Review

Current perspectives in engineering of viable hybrid photocathodes for solar hydrogen generation

Hoang V Le\textsuperscript{1,2}, Thi Ly Le\textsuperscript{3}, Ung Thi Dieu Thuy\textsuperscript{1,4} and Phong D Tran\textsuperscript{3}

\textsuperscript{1} Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam
\textsuperscript{2} Department of Physics and Technology, Thai Nguyen University of Sciences, Tan Thinh ward, Thai Nguyen, Vietnam
\textsuperscript{3} University of Science and Technology of Hanoi, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam
\textsuperscript{4} Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

E-mail: tran-dinh.phong@usth.edu.vn and dieuthuy@ims.vast.vn

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Abstract
Photoelectrochemical water splitting represents an attractive technological solution to harvest and then store the solar energy which is abundant but intermittent. It can be achieved by employing a photoelectrochemical cell, also called an artificial leaf. In order to construct viable photoelectrochemical cells, efforts are being dedicated to engineer robust and efficient photocathodes for solar H\textsubscript{2} generation and photoanodes for solar water oxidation reaction. In this article, we discuss on the recent achievements and current perspectives in engineering of viable hybrid photocathodes. The state of the art on the design of a hybrid photocathode, its performance as well as the current understanding of its mechanistic operation will be first described. We then discuss on the technical strategies that are currently being developed to enhance the robustness and performance of a hybrid photocathode.

Keywords: solar energy, water splitting, photoelectrode, catalysis, assemblage
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1. Introduction

Solar represents the most abundant renewable energy being available to the human. Thus, the exploitation of solar energy in an efficient manner could be a decisive action to address to the ever increasing of the global energy demand as well as to solve the environmental issues associated with the burning of the fossil fuel. However, the solar energy is intermittent. Therefore, viable technology to harvest and store the solar energy is urgently demanded. Solar-to-chemical energy conversion is such a desirable technology wherein the solar energy is harvested into the chemical energy that is stored within the small molecules like H\textsubscript{2}, HCOOH, CH\textsubscript{3}OH, etc [1–4]. These molecules, also named as solar fuels, could be then collected, re-distributed and used per demand as alternatives to the fossil fuels. Within the potential solar fuels, H\textsubscript{2} has highest energy density per weight of 273 KJ mole\textsuperscript{-1} but very low density per volume, being close to zero [5]. ‘Burning’ H\textsubscript{2} fuel within a proton exchange membrane fuel cell generates energy and only H\textsubscript{2}O as by-product. Therefore, H\textsubscript{2}
is considered as the best energy carrier (fuel) for the future. Recently, actions toward a H2 economy are being engaged in some states and regions.

\[
\begin{align*}
2H^+ + 2e^- & \rightarrow H_2, \\
2H_2O & \rightarrow 4H^+ + 4e^- + O_2, \\
2H_2O & \rightarrow 2H_2 + O_2.
\end{align*}
\]

Solar-to-H2 conversion via the photoelectrolysis of water (equation (3)) could be achieved by employing an appropriated photoelectrochemical cell (PEC) that is also named as artificial leaf [2, 4]. Actually, several configurations have been proposed for construction of such a PEC [6–8]. Among these configurations, the Z-scheme dual-photoelectrodes represents the most challenging one. It consists of a photocathode where the hydrogen evolution reaction (equation (1)) occurs and a photoanode where the oxygen evolution reaction (equation (2)) occurs. These two electrodes are wired by an Ohmic connector like metal, transparent conducting oxide (TCO) or carbon-based materials (figure 1). Ideally, these two electrodes are kept in two compartments separated by a proton exchange membrane like Nafion® that allows separately collect H2 and O2 products. Indeed, avoiding the formation of an explosive O2-H2 gas mixture is critical for the large scale production of H2 fuel in the industry.

To date, while significant advances have been achieved for the construction of a PEC composed of a photovoltaic-electrolyser assemblage [9–11], just few examples have been reported for the construction of a Z-scheme PEC [12–17]. It is quite controversy when seeing that great efforts have been mobilized and numerous achievements have been made in the development of photocathodes and photoanodes for solar water hydrogen production and solar water oxidation, respectively. However, majority of these photoelectrodes are not ‘matching’ to be wired within a Z-scheme PEC device. Figure 2 shows the typical I-V curves of two photoelectrodes within an operating Z-scheme PEC device (blue and red bulk traces). The primary requirement is suitable onset potential allowing these two photoelectrodes operate when they are wired without applying an external bias. However, majority of photocathodes shows small anodic onset potential while the photoanodes shows low cathodic onset potential (blue-dash and red-dash traces). Moreover, the solar-to-H2 conversion yield depends on the operating current \(j_{\text{op}}\) [2]. To achieve a conversion yield of 10% under the standard 1 Sun irradiation (100 mW cm\(^{-2}\)), a minimum \(j_{\text{op}}\) of 8.2 mA cm\(^{-2}\) is needed. This represents a great challenge for instance. Indeed, while several photocathodes can offer a short-circuit photocurrent \(j_{\text{SC}}\) of few-tens mA cm\(^{-2}\) (see following sections and table 1), most of the reported photoanodes showed low \(j_{\text{SC}}\) of 1 ÷ 4 mA cm\(^{-2}\) or even less. The record of 6.1 mA cm\(^{-2}\) was reported for a BiVO4/CoPi photoanode very recently [18]. Other than the H2 production yield, a PEC device is expected to operate continuously for over 1000h. The latter demand is critical in order to make solar H2 competitive with that produced from the natural gas. It means each single photocathode and photoanode should be stable for a longer period of operation. For instance, to the best of our knowledge, majority of promising photocathodes only last for minutes to few-hours under the operation.

Thus, efforts are being mobilized worldwide in order to address the technical challenges mentioned. In this article, we review the current trenches being developed in engineering of viable hybrid photocathodes for the hydrogen generation. The current development of photoanodes could be referred to several articles published elsewhere [7, 19–23]. We first describe the principal operation of a hybrid photocathode composed of a light harvester and a H2-evolving catalyst. We then discuss on potential strategies being employed to enhance the solar light harvesting performance, including the identification of novel component and the creation of innovative nanostructure for the light harvester. We last our discussion by highlighting the strategies being used to assemble a light harvester with an appropriate catalyst to create a hybrid photocathode with enhanced photocatalytic performance and stability.

![Figure 1. Schematic presentation of a Z-scheme dual-photoelectrodes PEC device.](Image 1)

![Figure 2. Overlaid I-V curves of a p-type semiconductor photocathode and an n-type semiconductor photoanode in perspective of constituting a bias-free PEC device for the solar water splitting. Bulk traces: desired performances; dash traces: actual performances of majority of photoelectrodes reported in the literature.](Image 2)
2. Principles of photocathode operation

2.1. Elemental steps

The elemental steps occurring within a hybrid photocathode for the solar H₂ generation are schematically presented in figure 3. The ‘wanted’ steps involve the light absorption (ia), charge separation (iia), charge diffusion within the bulk volume of light harvester (iib), electron quenching at the light harvester/catalyst interface (iica) and the catalytic evolution of H₂ on the surface of catalyst (iiv). The yield of the (i), (iia) and (iib) elemental steps could be tuned by selecting an appropriate semiconductor that has small or narrow band gap, high light absorption coefficient and high charge mobility. The yield of the (iica) step depends on the surface state, e.g. defects, dangling bonds of the light harvester. It also strongly depends on the band offset between the conduction band potential of the semiconductor and the work-function of the catalyst. The last step (iiv) is governed by the intrinsic catalytic activity of the H₂-evolving catalyst. Thus, it depends on the choice of catalyst.

In parallel to the wanted process, ‘un-wanted’ processes occur in any photoelectrode. These processes lower or even suppress the photoelectrode performance. These processes include light transmission and reflection (ib), charge recombination within the bulk volume (iib) and on the surface of the light harvester (iib), the photo-induced/chemical degradation of the light harvester (ivb) and the degradation of catalyst layer due to its intrinsic deactivation or its progressive detachment from the electrode surface during the operation (v). The (ib)–(ivb) steps depend on the choice of materials as well as its structure at the nanoscale. The choice of catalyst as well as the manner how it is grafted on the surface of light harvester could limit or even suppress the step (v).

In following sections, we discuss in details on current trenches being developed to promote the wanted processes while limit or remove the un-wanted ones.

2.2. Current achievement on H₂-evolving photocatalytic performance

2.2.1. Performance assay. Usually a three-electrode configuration is employed to assay the photoelectrochemical property of a photoelectrode (photocathode and photoanode). This assessment is usually called as a half-cell analysis. A typical photogenerated I-V curve, e.g. under the standard 1 Sun irradiation, is schematically presented in figure 4. From this measurement, key parameters are deduced: onset potential representing the smallest applied potential that is required to drive the photocathode functioning; short circuit photocurrent j_{sc} representing the maximal current when there is no external potential applied to the photocathode; j_{hv} representing the current generated at thermodynamic equilibrium potential of the 2H⁺/H₂ redox couple. Fill-factor (ff) can be also deduced suggesting how the photocathode is close to an ideal photodiode.

From this half-cell analysis, the half-cell solar-to-hydrogen conversion yield (HC-STH) could be deduced as the product of the potential gained and the photocurrent (1) [24]. The gain in potential of the photocathode is determined by the difference of the potential applied \(E_{\text{RHE}}\) to generate the photocatalytic current \(j\) from the hydrogen equilibrium potential \(E^{\circ}_{\text{H}^{+}/\text{H}_{2}}\). The latter is actually 0 V versus RHE. Whereas \(P_{\text{sun}}\) is the power density of the sun light reaching the photocathode. In practical, it is usually fixed at 100 mW cm⁻² (standard 1 Sun). We note that the calculated HC-STH value is only meaningful when the current-to-H₂ yield, namely Faradic yield \(n_{F}\), is unity. It means there is no other redox reaction occurred on the photocathode rather than the desired H₂-evolving reaction. Thus, an experimental quantification of the amount H₂ produced is compulsory.

\[
\text{HC-STH} = j x \left( E_{\text{RHE}} - E^{\circ}_{\text{H}^{+}/\text{H}_{2}} \right) / P_{\text{sun}}.
\]

Together with the performance, the stability of a photocathode is a critical figure-of-merits. Conventionally, it can be assayed by conducting a long-term photoelectrolysis at a constant applied potential under continuous light irradiation for hours. Evolution of the photocurrent as well as the \(n_{F}\) overtime provide a precise idea on the electrode stability.

2.2.2. Current achievements and remained technical challenges. Briefly, in perspectives of making a high performance PEC device, a photocathode is expected to provide high onset potential (\(V_{\text{OC}}\)), high photocurrent at applied potential of 0 V versus RHE (\(j_{\text{hv}}\)), close-to-unity fill factor, unity Faradic yield, and high stability under the operation conditions. Table 1 showed the best performances that have been reported for some selected photocathodes. The highest onset potential of ca. +0.75 V versus RHE was achieved for a p-GaP/Pt nanowires photocathode immersed in a pH 0 HClO4 electrolyte solution [25]. We note that the highest \(V_{\text{OC}}\) of ca. 0 V versus RHE was reported for a W-doped BiVO₄ photoanode [26]. It indicates the p-GaP/Pt photocathode suitable for assembling with the W-doped BiVO₄ photoanode for
Table 1. Evolving photocatalytic performance of some selected photocathodes.

| Photocathode | $V_{OC}/V_{RHE}$ | $j_0/j_{RHE}$ | $J_{SC}/mA \cdot cm^{-2}$ | $\eta_{STH}$ (%) | Robustness | pH | Remark | Reference |
|--------------|-----------------|---------------|--------------------------|------------------|------------|----|--------|-----------|
| Silicon      |                 |               |                          |                  |            |    |        |           |
| $p$-Si/SrTiO$_3$/Ti/Pt | +0.45 | 25 | 35 | 4.9 | Over 35 h at $-0.2 V_{RHE}$ | 0 | — | [28] |
| $p/n^+$ SIMWs/NiMo | 0.485 | 10.3 | 10.3 | 0 | 0 | 0 | [31] |
| $p/n^+$ Si/Mo/MoS$_2$/[Mo$_3$S$_2$]$^{2-}$ | 0.4 | 17.5 | 17.5 | 0 | 0 | 0 | [32] |
| Si/1T-MoS$_2$ | 0.25 | 17.6 | 26.7 | 0 | 0 | 0 | [33] |
| Si/[Mo$_3$S$_2$]$^{4+}$ | 0.15 | 8 | 12 | 0 | 0 | 0 | [34] |
| Si/$\alpha$-CoMoS$_3$ | 0.25 | 17.5 | 20 | 0 | Over 2 h at $0 V_{RHE}$ | 4.25 | [35] |
| III-V semiconductors |                 |               |                          |                  |            |    |        |           |
| GaP NWs/Pt | +0.76 | 9.8 | — | 2.9 | 5 h at $0 V_{RHE}$ | 0 | ff 0.39 | [25] |
| GaP MWs/MoS$_2$ | +0.71 | 6.4 | — | 1.5 | 0 | 0 | 0 | [25] |
| GaS/$\alpha$/AmGe/$\alpha$/Au/Pt | +1.022 | 22.5 | 22.5 | 17.0 | 11% current loss after 8 d at $0 V_{RHE}$ | 0 | ff 0.725: metal layers protect the cathode | [16] |
| Zn-doped GaP NWs | +0.5 | 0.09 | — | — | — | — | — | [36] |
| GaP/TiO$_2$/Pt | +0.7 | 1.4 | 1.4 | — | — | — | — | [37] |
| GaP/Nb$_2$O$_5$/Pt | +0.7 | 1.1 | 1.1 | — | — | — | — | [37] |
| InP planar/MoS$_2$ | +0.55 | 15 | — | — | — | — | — | [38] |
| InP NWs/MoSe$_2$ | +0.55 | 22 | 22 | 6.4 | 7% current loss after 1 h at $0 V_{RHE}$ | 0 | — | [38] |
| $p$-InP nanopillars/TiO$_2$/RuO$_x$ | +0.73 | 37 | 37 | 14 at $0.5 V_{RHE}$ | Stable for over 4 h at $+0.23 V_{RHE}$ | 0.5 | 6.5 | [39] |
| Chalcopyrite-type semiconductors |                 |               |                          |                  |            |    |        |           |
| Cu(In,Ga)Se$_2$/CdS/Ti/Pt | +0.65 | 25 | — | 5.4 at $+0.3 V_{RHE}$ | 3 h at $+0.3 V_{RHE}$ lost 20% activity | 6.8 | Stability depends on Ti or Mo protective layer | [29] |
| Cu$_2$ZnSnS$_4$/CdS/AMO/TiO$_2$/Pt | +0.25 | 0.6 | 1.5 | — | — | — | — | [40] |
| Cu$_{0.85}$Zn$_{0.15}$Ga$_{0.85}$Se$_{2}$/TiO$_2$/Pt | +0.9 | 9.1 | — | 1.7% at $0 V_{RHE}$ | Stable for over 10 h at $+0.6 V_{RHE}$ | 13 | Higher performance in alkaline pH13 than in neutral pH7 | [41] |
| CuInS$_2$/CdS/TiO$_2$/Pt | +0.6 | 13 | — | 1.82 at $+0.25 V_{RHE}$ | Over 1 h at $0 V_{RHE}$ | 10 | — | [42] |
| Cu$_2$S/CdS/TiO$_2$/RuO$_x$ | +0.48 | 6.0 | 7.0 | — | — | — | — | [43] |
| CuGaSe$_2$ | +0.1 | 3.0 | 10.5 | — | — | — | — | [44] |
| Si/$n^{++}$ - GaN/InGaN/p$^+$ - GaN | +0.5 | 40.6 | 40.6 | 8.7% at $+0.33 V_{RHE}$ | Stable for over 3 h at $0.06 V_{RHE}$ | 0 | 1.3 sun irradiation | [45] |
| Metal oxides |                 |               |                          |                  |            |    |        |           |
| $p$-Cu$_2$O/AMO/TiO$_2$/MoS$_2$ | +0.48 | 6.3 | — | 7.7 at $0 V_{RHE}$ | Degraded gradually over 10 h | 14 | — | [46] |
| Cu$_2$O/Cu$_2$O/BaTiO$_3$ | +0.45 | 4.0 | — | — | — | — | — | [47] |
| Au/Cu$_2$O/BaTiO$_3$/Pt | +0.9 | 1.2 | — | — | — | — | — | [48] |
| $p$-Cu$_2$O/AMO/TiO$_2$/Pt | +0.55 | 6.0 | 6.0 | — | — | — | — | [49] |
| $p$-Cu$_2$O/AMO/TiO$_2$/RuO$_2$ | +0.55 | 5.0 | 5.0 | — | — | — | — | [49] |
| $p$-Cu$_2$O/AMO/TiO$_2$/RuO$_x$ | +0.55 | 8.5 | >10 | — | — | — | — | [49] |
| $p$-Cu$_2$O/AMO/TiO$_2$/Pt | +0.4 | 7.6 | — | — | — | — | — | [49] |
| $p$-CuO | +0.8 | 2.1 | — | — | — | — | — | [50] |
| $p$-CuFeO$_2$/NiFeLDH/RGO | +0.8 | 2.4 | — | — | — | — | — | [51] |
| CuNb$_2$O$_6$ | +0.3 | 0.2 | — | — | — | — | — | [52] |
creating a functioning bias-free PEC. In principle, the highest \( V_{OC} \) of a photocathode is the valence band edge potential of the semiconductor used as light harvester. It means a semiconductor with more positive valence band edge potential could offer higher \( V_{OC} \). For example, the highest \( V_{OC} \) of +0.5 V versus RHE was achieved for a Cu_{2}O photocathode [27] while the highest value for a Si photocathode was ca. +0.4 V versus RHE [28]. Apparently the determined \( V_{OC} \) is a dynamic voltage. It means the electron and hole mobility within the electrode decide on the loss of photovoltage compared with the theoretical maximal. The charge mobility together with the conduction band edge potential and the catalytic activity of the H_{2}-evolving catalyst loaded govern the photo-generated current density, thus the short circuit current density \( j_{SC} \).

To date, the highest \( j_{SC} \) of 35 mA cm\(^{-2} \) was achieved for a \( p \)-Si photocathode protected by a thin epitaxial SrTiO\(_{3} \) [28]. In theory, under the ideal operation conditions, several semiconductors could offer \( j_{SC} \) at the level of over 10 mA cm\(^{-2} \), e.g. 42.3 mA cm\(^{-2} \) for CIGS [29], 14.7 mA cm\(^{-2} \) for Cu_{2}O photocathodes [30]. However, it is very challenging to idealize the structure and the operation of these photocathodes to obtain the theoretical performance. Indeed, the highest current density of ca. 8.0 mA cm\(^{-2} \) was achieved for a Cu_{2}O photocathode [27, 30] while that of ca. 25 mA cm\(^{-2} \) was recorded for a CIGS photocathode [29]. We note that even fill-factor (\( \text{ff} \)) is a critical parameter to appreciate the actually performance of a photoelectrochemical device, e.g. how it performs closely to an ideal photodiode, it is rarely reported for the case of photocathodes.

\[
\begin{align*}
\text{Cu}_{2}\text{O} + 2\text{H}^{+} + 2e^{-} & \rightarrow 2\text{Cu} + \text{H}_{2}\text{O}, \\
\text{Cu}_{2}\text{O} + \text{H}_{2}\text{O} + 2h^{+} & \rightarrow 2\text{CuO} + 2\text{H}^{+}, \\
\text{MS} + h\nu & \rightarrow \text{MS}^{*} + e^{-} + h^{+}, \\
 h^{+} + \text{MS}^{*} & \rightarrow \text{M}^{n+} + \text{S}. 
\end{align*}
\]

Robustness is a figure-of-merits that receives much attention but less remarkable progress has been achieved. To date, the best photocathode was usually assayed for few to few-10h, while the target was 1000h. Perhaps, the research community prefers to ‘wait’ for having operating PEC devices that display high solar-to-H\(_{2}\) conversion yield, before assaying for their long-run robustness. For instance, the best photocathode, namely GaAs/AuGe/Ni/Au/Pt, showed a stable performance for about 8 days during that period only ca. 11% of its initial performance was lost [16]. Majority of the reported photocathodes suffers of catalytic degradation in hour, even in minute scale, due to the dissolution or deactivation of catalyst and/ or the degradation of light harvester. Indeed, the narrow band gap light harvester suffers of a chemical and/ or photochemical corrosion process. The surface of Si electrode is quickly oxidized generating a thin layer of inactive SiO\(_{2} \) even at low concentration of dissolved O\(_{2} \) of 15 ppb [34, 53]. This oxidation process is faster in an alkaline solution than in an acidic solution. As a consequence, Si based photocathodes are usually assayed for their performance in a highly acidic solution, e.g. pH 0 H\(_{2}\)SO\(_{4} \) solution. Cu_{2}O, CIGS materials are chemically stable under the ambient conditions. Hence, handling these materials in air or in electrolyte containing dissolved oxygen is not an issue. However, because the Cu_{2}O/Cu reduction potential and the CuO/Cu_{2}O oxidation potential lie within the Cu_{2}O band gap, it is degraded into inactive Cu by the photogenerated electrons (equation (4)) or into less active CuO (equation (5)) by the photogenerated holes [30, 54–56]. The same oxidative corrosion was usually observed for sulfide or selenide based light harvesters like CdS [57] and CIGS [58]. Under the light irradiation, the photogenerated holes can oxidize these sulfides generating sulfur and metal ions that are subsequently dissolved into solution (equations (6) and (7)). Thus, the identification of appropriate strategies, that allow stabilize these light harvesters again the chemical and photo-induced electrochemical corrosion process, is highly demanded. To this end, few strategies have been developed that will be described in the following section 4.

3. Light harvester for photoelectrode construction

To date, several families of semiconductors have been used as light harvesters for the construction of the H\(_{2}\)-evolving photocathodes (figure 5). In this section we summary the main families with emphasizes on their advantages as well as drawbacks in perspective of a large scale H\(_{2}\) generation. The best performance achieved for photocathodes made of each family of semiconductors is also discussed.

3.1. Silicon

Si has narrow band gap of 1.1 eV that is efficient for harvesting the whole solar spectrum. We note that the theoretical simulation suggested the best material for engineering a photocathode within a PEC device showing ca. 30% solar-to-H\(_{2}\) conversion yield should have narrow band gap of 0.9 eV [59]. It says Si is close to an ideal photocathode material. That explains why Si is one of the photocathode materials that have been most largely investigated. Because Si conduction band lies at −0.5 V versus RHE, it offers enough driving force for driving the H\(_{2}\) evolution with several viable
H₂-evolving catalysts. Indeed, Pt [28, 60, 61], metal alloy like NiMo [31], crystalline MoS₂ [32, 33], amorphous molybdenum sulfide [35, 53, 62] etc were successfully employed as catalysts within Si photocathodes. The main drawback of Si is the rapid oxidation generating an isolating SiO₂ thin layer on the surface of the photocathode even with a trace level of dissolved O₂ in an electrolyte solution. It raises difficulty in manipulation with this material, e.g. the reproducibility of electrode fabrication varies from one electrode to other. Thus, an effective protecting layer is required for the construction of a robust Si photocathode (see following section for electrode protection strategies). Nevertheless, the best photocathode performance ever been reported was achieved with a Si protected by a n-SrTiO₃ layer (table 1) [28].

3.2. III-V semiconductors

p-GaP has small band gap of 2.3 eV being sufficient for harvesting the visible light. Under an irradiation of the standard 1 Sun, a p-GaP photocathode can generate a maximal photocurrent density of 12.5 mA cm⁻² [37]. Its conduction band lies at −1.0 V versus RHE, being extremely large for driving the H₂ evolution reaction [63]. Thus, high H₂ evolution rate of ca. 2 mA cm⁻² at an applied potential of 0 V versus RHE could be achieved with the p-GaP photoelectrode without any H₂-evolving catalyst decorated [25]. Replacing Ga by In reduces the band gap energy. The solid solution GaInP₂ has band gap of 1.8 eV [64] while that of p-InP is 1.3 eV [39]. The latter shows excellent absorption property but its conduction band energy is rather low, located at ca. −0.2 V versus RHE, that requires an efficient HER catalyst like Pt, Ru [39] or amorphous MoS₂ for accelerating the H₂-evolution [38]. Remarkable advantage of these III-V semiconductor photocathodes is the capacity to generate high onset potential, e.g. of 0.6 ÷ 0.7 V versus RHE, under the solar irradiation. That is about 0.2 V more anodic compared with the best Si-photocathode. Thus, for construction of a bias-free PEC device, these III-V photocathodes are more attractive candidates compared with the Si based photocathodes. However, efforts are needed to make these photocathodes viable for long-term application since they suffer from a rapid chemical and photochemical corrosion in air or in aqueous electrolyte, for instance [64, 65]. Furthermore, due to the scarcity and the very high demand of In, the III-V photocathodes may be not very relevant to the large scale generation of solar H₂.

3.3. Chalcopyrite-type semiconductors

Chalcopyrite-type semiconductors, CuInₓGa₁₋ₓS(Se), are popular light harvesters being used for developing the 2nd generation thin film solar cell [66, 67]. These materials show high absorption coefficient, e.g. of 10⁵ cm⁻¹ in the visible spectral range [42]. Their band gap energy, thus light absorption property, can be easily tuned by varying their chemical compositions, e.g. by changing the In/Ga atomic ratio. CIGSe has a narrow band gap of 1.2 eV, very close to that of the Si. However, its conduction band energy is quite deep, lying at −0.2 V versus RHE, that offers only moderate driving force for the H₂ evolution reaction. Thus, an efficient H₂-evolving catalyst requiring very low overpotential like Pt should be used. Indeed, a CIGSe/Cds/Pt photocathode generating an outstanding photocurrent density of ca. 25 mA cm⁻² at applied potential of 0 V versus RHE and a VOC of +0.65 V versus RHE under standard 1 Sun illumination and in a neutral pH electrolyte was reported [29]. Stronger driving force thanks to very negative conduction band edge potential of ca. −1.5 V versus RHE is achieved with a CuGeSe₂ photocathode. In this case, solar H₂ was generated even without any H₂-evolving catalyst loaded on the photocathode surface [44]. However, the valence band of this light harvester locates at ca. +0.2 V versus RHE. As a result, a moderate VOC of +0.05 V versus RHE was obtained. Even the short circuit current density of this electrode was rather high, 10.6 mA cm⁻², that obtained at 0 V versus RHE was only of ca. 3 mA cm⁻². In other words, this CuGeSe₂ photocathode is not likely suitable for assembling with a photoanode for construction of a bias-free PEC.
device. Furthermore, as stated this earlier, due to the scarcity and the very high demand of In element, the CuInGaS\(_x\)Se\(_{1−x}\) photocathode is less relevant for the construction of a viable PEC device that can be used for the large scale generation of solar \(\text{H}_2\). In this context, efforts were paid to search for potential alternatives to these chalcopyrite-type materials. An attractive example is Cu\(_2\)ZnSnS\(_4\) (CZTS) which has a direct band gap of 1.5 eV and conduction band edge potential of ca. −0.7 V versus RHE [40]. This material is composed of only elements being found abundant in the earth’s crust. However, considerable efforts are still needed to further improve the performance of this photocathode. For instance, a moderate performance with photocurrent density of only ca. 0.3 mA cm\(^{-2}\) at 0 V versus RHE and a small onset potential \(V_{OC}\) of +0.25 V versus RHE was achieved under the standard 1 Sun irradiation. Most recently, Tay et al reported an innovative solution wherein Zn within the CZTS was partly substituted by Cd ion [68]. Cd doping was able to passivate the surface and bulk defects, being usually high within a CZTS. Thus, the resultant Cu\(_2\)Cd\(_0.2\)Zn\(_0.8\)SnS\(_4\) photocathode, being interfaced with a \(n\)-type CdS layer, protected by a TiMo layer and activated by Pt HER catalyst, showed an outstanding performance with \(V_{OC}\) of +0.6 V versus RHE and a current density of +17.5 mA cm\(^{-2}\) at 0 V versus RHE.

Being similar to the case of \(n\)-type CdS light harvester, the chalcopyrite-type materials usually suffer of the photocorrosion phenomenon (equations (6) and (7)). Thus, appropriate strategies are needed to protect these photocathodes for long run application. For instance, \(n-p\) junction together with a conducting protective layer is usually employed to improve stability and performance of these photocathodes. Details will be discussed in the following section.

3.4. Metal oxide semiconductors

\(p\)-Cu\(_2\)O represents one of photocathode materials that gained the most attention in recent years thanks to its small band gap \(E_g\) of 2.0 ± 2.1 eV, being suitable for harvesting the visible light, and its high conduction band edge potential being largely sufficient for the \(\text{H}_2\) evolution. Preparation of \(p\)-Cu\(_2\)O can be achieved easily by various methods, including the chemical deposition bath [69–71], electrodeposition [72], or RF-magnetron sputtering [73, 74]. High theoretical photocurrent density of 14.7 mA cm\(^{-2}\) was calculated for an ideal \(p\)-Cu\(_2\)O photocathode suggesting a high photocatalytic performance, potentially [30]. For instance, the best photocatalytic current of 7.5 mA cm\(^{-2}\) was achieved for a \(p\)-CuO/AlO/\(\text{TiO}_2/Pt\) photocathode [30]. It indicates there are still rooms for further improvement of the Cu\(_2\)O-photocathode performance. Moreover, in perspective of making viable photocathodes for the large scale production of \(\text{H}_2\), the \(p\)-Cu\(_2\)O should overcome its intrinsic photocorrosion...
issue (equation (4)) [30, 75]. Due to this corrosion, most of Cu2O photocathodes only last for hours or even minutes under the operation conditions. It is worth noting here that the measured photocurrent is not a full figure-of-merits for evaluating the photocatalytic performance in this case. Indeed, the measured photocurrent maybe not solely relevant to the solar H2 generation but also the electrochemical degradation of Cu2O [54, 55]. Strategies being developed recently to deal with this photocorrosion will be discussed in the following section.

Some bimetal oxides, e.g. those with the spinel structure, have been examined as photocathode materials. Among them, CuBi2O4 is promising that could offer an exceptional positive onset potential of over 1.0 V versus RHE [48, 76]. Indeed, this VOC is suitable for assembling with several photoanode made of BiVO4, Fe3O4 etc for construction of a bias-free PEC device [21, 77]. It is now important to further enhance the H2-evolving rate on this photocathode that readily reaches the level of ca. 1.2 mA cm⁻² under the standard 1 Sun illumination at 0 V versus RHE [48].

4. Nanostructuring as a powerful strategy for improving photocathode performance and stability

As discussed earlier in the section 2.1, the performance of a photocathode is limited by several steps including the light absorption, light harvesting and transportation of charge carriers (photogenerated electron and hole) to the desired collectors, namely the H2-evolving catalyst and hole conductor. Thanks to the current advances in nanotechnology, these steps could be improved, by adopting an appropriate structure for the light harvester.

4.1. Via improving light absorption capability

For a given light harvester, the light absorption can be improved by limiting or removing un-wanted events, including the light scattering and transmission. In general, the light scattering is serious on a surface at nanoscale. However, by patterning the light harvester in a well ordered structure, the light scattering can be turned to positive contribution. In a photocathode made of Si nanowires or nanopillars, scattered photons from one wire can be absorbed by the neighbor ones. As a consequence, the photons are trapped within the Si nanowires and the light absorption is maximized (figure 6, top panel) [78]. Similar approach has been applied for the p-GaP [25], p-InP [38], Cu2O [27] nanowires photocathodes.

It is likely not a big issue to limit or remove the light transmission through the photocathode. First, the photocathode light harvester layer can be fabricated in a good thickness, even in µm scale, since it is supposed to harvest the long wavelength photons [6]. This is in a shape contrast to a photoanode where thin light harvester is desired to harvest the short wave-length photons. Second, the catalyst layer loaded on the electrode surface can act as a reflective or light blocking layer. It is because the light is sent to the photocathode light harvester via a back irradiation, through the photoanode (figure 1). This is also a specific feature of the photocathode in compared with a photoanode counterpart. In the latter case, the O2-evolving catalyst layer should express the highest light transparency.

4.2. Via improving charge separation and transportation

Except for the emerging perovskite where the diffusion length of the charge carriers was determined in µm scale [79–81], it is few to few tens nm for majority of semiconductors. Thus, to limit the charges recombination within the bulk volume, light harvester layer within a photocathode should be made in thickness of few to few-tens nm. However, such an engineering is challenging and likely not optimal since it will let light transmitted in a high yield. In this context, having photocathode with nanowires [27, 60, 62], microwire [82], nanorods or nano-pillars [39] morphology was demonstrated to be an advanced strategy. In a GaP nanowire electrode, the photogenerate hole is collected in the vertical direction while the photogenerated electron diffuses via the horizontal direction to the nanowire surface where the H2 evolution takes place. As a result, five-fold higher short circuit current density was achieved for a GaP nanowires photocathode compared with a planar counterpart (see also table 1) [25].

Another emerging strategy to improve the charge separation and transportation within a semiconductor is via the creation of a p-n junction that generates an internal electrical field to drive the photogenerated electron and hole in the opposite directions. As such, a thin layer of P-doped Si was created onto the surface of a B-doped Si. The P-doped Si layer is also named as the emitted layer. The p-n junction results in significant
enhancement of the charge separation and diffusion within the Si photocathode. Indeed, the best Si photocathodes were fabricated containing P-doped Si emitter [31, 32]. This strategy has been also applied for other semiconductor like InP with a TiO₂ layer [83], Cu₂O with a TiO₂ layer [30], Cu₂S with a CdS layer [43], CIGS with a CdS layer [29], CIS with a bilayer CdS/TiO₂ [42], and CZTS with a bilayer CdS/In₂S₃ [17]. To be used as an added top layer, the n-type semiconductor of choice should offer appropriate band alignment (figure 7). Within this junction scheme, the photogenerated electron drops its original high potential as it now migrates within the conduction band of the n-type layer. As a result, the choice of efficient H₂-evolving catalyst to ‘use’ these hot-pot electrons in an efficient manner may be narrower. Indeed, the conduction band edge potential of Cu₂O is about −0.7 V versus RHE. With this high driving force, most of the H₂-evolving catalysts could operate. However, the available driving force is lowered to −0.17 V versus RHE when a p-Cu₂O/n-TiO₂ junction is created. To operate, a H₂-evolving catalyst that requires low overpotential of about 100 mV for operation is demanded. In other words, the choice of H₂-evolving catalysts must be made carefully. For example, the best choice remains Pt nanoparticles [30]. However, it is worth noting that for a large scale production of H₂ this choice is not really judicious.

Several techniques have been developed to deposit the n-type semiconductor layer on top of the p-type semiconductor for creation of a p-n junction. They include the molecular beam epitaxy [28], atomic layer deposition [30], electrochemical deposition [84], and simple chemical deposition [43]. We note that a large set of experiment parameters needs to be worked out in order to optimize the effect of the added n-type semiconductor layer, thus the operation of the p-n junction. It includes, but not limited to, the thickness of the n-type semiconductor layer, the band gap ligament of the p and n materials, and specially the interface of these two layers. The latter is decided by the lattice constraint between the two materials employed. In fact, the interface between the two layers might contain a high density of defects that serve as recombination traps. Therefore, thermal treatment is usually needed in order to create high quality interface and thus an efficient p-n junction.

4.3. Via improving chemical and photochemical stability

Other than creating a p-n junction, the added n-type semiconductor layer on top of the photocathode, once it is well selected, could allow tuning the surface chemical property of the photocathode and thus changing its chemical or photochemical stability. Talking the case of a Cu₂O photocathode, the added TiO₂ thin layer not only creates an efficient p-n junction but also acts as a protective layer that suppress the diffusion of protons to the Cu₂O electrode surface. As consequence, the photocorrosion described in equation (4) was suppressed. Naturally, large band gap n-type semiconductor oxides that display outstanding chemical and photochemical stability like TiO₂ [30, 40, 42, 64], SrTiO₃ [28], BaTiO₃ [47], Nb₂O₅ [37] etc are valuable candidates for generating a top layer. This layer has a dual functionality, namely p-n junction and protective layer. It also means some n-type semiconductor like ZnO, even if it has suitable band alignment for junction creation, is not a popular choice since itself suffers of a chemical corrosion.

Alternative to a n-type semiconducting layer, a conducting layer could be considered for stabilizing the p-type semiconductor photocathode. To be used, the metal, e.g. Ti, should have lower work function compared with the conduction band edge potential of the light harvester (figure 8) [22, 53, 85]. For example a thin layer of Ti metal, 5 nm in thickness, successfully protected and activated a p-Si photocathode [53]. The activation was generated thanks to a p-Si/Ti Schottky junction. Nevertheless, Ti was not chemically inert causing in generation of a thin outermost layer of TiO₂. A monolayer of N-doped graphene was demonstrated as an outstanding metal-free protective layer that totally suppressed the oxidation, thus the photocatalytic degradation, of a p-Si photocathode [86]. Remarkably, the graphene layer was transferred from a commercial available graphene/Cu substrate onto the surface of the p-Si photocathode by a rather simple method with help of the poly(methyl methacrylate). Thus, it holds great potential for application to other photocathode materials. Graphene layer was also used as an electron acceptor that helped to improve the H₂-evolving activity of Cu₂O nanoparticle based photocatalyst [87]. Alternative to the graphene, amorphous carbon layer that was generated from glucose via a carbonization process showed a promising protecting effect for Cu₂O nanowires photocathode [88]. After a period of 20 min of operation, a carbon-layer-protected Cu₂O lost about 21% photocatalytic
activity while a bare electrode without a protective layer lost 87% of its activity.

Evidently, an isolating layer is not recommended since it blocks electrons that result in a complete passivation of the photocathode surface in regards of the solar H$_2$ generation. The same recommendation is for a conducting polymer. Indeed, adding a conducting polymer could allow tuning the hydrophilic property of the photocathode surface that is suitable to suppress the chemical or photochemical corrosion. As an example, a p-GaP photocathode was successfully protected by a polyvinylpyridine layer, generated via a photo-induced process using 4-vinylpyridine monomer [89]. Unfortunately, conducting polymers, e.g. the polyvinylpyridine, PEDOTs, or PANI, express good conductivity under oxidative potentials but not reductive potentials. Whereas, the H$_2$-evolution operates on the surface of the photocathode under (large) conductive potential. It says, a fine engineering is needed to fabricate a thin layer of polymer, e.g. reservoir and mediator between the light harvester and the proton.

**5. Catalyst/ light harvester assemblage**

**5.1. Catalyst requirement**

As described earlier, the H$_2$ evolution process on a semiconductor surface has slow kinetics. Furthermore, there is a considerable ‘lag’ between a one-photon-one-electron process within the light harvester and a two-electron-two-proton H$_2$-evolving process occurred on the surface of the light harvester. As a consequence, the surface recombination appears to be important that lowers the solar-to-H$_2$ conversion yield within a pure light harvester [90]. To deal with this issue, a H$_2$-evolving catalyst is loaded onto the surface of light harvester. It first quenches electron from the light irradiated harvester and then reduces proton generating H$_2$. By this way, the catalyst acts as an electron reservoir and mediator between the light harvester and the proton. To be used as a H$_2$-evolving catalyst in this configuration, the selected catalyst should satisfy several technical requirements. It should have working function at lower potential than the conduction band of the light harvester to create a suitable junction for a favorable charge transfer. Furthermore, the catalyst should generate a high catalytic current at the driving force offered by the light harvester, namely the conduction band edge potential. For instance, a catalytic current density of 10 mA cm$^{-2}$ is usually used as a figure-of-merits to appreciate whether the catalyst is suitable for assembling with a light harvester [91]. For long term application perspectives, catalyst itself should be last for over 1000h under operating conditions. Evidently, the noble metals like Pt or metal oxides like RuO$_2$ perfectly satisfy these requirements thanks to their outstanding chemical robustness. Alternatively, the transition metal chalcogenides like MoS$_2$ [92], MoS$_x$ [35, 93], MoSe$_x$ [94, 95], Cu$_2$MoS$_4$ [57, 96], phosphides [97, 98], and carbides [99, 100] are promising candidates to replace the above noble metal based catalysts in perspective of creating a viable device for the large scale H$_2$ generation.

**5.2. Fabrication of a light harvester/catalyst assemblage**

Catalyst could be simply loaded onto the surface of a light harvester by employing relative simple technics like dip-coating, drop-casting, spin-coating, spray-coating etc. For example, [Mo$_3$S$_4$]$^{3+}$ catalyst dissolved in a CH$_2$Cl$_2$ solution was drop-casted onto a p-Si pillar electrode surface for creation of a p-Si/[Mo$_3$S$_4$]$^{3+}$ photocathode [34]. We have spin-coated a layer of Cu$_2$MoS$_4$ catalyst onto a p-Cu$_2$O electrode surface protected by a thin layer of NiO for creating the multiple layers p-Cu$_2$O/NiO/Cu$_2$MoS$_4$ photoelectrode [55]. These preparation technics look rather simple that could be practically applied for all catalysts, ranging from small molecule, cluster to solid state compound. However, the resultant electrodes usually have poor mechanical stability wherein the loaded catalyst is slowly detached from the electrode surface during the evolution of the H$_2$ bubbles. As a consequence, the H$_2$-evolving
activity is slowly degraded over time. Vacuum methods like the chemical vapor deposition [33], sputtering [101] are also used e.g. for loading MoS$_2$ or Mo$_2$C thin film catalyst. Thin catalyst layer can be also loaded onto the surface via an electrochemical deposition process. This is applicable if the deposited catalyst requires a deposition potential (and medium) wherein the light harvester is stable without any degradation happened. As an example, amorphous molybdenum sulfide catalyst (MoS$_x$) was loaded via an electrodeposition process on a titanium-protected Si electrode [53]. An attractive strategy, namely photo-assisted electrochemical deposition, is created by innovating the electrochemical deposition process. The light harvester, when it is excited by the light irradiation, creates sufficient reducing potential to reduce [MoS$_4$]$^{2-}$ precursor into a solid MoS$_2$ catalyst that is self-assembled on the surface of the light harvester like CdS [92], $p$-Si [53, 62], or Cu$_2$O [46] electrode (figure 9). The same concept was also successfully applied for the deposition of noble metal oxides like RuO$_2$ [41, 43], or metal alloy catalysts like NiMo [46]. As the catalyst is resulted from the reduction of an appropriate precursor induced by the photogenerated electrons, it is well located on the hot-pot of the light harvester surface. Thus, the communication between the light harvester and the catalyst is somehow maximized to achieve the best electrode performance. However, it is challenging to quantify the amount of catalyst loaded in this technics since after certain deposition time, the H$_2$-evolution occurs in parallel with the catalyst deposition. Thus, kinetic parameters like turn over frequency TOFs for the H$_2$-evolving rate could not be easily quantified in this case.

5.3. Insights into the communication between light harvester and catalyst

The performance of a hybrid photocathode is decided by how the communication between the light harvester and the catalyst is efficient as well as how fast the catalytic H$_2$-evolution is on the catalyst. Roughly, the photocatalytic performance of a hybrid photoelectrode is assayed and compared back-to-back with that of a counterpart made solely of the respective
light harvester without any catalyst loading. As such, with a catalyst layer, superior catalytic current together with a shifting of the onset potential to more positive value are generally recorded [25]. However, to further improve the system, it is desirable to understand more in mechanistic details of the operation, e.g. which step is limiting either the electron transfer from the light harvester to the catalyst or the catalytic H2-evolving on the catalyst. Similarly, understanding the impacts of variable operating parameters on the photocathode performance is critical. Unfortunately, there are not much available tools to examine the mechanistic operation of a photocathode.

A possibility is by using the transient absorption spectroscopic analysis to track the population and lifetime of the photogenerated charge carriers (electron-hole) within a photocathode upon the light excitation. For the case of TiO2 light harvester activated by hybridizing with a CoP catalyst6, electron transfer events were well detailed by employing this technique. It was found that when a monolayer of CoP H2-evolving catalyst was used, photogenerated electron within the TiO2 quickly transferred to the catalyst (in less than 10 μs), resulting an accumulation of valence band holes and a fast depletion of conduction band electrons. Thus, the transient absorption signal of the photoexcited electron showed a lower amplitude while that of the photoinjected holes showed double amplitude compared with those within a pristine TiO2 light harvester without CoP catalyst decoration [90]. The accumulate hole displayed a slow decay dynamics (τ1/2 ∼ 1 ms). Interestingly, it was found that an increment of the excited density (e.g. by increasing laser intensity) caused a faster electron-hole recombination that is not necessary to improve the electron transfer to catalyst, and thus to improve the photocathode performance. With employment of a hole scavenger, the excited electron life time was increased to ~1 s. We noted that this rather better simulates the operation of a photocathode under the real condition where a hole scavenger is readily, e.g. the photoanode in the dual photoelectrode configuration or just an applied external bias in the single photocathode configuration. The ratio of photoinduced electron density per CoP catalyst is the key determinant for the electron transfer rate (figure 10). Lower catalyst coverage is lower electron transfer rate is. Importantly, not only the work function of catalyst but its redox potentials, e.g. CoIII/CoII and CoII/CoI, were found to be critical for the electron transfer rate. In other words, catalyst with lower overpotential for the H2 evolution is more desirable for achieving a higher light harvester-to-catalyst electron transfer rate. It is worth noting that the long-live electron life time was usually at ~1 s, at the best. The Pt catalyst offers a catalytic rate of 0.9 s−1[102], meaning Pt catalyst will be the best candidate for using these photogenerated electrons to reduce H+ into H2 molecule. While most of the Pt-free catalysts operates at 1–2 order of magnitude slower rate, for instance. Thus, there is a need to identify effective H2-evolving catalysts that operate closely like a Pt or a hydrogenase catalyst in perspectives of construction of effective photocathodes.

6 CoP is a cobaloxime catalyst, namely (Et3N)CoIIICl(dmgH)2-(pyridyl-4-hydrophosphonate).

Electrochemical Impedance Spectroscopy represents another method for tracking the electron transfer rate within a photocathode under operating condition. Impedance spectra are recorded at different applied potential, under light irradiation and at different frequency [35, 85]. Typically, a photocathode composed of only light harvesting component without any catalyst loading showed only a single arc corresponding to a direct electron transfer to the electrolyte. In that case, very huge resistance is calculated indicating for a slow kinetic of the H2 evolution on the surface of light harvester. When a HER catalyst layer was loaded, Nyquist plot shows two arcs representing the light harvester-to-catalyst and catalyst-to-electrolyte electron transfers (figure 11). Employing an appropriate electrical circuit equivalent, these experimental data could be fitted providing the resistances of each electron transfer event, e.g. harvester-to-catalyst (Rbapping) and catalyst-to-electrolyte (Rct) [35, 85]. Higher resistance means slower electron transfer rate that indicates a non-efficient event. For the case of Si/CoMoSx and Si/MoS2 photocathodes operated in a pH 4.25 and under 1 Sun illumination, we found that the limiting step was the excited Si-to-catalyst electron transfer whose resistance is about 1 order of magnitude higher than that of the catalyst-to-electrolyte event. This result indicates that to further improve the electrode performance attention should be paid to get a better Si/catalyst interfacing rather than creating more active sites on the catalyst layer. It was also found that the CoMoSx, acted both as a better electron accepter a more active HER catalyst compared with the MoS2 analogous. As a consequence, the Si/CoMoSx showed much higher H2-evolving performance [35]. In some cases, when the catalytic rate is slow and limiting step, the catalyst intermediates could be identified by spectroscopic analysis.

6. Conclusions

To conclude, several families of semiconductors have been examined as light harvesters for the construction of efficient photocathodes for the solar H2 generation. For the H2-evolving catalyst component, both noble-metal-catalysts like Pt, RuO2 and noble-metal-free catalysts like MoS2, CoMoSx have been employed to accelerate the H2 evolution process on the surface of light harvester. Large variety of methods have been developed for light harvester/catalyst assembling. Among these methods, the photo-assisted electrodeposition offers a relatively robust and efficient assemble that gains more and more attention recently. For instance, Si-based photocathode generates the highest photocurrent density (at applied potential of 0 V versus RHE) recorded of about 35 mA cm−2 under 1 Sun illumination [28]. Whereas the highest (most positive) onset potential, Voc of over +0.75 V versus RHE, was achieved for a p-GaP photocathode [25]. The latter also showed a relative high short-circuit current density jSC of over 10 mA cm−2. This current density is sufficient to generate a solar-to-H2 conversion yield of over 10%, that is expected for a viable PEC device. Thus, for generating a bias-free PEC device several efficient photocathodes are readily available. However, the robustness of these photocathodes till remains as a very challenging main issue. For instance, most of high performance photocathodes like Si,
Cu$_2$O, GaP etc suffers of a rapid chemical/photochemical corrosion during the photocatalytic operation. Thus, both development efforts to make these photocathodes more stable and research efforts to identify novel stable photocathode materials are urgently needed.

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