Solar-Driven Hydrogen Generation by Metal Halide Perovskites: Materials, Approaches, and Mechanistic View

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ABSTRACT: Solar-driven photocatalysis by metal halide perovskites (MHPs) is emerging as an exciting and promising field to promote several relevant catalytic reactions taking advantage of the superior optical properties of MHPs. Their electronic structure is suitable to run reduction reactions (H₂ generation, CO₂ reduction) and even oxidation reactions, in particular for perovskites with higher band gap values, and further extends their possible use in the field of photochemical organic syntheses. This Mini-Review focuses on the application of MHPs in the solar-driven hydrogen generation with particular emphasis on the materials’ design and mechanistic features involved in the catalytic reactions.

INTRODUCTION

Metal halide perovskites (MHPs) of general formula ABX₃ (A = methylammonium, MA, formamidinium, FA, Cs, etc.; B = Pb, Sn, Ge; and X = Cl, Br, I) have provoked a substantial revolution in the field of photovoltaics and optoelectronics because of their superior optical characteristics, physical properties’ tunability, ease of fabrication, and low cost. In very recent times, MHPs have attracted a significant interest for their possible use in various photocatalytic applications. The suitability of MHPs in relevant solar-driven reactions comes essentially from their highly tunable and narrow band gap, long carrier lifetimes, and high mobilities, together with a good defect tolerance. The band alignment of various MHPs, together with traditional photocatalysts, relative to the potentials of common redox half-reactions, is shown in Figure 1, indicating the thermodynamic suitability of these materials to effectively run reduction reactions (H₂ generation, CO₂ reduction) and even oxidation reactions for MHPs with higher band gap values (e.g., chloride-based). As it will be clear later in the text, the main mechanisms involved in the photocatalytic reactions by MHPs closely resemble those of conventional catalysts, involving the visible-light generation of charge carriers and their transfer to reaction sites, in many cases mediated by metal and/or semiconductor cocatalysts.

In addition to the thermodynamic suitability, MHPs also possess good charge carrier dynamics properties resulting in low excitation binding energies, efficient charge carrier generation, and long-lived excited states. Such features are advantageously exploited in the photocatalytic applications of MHPs and further enhanced by coupling them with other semiconductors in composites. Among the different solar-driven reactions of current interest, MHPs have been explored for their possible use in H₂ generation, CO₂ reduction, photodegradation of dyes and contaminants, and photosynthesis of organic compounds. In this Mini-Review, we will focus on the H₂ generation by showing the progressive research evolution from the first report by Park and co-workers up to the most recent developments in the field. It is well-known that MHPs are highly unstable in water, leading to their immediate decomposition, and for this reason, the Mini-Review is organized in terms of the environment where the photogeneration of hydrogen is carried out because this aspect, in turn, determines the experimental setup and the materials/device engineering.

H₂ Photogeneration in Hydrohalic Acids. The first report of H₂ photogeneration appeared in 2017 where Park and coauthors used methylammonium lead iodide, MAPbI₃, as photocatalysts. In order to overcome the water-induced instability of the perovskite, the reaction was carried out in aqueous HI solution. By controlling the I⁻ and H⁺ concentrations, powdered MAPbI₃ underwent a continuous dissolution and precipitation under a dynamic equilibrium, which allowed a stable photocatalytic HI splitting and evolution of H₂ (and I₃⁻). As a matter of fact, MAPbI₃ was found to be stable only at specific I⁻ and H⁺ concentrations (6.06−2.51 mol l⁻¹ of HI). The hydrogen evolution reaction (HER) activity by irradiating in a solar simulator was 11.31 μmol h⁻¹ g⁻¹, further enhanced by 2 and 2.8 times after a thermal annealing of MAPbI₃ in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) atmosphere to improve material crystallinity. Finally, approximately 57 μmol g⁻¹ h⁻¹ of H₂ was evolved from the sample with deposited Pt, and the final solar HI splitting efficiency was 0.81%.

Wu and co-workers further enhanced the photocatalytic hydrogen evolution activity by preparing powdered samples of MAPbBr₃−xIₓ having a iodide-concentration gradient pro-
gressively increasing moving from the interior to the surface of each sample particle. Such mixed MHPs was prepared by means of a facile light-assisted halide exchange method leading to a band gap funnel structure (see a sketch in Figure 2a). With this architecture, the authors observed, by means of photoluminescence (PL) experiments, a quick charge carrier transport from the bromide-rich to the iodide-rich region with the latter being the primary sites for charge recombination and the first serving as the absorbing and carrier generation sites. Such funnel structure allowed indeed an improvement of H2 photogeneration by reducing the carriers recombination as demonstrated by carrying out experiment under aqueous mixed HI/HBr acid-saturated solutions, together with H3PO2 which selectively reduced I3− ions interfering with the light absorption by darkening the solution. Visible light (λ ≥ 420 nm, 100 mW cm−2) irradiation of MAPbBr3−xIx led to a H2 evolution of 1021.20 μmol h−1 g−1 (with respect to 11.20 μmol h−1 g−1 of pristine MAPbBr3), which was further improved to 2604.80 μmol h−1 g−1 by a 3 wt % Pt loading, acting to separate the electron–hole pairs. The solar-to-light chemical efficiency defined at the beginning of the reaction without H2PO2 was 1.05%, and the apparent quantum efficiency of the MAPbBr3−xIx/Pt system under 450 nm irradiation was determined to be 8.10%. Finally, this last system showed an excellent stability after 30 h of experiments (repeated in 6 cycles of 5 h). The same authors further expanded the band gap funnel approach to all-inorganic mixed perovskite, by investigating the CsPbBr3−xIx system, prepared in the same way as the previous one. Also in this case, the hydrogen evolution of CsPbBr3−xIx (loaded with Pt) in aqueous HBr solution saturated with CsPbBr3 led to a H2 photogeneration (λ ≥ 420 nm, 120 mW cm−2) of 896.0 μmol h−1 g−1 with a high stability up to 50 h. Apparent quantum efficiency was in this case 2.15% under 450 nm irradiation.

An improvement in hydrogen photogeneration activity by metal halide perovskites in acid solutions was achieved by creating composites in analogy with the strategies employed for more traditional photocatalysts. Wu and co-workers prepared a composite of MAPbI3 with reduced graphene oxide (rGO) by dispersing GO powders in aqueous HI acid solution saturated with MAPbI3, which selectively reduced I3− ions interfering with the light absorption by darkening the solution.6,7 Visible light (λ ≥ 420 nm, 100 mW cm−2) irradiation of MAPbBr3−xIx led to a H2 evolution of 1021.20 μmol h−1 g−1 (with respect to 11.20 μmol h−1 g−1 of pristine MAPbBr3), which was further improved to 2604.80 μmol h−1 g−1 by a 3 wt % Pt loading, acting to separate the electron–hole pairs. The solar-to-light chemical efficiency defined at the beginning of the reaction without H2PO2 was 1.05%, and the apparent quantum efficiency of the MAPbBr3−xIx/Pt system under 450 nm irradiation was determined to be 8.10%. Finally, this last system showed an excellent stability after 30 h of experiments (repeated in 6 cycles of 5 h). The same authors further expanded the band gap funnel approach to all-inorganic mixed perovskite, by investigating the CsPbBr3−xIx system, prepared in the same way as the previous one. Also in this case, the hydrogen evolution of CsPbBr3−xIx (loaded with Pt) in aqueous HBr solution saturated with CsPbBr3 led to a H2 photogeneration (λ ≥ 420 nm, 120 mW cm−2) of 896.0 μmol h−1 g−1 with a high stability up to 50 h. Apparent quantum efficiency was in this case 2.15% under 450 nm irradiation.8

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Figure 1. Band alignment of various MHPs and of traditional photocatalysts and redox potentials of common half-reactions relative to the reversible hydrogen electrode (RHE). Reprinted with permission from ref 2. Copyright 2020 American Chemical Society.
achieved for a 50% loading of Pt (0.75 wt %)/TiO2 which corresponds to an improvement of 89 times with respect to pristine Pt/MAPbI3 and to 436.6 μmol of hydrogen evolved in 6 h. Composite stability was confirmed on four successive photocatalytic cycles. From PL measurements, the authors proposed a mechanism where MAPbI3 particles dispersed in saturated solution acted as the light absorber and generated electrons and holes upon light irradiation. Due of the proper band alignment between Pt/TiO2 and MAPbI3, the electrons generated on MAPbI3 were transferred to Pt/TiO2 and reduced protons to H2 on Pt. At the same time, the holes on MAPbI3 oxidized I− to I3− thus enhancing HI splitting efficiency. Schematic band-alignment diagram for the composite is reported in Figure 2d. The same authors created a composite with MAPbI3 using commercial Ta2O5 and Nb2O5 nanoparticles loaded with Pt.11 While Ta2O5 was relatively effective in promoting H2 evolution (even though less than TiO2), the possible unfavorable band-alignment with Ta2O5 led to negligible catalytic activity.11 However, these were preliminary data, and more efforts could be devoted to further investigate such composites.

TiO2 was also used in the form of nanorods by Luo et al. to promote hydrogen evolution from HI splitting.12 In this work, a MAPbI3 film was deposited onto a TiO2 nanorod array...
transporting channel.14 This was done by employing MAPbBr3 portation modulation, i.e., by creating an electron- and a hole-for electron transfer. An evolution of this concept was due to the loading of 1.2% of BP, that is, a 106-fold improvement with respect to pristine MAPbI3. By PL measurements, the authors observed a PL quenching and decreasing lifetime ascribed to the hydrogen photogeneration by creating e− including holes, the rate of hydrogen evolution was drastically enhanced with a facile nonradiative quenching channel, which is beneficial for enhanced charge separation of electron–hole pairs and a photocatalytic HER activity.12 To date, this composite showed the record activity in the H2 photogeneration by a MHP.

The creation of the above-mentioned composites, improved the hydrogen photogeneration by creating effective channels for electron transfer. An evolution of this concept was due to the formation of a cocatalyst to trap photogenerated electrons derived from MAPbI3 through a type I heterojunction in the interface of BP/MAPbI3. Under visible light (λ ≥ 420 nm) illumination with H3PO2 as sacrificial reagent, MAPbBr3 was stabilized for concentrations in HBr greater than 0.24 mol L−1, and the bare perovskite, under visible light irradiation (λ > 420 nm), has a hydrogen evolution of about 10 μmol h−1 g−1.14 A first enhancement of photocatalytic activity was achieved by creating a composite between MAPbBr3 (as light absorber) and nanoscale Pt/Ta2O5 (as electron transporter). However, the band structure analysis suggested that, while the reduction reaction of hydrogen was effective in this composite, the same was not true for the Br− oxidation. Therefore, a hole-transporting channel was further added in the form of poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS).14 With this dual-charge transportation modulation (Ta2O5 for the electrons and PEDOT:PSS for the holes), the rate of hydrogen evolution was drastically enhanced to 650.0 μmol h−1 g−1.14 According to PL and transient absorption (TA) measurements, the authors devised a mechanism where MAPbBr3 is responsible for visible light (λ > 420 nm) absorption, thus generating electrons and holes. The electrons transfer from the MAPbBr3 to the conduction band of Ta2O5 reduced protons to produce hydrogen on the Pt nanoparticles that were deposited on Ta2O5. In the meantime, the photogenerated holes transferred from MAPbBr3 to PEDOT:PSS and oxidized Br− to Br2.14 A schematic representation of the reaction mechanism proposed is depicted in Figure 2fg. By further optimizing the photocatalysts, in terms of different combinations of MAPbBr3, PEDOT:PSS, and Pt/Ta2O5, an optimal rate of hydrogen evolution from the HBr splitting reaction was found to be 1050 μmol h−1, which was 52 times that obtained on MAPbBr3, with an AQE of ca. 16.4% at 440 nm.14 The stability of hydrogen evolution in this complex composite was only about 3 h; however, after that, the activity gradually decreased, with the PEDOT:PSS component as the possible source of such instability.14

A very recent work by Cai and co-workers made use of a facile in situ photosynthesis to fabricate a MAPbI3/cobalt phosphide (CoP) hybrid heterojunction.15 MAPbI3 nanocrystals were first prepared by the microcrystalline-assisted antisolvent method, and then the MAPbI3/CoP hybrid was synthesized by the in situ photodeposition process in which CoCl2 and NaHPO2 were dissolved in MAPbI3-saturated HI solution to work as a precursor solution.15 TEM analysis revealed the presence, on the cubic-shaped crystals of the perovskite, of fine particles of CoP. Figure 2h reports a schematic diagram of the fabrication and photocatalytic hydrogen evolution of the MAPbI3/CoP hybrid heterojunction. Under visible light illumination, the photocatalytic HER rate of the optimal composite (MAPbI3:CoP 1:0.25) was 785.9 μmol g−1 h−1, that is, ≈8.0 times higher than that of pristine MAPbI3.15 The authors proposed that CoP nanoparticles not only favored the charge separation but also contributed to increasing the number of reaction active sites. Through PL measurements, the quenching of the PL signal was considered as an indicator of effective charge transfer in the composite catalysts which was further corroborated by the much shorter PL lifetime (τ PL) of MAPbI3/CoP (148.1 ns) with respect to the pristine MAPbI3 (232.6 ns).15 The further confirmation of the effective charge transfer and separation process in the composite was achieved by measuring the surface photovoltage (SPV) of pristine perovskite and of MAPbI3/CoP. A distinct negative signal found in the composite, with respect to no difference observed in MAPbI3 before and after illumination, confirmed the electron accumulation of the surface of CoP nanoparticles during illumination. Finally, the long-term stability of the photocatalytic activity of the composite was measured under continuous illumination for 27 h (differently from most of the works measuring the stability over cycles). The crystalline structure and the HER activity was maintained during this time course as well as for five successive cycles.15 Interestingly, the photocatalytic HER performance increased with the reaction time which could be probably ascribed to the improved crystallinity of MAPbI3 and the increased loading of CoP cocatalyst during the continuous photocatalysis reaction.15

In addition to the relatively vast literature on methylammonium lead halide perovskites, few examples used lead-free materials for effective HI or HBr splitting, with particular interest toward Bi-based materials.16,17 Guo and co-workers hydrothermally synthesized MA3Bi2I9, a semiconductor with a band gap around 1.98 eV, exhibiting an excellent phase stability in HI with different concentrations, differently from the above-reported results for MAPbI3.6 Pristine MA3Bi2I9 was capable to split HI into H2 and I3− evolving about 12.19 μmol h−1 g−1 but the activity was enhanced by Pt loading to about 169.21 μmol g−1 h−1 and a solar-to-chemical conversion efficiency of 0.48%.16 Stability was tested and found to be excellent over 70 h of illumination (10 cycles). The lead-free double perovskite Cs8Ag2Br9 (CABB) was combined with rGO to create CABB/rGO (x = 1%, 2.5%, 5%, mass ratio) composites by a facile photoreduction method.17
photocatalytic activities of the CABB-based composites were evaluated in aqueous saturated HBr and H₃PO₂ solutions under visible light irradiation (λ > 420 nm) at 5 °C. Pristine double perovskite showed a modest 0.61 μmol h⁻¹ g⁻¹ H₂ evolution while the addition of rGO (2.5%) improved by 80 times the photoactivity to about 50 μmol h⁻¹ g⁻¹ of evolved hydrogen. The photocatalytic stability of CABB/2.5%RGO was studied, and no significant decline in H₂ evolution was observed after 12 cycles of 10 h continuous photoreaction. The same mechanism observed for MAPbI₃/rGO was also proposed here by means of PL measurements. While the overall photocatalytic efficiencies of lead-free perovskites is lower with respect to the above presented data on lead halide perovskites, the research is still at infancy for these phases, and because of the availability of a huge number of different compositions, it is expected to see significant improvements for these systems in the near future.

**H₂ Photogeneration in Water and Organic Solvents.** As it is well-known, metal halide perovskites are highly unstable in water, and therefore, the strategy of using haloacids solutions has been extensively used to promote hydrogen photogeneration, as discussed above. However, in very recent times, few reports about water-stable metal halide perovskites appeared, and such feature was used to produce H₂ directly.
from water. At the same time, other results reported the possible photocatalytic use of MHPs in organic solvents. These two media, water and organic solvents, are of particular interest to further extend the photocatalytic applications of metal halide perovskites being the natural environments for water splitting and possible organic photo-reactions. Clearly, while the use of concentrated halocids may still be of relevance for basic studies, the extension of MHPs catalysts, in particular, to aqueous environments may pave the way to effective solar-driven water splitting by perovskites.

Ju and co-workers showed that DMASnI3 (DMA = dimethylammonium) is stable in pure water for up to 16 h and does not dissolve but rather undergoes a transformation from a black to yellow phase promoted by air exposure. XRD data before and after deionized (DI) water treatment confirmed the retention of the correct crystal structure, which was also preserved when DMASnI3 was immersed in different solvents for a long period of time (see Figure 3a). Its excellent water stability was used to promote photocatalysis for H2 evolution in DI water (under 300 W Xe lamp irradiation at 10 °C) rather than in the saturated HI solution with an H2 evolution rate of 3.20 μmol h−1g−1 with good recycling properties (see Figure 3b). The authors noted that because of the formation of O2 after the evolution of H2, the peaks of SnI3 were formed. While the activity reported was very low, this paper represents a milestone for future effective development of water-stable MHP photocatalysis, also considering the use of a lead-free material.

Following this first report on hydrogen photogeneration by a water-stable lead-free MHP, Malavasi and co-workers found an analogous stability for the bromide analogue, that is, DMASnBr3 (band gap around 2.9 eV). After assessing the air-stability of this phase by exposing it to laboratory conditions for 6 days without observing sample decomposition, DMASnBr3 was used to photogenerate hydrogen directly from DI water. Again, the perovskite did not dissolve but formed an opalescent dispersion, and once the material was dried, the pristine phase was found. The photocatalytic experiments were carried out by suspending 2 g L−1 of DMASnBr3 in DI water and irradiating the solution under simulated solar light with a power factor of 500 W m−2. The result was the observation of hydrogen photoproduction on the order of 6 μmol g−1 h−1 for DMASnBr3 (with a reference sample without the perovskite providing an undetectable amount of H2). The same authors performed an additional experiment in the presence of triethanolamine (as a donor) and 1 wt % of Pt which led to the production of 11 μmol g−1 h−1 of hydrogen. It is clear that these two systems, in virtue of their superior water-stability, whose origin is not yet clear but possibly due to the relatively high hydrophobic nature of the dimethylammonium cation, merits to be further explored by providing suitable composites.

In this respect, a very recent paper by Malavasi and co-workers, successfully coupled a novel water-stable 2D lead-free MHP, namely PEA2SnBr4 (PEA = phenylethylammonium), with graphitic carbon nitride (g-C3N4) to create efficient composites. PEA2SnBr4 is a 2D perovskite showing an orthorhombic crystal structure and a band gap around 2.7 eV. In this work, the authors first determined the water stability of the perovskite in two ways: (i) by suspending the powders in DI water under stirring and recovering them by filtration, and (ii) by measuring the amount of tin in DI water after perovskite removal (“leaching test”). As can be seen from Figure 3c, the XRD pattern of PEA2SnBr4 after 4 h in DI water under stirring was superimposable onto that of the starting material, and the leaching test confirmed the absence of tin into the water where the perovskite was stirred. Stability of the perovskite was also confirmed by XPS. PEASnBr4 evolved 4.0 μmol g−1 h−1 of hydrogen under irradiation and in the presence of 3 wt % of Pt. As mentioned above, however, the authors explored the creation of composites with a well-known photocatalyst, namely g-C3N4, in other to enhance the H2 evolution activity. By means of wet-chemistry, 5 and 15 wt % of perovskite were loaded onto g-C3N4 and the HERs were measured. At the optimal concentration of 5 wt %, the PEASnBr4/g-C3N4 composite (in the presence of TEOA and 3 wt % Pt) evolved 1613 μmol g−1 h−1 of hydrogen showing an impressive synergic effect, with a HER that was more than 20 times that of pure g-C3N4. As can be understood, in this case the authors made use of the MHP as a cocatalyst to improve the photoactivity of g-C3N4. The mechanism proposed by Malavasi et al. was based on a positive band-alignment between g-C3N4 and PEASnBr4 thus forming a heterojunction. Figure 3d shows the calculated band edge positions for two semiconductors relative to NHE potential. The photoinduced electrons from PEASnBr4 could easily move toward g-C3N4 due to the conduction band maximum (CBM) lying at a less negative potential with the accumulated electrons taking part in the photochemical reduction of water to generate H2. The heterojunction formed reduced the recombination rate of the photo generated electron–hole pairs and increased the photocatalytic activity for hydrogen evolution.

Few other examples of hydrogen generation were achieved in organic solvents by employing nanocrystalline MHPs which are excellent visible light emitting materials. Again, NCS MHPs are highly unstable in aqueous environments leading to an immediate phase decomposition. Pavliuk et al. employed a system composed of CsPbBr3 nanocrystals (NCS) and Ru@TiO2 nanoparticles as light harvesters and catalyst, respectively, to run a direct proton reduction in liquid solution. CsPbBr3 NCS (photosensitizer), capped with oleate and oleylammonium ligands, were combined with Ru@TiO2 nanoparticles (H2-evolution catalyst), TEOA (sacrificial electron donor), and trifluoroacetic acid (TFA, sacrificial proton donor) in the nondried toluene. Under optimal experimental conditions, the maximum hydrogen photoproduction rate was ≈160 μmol min−1 gcat−1 and the photon-to-hydrogen efficiency was estimated to be 0.4 ± 0.1%. Thanks to a rich set of spectroscopy measurements the following mechanism was proposed. Upon photon absorption with the correct energy to overcome the CsPbBr3 NCS bandgap, excitons were formed and dissociated into electron–hole pairs; subsequently, the excited electrons were transferred unidirectionally via collision events from CsPbBr3 NCS conduction band to n-type TiO2 nanoparticles conduction band. The electrons in the TiO2 conduction band were rapidly transferred to ruthenium nanoparticles, where protons coming from TFA were converted to gaseous H2. TiO2 nanoparticles had the dual function of shuttling electrons from photosensitizer to catalytic subunit and enhance excited electrons lifetime. At the ruthenium active sites, the electrons were accumulated and further stabilized in order to suppress the time gap between light absorption processes (fs to ps time scales) and catalysis (above μs). The perpetuation of the photocatalytic reaction was ensured by the irreversible quenching of the excited holes.
Table 1. Photocatalytic Systems Reviewed in the Present Paper Highlighting the Reaction Environment and Hydrogen Production

| System | Reaction Environment | H₂ (μmol g⁻¹ h⁻¹) | Ref |
|--------|----------------------|------------------|-----|
| MAPbI₃ | HI (6 M), saturated with MAPbI₃, with H₃PO₄ | 11.31 | 6 |
| MAPbI₃ | annealed in DMSO | 23 | |
| MAPbI₃ | annealed in DMF | 32 | |
| MAPbI₃ | with Pt | 57 | |
| MAPbBrₓIₓ | with Pt 3 wt% | HI/HBr saturated with perovskite, H₂PO₄ | 1021.20 | 7 |
| Cs₂AgBiBr₆ | HBr saturated with CsPbBr₃ | 896.0 | 8 |
| MAPbBr₃ | HBr, MAPbBr₃ saturated | 939 | 9 |
| MAPbBr₃ | (Pt⁺ – Ta₂O₅)/MAPbBr₃/(PEDOT:PSS) | 1050.0 | |
| CS₂AgBiBr₆ | HBr, perovskite saturated, H₂PO₄ | 0.61 | 17 |
| DMASnI₃ | DI water | 50 | |
| DMASnBr₃ | DI water | 6 | 19 |
| DMASnBr₃ | with Pt 1 wt% | triethanolamine aq (10%V) | 11 | |
| DMASnBr₃ | with Pt 3 wt% | triethanolamine aq (10%V) | 4.0 | 20 |
| C₃N₄/PEA₂SnBr₄ | toluene, with triethylamine (33 mM) and trifluoroacetic acid (33 mM) | 1613 | |
| Cs₂PbBr₃/Ru@TiO₂ | DI water, with N₂S and Na₂SO₃ | 7.72 | 22 |
| (Cs₂PbBr₃ₓZnₓ⁻)np (5.4 M) glass | | |
| x = 0 | 12.70 | |
| x = 0.5 | 12.54 | |
| x = 0.9 | 169.21 | |

The examples reported so far in the previous two sections are based on suspended materials in direct contact with the reaction environment where the MHPs play the direct role of photocatalyst in the form of pristine materials or in composites, which however still imposes more or less rigid limitations to the usable reaction medium. Another approach which has been recently explored to promote hydrogen photogeneration in water is the construction of photodevices including a MHP layer (not in contact with water), which however plays the only role of light absorber, using device architectures closely resembling those of perovskite solar cells. Another approach which has been recently explored to promote hydrogen photogeneration in water is the construction of photodevices including a MHP layer (not in contact with water), which however plays the only role of light absorber, using device architectures closely resembling those of perovskite solar cells. The construction of such PEC cells is complex, and the photocathodes employed so far are expensive. While this technology will surely have a significant evolution in the next years, it is clearly more interesting to push the research toward more stable and effective MHPs, which can be directly used for photocatalytic applications.

CONCLUSIONS AND FUTURE PERSPECTIVES

In this Mini-Review, we highlighted the state-of-the-art use of MHPs as photocatalysts in the evolution of hydrogen under visible light. Table 1 summarizes the various systems considered in the present work together with the reaction environment and the H₂ production activity. To date, most of the examples refer to applications for the HI/HBr splitting in order to avoid the well-known degradation of MHPs in aqueous environments. Few examples, however, are appearing in the current literature showing lead-free perovskites with an enhanced water-stability and their direct hydrogen production from water. While encapsulation strategies could for sure advance the field, it would be even more advantageous to explore novel compositions highlighting such improved stability in an aqueous environment which is closer to real application conditions and, in addition, getting rid of the...
presence of lead. Such route toward water-stable MHPs requires and extended use of materials chemistry and computational modeling and the exploration of Sn-, Bi-, and Ge-based compositions which have suitable optical properties. Moreover, 2D perovskites, containing highly hydrophobic organic groups between the inorganic octahedra framework, could enhance such stability in relevant aqueous environments while preserving optimal charge-carrier dynamics features. Together with this exciting materials discovery route, a further extension in the creation of MHPs-based photocatalytic composites could significantly extend the range of solar-driven utilization. This should also be seen not only with respect of adding a cocatalyst to MHPs but also considering the MHP as a cocatalyst itself to reduce the charge carrier recombination in conventional catalysts such as carbon nitride and titanium dioxide. The huge tunability in the band gap of MHPs allows to engineer the relative band-alignment between two semiconductors thus taking advantage of the relative efficiencies. Moreover, the ease of fabrication of MHPs in various forms such as microcrystals, nanocrystals, and films, add a further degree of freedom to design devices and Z-scheme architectures. In this respect, it is worth mentioning here a very recent report of the development of a direct Z-scheme photocatalyst based on FAPbBr3/Bi4WO12 with strong redox ability for solar-to-chemical energy conversion.25 Such an approach must be further exploited for overall water splitting by MHPs-based systems.

To conclude, MHPs photocatalysts, in addition to hydrogen generation discussed here, have already shown an impact on many solar-driven reactions such as CO2 reduction, pollutant degradation, and photochemical organic syntheses in full analogy to traditional catalysts. All these fields would highly benefit from the developments suggested and highlighted above, allowing us to shine a novel light on the future exploitation of MHPs.

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The authors declare no competing financial interest.

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