Solar-to-Chemical Fuel Conversion via Metal Halide Perovskite Solar-Driven Electrocatalysis

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**ABSTRACT:** Sunlight is an abundant and clean energy source, the harvesting of which, could make a significant contribution to society’s increasing energy demands. Metal halide perovskites (MHP) have recently received attention for solar fuels generation through photocatalysis and solar-driven electrocatalysis. However, MHPs photocatalysis is limited by low solar-energy conversion efficiency, poor stability and impractical reaction conditions. Compared tophotocatalysis, MHP solar-driven electrocatalysis not only exhibits higher solar conversion efficiency, but is also more stable when operating under practical reaction conditions. In this Perspective, we outline three leading types of MHP solar-driven electrocatalysis device technologies now in the research spotlight; namely, (1) photovoltaic-electrochemical (PV-EC), (2) photovoltaic-photoelectrochemical (PV-PEC) and (3) photoelectrochemical (PEC), approaches for solar-to-fuel reactions including water-splitting and the CO2 reduction reaction. In addition, we compare each technology to show their relative technical advantages and limitations, and highlight promising research directions for the rapidly emerging scientific field of MHP-based solar-driven electrocatalysis.

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**KEYWORDS** Metal halide perovskite, solar-driven electrocatalysis, solar-to-fuels conversion, water-splitting, CO2 reduction

Climate change and atmospheric pollution due the burning of fossil fuels are of significant, immediate and future, societal concern. Annually, roughly 35 GT of CO2 are released as the main combustion product of fossil fuels, which far exceeds the amount fixed by plants via photosynthesis.1 Developing renewable and environmentally benign technologies to replace fossil fuels is critical for securing the sustainable development of society. Among renewable energy sources, solar energy is the most abundant energy source; each year, thousands of times more solar energy reaches the earth than the global primary energy consumption.2 Therefore, the efficient utilization of solar energy is one of the most promising options toward sustainably addressing future energy demands and reducing our reliance on fossil fuels.

Metal halide perovskites (MHPs) are a family of ionic semiconducting materials with a general formula of ABX3, in which A is monovalence cation (methylammonium (MA+), formamidinium (FA+), Cs+, *etc*.); B is a bivalence metal ion (Pb2+, Sn2+, *etc.*); and X is a halide ion (Cl- , Br- or I-) (Figure 1A).3 Owing to their excellent optoelectronic properties, including large absorption coefficients, tunable bandgap, long charge carrier lifetimes and diffusion lengths, and relatively low trap densities,4–6 MHPs have recently emerged as a promising material for solar energy capture and utilization.7,8 In 2009, methylammonium lead iodide (MAPbI3) perovskite appeared for the first time in photovoltaics (PVs), converting solar energy to electrical energy with a reported efficiency of 3.81%.9 Since then, through the combined efforts of a relatively large, international research community, the solar energy conversion efficiency of MHP PVs has now surpassed 25%.10 However, the grid-scale application of PVs still requires effective energy storage for load matching and transportation applications. From this perspective, the direct conversion of solar energy into chemical energy/fuels represents a promising option that could help meet these needs and can also at least partially integrate into existing infrastructure increasing the economic viability.



**Figure 1.** (A) Crystal structure of a 3D halide perovskite ABX3. Different configurations of solar-driven electrocatalysis, (B) PV-EC, (C) PV-PEC, and (D) PEC.

Photocatalysis and solar-driven electrocatalysis represent promising and effective ways to transform sunlight into chemical energy directly.11–15 In general, photocatalysis and solar-driven electrocatalysis require three underpinning processes: (i) light harvesting, usually by a semiconductor, which absorbs photons with an energy equal to or greater than the bandgap and generates photoexcited electron and hole pairs; (ii) separation and independent migration of the photogenerated electrons and holes to the reactive sites on the surface of the catalyst/electrode and this without recombination; and (iii) reduction and oxidation of reactants, adsorbed at the surface of the catalyst/electrode (often decorated with additional redox cocatalyst), which are reduced and oxidized by the photogenerated electrons and holes, respectively, to produce target products.11

However, the reaction conditions of most photocatalytic reactions, such as H2O splitting, CO2 reduction, and environmental remediation, are not suitable for MHP, because they operate in aqueous mixtures or require polar solvents, which can cause the rapid decomposition of the ionic MHP structure.7 Therefore, although MHP PVs have continuously improved since 2009, the use of MHP for photocatalysis was not reported until 2016. The first report of MHP photocatalysis was by Park and coworkers, where they exploited the dynamic equilibrium strategy through the dissolution and reprecipitation of MAPbI3 in saturated HI aqueous solution for photocatalytic HI splitting.16 Subsequently, several alternative routes toward creating stable reaction environments when employing MHPs as photocatalysts have been proposed: (i) saturated haloacid solutions to establish a dynamic ionic equilibrium between the dissolved ionic species and the solid MHPs;16 (ii) nonpolar or low-polarity solvents to reduce the degradation of MHPs;17,18 (iii) core-shell structures to prevent the direct contact of MHPs with polar solvents.7,19–21 Even in these limited reaction environments, the stable operating time of MHP photocatalysts is still relatively short when compared to encapsulated MHP PVs, which can operate for thousands of hours.22,23 More importantly, the solar energy conversion efficiency of MHP photocatalysts is relatively low; the champion solar-to-fuels efficiency reported for MHP photocatalysts so far is 1.09%, where MoS2 modified with MAPbI3 was used for hydrogen generation.24 For comparison, this is much lower than the 25% solar-to-electric conversion efficiency of a single junction MHP PV.

Compared to photocatalysis, solar-driven electrocatalysis including PV-EC (Figure 1B), PV-PEC (Figure 1C), and PEC (Figure 1D) can integrate and optimize the advantages of both a solar harvester and electrocatalysis to promote charge separation, increase redox reaction rates and overall improve solar-to fuel conversion efficiency.11 The state‐of‐the‐art MHP solar-driven electrolysis of water has an 18.7 % solar-to-hydrogen conversion efficiency under 1-Sun irradiation and consists of a Si/Cs0.19FA0.81Pb(I0.87Br0.13)3 tandem PV, NiFe layered double hydroxide (LDH) anode and TiC-supported Pt nanocluster cathode.25 Furthermore, MHP solar-driven electrocatalysis does not require special reaction conditions and exhibits longer operational stability compared to MHP photocatalysis because the MHP is physically separated from the polar (electrolyte) solution.26,27 Therefore desired practical electrolytes, such as acidic and basic solutions, rather than non-polar solvents, can be used in MHP based solar energy conversion. In MHP PEC, MHP photoelectrodes have a layer-by-layer structure, in which the MHP layer is encapsulated between hole and electron transport layers (HTL and ETL, respectively), preventing direct contact with the electrolyte and significantly increasing MHP stability. Similar to MHP PV-EC and PV-PEC, a broad range of aqueous electrolytes can also be used for MHP PEC.28

Having established the clear advantages of solar-driven electrocatalysis technologies using MHP (Table S1), we discuss below the relative merits and challenges for the three configurations shown in Figure 1B-D, namely MHP PV-EC, MHP PV-PEC and MHP PEC. Furthermore, the most common solar-to-fuels conversion reactions, including water-splitting and CO2 reduction reaction, using these devices are evaluated. This analysis reveals the issues that hinder the progress of each technology in terms of efficiency and stability, and highlight the potential solutions that have been reported. With a clear perspective developed, the ongoing challenges and outlook of these solar-to-fuels technologies are summarized.

*PV-EC solar-to-fuels conversion based on MHPs.* In recent years, PV-EC has attracted attention due to the high solar-to-fuels conversion efficiencies it offers and ease of product separation. Here, the PV-EC device consists of two parts, an MHP-based PV and an electrochemical cell which operates in the dark. (Figure 1B). Consequently, the solar energy harvesting system and the electrocatalytic chemical fuel generation can be optimized independently to achieve a high solar-to-fuels conversion efficiency. In addition, it is challenging to maintain the long-term stability of MHP materials in polar solvents. However, with the MHP PV being physically separated from the electrolyte, the problem of MHP stability is significantly simplified.



**Figure 2.** (A) Illustration of a MAPbI3 PV-NiFe LDH electrochemical device for water-splitting and (B) the corresponding operating point under 1-Sun illumination26; Reproduced from ref 26, Copyright 2014, The American Association for the Advancement of Science. (C) Illustration of a Si/MHP tandem cell-TiC/Pt cathode-NiFe LDH anode PV-EC device and (D) the corresponding operating point under 1-Sun irradiation.25 Reproduced from ref 25, Copyright 2019, Elsevier.

In 2014, the first MHP PV-EC device was proposed and prepared by Luo and co-workers26 for the application of water-splitting in an aqueous alkaline electrolyte solution (1M NaOH; Figure 2A). Here, because the single junction MAPbI3 PV only provided an open-circuit voltage (VOC) of 1.06 V which is lower than the thermodynamic voltage required for water-splitting (1.23 V, as shown in Table S2), two perovskite PVs were connected in series to yield a VOC of 2.00 V. Both water oxidation and reduction redox reactions were mediated by bifunctional NiFe layered double hydroxide (LDH) electrocatalysts. A 1.7 V bias across the NiFe LDH anode and cathode was achieved, giving 10 mA/cm2 water-splitting current density and a solar-to-hydrogen conversion efficiency of 12.3% under 1-Sun irradiation (Figure 2B). This pioneering work combines two important research areas and opens up new opportunities for the use of MHP for solar energy conversion: not only converting solar energy into electricity, but also converting solar energy into fuel. In addition, a non-noble metal dual-function catalyst was developed with an activity comparable to Pt, but at a lower cost. Although the whole system showed a decrease of ca. 30% in performance during 10 h of operation, with a ca. 20% decrease in the first 2 h, the decreasing performance can be attributed to the instability of the perovskite PV caused by the immature preparation process at that time.

The short operating time of the first MHP PV-EC device severely limits practical application. Based on this pioneering work, Luo et al. in 2016 developed a more stable PV-EC system by optimizing both the EC and PV. A cobalt phosphate (CoP) electrocatalyst was used for the hydrogen evolution reaction (HER) in an acidic electrolyte solution and NiFe LDH for the oxygen evolution reaction (OER) in a basic electrolyte solution.29 This electrochemical cell showed improved stability of 100 h without any obvious degradation. In addition, Br- doping into the I-based MHP yielded the more stable FA1−xMAxPb(I1-xBrx)3 with a decreased trap state density going on increased perovskite phase stability.30,31 Furthermore, an improved encapsulation technology was employed to prepare the PV to prevent degradation of the air-sensitive MHP. With these efforts, this PV-EC system exhibited, less than ca. 20% decrease in performance over 16 h of operation. Furthermore, the solar-to-hydrogen (STH) conversion efficiency was increased to 12.7%, which was supported by the pH bias from the use of strong acid and base electrolytes to reduce the overpotential required for HER and OER, respectively. However, with EC operating the pH of the anolyte and catholyte will converge thus reducing the overall cell voltage unless the electrolytes are refreshed. Currently, state-of-the-art MHP PVs are stable for over 1000 operating hours and therefore investigation of the operational stability of the PV-EC system has shifted focus to the stability of the electrocatalyst electrodes.

Besides improving operational stability, increasing the efficiency of PV-EC systems is also a key objective. This can be achieved by increasing the efficiency of the PV, EC or both, taking into account the relationship between the IV curves of PV and EC under the operating conditions (e,g, Figure 1B and 1D). Park and coworkers prepared a Si/MHP[MAPb(Br0.15I0.85)3] tandem PV which yielded a VOC of 1.7 V and solar-to-electric conversion efficiency of 23.1%. By integrating this tandem PV with an anodized NiFe LDH OER electrocatalyst and a Ni4Mo HER electrocatalyst, they reported a STH efficiency of 17.52%.32 Gao et al. prepared a TiC-Supported Pt (TiC/Pt) nanocluster electrocatalytic cathode which exhibited a very low H2 evolution overpotential (35 mV) in an acidic electrolyte, which is comparable to commercial Pt/C. When this was integrated with a Si/MHP[Cs0.19FA0.81Pb(Br0.13I0.87)3] tandem cell and NiFe LDH anode, the STH efficiency was improved to 18.7% (Figure 2C and D).25 Furthermore, in a stability test over 10 h, the Si/MHP tandem cell retained 95% solar-to-electric conversion efficiency of the initial value after 10 h in ambient air and without any encapsulation, and separate electrocatalysis was stable for more than 100 h. Collectively, unassisted water-splitting of the overall PV-EC cell showed a small decrease of STH efficiency from 18.7% to 18.02% under 1-Sun irradiation over 2h.



**Figure 3.** (A) Illustration and (B) energy diagram of MAPbI3 photovoltaic-IrO2 anode-Au cathode for CO2 reduction. (C) The operating point under 1-Sun solar irradiation. (D) Current density, CO yield and solar-to-carbon monoxide conversion efficiency during an 18 h stability test.33 Reproduced from ref 33, Copyright 2015, Springer Nature.

Compared to water-splitting, the CO2 reduction reaction (CO2RR) poses some additional challenges, due not only to the slow kinetics of multi-electron/proton processes but also CO2 mass transport in aqueous media which present a considerable challenge for controlling product selectivity. The Grätzel group extended the MHP-based PV-EC system from water-splitting to CO2 reduction (Figure 3A).33 In this work, a Au cathode, which has an inherent high selectivity for CO2RR to CO, gave a faradaic efficiency (FE) for CO between 80 and 90%, and an IrO2 anode was used for water oxidation. Due to the thermodynamic requirement for the overall reaction (1.34 V) and the overpotential of each electrode (0.3 V for Au, 0.4 V for IrO2), a voltage larger than 2.04 V is necessary to drive this reaction. To meet this requirement, three MAPbI3 PVs were used in series to provide a VOC of 3.1 V (Figure 3B). Under 1-Sun irradiation, this PV-EC system exhibited an operating current of 5.9 mA/cm2 for up to 18 h with a 6.5% solar-to-fuels conversion efficiency in CO2-saturated 0.5 M NaHCO3 (Figure 3C and D). Beyond CO synthesis, MHP-based PV-EC systems can also be used to drive CO2RR on copper based electrocatalysts, which inherently promote C2+ product formation.34–36 In 2019, Huan and coworkers selected dendritic nanostructured copper oxide (DN-CuO) as both the anode and cathode materials, as part of a system comprising two series of three MHP (CsFAMA triple cation perovskite) PVs integrated with a continuous-flow electrochemical cell.37 CO2-saturated 0.1 M cesium bicarbonate (CsHCO3) solution and 0.2 M cesium carbonate (Cs2CO3) solution were selected as the anolyte and the catholyte, respectively. Under 1-Sun illumination, a stable current of 6.0 ± 0.2 mA at a potential of 2.8 ± 0.02 V was generated, producing C2H4 and C2H6 as the main products with a FE of 34 and 6.5%, respectively. This PV-EC system demonstrated a champion solar-to-fuels (ethylene and ethane) efficiency of 2.3%. Note that, in conventional electrocatalytic CO2RR, the selectivity depends on the relative partial current density of each product which is controlled by not only the electrocatalyst composition and structure, but CO2 mass transport which in turn is critically dependent on reactor design.38–40 Similarly, for a PV-EC system, the EC process will dominate the reaction selectivity. Meanwhile, the voltage available from the PV module could significantly affect selectivity if CO2RR is measured under mass transport limited conditions, which should be avoided and the general problem remains of limited stability of Cu electrocatalysts for CO2 reduction.

**Table 1.** Summary of reported solar-to-fuels generation via MHP PV-EC systems for water-splitting (WS) and CO2 reduction reaction (CO2RR).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| PV | Anode | Cathode | Reaction | Reaction conditions | Solar fuel(s) | Solar-to-fuels efficiency  (%) | Stability*a* | Ref |
| MAPbI3 | NiFe LDHb | NiFe LDH | WS | 1 M NaOH, 1-Sun | H2 | 12.3 | 2 h (80%) | 26 |
| (FAPbI3)1-x(MAPbBr3)x | NiFe LDH | CoPc | WS | 0.5 M H2SO4, 1 M KOH, 1-Sun | H2 | 12.7 | 16 h (70%) | 29 |
| MAPbI3-Organic PV | NrGO/NCNTd | NrGO/NCNT | WS | 1 M KOH, 1-Sun | H2 | 9.02 | 6 h (100%) | 41 |
| CH3NH3PbI3−xClx | NF-8-A/CFPe | NF-8/CFP | WS | 1 M KOH, 1-Sun | H2 | 9.7 | 500 s (90%) | 42 |
| MAPb(I0.85Br0.15)3-Si | NiFe(oxy)hydride | Ni4Mo | WS | 1 M NaOH, 1-Sun | H2 | 17.52 | 300 s (100%) | 32 |
| (Cs0.19FA0.81Pb(Br0.13I0.87)3-Si | NiFe LDH | TiC/Pt | WS | 1 M NaOH, 1-Sun | H2 | 18.7 | 2 h (96%) | 25 |
| MAPbI3 | CoP | CoP | WS | 1 M KOH, 1-Sun | H2 | 6.7 | 700 s (70%) | 43 |
| FA0.80MA0.15Cs0.05PbI2.55Br0.45 | Ni/FeNi(OH)X | CoP/Sn | WS | 0.5 M NaOH, 1-Sun | H2 | 8.54 | 3 h (90%) | 44 |
| MAPbI3 | IrO2 | Au | CO2RR and WS | 0.5 M NaHCO3, 1-Sun | CO, H2 | 6.5 | 18 h (100%) | 33 |
| CsFAMA triple cation perovskite | DN-CuOf | DN-CuO | CO2RR and WS | 0.1 M CsHCO3 CO2-saturated, 0.2 M Cs2CO3, 1-Sun | C2H4, C2H6, H2, CO | 2.3 | 50 min (100%) | 37 |

*a*In parentheses is the percentage of the initial current density remaining after the specified time; blayered double hydroxide (LDH); ccobalt phosphate (CoP); dnitrogen doped reduced graphene oxide(NrGO)/nitrogen doped carbon nanotube(NCNT); eNiFe alloy nanoparticle supported N,S-doped carbon annealed (NF-8-A)/carbon fiber paper(CFP), NiFe alloy nanoparticle supported N,S-doped carbon (NF-8); fdendritic nanostructured copper oxide (DN-CuO).

As summarized in Table 1, the reported PV-EC devices demonstrate promising performance for this emerging technology under 1-Sun irradiation, however there are challenges with respect to efficiency and long-term stability. For PV-EC, the driving force for the chemical reactions, e.g. water-splitting or CO2 reduction reaction, is fully provided by the MHP-containing PV. In addition to the thermodynamic voltage requirements for the target reactions, 1.23 V for water-splitting and over 1.05 V for CO2 reduction (Table S2), the overpotentials of the two electrodes (Table S4) are usually significant particularly for the OER. Therefore the total solar-to-fuel efficiency is largely determined by the collective optimization of the PV and EC efficiencies. For single-junction MHP photovoltaics, the VOC is between 0.9-1.5 V and is not sufficient to drive these chemical reactions and, thus, PV modules in series or multi-junction cells with a larger VOC are necessary. In principle, any electrocatalyst used traditional electrolyzers can be deposited on a suitable substrate and connected to an MHP PV, which is a distinct advantage of the PV-EC configuration. Thus, it should be possible to select a known electrocatalyst which is robust, low cost, and exhibits low overpotential, large current density and high selectivity. Although the two separate parts can be optimized independently to target high-efficiency solar-to-fuels conversion, the theoretical output matching between the photovoltaic and electrochemical components can be challenging. The operating current and voltage are determined by the crossing point between the current-voltage curves of the PV and EC under operating conditions. In Figure 4, two scenarios are presented for crossing points of PV-EC systems with different I-V characteristics. The maximum power point of a PV is determined by the maximum I x V area under the I-V curve (Figure 4). Ideally the EC process will cross at this point to maximize the use of the electrical power output from the PV. However, to maximize the quantity of fuel the total current should be maximized. This can be achieved by minimizing the EC overpotential and optimizing the surface area of the EC to cross at the maximum power point as shown by the EC curves 1 and 2. In principle this can be achieved using a single electrode or smaller electrodes in series. Therefore to maximize the solar-to-fuel efficiency the PV should be optimized to maximize the power output and the EC process optimized to extract the maximum current. It has been estimated that for STH an efficiency of ca. 60% is possible although this represents a significant engineering challenge to collectively optimize light absorption and electrocatalysis.45,46



**Figure 4.** Water-splitting using PV-EC: I-V curve of PV (purple) and LSV curve of EC with different of surface area (1 red and 2 green curves).

*PV-PEC solar-to-fuels conversion based on MHPs.* In PV-EC devices, multijunction PV or PV in series are required to deliver sufficient driving force for water-splitting or CO2 reduction on the non-photoactive dark electrodes. In a PV-PEC device, a photoelectrode is combined with a single-junction PV to provide the necessary driving potential and is similar to Z-schemes used in photocatalysis.47 The photoelectrode is multifunctional, not only absorbing light energy to generate voltage and current but also providing catalytic sites for the interfacial redox reaction. Depending on the type of photoelectrode used, MHP-based PV-PEC devices can be further classified into PV-photoanode or PV-photocathode devices.



**Figure 5.** (A) Illustration of the MAPbI3-BiVO4 PV-photoanode for water-splitting; (B) Electron flux for BiVO4 and MAPbI3 across the solar spectrum; (C) The operating point and (D) photocurrent density of the MAPbI3-BiVO4 PV-photoanode under 1-Sun irradiation.27 Reproduced from ref 27, Copyright 2015 American Chemical Society. (E) Illustration of the MHP PV-BiVO4 photoanode/3D TiN-ClFDH (clostridium ljungdahlii bacterium) cathode cell for solar-driven formate production from CO2, and (F) the formate yield over 24 h under visible light irradiation.48 Reproduced from ref 48, Copyright 2019 John Wiley & Sons, Ltd.

**Table 2.** Summary of reported solar-to-fuels generation using MHP photovoltaic-photoanode systems for water-splitting (WS) and CO2 reduction reaction (CO2RR).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| PV | Photoanode | Cathode | Reaction | Reaction conditions | Solar fuels | Solar-to-fuels efficiency (%) | Stabilitya | Ref |
| MAPbI3 | CoPb/BiVO4 | Pt | WS | 0.1 M aqueous phosphate solution, 1-Sun | H2 | 2.5 | 1 h (45%) | 27 |
| MAPbI3 | Co-Cic/Mo:BiVO4 | Pt | WS | 0.1 M bicarbonate, 1-Sun | H2 | 4.3 | 12 h (100%) | 49 |
| MAPbI3 | CoP/Mn:Fe2O3 | Pt | WS | 1 M NaOH,  1-Sun | H2 | 2.4 | 8 h (70%) | 50 |
| MAPbI3 | FeNiO*x*/Al2O3/nano-Fe2O3 | Ni-Mo | WS | 1 M KOH, 1-Sun | H2 | 1.9 | 8 h (70%) | 51 |
| MAPbI3 | TiO2/BiVO4 | Pt | WS | 0.1 M phosphate buffer, 1-Sun | H2 | 1.24 | 6 h (100%) | 52 |
| MAPbI3 | NiOOH/FeOOH/Mo:BiVO4 | Pt | WS | 0.5 M phosphate buffer, 1-Sun | H2 | 6.2 | 10 h (94%) | 53 |
| MAPbI3 | CoP/Sn:Fe2O3 | Pt | WS | 1 M NaOH, 1-Sun | H2 | 3.4 | 1 h (>95%) | 54 |
| FA0.83Cs0.17PbIBr2 | Mo:BiVO4/Fe(Ni)OOH | Pt | WS | 0.5 M potassium  Phosphate, 1-Sun | H2 | 6.3 | 6 h (100%) | 55 |
| MAPbI3-xBrx | CoP/Fe2O3 | Pt | WS | 1 M NaOH, 1-Sun | H2 | 3.25 | 10 h (100%) | 56 |
| Cs0.05(MA0.17FA0.83)0.95Pb(I0.83Br0.17)3 | CdS/TiO2 | Pt | WS with sacrificial reductant | 0.25 M Na2S, 0.35 M Na2SO3,e 1-Sun | H2 |  | 50 min (90%) | 57 |
| MAPbI3 | NiOOH/FeOOH/BaSnO3-x | Pt | WS | 1 M potassium borate, 1-Sun | H2 | 7.92 | 100 h (97%) | 58 |
| CsPbBrI2 | CoP/Mo:BiVO4 | Pt | WS | 0.5 M phosphate buffer, 1-Sun | H2 | 2.43 |  | 59 |
| MAPbI3 | CoP/BiVO4 | MoS2 | WS | 0.1 M phosphate buffer, 1-Sun | H2 | 3.1 | 6 h (65%) | 60 |
| (FAPbI3)0.85(MAPbBr3)0.15 | CoOx/Mo:BiVO4 | Pt/SiC | WS | 0.05 M KOH, 0.05 M H3BO3, 1-Sun | H2 | 0.55 | 30 min (44% ) | 61 |
| CsFAMA triple cation perovskite | FeOOH/BiVO4 | 3D TiN: CIFDH biocathoded | CO2RR | Sodium phosphate buffer (pH=6.5), 1-Sun | formate | 0.06 | 24 h (58%) | 48 |

aIn parentheses is the percentage of the initial current density remaining after the specified time; bcobalt phosphate (CoP); ccobalt bicarbonate (Co-Ci); dclostridium ljungdahlii (CIFDH); c Na2S and Na2SO3 as sacrificial reductants.

Photoanodes, typically made of n-type semiconductors, produce photoexcited holes that migrate in the valence band to the surface to oxidize water. Thus, the valence band should be more positive than the O2/H2O potential at the operating pH (+1.23 eV vs reversible hydrogen electrode (RHE) (pH = 0)). To date, several n-type semiconductors including BiVO4, Fe2O3, CdS and TiO2, have been coupled with an MHP-containing PV to drive water-splitting and the CO2 reduction reaction, as summarized in Table S5. In 2015, Chen et al reported a monolithic PV-PEC system containing a single-junction MAPbI3 PV, cobalt phosphate-modified BiVO4 photoanode (CoP/BiVO4), and Pt cathode (Figure 5A).27 Due to the relative band positions of the photoabsorbers, BiVO4 can selectively harvest the high-energy visible photons (< 500 nm) and can also catalyze oxygen evolution when decorated with a suitable co-catalyst (CoP). Simultaneously, MAPbI3 can capture the lower energy red photons and generate sufficient additional voltage for H+/H2 reduction at a dark electrode. Constructing a single-pass tandem device, combining a BiVO4 photoanode and MHP PV, ultimately achieved relatively efficient harvesting and utilization of the solar spectrum (Figure 5B) to give an STH conversion efficiency of 2.5% under 1-Sun irradiation, at neutral pH with no external bias (Figure 5C and D). Compared to PV-EC, in principle the single-junction PV in PV-PEC can reduce the complexity and fabrication cost associated with multijunction PV. However, multi-junction PV requires less external wiring and simpler management of light.

The STH efficiency was boosted to 7.92% by Kim and coworkers58 by improving the light absorption of the photoanode using barium stannate (BaSnO3) with oxygen vacancies. The light absorption edge extends from 400 to 660 nm with increased oxygen vacancy concentration and commensurate decrease in the bandgap from 3.08 to 1.84 eV. FeOOH/NiOOH cocatalysts were deposited on the surface of the photoanode to improve the oxygen production rate. With 8.7% oxygen-vacancy concentration and a 2.17 eV bandgap, the photocurrent density on the photoanode reached 7.32 mA/cm−2 at 1.23 V vs RHE under 1-Sun irradiation. For the overall device, a beam splitter was used to divide the light into two beams with complementary wavelengths, where the lower energy photons (> 635 nm) were absorbed by the MHP PV [Cs0.05(FA0.83MA0.17)0.95Pb(I0.83Br0.17)3] and the larger energy photons (< 635 nm) were absorbed by the photoanode. This PV-PEC device delivered an operating photocurrent density of 6.84 mA/cm2 under 1-Sun irradiation and was stable for 100 h. Unlike the usual single-pass device configuration, this work used a beam splitter to generate two beams, which can reduce the light scattering caused by the first light-absorbing layer, thereby possibly enhancing the light absorption, but at the expense of additional device components and complexity. However, since the bandgap of BaSnO3 can be tuned by changing the defect concentration, in principle the driving force of the PV-PEC system can be adjusted and the I-V curve of EC, PV and PEC components can be optimized to achieve the more efficient energy conversion.

Beyond water-splitting applications, the photovoltaic-photoanode device has also demonstrated promise for the solar-driven CO2 reduction reaction. In 2019, Kuk *et al.* constructed a tandem device consisting of an MHP PV (CsFAMA triple cation perovskite), FeOOH/BiVO4 photoanode, and a 3D-TiN-CIFDH (clostridium ljungdahlii) biocathode for bias-free CO2 to formate conversion (Figure 5E).48 Under visible light irradiation and bias-free operation, an average formate generation rate of 0.78 µmol/h, FE of 77.3% and STH of 0.06% could be achieved over 24 h, (Figure 5F). ClFDH is an effective CO2 enzyme because it has a suitable redox potential, fast interfacial electron transfer and surface active sites for stabilizing CO2 intermediates. However, the electron transfer between CIFDH and electrode requires a mediator, such as the nicotinamide adenine dinucleotide cofactor, which causes side reactions and efﬁciency loss. In this work, the authors avoided the need for an electron mediator by using 3D TiN with a periodically porous network and high conductivity which achieved not only high biocatalyst loading but also fast and direct electron transfer between TiN and ClFDH.



**Figure 6.** (A) Illustration of the MHP PV-CIGS photocathode with DSA (dimensional stable anode) for water-splitting and (B) the operating point of this tandem assembly;62 Reproduced from ref 62, Copyright 2015 John Wiley & Sons, Ltd. (C) Illustration of MHP PV-ZnO@ZnTe@CdTe photocathode for CO2 reduction and (D) faradaic efficiencies of CO and H2 over 3 h under 1-Sun illumination.63 Reproduced from ref 63, Copyright 2016 American Chemical Society.

**Table 3.** Summary of reported solar-to-fuels generation using MHP photovoltaic-photocathode systems for water-splitting (WS) and CO2 reduction reaction (CO2RR).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| PV | Anode | Photocathode | Reaction | Reaction conditions | Solar fuels | Solar-to-fuels efficiency (%) | Stabilitya | Ref |
| MAPbBr3 | DSAb | CuInxGa1-xSe2 | WS | 0.5 M H2SO4, 1-Sun | H2 | 6 |  | 62 |
| FAxMA1-xPbI3 | IrO2 | Cu2O | WS | 0.5 M Na2SO4, 0.1 M phosphate buffer, 1-Sun | H2 | 2.5 | 2 h (75%) | 64 |
| (Cs0.15FA0.65MA0.2)Pb(I0.8Br0.2)3 | IrOx | Cu(InGa)(S,Se)2 | WS | 0.5 M phosphate buffer, 1-Sun | H2 | 9.04 | 7 h (95%) | 65 |
| Cs0.10Rb0.05FA0.75MA0.15PbI1.8Br1.2 | DSA | Ti/Pt/p-n Si | WS | 1 M HCl, 1-Sun | H2 | 17.6 | 10 h (100%) | 66 |
| MAPbI3 | Co-Cic/Ni foam | ZnO/ZnTe/CdTe/Au | CO2RR and WS | 0.5 M KHCO3, 1-Sun | CO, H2 | 0.43 | 3h (73%) | 63 |
| MAPbI3 | IrO2 | Si/TiO2/CuAg | CO2RR | 0.1 M CsHCO3 | C2H4 | 3.5 |  | 67 |

aIn parentheses is the percentage of the initial current density remaining after the specified time; bdimensional stable anode (DSA); ccobalt bicarbonate (Co-Ci).

In addition, devices based on MHP-PV in combination with a photocathode have also been reported for solar-to-fuels conversion and are summarized in Table 3. In general, photocathodes where a reduction reaction takes place, are p-type semiconductors. However, most oxide, nitride, and sulphide semiconductors are n-type, and the number of p-type semiconductors is relatively small, and mainly consists of III-V semiconductors, or Cu based oxides, and all are prone to photocorrosion. In 2015, Luo *et al.* fabricated a MAPbBr3 photovoltaic-CuInxGa1-xSe2 (CIGS)photocathode device for water-splitting (Figure 6A).62 Here, due to the relative bandgaps of the MHP (2.3 eV) and CIGS PEC (1.1 eV) the MHP PV and CIGS PEC absorbed shorter and longer wavelengths of the solar spectrum, respectively. To improve the efficiency and stability of the photocathode, CdS/ZnO/Pt layers were deposited to overcome poor charge separation in CIGS, and an amorphous TiO2 layer was further deposited as a passivation layer to protect the photocathode from corrosion. A STH efficiency exceeding 6% was achieved with 1-Sun irradiation (Figure 6B). However, the photocathode remained stable for only 1 h in an acidic electrolyte (0.5 M H2SO4), which was attributed to H+ ions penetrating the amorphous TiO2 layer leading to dissolution of the underlying ZnO, CdS and CIGS layers. Besides chemical corrosion, ZnO and CdS are also unstable during light irradiation, potentially leading to additional deactivation of the photocathode. In this work, because the bandgap of MAPbBr3 is larger than that of CIGS, the MHP PV was placed before the CIGS PEC as the first light-absorbing component. To optimize both photoactive materials in PV-PEC, the relative position of PV and PEC needs to be considered. Specifically, the wide bandgap material should be positioned before the narrow one so that the lower energy photons can be absorbed separately by the narrow bandgap material. A 6% STH efficiency is still far below the 25% target set by the US Department of Energy.68

Si with a bandgap of 1.1 eV is an attractive candidate to replace the CIGS for constructing a dual-absorber tandem water-splitting cell because of lower cost and environmental concerns. Furthermore, the use of p-n Si junction promotes electron-hole separation improving the efficiency compared to an analogous CIGS system. Karuturi and coworkers developed a p-n junction Si photocathode and combined it with an MHP PV. To increase photocathode stability, Ti/Pt layers were deposited on the buried Si p-n junction photocathode.66 The photocathode remained stable for more than three days of continuous operation in 1 M H2SO4 electrolyte. When integrated with an MHP PV (Cs0.10Rb0.05FA0.75MA0.15PbI1.8Br1.2), a photocurrent of 14.3 mA/cm2 was achieved with a STH efficiency of 17.6%.

Beyond being applied to water-splitting, MHP PV-photocathode tandem devices have also been used to drive the CO2 reduction reaction. Jang et al. fabricated a tandem device with an MHP PV (MAPbI3), ZnO@ZnTe@CdTe photocathode and Co-Ci (cobalt bicarbonate) anode, which mediated the CO2 reduction reaction without external bias (Figure 6C).63 In this device, the two telluride light absorbers (ZnTe and CdTe) were combined into a photocathode to effectively absorb higher energy photons ( < 550 nm) and produce the required driving voltage in combination with the MHP PV placed behind. Au deposited on the top of photocathode as a cocatalyst for CO production. Under 1-Sun irradiation, the device gave a solar-to-fuels efficiency of 0.43% and CO product selectivity of 80% (Figure 6D) which is lower than the typical > 90% of a Au electrode. In addition, Te extrusion from the photocathode limited the stability to a few hours and reduced the FE. Illumination of the photocathode from the front can also result in the cocatalyst restricting light absorption.

Comparing Table 1 with 2 and 3, the efficiency and stability of PV-PEC systems is currently lower than that of PV-EC systems, but advances continue to be made. The maximum power output from these systems is determined by the crossing point of the PV and PEC I-V curves (Figures 5C and 6B). However, due to the differing photocurrent densities of the PV and PEC electrode, light management is a particular challenge to maximizing the power output. Light irradiance (intensity per unit area) requires both PV and PEC to be collectively optimized per unit area whereas for PV-EC, the dimensions of the PV and EC components are independent and can be optimized separately. Managing the light absorption between PV and PEC, coupled with catalysis at the PEC surface is a significant technological challenge if efficiencies are to approach those of PV-EC systems. Furthermore, with respect to stability, although in PV-PEC devices the sensitive MHP PVs are physically separated from the electrolyte, the photo/electrochemical corrosion of the PEC, especially photocathodes, is often limiting.

*Solar-to-fuels conversion based on an MHP buried junction photoelectrode.* While PV-EC and PV-PEC devices benefit from the stability of the external MHP PV, there are disadvantages with respect to the costs of metal electrodes and peripherals, and particularly for PV-PEC, the complex design configurations often used.69 Furthermore, ohmic resistance in external wiring results in further losses. An alternative to PV-PEC is to directly use an MHP as a PEC, or part of a buried multijunction PEC coupled with an EC, or as part of a fully integrated ‘wireless’ device. MHPs exhibit long electron and hole diffusion lengths supporting their use in either a photocathode or photoanode. However, as already stated a major challenge is the chemical stability of MHP’s in aqueous media which prevents direct use as a PEC electrode. Coating or encapsulation with other functional layers to give a buried junction not only increases stability but could improve the solar-to-fuels efficiency, by supporting charge extraction and catalysis.7 The traditional MHP PV structure comprises the HTL deposited on the top of the MHP with the ETL below giving an MHP photoanode. Using an inverted MHP PV structure, gives a photocathode. Many types of functional layers including metal foils and alloys, carbonaceous materials, and conductive polymers have been deposited on an MHP to create more efficient and stable MHP buried junction photoelectrodes, which are summarized in Tables 4 and 5, along with the reported solar-to-fuels conversion efficiencies.



**Figure 7.** (A) Illustration and energy diagram of Ni-coated MHP photoanode. (B, C) Stability of Ni-coated MHP photoanode under chopped and continuous 1-Sun illumination;70 Reproduced from ref 70, Copyright 2015 American Chemical Society. (D) Illustration of CsPbBr3 photoanode coated with mesoporous carbon and graphite sheets and (E) stability to water oxidation under 1-Sun irradiation.71 Reproduced from ref 71, Copyright 2019 Springer Nature.

**Table 4.** Summary of reported photoanodes for water-splitting(WS) and CO2 reduction reaction(CO2RR) using a buried metal halide perovskite junction.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| MHP photoanode | Cathode | Reaction | Reaction conditions | Solar fuels | Current | Stabilitya | Ref |
| MAPbI3/spiro-OMeTADb/Au-Ni | Pt | WS with sacrificial reductant | 0.1 M Na2Sg, 1-Sun | H2 | 10 mA cm-2 at 0 V vs. Ag/AgCl | 1000 s (17%) | 70 |
| CsPbBr3/m–Carbonc/GSd-Ir | Pt | WS | 0.1 M KNO3, 1-Sun | H2 | 2 mA cm-2 at 1.23 V vs. RHE | 30 h (63%) | 71 |
| MAPbI3/spiro-OMeTAD/Au-Ni | Pt | WS | Buffer (pH = 9.2) , 0.7-Sun | H2 | 17.4 mA cm-2 at 1.23 V vs. SHE | 30 min (60%) | 72 |
| MAPbI3/spiro-OMeTAD/Ag-Ni | Pt | WS with sacrificial reductant | 0.1 M Na2Sg, 1-Sun | H2 | 2.1 mA cm-2 at 0 V vs. Ag/AgCl | 30 min (100%) | 73 |
| MAPbI3/spiro-OMeTAD/Au/FMe-Ni | Pt | WS | 1 M KOH, 0.7-Sun | H2 | >15 mA cm-2 at 1.23 V vs. RHE | 5h (93%) | 74 |
| (5-AVA)x (MA)1-xPbI3f/Carbon/Ag/Carbon | Pt | WS | 1 M KOH, 1-Sun | H2 | 12.4 mA cm-2 at 1.23 V vs. RHE | 12 h (70%) | 75 |
| FA0.83Cs0.17Pb(I0.8Br0.2)3-GS/Ni | Pt | WS | 1 M KOH, 1-Sun | H2 | 17.4 mA cm-2 at 1.23 V vs. RHE | 40 h | 76 |

aIn parentheses is the percentage of the initial current density remaining after the specified time; b2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene; cmesoporous carbon(m-Carbon); dgraphite sheets(GS); eField metal (FM); fHOOC(CH2)4NH3I (5-AVA); gNa2S as. sacrificial reductant.

The first MHP photoanode was prepared by Da and coworkers in 2015,70 comprising as multi-layered photoanode of TiO2, MAPbI3, spiro-MeOTAD, Au, and Ni layers as shown in Figure 7A. Using FTO as a transparent conducting support, TiO2 as ETL was initially deposited below the MHP layer, followed by spiro-MeOTAD and Au as HTLs, and finally Ni was sputtered on top. The photoanode exhibited a photocurrent density exceeding 10 mA/cm2 in 0.1 M Na2S at 0 V bias vs Ag/AgCl under 1-Sun irradiation (Figure 7B) when combined with Pt as a cathode for H2 evolution. However, the photocurrent decreased to 2 mA/cm2 after 1000s (Figure 7C) and it should be noted that in this sacrificial system sulfide rather than water oxidation is occurring at the photoanode. Nevertheless, this work demonstrated the need to form protective layer(s), to prevent degradation by the electrolyte. In subsequent years, developing lamella structures using more dense HTL and a low-melting-point Field's metal layer, has increased operational stability to up to 6h and supported oxidation of water to dioxygen.72, 74

Carbon-based protective layers have also been investigated. In 2019, Cameron et al. encapsulated a CsPbBr3-based photoanode with mesoporous carbon(m-C) and graphite sheets(GS) for water oxidation (Figure 7D).71 Under 1-Sun illumination, the photoanode achieved a photocurrent density of 2 mA/cm2 at 1.23 V vs RHE and stability for 30 h, in 0.1 M KNO3 solution (pH 9, Figure 7E). The greater stability of the MHP photoanode can be attributed to: (i) the graphite sheets are hydrophobic and (ii) the thickness of the graphite sheets (25 µm) which effectively seals the MHP from water. However, the 25 µm graphite sheets could also affect the conductivity of the photoanode, leading to a small photocurrent density and, in general, it is a challenging to achieve device stability without sacrificing efficiency.



**Figure 8.** (A) Illustration of MAPbI3 photocathode with a InBiSn alloy encapsulating layer and (B) the photocurrent recorded at an applied potential of 0 V versus RHE.28 Reproduced from ref 28, Copyright 2016 Springer Nature. (C) Illustration of the InBiSn alloy compositional screening and the alloy protected MAPbI3 photocathode, and (D) stability test at −0.6 V versus RHE under 1-Sun irradiation.77 Reproduced from ref 77, Copyright 2019 American Chemical Society. (E) Illustration of MHP photocathode with a cobalt(II) meso-tetrakis(4-methoxyphenyl)porphyrin (CoMTPP) molecular catalyst for CO2 reduction and (F) stability test under 0.1 sun irradiation.78 Reproduced from ref 78, Copyright 2019 Springer Nature.

**Table 5.** Summary of reported photocathodes for water-splitting(WS) and CO2 reduction reaction(CO2RR) using a buried metal halide perovskite junction.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Anode | MHP photocathode | Reaction | Reaction conditions | Solar fuel | Current | Stabilitya | Ref |
| Pt | CsFAMA triple cation perovskite/PCBMb/TiO2 | WS | 0.5 M H2SO4, 0.5-Sun | H2 | >10 mA/cm2 at 0 V vs. RHE | 2 h (75%) | 79 |
| Pt | Cs0.05(MA0.17FA0.83)0.95Pb(I0.83Br0.17)3/PCBM/AZOc/FMd | WS | 0.1 M potassium phosphate, 1-Sun | H2 | 14.3 mA/cm2 at 0 V vs. RHE | 18 h (0%) | 80 |
| Pt | MAPbI3/PCBM/Ag/FM | WS | 0.1 M borate, 1-Sun (>400 nm) | H2 | 9.8 mA/cm2 at 0 V vs. RHE | 1.5 h (80%) | 28 |
| Pt | CsPbBr3/ZnO/Ag/FM | WS | 0.2 M Na2HPO4/ NaH2PO4, 1-Sun | H2 | 1.2 mA/cm2 at 0 V vs. RHE | 1 h (94%) | 81 |
| Pt | MAPbI3/PCBM/Ag/Ti | WS | 0.5 M H2SO4, 1-Sun | H2 | 18 mA/cm2 at 0 V vs. RHE | 12 h (75%) | 82 |
| Pt | Pt/Ti foil/In-Ga alloy/MAPbI3 | WS | 0.5 M H2SO4, 1-Sun | H2 | 21.7 mA/cm2 at 0 V vs. RHE | 54 h (60%) | 83 |
| BiVO4/TiCo | MHP/Graphite/Pt | WS | 0.1 M potassium borate buffer, 0.1 M K2SO4, 1-Sun | H2 | 1.5 mA/cm2 at zero applied bias | 96 h (25%) | 84 |
| Pt | MAPbI3/C60/BCPe/Cu/In0.4 Bi0.6 | CO2RR and WS | 0.1 M KHCO3, 1-Sun | CO, H2, CHOOH | 5.5 mA/cm2 at −0.6 V vs RHE | 1.5 h (100%) | 77 |
| IrOx/a-Si | CoPcf/CNTg-Carbon plate-CsFAPb(IBr)3 | CO2RR and WS | 0.5 M KHCO3, 1-Sun | CO, H2 | 3.3 mA/cm2 at 0.09 V vs. RHE | 1.5 h (100%) | 85 |
| BiVO4 | Perovskite/CoMTPPh@CNT | CO2RR and WS | 0.5 M KHCO3 buffer, 1-Sun | CO, H2 | 100 µA/cm2 at no applied bias | 67 h (100%) | 78 |
| BiVO4 | Perovskite/CuxIny | CO2RR and WS | 0.5 M KHCO3, 1-Sun | CO, H2 | 195 µA/cm2 at no applied bias | 10 h (50%) | 86 |

aIn parentheses is the percentage of the initial current density remaining after the specified time; b[6.6]-phenyl C61 butyric acid methyl ester (PCBM); cAluminium-doped zinc oxide (AZO); dField metal (FM); eBathocuproin (BCP); fcobalt phthalocyanine (CoPc); gcarbon nanotube (CNT); hcobalt(II) meso-tetrakis(4-methoxyphenyl)porphyrin (CoMTPP).

MHP photocathodes have also been fabricated and used for water-splitting, with several seminal contributions from Reisner and coworkers. The first MAPbI3-based photocathode was reported in 2016 (Figure 8A), with an InBiSn alloy layer used to protect the MHP during hydrogen evolution whilst immersed in water.28 To further improve the H2 evolution rate, Pt cocatalysts were deposited on the surface of the InBiSn alloy layer. Pt was also used for the water oxidation counter electrode. With an aqueous buffer solution (0.1 M borate, pH 8.5) and 1-Sun irradiation, a photocurrent density of 9.8 mA/cm2 at 0 V vs RHE was achieved and 80% of the initial photocurrent was retained after 1.5 h of operation (Figure 8B). In 2018, Andrie et al. further improved the MHP photocathode to achieve better performance and stability, using a CsFAMA triple cation MHP, a robust nickel oxide (NiOx) hole transport layer and an improved encapsulation technique.87 This MHP buried junction photocathode was combined with Pt as an H2 evolution cocatalyst and a stable BiVO4 photoanode for bias-free water-splitting as an ‘artificial leaf’. Unlike the dark counter electrode approach, a dual PEC system with two photo-active electrodes, is challenged by the need to current match the electrodes to avoid significant losses. Furthermore, to achieve bias-free water-splitting, the valence band of the BiVO4 photoanode in contact with the aqueous electrolyte should be more positive than the potential of water oxidation. This MHP buried photocathode-BiVO4 photoanode tandem device gave a solar-to-fuels efficiency of 0.35 ± 0.14% and was stable for 20 h. The loss in activity was attributed to H2 bubble formation which can affect the mechanical stability of the Field’s metal/epoxy interface causing water ingress. More recently, the STH efficiency was increased to 1.1% using [NiFeSe] hydrogenase enzyme as a cocatalyst for hydrogen evolution,88 which also showed that the encapsulation layer of the MHP can also act as a biocompatible scaffold for a metalloenzyme.

In 2019, Chen *et al*. first demonstrated buried MAPbI3-based photocathodes for CO2RR (Figure 8C).77 Similar to related water-splitting work, an InBiSn alloy layer functioned as catalytic and protective layer stabilizing the MHP photocathode in the 0.1 M KHCO3 electrolyte. However, unlike water-splitting, the products of CO2 reduction reaction, including HCOOH, CO, CH4 and C2+ hydrocarbons, are partially determined by the composition and surface structure of the catalyst(s). To promote selectivity for HCOOH, a series In−Bi−Sn ternary alloys were prepared and after systematic screening, In0.4Bi0.6 alloy without Sn gave the best catalytic performance, of nearly 100% FE for HCOOH using a bias of -0.52 V vs RHE and 1-Sun irradiation. Furthermore, a stability test at -0.6 V versus RHE showed 5.5 mA/cm2 current density for more than 1.5 h and a solar-to-fuels efficiency of 7.2% under 1-Sun irradiation (Figure 8D).

In 2020, Andrei and coworkers also applied the buried MHP photocathode-BiVO4 photoanode dual PEC ‘artificial leaf’ system to CO2RR by replacing the H2 evolution cocatalysts with a CO2 reduction cocatalyst, cobalt(II) meso-tetrakis(4-methoxyphenyl)porphyrin (CoMTPP) (Figure 8E).78 Under 1-Sun irradiation with no applied bias, reduction of CO2 in water led to simultaneous CO2 reduction and water-splitting giving a mixture of CO and H2 (syngas) with the solar-to-CO and STH efficiencies of 0.02% and 0.06%, respectively, over 67 h (Figure 8F). This work also demonstrated that the system could drive syngas production with a low light intensity of 0.1-Sun giving ca. 17% of the activity observed under 1-Sun, suggesting use under diffuse light conditions. However, due to losses inside the device and the performance of the surface catalysts, the efficiencies of these devices are still very low. Nevertheless, considering the advances in related technologies using these complex layered devices, such as PVs, there is significant scope to improve the STF efficiency of these stand-alone monolithic devices.

Following this work, recently, Li and coworkers assembled a tandem PEC cell with an MHP-photocathode and an amorphous Si photoanode for CO2 reduction.85 The addition of a hydrophobic carbon plate onto the MHP layer not only protects the light absorber, but also allows efficient photogenerated electrons to migrate to the surface. A cobalt phthalocyanine molecular cocatalyst was deposited to lower the onset potential of CO2 reduction on the photocathode giving a photocurrent of 15.5 mA/cm2 at −0.11 V versus RHE in CO2-saturated 0.5 M KHCO3 under 1-Sun irradiation for up to 25 h. Pairing this MHP photocathode with the a-Si photoanode, the solar-to-CO and solar-to-fuels efficiency reached 3.34% and 3.85%, respectively, under 1-Sun irradiation.85

It is clear that compared to PV-(P)EC systems, MHP PEC have two significant weaknesses: relatively short operational stability and currently low solar-to-fuels conversion efficiency. For MHP PEC, the MHPs are integrated into photoelectrodes and immersed into the aqueous electrolyte solution. Although several protective layers are deposited onto the MHP layer and the photoelectrode edges are additionally protected, water can still penetrate to destabilize the MHP because of (i) the (photo)chemical corrosion of protective layers and (ii) gas bubble formation causing mechanical stress and leakage. Selectively deposited robust and dense HTL/ETL layers in combination with cocatalyst layers on the top of MHP based photoelectrodes can limit corrosion. In addition, developing improved encapsulation technologies and increasing the number, impermeability (thickness and/or density) of protective coatings, are generally seen as effective methods to prolonging the stable operation time of MHP photoelectrodes. However, increasing the overall thickness and density of the protective layers limits photon penetration depth to the MHP layer and increases photogenerated charge carrier loss, lowering the solar-to-fuels conversion efficiency. Furthermore, optimizing the current matching between the MHP photoelectrode and counter photoelectrode in dual PEC systems is challenging. Using two junctions also limits collection of the solar spectrum and it has been estimated that the maximum STH efficiency lies between 23 and 32%, much lower than that predicted for multijunction PV-EC systems.

*S**ummary, Prospects and Concluding remarks*. Due to their interesting optoelectronic properties, MHPs have been proposed for a wide variety of useful optoelectronic applications, including solar cells, LEDs, photodetectors, photocatalysis, and solar-to-fuels conversion. Compared to MHP-based powder photocatalysis, the three device configurations described herein offer the prospect of viable stability under realistic conditions, easier product separation, and higher solar-to-fuels conversion efficiency. However, the relatively soft, ionic nature of their crystal structure has thus far presented significant technical obstacles to applying these materials for effective solar-to-fuels conversion.

In this perspective, we have provided an overview of the recent progress in the field of MHP solar-driven electrocatalysis using MHP PV-EC, MHP PV-PEC, and MHP PEC, for solar-driven water-splitting and CO2RR. Based on our summary of current progress, several themes emerge and strategies can be envisioned to guide further advances:

(1) Prolonging the operational stability of MHP solar-driven electrocatalysis devices. For MHP PV-EC and PV-PEC systems, because the MHP PV are not immersed in an electrolyte the operational time is determined by the non-MHP (photo)electrode stability in contact with the electrolyte. For MHP PEC, although current encapsulation methods initially eliminate contact between the MHP and electrolyte, as the reaction proceeds, gas bubbles and photo(corrosion) of MHP overlayers eventually cause ingress to the MHP layer inducing decomposition and device failure. Strategies to improve stability are required that provide physical protection but also promote electron-hole separation and support catalysis, whilst maximizing light absorption. Protective layers, passivating ligands, and nanostructuring can all be developed to control local current density, bubble formation, and electrolyte wetting to improve operational stability and have been applied successfully to other (photo)electrochemical systems.89

(2) Solar-to-fuels conversion efficiency using MHP solar-driven electrocatalysis. To date, the maximum recorded solar-to-electric conversion efficiencies for single junction and tandem junction MHP PVs are 25.5 and 29.5%,10 respectively, which is higher than that for MHP solar-driven electrocatalysis at 18.7%.25 In common with all PV driven electrocatalysis the operating point of the system is at the intersection of the (photo)electrochemical cell polarization curve and the MHP PV I-V curve. Thus, it follows that further optimizing the (photo)electrochemical components in the device to match the output of PVs is required to enhance the efficiency of MHP solar-driven electrocatalysis devices. This could take the form of developing high-performance (photo)electrocatalysts, optimizing the current transport layers and electrolytes, and designing new system configurations e.g. using EC cells in series. Moreover, development of additional MHP/PV junctions to increase light absorption across the solar spectrum and hence the power available to generate greater current and fuel production can complement improvements in EC technology. Similarly, engineering of PV-EC systems is significantly more straightforward than PV-PEC or all PEC systems where collective optimization of light absorption, matching current densities and catalysis, whilst retaining stability is extremely challenging.

While it is a challenging task to fully exploit the excellent photophysics of MHP semiconductors, and ensure both material stability alongside optimum performance, identifying the systemic challenges and developing principles to mitigate their effects will be critical to seeing real advances in MHP solar-driven electrocatalysis. In particular, the photophysics and chemistry of the interfacial regions and exposed surfaces are critical areas to gain further understanding to improve overall stability and efficiency. Significant progress has already been achieved, particularly in MHP PV-EC systems applied to hydrogen production. As developments in MHP PV technology, wider electrocatalysis, and reactor design emerge it is anticipated that these can be integrated into new systems with increasing efficiency and critically their stability. By shedding light on these topics, we hope that this perspective will help stimulate further discussion and advances in this rapidly developing field.

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Johan Hofkens graduated from the Laboratory of Photochemistry and Spectroscopy, KU Leuven (Belgium), in 1993 studying TICT-states in organic molecules by time-resolved fluorescence measurements. After a postdoctoral stay (1994-1995) with Prof. Masuhara at Osaka University (Japan) on the development of optical trapping and with the late Prof. Barbara at University of Minneapolis (United States) on single-molecule spectroscopy, he returned to the KU Leuven were he started the single-molecule group, focusing on the development of optical microscopy tools to study challenging topics at the boundary of chemistry, biology, and physics.

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SUPPORTINHG INFORMATION

Additional tables, including the comparison between MHP photocatalysis and MHP solar-driven electrocatalysis, the redox potential of half reactions of water splitting and CO2 reduction, the overpotential of electrodes in MHP PV-EC systems for water oxidation, water reduction and CO2 reduction.

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