of performance, photoanodes with a more negative onset potential for water oxidation and photocathodes with a more positive onset potential for water reduction should be considered, and the interface between the photoanode surface and the electrolyte deserves more attention [96]. To decrease the onset potential of the photoanodes, improving the preparation method and employing more effective catalysts may be useful. In addition, applying new materials can bring hope to tandem cell. A Cu$_2$ZnSnS$_4$ photocathode has been recently reported for its excellent performance. A stable photocurrent density of 11.1 mA cm$^{-2}$ at 0 V$_{\text{RHE}}$ has been obtained. Cu$_2$ZnSnS$_4$ may be a very promising absorber for solar driven photovoltaics and water splitting applications [97].

The most important aspects in the future are to continue the research for improving the performance of existing materials [98] and to find new materials, coupled with an optimized configuration. Lastly, it is reasonable to believe that an efficient, inexpensive and stable tandem device for the unassisted overall water splitting will someday be realized.

Disclosure statement

No potential conflict of interest was reported by the authors.

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