Photoelectrochemical solar water splitting: From basic principles to advanced devices

Bandar Y. Alfaifi1,*, Habib Ullah1, Sulaiman Alfaifi2, Asif A. Tahir1, Tapas K. Mallick1
1 Environment and Sustainability Institute (ESI), University of Exeter, Penryn Campus, Penryn, Cornwall, TR10 9FE, United Kingdom
2 Department of Chemistry, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Abstract

Photoelectrochemical water splitting (PEC) offers a promising path for sustainable generation of hydrogen fuel. However, improving solar fuel water splitting efficiency facing tremendous challenges, due to the energy loss related to fast recombination of the photogenerated charge carriers, electrode degradation, as well as limited light harvesting. This review focuses on the brief introduction of basic fundamental of PEC water splitting and the concept of various types of water splitting approaches. Numerous engineering strategies for the investigating of the higher efficiency of the PEC, including charge separation, light harvesting, and co-catalysts doping, have been discussed. Moreover, recent remarkable progress and developments for PEC water splitting with some promising materials are discussed. Recent advanced applications of PEC are also reviewed. Finally, the review concludes with a summary and future outlook of this hot field.

Introduction

The traditional sources of energy such as coal, oil and natural gas have supplied the world with energy that drives society for long decades. But the energy consumption around the world is incredibly increased and is estimated to be double by 2050 [1]. Since the fossil fuel resources are limited and concentrated in certain region around the world, while global demand is increasing; subsequently, a secure supply is increasingly challenging to assure [2]. Furthermore, pollution created from fossil fuel plants has significant impact on our health. Moreover, the emissions of greenhouse gas and Carbon dioxide have negative impact on our planet.

Renewable energy resources such as wind, biomass and solar fuel have been investigated for years to help in the replacement of fossil fuels. Extensive research and development are required to produce such a technology that can compete the fossil fuel and commercially available everywhere. However,
the most developed renewable energy sources are based on electricity generation, producing transportable and storable fuel, which is remains a challenge.

Among these energy resources, solar energy is considered a primary carrier that may hold potential promise for a sustainable and clean energy future [3]. Solar energy focused on direct conversion of sunlight into chemical fuels in the form of hydrogen gas (H₂) [4]. The advantages and attractiveness of solar water splitting, include sufficient water resources, small reaction potential required (1.23 eV), and zero CO₂ emission [5].

In this review, we are aiming to briefly introduce the basic principles of PEC. An overview of the common used materials that have been investigated for photoelectrochemical water splitting will be presented. In addition, the current state of the technology is discussed. Finally, the review concluded with a summary and future viewpoint in this hot topic of research.

**Basic principles of photocatalytic water splitting**

Generating Hydrogen fuel directly from sunlight, comes from natural phenomena called natural photosynthesis (NP), exist in plants [6,7], where sunlight is used to convert water and carbon dioxide into oxygen and carbohydrates. The potential technology that converts water into H₂ and O₂ using sunlight for generation of solar fuel is called artificial photosynthesis (AP), which aims to mimic NP using man-made materials [7,8].

The water splitting reactions (see reactions 1–3) is an uphill reaction with a net Gibbs free energy of 238 kJ/mol or 1.23 eV, as shown in Equation (1),

\[
\begin{align*}
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \rightleftharpoons 2\text{H}_2\text{O} \quad \text{Water Oxidation} \\
4\text{H}^+ + 4\text{e}^- & \rightleftharpoons 2\text{H}_2 \quad \text{Water Reduction} \\
2\text{H}_2\text{O} & \rightarrow 2\text{H}_2 + \text{O}_2 \quad \text{Water Splitting}
\end{align*}
\]

The basic mechanism of photocatalysis water splitting in general is based on the generation of photoexcited charge carriers. Generally, photocatalytic water splitting reaction on semiconductor particles involves three main steps: (1) absorption of light irradiation with energies exceeding the semiconductor bandgap, generate electrons (e⁻) and holes (h⁺) pairs inside the semiconductor particles; (2) the generated electrons and holes are separated followed by migration of these charges to the interface of the semiconductor particles; (iii) surface chemical reactions between these carriers with various compounds (e.g., H₂O); electrons and holes to produce H₂ and O₂, respectively as it shown in Figure 1 [9,10]. Recombination of electrons and holes may also occurs on a very fast timescale without participating in any chemical reactions [5,9,11,12].

**General approaches for water splitting**

Production of Hydrogen, using water splitting technique mainly fall into three categories; photocatalyst system (PC), photoelectrochemical system (PEC), and photovoltaic-photoelectrochemical system (PV-PEC) [13,14]. In photocatalytic system (PC), which is considered as the simplest, cheapest, and for potential scalable method for water splitting. Photocatalyst which form as powders are dispersed in water for water splitting under light irradiation (Figure 2). Photocatalysts possess the advantage that the water splitting can occur in the homogeneous phase without the need of transparent electrodes and without the need of directional illumination [10]. Whereas, PC have many disadvantages that limit its use for water splitting. (1) Separation of the generated hydrogen and oxygen immediately when formed are required, which will consume additional energy, causing low efficiency of water splitting process. (2) The illumination of PC systems without fast removal of the catalysts will eventually cause a photostationary state, where all forward and backward reactions have identical rates, and no more water splitting can take place. (3) Implementing PC system at high scale still challenging. Due to these limitation, PC system will not be covered in this review.
Photoelectrochemical water splitting has been reported for the first time early 1968 by illumination a conductive electrode made from TiO₂ in aqueous solution [15]. The interaction of incident light with TiO₂, generate electron hole pairs, where the holes oxidize water at the TiO₂ surface to generate oxygen, and the electrons travel to the Pt counter electrode to reduce water to produce hydrogen (Figure 3a)[11–14]. In PEC technique, the photocatalysts initially prepared on conductive substrates as electrodes and additional small bias applied for water splitting.

To make this cell, one or both electrodes should be a photoactive semiconductor, where the charge separation forms at the semiconductor/liquid interface (Figure 3b and 3c). When the cell is exposed to sun-light, photogenerated carriers are separated by the space-charge field and the minority charges (holes for an n-type photoanode and electrons for a p-type photocathode) travel to the semiconductor electrode-liquid interface for reaction [17]. Compared to photocatalyst system (PC), PEC have advantage that there is no need for gas separation in PEC systems because the generation of H₂ and O₂ is spatially separated at different electrode sides [17,18]. PEC will be described in this review with focus on different semiconductor materials used to fabricate both photoanode and photocathode.

**Photocathode for hydrogen evolution**

Water splitting photocathodes are generally p-type semiconductors and must generate the required cathodic current to reduce water to hydrogen and need to have high stability in aqueous environments. The optimal photocathode material, need to have the conduction band edge potential to be more negative than the hydrogen redox potential. Many earlier studies on electrochemical photocathodes mainly focused on p-type silicon and III–V semiconductor such as InP and GaP. Recently, p-type semiconductor including oxides and sulphide have received lots of attention. In this section, the review is focused on various photocathodes materials, which include monometallic and bimetallic oxides, chalcopyrites, silicon, and III–V semiconductors.

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Figure 1. Fundamental principle of photocatalytic water splitting on semiconductor.

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Cuprous oxide (Cu₂O), cupric oxide (CuO), and nickel oxide (NiO) are among the forefront p-type semiconductors oxide that have been investigated for solar water splitting. They are favourable photocathodes having low cost, earth abundance, and ideal band-gap energies that allow for the absorption of visible light.
Cu₂O
Cuprous oxide is one of the most investigated p-type semiconductors, used for solar water splitting. Cu₂O has a direct band gap of 1.9–2.2 eV [19], which makes it an excellent solar absorber; however, the photocorrosion is the major limitation of Cu₂O [19,20]. Recent studies show that there is a possibility to suppress the photocorrosion of Cu₂O by adding a passivation layer on the surface of Cu₂O (Figure 4a). This layer prevents the direct contact between the Cu₂O surface and the surrounding electrolyte [21]. The best performance of Cu₂O was demonstrated from cathodic reduction of Cu²⁺ ions in aqueous solution with pH 12, where TiO₂ was as a protective layer with photocurrent of −7.6 mA/cm² at 0V vs RHE as shown in Figure 4c [22].

CuO
Cupric oxide (CuO) is another p-type copper oxide with an indirect band gap of 1.2–1.8 eV [23,24], where its small band gap allows CuO to achieve more photocurrent than Cu₂O. However, CuO as a photocathode for water splitting has received less attention than Cu₂O, due to its conduction band, more positive than that of the Cu₂O [25–27]. Though, recent studies on hydrogen evolution by CuO
with composites photocatalysts, confirm the possibility of CuO to reduce water to hydrogen [28–31]. Similar to Cu2O, photocorrosion is another major drawback with CuO as photocathode in water splitting. However, some recent studies show that a reduction in photocorrosion of Cu2O may apply to CuO [31–33].

NiO
Nickel oxide (NiO) is a semi-transparent p-type semiconductor with direct band gap of 3.6–4.0 eV [34]. This wide band gap NiO possess low resistance, high p-type concentration, high hole mobility, and low lattice mismatch with ZnO, which are favourable for formation of p-n heterojunction [34–37]. On the other hand, the photocurrents obtained by NiO photocathode are low due to low potential of its valence band (0.3V vs RHE) [38]. However, sensitizing NiO photocathodes with quantum dots (e. g., CdSe) possess high photocurrent and photopotential as shown in Figure 5a and 5b [37,39].

Bimetallic
CuFeO2
CuFeO2 has a ABO2-type semiconductor delafossite structure with bandgap of 1.5–1.6 eV, which can absorb the entire range of visible light [40]. In addition to its small band gap, CuFeO2 is an earth abundant material with high onset potential and good stability in aqueous solution [40,41]. However, the lack of poor charge transfer, limit its performance for PEC water splitting. Recent studies show that the fabrication techniques, involving post treatment in air with hybrid microwave annealing, enhanced the activity of the electrode which make the CuFeO2 attractive candidate for PEC water splitting as shown in Figure 6a [42]. In Figure 6b and 6c, photocurrent activity of CuFeO2 possess enhancement after modifying with electrocatalyst such as nickel-iron (NiFe) and reduced graphene oxide (RGO) [42].

LaFeO3
Perovskite oxides are quite encouraging materials for PEC water splitting due to their high efficiency and stability in water. LaFeO3 with ABO3 perovskite structure is a promising candidate to be used for water splitting due to its high stability, optoelectronic properties and small band gap energy [43–46]. However, failure to improve their photosresponse limit their use as photocathode which is because of the lack of preparative technique for LaFeO3 photocathode with effective quality [46]. Recent effort
show that the efficiency of LaFeO₃ as photocathode can be improved via doping with metals which have 2⁺ oxidation state similar to that of Fe³⁺, such as Mg²⁺ and Zn²⁺. These dopant agents lead to change the structure and electrical properties of the photocathode which enhanced the overall photoelectrochemical response of LaFeO₃ (Figure 7a and 7b) [47].

CaFe₂O₄
Calcium iron Oxide (CaFe₂O₄) has been discovered for the first time as a p-type semiconductor oxide for use of electrolyse of water [48]. It has band gap of 1.9 eV with suitable conduction and valance band edges of −0.6 and +1.3 V vs RHE, respectively, which is suitable for splitting water [49]. However, the photoresponse of CaFe₂O₄ is relatively low, because of its poor charge separation and charge carrier mobility [50,51]. Moreover, CaFe₂O₄ photocathode with metal doping such as, CuO and Au shows a higher photocurrent response due to the increase absorption wavelength range [52]. Furthermore, CaFe₂O₄ doped with Ag, exhibited 23 times higher photocurrent response than undoped CaFe₂O₄ as shown in Figure 8 [53].

Chalcogenides
To date, some p-type chalcogenides have been studied as a photocathode for solar water splitting. Semiconductors with chalcopyrite structure (e.g., CuInS₂, CuGaS₂), have recently shown significant photocathode performance for solar water splitting due to their excellent photovoltaic properties.
CuInS₂
Copper indium disulphide (CuInS₂) is considered as a promising candidate to be used in thin film solar cells due to its direct bandgap (1.5 eV) and large absorption coefficient \((10^5 \text{ cm}^{-1})\) in the visible spectral range \([54–56]\). Moreover, it is environmentally friendly \([56]\), but the fabrication of CuInS₂ thin film is expensive. Fabrication techniques such as chemical deposition, especially spray pyrolysis possess an attraction solution to this issue where the large area of thin film can easily be coated \([57]\).
Spray pyrolysis at low temperature (about 150–200°C) shows the possibility of CuInS$_2$ thin film on cheap and flexible substrates [57].

**CuGaS$_2$**

Copper gallium disulphide (CuGaS$_2$) is less interesting to be used as photocathode in solar cell than CuInS$_2$ due to its wide direct band gap of 2.4 eV [58]. However, CuGaS$_2$ has conduction band located at more negative potential than that of CuInS$_2$ which make it a possible photocathode for solar water splitting [21,59,60]. In addition to its wide band gap, gallium deposition requires more cathodic potential than that of indium metal, where the fabrication of uniform film remain is challenging [21]. Recent studies suggested that doping CuGaS$_2$ film with co-catalyst such as Zn and Ti enhanced the morphology and phase structure of Cu-Ga photocathode film [61].

**III-V Semiconductors**

**GaP**

Gallium phosphide (GaP) has an indirect band gap (2.2–2.3 eV) and band edges above the reduction potential of hydrogen which is make it suitable material for water splitting [62,63]. The n-type of GaP is unstable in water, but the p-type form has more stability for longer periods of time in electrolytes under cathodic conditions [62]. Despite the wide bandgap of GaP, still it does not show the expected photocurrent [64,65]. Recent investigation show that the influence of the interface structure region between the semiconductor and the electrolyte, depositing of platinum particles on top of GaP notable increased the efficiency of the photoelectrochemical cell [63].

**InP**

Indium phosphide (InP) has a direct band gap of 1.35 eV, which makes it well-matched to the solar spectrum [66–69]. Moreover, its conduction band edge is slightly above the water reduction potential [69]. For these reasons, InP is considered as a promising photocathode for water splitting. Although p-type InP is suffer from photocorrosion in acidic solution [70,71], but the stability and efficiency of InP electrode can be enhanced with protective coat-layer of TiO$_2$ [72]. Despite its efficiency, high cost of bulk materials and fabrication process, InP photocathode limits its scalable application [72]. Latest studies demonstrated a low-cost and high efficiency solar device, implemented using the thin-film vapour–liquid–solid (TF-VLS) growth technique that decreases usage of feedstock materials [73].

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Figure 9. (a) Current-voltage curve of Si coated with various STO thicknesses as protective layer. (b) Voltage versus time curve.

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Silicon

Silicon (Si) has been extensively used for water reduction over the past few decades due to its narrow band gap (1.1 eV) [74,75]. In addition to its small band gap energy, silicon is one of the most promising materials for photoelectrodes in a PEC due to its natural abundance, environmental friendly and ability for large-scale production [76–78]. The practical use of Si as photocathode electrode in water splitting was originally limited due to its instability in water [75]. However, several approaches have been developed to protect its surface from corrosion using protective layers (e.g., ALD of TiO2, Al2O3, and different catalysts layers) to enable more stable PEC performances of Si electrodes in different aqueous environments [70,79–83]. Latest study indicated that Si photocathode deposited with strontium titanate, SrTiO3 (STO), as protective layer achieved photocurrent density of (35 mA/cm2) and long-term stability as illustrated in Figure 9 [77].

Photoanode for water splitting

Photoanode materials, responsible for oxygen evolution must be; an n-type semiconductor, band gap that are suitable for absorb wide range of spectrum, and efficient charge collection and charge carriers’ motilities. In addition to that, the materials must be stable in aqueous solution, low cost, and environmental friendly. This section will focus on the n-type semiconductors that have been investigated as a photoanodic electrode in PEC water splitting. Examples of these materials are monometallic and bimetallic oxides, chalcogenide, and nitride.

Monometallic

TiO2

Titanium dioxide (TiO2), which is an n-type semiconductor having band gap of ~3.2 eV, is considered to be the most promising oxides used in PEC [84–87]. It’s reported for the first PEC water splitting as photoanode under UV irradiation by Honda and Fujishima in 1972 [11]. Due to its excellent stability in aqueous solution, it has been implemented as protection layers for photoelectrodes (e.g., Cu2O, Si, InP, etc.) that are not stable in water [72,81,82]. However, the applications of TiO2 photoanode in PEC water splitting is limited due to its wide band gap. Several techniques have been explored to improve the light absorption and charge carries transport of TiO2 such as doping with cocatalyst (e.g., Co and Ag) (Figure 10). For example, N-modified TiO2 photoanode,

Figure 10. (a) Linear sweep voltammetry of, TiO2 nanowire arrays (blue), Cobalt doped TiO2. (b) Chronoamperometry measurement of TiO2 nanowire arrays and the same film after treated with cobalt and silver.
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which were synthesized via the nitridation of hydrothermally synthesized TiO$_2$ nanowire arrays in NH$_3$ atmosphere, obtained a band gap of 2.4 eV [88]. Additionally, TiO$_2$ nanotubes treated with heat and chemical reduction demonstrated enhanced photocatalytic activity, with a photocurrent of 2.0 mA/cm$^2$ at 1.23 V [89].

ZnO
Zinc oxide (ZnO) is also an n-type semiconductor which is environmentally friendly and inexpensive [90–92]. It has band gap of 3.2 eV, similar to TiO$_2$ but higher carrier mobility [91–96]. Nevertheless, the effective applications of ZnO as photoanode for water splitting still requires the improved design and synthesis technique to overcome the limitations of ZnO [97]. Recent studies revealed that by controlling the morphology of ZnO, the light harvesting ability can be enhanced by thermal evaporation approaches and a photocurrent of ~0.4 mA/cm$^2$ at applied potential of 0.8 V$_{Ag/AgCl}$ is achieved [97,98].

WO$_3$
Tungsten oxide (WO$_3$), an n-type semiconductor has been well studied as photoanode for water splitting compared to their other metal oxides. It has an indirect band gap of 2.5–2.8 eV which can harvest about 12% of the solar spectrum [99]. WO$_3$ is an inexpensive, nontoxic, and possess high stability in acidic aqueous solution [99–101]. However, this material can only absorb a limited portion of visible light due to its wide band gap [99]. Moreover, its conduction band is too low (0.3 V vs RHE) compared to Hydrogen evolution reaction redox potential [102]. Recent studies have demonstrated that morphological control and hydrothermal treatment can significantly affect the morphology of the synthesized electrode and may exhibit a far higher enhancing photocurrent of WO$_3$ [103,104]. In particular, it was shown that fabricated WO$_3$ nanospheres by removing the top platelets of WO$_3$ via a hydrothermal method exhibited a photocurrent of 2.6 mA/cm$^2$ at 1.2 V [104].

$\alpha$-Fe$_2$O$_3$
Alpha-Hematite ($\alpha$-Fe$_2$O$_3$) is undoubtedly the most extensively studied n-type semiconductor to be used in water splitting. It has band gap of 2.0–2.2 eV which absorb a significant portion of visible light with efficiency exceeds 12% [17,105–107]. It is also stable in most of the aqueous media, and has high resistance towards photocorrosion [17,108,109]. In addition, it is environmental friendly and inexpensive but it has low absorption efficiency, low electrical conductivity, short diffusion length (2–4 nm), and facile surface recombination are serious challenges for its used in practical application as a photoanode [110]. To overcome these limitations, several synthesis techniques and strategies have been developed, which include surface modification and composition [108,111,112]. Surface modification with catalysts such as IrO$_2$, aim to reduce the overpotential and thus enhanced the efficiency [113,114], while composition aims to increases charge mobility [114]. Recent study reported that preparing $\alpha$-Fe$_2$O$_3$ film by electrodeposition method followed by surface decorating with Co-Pi catalyst showed a stable photocurrent of ~1.89 mA/cm$^2$ at 1.23 V vs RHE as presented in Figure 11 [115].

Bimetallic
BiVO$_4$
Another n-type semiconductor is Bismuth vanadate (BiVO$_4$), which is recently emerged as a viable candidate for photocatalytic water splitting. It has band gap of 2.4 eV and can absorb a significant portion of the visible spectrum [116,117]. It has a suitable conduction band position very near to the H$_2$ evolution potential, and relatively low onset potential for O$_2$ evolution [118,119]. However, BiVO$_4$ lacks low photocurrent efficiency under solar radiation, fast electron–hole recombination, slow charge transfer, and low water oxidation kinetics [120–122]. To overcome these drawbacks, several
techniques has be applied such as construction of heterojunction structures, morphology control, and doping. Previous works have demonstrated that BiVO$_4$ heterojunction WO$_3$/BiVO$_4$ less than 1.0 mA/cm$^2$ at 1.0 V vs RHE [123,124]. A significant enhancement has been achieved using a double-heterojunction photoanode based on BiVO$_4$/WO$_3$/SnO$_2$ triple layers prepared by spin coating, which has increased the PEC photocurrent to 3.1 mA/cm$^2$ at 1.23 V vs RHE as presented in Figure 12 [125].

Figure 11. (a) J-V measurements with chopped light for Co-Pi/$\alpha$-Fe$_2$O$_3$ films at different deposition times (300 s, 600 s, and 1,200 s). (b) Photocurrent versus time curve of $\alpha$-Fe$_2$O$_3$ and 600s Co-Pi/$\alpha$-Fe$_2$O$_3$ photoanode.

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Figure 12. (a) PEC photocurrent potential (J-V) curves of five photoanodes (i.e., BVO = BiVO$_4$, B/W = BiVO$_4$/WO$_3$, B/S = BiVO$_4$/SnO$_2$, B/S/W = BiVO$_4$/SnO$_2$/WO$_3$, B/W/S = BiVO$_4$/WO$_3$/SnO$_2$). (b) Photocurrent density and solar to hydrogen conversion efficiency as a function of time for the BiVO$_4$/WO$_3$/SnO$_2$ photoanode tandem cell.

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CuWO$_4$

Copper tungstate, also known as copper tungsten oxide (CuWO$_4$) is an n-type semiconductor with indirect optical band gap of 2.3 eV [126–128]. It has been widely studied for different applications such as detector, lasers, and optical sensor [127–129]. Due to its small band gap, it is very close to ideal...
potential for PEC water spiting as promising photoanode material [128,130]. In addition, single crystal of this materials have maximum conversion efficiency of 0.52% [127]. The PEC of CuWO4 is significantly low due to its low absorption light and high bulk charge transfer resistance [130–133]. Several approaches such as surface modification and construction of heterojunction structures can help to mitigate some of its PEC water splitting limitations. Recent studies demonstrated that modification of the CuWO4 photoanode surface with TiO2-coated Au NPs can significantly increase the PEC water-splitting performance and increased the water splitting photocurrent from 0.03 to 0.1 mA/cm² (Figure 13) [134]. Coupling CuWO4 with WO3, to form heterojunction photoanode can enhanced the absorbed photon density and charge mobility [135,136].

Nitride and Oxynitride

TaON

Tantalum oxynitride (TaON) with band gap of 2.5 eV is another n-type semiconductor, suitable for solar water splitting [137–139]. It has achieved a maximum quantum efficiency of 34% [140]. Moreover, TaON shows reasonably alignment of its CB and VB edges relative to the OH⁻/O₂ oxidation and H⁺/H₂ reduction potentials, generate H₂ and O₂ [137]. However, the activities for H₂ production is lower than those for O₂ evolution, which is sufficiently negative for H₂ production [141]. TaON suffer from low stability due to the introduction of N 2p orbitals in the valence band [137]. Recent studies has demonstrated that the photocatalytic activity of TaON for water splitting can be enhanced through photo-deposition with noble nanoparticles such as Ru [142]. Also, a significant enhancement to the photocurrent in TaON photoanode by heat treatment of the surface with TiCl₄ has been reported (Figure 14) [143].

Ta₃N₅

Tantalum nitride (Ta₃N₅) has received significant attention over the past years due to its small band gap (2.1 eV) and stability [139,144–147]. It has CB lies at ca.–0.4 V vs. RHE, and VB lies at ca. +1.6 V vs. RHE, which possibly allow Ta₃N₅ to perform unassisted solar water splitting [144,148]. Due to these band energies, Ta₃N₅ can theoretically split water spontaneously as a single photoanode with maximum solar to hydrogen efficiency of about ~15% [148–150]. However, Ta₃N₅ suffer from the poor charge transport, low photocurrent efficiency and insufficient light absorption [151–153]. Effective strategies have been developed to enhance the PEC performance of Ta₃N₅ photoanode, such...
as nanostructuring and morphology control [154,155]. Particularly, Ta₃N₅ photoanode with a 1D configuration, such as nanotubes (NTs), nanorodes (NRs), have been considerably investigated [151,152,156–160]. These 1D nanostructure offer advances of charge transfer to the solid-liquid interface without recombination and high absorption of incident light. Ta₃N₅ nanorod arrays modified by Co(OH)ₓ co-catalyst yields a stable photocurrent density of 2.8 mA/cm² at 1.23 V vs RHE as illustrated in Figure 15 [157].

Chalcogenides

CdS

Cadmium sulphide (CdS) is the most investigated metal chalcogenide materials for water splitting under visible light irradiation due to its favourable direct band gap (2.4 eV). Furthermore, its band edge positions are suitable for water splitting to produce hydrogen and oxygen [161,162]. Despite these advantages, the photocurrent activity of CdS is not sufficient due to the photogenerated charges (electrons and holes) which cannot be efficiently separated and transferred [162–164]. Additionally, CdS suffer from photocorrosion in aqueous media which hampers their long term stability in solar water splitting [161,165]. To overcome these drawbacks, extensive studies have been investigated to improve the stability and efficiency of CdS photoanode. Recent studies demonstrated that, formation of CdS 2D-nanostructure offer significant advantages such as, reduction of the scattering rate which increase the carrier collection efficiency and increase the absorption of incident light [166].
ZnS

Zinc sulphide (ZnS) is a promising candidate for photocatalysis of hydrogen production due to its ability, generation of mobile photo excited charge carriers, and high conduction band potential which ensures fast electron transfer [167–170]. Moreover, it has active sites for hydrogen evolution without the need to deposit expensive charge transfer co-catalyst like Pt or RuO₂ [171]. But due to its large band gap (≈3.6 eV), the performance in photocatalysis is limited, which means that pure ZnS are only active under UV irradiation [172,173]. Therefore, several studies have been investigated to improve the light absorption behaviour of ZnS photoanode. For instance, it has been reported that doping ZnS with transition metal ions such as Ni, Sn, and Cu has improved the H₂ production under visible light irradiation [174–176]. An alternative approach to doping is the defect engineering, which also increase the overall efficiency of ZnS [177]. Moreover, the modification of the fabrication conditions can lead to defect states in ZnS thin films which also enhance visible-light absorption, charge separation, and photocurrent up to 1.6 mA/cm² [177].

Current state of the art for water splitting

Tandem approach

Photoelectrochemical (PEC) water splitting is considered as a promising technology to convert solar energy into storable and transportable fuel. Potential energy greater than 1.23 eV should be sufficient to split water. However, the actual required energy is considerably greater due to the different kinetic and thermodynamic non-idealities in the oxidation and reduction reactions. Therefore, using a single semiconductor absorber, requires a semiconductor with large energy bandgap to absorb a maximum portion of the solar spectrum [178]. This drawback, can be solved by dual-absorber-four photon (D4) tandem approach (Figure 16) [179]. In PEC tandem device, the cell configuration is composed of two sided light absorption electrodes, a p-type photoanode and a n-type photocathode, where hydrogen evolution (water oxidization) and oxygen reduction (water reduction) reactions take place on the photocathode and photoanode, respectively [179].

Tandem cell has an improved overall efficiency due to the two different band gaps used and the high portion of the light absorbed. It show a theoretical estimated light conversion efficiency of 18% [180]. Tandem cell used a III–V semiconducting materials have been shown to perform with efficiencies of 12.4% under concentrated sun light [181]. Though, their commercial applications still far to achieve
due to poor stability, high cost and complexity of their fabrication [182]. To reduce the cost, increase stability, and enhance the efficiency, several methods have been proposed [179,183–188]. Recently, Graetzel et al. reported a perovskite tandem solar cell based on CH3NH3PbI3 and achieved solar-to-hydrogen efficiency of 12.3% [189].

PEC/PV approach

Due to the difficulties in designing PEC tandem cell with sufficient bandgap energies and band edge positions of photocathodes and photoanodes; photovoltaic-integrated photovoltaic-electrochemical cells are attractive approach for mitigating this aspect. In this configuration, the bandgap energy levels in PEC cells have no role with the water redox due to PV cells could play the direct role of potential supply; therefore, there are no limitations on selecting the material type (Figure 17) [184]. PV-PEC systems possess many advantages for water splitting compared with PEC systems, excluding major cost. PV-PEC device has been developed for the first time for hydrogen production via water
splitting in 1998, using a GaInP₂/GaAs tandem cell which has achieved more than 10% efficiency [181].

Moreover, coupling a WO₃/BiVO₄ photoanode with a double junction GaAs/InGaAsP solar cell, to build a self-operating integrated PEC device, generated solar to hydrogen efficiency of up to 8.1% [118]. The highest efficiency of PV-PEC approach was recently achieved through fabrication of an integrated system with Ni electrodes and multi-junction GaInP/GaAs/Ge solar cell, delivered solar water splitting efficiency of about 22.4% [190]. Despite this high efficiency, the fabrication of PV-PEC solar cells is complicated and expensive. Without considering the cost factor, PV-PEC systems are the most viable hydrogen production method for the practical applications. PV-PEC system based hydrogen production is expected to be primarily used in navigation, military, and aerospace applications to provide fuel for these special situations.

Conclusion and outlook

Significant increase in research activity around the solar hydrogen production via direct water splitting under sunlight has been achieved in the last decade.

- In this review, we present the fundamental mechanisms and basic principle of water splitting.
- We investigated the common engineering strategies of hydrogen production via solar water splitting.
- Many semiconducting materials such as p-type, n-type, nitride, and chalcogenide have been successfully developed as a photocathode and photoanode for PEC.
- Advanced PEC applications such as tandem cell and PV-PEC hybrid system have possessed significant solar to hydrogen efficiency.
- The solar to hydrogen efficiency of different approaches has been improved to more than 12.3% and 22.4% for PEC and PV-PEC water splitting systems, respectively.
- Solar driven hydrogen production is ideal pathway to produce green energy but it faces many challenges to achieve this goal.
- Significantly, several factors such as stability, electronic properties, structure, surface states and morphology of catalysts, cost, and toxicity need to be carefully considered to drastically improve the hydrogen production efficiency through solar water splitting in practical applications.

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Competing interests

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