

Halide Perovskite Photocatalysts for Clean Fuel Production and Organic Synthesis: Opportunities and Challenges

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The need to constrain the use of fossil fuels causing global warming is motivating the development of a variety of photocatalysts for solar-to-fuel generation and chemical synthesis. In particular, semiconductor-based photocatalysts have been extensively exploited in solar-driven organic synthesis, carbon dioxide (CO₂) conversion into value-added products, and hydrogen (H₂) generation from water (H₂O) splitting. Recently, metal halide perovskites (MHPs) have emerged as an important class of semiconductors for heterogeneous photocatalysis owing to their interesting properties. Despite key issues with long-term stability and degradation in polar solvents due to their ionic character, there has been significant progress in halide perovskite-based photocatalysts with improving their stability and performance in the gas and liquid phases. This review discusses the state-of-the-art for using halide perovskite-based photocatalysts and photoelectrocatalysis in hydrogen production from water and halogen acid solutions, CO₂ reduction into value-added chemicals, and various organic chemical transformations. The different types of halide perovskites used, design strategies to overcome the instability issues in polar solvents, and the efficiencies achieved are discussed. Furthermore, the outstanding challenges associated with the use of polar electrolytes and how the stability and performance can be improved are discussed.

1. Introduction

Global warming caused by burning fossil fuels is one of the world's most significant concerns.^[1,2] The annual release of CO₂ equivalent (CO₂eq) emissions (>37 tonnes per year in 2023) has been increasing each year and already exceeds the amount consumed by plants for photosynthesis.^[3] Therefore, clean energy generation from renewable energy sources, as well as effective approaches for CO₂ capture and removal, are crucial to limit the effects of climate change.^[4,5] Solar energy is the most abundant source of clean energy.^[6–8] Harvesting solar energy can be used not only to produce clean electricity, but also to decarbonize the chemicals industry, producing fuels sustainably. These fuels are needed for transport, the production of plastics, as well as fertilizer, among many other examples. Hence, alongside the need for electrification, it is equally important to shift towards zero- or low-emission fuels, such as hydrogen, or net-zero fuels, such as hydrocarbon fuels generated from

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captured CO₂.^[9] Hydrogen as a fuel source can be burnt in a combustion engine or used in a fuel cell, with the latter constituting a “cleaner” option,^[10] since the only by-product is water. Hydrogen is classified into various categories depending on the way it is sourced, two of which are *grey hydrogen* and *green hydrogen*. The former relies on the use of natural gas, and there is therefore a non-zero CO₂eq footprint associated with it. In contrast, green hydrogen refers to H₂ produced by splitting water using clean energy sources, such as by harvesting solar energy. This involves the use of a photocatalyst that absorbs light to generate free charge carriers which then drive the required chemical reactions. Considering the whole lifecycle, hydrogen is not necessarily the most sustainable source of energy. Green hydrogen production requires the input of electrical energy. Reconverting H₂ into electrical energy further downstream constitutes a significant overall energy loss. Whilst the direct use of electricity may be more efficient in certain applications (e.g., heating), H₂ nevertheless holds importance as a feedstock in several industries on which modern-day life depends, the most important of which are fertilizer synthesis, oil refining, and steel production. In 2022, green hydrogen constituted only 3% of all hydrogen produced worldwide, while grey hydrogen constituted nearly 96%.^[11]

Another way of storing solar energy in green fuels is by making hydrocarbons via CO₂ capture and reduction.^[12] While these fuels do not contribute to decarbonizing the energy sector, they are critical for achieving net-zero CO₂eq emissions goals. Although the specific energy density (MJ kg⁻¹) of H₂ is three times that of gasoline,^[13,14] synthetic hydrocarbon fuels offer advantages in that their use requires no change to existing infrastructure, such as pipelines for gas transport. This is in contrast with the significant costs associated with building new specialized networks or adapting existing ones to mitigate the risks of structural damage due to hydrogen exposure (e.g., hydrogen embrittlement of steels).^[15] Furthermore, photocatalytic conversion of CO₂ into chemical fuels like ethanol does not pose a threat to food security as in the case of bioethanol, which competes for agricultural land.^[16] Nonetheless, CO₂ reduction can lead to a variety of products depending on catalyst choice and reaction conditions,^[17] making selectivity an added issue compared to photocatalytic hydrogen evolution. Furthermore, while CO₂ reduction to certain alcohols and hydrocarbons is more thermodynamically favorable than proton reduction, given the more positive reduction potentials, these reactions suffer from a kinetic barrier associated with the requirement of multiple proton-coupled electron transfer steps.^[18]

In addition to using sunlight to drive the production of hydrogen and synthetic fuels, another application of interest is organic synthesis. Indeed, the realization of the importance of photochemistry dates back to the early 1900s, when scientists recognized the need to optimize synthetic processes by relying on light energy rather than conditions involving high temperatures

and harsh chemicals.^[19] In addition to optimized reaction conditions, photochemistry also opens the door to previously inaccessible transformations, since the reactivity of molecules in the excited state differs from that in the ground state.^[20]

Considering the above, solar-driven fuel production and chemical synthesis are important. Efforts to drive photoelectrocatalytic and photocatalytic generation of hydrogen and synthetic hydrocarbons date back to the 1970s and 1980s,^[21–24] following the pioneering work by Fujishima and Honda in 1972, when they used a photoelectrochemical cell to drive overall water splitting (OWS), with TiO₂ as a photoanode and Pt as a cathode.^[24] Since then, research so far has focused primarily on inorganic, wide-bandgap semiconductors. But the performance of these materials is limited by their inability to harness solar energy in the visible wavelength range, which has significantly higher solar irradiance than in the UV.^[25] While certain lower-bandgap inorganic semiconductors can utilize visible light, another bottleneck of these materials is fast charge-carrier recombination, which limits the supply of photogenerated charge-carriers for redox reactions.^[26–28] Similarly, various types of photoredox catalysts may be used to catalyze organic synthesis, such as transition metal complexes and organic catalysts. However, these may be limited by their reliance on precious metals, moderate extinction coefficients, as well as challenges with synthesizing these catalysts at scale.^[29,30]

Over the last decade, metal halide perovskites (MHPs) have garnered significant attention due to their exceptional optoelectronic properties.^[31,32] They are categorized into two types: organic–inorganic hybrid and all-inorganic perovskites. They are commonly denoted by the chemical formula ABX₃, where the A-site can be either a monovalent inorganic or organic cation (such as Cs⁺ or CH₃NH₃⁺), B-site a divalent cation (like Pb²⁺, Sn²⁺, Sr²⁺, or their combinations), and the X-site a halide anion (Cl⁻, Br⁻, I⁻, or their combinations) (Figure 1a). The hybrid perovskites can also exist in layered structures. These include Ruddlesden–Popper perovskites, which have the general formula L₂A_{n-1}Pb_nX_{3n+1}, where the L-site is occupied by a long-chain organic amine cation (spacer), the A-site is a short-chain organic cation, and *n* is an integer.^[33] Since 2009, when Miyasaka and co-workers published the first report on the use of 3D MHPs in solar cells,^[34] a broad set of materials within the halide perovskite family have been used in photovoltaics, demonstrating remarkable efficiencies of up to a certified value of 27.0% in single-junction cells and 34.6% in perovskite/Si tandem photovoltaics (exceeding the practical limit of single-junction crystalline Si solar cells of 28%).^[35] These figures underscore the exceptional light-absorbing properties of MHPs across a wide spectrum, coupled with their extended charge-carrier diffusion lengths.^[31] The properties of MHPs, in terms of their ease of synthesis, tunable bandgaps, defect tolerance, and charge transport, make them promising candidates in solar cells and as photocatalysts to drive solar-fuel generation and organic synthesis. For instance, the bandgap of MHPs could be finely tuned approximately from 1.2 to 3 eV (Figure 1b).^[36] This enables the valence and conduction band edges to be optimized to fulfill the thermodynamic requirements to drive a variety of chemical reactions (Figure 1b).

However, despite these favorable characteristics, the ionic nature of MHPs renders them prone to dissolution in moisture and polar solvents, thereby imposing significant challenges to their

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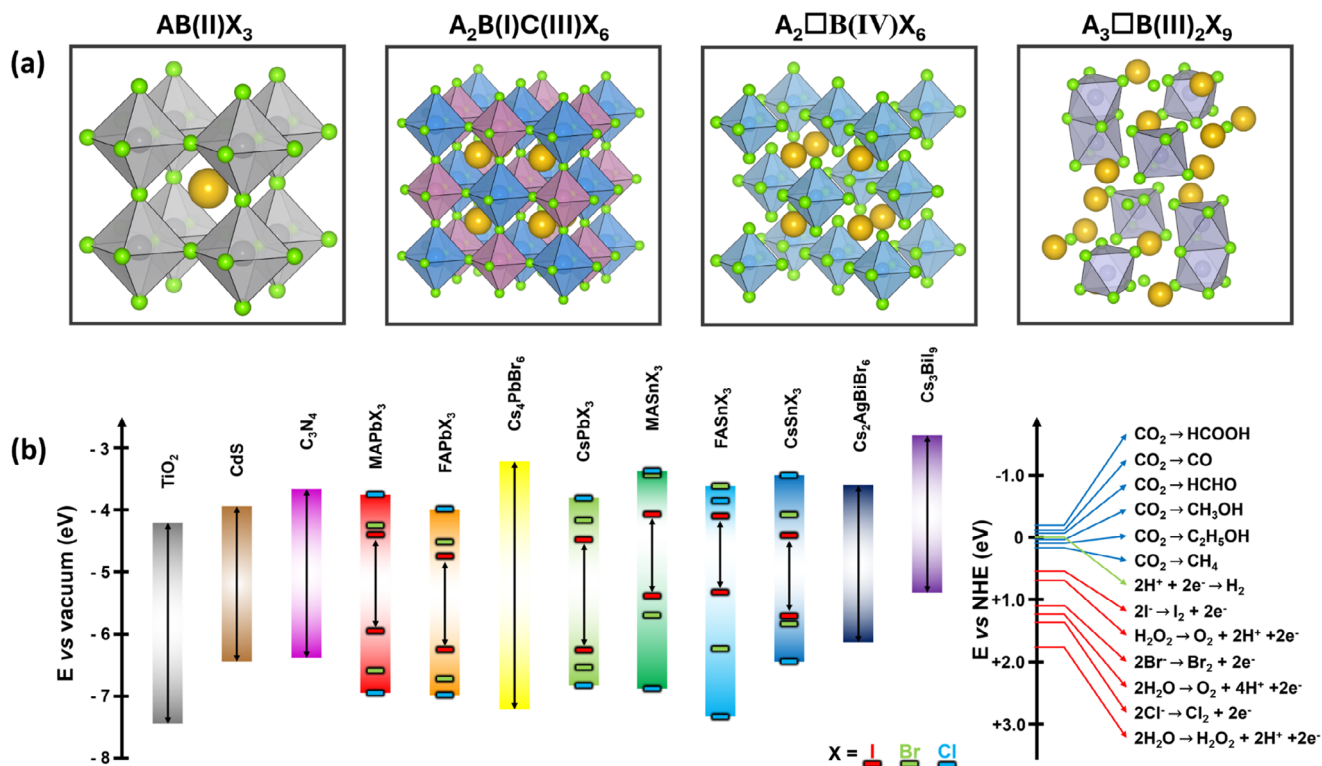


Figure 1. a) Crystal structures of ABX_3 halide perovskites, $A_2B(I)B(III)X_6$ double perovskites, $A_2\Box B(IV)X_6$ vacancy-ordered perovskites ($\Box$: vacancy), and $A_3\Box B(III)_2X_9$ 0D perovskite derivatives, which are potential photocatalysts for H_2 evolution, CO_2 reduction and organic synthesis.^[37] The crystal structures were drawn using the VESTA software. b) Band edge positions of different types of perovskite and perovskite-derivative photocatalysts relative to vacuum and the reversible hydrogen electrode (RHE).^[38]

employment in photocatalytic applications in polar solvents.^[39] To tackle this issue, various strategies have been used, such as H_2 generation in saturated hydrohalic acid solution, the use of non-polar or low-polar solvents, lowering the structural dimensionality, and relying on heterojunctions or encapsulants.^[40–46] The first strategy was pioneered by Park and co-workers when they relied on the common-ion effect to produce water-stable MHPs in aqueous environments to produce H_2 from HI splitting.^[47] Employing heterojunctions or encapsulants based on organic ligands, polymers, MOFs, and inorganic materials has also been a strategy used to enhance their stability in water.^[42,48–52] For example, in recent literature, bola-amphiphilic ligands (organic ligands) utilized to cap $CsPbBr_3$ NCs and successfully employed in a photocatalytic acrylamide polymerization in an aqueous medium.^[42,53,54] Other than that, few all inorganic MHPs were realized for their inherent stability in polar environments or moisture, attributed to their composition, which includes materials such as $Rb_3Bi_2I_9$, $Cs_3Bi_2I_9$, $MA_3Bi_2I_9$, $Cs_2AgBiBr_6$, among others.^[55–58] Nonetheless, while the above approaches can improve stability, photocatalytic activity remains low. Indeed, another bottleneck to overcome is the presence of active sites, whether intrinsic or co-catalyst incorporation. Such sites are key to reducing the energetic barriers associated with the reactions involved, thus enhancing activities.

Bearing in mind the importance of the photocatalytic applications outlined above, and the pros and cons of MHPs in photocatalysis, this review aims to discuss the research progress in

using MHPs as photo(electro)catalysts for hydrogen evolution, CO_2 reduction, and organic synthesis. While various existing reviews tackle the same topics independently at different levels of depth,^[59–65] this review provides a comprehensive overview of halide perovskite-based photocatalytic applications covering solar-to-fuel generation as well as a wide range of organic reactions along with discussions on associated challenges. Especially, the challenges associated with water oxidation are often neglected when focusing on the proton reduction half-reaction but are key to moving away from relying on sacrificial oxidation half-reactions to drive fuel synthesis.

2. Design Strategies for Perovskite Photocatalysis

The reaction medium or solvent in which heterogeneous photocatalytic reactions are performed plays a crucial role in the efficiency and long-term stability of catalysts.^[66–69] In general, photocatalytic H_2O splitting, CO_2 reduction, and dye degradation reactions require water or polar solvents.^[17,70–72] However, unlike traditional photocatalysts, such as oxides (e.g., TiO_2) and metal chalcogenides (e.g., CdS), halide perovskites are prone to degradation in water due to the soft and ionic nature of these materials.^[40,45,46,62,64,73–77] This section briefly discusses the most widely implemented strategies for performing perovskite photocatalysis by overcoming their degradation in polar solvents.^[46,78–80] These methods include the use of hydrohalic acid solutions (e.g., HBr , HCl) instead of pure water for

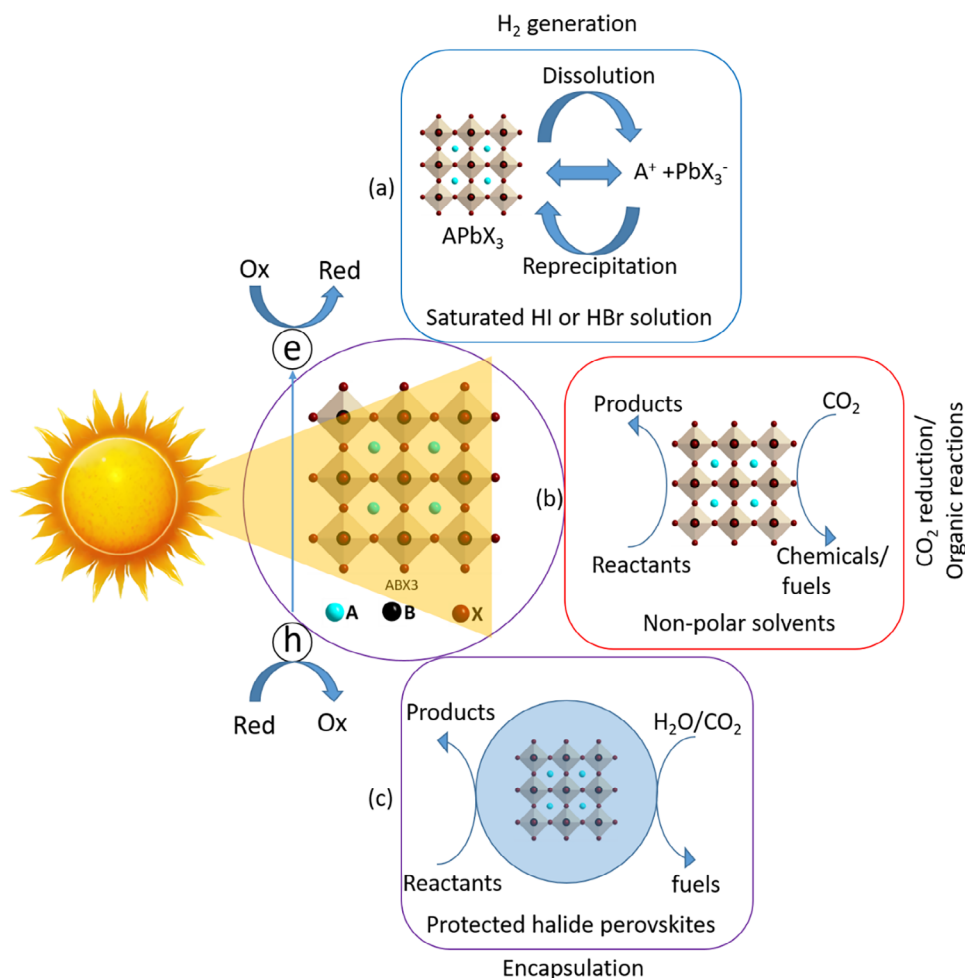


Figure 2. Strategies used to avoid polar solvent-induced degradation in perovskite photocatalysis for H₂ generation and CO₂ reduction: a) Using saturated haloacid (HI or HBr) solutions that prevent the dissolution of perovskites by establishing a dynamic equilibrium between the dissolved ions (Cs⁺/MA⁺/FA⁺ and PbX₃⁻) and perovskites. b) Using relatively less polar or non-polar organic solvents to dissolve CO₂ for its reduction. c) Encapsulation with bulky ligands or shell structures that prevent direct contact of colloidal or thin film perovskites with polar solvents. The materials used for encapsulation should not degrade in electrolyte solution but should transport photogenerated charges.

hydrogen evolution reactions,^[47] low-polarity solvents for dissolution of CO₂ for its reduction (e.g., ethyl acetate),^[81] encapsulated perovskites (thin films and colloids) that survive in aqueous solutions,^[39,82–84] surface and ligand engineering of perovskites that offers the inherent stability in water, which are schematically illustrated in **Figure 2**.

2.1. Saturated Hydrohalic Acid Solutions

An innovative approach that has been used to overcome the instability of MHPs in polar solvents is the use of saturated hydrohalic acids (HBr or HI) as a solvent medium that helps to establish a dynamic equilibrium between the disintegration of perovskites into ions (A⁺ and PbX₃⁻) and their recrystallization, thereby enabling the photocatalytic transformation of HX into hydrogen (Figure 2a).^[47,85–88] Park and co-workers first reported this approach to convert HI into H₂ using MAPbI₃ as the photocatalyst.^[47] The idea behind this approach is that the

perovskites precipitate in a saturated solution as the concentration of ions exceeds the solubility limit, thus stabilizing the perovskite material. Therefore, the minimum concentration of perovskites required for a stable colloidal dispersion, i.e., a saturated perovskite, in HI solution can be obtained from solubility measurements. For MAPbI₃, the solubility limit at 20 °C was found to be ≈0.645 mol L⁻¹. In addition, the concentration of H⁺ and I⁻ ions was found to be crucial for the stabilization of the perovskite crystals in the saturated aqueous solution. This is because PbI₂, which is less soluble in aqueous solution, dissolves in water in the form of PbI₃⁻ or PbI₄²⁻ at high iodide concentrations.^[47] On the other hand, the intermolecular hydrogen bonding between water molecules at highly acidic conditions can decrease the hydration of perovskites. Therefore, a high ionic strength along with a low iodide concentration ([I⁻] ≤ [H⁺]) and high acidic conditions are required for the long-term stability of a perovskite phase. This (i.e., [I⁻] ≤ [H⁺]) can be achieved by the addition of HClO₄ to a saturated HI solution.^[47] Under these optimum conditions, the MAPbI₃ photocatalyst remains stable

under continuous light irradiation for 160 h and splits HI into H_2 with constant efficiency. It should be noted that the I^- of HI converts into I_3^- during the photocatalytic reaction, and the solution turns brown, affecting light absorption by the MHP. To overcome this, H_3PO_2 was added as a selective reducing agent to reconvert I_3^- into I^- , enabling constant H_2 production from HI (This is also briefly repeated in section 3: H_2 evolution). This approach has been extensively used in perovskite photocatalysis for H_2 production using different photocatalysts, including Pb-based (e.g., $MAPbBr_3$, $CsPbBr_3$) and Pb-free (e.g., $A_2^{I}B^{III}X_6$, $MA_3Bi_2I_9$) materials.^[31,40,43,44,46,85,89–94] Currently, perovskite photocatalysts are undergoing further chemical engineering (tuning halide composition and combining them with co-catalysts such as TiO_2 , Pt, black phosphorus, and graphene oxide) to improve their stability and efficiency.^[87,88,90,95–104] Some examples are discussed in section 3 regarding their preparation and H_2 evolution efficiency ($\mu mol\ g^{-1}\ h^{-1}$).

2.2. Organic Solvents for CO_2 Reduction and Organic Chemical Reactions

Another solution to the problem of perovskite instability in polar electrolytes would be to use lower-polarity or non-polar organic solvents to perform perovskite photocatalysis for CO_2 reduction and organic chemical reactions (Figure 2b).^[29,81,105–109] Organic solvents do not dissociate ionic perovskite crystals as they do not coordinate well with the corresponding ions. For this reason, organic solvents have been commonly used as antisolvents in perovskite crystallization on a substrate and colloidal solution.^[29,81,105–109] In addition, ligand-capped colloidal perovskite nanocrystals can be well dispersed in organic solvents, which makes them ideal candidates for photocatalytic CO_2 reduction and organic chemical transformations.^[110,111] However, the solubility of CO_2 is also crucial in choosing the most appropriate solvent for efficient photocatalysis. In addition, one has to be cautious in the analysis of the reaction products of photocatalysis in organic solvents. This is because perovskite photoreduction of organic solvents can lead to CO production up to a rate of $1000\ \mu mol\ g^{-1}\ h^{-1}$. Such photoredox organic molecules can produce CO and CH_4 at a much higher rate than in typical photocatalytic CO_2 reduction reactions. There is a chance the reaction products could simply be due to the organic chemical transformation, rather than CO_2 reduction. Therefore, control experiments, e.g., analysis of reaction products without CO_2 in the reaction medium, are needed to avoid the overestimation of efficiencies.^[112] Furthermore, the photodecomposition of organic capping ligands can also lead to the production of CO without CO_2 in the reaction medium. However, the process mainly occurs under UV light irradiation. Therefore, it is important to cut off UV light from the excitation source using a UV filter.^[113] Despite many available organic solvents, acetonitrile and ethyl acetate, which have relatively low polarity, have been the most widely used in perovskite photocatalysis for CO_2 reduction.^[46,111] In addition, a trace amount of water is also used as a hole scavenger and thus generates oxygen and hydrogen through a water-splitting reaction that competes with CO_2 reduction (Figure 2b). On the other hand, for organic chemical reactions, organic solvents, such as acetonitrile, dichloroethane, dichloromethane, toluene, chloro-

reform, tetrahydrofuran, dichloroethane, dioxane, and ethanol have often been used depending on the required reaction conditions.^[29,114–120] Over the years, both Pb-based and Pb-free perovskites (e.g., $CsPbBr_3$, $Cs_2AgBiBr_6$, Cs_2SnI_6 , $Cs_3Bi_2I_9$) in combination with co-catalysts, such as graphene oxide, graphene, carbon nitride, TiO_2 , MOFs, and Mxene, have been studied as photocatalysts for CO_2 reduction.^[43,46,111,121–129] Some of these are discussed in Section 4 on perovskite photocatalytic CO_2 reduction. On the other hand, colloidal NCs of inorganic halide perovskites, especially, $CsPbBr_3$, have been used in photocatalytic chemical transformations (See Section 5 about chemical transformations).^[29,31,130]

2.3. Encapsulation of Perovskites

Physically separating the perovskite material from the dispersant/electrolyte is another effective way to prevent their degradation.^[53,73,131–133] This can be achieved through a core-shell structure (for nanocrystals), or the use of a protective over-layer in the case of thin films (Figure 2c).^[41–43,80,132,134,135] These protective layers can also prevent the degradation of perovskites by harsh conditions, such as heat and UV light, and provide long-term stability.^[73] However, the shells must be transparent to light and allow charge carriers to pass through to reach their surface where light-induced chemical transformations (water splitting, CO_2 reduction, and chemical synthesis) occur.^[136,137] In addition, the protective materials also act as co-catalysts for enhanced charge separation.^[81,137]

Various inorganic coatings have been explored using techniques like atomic layer deposition (ALD) and solution processing to apply thin layers onto the perovskites with an organic buffer layer in between. Materials such as AlO_x , zeolites, and glassy substances (including silicates and lead oxide) offer stability for up to 3–4 months against water but fail to address photocatalytic challenges due to their insulating properties.^[39] In contrast, inorganic semiconducting coatings of a few nanometers (1–10 nm) resolve this issue while facilitating charge-carrier transport. For example, Li et al. reported coating $CsPbBr_3$ with TiO_2 using a titanium precursor followed by calcination at $300\ ^\circ C$ (higher temperatures could lead to perovskite degradation). The resulting composites maintained stable charge transport properties for over three months. The composite exhibited reduced resistance for charge transport and thus led to enhanced photocurrent compared to pure $CsPbBr_3$, as revealed by electrochemical impedance spectroscopy and photocurrent measurements, respectively.^[52] Similarly, Xu et al. coated $CsPbBr_3$ with amorphous TiO_2 and used it as a photocatalyst for CO_2 reduction.^[83] In this case, charge consumption increased by 6.5 times, and CO_2 adsorption improved significantly. Such coatings are of great interest to the catalysis community, offering a synergistic effect that enhances charge separation and reactant adsorption. Although these structures possess poor dispersibility in water and thus are not well suited for solution-based photocatalysis.^[138] However, in the case of photoelectrochemical water-splitting devices, the hole and electron transport layers, as well as the electrodes coated on the perovskite layers, also serve as protective layers.^[40,131,139] Further details on the use of encapsulated colloidal perovskite NCs and

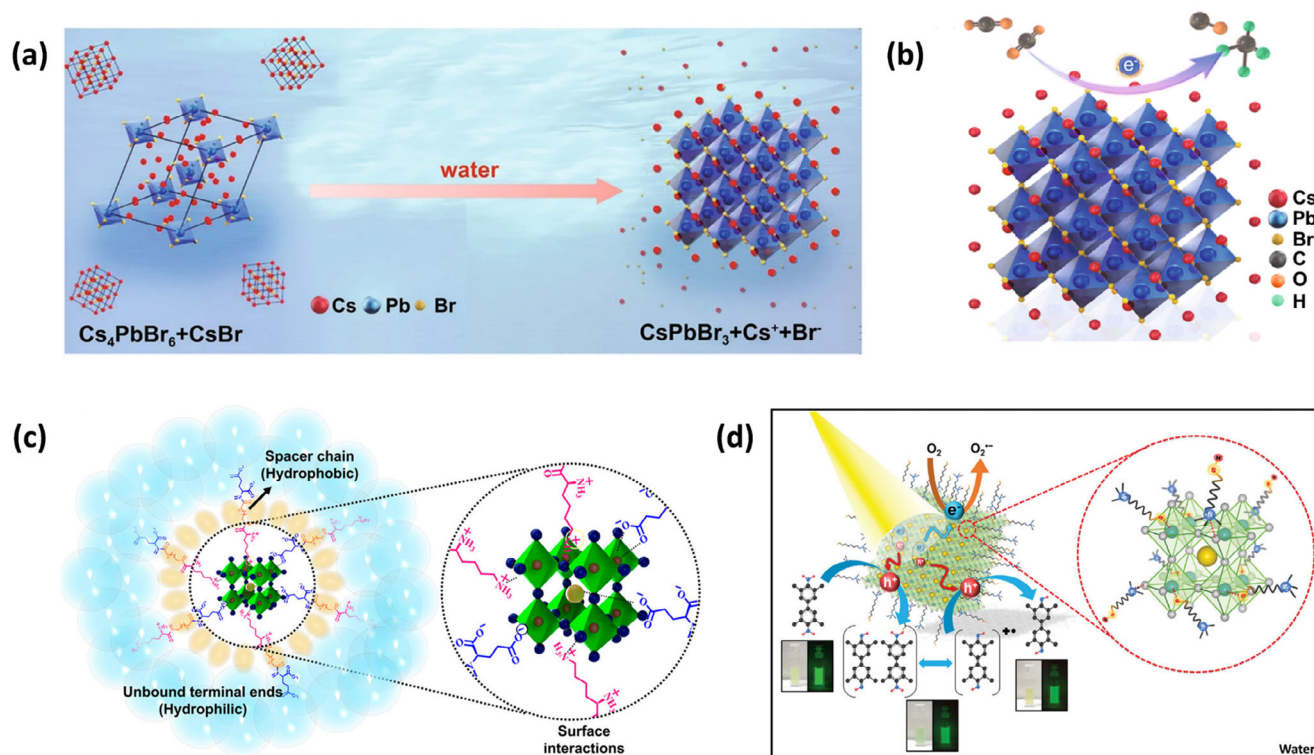


Figure 3. a) Schematic illustration of the phase transition from Cs_4PbBr_6 to CsPbBr_3 in water. b) Illustration of CO_2 reduction reaction using water-dispersed CsPbBr_3 . Reproduced with permission.^[138] Copyright 2021, the Author(s). c,d) Schematic representation of NKE-12 (c) (Reprinted with permission.^[42] Copyright 2023, American Chemical Society) and MUTAB (d) ligand anchored on perovskite surface and their interaction with water. Reproduced with permission.^[141] Copyright 2024, Wiley-VCH.

perovskite photoelectrochemical cells for water splitting, CO_2 reduction, and chemical reactions are discussed in later sections.

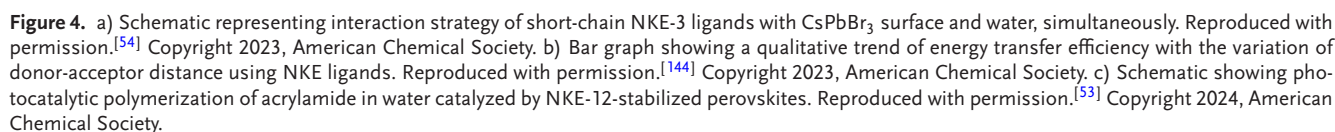
2.4. Surface Engineering

Another strategy to maintain charge transfer properties with improved stability in polar solvents is surface engineering. This approach involves modifying the surface of perovskites to prevent polar molecules, like water, from interacting with the core structure. Using non-stoichiometric precursors creates different intermediates, leading to the formation of various phases. An example of a core-shell structure investigated is CsPbBr_3 core with Cs_4PbBr_6 shell, doped with cobalt prepared while capping with hexafluoro butyl methacrylate. The structures were further employed for photocatalytic CO_2 reduction in pure water.^[140] Chen et al. synthesized water-dispersible CsPbBr_3 nanocrystals (NCs) by utilizing a hot-injection method under non-stoichiometric conditions.^[138] Unlike encapsulated structures, these nanocrystals demonstrated remarkable water dispersibility and exceptional stability for over 200 days. The synthetic process was designed to create a Cs- and Br-rich environment while maintaining low Pb conditions, resulting in mixed-phase $\text{CsBr}/\text{Cs}_4\text{PbBr}_6$ structures. An optimized washing procedure further facilitated the formation of water-dispersible CsPbBr_3 NCs, schematically presented in Figure 3a.^[11] These findings were attributed to the well-passivated CsBr termination on the nanocrystals, which can

potentially form an electrical double layer, acting as a protective barrier. When tested for catalytic applicability, these nanocrystals were successfully employed in electrochemical CO_2 reduction in water (Figure 3b). These strategies have met almost all the essential requirements for photocatalysis in polar solvents, making them a promising area for further exploration.

2.5. Ligand Engineering

Catalysis requires more than just water-stable hybrid perovskites. It also necessitates water-dispersible perovskites with enhanced charge localization to catalytically active sites. Achieving this involves engineering ligands that can stabilize colloidal lead halide perovskite nanocrystals in water. To date, ligands with dual functionality offering both hydrophobicity and strong anchoring properties have been investigated to improve water stability. For example, Haug and colleagues successfully stabilized CsPbX_3 ($\text{X} = \text{Br}/\text{I}$) nanocrystals in water for nearly 10 weeks by using polyhedral oligomeric silsesquioxane (POSS). POSS formed a cage-like structure around the nanocrystals, with lead-sulfur bonds providing stability.^[142] Additionally, metal stearates have been explored as ligands, where the stearate imparts hydrophobicity, leading to excellent water stability.^[143] However, despite these promising approaches, they have not been widely applied in photocatalysis due to challenges related to charge transport, surface accessibility, and water dispersibility.



Building on these foundational studies, subsequent research from the group confirmed the practical applicability of these systems in photocatalysis. The stabilized halide perovskites successfully catalyzed polymerization reactions and redox transformations in aqueous media.^[53,141] As shown in Figures 3d and 4c, these reactions leveraged the robust stability and enhanced charge transfer properties imparted by the engineered ligands. This work represents a significant advancement in the development of halide perovskite materials for use in polar solvents, offering a pathway to simultaneously improve their stability and preserve their photocatalytic functionality.

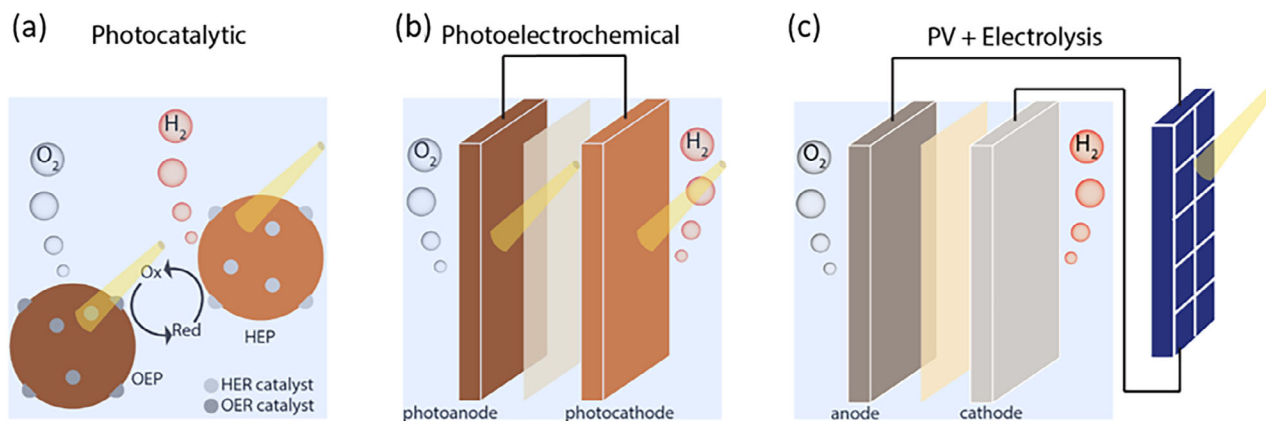


Figure 5. Diagram showing the three main technologies for generating hydrogen from sunlight: a) photocatalytic, b) photoelectrochemical, and c) photovoltaic-electrolyzer systems. OEP and HEP in (a) correspond to the oxygen evolution photocatalyst and hydrogen evolution photocatalyst, respectively. The illustrations are representations of example systems of each technology, but other configurations are possible for each. For example, in the photocatalytic case represented here, the photogenerated electron on the HEP component reduces protons to make H_2 , while the photogenerated hole is consumed by a redox mediator to form the “Ox” species. Similarly, the photogenerated hole on the OEP oxidizes water, while the corresponding electron is consumed by the oxidized mediator to regenerate the “Red” species. This is referred to as a redox-mediated Z-scheme. Another possible device is a hybrid between PEC and PV-EC, with one of the photoelectrodes in (b) relying on a catalyst-coated PV cell, and the whole system being fully integrated and wireless. This is referred to as integrated PV-PEC tandem or artificial leaf.^[154,156]

The strategies described in these studies could serve as a blueprint for advancing the stability of halide perovskites in challenging environments, particularly in polar media, without compromising their desirable photophysical and photocatalytic properties. This strategy holds transformative potential for the future of halide perovskite-based catalysis.

3. H_2 Evolution

In the context of hydrogen evolution, we start with a discussion of the main technologies for hydrogen production using sunlight and outline the limiting factors associated with some of these processes both in terms of the technology itself (Section 3.1.), as well as from the viewpoint of thermodynamic and kinetic limitations of the underlying chemistry (Section 3.2.). Specifically, in the case of the latter, we include a discussion of the mechanistic intricacies of the oxygen evolution reaction (OER). This is often neglected in the context of lead-halide perovskites. Granted, these materials are not a straightforward candidate for water oxidation due to moisture sensitivity. Nonetheless, it is often suggested or implied that MHPs can act as photocatalysts for oxygen evolution, whether in the context of OWS or performing gas-phase CO_2 reduction in the presence of water vapor. After discussion of the thermodynamic and kinetic aspects, we outline the metrics used to evaluate catalytic activity (Section 3.3). In Section 3.4., we review the literature relevant to MHP photocatalysts for hydrogen evolution. This is followed by a brief review of the application of these materials in the context of photoelectrochemical water splitting in Section 3.5.

3.1. Green Hydrogen Production

There are three device types that absorb solar energy to drive water or HI splitting.^[47,145] These are, in order of increasing complexity: a particulate system, a photoelectrochemical cell (PEC),

or a photovoltaic-electrolyzer (PV-EC) tandem system (Figure 5). PV-EC tandems have already surpassed the 10% solar-to-fuel efficiency threshold required for commercialization,^[146] and are the most mature technology, with a technology readiness level of 9.^[147] The particulate device is the simplest in many respects, requiring no wiring, multi-component devices, or a corrosive electrolyte, making it the most promising in terms of yielding low cost green hydrogen.^[148] Nonetheless, there are significant hurdles yet to overcome for this to be viable on a large scale, namely system efficiency, stability, and safety in terms of gas separation in the context of OWS. As for the other two technologies, it is increasingly believed that traditional PECs can no longer compete against PV-EC, a technology that has benefitted from the low cost of electricity produced by silicon PV cells.^[147,149–151] In fact, the leveled cost of hydrogen is estimated at 6.22 and 8.43 \$ $kg_{H_2}^{-1}$ for a PV-EC and a PEC system, respectively.^[150] Nonetheless, these costs remain significantly higher than that of grey hydrogen, which averaged 2.13 \$ $kg_{H_2}^{-1}$ in 2023,^[145,149,151,152] as well as the US Department of Energy Hydrogen Shot target of 1 \$ $kg^{-1} H_2$ by 2031.^[153] This highlights the importance of ongoing research into particulate systems, as well as the promising PV-PEC hybrids, also termed artificial leaves.^[154,155] The latter offers the advantage of more compact devices compared to traditional PV-EC. Furthermore, their potential for commercialization can benefit from the increased flexibility, weight reduction, and cheaper manufacturing, which are afforded by thin-film PV technologies, such as perovskite solar cells.

3.2. Thermodynamics and Kinetics of Water and HI Splitting

Overall Water Splitting (OWS): The light-driven splitting of water was first reported in 1972 by Fujishima and Honda using a photoelectrochemical cell with TiO_2 as a photoanode and Pt as a

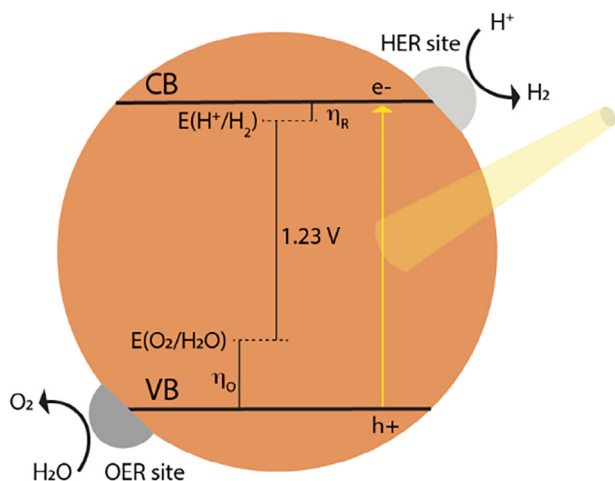


Figure 6. Schematic energy diagram of single-component-mediated photocatalytic water splitting. The diagram shows the overpotentials η_O and η_R for the oxidation and reduction half-reactions, respectively; the water-splitting redox potential (1.23 V); photoexcited charges; co-catalyst active sites for HER and OER.

cathode.^[24] This was followed by the use of particulate photocatalytic systems in 1980.^[157]

The major limitation to commercial-scale green hydrogen production via water-splitting is finding a system that combines high efficiency, stability, and low cost. The reaction is thermodynamically uphill and requires a standard Gibbs free energy (ΔG^0) of 237.2 kJ mol⁻¹, or 1.23 V per electron (Equations 1–3). A semiconductor capable of OWS needs to have a bandgap of at least 1.23 eV, with its conduction band (CB) being shallower than the redox potential of the reduction half-reaction, and its valence band (VB) deeper than the redox potential of the oxidation half-reaction (Figure 6).

Proton reduction : $2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O}$

$$E^\theta = 0.00 \text{ V versus RHE at pH} = 0 \quad (1)$$

Water oxidation : $6\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}_3\text{O}^+ + 4\text{e}^-$

$$E^\theta = 1.23 \text{ V versus RHE at pH} = 0 \quad (2)$$

Water splitting : $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

$$E^\theta = 1.23 \text{ V versus RHE at pH} = 0 \quad (3)$$

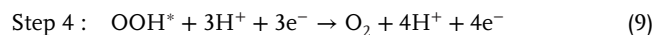
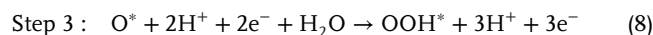
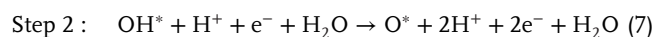
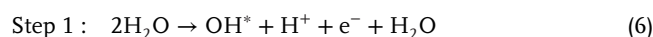
The steps involved in OWS are: i) light absorption by the semiconductor, ii) charge separation in the light harvester, iii) migration of the electron (hole) to the reduction (oxidation) site, where iv) charge transfer to H^+ (H_2O) occurs, followed by v) H_2 (O_2) desorption and collection. Each step presents limitations that depend on the photocatalyst (PC) in question, as well as on the device employed.

Proton reduction is a relatively simple two-electron process that proceeds via a single adsorbed intermediate and is suggested to proceed via one of two possible mechanisms: Volmer-Tafel or

Volmer-Heyrovsky.^[158] The reactions involved in the latter are illustrated in Equations (4) and (5).



This is in stark contrast with the sluggish, four-electron transfer, oxygen evolution reaction (OER).^[159] The conventional mechanism for OER is the adsorbate evolution mechanism (AEM). Herein, discussion of the mechanism for OER will focus on the example of the extensively studied metal-oxide catalysts, which include perovskite oxides. AEM occurs via three intermediates: OH^* , O^* , and OOH^* .^[160,161] These occur at active metal ion sites, and the proposed mechanism involved is shown in Equations (6–9).



The activation energy barrier for each step varies depending on the material, and the largest barrier defines the potential-determining step (note that this may be different from the rate-determining step).^[162,163] This results in the need for an overpotential (η) to be supplied beyond the thermodynamic requirement of 1.23 eV to drive OWS. In fact, the band gap of the light-harvesting semiconductor required for OWS is around 1.9–2.3 eV when taking into account thermodynamic losses (0.3–0.5 eV) and the required overpotential (0.4–0.6 eV).^[164]

This is clearly illustrated in the energy diagram in Figure 7, which shows that based on the equilibrium potential, a reaction free-energy equivalent to +1.23 eV is expected for each of the four OER steps at no applied bias ($U = 0$ V). It follows that the ideal catalyst would mean that all four reactions have a free-energy of 0 kJ mol⁻¹ at an applied potential of $U = 1.23$ V (i.e., all steps are thermoneutral), and that at $U > 1.23$ V, the reactions are exothermic. However, this is never observed, since a potential-determining step always occurs, such that a significant overpotential is required ($U \gg 1.23$ V) to render all steps exothermic. The reason for this is the scaling relation that has been observed between the binding energies of OH^* and OOH^* on a wide range of oxide catalysts, as shown in Figure 8a,^[162] and which is caused by the similar binding of both intermediates, on the same active site.^[162,163]

As a result, a constant free energy difference of 3.2 eV occurs between the two reactions (between steps 2 and 4), as shown in Figure 6, which translates to a minimum overpotential of ≈ 0.4 eV when we take into account the ideal free energy difference of 2.46 V ($[(3.2 - 2.46 \text{ V})/2]$). It thus follows that the difference $\Delta G_{\text{Oads}} - \Delta G_{\text{OOHads}}$ determines the overpotential, i.e., whether step 2 or 3 is the potential-determining step.^[162,163] Reaction 4 is never potential-determining in this model.^[162,163] Given the above, $\Delta G_{\text{Oads}} - \Delta G_{\text{OOHads}}$ is used as a descriptor to compare the activity of different OER catalysts in a volcano plot, with higher

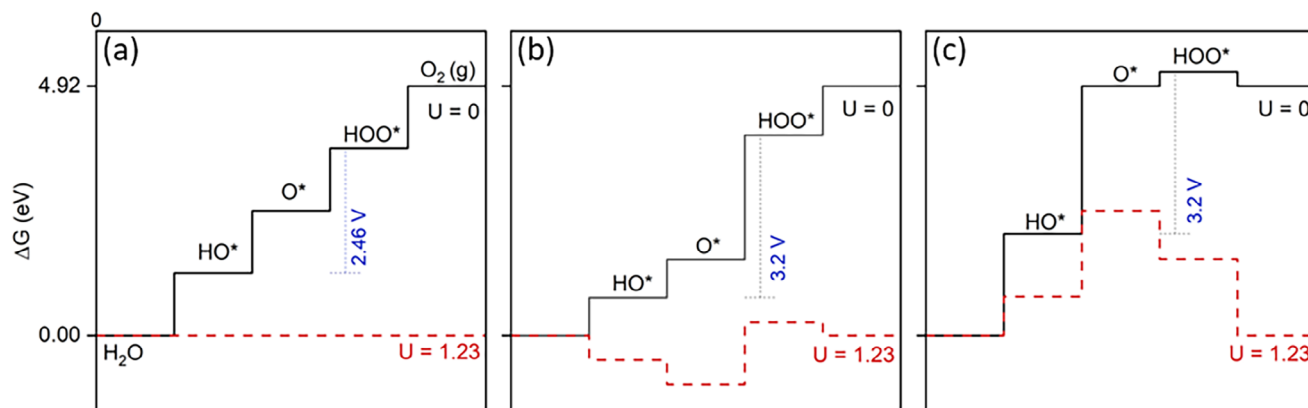


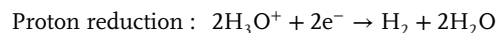
Figure 7. The free energy diagram for three types of metal oxide-based OER catalysts modeled according to ref. [162]. a) The (non-existent) ideal catalyst, where thermoneutrality is achieved at an applied potential $U = 1.23$ V (dashed red curve); b) a catalyst which binds the intermediates too strongly, making oxidation of O^* (step 3) potential-determining; c) a catalyst which binds the intermediates weakly, making oxidation of OH^* (step 2) potential determining. In (b) and (c), U has to be significantly larger than 1.23 V to make all steps exothermic ($U > 1.23$ V not represented above for simplicity). The dashed blue lines and values in blue represent the difference between the binding energies of HOO^* and HO^* .

activity being synonymous with lower overpotential (Figure 8b). The minimum overpotential requirement means the apex of the volcano occurs around $\eta = 0.4$ V.

In the case of the hydrogen evolution reaction (HER), the descriptor is the adsorption energy of the only intermediate involved, i.e., H_{ads} . To maximize activity, H_{ads} needs to interact sufficiently strongly with the catalyst for the second step to occur, but not too strongly in order to minimize the back reaction. Pt, at the apex of the volcano, is known to be the most efficient catalyst for HER due to optimal adsorption energy ($\Delta G_{H_{ads}} \approx 0$).^[90,165] Given the above considerations regarding thermodynamic and kinetic requirements for the two half-reactions involved in OWS, photo-

catalytic H_2 production has largely relied on sacrificial oxidations to replace the demanding water oxidation half-reaction.

HI Splitting: The process of splitting hydrohalic acids is thermodynamically and kinetically easier than OWS, as it involves a Gibbs free-energy change of $103.3 \text{ kJ mol}^{-1}$ (less than half that of OWS), and is a two-electron process, as shown in Equations (10–12).



$$E^0 = 0.00 \text{ V versus RHE at pH} = 0 \quad (10)$$

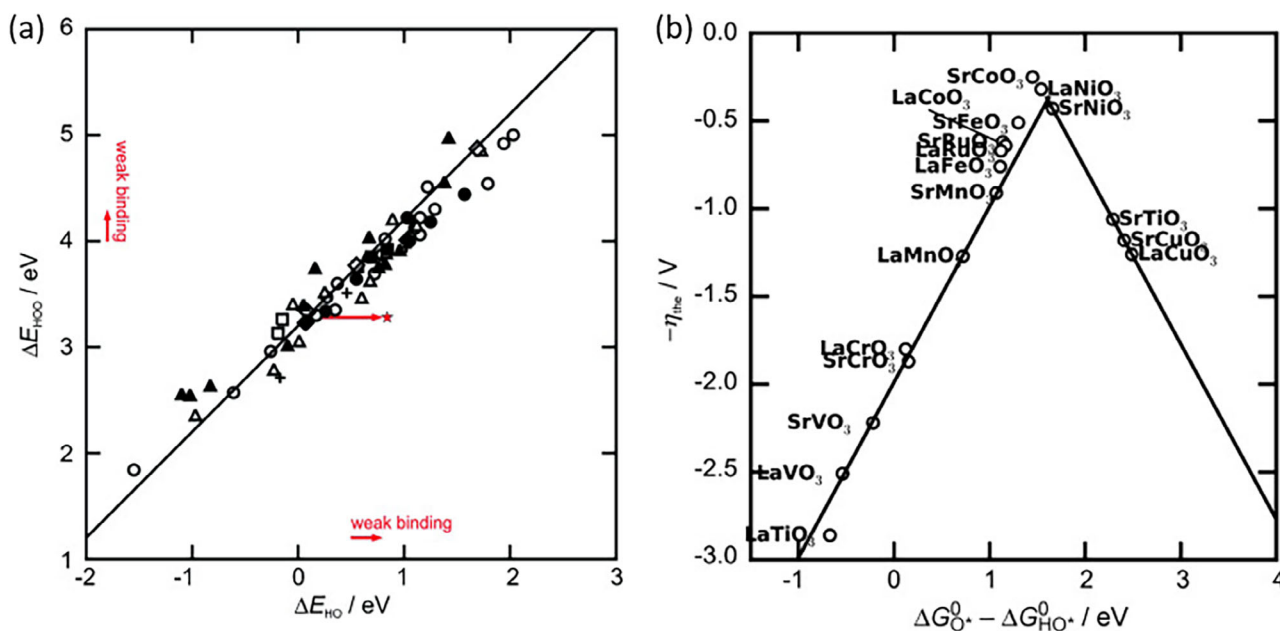


Figure 8. a) Adsorption energy ΔE of OOH^* intermediate versus that of OH^* , showing a linear scaling relation with an intercept of 3.2 V for a range of metal-oxide catalysts. b) Volcano plot of the theoretical overpotential as a function of the free energy of the OH^* oxidation (step 2) for a range of oxide perovskites. Both figures are reproduced with permission.^[162] Copyright 2011, Wiley-VCH.

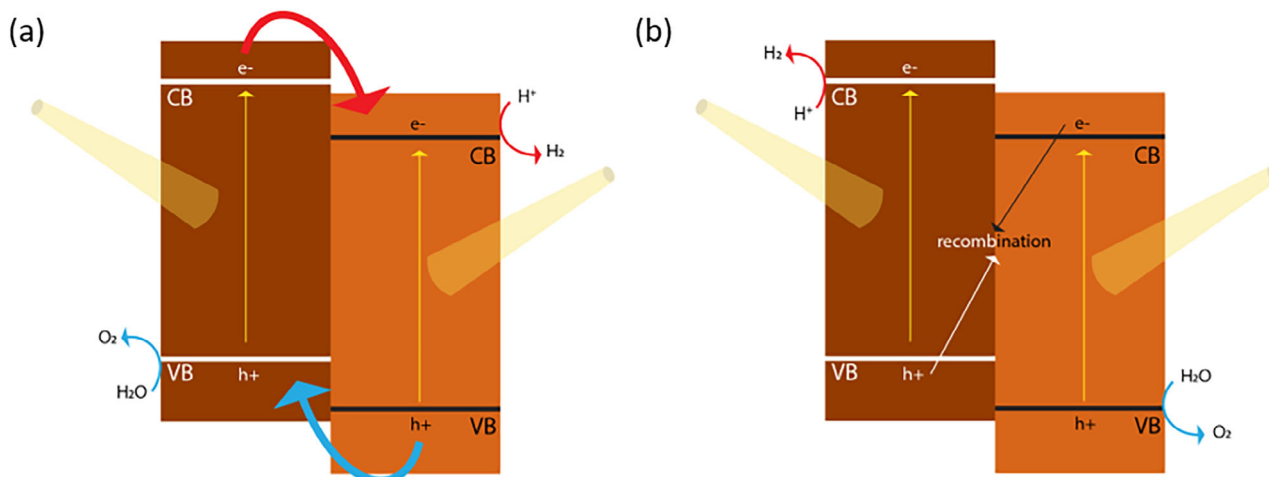
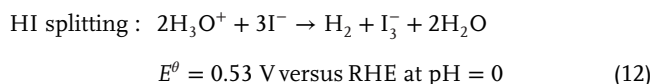
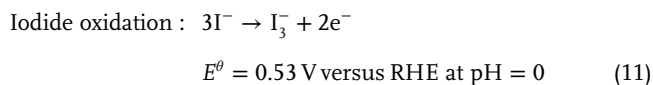
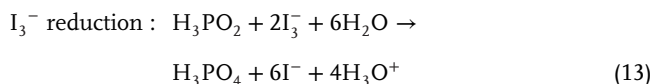


Figure 9. Schematic diagrams of a) type-II heterojunction and b) Z-scheme heterojunction. Note that the Z-scheme represented here illustrates a *direct* Z-scheme. In alternative configurations, consumption of the low-energy electron and low-energy hole occurs via a redox mediator, as illustrated in Figure 5a.



The overpotential is negligible for iodide oxidation, such that photocatalysts displaying smaller bandgaps (i.e., harvest sunlight more efficiently) can be used. As mentioned above, H_3PO_2 is added to circumvent browning of the medium with increasing I_3^- formation, as shown in Equation (13).



Control experiments show that H_3PO_2 is not oxidized in the absence of I_3^- , confirming that photogenerated holes do not react with H_3PO_2 directly.^[47,166] The reaction in Equation (13) regenerates I^- and also replenishes the consumed aqueous H^+ (i.e., H_3O^+) at the same ratio at which they react in Equation (12). This highlights the role of H_3PO_2 in not just preventing parasitic I_3^- absorption but also in maintaining the delicate balance required between $[\text{I}^-]$ and $[\text{H}^+]$ to suppress side reactions.^[47]

3.3. Evaluating Photocatalytic Activity

Strategies to boost the performance of photocatalysts include relying on low-bandgap semiconductors to harness abundant visible-light photons; in fact, traditional wide-bandgap semiconductors used to drive overall water splitting can only harness UV radiation and thus are restricted to a solar-to-fuel energy conversion efficiency of around 2% at a quantum efficiency of 100% (i.e., assuming that all photogenerated charge-carriers react).^[25] Other important strategies to enhance activity include improving charge separation efficiency and charge transport, extending

charge lifetime, and reducing the barrier for charge transfer at active sites.

Traditional OWS photocatalysts consist of transition metal oxides given their stability and suitable band edge positions relative to the redox potentials for OWS. While the addition of metal cocatalysts can be used to reduce the energetic barrier, the reliance on a single component to drive both HER and OER, while also harnessing a significant proportion of visible light photons, is very challenging. Hence the use of two-component systems in binary heterojunctions, which allows the use of smaller bandgap semiconductors to drive OER and HER separately. In a type-II heterojunction (Figure 9a), the energetic offsets between CB edge (VB edge) and HER (OER) potential at the interface contribute to enhancing charge separation efficiency and reducing recombination. Z-schemes are difficult to achieve, but compared to type-II heterojunctions, they present smaller energetic losses since recombination occurs between the lower-energy electron and hole, leaving the higher-energy photogenerated charges free for driving the desired redox reactions (Figure 9b).

In terms of evaluating a system's performance, the rate of H_2 evolution ($\mu\text{mol h}^{-1}$) is a useful parameter within a single study, but cannot be used to draw meaningful comparisons between different studies. Firstly, it does not take into account variables related to the experimental set-up, like photocatalyst loading, incident energy, and reactor surface area. Normalizing to mass ($\mu\text{mol g}^{-1} \text{ h}^{-1}$) is not meaningful either as the relationship between activity and mass will depend on the experimental setup, and may be limited at higher concentrations by the stability of the dispersion.^[167,168] As a result, apparent quantum yield (AQY) is a more reliable wavelength-specific metric to assess efficiency and compare across systems (Equation 14). The term "apparent" arises from the fact that it depends on the number of incident photons, rather than the number of photons absorbed.^[167]

$$\text{AQY} (\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \quad (14)$$

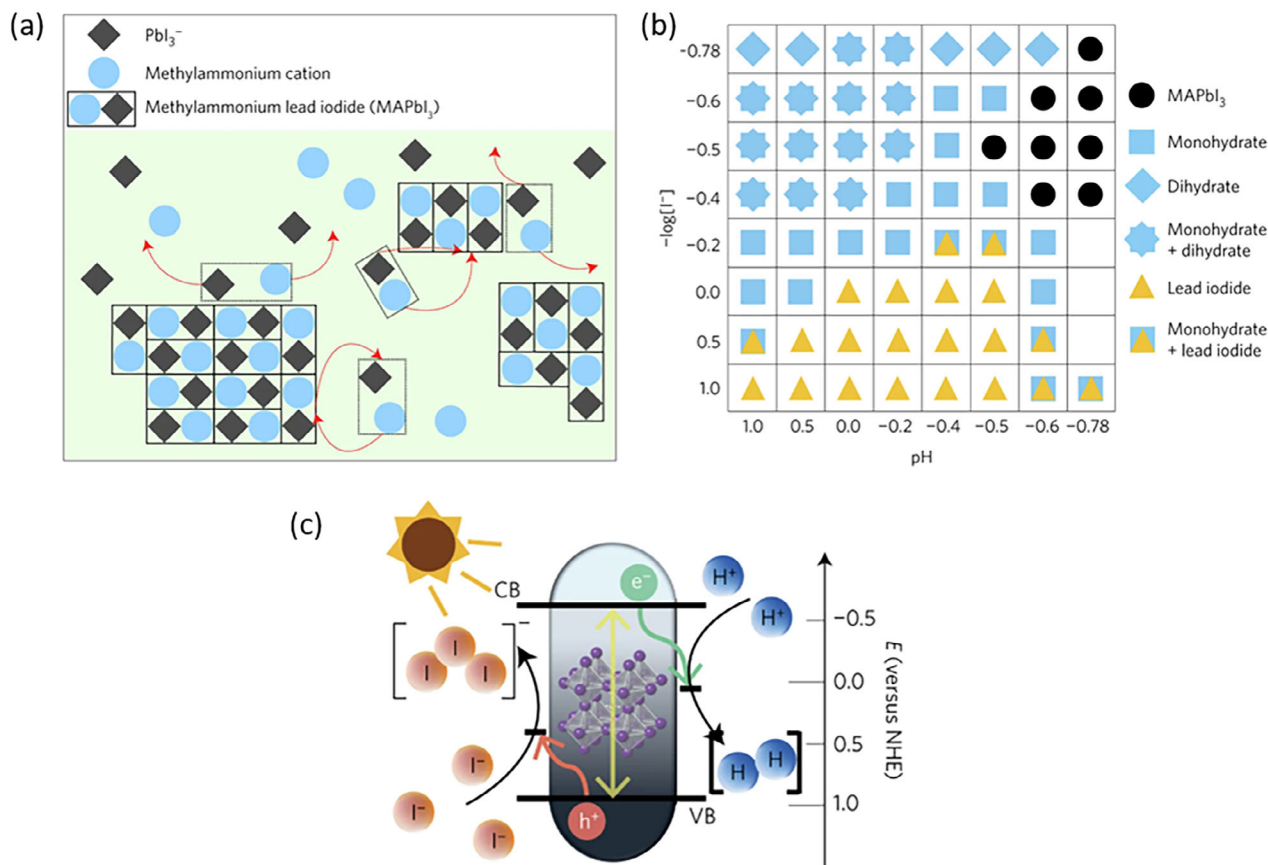


Figure 10. a) Schematic illustrating the dynamic equilibrium between dissolution and reprecipitation of MAPI in HI solution. b) Phase map showing the range of concentrations of I⁻ and H⁺ within which MAPI is stable in HI solution. c) Schematic energy band diagram illustrating H₂ evolution via HI splitting on MAPI. a–c) Reproduced with permission.^[47] Copyright 2017, Springer Nature.

The solar-to-fuel (STF) conversion efficiency provides an estimate for the ratio between energy output and energy input. In the case of HER, it is referred to as the STH (solar-to-hydrogen) conversion efficiency (Equation 15).

$$\text{STH} = \frac{\text{evolved H}_2 \text{ (mol)} \times N_A \times 2 \times E_{\text{redox}} \text{ (eV)} \times e}{P_{\text{sol}} \text{ (W.cm}^{-2}\text{)} \times \text{area (cm}^2\text{)} \times \text{time (s)}} \times 100\% \quad (15)$$

where N_A is Avogadro's number, $E_{\text{red/ox}}$ indicates the redox potential of the reaction in question (whether water splitting or HI splitting), e is the elementary charge, and P_{sol} is the power density of incident light.

3.4. Halide Perovskites for Photocatalytic H₂ Evolution

As discussed in the introduction, lead-halide perovskites display tunable bandgaps with strong light absorption in the visible region, as opposed to many of their wider-bandgap oxide counterparts. However, their instability in the presence of moisture makes their employment as PCs for OWS counterintuitive. In fact, as will be discussed further below, they are thus far mostly employed in the context of splitting hydrohalic acids. Under such conditions, the integrity of the perovskite photocatalyst is main-

tained by the dynamic equilibrium established between dissolution and reprecipitation (Figure 10a).^[47]

Strategies to stabilize MHPs towards moisture in the field of photovoltaics involve the use of external encapsulation of the device as a whole.^[169] This cannot be directly applied in the context of perovskite-based photoelectrodes in PEC devices, since the encapsulants need to be conductive to allow charge transport to the surface of the electrode.^[154] Other methods involve composition tuning or structural modifications (3D to 2D or ligand-stabilized QDs).^[170] However, moisture stability is a significant challenge in photocatalysis, as water molecules need to come in close contact with the surface of perovskite particles in the context of photocatalytic water splitting.

In the next two sections, we review the progress in lead-halide perovskites (LHP) and lead-free halide perovskites as photocatalysts for HER, with data from the literature summarized in Table 1.

3.4.1. Lead Halide Perovskites

Herein, we start with the first example of LHP reported for HI splitting in 2017. We then review the reported works focusing on boosting activity and mitigating the reliance on precious metals.

Table 1. Summary of reported photocatalytic hydrogen evolution systems using halide perovskites.

#	Photocatalyst	Reaction	Cocatalyst [wt%]	Light source	Medium	Performance	Measured stability [h]	Refs.
1	MAPbI ₃ /Pt	HI splitting	1.7 wt% Pt	Solar simulator, $\lambda \geq 475$ nm, 100 mW cm ⁻²	aq. HI + H ₃ PO ₂	11.4 $\mu\text{mol h}^{-1}$ (200 mg), STH = 0.81%	160	[47]
	MAPbI ₃ (solvent anneal)					6 $\mu\text{mol h}^{-1}$		
	MAPbI ₃					2 $\mu\text{mol h}^{-1}$		
2	MAPbI ₃ /rGO	HI splitting	3.4 wt% rGO	300 W Xe lamp, $\lambda \geq 425$ nm, 120 mW cm ⁻²	aq. HI + H ₃ PO ₂	93.9 $\mu\text{mol h}^{-1}$ (100 mg), AQY = 1.5% at 450 nm	200	[99]
	MAPbI ₃ /Pt		1.9 wt% Pt			4 $\mu\text{mol h}^{-1}$		
	MAPbI ₃					1.4 $\mu\text{mol h}^{-1}$		
3	Pt/TiO ₂ /MAPbI ₃	HI splitting	0.75 wt% Pt	300 W Xe lamp, $\lambda \geq 425$ nm, 200 mW cm ⁻²	aq. HI + H ₃ PO ₂	72.8 $\mu\text{mol h}^{-1}$ (10 mg), AQY = 70% at 420 nm, STH = 0.86%	12	[95]
	Pt/Ta ₂ O ₅ /MAPbI ₃		0.75 wt% Pt			39.9 $\mu\text{mol h}^{-1}$		
	MAPbI ₃ /Pt		0.5 wt% Pt			0.93 $\mu\text{mol h}^{-1}$		
	MAPbI ₃					0.47 $\mu\text{mol h}^{-1}$		
4	MAPbBr _{3-x} I _x /Pt	HBr splitting	1.2 wt% Pt	Xe lamp, $\lambda \geq 420$ nm, 100 mW cm ⁻²	aq. HI/HBr + H ₃ PO ₂	651.2 $\mu\text{mol h}^{-1}$ (250 mg), AQY = 8.10% at 450 nm, STH = 1.05%	30	[171]
	MAPbBr _{3-x} I _x					255.3 $\mu\text{mol h}^{-1}$		
	MAPbBr ₃ /Pt		1.2 wt% Pt			8.4 $\mu\text{mol h}^{-1}$		
	MAPbBr ₃					2.8 $\mu\text{mol h}^{-1}$		
5	CsPbBr _{3-x} I _x /Pt	HBr splitting	1.13 wt% Pt	Xe lamp, $\lambda \geq 420$ nm, 120 mW cm ⁻²	aq. HBr + H ₃ PO ₂	224 $\mu\text{mol h}^{-1}$ (200 mg), AQY = 2.15% at 450 nm	50	[172]
	CsPbBr _{3-x} I _x					23.6 $\mu\text{mol h}^{-1}$		
	CsPbBr ₃					negligible (≈ 0 $\mu\text{mol h}^{-1}$)		
6	MAPbI ₃ /Ni ₃ C-15%	HI splitting		Xe lamp, $\lambda \geq 420$ nm, 100 mW cm ⁻²	aq. HI + H ₃ PO ₂	118 $\mu\text{mol h}^{-1}$ (50 mg), AQY = 16% at 450 nm	200	[173]
	MAPbI ₃ /Pt					26.7 $\mu\text{mol h}^{-1}$		
	MAPbI ₃					2.15 $\mu\text{mol h}^{-1}$		
7	Pt/Ta ₂ O ₅ /MAPbBr ₃ /PEDOT:PSS	HBr splitting	0.75 wt% Pt	Xe lamp, $\lambda \geq 420$ nm, 150 mW cm ⁻²	aq. HBr + H ₃ PO ₂	105 $\mu\text{mol h}^{-1}$ (150 mg), AQY = 16.4% at 420 nm	4	[174]
	Pt/Ta ₂ O ₅ /MAPbBr ₃		0.75 wt% Pt			6 $\mu\text{mol h}^{-1}$		
	Pt/MAPbBr ₃		0.75 wt% Pt			2 $\mu\text{mol h}^{-1}$		
8	Pt/CsPbI ₃ /pCN	HER	3.9 wt% Pt	300 W Xe lamp, $\lambda \geq 420$ nm, 120 mW cm ⁻²	TEOA + aq. H ₂ PtCl ₆	10 $\mu\text{mol h}^{-1}$ (10 mg)	16	[175]
9	MAPb(I _{1-x} Br _x) ₃ (x = 0.1)	HI splitting	n/a	300 W Xe lamp, $\lambda \geq 420$ nm, 100 mW cm ⁻²	aq. HI/HBr + H ₃ PO ₂	29.4 $\mu\text{mol h}^{-1}$ (20 mg), STH = 1.42%	252	[85]
	MAPbI ₃					0.74 $\mu\text{mol h}^{-1}$		
10	Pt/TiO ₂ /CsPbBr ₃ QDs-9.9wt%	sacrificial WS	1 wt% Pt	300 W Xe lamp, $\lambda \geq 420$ nm	H ₂ O/MeOH vapor	4.05 $\mu\text{mol h}^{-1}$ (30 mg)	160	[176]
11	MAPbI ₃ (piezophotocatalytic)	HI splitting		500 W tungsten-halogen lamp, 100 mW cm ⁻²	aq. HI	23.3 $\mu\text{mol h}^{-1}$ (50 mg)	15	[177]
	MAPbI ₃ (piezocatalytic)					2.21 $\mu\text{mol h}^{-1}$		
	MAPbI ₃ (photocatalytic)					3.42 $\mu\text{mol h}^{-1}$		

(Continued)

Table 1. Continued

#	Photocatalyst	Reaction	Cocatalyst [wt%]	Light source	Medium	Performance	Measured stability [h]	Refs.
12	MAPbI ₃ /CoP	HI splitting	20 wt% CoP (theoretical)	150 W Xe lamp, $\lambda \geq 420$ nm	aq. HI + H ₃ PO ₂	1.96 $\mu\text{mol h}^{-1}$ (2.5 mg MAPbI ₃)	3	[98]
13	MAPbI ₃ PMA ₂ PbI ₄ /Pt (labelled PMPI)	HI splitting	2 wt% Pt	300 W Xe lamp, $\lambda \geq 420$ nm, 200 mW cm ⁻²	aq. PMAI + H ₃ PO ₂	0.24 $\mu\text{mol h}^{-1}$ 333 $\mu\text{mol h}^{-1}$ (150 mg), STH = 1.57%	16	[178]
14	PMA ₂ PbI ₄ MAPbI ₃ /BP	HI splitting	1.2% BP 2D nanoflakes	300 W Xe lamp, $\lambda \geq 420$ nm	aq. HI + H ₃ PO ₂	17 $\mu\text{mol h}^{-1}$ 112.3 $\mu\text{mol h}^{-1}$ (30 mg), AQY = 23.2% at 420 nm, STH = 0.93%	200	[97]
	MAPbI ₃ /bulk-BP MAPbI ₃ /Pt MAPbI ₃		5% bulk BP			17.4 $\mu\text{mol h}^{-1}$ 5.76 $\mu\text{mol h}^{-1}$ 1.05 $\mu\text{mol h}^{-1}$		
15	ML-MoS ₂ /MAPbI ₃ -MCs (intercalated)	HI splitting		300 W Xe lamp, $\lambda \geq 420$ nm	aq. HI + H ₃ PO ₂	1360 $\mu\text{mol h}^{-1}$ (100 mg), AQY = 11.6% at 450 nm, STH = 1.09%	208	[166]
	ML-MoS ₂ /MAPbI ₃ -MCs (physical mixture) bulk-MoS ₂ /MAPbI ₃ -MCs					97.2 $\mu\text{mol h}^{-1}$ 57.4 $\mu\text{mol h}^{-1}$		
	MAPbI ₃ -MCs/Pt MAPbI ₃ -MCs		1.88 wt% Pt			57.5 $\mu\text{mol h}^{-1}$ 6 $\mu\text{mol h}^{-1}$		
16	FAPbBr _{3-x} I _x /PtSA (single-atom Pt)	HI splitting	1.8 wt% (ICP-OES value)	300 W Xe lamp, AM1.5G, 100 mW cm ⁻²	aq. HI + H ₃ PO ₂	682.6 $\mu\text{mol h}^{-1}$ (100 mg), AQY = 33.4% at 530 nm, STH = 4.5%	30	[90]
	FAPbBr _{3-x} I _x		n/a			39.8 $\mu\text{mol h}^{-1}$		
17	Cs ₂ AgBiBr ₆ /N-C-140	HBr splitting	n/a	300 W Xe lamp, $\lambda \geq 420$ nm, 100 mW cm ⁻²	aq. HBr + H ₃ PO ₂	3.8 $\mu\text{mol h}^{-1}$ (50 mg), AQY = 0.59% at 420 nm	24	[179]
	Cs ₂ AgBiBr ₆		n/a			0.2 $\mu\text{mol h}^{-1}$		
18	MA ₃ Bi ₂ I ₉ /Pt	HI splitting	1.9 wt% Pt	300 W Xe lamp, $\lambda \geq 400$ nm	aq. HI + H ₃ PO ₂	6.76 $\mu\text{mol h}^{-1}$ (40 mg), STH = 0.48%	70	[102]
	MA ₃ Bi ₂ I ₉		n/a			0.49 $\mu\text{mol h}^{-1}$		
19	Cs ₂ AgBiBr ₆ /rGO	HBr splitting	2.5 wt% rGO	300 W Xe lamp, $\lambda \geq 420$ nm	aq. HBr + H ₃ PO ₂	9.78 $\mu\text{mol h}^{-1}$ (200 mg), AQY = 0.16% at 450 nm	120	[180]
	Cs ₂ AgBiBr ₆ /Pt Cs ₂ AgBiBr ₆		2.5 wt% Pt n/a			0.19 $\mu\text{mol h}^{-1}$ 0.12 $\mu\text{mol h}^{-1}$		
20	Cs ₃ Bi _{2x} Sb _{2-2x} I ₉ /Pt (denoted CBSI-0.3)	HI splitting	missing SI	AM1.5G, 100 mW cm ⁻²	aq. HI	92.6 $\mu\text{mol h}^{-1}$ (100 mg), AQY = 1.206% at 420 nm, STH = 0.32%	50	[181]
	Cs ₃ Bi _{2x} Sb _{2-2x} I ₉		n/a			4.2 $\mu\text{mol h}^{-1}$		
21	DMASnI ₃	OVS	n/a	300 W Xe lamp	DI water	0.64 $\mu\text{mol h}^{-1}$ (200 mg)	16	[182]
22	33wt%-DMASnBr ₃ @g-C ₃ N ₄ /Pt	sacrificial WS	3 wt% Pt	1500 W Xe lamp, $\lambda = 300\text{--}800$ nm, 50 mW cm ⁻²	H ₂ O + 10% (v/v) TEOA	36.3 $\mu\text{mol h}^{-1}$ (21 mg), AQY = 6.6% at 300–800 nm	6	[183]

(Continued)

Table 1. Continued

#	Photocatalyst	Reaction	Cocatalyst [wt%]	Light source	Medium	Performance	Measured stability [h]	Refs.
	33wt%-DMASnBr ₃ @g-C ₃ N ₄	sacrificial WS	n/a		H ₂ O + 10% (v/v) TEOA	0.39 $\mu\text{mol h}^{-1}$		
	33wt%-DMASnBr ₃ @g-C ₃ N ₄ /Pt	OWS	3 wt% Pt		H ₂ O	0.29 $\mu\text{mol h}^{-1}$		
	DMASnBr ₃ /Pt	sacrificial WS	3 wt% Pt		H ₂ O + 10% (v/v) TEOA	0.13 $\mu\text{mol h}^{-1}$		
23	Cs ₂ AgBiBr ₆ -10/g-C ₃ N ₄	HBr splitting	9.1 wt% g-C ₃ N ₄	300 W Xe lamp, $\lambda \geq 420$ nm	aq. HBr + H ₃ PO ₂	3 $\mu\text{mol h}^{-1}$ (50 mg)	42	[184]
	Cs ₂ AgBiBr ₆		n/a			1.2 $\mu\text{mol h}^{-1}$		
24	MA ₃ Bi ₂ I ₉ /DMA ₃ BiI ₆ (BBP-5)	HI splitting	n/a	300 W Xe lamp, $\lambda \geq 420$ nm	aq. HI + H ₃ PO ₂	19.82 $\mu\text{mol h}^{-1}$ (100 mg)	100	[185]
	MA ₃ Bi ₂ I ₉ (BBP-0)					1.32 $\mu\text{mol h}^{-1}$		
	DMA ₃ BiI ₆ (BBP-10)					2.48 $\mu\text{mol h}^{-1}$		
25	Cs ₂ SnI ₆ /PtSA	HI splitting	0.12 wt% Pt	300 W Xe lamp, $\lambda \geq 420$ nm	aq. HI + H ₃ PO ₂	4.3 $\mu\text{mol h}^{-1}$ (10 mg), TOF = 70.6 h ⁻¹	180	[186]
	Cs ₂ SnI ₆ /PtNP		3.88 wt% Pt			1.45 $\mu\text{mol h}^{-1}$		
	Cs ₂ SnI ₆					0.25 $\mu\text{mol h}^{-1}$		
26	2.5wt%-Cs ₃ Bi ₂ Br ₉ /g-C ₃ N ₄ /Pt	sacrificial WS	3 wt% Pt	1500 W Xe lamp, $\lambda = 300\text{--}800$ nm, 50 mW cm ⁻²	H ₂ O + 10% (v/v) TEOA	22.05 $\mu\text{mol h}^{-1}$ (21 mg)	6	[187]
	Cs ₃ Bi ₂ Br ₉ //Pt		3 wt% Pt			0.46 $\mu\text{mol h}^{-1}$		
27	Cs ₂ Pt _{0.05} Sn _{0.95} Cl ₆ /Pt	sacrificial WS	5 wt% Pt	300 W Xe lamp, $\lambda \geq 420$ nm	H ₂ O + 10% (v/v) TEOA	0.85 $\mu\text{mol h}^{-1}$ (50 mg)	4	[188]
28	5wt%-PEA ₂ SnBr ₄ /g-C ₃ N ₄ /Pt	sacrificial WS	3 wt% Pt	1500 Xe lamp, 50 mW cm ⁻²	H ₂ O + 10% (v/v) TEOA	33.9 $\mu\text{mol h}^{-1}$ (21 mg)	6	[189]
	PEA ₂ SnBr ₄ /g-C ₃ N ₄		3 wt% Pt			0.084 $\mu\text{mol h}^{-1}$		
29	[(CH ₃) ₂ NH ₂] ₃ [BiI ₆]/Pt	HI splitting	1 wt% Pt	425 nm LED	aq. HI + H ₃ PO ₂	23.3 $\mu\text{mol h}^{-1}$ (500 mg)	100	[190]
	[(CH ₃) ₂ NH ₂] ₃ [BiI ₆]					1.9 $\mu\text{mol h}^{-1}$		
30	PMA ₂ PbI ₄ /MoS ₂	HI splitting	2.5 wt% MoS ₂	300 W Xe lamp, 100 mW cm ⁻²	aq. HI	368.3 $\mu\text{mol h}^{-1}$, AQY = 14.26% at 500 nm, STH = 2.31%	25	[191]
31	PMA ₂ PbI ₄ /MoS ₂ -WO ₃ /RuO _x	OWS	2.5 wt% MoS ₂	300 W Xe lamp, 100 mW cm ⁻²	aq. HI	154.5 $\mu\text{mol h}^{-1}$, STH = 2.07%	25	[191]

Works are categorized based on the dominant strategy: compositional engineering, dimensionality, heterojunction composites, and multi-catalytic devices. Where overlap occurs between two or more strategies, priority is given to the one that allows interesting comparisons between different studies. HER rates ($\mu\text{mol h}^{-1}$) constitute meaningful comparisons within the same study only.

The first successful report of MHPs for photocatalytic H₂ generation was published in 2017.^[47] By employing a saturated solution of MAPbI₃ in hydriodic acid, the authors reported a 0.44% STH efficiency, which reached 0.81% with the incorporation of 1.7 wt% Pt as cocatalyst. To stabilize the MAPbI₃ powder in solution, precise control of the concentration of I⁻ and H⁺ ions was required, with the perovskite lattice being stable at $[\text{I}^-] \leq [\text{H}^+]$ when $[\text{H}^+] \leq 3.16 \text{ mol L}^{-1}$ (Figure 10). This led to stable H₂ evolution for up to 160 h. The catalytic activity was optimized by annealing under a polar solvent atmosphere to increase crystallinity for more efficient charge transport and reduced non-radiative re-

combination, which led to a 2-to-3-fold increase in H₂ evolved depending on the solvent used.

Since this report, there have been various attempts to boost the efficiency of photocatalytic hydrogen evolution by A) composition engineering (including co-catalyst decoration); B) varying the dimensionality; and C) employing perovskite/semiconductor composites. Some studies have also explored the effect of D) combining photocatalysis with piezocatalysis or electrocatalysis.

Compositional Engineering: X-Site Tuning: Tuning the composition of lead-halide perovskite involves employing (i) mixed halides (X-site tuning), and (ii) replacing the organic cation with an inorganic equivalent (A-site tuning). As most efficient systems incorporate Pt as a co-catalyst, we also review in this sub-section alternative co-catalysts.

Various studies investigated the effect of mixed halide compositions, either by doping the bulk of the perovskite or by inducing a gradient in composition. Two such reports made use of light-induced ion exchange to establish a gradient of iodide ions

across $\text{MAPbBr}_{3-x}\text{I}_x$ and $\text{CsPbBr}_{3-x}\text{I}_x$.^[171,172] This induced a gradual narrowing of the bandgap from the deeper (bromide-rich) regions towards the surface (iodide-rich) regions, thus accumulating photogenerated electrons at the surface. The MA-based system yielded better HER rates: the bandgap-funnel structure in $\text{MAPbBr}_{3-x}\text{I}_x$ presented a 91-fold improvement in rate relative to MAPbBr_3 (from 2.8 to 255.3 $\mu\text{mol h}^{-1}$), compared to a maximal 24-fold improvement in the cesium-based system (from ≈ 0 to 23.6 $\mu\text{mol h}^{-1}$). The addition of 1.2 wt% Pt more than doubled the rate for $\text{MAPbBr}_{3-x}\text{I}_x$, reaching 651.2 $\mu\text{mol h}^{-1}$, with an AQY of 8.1% at 450 nm and a STH efficiency of 1.05%.^[171] It is worth noting that the authors report STH efficiency based on the HER rate in the first hour only. However, their data shows an induction period at the beginning of the experiment before the rate stabilizes. We re-calculate STH using the hourly rate based on the total H_2 evolved by the end of the experiment (651.2 $\mu\text{mol h}^{-1}$, as opposed to 161.5 $\mu\text{mol h}^{-1}$ in the first hour). This yields an STH of 4.2% which we will refer to further below to compare with a similar system in section B, where STH is reported based on the same calculation we made.

Another study investigated the same MA-based mixed-halide perovskite, but by doping the bulk of MAPbI_3 with bromide, rather than inducing a gradient.^[85] The authors see a more modest 40-fold improvement in HER rate (0.74 to 29.4 $\mu\text{mol h}^{-1}$), with an STH of 1.42% without the use of Pt. They attribute the improved performance to a combination of longer-lived charges, more efficient charge separation, and better transport. Furthermore, they suggest that the incorporation of the smaller Br ions induces the formation of Pb defect sites due to the breaking of the X-Pb-X linkage, which does not occur in pure MAPI . These defect sites are proposed to act as H_2 evolution sites within an amine-assisted mechanism where MA^+ cations are the source of “H” for H_2 formation. However, this seems unlikely as it would lead to degradation of the perovskite, and it is mechanistically unclear how MA^+ cations can transfer “H” to form PbH^- , as suggested by the authors.

Co-Catalyst Modifications: In one report, the authors rely on the same bandgap-funnel structure discussed above, but their main aim was to enhance the utilization of photogenerated charge-carriers by optimizing Pt-loading.^[90] They suggest that the limited HER rates in Pt-loaded MHP photocatalysts thus far are likely due to poor utilization of photogenerated charges. Two reasons are proposed: i) the dynamic dissolution/precipitation equilibrium existing at the surface of the perovskite particles dispersed in saturated HX solutions prevents the formation of static Pt active sites, and ii) the size of Pt clusters. Larger clusters are undesirable as they constitute a poor ratio of available active sites to the amount of Pt used, meaning a lower efficiency of extracting photogenerated electrons. With the aim of enhancing charge extraction, they rely on $\text{FAPbBr}_{3-x}\text{I}_x$ as a photocatalyst given FA-based MHP’s superior carrier lifetime and diffusion compared to its MA-based counterpart, with the bandgap-funnel structure acting as an additional driving force to drive electrons to the surface. However, while the authors report an STH of 4.5% and compare it to the 1.05% found for the $\text{MAPbBr}_{3-x}\text{I}_x/\text{Pt}$ system mentioned above, the two systems perform similarly since, as explained above, the re-calculated STH for $\text{MAPbBr}_{3-x}\text{I}_x/\text{Pt}$ yields 4.2%. Furthermore, despite evidence of photodeposited single-atom Pt (PtSA) on $\text{FAPbBr}_{3-x}\text{I}_x$, the 1.8wt% loading determined

from ICP-OES remains quite high and is comparable to other reports relying on regular Pt nanoparticles.^[47,186] Nonetheless, thanks to the efficient trapping of photogenerated electrons and the significant reduction in the activation barrier for H_2 evolution, a 17-fold improvement in rate was achieved by deposition of Pt, leading to a HER rate of 682.6 $\mu\text{mol h}^{-1}$. We estimate that this corresponds to a turnover frequency (TOF) of 24.7 h^{-1} , assuming that the totality of the 1.8wt% Pt used does indeed correspond to single-atom active sites. Despite the ability of Pt to efficiently catalyze hydrogen evolution, its use on a commercial scale is prohibitive given its cost and scarcity. With this in mind, there are various examples of employing co-catalysts based on abundant transition metals.

TiO_2 is an established metal oxide catalyst for OWS. In 2018, the effect of combining TiO_2 and MAPI for HI splitting was explored, relying on 33 wt% Pt- TiO_2 (with a Pt loading of 0.75wt% on TiO_2).^[95] They observe a HER rate of 72.8 $\mu\text{mol h}^{-1}$, an 89-fold improvement on using only Pt-decorated MAPbI_3 . The authors use a higher light intensity of 2 suns. While TiO_2 is a photocatalyst in its own right, it requires UV photons to excite electrons across its bandgap. Since only visible light is involved in this study, it is worth highlighting that its role is purely co-catalytic in this instance. Depositing the Pt co-catalyst on TiO_2 rather than the perovskite leads to better activity as it avoids the instability associated with Pt sites on MAPbI_3 given the dissolution/precipitation equilibrium at the surface of MAPI crystals. Following optimization of (i) the amount of Pt/ TiO_2 , (ii) Pt-loading, and (iii) composite fabrication with a preheating treatment, they suggest the enhanced performance is due to a dynamic heterojunction which allows efficient electron transfer from MAPI to TiO_2 , where proton reduction is catalyzed on stable Pt active sites. They apply the same rationale to composites of either Pt- Ta_2O_5 or Pt- Nb_2O_5 with MAPI . The former yields more modest rates, which is assigned to a reduction in surface area, while the latter shows negligible activity due to unsuitable band positions. The same group then extended this idea. They employed a hole-extraction layer to try to boost the performance of their Pt/ Ta_2O_5 - MAPbBr_3 system.^[174] They tested various hole-transporting materials (HTM) in the composite Pt/ Ta_2O_5 - MAPbBr_3 -HTM, and PEDOT: PSS yielded the best performance under 1.5 sun (105 $\mu\text{mol H}_2 \text{ h}^{-1}$) due to enhanced hole transfer from MAPbBr_3 and a superior ability to catalyze Br^- oxidation. While this represented a 17-fold improvement on the photocatalyst without PEDOT: PSS, stability was limited by aggregation of the hole-transport material.

A photocatalyst based on nickel carbide as a co-catalyst displayed a four-fold improvement in HER rate compared to the Pt-loaded MAPI equivalent.^[173] The reported $\text{MAPbI}_3/\text{Ni}_3\text{C}$ -15% yielded a HER rate of 118 $\mu\text{mol h}^{-1}$, four times that of its Pt-loaded counterpart and 55-fold higher than MAPbI_3 . The Ni_3C -decorated perovskite was obtained via electrostatic self-assembly and was stable over 200 h of operation. The origin of the improved performance is attributed to efficient electron transfer onto Ni_3C , supported by the observed reduction in the lifetime of charge decay. Furthermore, they find that the composite can separate charges more efficiently and improve the kinetics of proton reduction, as evidenced by a reduction in the overpotential required compared to pure MAPI .

Drawing inspiration from electrocatalysis, one study investigated the effect of decorating the perovskite with cobalt phosphide (CoP).^[98] At a theoretical loading of 20wt% CoP, an 8-fold improvement in rate was observed in the performance of MAPbI₃ nanocrystals (0.24 to 1.96 $\mu\text{mol h}^{-1}$), with an AQY of 1.5% at 450 nm. The CoP was photodeposited onto the perovskite, and the loading was optimized for enhanced catalytic activity while mitigating recombination induced by excessive loading. Similar to the effect of other co-catalysts, it was found that CoP decoration led to enhanced charge transfer from the perovskite to the co-catalyst, as evidenced by enhanced PL quenching and reduced charge lifetime. Another strategy employed in this study was reducing the size of the perovskite crystals to increase the exposed surface area. An increase in the HER rate is observed over the first 21 hours, which the authors attribute to enhanced crystallinity of MAPI and more CoP being photodeposited onto the surface.

Dimensionality: The dimensionality can be tuned on two levels: form factor and material structural dimensionality.^[192,193] In 2D perovskites (discussed here in terms of material-dimensionality), the layer of hydrophobic R groups can act as a barrier against water ingress, making these materials potential candidates for water splitting. Some limitations of 2D perovskites compared to their 3D counterpart are stronger exciton binding energies and wider bandgaps. The latter is not necessarily a limitation in the context of photocatalysis given the large overpotentials required to drive some of the desired reactions.

One study employed a bulky organic cation to induce the formation of a 2D perovskite, namely PMA₂PbI₄, (abbreviated PMPI).^[178] It was expected that the bulky cation should confer stability in water for H₂O splitting. Since this was not the case, the authors used PMPI to drive HI splitting, and observed a HER rate of 333 $\mu\text{mol h}^{-1}$ with 2 wt% Pt (up from 17 $\mu\text{mol h}^{-1}$ without Pt). The authors stabilize the perovskite by tuning the concentration of PMAI salt in aqueous solution. In contrast to the more established scenario where a saturated solution of the perovskite is used to stabilize the photocatalyst powder,^[47,174] a negligible amount of PMA₂PbI₄ is dissolved, likely an effect of the more hydrophobic PMA⁺ compared to MA⁺. Furthermore, they observe that increasing the hydrophobicity further by increasing the length of the organic cation leads to a significant drop in performance, which they attribute to less efficient charge separation/migration and slower charge transfer to Pt. Another study focused on reducing form factor dimensionality by studying 0D quantum dots (QD).^[176] CsPbBr₃ QDs were employed in a composite with Pt-loaded TiO₂ to promote proton reduction and vapor-phase methanol oxidation. It was found that control of the ligand density was critical. They observe longer induction times at higher ligand densities, but a more stable perovskite structure. The proposed rationale is based on irradiation-induced ligand degradation/removal in the first minutes/hours of photocatalysis, until a suitable density is reached to allow electron transfer onto TiO₂, while also protecting against moisture. A loading of 9.86 wt% perovskite yielded the best rate (4.05 $\mu\text{mol h}^{-1}$), with 1 wt% Pt photodeposited on TiO₂ and a stability of 160 h (compared with ≤ 23 h at lower initial ligand densities).

Perovskite/Semiconductor Heterojunction Composites: Rather than catalyzing both half-reactions on the same semiconductor, binary heterojunction composites can be used to enhance

charge-carrier separation, as discussed earlier. Below we review the MHP/semiconductor composites employed for HX splitting.

Inorganic Semiconductors: The metal chalcogenide MoS₂ is another example of a well-known metallic electrocatalyst,^[194] that can also display semiconducting properties with a visible-light response.^[195] Its behavior is dictated by the formation of the metallic 1T phase or the semiconducting 2H phase. One study investigated the composite ML-MoS₂/LHP-MC based on monolayers (ML) of MoS₂ intercalated into microcrystals (MCs) of various LHPs.^[166] Of the four LHPs tested, MAPbI₃ was by far the best-performing. The authors confirm the presence of both 1T and 2H phases of MoS₂ using Raman spectroscopy and XPS. It is worth noting that while the reported absorption spectrum of ML-MoS₂ suggests a dominant metallic behavior, we classify this system under perovskite/semiconductor heterojunction composites rather than perovskite/co-catalyst composites, given the known visible-light response of ML-MoS₂.^[196] The resultant type-II heterojunction successfully enhanced charge separation efficiency. In fact, they observe a clear spatial separation of electrons and holes on ML-MoS₂ and MAPbI₃-MC, respectively. They also find that careful control of the thickness of ML-MoS₂ and size of MAPbI₃-MC is required to reach the optimal rate of 1360 H₂ $\mu\text{mol h}^{-1}$ and an STH efficiency of 1.09%. Simple mixing of ML-MoS₂ and MAPbI₃-MC leads to a 93% drop in the HER rate, while employing bulk-MoS₂ leads to a 96% drop. Furthermore, an intermediate size of the MAPbI₃-MC is needed, indicating the required balance between a high surface area but also an appropriate density of intercalated ML-MoS₂.^[185]

Also relying on a perovskite/MoS₂ composite, a recent study offers an elegant solution to the additional costs associated with relying on H₃PO₂ as a sacrificial agent in HX splitting by replacing it with a water-oxidation catalyst, namely WO₃ decorated with RuO_x. This not only serves as a more useful oxidation, but also regenerates I⁻ from I₃⁻. Furthermore, the reaction medium is much less corrosive than the traditional HI-reliant systems (pH = 2.9 vs -0.5).^[47,191] OWS proceeds at a promising STH of 2.07%.^[191]

In another approach, a 1.2 wt% black phosphorous (BP)/MAPbI₃ system showed a 19-fold improvement in rate compared to Pt-loaded MAPI (112.3 vs 5.76 $\mu\text{mol h}^{-1}$).^[97] This required the use of 2D few-layer BP, as opposed to bulk BP which yielded a rate of only 17.4 $\mu\text{mol h}^{-1}$ due to a more limited number of active sites. A promising AQY of 23.2% at 420 nm was reported, the highest so far amongst Pt-free LHP composites. Despite the type-I heterojunction formed, with the associated risk of recombination on the smaller-bandgap material, photoelectrochemical and spectroscopic characterization indicate efficient charge separation and transfer at the semiconductor interface, as well as improved transport.

Organic Semiconductors: Initial efforts following the first 2017 report of MAPI for hydroiodic acid splitting were directed towards perovskite/organic heterojunction composites. One study published in 2018 showed a 23-fold increase in the activity of MAPbI₃ by replacing 1.9 wt% Pt with 3.4 wt% reduced graphene oxide (rGO), going from 4.0 to 93.9 $\mu\text{mol h}^{-1}$.^[99] The system was stable during 200 h of testing and achieved an AQY of 1.5% at 450 nm. The improved performance was attributed to enhanced charge separation via favorable electron transfer from perovskite to rGO, thus reducing recombination.^[180]

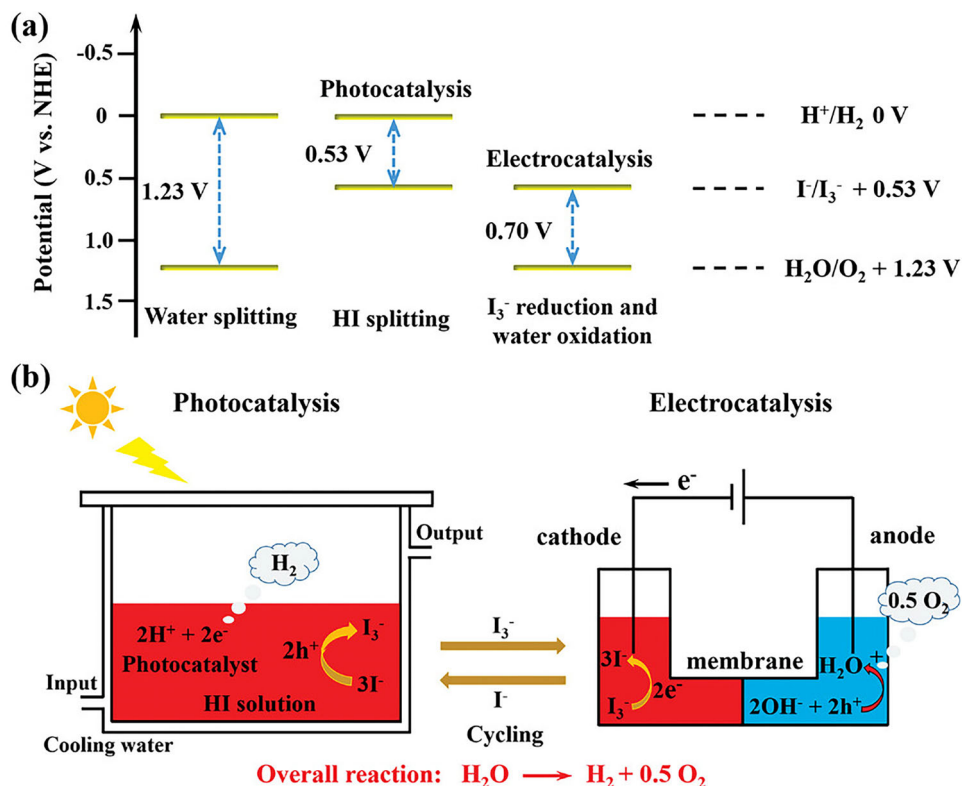


Figure 11. a) Redox potentials for the photocatalytic/electrocatalytic system for sequential HI splitting and water oxidation and b) schematic illustration of the steps involved. Reproduced with permission from ref. [197]. Copyright 2023 Wiley-VCH.

Photocatalysis + Piezocatalysis/Electrocatalysis: While the focus so far has been on purely photocatalytic redox processes, two studies combine photocatalysis with a second technology to boost activity.

An interesting study used the piezoelectric properties of MAPbI₃ to induce a built-in electric field for enhanced charge separation and accumulation of charges in opposite directions, favoring a spatial separation of oxidation and reduction processes.^[177] The piezophotocatalytic effect led to an HER rate of 23.3 $\mu\text{mol h}^{-1}$, a 7-fold and a 11-fold enhancement in rate compared to photocatalytic and piezocatalytic, respectively. The study relied on ultrasonic vibration as a source of mechanical stress, and it was observed that control of sonication power was critical to avoid conversion from the piezoactive tetragonal MAPbI₃ to the piezoinactive orthorhombic structure. Even if catalytic activity is improved, such a system seems difficult to scale-up; larger-scale ultrasonication is more difficult to control. Furthermore, the authors rely on measuring the concentration of I_3^- in solution to quantify evolved H_2 . However, the absorption of I_3^- , especially at higher concentrations, limits the absorption of MAPI in the visible range.^[47]

A more recent study combines photocatalytic HI splitting with electrocatalytic water oxidation to carry out OWS using I_3^-/I^- as a redox shuttle between the two systems (Figure 11).^[197] The authors couple a metal chalcogenide co-catalyst (MoSe₂) to a mixed-halide perovskite, MAPbBr_{3-x}I_x, and observe the same positive effects as mentioned for the ML-MoS₂ system discussed above. In fact, both the 1T and 2H phases of MoSe₂ are also detected in

this study, with an optimized loading of 3wt% MoSe₂. The importance of the more catalytically active 1T phase is illustrated by the reduced performance of 3wt% 2H-MoSe₂/MAPbBr_{3-x}I_x. The highest performing system yielded an HER rate of 3440 $\mu\text{mol h}^{-1}$, 153- and 2-fold higher than the pure perovskite or its Pt-loaded counterpart, respectively. In the presence of H₃PO₂ as a sacrificial agent to reduce I_3^- , the authors reported an STH of 3.85% and an AQY of 37.67% at 530 nm. Without H₃PO₂, an impressive STH of 1.02% is obtained when HI splitting and water oxidation are performed sequentially. While offering an elegant way to circumvent the large overpotential required to drive OWS, one major drawback of this system is the sequential HI splitting/water oxidation, which requires double the time compared to another system performing concerted hydrogen and oxygen evolution. Furthermore, the activity of the photocatalyst seems to drop progressively after the first cycle.

3.4.2. Lead-free halide perovskites

Replacing lead with non-toxic metal cations is an important step towards a system suitable for commercialization. Various substitutions have been tested since 2018, but performances remained weaker than lead-based counterparts until a study published in 2020 reported an activity comparable to MAPI using Cs₃Bi_{2x}Sb_{2-2x}I₉.^[181] Lead-free perovskites tend to display superior stability towards moisture compared to their lead-based counterparts, as illustrated by the higher number of applications in the

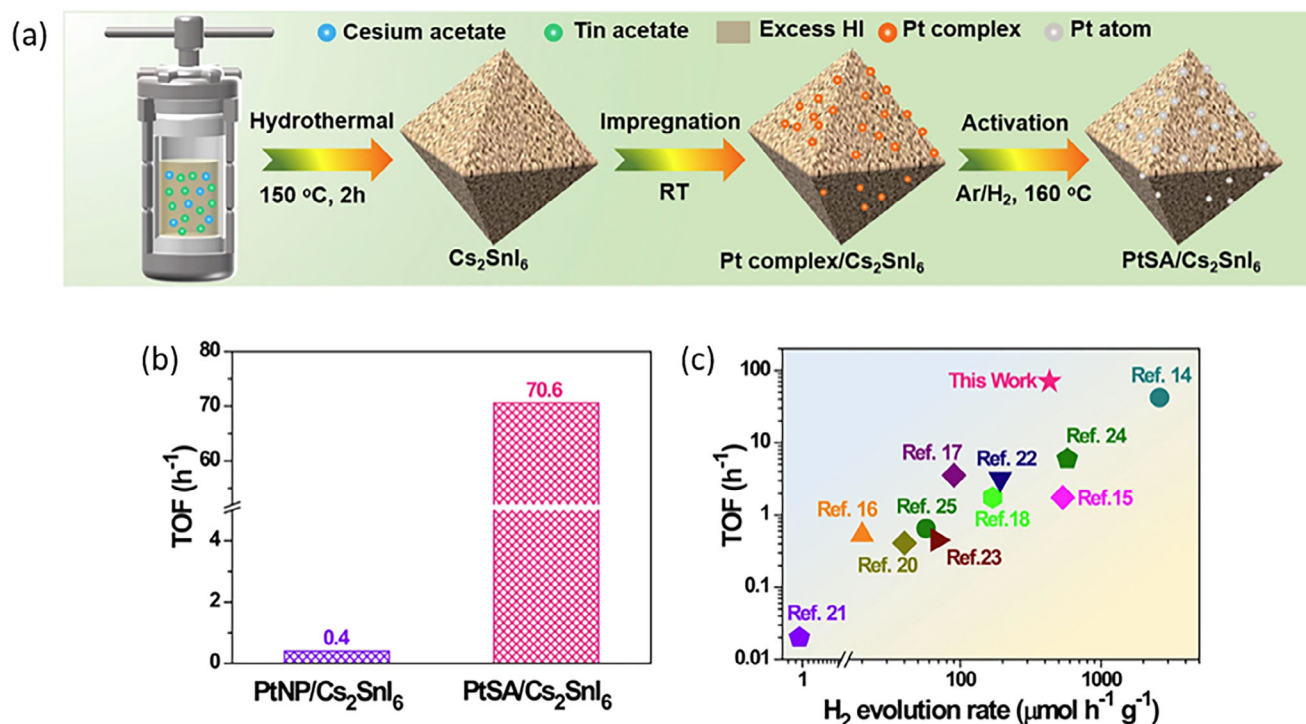


Figure 12. a) Schematic illustrating fabrication procedure of Cs₂SnI₆ photocatalyst decorated with PtSA as co-catalyst. b) TOF of the perovskite photocatalyst with Pt nanoparticles vs single-atoms. c) Literature comparison of TOF values, showing the record achieved for PtSA/Cs₂SnI₆. a–c) Reproduced with permission.^[186] Copyright 2021. Springer Nature.

context of water splitting. These developments are discussed below.

Compositional Engineering: Bi and Sn are common substitutes for Pb in lead-free perovskites. In 2018, DMA₃SnI₃ was found to be stable in water for 16 h,^[182] and was tested as a photocatalyst for hydrogen evolution/methanol oxidation. A very modest HER rate of 0.64 μmol h⁻¹ was reported, but the authors state that O₂ evolution from water oxidation induces Sn oxidation. One study employing a Bi-based perovskite reported photocatalytic activity based on a mechanism of charge transfer by collision, initially reported for a CdZnS-based HER photocatalyst.^[198] In the study in question,^[102] it was suggested that electron transfer occurs via a collision between dispersed MA₃Bi₂I₉ powder and dissolved Pt²⁺ ions, generating 6.76 μmol H₂ h⁻¹, in contrast to 0.49 μmol h⁻¹ without Pt. The material's activity corresponds to an STH of 0.48%. The first lead-free system yielding comparable results to that of MAPI was reported in 2020 and was based on Pt-decorated Cs₃Bi₂Sb_{2-2x}I₉ with $x = 0.3$ (labeled CBSI-0.3). They report an AQY of 1.21% at 420 nm. The incorporation of Sb alongside Bi as B-site cations is suggested to be the main reason behind the enhanced performance due to the reduction in Bi-vacancy defect sites. Employing a tin-based (Sn⁴⁺) double perovskite (Cs₂Pt_xSn_{1-x}Cl₆), one study showed that by introducing different amounts of Pt⁴⁺, the material displays switching behavior between photoluminescence and photocatalytic proton reduction in water.^[188] The latter process occurred at the lower Pt concentrations, namely Cs₂Pt_{0.05}Sn_{0.95}Cl₆. The photocatalytic activity at low Pt composition was attributed to the higher density of sub-gap states promoting thermal de-trapping of electrons,

thus suppressing radiative decay and increasing the number of electrons available to drive proton reduction. The authors report that the perovskite is stable during immersion in water for 25 days, and attribute this to the formation of an amorphous tin oxide protective layer.^[199] Similar to the principle of single-atom Pt reported in the study on FAPbBr_{3-x}I_x discussed above,^[90] a new way of forming single-atom Pt active sites was reported for a lead-free system (Figure 12).^[186] The authors relied on a Sn-based MHP to mitigate the issue of lead toxicity. Furthermore, the all-inorganic Cs₂SnI₆ perovskite was found to be more stable in HI aqueous solution than those based on organic cations. While the HER rate (4.3 μmol h⁻¹) is less than in other systems, the novelty of the study is the formation of single-atom Pt-I₃ sites. They report a record TOF of 70.6 h⁻¹, indicating much more efficient utilization of Pt active sites compared to the report on FAPbBr_{3-x}I_x/PtSA.^[90] The authors suggest three key reasons behind their system's performance: i) coordination structure, whereby I⁻ acts as anchoring sites, leading to atomic dispersion of Pt coordinated with three I⁻; ii) electronic properties of the Pt-I₃ species, which promote more efficient charge separation and transport; and iii) higher electron density at single-atom Pt sites compared to Pt NPs due to the favorable metal-support interaction (SMSI). TOF for the single-atom system is 176.5 times higher than that of Cs₂SnI₆ decorated with Pt NPs (0.4 h⁻¹).

Perovskite/Semiconductor Heterojunctions: A perovskite/perovskite heterojunction has also been reported, with the aim of mitigating recombination in Bi-based perovskites. The authors employ MA₃Bi₂I₉/DMA₃BiI₆ (BBP-5) as a binary, lead-free, perovskite heterostructure and achieve a rate of 19.82 μmol h⁻¹

without a noble metal co-catalyst.^[185] This constitutes a 15- and 8-fold improvement relative to the individual components, respectively. The heterostructure is formed in situ and requires control of the amount of DMF used, which acts as a co-solvent and as the source of DMA⁺ cations. At 5 vol% DMF, the resultant type-II heterojunction leads to efficient charge separation and suppressed recombination. Following the same rationale as for the lead halide perovskite/organic semiconductor heterojunctions, such heterojunctions were adopted for lead-free systems. Similar to the enhancement observed by replacing MAPI-Pt with MAPI-rGO (discussed above), a comparable effect was observed using Cs₂AgBiBr₆.^[180] While photo-deposition of 2.5wt% rGO did lead to a 51-fold improvement in HER rate compared to the Pt-analogue, the efficiency of the system is limited by the wider and indirect band gap in Bi-based perovskites,^[200] evidenced by the more modest AQY of 0.16% at 450 nm, compared to 1.5% in the case of MAPI-rGO. One group relied on the expected superior stability of 2D perovskites to test PEA₂SnBr₄ for H₂ generation under sacrificial water splitting conditions, with TEOA as a hole scavenger.^[189] Having confirmed the material's stability in water over a period of 4 h, they employ the lead-free perovskite in a composite with g-C₃N₄. At a low perovskite composition of 5 wt% and with 3 wt% Pt as a co-catalyst, they observe a HER rate of 33.9 $\mu\text{mol h}^{-1}$. The neat perovskite with 3 wt% Pt displayed a very modest rate of 0.084 $\mu\text{mol h}^{-1}$. The same group later also explored the 3D perovskite DMASnBr₃ in a similar system,^[183] encouraged by the relative stability of DMASnX₃ towards water (X = Br or I).^[182,201] The highest-performing composite DMASnBr₃/g-C₃N₄ contained 33 wt% DMASnBr₃ and 3 wt% Pt, leading to a HER rate of 36.3 $\mu\text{mol h}^{-1}$ with TEOA as hole scavenger. Based on the favorable impact of nitrogen-doped carbon materials on electron transport and lifetime,^[202] one study in 2021 relied on nitrogen-doped carbon support (N-C-140) in their CABB-based composite.^[179] Cs₂AgBiBr₆/N-C-140 yielded an AQY of 0.59% at 420 nm, an improvement relative to CABB-rGO mentioned above. Apart from the favorable CB alignment to promote electron transfer onto N-C-140, the material also performs the role of support onto which CABB is grown and helps prevent aggregation. In fact, a physical mixture of CABB and N-C-140 leads to only 25% of the activity achieved with in-situ growth. The optimized composite evolved H₂ at a rate of 3.8 $\mu\text{mol h}^{-1}$, 19 times higher than pure CABB. While the aforementioned study relied on g-C₃N₄ as a precursor to make N-C-140, g-C₃N₄ is a promising visible-light, metal-free semiconductor photocatalyst in its own right.^[203] Various lead-free halide perovskite/g-C₃N₄ composites have also been reported in the context of HX splitting, employing either CABB or Cs₃Bi₂Br₉.^[184,187] In-situ self-assembly of the CABB composite yields a type-II heterojunction where H₂ evolution occurs on the CABB at a rate of 3 $\mu\text{mol h}^{-1}$, a modest 2.5-fold improvement on the neat perovskite (1.2 $\mu\text{mol h}^{-1}$).^[184] A different mechanism is proposed for Cs₃Bi₂Br₉/g-C₃N₄/Pt (3wt%), where the best-performing composition involves a low perovskite content (namely 2.5wt%). The composite yields a HER rate of 22.05 $\mu\text{mol h}^{-1}$.^[187] According to the proposed mechanism, self-trapping of photogenerated electrons occurs on the perovskite at higher contents, leading to a drop in HER rates. Inspired by an effect observed in dye-sensitized solar cells, they suggest a direct excitation from the VB of the

perovskite to the CB of g-C₃N₄ is effective at low perovskite content.^[187]

Porous g-C₃N₄ (pCN) has also been combined with 16.7 wt% CsPbI₃ and decorated with 3.9 wt% Pt. In the resultant type-II heterojunction, H₂ evolution occurred on pCN at a rate of 10 $\mu\text{mol h}^{-1}$ while sacrificial oxidation of TEOA occurred on the perovskite. It is worth noting that proton reduction is a competing reaction when performing CO₂ reduction. In fact, negligible H₂ evolution has been observed as a by-product in gas-phase CO₂ reduction performed with concomitant water oxidation (without a hole scavenger),^[204] but further work is needed to understand the feasibility of water oxidation on halide perovskites and how to control it, as evidenced by the studies reviewed above.

3.5. Lead-Halide Perovskites for Photoelectrochemical Water Splitting

As mentioned in section 3.1, PEC and PV-EC systems are two of the main technologies for green H₂ production. PEC systems have historically been limited by low solar to fuel conversion efficiencies, while PV-EC systems have been limited by complex device configurations and high costs.^[205] Meeting the US Department of Energy target of achieving <\$2 kg⁻¹ H₂ requires an STH of > 20% and a device lifetime of >10 years.^[206] However, after over four decades of research, traditional earth-abundant materials for PEC systems, including metal oxides, metal nitrides, III-V materials, and crystalline silicon have low STH values well below this target, and poor stability.^[207] Lead-halide perovskites offer opportunities to achieve improved performance, and using integrated PV-PEC systems provides an opportunity to make use of the extensive work in the wider field of fabricating efficient LHP photovoltaic devices. LHPs have a theoretical STH of 28.7% for single-junction photoelectrodes,^[207] and can readily be combined with silicon photovoltaics to achieve efficient tandem devices that have now enabled integrated PV-PEC systems with >20% STH.^[208] This section discusses the advances made in the application of LHPs for water splitting in terms of performance, but also in terms of durability.

3.5.1. Single-Junction Photoelectrodes

LHPs readily dissolve in water, which severely limits the ability to directly use halide perovskites as photoelectrodes for water splitting in direct PEC systems.^[82,139,209] Over the past decade, substantial progress has been made to overcome this limitation to enable LHPs to be feasible photoelectrodes through the use of effective encapsulation methods (discussed later in section 3.5.3). At the same time, unlike traditional photoelectrodes, in which the bare photoactive layer is often used, LHPs benefit from the use of the charge transport layers developed by the photovoltaics field to enhance the separation and extraction of photogenerated charge carriers to the catalyst. The use of these charge transport layers also improves the open-circuit voltage, leading to a higher onset potential, thus improving the ability of these devices to overcome the overpotentials necessary to drive solar water splitting.

LHPs are typically intrinsic or close to being intrinsic, and so are sandwiched between electron- and hole-selective transport

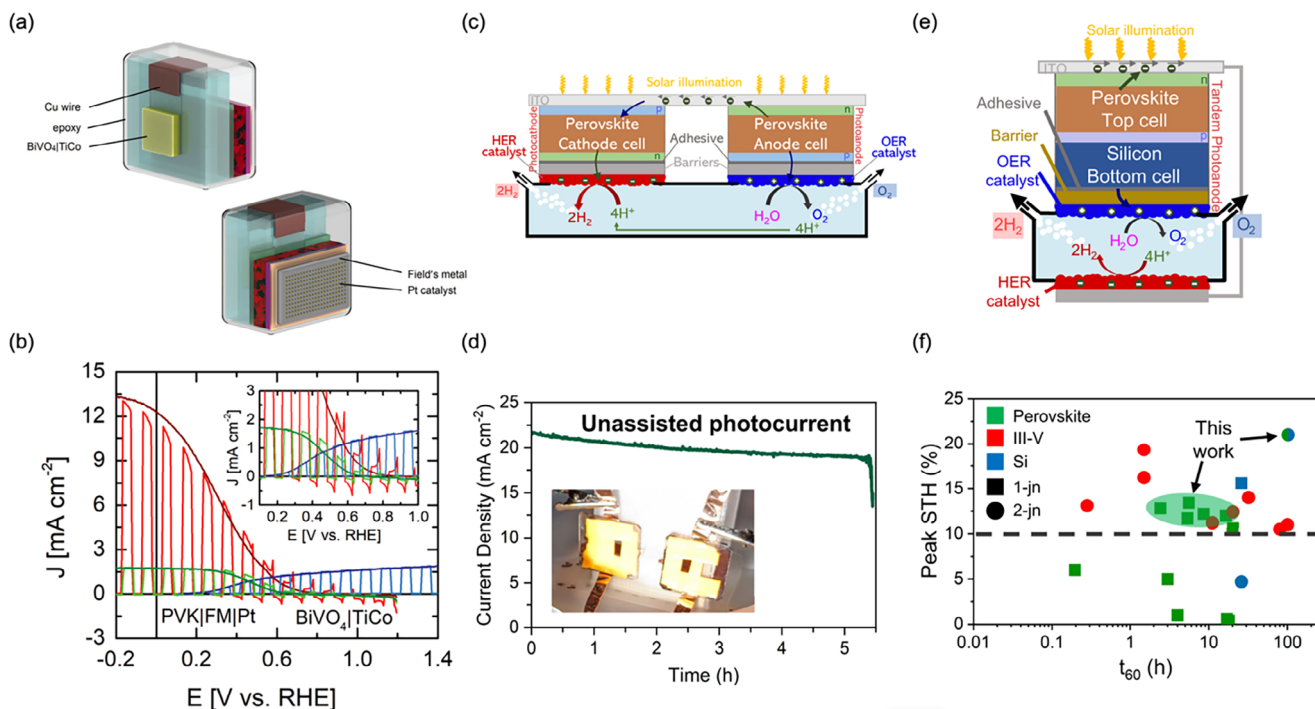


Figure 13. Device architectures for halide perovskite photoelectrodes. a) Photocathode formed from a metal-halide perovskite heterojunction device, connected to a BiVO₄ photoanode. b) Continuous and chopped voltammograms of BiVO₄/TiCo photoanodes (blue), and halide perovskite photocathode without filtering (blue), and with filtering from BiVO₄/TiCo (green). The device area was 0.25 cm². Parts (a) and (b) are reproduced with permission from Ref.[211] Copyright 2018, Wiley. c) Tandem device with halide perovskite photoelectrodes connected together to achieve unassisted water splitting, and d) stability of the photocurrent with no external bias applied. e) Unassisted water splitting from perovskite-silicon tandem photoanode, combined with a Pt/C hydrogen evolution reaction (HER) catalyst. f) Comparison of the peak solar-to-hydrogen (STH) efficiency of a range of PEC devices based on different light-harvesting materials. "This work" refers to devices based on halide perovskite-silicon tandem photoanodes. Parts (c) to (f) are reproduced under the terms of the CC-BY license from Ref. [208].

layers (ETLs and HTLs, respectively). By adjusting the order of these carrier-selective contact layers when deposited onto the transparent conducting oxide (TCO)-coated substrate, the devices can be prepared as photocathodes (*p-i-n*-structured devices) or photoanodes (*n-i-p*-structured devices). The materials used as charge-transport layers significantly influence the STH and stability of the devices. For example, replacing poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) with NiO_x as the hole transport layer improved the open-circuit voltage of *p-i-n*-structured perovskite photovoltaics from 0.6–0.9 V (PEDOT: PSS) to 1.00 ± 0.02 V (NiO_x), and this led to an improvement in the early-onset potential of these devices used in photocathodes (refer to Figure 13a for an illustration of the device). Improvements in open-circuit voltage and early onset potential were also achieved by covering the PEDOT:PSS layer with poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], or PTAA.^[154] This reduced interface recombination,^[210] thus giving rise to an increase in open-circuit voltage to 1.04 ± 0.02 V. The PTAA layer was also doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) to improve the conductivity of this layer. Increasing the early onset potential of these photocathodes leads to greater overlap in their cyclic voltammetry (CV) curves with the CV curves of the photoanode (see Figure 13b for an example),^[211] thus enabling the development of self-driven photoelectrochemical tandem devices (see section 3.5.2 for more details). The use of PTAA rather

than NiO_x to improve the open-circuit voltage of these devices is advantageous in that PTAA can be deposited at lower temperatures than NiO_x, and is compatible with flexible polymer substrates (rather than bulky glass substrates), which enabled the demonstration of lightweight, floating LHP photoelectrochemical tandem devices.^[154] Similarly, for *n-i-p*-structured devices, making use of charge transport layers that have enabled reduced interface recombination has led to photoanodes with improved performance.^[208] There is therefore substantial work that can be done in the LHP photoelectrochemical field by drawing off the many varied improvements made in the photovoltaics field.

LHP photoanodes can be achieved using *n-i-p*-structured devices with an oxygen evolution catalyst (e.g., Ni, NiFe, or NiFeOOH) connected to the hole transport layer.^[82] The advantage of LHPs is that their bandgaps can be readily tuned through the composition. MAPbI₃ and triple-cation perovskites, which have been widely explored for photocathodes, have also been investigated for photoanodes. However, the valence band maximum of MAPbI₃ is too high for water oxidation to oxygen.^[209] Replacing I with Br in these LHPs increases the ionization potential, such that water oxidation can proceed. For example, CsPbBr₃ and FAPbBr₃ have both been demonstrated in photoanodes, achieving photocurrent densities of up to 3.8 mA cm⁻²^[82] and 8.5 mA cm⁻² photocurrent density^[212] at 1.23 V (RHE), respectively. The latter exceeds the photocurrent of state-of-the-art metal

oxide-based photoanodes ($5\text{--}7\text{ mA cm}^{-2}$ at 1.23 V (RHE)).^[207] Very recently, a substantially higher photocurrent of 22.82 mA cm^{-2} was achieved at 1.23 V (RHE) using an α -phase FAPbI_3 perovskite photoanode, encapsulated with Ni foil, and with a NiFeOOH oxygen evolution reaction photocatalyst^[207] (as measured in a three-electrode setup). α - FAPbI_3 has a deeper band position than MAPbI_3 , although, the same spiro-OMeTAD hole transport layer was used.^[207] When these α - FAPbI_3 photoanodes (0.25 cm^2 active area) were wired to an external α - FAPbI_3 photovoltaic device, and also wires to a Pt cathode (dark; only acts as an electrocatalyst) to achieve a hybrid PEC-PV device, unassisted solar water splitting with an STH of 9.8% was realized.^[207]

3.5.2. Perovskite-Based Tandem Devices for Photoelectrodes

Single-junction halide perovskites face significant limitations when it comes to unassisted solar water splitting. The open-circuit voltage produced by a single-junction lead-iodide-based device falls below the minimum practical voltage required to drive both the hydrogen and oxygen evolution reactions ($1.5\text{--}1.9\text{ V}$).^[213] Increasing the bandgap of the halide perovskite increases the open-circuit voltage (but also increases non-radiative voltage losses) but at the cost of a reduced photocurrent. This trade-off can be overcome by combining multiple photovoltaic devices together, harvesting light from complementary parts of the solar spectrum. This can be in the form of separate devices operating as the photocathode and photoanode (see Figure 13c for an example), or from a tandem photovoltaic device either driving an electrocatalyst or integrated into a photoelectrochemical system (see Figure 13e for an example).

For example, Mohite and co-workers recently developed *p-i-n* photocathodes based on triple-cation halide perovskites, and *n-i-p* photoanodes based mostly on α - FAPbI_3 , with a small amount of methylammonium mixed into the A-site.^[207] The perovskite photocathode had a Pt hydrogen evolution catalyst, while the perovskite photoanode had an IrO_x oxygen evolution catalyst (Figure 13c). The back contacts of these two devices were connected, and, when both photoelectrodes were illuminated with AM 1.5G radiation, were shown to achieve unassisted solar water splitting with an initial photocurrent of 22.1 mA cm^{-2} and STH of 13.4% (Figure 13d). These devices operated for just over 5 h, with an average decrease in photocurrent of approximately $0.5\text{ mA cm}^{-2}\text{ h}^{-1}$ before failure (Figure 13d).^[207]

A similar wired design was demonstrated earlier by Andrei et al. for halide perovskite (photocathode)– BiVO_4 (photoanode) tandems.^[154] In both cases, Pt was used as the hydrogen evolution catalyst, while the BiVO_4 photoanode used TiCoO_x oxygen evolution catalysts. Increasing the open-circuit voltage of the halide perovskite photocathode to $> 1\text{ V}$ by reducing interface recombination between the perovskite and hole transport layer (by using an interfacial layer of PTAA) was important to increase the overlap in the CV curves of photocathode and BiVO_4 in order to achieve unassisted solar water splitting. The STH reached was $< 1\%$ in both cases.^[154,211] An important loss in performance came from the shading of the photocathode by the photoanode when these devices were wired together back-to-back (Figure 13a).^[211] This was overcome by having the two photoelectrodes placed next to each other, thereby taking a

larger area, but avoiding any shading losses (see Figure 13c for an example).^[154,207]

An important limiting factor of the wired-tandem design described above is that it is difficult to achieve an ideal overlap in the maximum power points of the two photoelectrodes. An alternative approach is to fabricate a monolithic tandem photovoltaic device that can provide sufficient photovoltage to drive unassisted solar water splitting. Mohite and co-workers demonstrated this with a perovskite-silicon tandem photovoltaic device (with 29% power conversion efficiency under 1-sun illumination, along with 1.9 V open-circuit voltage), with the Ir/IrO_x oxygen evolution catalyst attached to the silicon cell. The perovskite top cell was wired to a Pt foil counter electrode for hydrogen evolution (Figure 13e). This PEC–PV–EC hybrid device achieved unassisted solar water splitting with 20.8% STH. This peak STH exceeds previous reports of halide-perovskite-based PEC systems (Figure 13f), also exceeds the performance of III–V tandem PEC systems,^[208] and is competitive with PV–EC systems using a separate monolithic perovskite-silicon tandem photovoltaic device driving electrolysis.^[214]

Monolithic perovskite-perovskite tandem devices for PEC–PV–EC systems have also been demonstrated by Yan and co-workers.^[213] A mixed iodide-bromide perovskite top-cell (1.75 eV bandgap) was monolithically integrated over a mixed Pb–Sn perovskite bottom-cell (1.25 eV bandgap), leading to photovoltaic devices with 26% power conversion efficiency and 2.1 V open-circuit voltage. In a PV–EC system, 17% STH was achieved (using Pt and IrO_x catalysts). To create a hybrid system, the monolithic perovskite-perovskite tandem was encapsulated with metal foil and graphite/Ag paste, and a Pt catalyst connected to the top electrode of the narrow-gap perovskite device, while the back contact of the tandem was wired to an IrO_x electrocatalyst. These hybrid systems achieved an STH of 15% and retained 95% of the initial performance after 120 h of continuous operation under chopped illumination. Whilst the performance of these devices is lower than that obtained from III–V tandems, techno-economic analyses showed that the fabrication cost of the all thin film perovskite tandem is two orders of magnitude smaller, and hybrid PEC–PV–EC systems that can operate for 3 years could reach a levelized cost of hydrogen of $\text{US\$1 kg}^{-1}$.^[213]

3.5.3. Improving Stability and Minimizing Lead Release from Halide Perovskite Photoelectrodes

While directly integrating a photovoltaic device into a photoelectrochemical system can improve the simplicity of the design, it places more stringent requirements on the stability of the device. Halide perovskites readily dissolve in water, and effective encapsulation is therefore essential. Early efforts at developing halide perovskite photoelectrodes encapsulated the perovskite device stack with metal foil. For example, a thin layer (8 nm) of nickel was used to protect *n-i-p*-structured MAPbI_3 photovoltaic devices, giving rise to the first demonstration of halide perovskite photoanodes.^[209] Nickel was selected because it had been shown previously to protect silicon photoanodes from corrosion and to act as an oxygen evolution reaction catalyst.^[139,215] Although the Ni top layer was more effective than Au as a top layer, the stability of the halide perovskite photoanodes was only on the order of

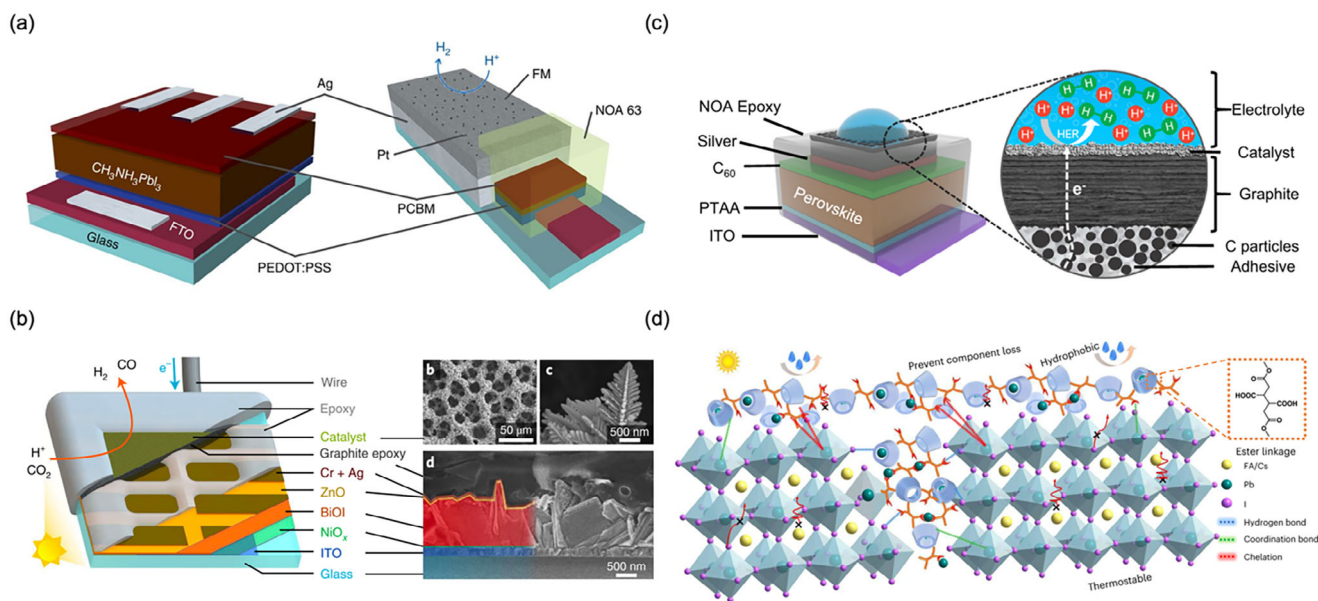


Figure 14. Mitigating the release of Pb from halide perovskite PEC devices. a) Illustration of the use of metallic encapsulating layers, such as Field's metal (FM). In this case, FM was deposited over a methylammonium lead iodide photovoltaic device, which was used as a photocathode by depositing Pt over the FM. Reproduced under the terms of the CC-BY license from Ref. [131]. b) Illustration of BiOI photocathodes, which are stabilized using graphite epoxy. Reproduced with permission from Ref. [220] Copyright 2022, Springer Nature. c) Halide perovskite photocathodes stabilized with a conductive adhesive barrier (CAB), comprised of graphite sheets with a pressure-sensitive adhesive. Reproduced under the terms of the CC-BY license from Ref. [208]. d) Use of supramolecular complexes to sequester Pb^{2+} from degraded halide perovskite grains. The supramolecular complex in this case was comprised of cyclodextrin cross-linked with butyltetracarboxylic acid. Reproduced with permission from Ref. [221]. Copyright 2023, Springer Nature.

tens of minutes.^[209] However, the degradation of the photoanode was partly due to the low stability of the MAPbI_3 perovskite layer. Recently, Hansora et al. used the more stable $\alpha\text{-FAPbI}_3$ as the photoanode active layer, which was made into a photoanode with a similar architecture at the MAPbI_3 device, and again with Ni foil encapsulation.^[207] But this time, the Ni foil was thicker (25 μm , rather than 8 nm), and this was critical for improving the stability of these photoanodes. When the Ni foil was <10 nm thick, the photoanodes were only stable for a few minutes because they were insufficient for preventing electrolyte permeation. Foils >10 μm thick were needed to prevent Pb leaching into the electrolyte after >5 h of operation, and these thick foils were attached to the perovskite device stack using Ag paste, which was adequate for forming an ohmic contact.^[207]

A similar idea was used to protect monolithic perovskite-perovskite tandems by using $\approx 100\ \mu\text{m}$ thick Pt foil to encapsulate these devices and using a mixed graphite/Ag paste to glue these foils onto the device stack.^[213] Pt was also effective as a hydrogen evolution catalyst, and these devices were stable under operation for 120 h.^[213] Leading on from the concept of metal-foil-encapsulation, Reisner and co-workers introduced the idea of using Field's metal (eutectic alloy of 51% In, 32.5% Bi, and 16.5% Sn).^[131] This has the advantage of being able to directly integrate onto the perovskite devices, since this alloy melts at 62 $^\circ\text{C}$, and can therefore be integrated by placing a solid piece of Field's metal onto the device and heating at 70 $^\circ\text{C}$, which melts the Field's metal but does not degrade the perovskite device. As a result, the use of Ag paste is unnecessary. At the same time, the perovskite devices still had Ag top electrodes deposited because it was found that Field's metal effects wet this surface

(Figure 14a). Where Field's metal spread to could therefore be controlled by the pattern of the Ag electrode.^[131] Catalysts could then be deposited on top of the Field's metal, e.g., Pt for hydrogen evolution reactions. The stability of MAPbI_3 photocathodes encapsulated with Field's metal was initially poor (degrading after only 2 h of operation),^[131] but was improved to >15 h by replacing the acidic PEDOT: PSS hole transport layer in contact with the perovskite thin film with NiO_x .^[211]

Further stability improvements were obtained by integrating conductive particles into an epoxy to provide more effective encapsulation, whilst still allowing photogenerated charge carriers to be transported to an electrocatalyst. Andrei et al. developed graphite epoxy by mixing in graphite powder with Araldite Standard epoxy adhesive.^[154] This is advantageous over Field's metal by requiring no heating and can be easily spread in a controlled manner, even when the substrate used is a polymer. As a result, Andrei et al. demonstrated the stable operation of the perovskite photocathodes for both H^+ and CO_2 reduction for >30 h and also were able to fabricate the photocathodes on flexible plastic substrates, giving rise to lightweight photocathodes that could float based on the bubbles produced.^[154] Such devices could be used in the future for offshore photoelectrochemical reactors for producing solar fuels. Graphite epoxy has also been demonstrated as an effective encapsulant for BiOI photocathode devices (Figure 14b).^[216] BiOI photocathodes directly used in contact with electrolytes degrade within minutes, and applying a bias to these devices results in Bi^{3+} being reduced to Bi^0 . Encapsulating these photocathodes with the oxide charge transport layers developed for photovoltaics,^[217] as well as graphite epoxy encapsulant, improves the stability to ≈ 500 h. Indeed, the BiOI photocathode was

more stable than the Pt catalyst used for H^+ reduction, which is unusual among novel light harvesters.^[217] Similarly, Mohite and co-workers developed a conductive adhesive barrier, comprised of a graphite barrier glued to the perovskite device with a pressure-sensitive adhesive mixed with conductive particles (Ag, Cu, and amorphous C) to improve the conductivity (Figure 14c).^[208] In photovoltaic devices measured in air, perovskite devices encapsulated with this conductive adhesive barrier retained 95% of their initial efficiency after 10 h of continuous maximum power point tracking, whereas perovskite photovoltaic devices covered only with graphite and carbon paste lost 40% of their initial performance. Encapsulating perovskite photoelectrodes, connected together in tandem (Figure 13c), with this conductive adhesive barrier enabled the tandem photoelectrochemical system to be stable for 5 h (Figure 13d) with >10% STH. Improved stability was achieved in monolithic perovskite-silicon tandems (Figure 13e), which achieved unassisted water splitting for >100 h.^[208]

Further enhancements in stability were achieved by Eslava and co-workers using glassy carbon and boron-doped diamond as encapsulation,^[218] achieving $CsPbBr_3$ photoanodes with 168 h and 210 h stability, respectively. This was a substantial improvement over $CsPbBr_3$ and $FAPbBr_3$ photoanodes with graphite encapsulation, which has stabilities on the order of tens of hours.^[82,212,219] The limitation of graphite is that these layered materials suffer from chemical and mechanical stresses during operation, particularly when bubblers nucleate and grow. Both glassy carbon and B-doped diamond are more chemically stable and maintain high electrical conductivity. These sheets were prepared separately to the perovskite device stack, and glued on using a thin layer of epoxy that did not completely isolate the perovskite device from these sheets, thus allowing photogenerated holes to still be transported through the encapsulation layer to the $NiFeOOH$ catalyst loaded onto the sheet.^[218]

Finally, it is important to consider what mitigation measures can be put in place to prevent the release of lead in aqueous solution following the catastrophic failure of encapsulation. This has led to the exploration of lead sequestration strategies, which make use of high surface area structures that can bind to Pb^{2+} before it is released into flowing water.^[222] One of these strategies is to use a supramolecular complex comprised of a β -cyclodextrin derivative, linked together with 1,2,3,4-butane tetracarboxylic acid (Figure 14d). These supramolecular complexes can be integrated into the perovskite active layer during thin film deposition and have been shown to reduce the leaching rate of Pb^{2+} by a factor of 18 without affecting device performance.^[221] As discussed above, a wide range of internal and external encapsulation strategies are being developed to enhance the stability of perovskites in polar solvents, thus reducing Pb's leaching into the solvent medium. Some of the external strategies include the encapsulation of perovskites with conductive materials like Ni, Pt, Au, alloys (Field's metal), graphite, carbon, conductive epoxy (conductive particles combined with epoxy), and organic supramolecules like cyclodextrins. Although these enhancement strategies enabled the operation of perovskite photoelectrodes from a few hours to a few days depending on the encapsulant, achieving long-term stability (months and years) is still an outstanding challenge. The material space of encapsulants should be expanded while keeping in mind that they have to be highly conductive. For example, internal encapsulation through direct interactions

with Pb^{2+} through lead-coordinating functional groups such as carbonyl, hydroxyl, and thiol can effectively suppress lead leakage. Explored encapsulants including the use of functional hole-transporting materials like spiro-NPU that form Pb-O bonds,^[223] thiol-functionalized 2D MOFs with strong Pb-S interactions,^[224] polymers like PBAT containing carbonyl groups,^[225] and small molecules like thiol-functionalized perfluoroalkyls.^[226] In addition, one should think of designing photoelectrochemical devices in which the perovskites are not in direct contact with the reaction medium. Therefore, more studies should be devoted to improving the stability and thus reducing Pb leaching in polar reaction mediums.

3.5.4. Strategies for Device Scale-Up

The conventional approach to scaling up devices is making one with a larger area. This leads to reductions in performance because of an increased likelihood of shunt pathways (e.g., pinholes in any of the thin film layers) being present, as well as increased series resistance from the longer pathway for charge carriers to travel through the transparent electrode. But unlike photovoltaics, in photoelectrochemical cells, it is not necessary to have one continuous large pixel. Rather, smaller pixels, operating simultaneously and side-by-side on a large substrate can be used since photoelectrochemical reactions take place on any exposed surface that has photogenerated charge-carriers introduced to it (Figure 15a).^[216] Andrei et al. demonstrated this concept for BiOI photocathodes, showing that combining several smaller pixels leads to a higher photocurrent and larger early onset potential because of reduced losses due to shunting, and this improved performance was essential to achieve unassisted water splitting working in tandem with $BiVO_4$ photoanodes. Furthermore, the BiOI pixels can be pre-screened to identify shunted or faulty pixels, and these can be covered using epoxy encapsulating.^[216]

Similarly, Hansora et al. fabricated α -FAPbI₃ mini-modules by combining multiple individual cells (3.84 cm² each) altogether (Figure 15b). As a result, there was little decrease in the STH from small photoelectrochemical cells (1 cm²; 9.2% STH) to 123.2 cm² area panels (8.5% STH). The STH values obtained from the large-area panels are competitive compared to oxide-based systems (Figure 15c). Furthermore, the 3.84 cm² area devices had similar performance to the smaller lab-scale 0.25 cm² cells (20.5 mA cm⁻² vs 22.82 mA cm⁻² photocurrent at 1.23 V (RHE), respectively).^[207]

4. CO₂ Reduction

Converting carbon dioxide (CO₂) into fuels like methane or methanol using solar energy offers a promising solution to both environmental concerns and future energy needs.^[227] This process not only mitigates the increasing levels of CO₂ in the atmosphere, but also offers a convenient means of energy storage.^[228] In this regard, several methods and materials have been developed primarily by harnessing solar energy for CO₂ reduction.^[139,229,230] One of the early notable contributions to this field was made by Bard et al.^[231,232] who developed a photocatalytic device based on a particle suspension system. This device

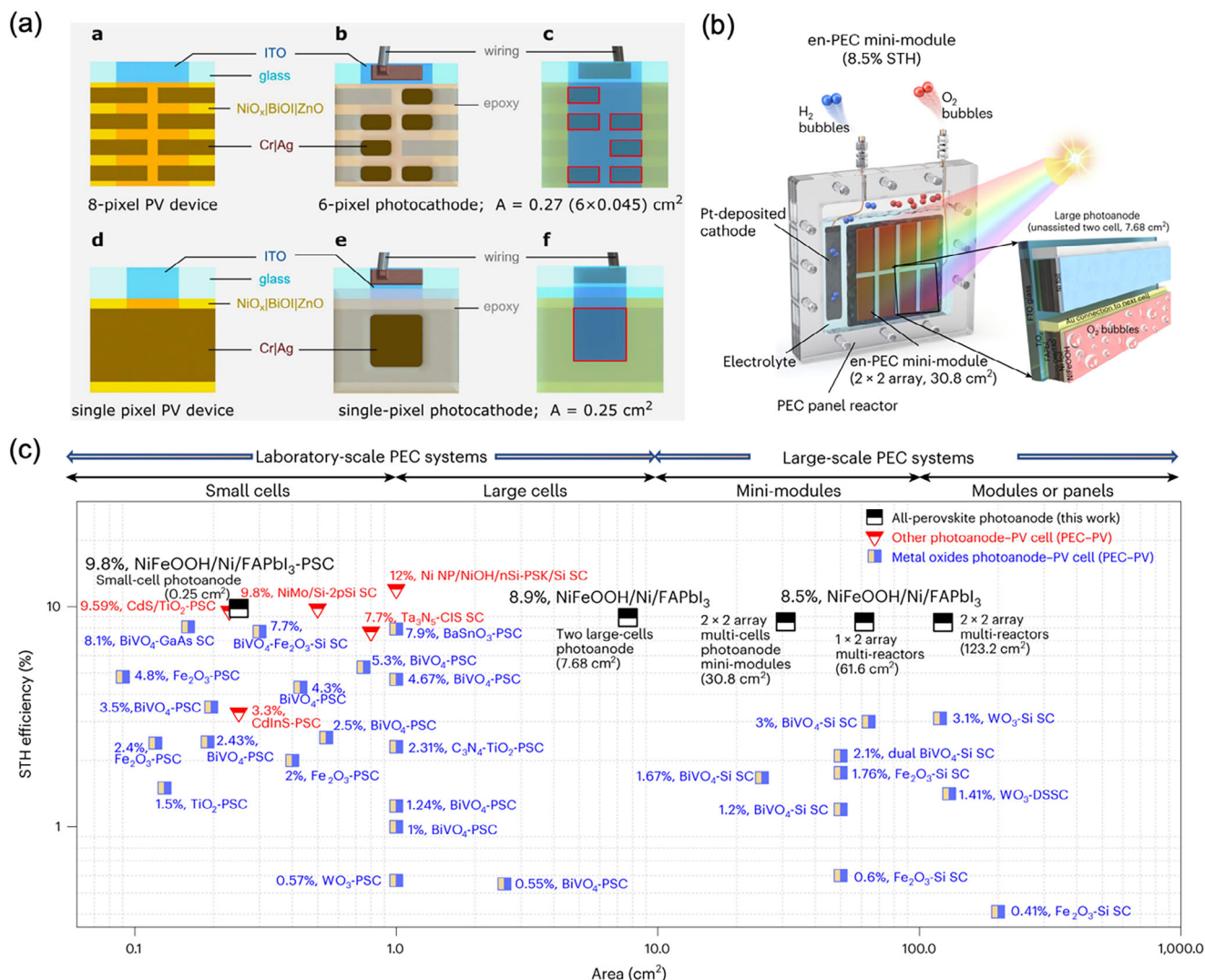


Figure 15. Strategies to scale up halide perovskite photoelectrodes. a) Illustration of two strategies for scale-up: the traditional use of a large single-pixel device, versus the combination of several smaller pixels that add up to a larger device area. Reproduced with permission.^[220] Copyright 2022, Springer Nature. b) Formation of mini-modules of photoelectrochemical cells by combining halide perovskite photoanodes. c) Comparison of the solar to hydrogen (STH) conversion efficiency against device area for a wide range of photoelectrochemical cells, ranging from small cells to modules. Parts (b) and (c) are reproduced with permission.^[207] Copyright 2024, Springer Nature.

was initially employed for water-splitting studies, following the pioneering discovery of photocatalytic water splitting at titanium dioxide electrodes by Honda and Fujishima in the early 1970s.^[24] The utilization of solar energy in such photocatalytic systems enables the conversion of CO_2 into useful fuels and has opened doors to sustainable energy and remediation. Ever since the early report of photocatalytic CO_2 reduction in 1979,^[21] numerous research efforts have been devoted to finding suitable photocatalysts. They play a vital role in converting solar light into charge carriers, namely electrons and holes, which are then utilized for oxidation and reduction reactions.^[233–236] A wide range of semiconducting materials, e.g., TiO_2 ,^[237–241] Cu_2O ,^[242–248] CdS ,^[249,250] C_3N_4 ,^[251–254] and perovskite oxides,^[255–258] have been developed for solar-driven photocatalytic CO_2 reduction. However, most of these materials are far from ideal photocatalytic systems because of various limitations, e.g., rapid recombination of photo-

generated charge-carriers, wide bandgaps, and poor photoreduction potentials (Figure 16). Over the past decade, MHPs have received significant attention as one of the most promising photocatalysts for reduction of CO_2 because of their high absorption coefficient,^[259–265] large charge carrier motility,^[259,266,267] and wide tunability of their optoelectronic properties through the composition (Figure 16).^[268–271] In the last few years, several review articles have been published on halide perovskite-based photocatalysts for CO_2 reduction, which mainly address the stability issues and basic mechanisms.^[38,40,111,227] However, demand remains for a timely and comprehensive review that explores deeper into the photoreduction mechanisms, reductants, and products, as well as the structure-photocatalytic performances relationships of halide perovskites and their composites. In this section, we highlight recent advances in solar-driven CO_2 conversion into fuels using organic-inorganic and all-inorganic

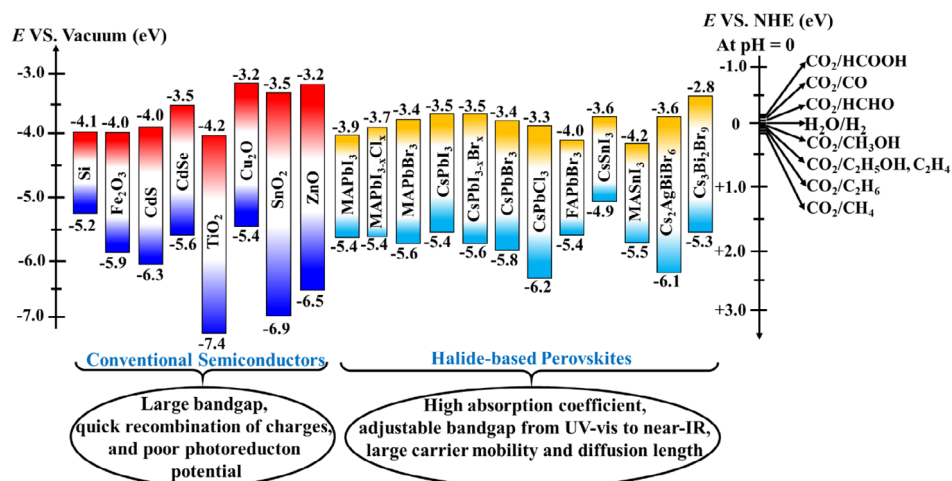


Figure 16. Conduction and valence band positions of conventional and halide-based perovskite materials relative to CO_2 reduction potential. The relative potentials at pH 0 involved in CO_2 reduction are plotted versus vacuum (left). This plotting helps to compare the energy levels of different electrochemical reactions with a common reference point, which is the vacuum level.

colloidal perovskite materials including their heterojunction construction, defects engineering, architectural modifications, and other strategies with the aim of enhancing the efficiency and selectivity of these materials for CO_2 conversion.

4.1. Typical Experimental Setup and Mechanism of Photocatalytic CO_2 Reduction

A photocatalytic reaction is generally carried out in a closed gas-circulation reactor containing semiconductor particles (in the form of thin film, colloidal dispersion, or colloided deposited on a substrate) as the photocatalysts, and dissolved CO_2 in various reaction medium (as shown in Table 3).^[233–235,272,273] The typical experimental setup is illustrated in Figure 17. The reduction of CO_2 takes place in the presence of semiconductor materials under light irradiation. The CO_2 reduction process proceeds when the incident light has a photon energy equal or greater than that of the bandgap (E_g) of the semiconductor materials. In general, the basic mechanism of the photocatalytic CO_2 reduction consists of three synergistic steps (see Figure 17). In the first step, the absorption of light by the photocatalyst generates electrons and holes. Then, the second step involves the separation and migration of electrons to the interface, leaving an equal

number of electrons and holes in the conduction band (CB) and valence band (VB), respectively. At this stage, a large fractions of photogenerated electron-hole pairs could be consumed by recombination, because of the dominance of recombination over charge separation or vice versa, depending on their relative time scales. This recombination issue can be reduced by carefully engineering various structural and material properties. Creating complex interactions among factors such as dimension, surface properties, material crystallinity, and making heterostructures with co-catalysts can improve the charge separation.^[38] In the final step, the transfer of electrons from the photocatalyst to respective sites, and then undergoes an electrochemical catalytic reaction to produce fuels. In general, an efficient photocatalyst should exhibit four important features; (i) the ability to enhance the charge separation and transfer them to reaction sites, (ii) the selectivity of photoreduction of CO_2 , (iii) durability in a peculiar environment (e.g., high humidity and high temperature), and (iv) suppressing the side reactions (e.g., H_2 reduction). In addition, other factors such as photocatalyst loading, particle size, structure, dispersion, crystal facets, composition, alloy phase, morphology, and valence states play an important role in the efficiency and selectivity of photocatalytic CO_2 reduction. In particular, the loading of an optimum amount of photocatalysts

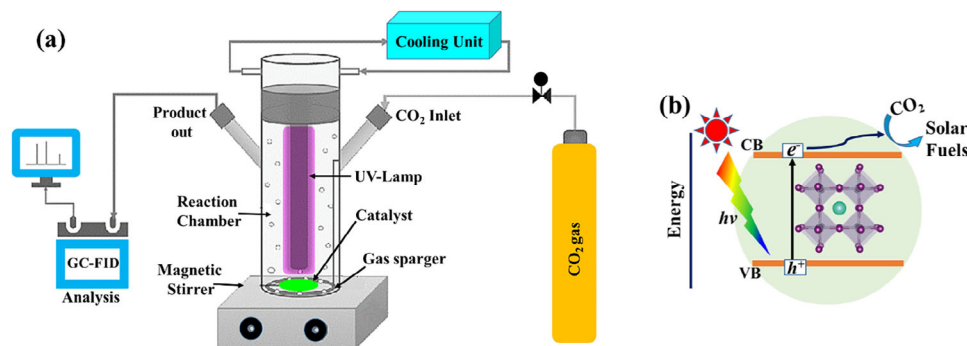


Figure 17. Schematic illustrations of a Photocatalytic reaction operator (a) and a typical mechanism for the photocatalytic CO_2 reduction (b).

Table 2. Common products from CO₂ reduction with their simplified redox equations.

S. No.	Equation	Product	E° (V)
01	CO ₂ + 1e ⁻ = CO ₂ ⁻	Carbonate anion radical	-1.90
02	CO ₂ + 2H ⁺ + 2e ⁻ = HCOOH (aq)	Formic acid	-0.61
03	CO ₂ + 2H ⁺ + 2e ⁻ = CO(g) + H ₂ O	Carbon monoxide	-0.53
04	CO ₂ + 4H ⁺ + 4e ⁻ = HCOH (aq) + H ₂ O	Formaldehyde	-0.48
05	CO ₂ + 6H ⁺ + 6e ⁻ = CH ₃ OH(aq) + H ₂ O	Methanol	-0.38
06	CO ₂ + 8H ⁺ + 8e ⁻ = CH ₄ (g) + 2H ₂ O	Methane	-0.24

is important for maximum performance, otherwise, excess or lack of catalyst may lead to a reduction in the performance owing to the low yield and poor selectivity.

Photocatalytic CO₂ reduction requires high energy because CO₂ is one of the most thermodynamically stable carbon-based molecules, with stronger C=O bonds (750 kJ/mol bond dissociation energy) than C–H bonds (411 kJ/mol bond dissociation energy) and C–C bonds (336 kJ mol⁻¹ bond dissociation energy).^[274] Hence, CO₂ needs to be activated before the photocatalytic reduction. This process occurs on the surface of photocatalysts through chemisorption by converting a linear molecule into a bent carbonate anion radical (CO₂⁻) via monodentate or bidentate coordination. Thus, the reactive carbonate anion is responsible for the various products obtained from the photoreduction of CO₂, as given in Table 2. These hydrocarbon products are evaluated through two different pathways, one is carbene (highly reactive species that can further react to form various hydrocarbons) and the other one is aldehyde (which also undergoes further reduction to form hydrocarbons).^[275] Both pathways ultimately lead to the formation of methane (CH₄) as a major product. Beside methane, other hydrocarbons such as ethane, ethylene, and propane (C1–C3 products) are also produced as side products during the CO₂ reduction process, which are shown in Table 2. It was proposed that the selective conversion of CO₂ to CO or HCOOH by reactive CO₂⁻ intermediates depends on the catalyst and media (aqueous or nonaqueous).^[276] In the aqueous media, the reactive CO₂⁻ takes protons from water and photo-generated electrons from the catalyst leading to the formation of HCOOH or CO depending on the type of catalyst. However, the selectivity of the product is still challenging, and it depends on many factors, such as reaction condition, active site of the photocatalysts, medium, etc. The efficiency of the photoreduction of CO₂ can be expressed in terms of CO₂ conversion rate, product formation rate, turnover frequency (TOF), and quantum efficiency.^[277] Furthermore, the photocatalytic reduction of CO₂ is a multielectron reduction process assisted by protons, and it consists of numerous intermediate steps that lead to different products (e.g., CO, formic acid, methanol, and methane), as shown in Table 2.^[18,278]

4.2. Organic–Inorganic Hybrid Perovskites

The photocatalytic activity of organic-inorganic hybrid perovskites (OIHP) towards CO₂ reduction has been mainly focused using MAPbI₃, and FAPbBr₃ perovskites.^[28] It is well known that the halide perovskites suffer from poor stability due to their ionic character, leading to their degradation un-

der moisture. Therefore, the halide perovskite photocatalyst needs to be encapsulated to obtain a stable photocatalyst. The encapsulant matrix could also assist in charge carrier separation upon excitation of a photocatalyst. In addition, the band gap and band position of halide perovskites are important to build efficient photocatalysts. Various strategies have been reported to encapsulate halide perovskites to obtain stable photocatalysts. For instance, Lu and co-workers developed a series of efficient photocatalysts for CO₂ reduction by encapsulating CH₃NH₃PbI₃ (MAPbI₃) perovskite NCs into earth-abundant porous Fe-porphyrin-based metal-organic framework (MOF) PCN-221(Fe_x), *x* = 0–1 by a sequential deposition process (see in Figure 18).^[279] The MAPbI₃/PCN-221(Fe_x) composite showed much improved photocatalytic activity towards CO₂ reduction compared with their individual counterparts (MAPbI₃ NCs and PCN-221(Fe_x), *x* = 0–1). In addition, the composite photocatalyst exhibited record stability over 80 hours with a total production yield of 1559 μmol/g for CO (34%) and CH₄ (66%). Besides, the halide perovskites combined with 2D materials exhibit enhanced photocatalytic activity. For example, FAPbBr₃ NCs anchored on Ti₃C₂ nanosheets form a Schottky heterojunction (Figure 18) for an efficient photocatalytic CO₂ reduction under visible light.^[280] In this composite system, the Ti₃C₂ ultrathin 2D nanosheet is an electron acceptor that promotes the prompt separation of excitons and helps to supply the charge carriers to specific catalytic sites. The FAPbBr₃/Ti₃C₂ composite demonstrated significantly enhanced production of CO from CO₂, which is over 1.84-fold higher than that of pure FAPbBr₃ quantum dots. In addition, the system exhibited an optimal electron consumption rate of 717.18 μmol g⁻¹ h⁻¹, which was far larger (2.08-fold improvement) than that of 343.90 μmol g⁻¹ h⁻¹ observed of pristine FAPbBr₃ QDs. Besides, pure perovskite NCs have also been explored for photocatalytic CO₂ reduction. In this regard, Que et al.^[281] demonstrated that pure colloidal FAPbBr₃ and CsPbBr₃ NCs exhibit photocatalytic activity toward CO₂ reduction in a mixture of deionized water/ethyl acetate solvent without further encapsulation. They found that the FAPbBr₃ NCs exhibit much better catalytic activity than CsPbBr₃ NCs towards CO₂ reduction into CO. The CO production rate for FAPbBr₃ NCs has reached 181.25 μmol g⁻¹ h⁻¹, which is ≈13.8-fold higher compared to 9.73 μmol g⁻¹ h⁻¹ achieved with CsPbBr₃ NCs.

4.3. All-Inorganic Perovskite NCs and Their Composites

All-inorganic lead halide perovskites have been extensively explored in the photocatalytic application. In particular, they

Table 3. Summary of reported Photocatalytic CO₂ reduction reactions using halide-based Perovskites.

Photocatalyst	Medium	Light source	Product	Yield [$\mu\text{mol g}^{-1} \text{h}^{-1}$]	Highest efficiency [%]	Stability [h]	Refs.
CsPbBr ₃ NCs	Ethyl acetate/water	300 W Xe lamp (AM 1.5G)	CO + CH ₄ + H ₂	4.3 + 1.5 + 0.1	—	> 8	[282]
CsPb(Br _{0.5} /Cl _{0.5}) ₃ NCs	Ethyl acetate	"	CO + CH ₄	85.2 + 12.0	—	> 9	[294]
CsPbBr ₃ NCs/g-C ₃ N ₄	"	400 W Xe lamp (AM 1.5G)	"	2.1 + 22.8	—	> 12	[283]
CsPbBr ₃ NCs/g-C ₃ N ₄	Acetonitrile/water	300 W Xe lamp (≥ 400 nm)	CO	148.9	—	> 6	[293]
CsPbBr ₃ NCs/GO	Ethyl acetate	150 mW cm ⁻² (AM 1.5G)	CO + CH ₄ + H ₂	58.7 + 29.6 + 1.58	0.025	> 12	[81]
CsPbBr ₃ @TiO ₂ -CN	Ethyl acetate/water	300 W Xe lamp (≥ 400 nm)	CO	12.9	—	> 10	[285]
CsPbBr ₃ NCs/MXene	Ethyl acetate	300 W Xe lamp (≥ 420 nm)	CO + CH ₄	26.3 + 7.3	—	> 9	[292]
CsPbBr ₃ NCs/BZnW/	(CO ₂ + water vapor)	150 mW cm ⁻² (AM 1.5G)	"	0.9 + 6.3	—	> 3	[290]
MRCO							
CsPbBr ₃ NCs/Pd NS	(CO ₂ + water vapor)	150 W Xe lamp (≥ 420 nm)	CO + CH ₄ + H ₂	1.9 + 3.5 + 1.1	0.035	"	[291]
CsPbBr ₃ -Re(600)	Toluene/isopropanol	150 W Xe lamp (≥ 420 nm)	CO + CH ₄	104.4 + 5.6	—	"	[345]
CsPbBr ₃ NCs/a-TiO ₂	Ethyl acetate/isopropanol	150 W Xe lamp (AM1.5G)	CO + CH ₄ + H ₂	3.9 + 6.7 + 1.5	—	"	[83]
CsPbBr ₃ NCs@ZIF-67	(CO ₂ + water vapor)	150 mW cm ⁻² (AM 1.5G)	CO + CH ₄	2.1 + 3.5	0.035	"	[288]
CsPbBr ₃ NCs@ZIF-8	(CO ₂ + water vapor)	100 W Xe lamp (AM1.5G)	"	0.7 + 2.0	—	"	[288]
CsPbBr ₃ QDs/	Ethyl acetate/water	300 W Xe lamp (≥ 420 nm)	"	8.2 + 0.3	—	> 12	[289]
UiO66(NH ₂)	"	300 W Xe lamp (≥ 400 nm)	"	4.2 + 13.0	—	25	[279]
MAPbI ₃ @PCN221(Fe _x)	"	450 W Xe lamp 150 mW cm ⁻²	"	3.2 + 6.1	—	> 3	[305]
Fe-CsPbBr ₃ NCs	Benzyl alcohol	150 W Xe lamp AM 1.5G 100 mW cm ⁻²	CO + Benzaldehyde	170.0 + 250.0	—	—	[323]
FAPbBr ₃ /Bi ₂ WO ₆							
FAPbBr ₃ QDs	Ethyl acetate/water	300 W Xe lamp 100 mW cm ⁻²	CO + CH ₄ + H ₂	181.3 + 16.9 + 2.37	—	> 3	[281]
CsPbBr ₃ QDs/Bi ₂ WO ₆	"	100 mW cm ⁻² > 400 nm	CO/CH ₄	50.3	—	> 10	[327]
Cs ₂ SnI ₆ /SnS ₂ NCs	(CH ₃ OH + CO ₂ + water vapor)	150 mW cm ⁻² (≥ 400 nm)	CH ₄	6.1	—	> 3	[319]
Cs ₃ Sb ₂ Br ₉	Octadecene	300 W Xe lamp 100 mW cm ⁻²	CO	127.2	—	> 6	[313]
a-Fe ₂ O ₃ /Amine-RGO/	(CO ₂ + water vapor)	150 W Xe lamp AM 1.5G, > 420 nm	CO + CH ₄ + H ₂	2.4 + 9.5 + 0.3	—	> 15	[324]
CsPbBr ₃	Ethyl acetate/water	300 W Xe lamp 4400 nm 100 mW cm ⁻²	CO + CH ₄	431.0 + 48.8	0.23	> 4	[337]
CsPbBr ₃ -Ni(tpy)							
Cs ₂ AgBiBr ₆ NCs	Ethyl acetate	150 mW cm ⁻² (AM 1.5G)	"	2.4 + 1.6	0.028	> 6	[311]

(Continued)

Table 3. (Continued)

Photocatalyst	Medium	Light source	Product	Yield [$\mu\text{mol g}^{-1} \text{h}^{-1}$]	Highest efficiency [%]	Stability [h]	Refs.
$\text{Cs}_3\text{Bi}_2\text{I}_9$	(CO_2 + water vapor)	80 mW cm^{-2} (AM 1.5G)	"	7.7 + 1.5	—	> 10	[312]
$\text{Co-CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$	Water	300 W Xe lamp 100 mW cm^{-2}	"	12.0 + 1.8	—	> 20	[308]
Mn-CsPb(Br/Cl)_3	Ethyl acetate	300 W Xe-lamp with AM 1.5 filter	"	213 + 9.1	—	9	[310]
$\text{Co-CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$	Acetonitrile/water/ Methanol	300 W Xe lamp 100 mW cm^{-2}	CO	122	—	15	[309]
Pt-CsPbBr_3	Ethyl acetate	150 W Xe-lamp with 380 nm cut o filter	"	5.6	0.012	30	[69]
Ni and Mn-CsPbCl ₃ NCs	(CO_2 + water vapor)	300 W Xe-lamp with AM 1.5 filter	Ni = CO, Mn = CO	169.37, 152.49	—	6	[307]
$\text{Cs}_4\text{PbBr}_6/\text{rGO}$	Ethyl acetate/water	300 W Xe-lamp with 420 nm filter	CO	11.4	—	60	[284]
Cu/RGO/CsPbBr_3	(CO_2 + water vapor)	Xe-lamp irradiation with a 400 nm filter	CH_4	12.7	1.1	12	[306]
$\text{TiO}_2/\text{CsPbBr}_3$	Acetonitrile/water	300 W Xe-arc lamp	CO	9.02	—	16	[137]
$\text{Cs}_2\text{AgBiBr}_6/\text{g-C}_3\text{N}_4$	Ethyl acetate/ Methanol	Xe-lamp (80 mW cm^{-2} light intensity)	CO/CH_4	2	—	12	[328]
CsPbBr_3 QDs/ $\text{g-C}_3\text{N}_4$	Acetonitrile/water	300 W Xe-lamp with a 420 nm filter	CO	149	—	—	[293]
CsPbBr_3 NCs/ Cu_2O	"	"	CO/CH_4	—	—	—	[331]
CsPbBr_3 QDs/2D-PbSe	"	"	CO	322	—	—	[296]
$\text{CsPbBr}_3/\text{SO}_4$	Methanol /water/ Acetone	"	CO/CH_4	56	—	8	[297]
$\text{CsPbBr}_3/\text{SOBr}_2/\text{g-C}_3\text{N}_4$	Acetonitrile/water	"	CO/CH_4	190	—	—	[286]
ZnSe/CsSnCl_3	Toluene/Isopropanol	"	CO/CH_4	57	—	—	[128]
CsPbBr_3 QDs/BiOBr	Acetonitrile/water	"	$\text{CO} + \text{CH}_4$	104.4 + 10.0	—	4	[332]
$\text{CsPbBr}_3/\text{CdIn}_2\text{S}_4$	"	"	CO	100	—	—	[341]
$\text{Cs}_2\text{CuBr}_4/\text{KIT-6}$	"	300 W Xe lamp	$\text{CO} + \text{CH}_4$	51.6, 17.2	0.122	28	[320]
$\text{Cs}_2\text{CuBr}_4/\text{CeO}_2$	"	"	$\text{CO} + \text{CH}_4$	54.31, 16.65	—	> 5	[333]

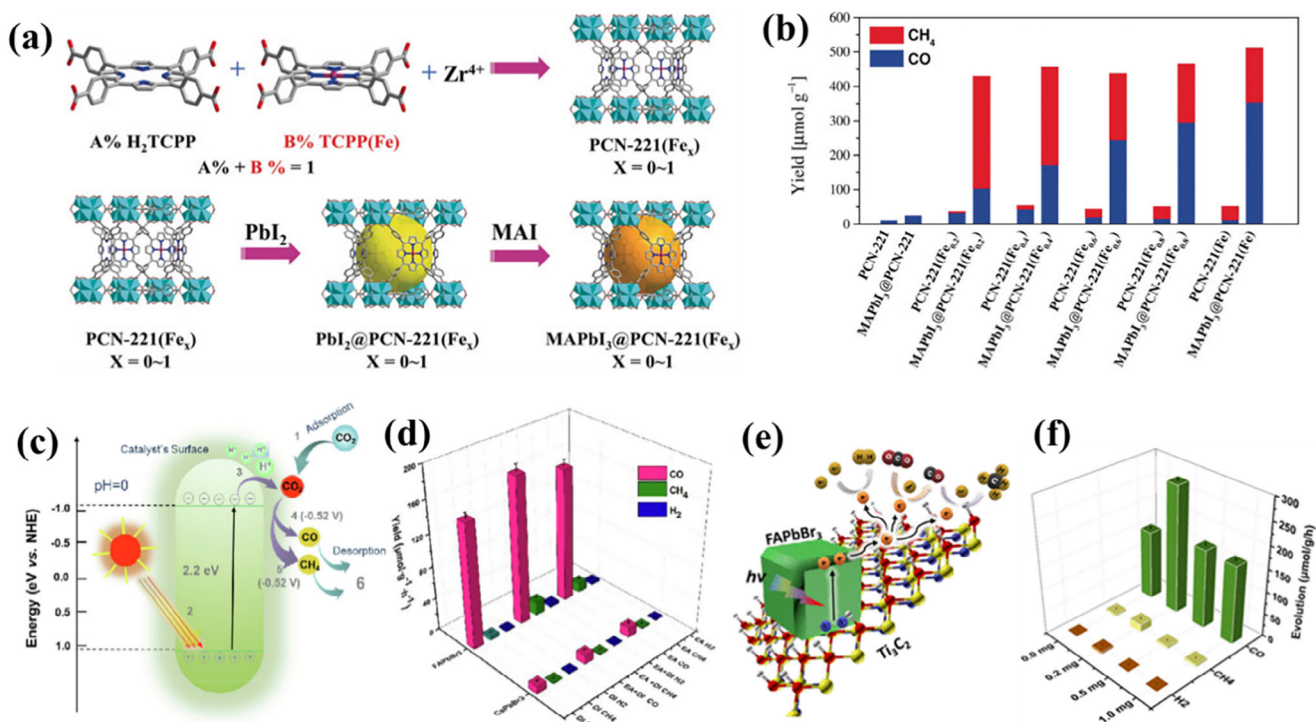


Figure 18. a) Schematic presentation for synthesis of PCN-221(Fe_x) MOF and MAPbI₃/PCN-221(Fe_x) composite photocatalyst for stable and product-selective CO₂ reduction. b) Histogram of product formation using PCN-221(Fe_x) and MAPbI₃/PCN-221(Fe_x) after 25 h of photocatalytic reaction. a,b) Reproduced with permission.[279] Copyright 2019, Wiley-VCH. c) Schematic illustration on band diagram of photocatalytic CO₂ reduction to chemical fuels of FAPbBr₃ QDs, and d) its product histogram in DI, the DI/EA system, and EA. (c) and (d) reproduced with permission from ref. [281]. Copyright 2021, with permission from Elsevier. e) Schottky heterojunction photocatalytic system for CO₂ reduction in FAPbBr₃/Ti₃C₂, and (f) its product histogram in deionized water. (e) and (f) reproduced with permission from ref. [280]. Copyright Copyright 2021, American Chemical Society.

emerged as one of the most promising candidates for conversion of CO₂ into value-added chemicals and fuels in recent years due to their facile synthesis, tunable bandgap, and relatively higher stability than hybrid counterparts. In this regard, one of the early reports came from Hou et al.,[282] in which they demonstrated the potentiality of colloidal CsPbBr₃ QDs for photocatalytic reduction of CO₂ with a yield of 20.9 μmol g⁻¹ and a high selectivity greater than 99%. In addition, the high product yields of ≈4.3, 1.5, and 0.1 μmol g⁻¹ h⁻¹ achieved for CO, CH₄, and H₂, respectively. To enhance their photocatalytic efficiency, the inorganic perovskite NCs were combined with carbon nitride (g-C₃N₄) through improved charge separation.[124,283] Halide Perovskite combined with various other semiconductors and metal complexes for enhanced photocatalytic CO₂ reduction are summarized in **Figure 19**. The CsPbBr₃-g-C₃N₄ composite showed improved stability for about 12 h with high yields of gaseous products (CH₄ and CO) (≈300 μmol g⁻¹) even at low concentrations of CO₂ with a selectivity upto 91%. The photocatalytic activity of the composite was found to be ≈6-fold and 4-fold higher than that of pure g-C₃N₄ and CsPbBr₃, respectively. Similarly, the combination of perovskite NCs with GO has been significantly exploited for photocatalytic CO₂ reduction. It was demonstrated that CsPbBr₃ NCs/graphene oxide (GO) composite exhibits enhanced photocatalytic reduction of CO₂.^[81] Notably, CsPbBr₃ NCs/GO composite demonstrates an improved rate of the electron consumption from 23.7 to 29.8 μmol g⁻¹ h⁻¹ compared with individual CsPbBr₃ QDs. The enhanced pho-

tocatalytic activity was attributed to electron extraction ability of conductive GO. Moreover, the CsPbBr₃ QD/GO composite exhibits superior stability of 12 hours with a high amount of gaseous products, 58.7 and 29.6 μmol g⁻¹ for CH₄ and CO, respectively, with a selectivity of the product greater than 99%. Another potential nanocomposite systems for CO₂ reduction was reported based on reduced-GO (rGO) and zero-dimensional (0D) Cs₄PbBr₆ perovskite.[284] The combined composite demonstrated a high rate CO production at 11.4 μmol g⁻¹ h⁻¹, maintaining long-term stability for about 60 h and exhibited a high selectivity of 94.6%. This performance is nearly 6.2-times higher than that of pristine Cs₄PbBr₆ perovskite. Similarly, the CO productivity of yield of 129 μmol g⁻¹ was achieved for 10 hrs of visible light illumination using multi-layer CsPbBr₃ NCs/graphitic carbon nitride (CN)-Titanium-oxide (TiO) composite system.[285] The production rate of CO is ≈3 and 6-fold higher than pristine CsPbBr₃ NCs and TiO-CN nanosheets, respectively. The enhanced productivity was attributed to an increase of active sites and swift interfacial charge separation between CsPbBr₃ and TiO-CN. Likewise, multi-layer CsPbBr₃/g-C₃N₄/thionyl bromide (SOBr₂) composite also showed enhanced photocatalytic activity toward CO₂ reduction.[286] In this case, the SOBr₂ does not only repair Br vacancies but also promotes the stripping of native ligands that effects charge transfer to nearby cocatalysts.[287] The multilayer-CsPbBr₃/g-C₃N₄/SOBr₂ composite exhibits superior performance in reduction of CO₂ into CO and CH₄ evaluation with a high yield rate of 190 μmol g⁻¹ h⁻¹ under visible

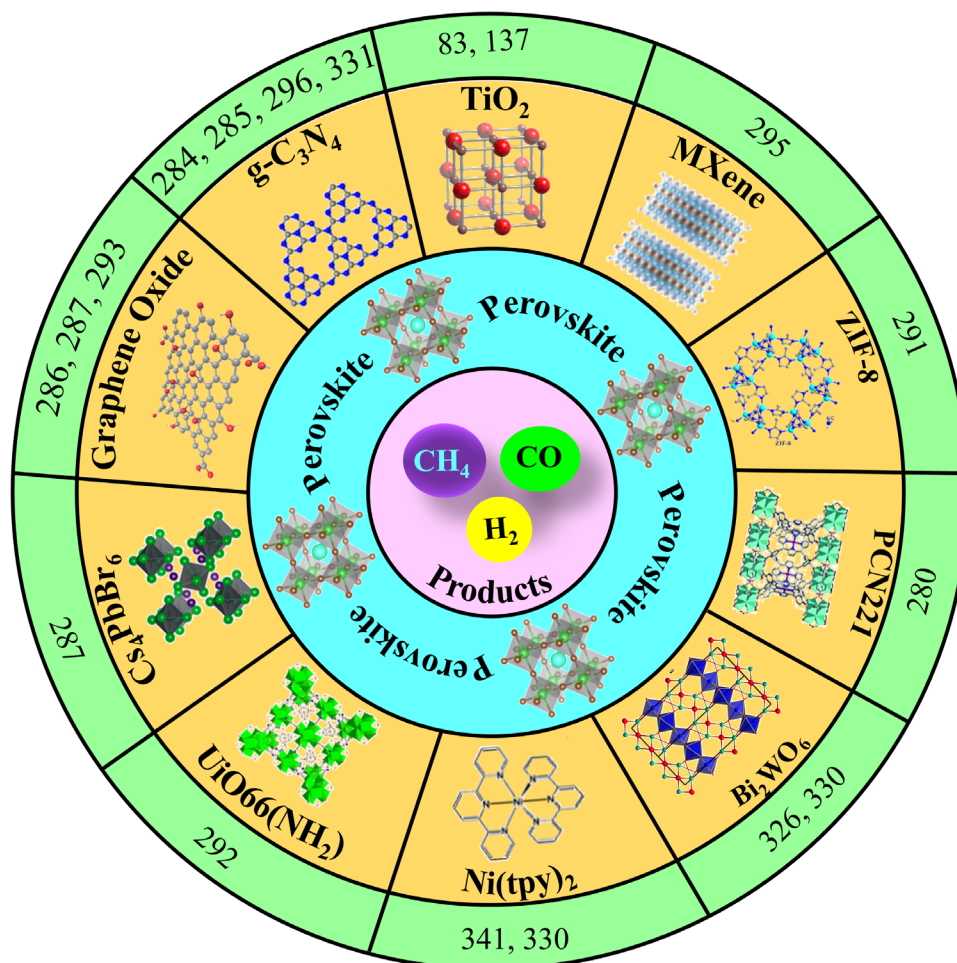


Figure 19. Halide perovskites combined with various other semiconductors and metal complexes for photocatalytic CO₂ reduction. The related works can be found in these references: 1) refs. [83, 137], 2) ref. [292], 3) ref. [288], 4) ref. [279], 5) refs. [323, 327], 6) refs. [327, 337], 7) ref. [289], 8) ref. [284], 9) refs. [81, 284, 290], 10) refs. [124, 283, 293, 328].

light irradiation, which is nearly 16 times higher than the pristine CsPbBr₃. Besides, porous materials such as TiO₂ have been used to extract the charge carriers and stabilize the NCs. The electron acceptor materials also can protect the NC surface in some cases. For instance, amorphous TiO₂ (a-TiO₂) was used for encapsulation of CsPbBr₃ NCs through a solution process.^[83] The encapsulated CsPbBr₃ NC/a-TiO₂ composite exhibits ≈6.5-fold higher photocatalytic activity toward CO₂ reduction as compared with the pristine CsPbBr₃ NC. Besides, CsPbBr₃ NCs were combined with Cobalt/Zinc-based zeolitic imidazolate framework (ZIF) through encapsulation and demonstrated a large enhancement of moisture stability, CO₂ capturing ability, and charge separation efficiency.^[288] The electron consumption rate of CsPbBr₃@ZIF for gaseous CO₂ reduction is 2.66-fold higher than that of pristine CsPbBr₃. Another potential application of metal-organic framework encapsulation has been reported by Wang and his co-workers, where CsPbBr₃ NCs/UiO-66(NH₂) nanohybrid demonstrated considerable improvement in photocatalytic CO₂ reduction under visible light irradiation than that of pristine CsPbBr₃ QDs and UiO66(NH₂).^[289] The improved photocatalytic performance was also attributed to the enhanced electron extraction and transfer between UiO66(NH₂) and CsPbBr₃ QDs, facilitated

by the large accessible specific surface area and enhanced visible light absorption capacity of the nanojunction composite. Furthermore, CsPbBr₃ NCs were loaded on hierarchical branched ZnO nanowire (BZNW) and microporous graphene scaffold (MRGO) to construct a multi-layer device for fast charge transport and improved CO₂ capture ability afforded by ZnO nanowire-branched macroporous graphene.^[290] Due to the favorable synergistic effect, an enhanced photocatalytic performance was achieved with a photoelectron consumption rate of 52.02 μmol_{cat}⁻¹ h⁻¹, which is ≈4.98 and 1.65 times higher than that of CsPbBr₃ NC (10.44 μmol_{cat}⁻¹ h⁻¹) and CsPbBr₃ NC/MRGO (31.52 μmol_{cat}⁻¹ h⁻¹), respectively, with ≈96.7% selectivity of desirable CH₄ production. Nanocomposites of certain types of materials can form Schottky-junction at the interfaces. For example, Schottky-junction photocatalyst was obtained by combining CsPbBr₃ NCs with palladium nanosheet (Pd NS).^[291] In this composite system, the Pd NS acts as an electron reservoir to promptly separate the photogenerated electron-hole pairs of CsPbBr₃ NC through a Schottky contact and thus provides an ideal site for CO₂ reduction. The Schottky-junction photocatalyst showed a high electron consumption rate of 33.79 μmol g⁻¹ h⁻¹, which is ≈2.43-fold higher than that of pristine CsPbBr₃ NCs (9.86 μmol g⁻¹ h⁻¹). Another interesting 2D

material that has been exploited to enhance the charge separation and extraction in perovskite NCs is Mxenes. For instance, Pan et al. Demonstrated an In situ growth of uniform CsPbBr₃ NCs in on the surface of two-dimensional MXene nanosheets.^[292] The resulting nanocomposite exhibited enhanced charge separation than in pristine CsPbBr₃. The yields of the obtained CO and CH₄ increased linearly with the light illumination time. The rate of the CO and CH₄ evaluation are 26.32 and 7.25 $\mu\text{mol g}^{-1} \text{h}^{-1}$ respectively, which are far higher than that of pristine CsPbBr₃ NCs (<4.4 $\mu\text{mol/gh}$) as well as a few newly developed CsPbBr₃ NCs-based heterostructure photocatalysts.^[81,282,293] The bandgap of the CsPbX₃ NCs is easily tunable by the halide ion composition, which enables the tunability of VB and CB energy levels according to the requirements. It has been shown that activity of mixed halide perovskites (CsPb(Cl_{0.5}/Br_{0.5})₃) exhibits photocatalytic activity toward CO₂ reduction without using a photosensitizer, and maintains 99% selectivity toward CO and CH₄ production with a total yield up to 875 $\mu\text{mol g}^{-1}$.^[294] The yields in this case are far better than any other reported halide perovskites.^[81,282] Moreover, the photocatalytic activity of the mixed halide perovskite toward CO₂ reduction is $\approx$ 4.5- and 9.1-fold higher than that of CsPbBr₃ and CsPbCl₃ under the same experimental conditions. The enhanced performance of mixed halide perovskites could be due to the better band alignment for efficient charge separation.

4.3.1. Amino Acid-Assisted Anchoring

To have a better charge transfer from perovskite NCs to acceptor materials, both need to be closely connected. Although physical adsorption of one material on top of other materials could lead to charge separation, linking the two systems through covalent functionalization can significantly increase the charge separation efficiency. For example, CsPbBr₃ NCs were coupled to the surface of porous g-C₃N₄ nanosheets by anchoring the amino group via N-Br chemical bonding.^[293] The covalently linked composite showed superior stability and outstanding photocatalytic activity for CO₂ reduction with a high CO production rate of 149 $\mu\text{mol/gh}$ under visible light irradiation, which is almost 15 times higher than that of pristine CsPbBr₃ NCs. The covalently-bond composite exhibited superior stability and outstanding photocatalytic activity for CO₂ reduction with a high production yield rate of 149 $\mu\text{mol/gh}$ for CO evaluation under visible light irradiation, which is almost 15 times higher than that of pristine CsPbBr₃ NCs. Despite the covalent binding between the two systems of photocatalytic nanocomposites, the incoherent interfaces caused by large lattice mismatches create high energy barriers for charge separation.^[295] Consequently, the catalytic activity of such composite systems can be significantly affected. To address this issue, Zhang et al.^[296] developed a semicoherent lattice-matching composite by combining CsPbBr₃ NCs and two-dimensional (2D) PbSe. The photocatalytic activity of CsPbBr₃/PbSe composite towards CO₂ reduction showed selective CO evaluation with a rate of 322.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is 3 times higher than that of pristine CsPbBr₃ NCs. Besides, the photocatalytic activity of perovskite NCs and their stability is their surface defects (halide vacancies and uncoordinated Pb²⁺ atoms). It was shown that the addition of SO₄²⁻ removes the uncoordinated Pb²⁺ ion from the surface of CsPbBr₃ NCs through the formation of a water-

resistant PbSO₄ product, and thus offers better stability in water. In this regard, Wang et al.^[297] found that the water-stable CsPbBr₃-SO₄ NCs exhibit photocatalytic CO₂ reduction into CO and CH₄ production. The CsPbBr₃-SO₄ composite exhibits improved stability in water and high CO₂ consumption with a rate of 56 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is nearly 8 times higher than that of pristine CsPbBr₃.

4.3.2. Metal Atoms Doping

Doping refers to the process of incorporation of a small percentage of hetero atom into a target lattice without significantly affecting the host crystal structure and basic characteristics. It is a general and effective approach for the modification of fundamental properties of semiconductors and improves their stability with a particular interest in optoelectronic application.^[298] Doping of metal ions in perovskites both the bulk and NCs have been extensively exploited to induce new optical features as well as enhance their stability and luminescence efficiency.^[298–302] However, the effect of doping on the photocatalytic performance has been relatively less explored. As discussed in above section, the selectivity of final product is very important but extremely challenging in photocatalytic CO₂ reduction.^[303] Tang et al.^[304] theoretically predicted that Co and Fe-doping in CsPbBr₃ NCs lead to high selectivity of methane (CH₄) production in photocatalytic CO₂ reduction. The high selectivity was attributed to the decreased band gap of Co and Fe-doped CsPbBr₃ NCs, leading to broadened absorption toward visible light. Inspired by this report, furthermore, it was experimentally found that Fe(II) doped CsPbBr₃ NCs exhibit high selectivity toward CH₄ production instead of CO, while undoped CsPbBr₃ NCs yield a mixture of CO and CH₄.^[305] In another work, Kumar et al.^[306] investigated the photocatalytic ability of different morphologies of CsPbBr₃ NCs for photocatalytic CO₂ reduction and found that nanosheets produce CH₄, CO, and H₂ with a low yield of 0.43, 2.25, and 0.08 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively, however when the nanosheets combined with Cu-loaded rGO (Cu-rGO), the reaction yields CH₄ with 98.5% selectivity and an yield of 12.7 $\mu\text{mol g}^{-1} \text{h}^{-1}$. The improved activity, selectivity, and stability were attributed to efficient charge separation and the hydrophobic character of the composite. Similarly, Pb-rich Mn and Ni-doped CsPbCl₃ NCs were also found to exhibit efficient photocatalytic ability toward CO₂ reduction, where the Ni-doped CsPbCl₃ NCs exhibits higher product yields with a rate of 169.37 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in comparison to the rate of 152.49 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for Mn-doped CsPbCl₃ NCs under similar operating conditions.^[307] As discussed in the earlier section, the solvent plays an important role in the selectivity and efficiency of the product. In this regard, Kuang and co-workers studied the effect of various non-aqueous solvents such as toluene, ethyl acetate, isopropanol, acetonitrile, dimethyl formamide, and methanol on the photocatalytic CO₂ reduction and found that the rate of product evolution was improved by 25 times when toluene was replaced with ethyl acetate.^[69] Moreover, the rate of CO₂ consumption doubled when Pt co-catalyst was photodeposited on CsPbBr₃ NCs. Although the doping and introduction of co-catalysts improve the efficiency of activity, the instability in water is a major challenge. A few studies reported that the stability of CsPbBr₃ NCs can be greatly improved

by forming a shell of Cs_4PbBr_6 . This approach was also used to carry out the photocatalytic CO_2 reduction in water using $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ -composite photocatalysts.^[308] The whole catalytic reaction was carried out in pure water with an overall yield of CO and CH_4 evaluation is $247 \mu\text{mol g}^{-1}$ after continuous irradiation of 20 h. The catalyst was also tested in acetonitrile and water medium and achieved a considerable enhancement of CO evolution with a yield of $1835 \mu\text{mol g}^{-1}$ under visible light continuous irradiation of 15 h.^[309] Furthermore, Mn-doped $\text{CsPb}(\text{Cl}/\text{Br})_3$ mixed halide perovskite system was also tested for photocatalytic CO_2 reduction and found that they produced CO and CH_4 with optimum yields of 1917 and $82 \mu\text{mol g}^{-1}$ respectively, under visible light irradiation for about 9 h. These yields are significantly higher than those obtained using CsPbBr_3 alone, by factors of approximately 14.2 and 1.4 times for CO and CH_4 , respectively.^[310]

4.3.3. Pb-Free All-Inorganic Perovskites

Despite tremendous progress in lead halide perovskite-based photocatalytic CO_2 reduction, water oxidation, and organic transformation, their toxicity is a major concern for further use in real-world applications.^[282,124,290,296,259] Therefore, researchers have been trying to find alternative halide perovskites with the same efficiency as Pb-based counterparts. In this regard, Zhou et al.^[311] demonstrated the potentiality of $\text{Cs}_2\text{AgBiBr}_6$ double perovskite NCs as active materials for photocatalytic CO_2 reduction into solar fuels. The double perovskite exhibits the total electron consumption of $105 \mu\text{mol/g}$ for evaluation of CO and CH_4 after continues irradiation of 6 hours. In addition, 2D-nanoplatelets of $\text{Cs}_2\text{AgBiBr}_6$ double perovskites were also synthesized and exploited in photocatalytic CO_2 reduction into CO and CH_4 selective products.^[127] During the course of the reaction time (about 6 h), the electron consumption of $\text{Cs}_2\text{AgBiBr}_6$ double perovskite nanoplates showed 8-fold ($255 \mu\text{mol g}^{-1}$) larger in comparison to the $\text{Cs}_2\text{AgBiBr}_6$ double perovskite NCs ($30.8 \mu\text{mol g}^{-1}$). Furthermore, a series of non-toxic zero-dimensional (0D) $\text{A}_3\text{Bi}_2\text{I}_9$ perovskite NCs ($\text{A} = \text{Rb}^+$, Cs^+ , and CH_3NH_3^+) were tested for photocatalytic reduction of CO_2 into CO and CH_4 at a gas-solid interface approach, and the conversion mechanism was investigated by electron paramagnetic resonance and diffuse-reflectance infrared spectra.^[312] The photocatalytic activity was found to be efficient for reduction of CO_2 at the gas–solid interface with formation yields $14.9 \mu\text{mol g}^{-1}$ of methane and $77.6 \mu\text{mol g}^{-1}$ of CO, and indicating that significantly more effective catalyst than TiO_2 under similar experimental conditions. Another type of 0D all-inorganic $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs was also tested for CO_2 reduction and found that only CO evolved with a rate of $510 \mu\text{mol g}^{-1}$ after 4 hours of continuous irradiation, which is ≈ 10 -fold higher than that of well-established CsPbBr_3 perovskite under similar conditions.^[313] A heterojunction is an interface between two layers of different semiconductors to suppress the rapid charge recombination and prolong their lifetime, as well as increases carrier density.^[314–318] However, initially, Wang et al.^[319] fabricated a heterojunction photocatalyst for CO_2 reduction using 0D Cs_2SnI_6 NCs and 2D SnS_2 chalcogenide nanosheet in an in situ process. The $\text{Cs}_2\text{SnI}_6/\text{SnS}_2$ composite showed a prolonged photogenerated electron lifetime of 3080 picoseconds compared to its pris-

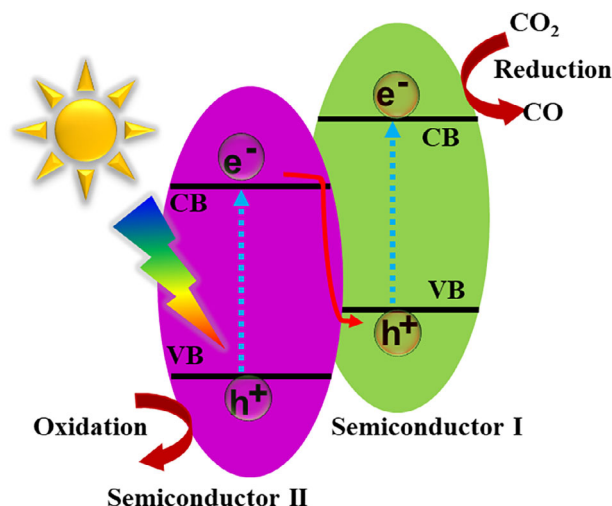


Figure 20. Schematic illustration of direct Z-scheme heterojunction of photocatalyst for CO_2 reduction.

time SnS_2 lifetime of 1290 picoseconds. Subsequently, a boosted photocatalytic activity was achieved, which is approximately 5.4 and 10.6-fold higher than that of pristine Cs_2SnI_6 NCs and SnS_2 nanosheet, respectively. In addition to the above, copper-based Cs_2CuBr_4 QDs synthesized before loading on a mesoporous molecular sieve of KIT-6 for a heterojunction photocatalyst to explore CO_2 reduction.^[320] The optimized Cs_2CuBr_4 QDs/KIT-6 showed noteworthy performance in the evaluation of CO and CH_4 products with rates of 51.6 and $17.2 \mu\text{mol g}^{-1} \text{h}^{-1}$, respectively, indicating far exceeding activity than that of pristine Cs_2CuBr_4 QDs.

4.4. Z-Scheme

Z-scheme photocatalysis for CO_2 reduction offers a promising approach to convert CO_2 into valuable fuels and chemicals using solar energy. This photocatalyst operates in a similar manner to the photosynthesis process observed in nature. In a typical photosynthesis process, electrons are transferred between different components to facilitate energy conversion, whereas in the Z-scheme composite, photogenerated electrons move between two photocatalysts with staggered band alignments, as shown in **Figure 20**. By optimizing the interaction between the two photocatalysts and ensuring efficient charge transfer, the Z-scheme system can significantly improve the overall photocatalytic performance. This is because the Z-scheme photocatalyst effectively promotes light harvesting by utilizing two different photocatalysts, each absorbing different wavelengths of light and thereby broadening the range of the solar spectrum that can be utilized. Moreover, the operation of the Z-scheme photocatalyst involves the following three key steps: i) it promotes light harvesting and maintains strong reducibility and oxidizability of reduction and oxidation of semiconductors, respectively. ii) the rapid charge transfer due to the Z-scheme system significantly decreases the recombination of photoinduced electron-hole pairs and then enhances the separation efficiency of effective charge carriers. iii) the separation of charge carriers can further promote the spatial separation of reductive

and oxidative active sites, which ensures that specific photocatalytic reactions can occur in their corresponding active sites.^[321,322]

4.4.1. Organic–Inorganic Hybrid Perovskites

Taking advantage of the Z-scheme, Huang et al.^[323] developed a direct Z-scheme photocatalyst for CO₂ reduction using the combination of formamidinium lead bromide and bismuth tungstate (FAPbBr₃/Bi₂WO₆) semiconductors with a strong redox ability. The reaction produced CO and benzaldehyde with an evolution rate of 170 μmol g⁻¹ h⁻¹ and 250 μmol g⁻¹ h⁻¹, respectively. The quantum yields of CO and benzaldehyde were determined to be 1.2% and 1.7% respectively, which are far larger in comparison to some of the reported perovskite-based photocatalysts.^[324–326]

4.4.2. All-Inorganic Perovskites

As discussed in earlier sections, pristine CsPbBr₃ exhibits low catalytic performance mainly due to quick recombination and low carrier mobility of charges. Therefore, it was combined with other semiconductor materials to achieve Z-scheme configuration and thus to improve the performance. In this regard, Wang et al.^[327] fabricated heterogeneous Z-scheme photocatalyst by joining CsPbBr₃ NCs and Bi₂WO₆ Nanosheets for efficient CO₂ reduction. This Z-scheme composite produced CO and CH₄ with a total yield of 503 μmol g⁻¹, which is nearly 9.5 times greater than that of pristine CsPbBr₃ NCs during 10 h of reaction. The enhanced photocatalytic activity exhibits due to high spatial separation of photoexcited charge carriers, and strong individual redox abilities of two components. Likewise, another effective Z-scheme photocatalyst for CO₂ reduction was fabricated by selecting α-Fe₂O₃ (2.2 eV) and CsPbBr₃ NCs (2.3 eV) on account of their similar bandgap.^[324] The catalytic efficiency was further improved when combined with amine-functionalized reduced graphene oxide (rGO), which helped to prolong the charge carrier lifetime.

4.4.3. Pb-Free All-Inorganic Perovskites

The development of Pb-free Z-scheme photocatalysts represents a significant advancement in the field of photocatalytic CO₂ reduction. These systems offer enhanced stability, higher selectivity, and improved efficiency while being environmentally friendly. Wang et al.^[328] reported a Pb-free Z-scheme photocatalyst for a selective evaluation of CH₄ by the reduction of CO₂ using Cs₂AgBiBr₆ double perovskite and carbon nitride (g-C₃N₄) combination. In this composite, g-C₃N₄ conduction band acts as a reducing agent, and Cs₂AgBiBr₆ double perovskite valance band acts as an oxidizing agent in the catalytic reaction. The Pb-free Z-scheme photocatalyst exhibits excellent stability for about 4 h and the CH₄ selectivity of over 70% with a rate of 2.0 μmol g⁻¹ h⁻¹, which is 10-fold and 16-fold higher than that of pure g-C₃N₄ and Cs₂AgBiBr₆ double perovskite, respectively. Another Pb-free and eco-friendly Z-scheme photocatalyst was developed by decorating the ZnSe nanorods on the surface of CsSnCl₃

NCs through an electrostatic self-assembly approach.^[128] The ZnSe/CsSnCl₃ composite produced CO and CH₄ with a total rate of 57 μmol g⁻¹ h⁻¹, which is ≈5-fold higher when compared to pristine ZnSe nanorods.

4.5. S-Scheme Photocatalyst

The motivation behind the use of the S-scheme heterojunction is aimed at overcoming the limitations of Z-scheme photocatalysts, particularly the issue of low charge-carrier separation efficiency.^[329] While both systems share similar charge transfer mechanisms, the S-scheme was proposed as a refinement of the conventional Z-scheme to provide a more precise depiction of charge transfer pathways. The key difference between these two systems lies in the electron-hole pair generation mechanism. In Z-scheme photocatalysts, electron-hole pairs are generated sequentially through two different semiconductors connected in series. In contrast, S-scheme photocatalysts generate electron-hole pairs simultaneously through connected semiconductors in parallel. The crucial advantages of the S-scheme include Fermi level alignment, work function, band alignment, band bending, and the generated interfacial electric field (E).^[329,330] These aspects enable a more accurate representation of charge transfer pathways. Z-scheme systems, however, do not account for these factors, often leading to an ambiguous depiction of charge transfer mechanisms.

Xu et al.^[137] developed a unique S-scheme heterojunction by fabricating CsPbBr₃ QDs onto mesoporous TiO₂ nanofibers through an electrostatic self-assembling approach for a boosting outcome in photochemical CO₂ reduction. The S-scheme TiO₂/CsPbBr₃ nanohybrid reduced the CO₂ into solar fuels with a high rate of 9.02 μmol g⁻¹ h⁻¹, which is almost double than that of 4.68 μmol g⁻¹ h⁻¹ of pristine TiO₂ under UV–vis irradiation. This high performance of S-scheme composite is likely due to non-aggregation of TiO₂ nanofibers upon dispersion in solution, which fascinates to have high photocatalytic active sites for greatly encourage the separation of electron-hole pairs in CO₂ reduction. Furthermore, Dong et al.^[331] originated a S-scheme heterojunction by incorporating CsPbBr₃ NCs into a microporous Cu₂O microsphere for exploration of CO₂ reduction under visible light irradiation. Due to staggered band alignment between CsPbBr₃ and Cu₂O, the Fermi level (E_F) of Cu₂O is much lower than that of CsPbBr₃. Consequently, the S-scheme composite acts as an efficient charge separator with a highly energetic electron and holes for excellent photocatalytic activity. Another novel S-scheme photocatalyst of CsPbBr₃ QDs and BiOBr nanosheets fabricated via a facile self-assembly process.^[332] The resultant CsPbBr₃/BiOBr composite delivered notable photocatalytic activity in CO₂ reduction, with an electron consumption rate of 72.3 μmol g⁻¹ h⁻¹, which is almost 4.1 and 5.7 times higher when compared to the pristine CsPbBr₃ NCs and BiOBr nanosheet, respectively.

4.5.1. S-Scheme with Pb-Free Perovskites

In view of the high oscillator strength associated with Cu 3d states, Cs₂CuBr₄ perovskite nanodots grown in mesoporous

CeO₂ through a facile impregnation approach for a heterojunction S-scheme have been applied for CO₂ reduction.^[333] An outstanding photocatalytic activity was achieved with optimally loaded Cs₂CuBr₄/CeO₂ composites, with yields of 271.56 and 83.28 $\mu\text{mol g}^{-1}$ for CO and CH₄ products, respectively. These results are almost 22.02 and 2.46 times larger than that of individual CeO₂ and Cs₂CuBr₄, respectively.

4.6. Perovskites with Metal Complexes

Usually, metal complexes are superb candidates for CO₂ reduction because of their tunable catalytic sites with high activity.^[334–336] But, most of the metal complexes have limits in absorbing visible-light, which hinders their wide-range applications in CO₂ reduction.^[337] In view of this, metal complexes are coupled with organic or inorganic sensitizers to broaden their absorption range including visible-light extent.^[338–340] Particularly, Chen et al.^[337] CsPbBr₃ NCs coupled on the surface of Ni(tpy) (nickel complex with 2,2':6',2''-terpyridin) and used as a photocatalyst for CO₂ reduction in visible-light-driven. The catalytic activity of coupled system showed a total yield of 1724 $\mu\text{mol g}^{-1}$ for the evaluation of CO and CH₄, which is ≈ 26 -fold higher than that achieved with the pristine CsPbBr₃ NCs. Additionally, CsPbBr₃ QDs also coupled on the surface of several transition-metal chalcogenides (TMC; CdIn₂S₄, ZnIn₂S₄, and In₂S₃) in an interfacial contact, which enables uniform self-assembly and boosted photoactivity toward CO₂ conversion into CO compared to that of pristine CsPbBr₃.^[341] Recently, Co- and Cu-based metal complexes were coupled with lead-free Cs₂AgBiBr₆ double perovskite^[342] and CsPbBr₃ perovskite,^[343] respectively, for photocatalytic CO₂ reduction. In this regard, Cs₂AgBiBr₆ nanosheets were anchored on cobalt tetraamino phthalocyanine (CoTAPc) and cobalt phthalocyanine tetracarboxylic acid (CoTCPC) for CO₂ photoreduction to CO, using water as the electron source. The Cs₂AgBiBr₆@CoTCPC hybrid photocatalyst exhibited the highest CO generation rate of $150 \pm 6 \mu\text{mol g}^{-1} \text{ h}^{-1}$ with a stoichiometric O₂ formation from water oxidation, which is over eight times higher than that of pure Cs₂AgBiBr₆ catalyst. It also showed a record-high electron consumption rate of $300 \pm 13 \mu\text{mol g}^{-1} \text{ h}^{-1}$ among metal halide perovskite photocatalysts for CO₂ reduction. Experimental and computational studies highlight the critical role of carboxyl groups in anchoring Bi atoms, facilitating electron transfer between CoTCPC and Cs₂AgBiBr₆, thereby enhancing photocatalytic performance. In addition, ultrathin film devices were developed by leveraging synergistic effects from steric hindrance and electrostatic attraction for efficient CO₂ reduction with H₂O as the electron donor. These devices combine dinuclear-metal molecular catalysts (DMC) and perovskite (PVK) quantum dots (QDs) as photosensitizers, integrated onto a conductive metal-organic framework (cMOF), namely the copper cathelate of 2,3,6,7,10,11-hexahydroxytriphenylene. The resulting [DMC@Cu-CAT]-PVK composite films produced CO with a rate of $133.36 \mu\text{mol g}^{-1} \text{ h}^{-1}$, significantly surpassing the performance of PVK or DMC-PVK alone. This enhanced photocatalytic activity is attributed to the precise spatial assembly of DMC and PVK together with the scalable fabrication of Cu-CAT-based film photocatalysts. In addition, a Zn-phthalocyanine (ZnPc) complex was coupled with CsPbBr₃ perovskite in a heterojunction

Z-scheme process for photocatalytic CO₂ methanation with a CH₄ selectivity of up to 89% and an activity of $168 \mu\text{mol g}^{-1} \text{ h}^{-1}$ for CH₄ production.^[108] This performance surpassed all previously reported perovskite-based photocatalysts and was nearly 114 times higher than that of bare ZnPc. (Figure 20)

4.7. Photoelectrocatalytic CO₂ Reduction

Reduction of CO₂ through photoelectrocatalytic process using halide-based perovskite has scarcely been reported.^[40] Encouragingly, for the first time, Chen et al.^[248] developed a photoelectrocatalyst using In-Bi alloy coated MAPbI₃-based photocathodes for selective CO₂ reduction into formic acid production in aqueous solution with nearly 100% faradaic efficiency. The photoelectrocatalyst operated at -0.6 V versus RHE under simulated AM 1.5G irradiation for more than 1.5 h and achieved a photo-assisted electrolysis system efficiency of 7.2%. Addition to above, recently, heterojunction photoelectrocatalyst greatly fabricated PbS nanocrystals anchoring on the surface of CsPbBr₃ with the help of 12-aminododecanoic acid.^[344] Here, the anchoring is likely possible due to direct interaction between $-\text{COO}^-$ ($-\text{NH}_3^+$) and Pb^{2+} (Br^-). However, photoelectrocatalytic activity of CsPbBr₃-PbS exhibits approximately 2.4 times higher than that of pristine CsPbBr₃ NCs in a selective reduction of CO₂ into evaluation of CO and CH₄ with a rate of 2.94 and $0.36 \mu\text{mol cm}^{-2} \text{ h}^{-1}$, respectively (Figure 21).

5. Photocatalytic Organic Reactions Using Colloidal Nanocrystal Catalysts

Recent advances in visible light photocatalysis have greatly expanded the synthetic protocols available to chemists. In photocatalysis, photon absorption by transition metal complexes, organic dyes, or semiconductors facilitates these materials to attain an electronically excited state. This state can take part in charge transfer interactions with organic molecules, enabling various redox processes that open up new pathways for organic synthesis. Although homogeneous photocatalysts are widely used, their recovery and reuse after reactions are challenging, often requiring extra purification steps to separate the photocatalyst from the product. In contrast, heterogeneous photocatalysts such as metal oxide semiconductors, perovskite semiconductors, and graphitic carbon nitrides offer the advantage of easy recyclability due to their solid phase, making them a more sustainable and cost-effective choice for photocatalytic applications.^[346–348]

Over the years, colloidal nanocrystals (NCs) of different materials have been exploited as heterogeneous catalysts for chemical transformations. They offer unique properties compared to their bulk counterparts, such as a high surface-to-volume ratio and thus more active sites, tunable composition, size, and shape. In this context, perovskite NCs have demonstrated their promise through their ability to achieve high Photocurrent Conversion Efficiency (PCE), due to their high absorption coefficients and outstanding optoelectronic properties, as previously mentioned. As discussed above, MHPs have high stability in organic solvents and are thus expected to be highly suitable for organic transformations. Motivated by this, we here discuss the recent liter-

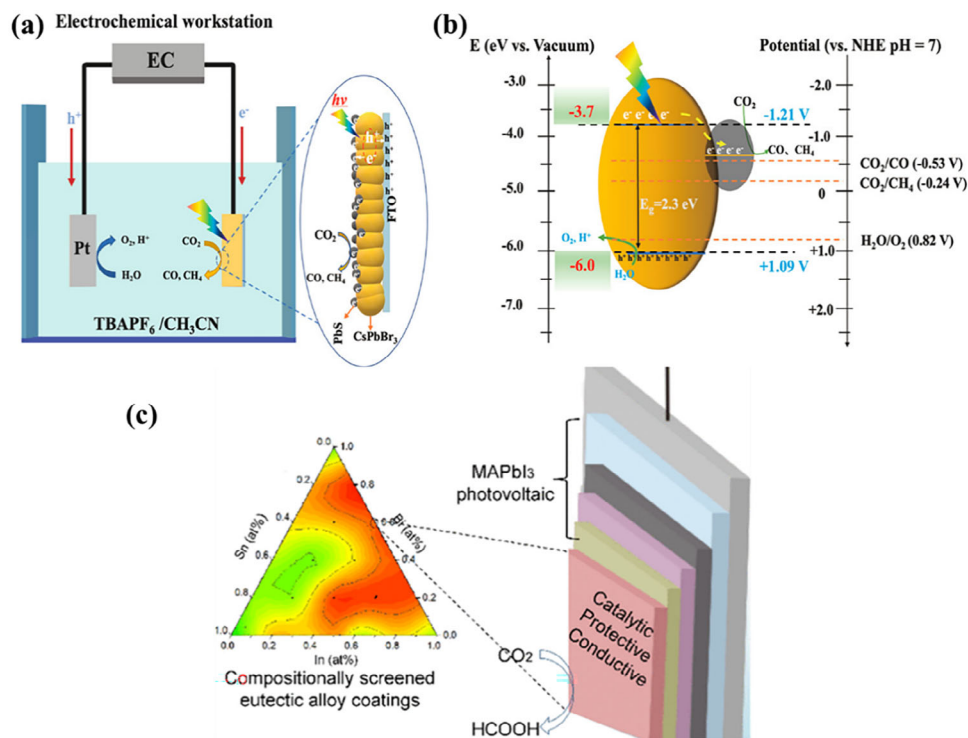


Figure 21. a) Schematic illustration of the photoelectrocatalytic CO₂ reduction, b) energy-band alignment of PbS/CsPbBr₃-12AA, and c) Schematic illustration of the compositional screening and photocathode structure of the catalytic alloy-protected MAPbI₃ photocathode for CO₂ reduction into formic acid. (a) and (b) reproduced with permission from ref. [344]. Copyright 2022, American Chemical Society.

ature to showcase the different chemical transformations employing MHP NC catalysts. Surprisingly, MHPs have been employed in a diverse range of reactions, such as C-C, C-N, and C-O coupling, cyclization, ring-opening reactions, polymerization, aromatization, decarboxylation reactions, asymmetric synthesis, and more (Table 4). A comprehensive review of these varied reactions necessitates an in-depth understanding of the essential factors at play. This discussion is instrumental in developing highly efficient photocatalytic methods in chemistry that yield selective product outcomes.

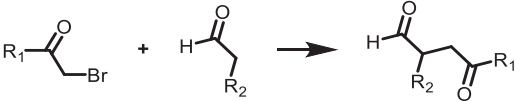
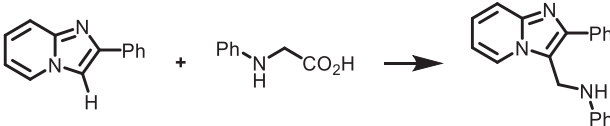
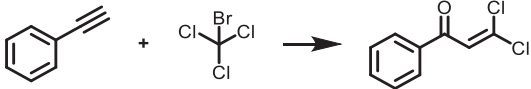
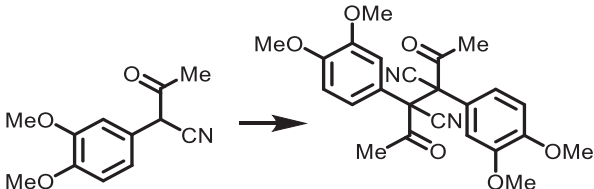
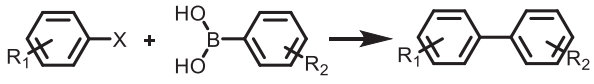
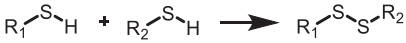
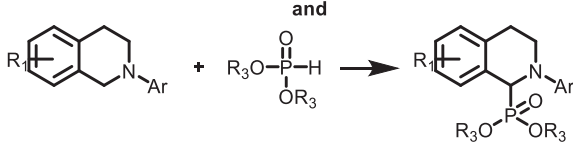
5.1. Charge and Energy Extraction: NC-Chromophore Composites

Despite exhibiting strong interaction with light and near-unity PLQY,^[31] MHP's primary obstacle resides in their incapacity to attain optimum photoconversion efficiency. This limitation stems from the lack of readily available charge carriers on their surface for catalytic processes, unlike metal NCs. To tackle this issue, employing small molecules capable of channeling energy and extracting charge carriers to the catalytic site becomes imperative for facilitating reactions. Interestingly, this has been achieved by anchoring MHP NCs with a variety of molecules capable of selectively extracting electrons and holes, such as methyl viologen, fullerene, benzoquinone, ferrocene, coumarin derivatives, and many more (Figure 22).^[42,337,375–385] These molecules must exhibit energetically favorable alignment with the perovskite and strong interaction with the NC surface, which can be achieved either through anchoring groups, electrostatic interactions, or physisorption.^[386] As of now, the highest reported association

constant, K_{app} , is approximately 10^8 M^{-1} .^[387] This was achieved using -COOH functionalized ferrocene on the surface of CsPbBr₃ NCs, enabling the extraction of holes in significant quantities and within a femtosecond timescale. On the other hand, methyl viologen exhibits a K_{app} around 10^6 M^{-1} with CsPbBr₃, demonstrating its high capacity to extract electrons in substantial amounts to the nanocrystal surface.^[376,388] These numerical values pave the way for hole and electron-driven chemical transformations, maximizing the turnover number (TON) when utilizing these composites as a photocatalyst. For example, Jin et al. showed how the photoexcitation of CsPbBr₃ NCs led to the polymerization of trithiocarbonate (TTC) ligands on their surface.^[389] The polymerization reaction was initiated by the transfer of charges from perovskite NCs to the TTC ligands anchored on the surface.

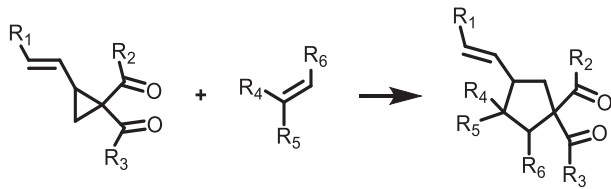
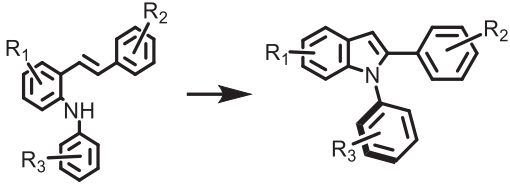
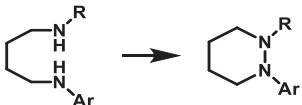
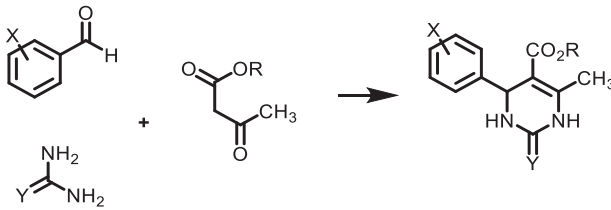
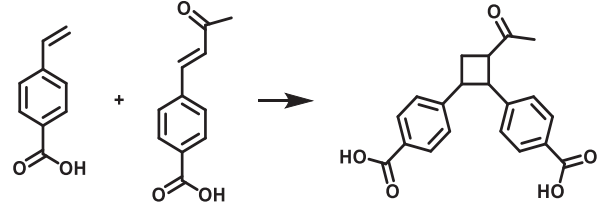
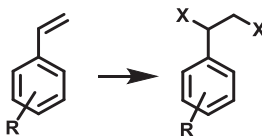
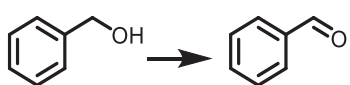
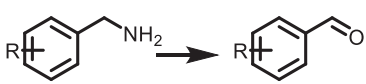
An alternative approach for extracting charge carriers from semiconductors includes transferring energy to an acceptor molecule. Upon photoexcitation, this process facilitates the transfer of the semiconductor's excitons to an acceptor molecule, thereby generating an excited state in the acceptor. Numerous studies have documented singlet and triplet energy transfer phenomena between excited MHPs and acceptor molecules. Singlet energy transfer to an acceptor requires the singlet energy level (S_0-S_1) to be lower than the semiconductor's bandgap. Whereas to generate a triplet excited state, which is typically spin-forbidden upon direct excitation, a chromophore in the S_1 state can undergo intersystem crossing or singlet fission. Alternatively, a triplet excited state can be produced through direct energy transfer from an excited semiconductor, provided that the sensitizer's band gap is lower than the acceptor's singlet energy level but higher than its triplet energy level.^[386] Moreover,

Table 4. Summary of diverse photocatalytic reactions employing metal halide perovskites.

Entry	Photocatalyst	Reaction	Illumination wavelength and intensity	Conversion/ Yield	Refs.
1) C–C, C–N, and C–O bond formation					
1.	APbBr ₃ (A = Cs, MA)		455 nm blue LED, 12 W	> 99%	[349]
2.	CsPbBr ₃		447 ± 20 nm blue LEDs	83%	[350]
3.	CsPbBr ₃		25 W white LEDs	Up to 94%	[351]
4.	CsPbBr ₃	C–H activation, C–O cross-coupling	455 nm blue LED, 12 W	52–90%	[29]
5.	CsPbBr ₃ NCs		Sunlight or 3 W blue LED	63–94%	[352]
6.	MAI-terminated MAPbI ₃		420 nm, 500 W Xe lamp	77 mg L ^{−1}	[353]
7.	ZW-CsPbBr ₃ NCs		435–445 nm blue LED	99%	[354]
8.	Pd/CsPbBr ₃		150 W Xe lamp, AM 1.5G	99.6%	[355]
9.	CsPbBr ₃		White light (450 mW cm ^{−2}), Blue LEDs	73 and 94%	[356,357]
1) S–S and C–P bond formation					
10.	CsPbBr ₃ NCs	 	White LEDs	Up to 98%	[358]
1) Cyclization reaction					
11.	CsPbBr ₃	N- hetero cyclization	455 nm blue LED, 12 W	52–90%	[29]

(Continued)

Table 4. (Continued)

Entry	Photocatalyst	Reaction	Illumination wavelength and intensity	Conversion/ Yield	Refs.
12.	CsPbBr ₃ NCs		456 nm blue LED, 40W	94%	[359]
13.	PEA-CsPbBr ₃ NCs		456 nm blue LED	72%	[360]
14.	Cu: CsPbBr ₃ NCs		456 nm blue LED	92%	[361]
15.	CsPbBr ₃		Blue LED, 7 W	94%	[362]
16.	CsPbBr ₃ NCs		Blue LED bulbs, 14 W	64%	[363]
1) Halogenation reaction					
17.	CsPbBr ₃ / Cu-CsPbBr ₃ NCs		White LED, 165 mW cm ⁻²	24-84%	[364]
1) Dehydrohalogenation reaction					
18.	CsPbBr ₃ NCs		White light, 300 mW cm ⁻²	N.A.	[365]
1) Oxidation reactions					
19.	CsPbBr ₃ /Ni ₄ P ₂ and FAPbBr ₃ , TiO ₂		>400 nm, 300 W Xe lamp, and AM1.5G	≈100 and 99%	[109,366]
20.	CsPbBr ₃		Blue LEDs	98%	[356]

(Continued)

Table 4. (Continued)

Entry	Photocatalyst	Reaction	Illumination wavelength and intensity	Conversion/ Yield	Refs.
21.	CsPbBr ₃		Blue LEDs	> 99%	[356]
22.	CsPbBr ₃		50 W blue LEDs	Up to 95%	[367]
23.	CsPbBr ₃ NCs		456 nm blue LED, 40 W	1000 μmol g ⁻¹ h ⁻¹	[112]
24.	Cs _x MA _{3-x} Sb ₂ Br ₉ NPs and Cs ₃ Bi ₂ Br ₉ /SBA-15s		> 420 nm visible light	1.98 mmol g ⁻¹ h ⁻¹ and 12 600 μmol g ⁻¹ h ⁻¹	[368,369]
25.	MAPbBr ₃		450 nm blue LEDs, 170 mW cm ⁻²	100%	[370]
1) Polymerization reaction					
26.	CsPbBr ₃ /NKE12		UV Light	N.A.	[53]
27.	CsPbI ₃ NCs		Solar simulator	NA	[371]
1) Decarboxylation, dehydrogenation, and aromatization reactions					
28.	(HDA) ₂ PbI ₄ and (HAD) ₂ SnI ₄		Visible light	Up to 98%	[372]
29.	CsPbBr ₃ NCs		461 nm blue LED, 40 W	Up to 95%	[373]
1) Ring opening reactions					
30.	Cs ₃ Bi ₂ Br ₉		> 420 nm visible light	88%	[374]

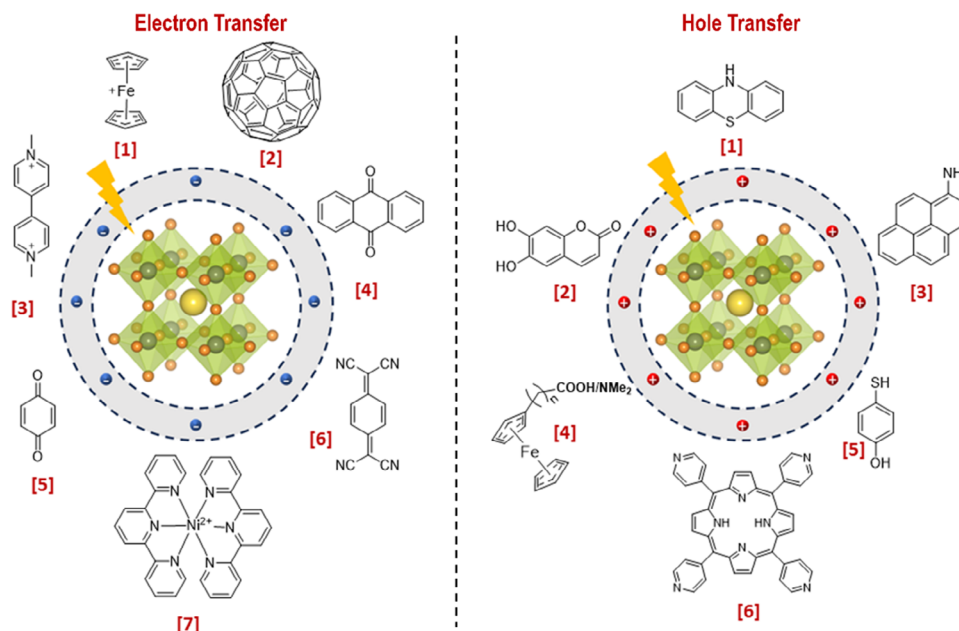


Figure 22. Summary of the molecules utilized for selectively extracting charge carriers (Either electron or hole) from MHPs. The molecules are chosen from references^[337,375–379] for electron transfer and references^[42,380–385] for hole transfer.

under specific conditions where the triplet energy is only 100–200 meV less than the exciton energy, the triplet excited states can repopulate the sensitizer's excited state via thermally activated reverse triplet energy transfer (rTET), thereby extending its lifetime significantly.^[390]

Various works have demonstrated the excitation of acceptor chromophores via energy transfer from MHP NCs. A wide range of chromophores including porphyrazine, rhodamine derivatives, rose bengal, pentacene, and 9-phenanthrene carboxylic acid, among others have been studied (Figure 23).^[391–398] These indirectly excited chromophores could find applications in photocatalysis by extracting the charge carriers and thus facilitating their availability on the catalyst's surface for a longer duration. The lifetime of charge carriers in MHPs can reach several microseconds when complexed with energy acceptors; however, without these acceptors, the lifetime is limited to just a few nanoseconds. For example, He et al. reported triplet energy transfer (TET) from CsPbBr₃ NCs to 9-phenanthrene carboxylic acid (PTA).^[390] Subsequently, the excited triplet states repopulated the NCs' excited state through reverse triplet energy transfer (rTET), resulting in an enhanced lifetime of 80 μs. This composite system was then used for steady-state photoreduction of anthraquinone, which was not achievable using only CsPbBr₃ NCs. In addition, direct ET has been utilized for chemical transformations such as [2+2] cycloaddition, and cis-trans isomerization, highlighting recent advancements.^[363,397]

5.2. Approaches for MHP-Photocatalyzed Reactions

5.2.1. O₂ Activation Approach

Oxygen is often deemed an excellent oxidant due to its widespread availability, lightweight nature, and tendency to pro-

duce water as a harmless by-product in many instances. The growing emphasis on eco-friendly and sustainable synthetic techniques has sparked significant interest in utilizing O₂ as a reagent in synthesis processes.^[399] In photocatalysis, two types of oxidation reactions are known to employ O₂ as an oxidant. In type I, photoexcited holes take part in oxidation, while O₂ accepts electrons to regenerate the catalyst without incorporating into the product. The example of type I includes dehydrogenation of alcohols to form aldehydes and ketones are such types of reactions employing MHPs as photocatalysts.^[366,370] Conversely, Type II reactions involve the incorporation of one or both oxygen atoms from O₂ into the final product. These reactions typically follow a radical pathway, with oxygen being assimilated after transformation into superoxide radicals by utilizing photoinduced electrons. Such reactions were also widely reported using MHP NC photocatalysts. These include the oxidation of toluene, thioether, benzylamine, etc.^[356,357,368,369] Based on an in-depth review of the literature, it appears that O₂ strongly interacts with MHP surfaces and is readily reducible due to favorable energetics (0.33 eV versus RHE).^[46] As a result, it has been extensively utilized in both the types of reactions (Figure 24).

5.2.2. C–X Activation Approach

Another aspect of MHPs-based photocatalysis involves the activation of the C–X bond, originating from a photoinduced halide exchange reaction, where the bond can be broken simply by irradiating a white or blue light (Figure 25a). Subsequently, the generated halide (X) exchanges with the intrinsic halides of MHPs (X' of ABX₃). Using dichloromethane as the reactant, this idea was first demonstrated by Parobek et al., later Wong and coworkers found that this exchange process is not limited to perovskite only, whereas this also brought a chemical change in C–X

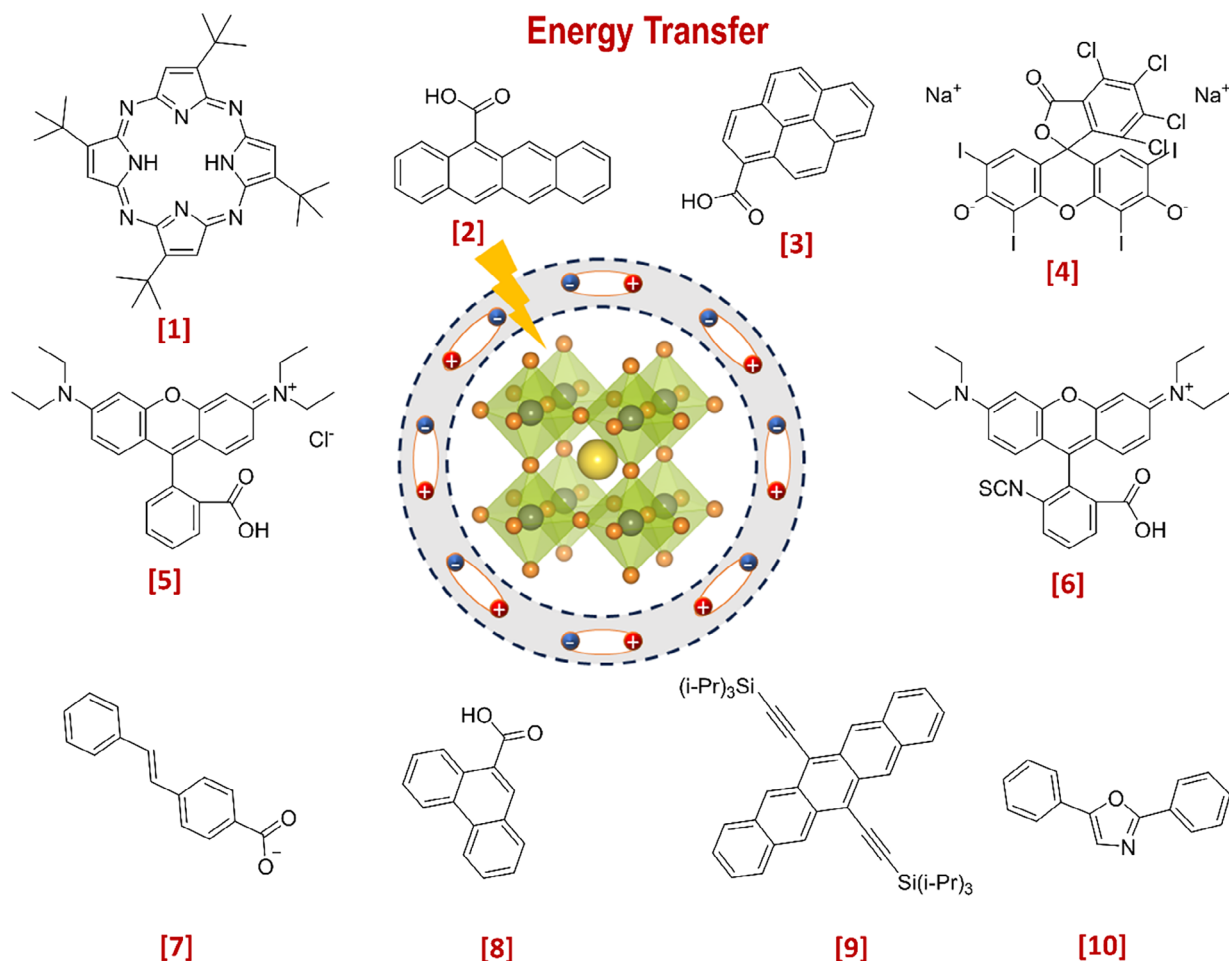


Figure 23. Summary of the molecules utilized for extracting charge carriers in the form of electron-hole pairs or demonstrated to show energy transfer from MHPs. The molecules are chosen from the references.^[391–398]

containing substrates.^[400,401] The suggested mechanism indicates that the C–X interacts with MHPs because of halide vacancies on the surface. These vacancies allow halides to coordinate with metal cations (B), leading to subsequent activation.^[402] Furthermore, this key concept was utilized in many organic reactions such as C–C coupling, N-hetero-cyclization, C–O cross-coupling, dehydrohalogenation, halogenation reactions, etc.^[46] (Figure 24).

5.2.3. Choice of Reactants

Another method used in MHPs-based photocatalysis is the choice of reactants containing functional groups or atoms that are prone to the perovskite surface. Carboxylic acid and amine groups are known to passivate the MHP surface,^[130,261] and thus the introduction of these groups to the reactants facilitates the organic transformations. For example, the presence of –COOH group in the substrate enabled a highly selective [2+2]-cycloaddition, while interactions with amines were utilized for N-hetero-cyclization and benzylamine oxidation.^[29,357,363] Additionally, sulfur and oxygen atoms can also interact with MHP surface through their Lewis basicity based on the HSAB principle.^[403–405]

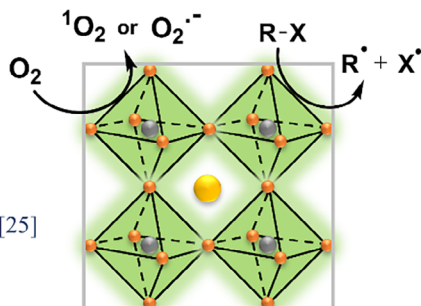
This could be seen in the organic transformations such as EDOT polymerization, thiol coupling, sulfide oxidation, and alcoholysis of styrene oxide, etc.^[356,358,371,374] Alkyl phosphonic acids and phosphines are also known for the strong passivation of the MHP surface.^[130] In a correlation, the phosphorous-containing substrates were also noted in a phosphorylation reaction where a dehydrogenative coupling was demonstrated between tertiary amines and phosphite esters.^[358] Thus the substrate choice could be made based on the existing passivating strategies to achieve efficient photocatalysis employing MHPs (Figure 24).

5.3. C–C, C–N, and C–O Bond Formation

In this regard, Yan's group in 2019, has taken phenacyl bromide and octanal as substrates, with CsPbBr₃ NCs as a photocatalyst to achieve various products via C–C coupling.^[349] Different products were achieved by varying the co-catalysts, and sacrificial donors in the reaction mixture. Introducing *N,N*-di isopropyl-ethylamine (DIPEA) without any cocatalyst resulted in a highly selective conversion to acetophenone (**3a**) whereas replacing amine with **6**, (5*S*)-(–)-2,2,3-trimethyl 5-benzyl-4-imidazolidinone resulted in

1. Oxygen Activation Approach

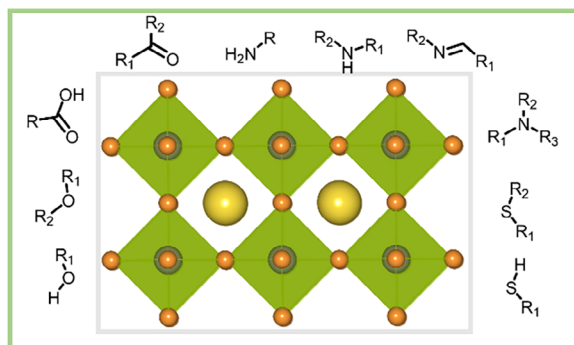
1. Benzyl Amine Oxidation[9,20]
2. Thio-Ether Oxidation[21]
3. Benzyl Alcohol Oxidation[19]
4. Alcoholysis of Styrene Oxide[30]
5. Toluene Oxidation[24]
6. Oxidation of 5-Hydroxymethylfurfural[25]
7. Acrylamide Polymerization[26]



2. C-X Activation Approach

1. α -Alkylation of Aldehydes[1]
2. Dehydrohalogenation Reaction[18]
3. Vicinal Dihalogenation[17]
4. C-C and C-O Bond Formation[4]
5. N-Heterocyclization[11]
6. [3+2] Cycloaddition[12]
7. Suzuki Reaction[8]

3. Choice of Reactants



1. EDOT Polymerization[27]
2. C-C Oxidative Coupling[7]
3. Thiol Coupling and C-H Activation[10]
4. N-Heterocyclization[11]
5. Asymmetric Organic Synthesis[13]
6. N, N- Heterocyclization[14]
7. [2+2]-Cycloaddition[16]
8. Decarboxylation and Aromatization Reaction[28]
9. Alcoholysis of Styrene Oxide[30]

Figure 24. Diagram illustrating three approaches that have been employed to showcase photocatalytic chemical transformations catalyzed by Metal Halide Perovskites (MHPs). [] represents the entry of the corresponding reaction in Table 3.

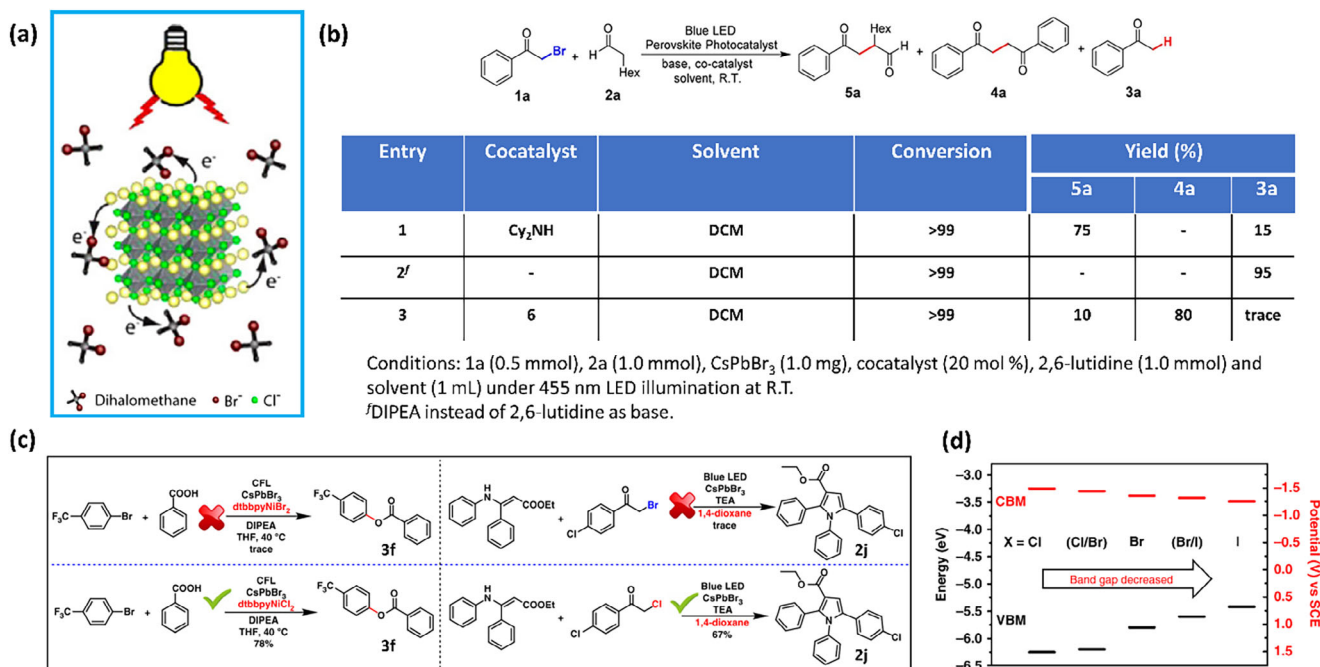


Figure 25. a) Proposed mechanism of photoinduced halide exchange reaction. Reproduced with permission.[400] Copyright 2017, American Chemical Society b) The chemical process (C-C coupling) and the tabulated data illustrating varied yields under distinct conditions. Reproduced with permission.[349] Copyright 2019, American Chemical Society c) Two instances of effective reactions showcasing the tuning of perovskite band characteristics with different halide contents. Reproduced with permission.[29] Copyright 2019, Nature.

sp³-C coupling product (**4a**) with 80% yield. Additionally, the presence of dicyclohexylamine and 2,6-lutidine produces (**5a**) with 75% yield by activating C-Br and C-H bond in a single catalytic cycle according to the provided mechanism. (Figure 25b) The investigated mechanism suggested that all the products were formed following the key step of C-Br activation (phenacyl bromide) via photoinduced electron transfer from perovskite NCs. Phenacyl radicals were trapped using TEMPO, isolated, and analyzed using NMR. Another report from the same research group employed not only C-Br activation as a pivotal step but also activated the comparatively stronger C-Cl bond to showcase C-C coupling, N-hetero-cyclization, and C-O cross-coupling reactions by using other cocatalysts and reagents.^[29] This report highlights a correlation between nanocrystal size, reaction rate, and product yield. It was observed that smaller-size NCs facilitated a faster reaction rate, albeit without achieving a high yield in a longer reaction time (6h). Conversely, larger-sized NCs led to a higher yield but with a slower reaction rate. The explanation lies in the fact that the larger surface-to-volume ratio of smaller NCs facilitates higher rates, while the detrimental effects due to moisture and light irradiation are more pronounced in these NCs than in larger NCs. Another intriguing aspect is the band tuning of halide perovskite NCs, which broadens the range of substrates that can be activated by facilitating their thermodynamic feasibility. As presented in Figure 25c, **3f** is formed in trace amounts when CsPbBr₃ NCs acts as photosensitizer and dtbbpyNiBr₂ as cocatalyst, while replacement of cocatalyst with dtbbpyNiCl₂ resulted in 78% of yield. This observation was cross-confirmed by replacing CsPbBr₃ NCs with an Ir-based photo sensitizer where no such effect was detected. A similar kind of observation was drawn in another reaction (**2j**) shown in Figure 25c, where replacing α -bromoketone with α -chloroketone resulted in an enhancement in yield to 67%. These observations were not only anticipated but also validated through various controls, confirming their existence due to an in-situ halide exchange. This exchange leads to a shift in the conduction and valence bands, consequently resulting in enhanced reaction yield. (Figure 25d)

Rosa-Pardo and coworkers have reported lipophilic ligand-capped CsPbBr₃ NCs, concentrating benzyl bromide and tertiary amine (electron donor) to the catalyst surface due to van der Waals interactions (Figure 26a).^[350] This strategy resulted in the facile activation of the C-Br bond of benzyl bromide, which is otherwise thermodynamically unfavorable. This led to the homo-/cross-coupling of benzyl bromide with a turnover number of up to 17500. Recently, Shi et al have recognized the recyclability of the photocatalysts as one of the major issues and paved their effort to demonstrate CsPbBr₃ catalyzed decarboxylative aminomethylation of imidazo-fused heterocycles.^[351] For this reaction, CsPbBr₃ was recycled and used five times without any significant reduction in the reaction yield. (Figure 26b) Mechanistic studies have revealed that hole-driven decarboxylation is followed by the formation of an amino methyl radical, which subsequently interacts with imidazo-fused heterocycles to produce an aminomethylated product.

In 2020, Yuan and colleagues demonstrated the stereoselective C-C oxidative dimerization of α -aryl keto nitriles using zwitterionic ligand-stabilized CsPbBr₃ NCs as the photocatalyst.^[354] The requirement for zwitterionic ligand arose because of stability issues encountered with the recycling of the catalyst capped

with oleic acid/oleyl amine-coated NCs. The zwitterionic ligand-stabilized NCs not only exhibited recyclability for up to three cycles but also led to an increased reaction rate, attributed to the reduced density of surface ligand coverage. Furthermore, a high stereoselectivity (>99%) was observed favoring *dl*- isomers over *meso*-isomers in cases involving NCs, which was attributed to reduced steric hindrance between the two benzene rings of the substrates when the substrate interacts with the NCs' surface in a *trans*-orientation (Figure 26c). Wang et al. showcased an intriguing study where they synthesized a CsPbBr₃/Pd composite to enhance Suzuki coupling (coupling between aryl halides and phenylboronic acid).^[355] Whereas for pure CsPbBr₃, the conversion and selectivity was 11% and 81%, respectively, but the introduction of 3% wt. Pd leads to 96.5% conversion with a selectivity of nearly 100%. To rationalize the thermal effect, the temperature was fixed at 30 °C and the reactions were performed at different light intensities including dark. A linear increase in the conversion with light intensity was observed in Figure 26d, suggesting the key role of light in the reaction. Finally, the stability test of the catalyst has revealed no significant decline in activity even after six cycles. Moreover, the integrity of the crystal structure and the presence of deposited Pd were confirmed through XRD and ICP-MS analyses.

5.4. S-S and C-P Bond Formation

Disulfides play a crucial role in facilitating the folding of proteins into biologically active structures and have extensive applications in the fine chemical industry. The known methods utilize typical oxidants for the oxidative coupling of thiols, which can lead to overoxidation and have challenges with selectivity in the synthesis of unsymmetrical disulfides. To tackle these, Wu and coworkers have utilized CsPbBr₃ NC catalysts to couple thiols in a symmetrical as well as in an unsymmetrical manner.^[358] The thiol binding to the nanocrystal surface was verified through the photoluminescence spectrum, showing a gradual increase in intensity attributed to Pb-S binding, which was further confirmed using FTIR spectroscopy. The reaction yield significantly improved in the presence of oxygen, reaching up to 98%. In contrast, under oxygen-free conditions, the yield was notably reduced to 65%. This establishes that oxygen accepts electrons and turn into superoxide, while holes participate in oxidizing thiols into thiyl radicals, which then couple with another radical to form disulfides. In the absence of oxygen, thiol protons accept electrons and release hydrogen gas as a byproduct. Moreover, the uniqueness of NC catalysts was explored through a reaction conducted with bulk CsPbBr₃, resulting in a significantly decreased yield of <8%, indicating the necessity of a large surface area for efficient catalytic activity. Furthermore, during the synthesis of unsymmetrical disulfides, noticeable selectivity was observed, with a 3:1 ratio of unsymmetrical to symmetrical products. In the same article, phosphorylation of tertiary amines using CsPbBr₃ NCs was also demonstrated, achieving a maximum yield of up to 98%. Additionally, the confirmation of substrate (tetrahydroisoquinoline and phosphite) interaction with the catalytic surface was established by the enhancement in photoluminescence when exposing the substrates to the catalyst individually. The involvement of oxygen in the reaction was deemed significant, as photo-

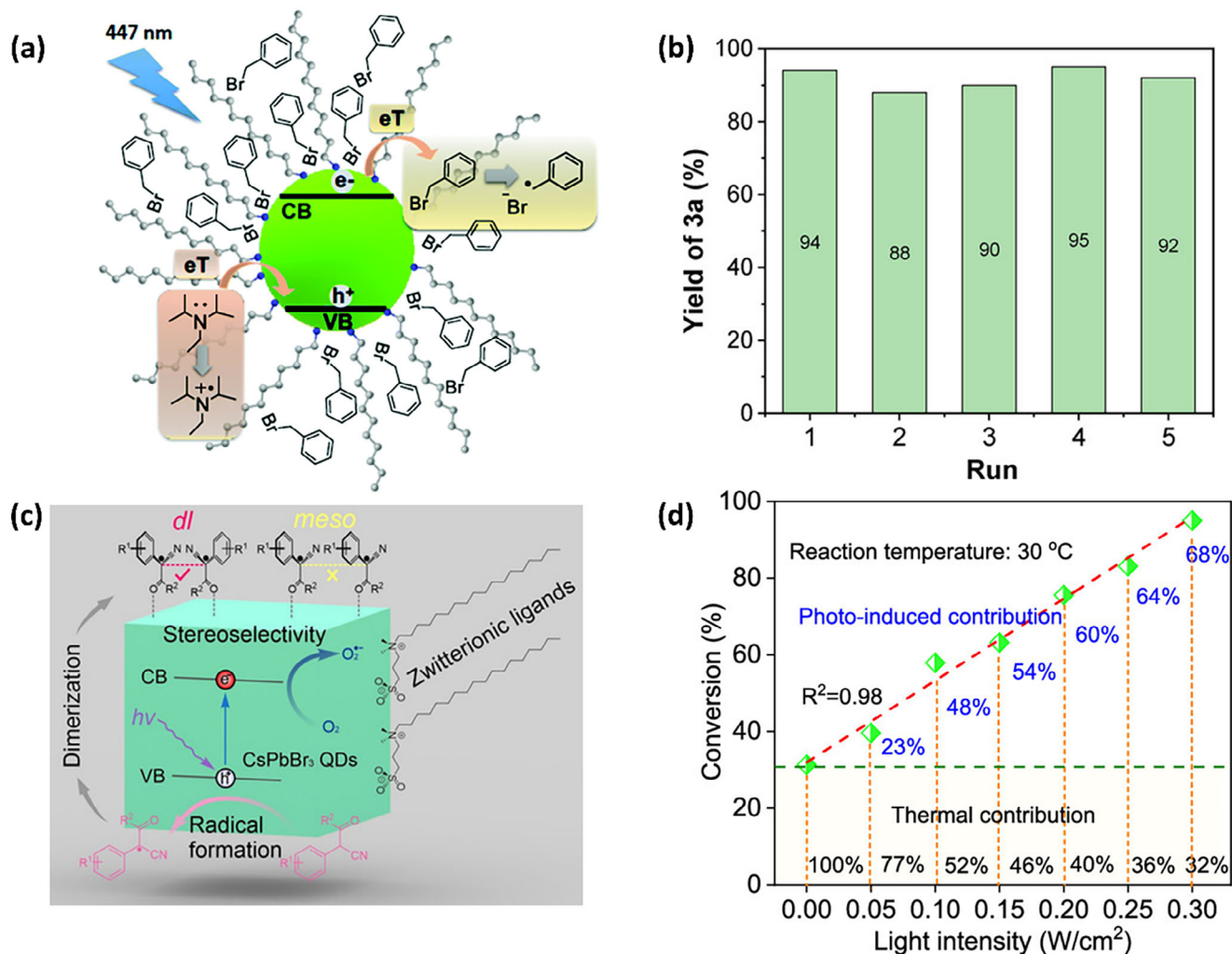


Figure 26. a) The proposed path of electron and hole transfer after light excitation of the CsPbBr₃ in the presence of the benzyl halide and DIPEA encapsulated within the lipophilic shell. Reproduced with permission.^[350] Copyright 2020, The Royal Society of Chemistry. b) Recyclability test of the catalyst up to 5 cycles for CsPbBr₃ catalyzed aminomethylation of Imidazo fused heterocycles. Reproduced with permission.^[351] Copyright 2020, Wiley-VCH. c) Suggested reaction path for photocatalytic stereoselective oxidative dimerization of α -aryl ketonitriles catalyzed by zwitterionic ligands capped lead halide perovskites. Reproduced with permission.^[354] Copyright 2020, Wiley-VCH. d) The catalytic activity of Pd/CsPbBr₃ for the Suzuki coupling reaction at varying solar light intensities when maintained at 30 °C for 4 h. Reproduced with permission.^[355] Copyright 2022, American Chemical Society.

generated superoxide was proposed to extract protons from the radical cation intermediate and transform into an α -amino radical. C-P coupling reaction serves as a significant synthetic approach due to the considerable structural complexity found in nitrogen-containing pharmaceutical compounds.

5.5. Cyclization Reactions

As established above, dichloro/dibromo-methane is susceptible to perovskite for photoinduced halide exchange reaction, which results in the formation of chloride/bromide radical as an intermediate.^[400] The Yan group^[359] employed a co-catalyst strategy in which the utilization of in-situ generated bromine radicals derived from the oxidation of bromide ions (photogenerated via a single electron transfer to the C-Br bond) for [3+2]-cycloaddition.

Following the mechanism in **Figure 27a**, the bromine radical first corroborated with molecule **2a** which subsequently reacted with alkene **3a** to form benzyl-based radical **III**. Ultimately, the release of a bromine radical led to the formation of the final product **4a**. Interestingly, the reaction was diastereoselective and resulted in *cis*-**4a** as a major product, which was confirmed by nuclear Overhauser effect spectroscopy (NOSEY NMR). This selectivity was attributed to the formation of transition state **III-a**, which lacks 1,3-diaxial interaction and is thus more stable than **III-b**. Regarding recyclability, CsPbBr₃ NCs have shown no decrement in their activity up to 3 cycles, attributed to a self-healing process to the presence of excess bromine in the system.

In another report, the Yan group has introduced an innovative approach by employing triplet energy transfer (TET) with reactant molecules having a -COOH anchoring group. This has been employed to demonstrate a remarkable diastereomeric *syn*-

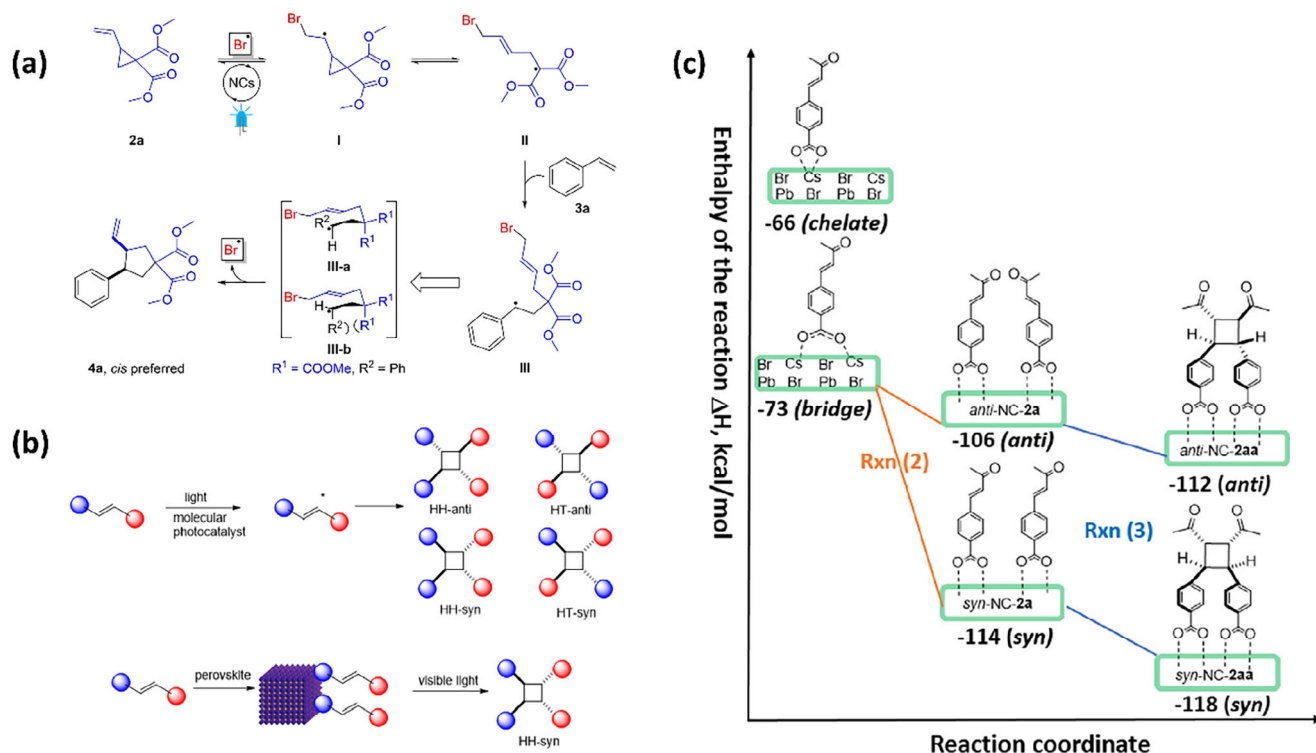


Figure 27. a) Proposed pathway for the [3+2] cycloaddition catalyzed by nanocrystals via bromine mediation. Reprinted with permission.^[359] Copyright 2023, The Authors. ChemSusChem published by Wiley-VCH GmbH. b) Schematic of [2+2]-cycloaddition in the presence and absence of perovskite NCs, showcasing how substrate binding dictates the formation of diastereomeric *syn*-selective product. c) Binding enthalpies of the intermediates involved in the reaction. Reprinted with permission.^[363] Copyright 2022, American Chemical Society.

selective [2+2] cycloaddition by utilizing lead halide perovskites as a triplet energy donor.^[363] As shown in Figure 27b, employing a molecular triplet energy donor generates triplet states in unbound reactant molecules, resulting in the formation of all possible products. In contrast, when using MHPs as donors (CsPbBr_3), the $-\text{COOH}$ groups on the reactants anchor them to the perovskite surface, which enforces selective product formation and promotes *syn* addition. The scanning of functional groups indicated that the substrates containing $-\text{COOH}$ with appropriate energy alignment exhibited the TET, while other substrates remained inert. As expected, TET-activated molecules have shown successful [2+2]-cycloaddition with yields up to 64%. To understand the diastereomeric selectivity, Density Functional Theory (DFT) studies were performed. In the free state, the reaction was exothermic for both *anti*- and *syn*-mode with ΔH_{rxn} of -8 and -6 kcal/mole, respectively, resulting in an *anti*-selective product. Whereas in the bound state, *syn*-mode binding is preferred, having lower energy than *anti*-mode, resulting in a *syn*-selective product (Figure 27c). Here, the strong $-\text{COOH}$ binding was attributed to the positively charged Cs-rich CsPbBr_3 NC surface.

Another report from the Yan group has demonstrated an asymmetric synthesis using chiral CsPbBr_3 NCs through amine-based surface interactions.^[360] First, to formulate chiral perovskite NCs ($\text{L}_2(\text{APbBr}_3)_{n-1}\text{PbBr}_4$, where $n = \infty$, L = chiral ligand and $\text{A} = \text{Cs}^+$, Figure 28a), diverse methods were tried and ultimately employed the tip sonication. Through this method maximum coverage ($\approx 47\%$) of the chiral ligand (chiral 1-phenylethylamine) on

the perovskite surface was achieved. These perovskites, denoted as NC-3, exhibited a characteristic signal at 515 nm in circular dichroism (CD) spectra (Figure 28b), indicating the establishment of electronic coupling between the chiral ligand and the perovskite nanocrystal lattice. The NC catalysts were further employed to control the chirality of N-hetero-cyclization reactions by inducing prochirality in substrate 1a (Figure 28c). Consistent with the hypothesis, the photocatalytic outcomes indicated that increased chiral-surface coverage leads to higher enantioselectivity, as shown in the table provided in Figure 28c. According to HPLC data, the nanocrystals synthesized using the tip sonication method (NC-3) exhibited an enantiomeric excess (*ee*) of over 99% for product 2a. In elucidating the mechanism, the atroposelective formation of N-aryl indole was ascribed to simultaneous hole transfer during the ring-closing step. This association was substantiated through DFT, revealing a subtle hydrogen bond between the N-arylamine substrate and the chiral organic site (1-phenylethylammonium) on the surface. During the recycling and regeneration of the catalyst, the enantiomeric excess (*ee*) of product 2a gradually declined from 99% to 90% after four cycles, likely due to the reduction of chiral ligand surface coverage.

Furthermore, intramolecular *N-N* hetero-cyclization was accomplished by Martin et al. via multiple hole transfer from copper (I)-doped CsPbBr_3 (Cu : CPB) to the diamine substrates.^[361] The introduction of copper into the nanocrystals was achieved through post-synthetic cation exchange with cesium, employing CuBr . Upon suspending Cu : CPB NCs in dichloromethane together with substrate, pyridazine was produced with a 90% yield

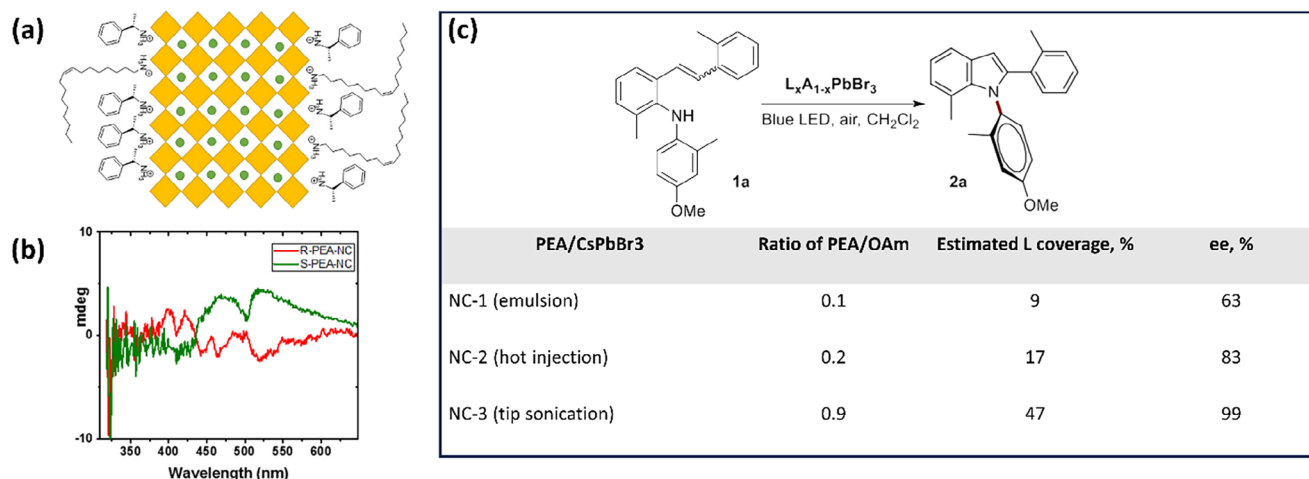


Figure 28. a) The proposed structure of chiral perovskite NCs formulated with $L_2(APbBr_3)_{n-1}PbBr_4$ with 'n' approaching infinity. b) Circular dichroism spectra of R-NC-3 and S-NC-3. c) The synthesis of chiral perovskites using various methods and their respective performance in the reaction. Reproduced with permission.^[360] Copyright 2023, American Chemical Society.

under aerobic conditions under 450 nm LED illumination. Mechanistic investigation revealed the catalytic role of copper, where the Cu(I)/Cu(II) redox couple played a significant role in achieving the multiple-hole transfer via capturing the hole generated upon photoexcitation (Figure 29a). The confirmation of Cu(II) formation was observed through EPR spectroscopy, recorded under both light-on and -off conditions. Moreover, inhibited conversion in the absence of oxygen indicated that the photoexcited electrons were efficiently quenched by oxygen, thereby regenerating the catalyst. The N–N heterocyclizations demonstrated significant success in synthesizing pyridazines and 5-membered pyrazolidines, involving 52 substrates.

5.6. Dehydrohalogenation and Halogenation Reactions

In the search for dehydrohalogenation reaction protocols under mild conditions, Singh *et al.* used CsPbBr₃ NCs as a catalyst-cum-reactant, and tetrachloroethane as a halogen-containing substrate.^[365] Exposure to white light led to the generation of a mixed halide perovskite (CsPbCl_xBr_{3-x}), serving as an effective photo-catalyst for the reaction until its transformation into CsPbCl₃ has occurred. The mechanism suggested the key step of the reaction is the activation of the C–Cl bond to form carbon radical which further releases a proton to quench the hole present on the photocatalyst, resulting in the formation of trichloroethylene.

The synthesis of two neighboring carbon-halogen bonds in a molecule is synthetically significant. Li *et al.* reported vicinal dibromination and dichlorination of alkenes using CsPbBr₃ and copper (Cu)-doped CsPbBr₃ NCs as photocatalysts where halide sources were taken as dibromoethane (DBE) and tetrachloroethane (TCE).^[364] White light irradiation initiates the generation of two photon-mediated hot charge carriers, aligning with the energy requirements for the reduction of DBE and TCE. The confirmation of the participation of hot charge carriers in the reaction was established by recording transient absorption spectra of CsPbBr₃ NCs, revealing accelerated bleach recovery in the presence of DBE (Figure 29b). Interestingly, using pristine

CsPbBr₃ NCs, dichlorination could not be achieved with a high yield due to a difficulty in the extraction of the second chlorine from the TCE. To tackle this, copper was doped to slow down the relaxation of hot electrons, which were then available for a longer time to facilitate reduction. This was assured again by comparing the bleach recovery profile of copper-doped and pristine CsPbBr₃ NCs as shown in Figure 29c. The faster recovery was attributed to the accelerated non-radiative recombination as the copper captured the holes. This process resulted in prolonged availability of electrons at the 1Se level for a longer time. Subsequently, these electrons were further excited to higher energy levels by absorbing a second photon, facilitating reduction (Figure 29d,e).

5.7. Oxidation Reactions

Given the significance of oxidation reactions in synthetic organic chemistry for introducing or transforming functional groups, it's imperative to delve into catalytic reactions using MHPs in this field. Huang and coworkers have demonstrated the oxidation of benzyl alcohols to benzaldehyde by using a hybrid of TiO₂ with FAPbBr₃.^[366] As such, the conversion was found to be enhanced up to 4x in comparison with the pure substances (FAPbBr₃ or TiO₂) whereas the selectivity of benzaldehyde differs from 99% to 95% (Figure 30a). In another report, Dong *et al.* achieved 100% selective conversion to benzaldehyde using CsPbBr₃/Polyoxometalate composites (CsPbBr₃/Ni₄P₂).^[109] The combination of steady-state and time-resolved photoluminescence (PL) revealed the enhanced dissociation of the exciton into free charge carriers, which was attributed to the optimum conversion obtained with the composite. Mechanistic studies revealed that the TiO₂/Ni₄P₂ served as a location for reduction (from O₂ to O₂^{•−}), while FAPbI₃/CsPbBr₃ acted as an oxidation site (from RCH₂OH to RCH₂OH*), ultimately resulting in the formation of the oxidation product.

In addition, Fan and coworkers have utilized CsPbBr₃ NC catalysts for the oxidation of amines and sulfides in aerobic and non-aerobic conditions with high selectivity (>99%) and conversion

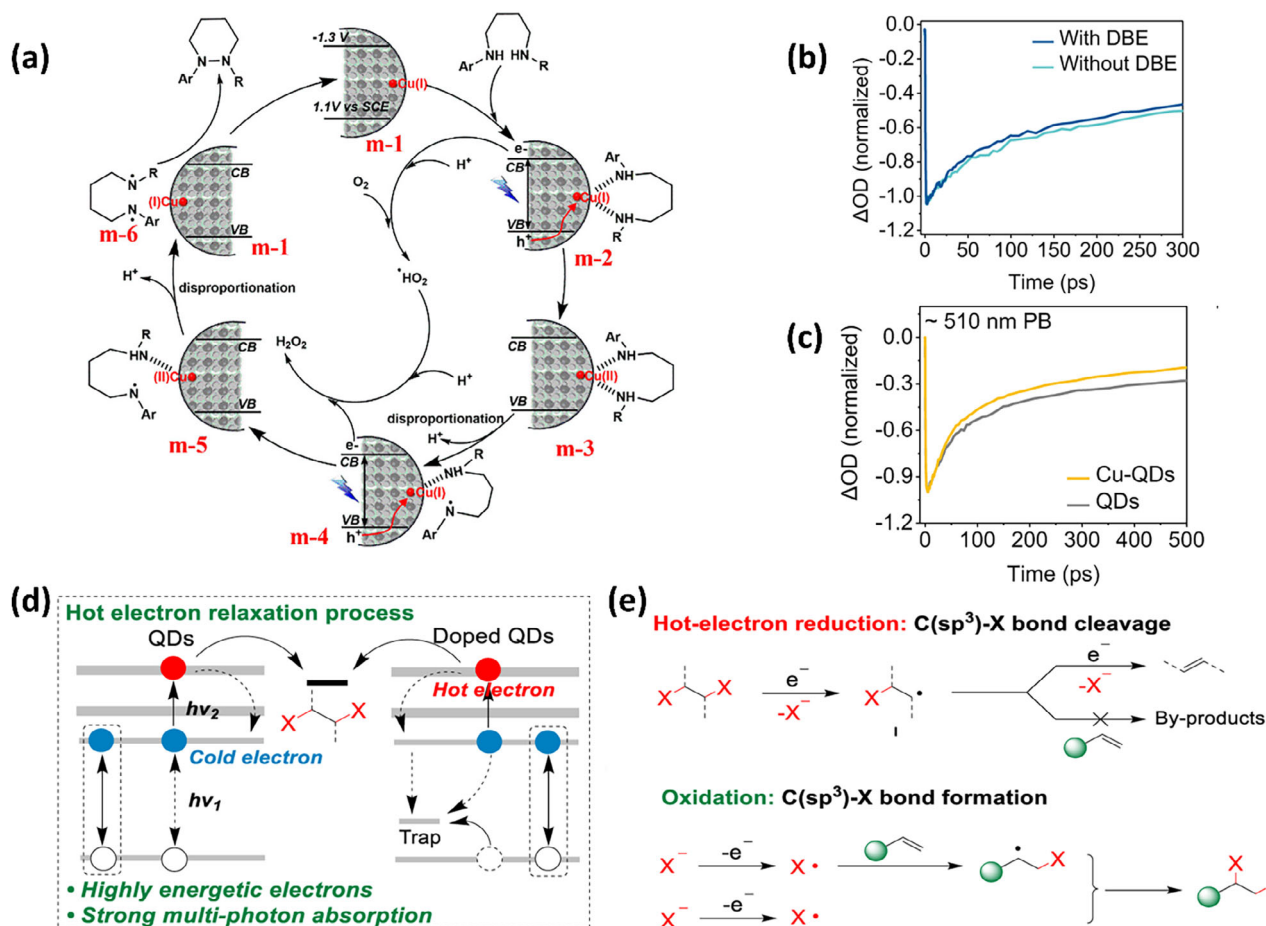


Figure 29. a) Proposed mechanism for intramolecular N-N hetero-cyclization by using copper-doped CsPbBr₃ as a photocatalyst. Reprinted with permission.^[361] Copyright 2021, American Chemical Society. b) Transient absorption (TA) kinetics of CsPbBr₃ NCs at 510 nm in presence and absence of 1,2-dibromoethane (DBE). c) Comparison of TA kinetics of CsPbBr₃ NCs and copper-doped CsPbBr₃ NCs at 510 nm. d) Energy requirements for photocatalytic shuttle reactions. e) Photocatalytic steps showcasing reduction and oxidation processes involved in vicinal di-halogenation reaction. Reproduced with permission.^[364] Copyright 2023, The Author(s). Nature.

(>99%).^[356] The products, imines, and sulfoxides have attracted considerable attention because of their crucial role as valuable components in the production of fine chemicals and bioactive substances. Interestingly, the electron-donating group containing benzylic amines has resulted in the formation of aldehydes as major products, whereas the electron-withdrawing group promoted the formation of imines as a major constituent. In the oxidation process, oxygen was identified as the crucial element in sulfide oxidation, otherwise the conversion was significantly suppressed in its absence. Conversely, the conversion of amine to imine did not show any such effect. Mechanistic studies established the crucial role of superoxide radicals through scavenging with 1,4-benzoquinone, and of holes with potassium iodide. Intriguingly, both the oxidations get inhibited in the presence of singlet oxygen (generated via energy transfer) scavenger 1,4-diazabicyclo[2.2.2]octane (DABCO), suggesting the involvement of both the energy and single electron transfer (ET and SET) in the reaction.

Given the formation of reactive oxygen species (ROS) upon photoexcitation of CsPbBr₃, Fan et al. have utilized the in-situ generated superoxide and singlet oxygen to facilitate the cleav-

age of C = C bonds, leading to the production of carbonyl compounds under aerobic conditions.^[367] This approach resulted in a 95% yield of benzophenone from 1,1-stilbene under standard optimized conditions. The investigated mechanism provided in Figure 30b, which clarifies the role of oxygen in activating the olefin forming [2+2]-adduct (IM₂) via SETs. The EPR spectrum in Figure 30c displayed the presence of the superoxide radical intermediate. Concurrently, DFT studies supported the formation of IM1, revealing a low energy barrier for the addition of superoxide to C1 (Figure 30d).

Furthermore, the oxidation of toluene to benzaldehyde was demonstrated using lead-free perovskites A₃Sb₂Br₉ and Cs₃Bi₂Br₉.^[368,369] Zhang et al. in their report highlighted the role of A-site cation in lead-free A₃Sb₂Br₃ perovskite, transforming toluene to benzaldehyde by hole-driven C-H activation.^[368] In the context of Cs_xMA_{1-x}SbBr₉, XPS investigations presented in Figure 30e indicated that increasing the value of x led to a noticeable decrease in the binding energy of Sb²⁺. This observation implies the creation of Sb with a relatively higher electron density, consequently generating sites on Br that are electron deficient. Further, these electron-deficient sites promoted the

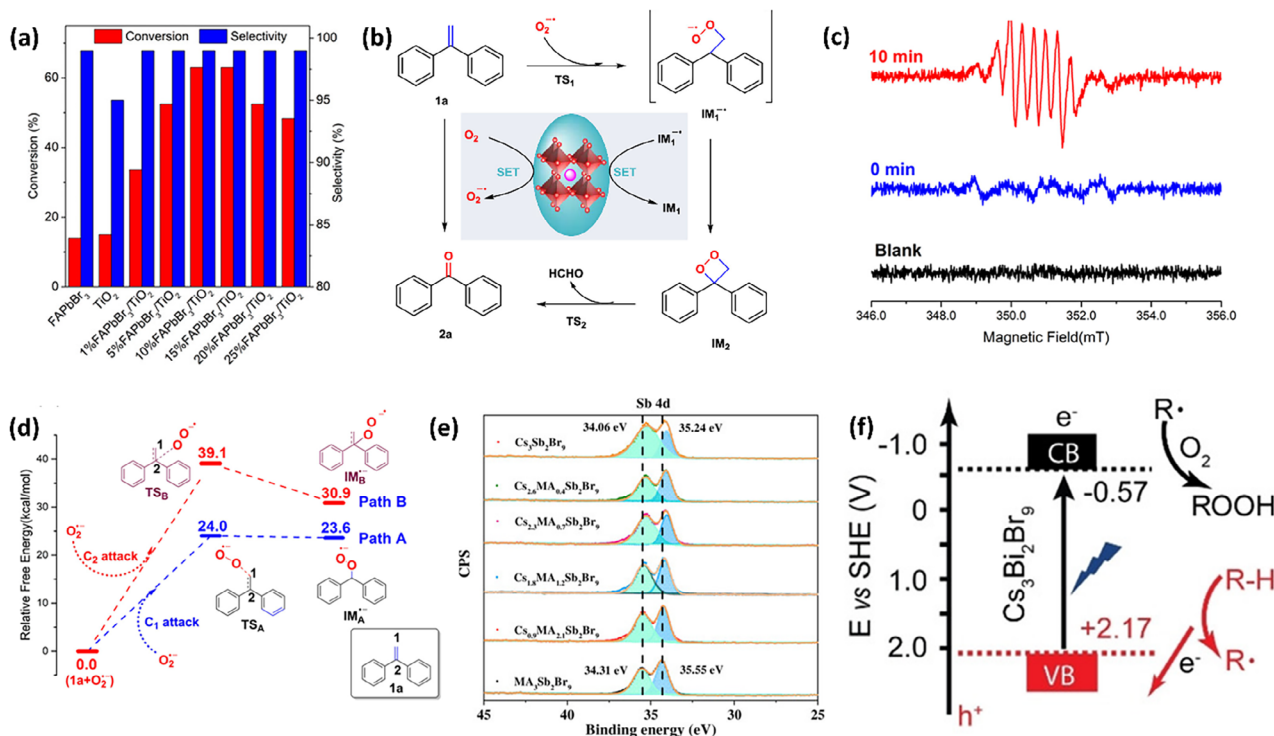


Figure 30. a) Conversion and selectivity obtained in benzyl alcohol oxidation by loading different amounts of FAPbBr₃ over TiO₂. Reprinted with permission.^[366] Copyright 2018, American Chemical Society. b) The suggested mechanism for the oxidative cleavage of C=C bonds to produce carbonyl compounds. c) EPR spectra for detecting superoxide radicals. d) Gibbs energy diagram illustrating two pathways for the incorporation of superoxide, as determined through DFT. Reprinted with permission.^[367] Copyright 2023, American Chemical Society. e) X-ray Photoelectron Spectroscopy (XPS) spectra of Sb 4d for nanoparticles (NPs) of Sb-based halide perovskites with varying Cs and MA (Cs_xMA_{3-x}Sb₂Br₉) composition ($x = 0-3$). Reprinted with permission.^[368] Copyright 2020 Wiley-VCH GmbH. f) The band positions of Cs₃Bi₂Br₉ nanoparticles and their plausible catalytic mechanism as a photocatalyst for oxidizing hydrocarbons under visible light in the presence of air. Reprinted with permission.^[369] Copyright 2019, The Authors. Published by Wiley-VCH.

enhanced rate of C-H activation and thus the corresponding product formation. The study by Dai and colleagues investigated the oxidation of toluene using Cs₃Bi₂Br₉ as a photocatalyst.^[369] In a control experiment conducted under anaerobic conditions, the reaction yielded 1,2-diphenyl ethane instead of benzaldehyde and benzyl alcohol, underscoring the essential role of O₂ in the conversion process (Figure 30f). Furthermore, control experiments revealed a significant decrease in yield when using hole and radical scavenging reagents.

5.8. Polymerization Reactions

In a recent study, Ahlawat et al. demonstrated the polymerization of acrylamide (amine-based) monomers in an aqueous solution using water-stable CsPbBr₃ NC catalysts.^[53] The stabilization of NCs in water was achieved using a bola amphiphilic ligand called NKE-12, which is shown in the accompanying Figure 31a. NKE-12 is distinguished by multiple polar functional groups at both terminals. One terminal effectively passivated the nanocrystal, while the remaining terminal was incorporated to prevent water molecules from infiltrating and disrupting the perovskite structure. This rendered an enhanced photogenerated charge separation and transport ability in modified nanocrystals, evidenced by electrochemical impedance spectroscopy (EIS) and photocur-

rent response measurements. Subsequently, these NCs were employed for the polymerization of acrylamide using of both holes and electrons according to the mechanism shown in Figure 31a. The significance of O₂ as a co-reactant was verified through a series of control experiments. Additionally, the presence of hydroxyl radicals was confirmed using EPR spectroscopy.

Chen et al. in 2017,^[371] polymerized 2,2',5',2''-ter-3,4-ethylene dioxothiophene (Ter-EDOT) to PEDOT presented in Figure 31b, based on oxidation using CsPbI₃ NCs as a photocatalyst. Here, again dissolved oxygen regenerated the photocatalyst by accepting an electron from the reduction site. Notably, the replacement of oxygen with benzoquinone, having a comparable reduction potential, preserved the stable cubic phase of the quantum dots, a contrast to the situation in the presence of oxygen. Polymerization provided a protective layer for the quantum dots, ensuring their encapsulation and stability.

5.9. Decarboxylation, Dehydrogenation, and Aromatization Reactions

In the search for heterogeneous photosensitizers capable of covering the visible spectrum and possessing suitable redox properties to achieve photo-redox reactions, Hong et al. synthesized 2D perovskites with hydrophobic hexadecyl ammonium (HDA)

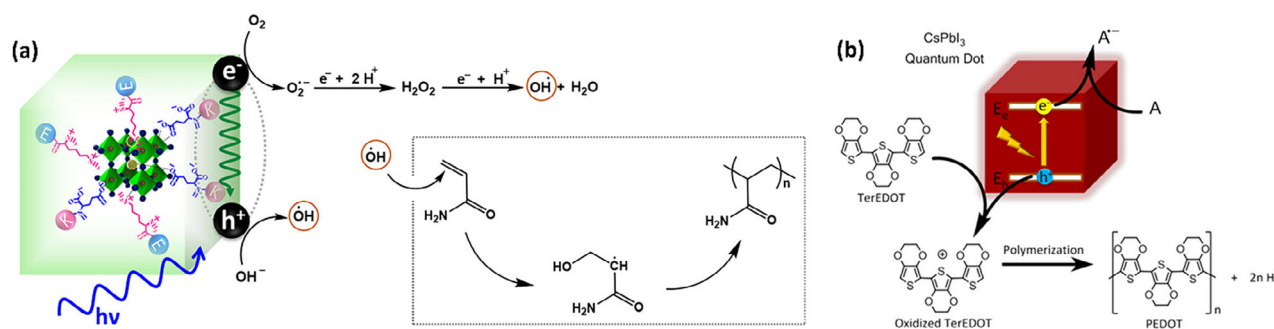


Figure 31. a) Proposed mechanistic pathway for photocatalytic polymerization of acrylamide. Reproduced with permission.^[53] Copyright 2024, American Chemical Society. b) Photocatalytic polymerization of Ter-EDOT on the catalytic surface of CsPbI₃ NCs. Reproduced with permission.^[371] Copyright 2017, American Chemical Society.

cations, thus forming metal halide nanosheets (HAD)₂MI₄ (M = Pb, Sn) (Figure 32a,b).^[372] Further, (HAD)₂PbI₄ nanosheets were utilized to catalyze the decarboxylation of indoline-2-carboxylic acid, yielding indoline in the presence of N₂ and both indoline and indole in the presence of O₂. Moreover, experiments were conducted on the direct dehydrogenation of 5-trifluoromethylindoline and 2-methylindoline, resulting in the production of indoles with yields of 48% and 71%, respectively. The utilization of lead-free (HAD)₂SnI₄ sheets achieved a 30% yield for the decarboxylation of 5-methyl-indoline-2-carboxylic acid and a 47% yield for the dehydrogenation of 2-methylindoline. The role of oxygen in the dehydrogenation reaction was established by scavenging superoxide radicals using Tiron.

So far, photocatalysis with MHPs has primarily utilized weakly confined or bulk crystals, limiting the full exploitation of their quantum confinement properties in catalysis. Conventionally synthesized MHP NCs showed limited activity in photocatalysis due to their vulnerability to moisture, oxygen, substrates, and reaction solvents. Pradhan and team have realized these issues and utilized halide passivated air-stable, monodisperse CsPbBr₃ NCs for oxidative aromatization of azaheterocyclic substrates (such as Hantzsch ester) in open air.^[373] These NCs have shown two to five times higher reaction rates with a turnover number (TON) of 200 than bulk CsPbBr₃ (TON = 177) and conventionally synthesized one (TON = 166). Through mechanistic investigation (presented in Figure 32c), it was confirmed that oxygen serves as an electron acceptor, leading to its conversion into superoxide. Simultaneously, the hole oxidizes the substrate, which is then transformed into the product by reacting with superoxide, converting it into H₂O₂. Figure 32d compares the reaction rate of halide-passivated NCs (abbreviated as QD1) with other photocatalysts like bulk perovskites (PNCs), Rhodamine 6G, and conventionally synthesized NCs (QD4). It demonstrates that QD1 has the highest reaction rate, indicating its robustness and quantum confinement properties.

5.10. Ring Opening Reaction

The nucleophilic addition of alcohols to epoxides, producing β -alkoxy alcohols, is crucial for synthesizing anti-tumoral drugs. Traditional methods often rely on strong corrosive acids or

harsh conditions. To address this challenge, Dai et al. integrated Bismuth-based MHP (Cs₃Bi₂Br₉) synthesis with the reaction of epoxide alcoholysis.^[374] They directly added a solution containing perovskite precursors (CsBr and BiBr₃) in DMSO to the reaction mixture with the targeted epoxide and alcohol. This approach yielded 2-isopropoxy-2-phenyl ethanol from the photocatalytic reaction between styrene oxide and isopropanol, achieving an 86% yield and a selectivity of $\geq 86\%$. The method was successfully applied to other nucleophiles like thiols, producing thia-compounds with up to 84% yield. Since epoxide ring openings require acidic conditions for activation, the catalyst surface was expected to contain acidic sites, which was confirmed by DRS analysis. Using alizarin as an adsorbate, a shift in absorbance from 2.856 eV to 2.42 eV was observed upon exposure to Cs₃Bi₂Br₉, as shown in Figure 33a. CsPbBr₃, in contrast, exhibited weaker acidity, explaining its low activity with a yield of < 1% in the reaction. The investigated mechanism highlighted the role of photoinduced superoxide ions and holes in activating the alcohol by converting it into radical and anion as shown in Figure 33b, while epoxides were activated by adsorption on bismuth acidic sites on the surface.

6. Conclusions and Prospects

Halide perovskite semiconductors, both in the form of thin films and nanocrystals, present unique advantages as photocatalysts, particularly due to their ability for efficient charge-carrier generation and extraction, as well as their fine bandgap tunability through the composition and size. However, their intrinsic instability in polar solvents caused by their ionic nature is a major hurdle in advancing their progress in terms of efficiency and durability. Despite the stability issues, significant progress has been made in developing methods to overcome the challenges posed by the degradation of perovskites in polar solvents. In addition, perovskites with different dimensionality and compositions in combination with different co-catalysts have been tested for solar-to-fuel production and photochemical organic synthesis. In this review, we have discussed the research progress of perovskite photocatalysts for H₂ generation, CO₂ reduction, and organic synthesis, regarding the design strategies to overcome the instability in polar solvents, different types of perovskites, different co-catalysts, different encapsulating materials, and different organic reactions. To overcome the instability in polar solvents,

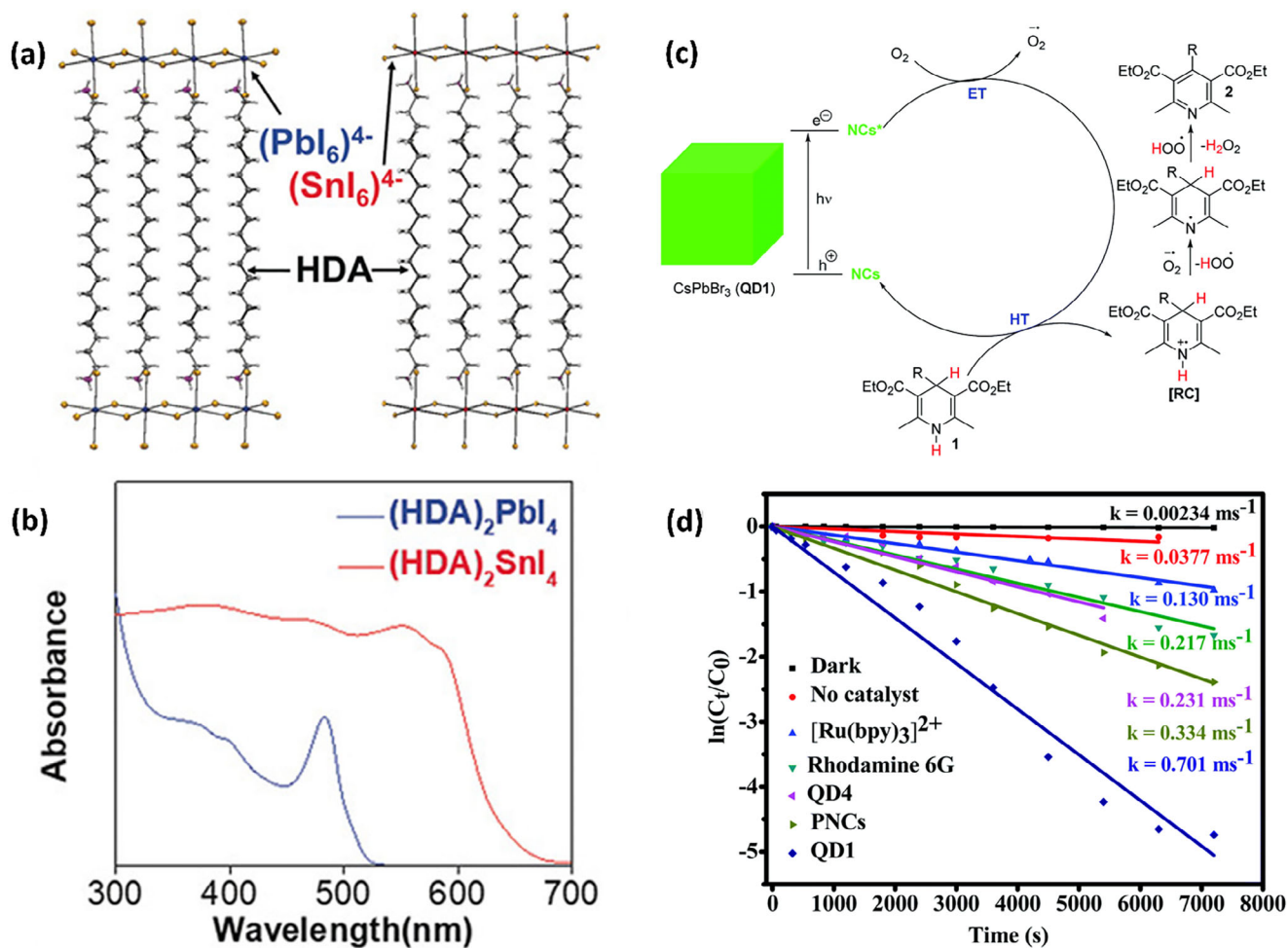


Figure 32. Crystal structure (a) and UV/Vis diffuse reflectance spectra (DRS) (b) of $(\text{HDA})_2\text{PbI}_4$ and $(\text{HDA})_2\text{SnI}_4$. Reproduced with permission.^[372] Copyright 2019, Wiley-VCH. c) Proposed mechanism of photocatalytic aromatization reaction catalyzed by CsPbBr_3 quantum dots (QD1). d) Demonstrating the superior catalytic activity of QD1 compared to other established photocatalysts by plotting $\ln(C_t/C_0)$ versus reaction time. Reproduced with permission.^[373] Copyright 2021, The Royal Society of Chemistry.

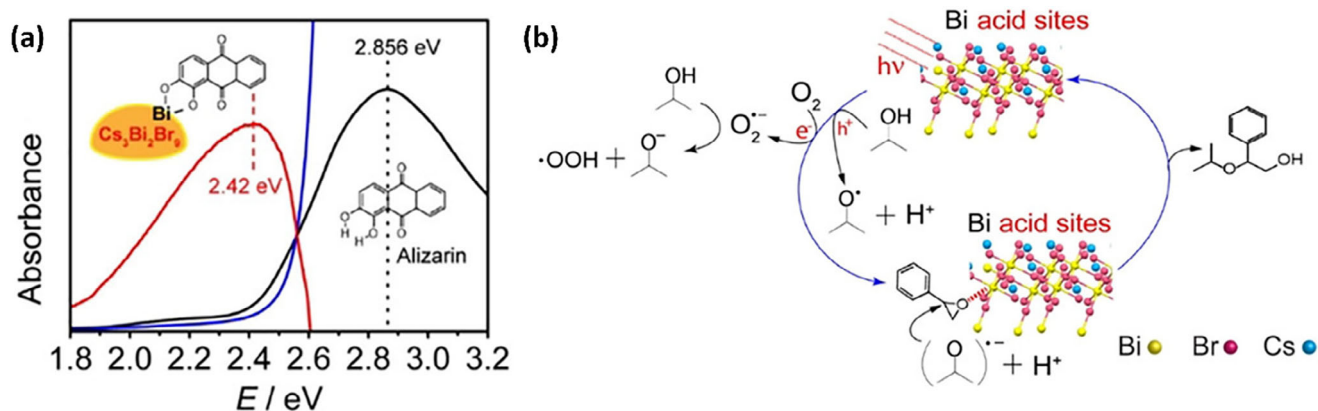


Figure 33. a) UV/Vis DRS spectra of pure alizarin (black), $\text{Cs}_3\text{Bi}_2\text{Br}_9$ (blue), and alizarin adsorbed $\text{Cs}_3\text{Bi}_2\text{Br}_9$ (red), showing a low energy shift on exchanging protons with bismuth. b) The suggested mechanism for the alcoholysis of epoxides, illustrating the adsorption of epoxide molecules on Bi acidic site. Reproduced with permission.^[374] Copyright 2019, Wiley-VCH.

methods like H_2 generation from saturated hydrohalic solution, CO_2 reduction in nonpolar or less polar solvents, encapsulation of NCs and thin films have been developed for photochemical and photoelectrochemical water splitting, and CO_2 reduction. The materials range includes lead halide perovskites to lead-free and 3D to 0D with the combinations of various co-catalysts like Pt, TiO_2 , GO, and C_3N_4 . We have discussed the product yield and efficiency of each systems in terms of $\mu mol\ cm^{-2}\ h^{-1}$ and % and compared with and without co-catalysts. In some cases, the co-catalysts can also be encapsulants, e.g., TiO_2 and graphene oxide. Furthermore, we examined a wide range of photocatalytic organic reactions using perovskite NC catalysts. Despite significant progress on perovskite photocatalysis recently, there are still several challenges that need to be addressed to improve the efficiency of photocatalysts for H_2 generation, CO_2 reduction, and organic synthesis.

6.1. H_2 Evolution

Photocatalytic hydrogen evolution based on halide perovskites remains severely limited by performance. To the best of our knowledge, the highest reported STH efficiency for perovskite materials for photocatalysis is around $\approx 2\%$,^[191] reaching $\approx 4\%$ with added Pt. The approach so far has been largely based on trial and error, drawing on materials from electrocatalysis and organic semiconductor-based photocatalysis to enhance performance and stability relative to pristine perovskite systems. While this may lead to a successful combination that would boost activities, mechanistic understanding and tailored engineering of composite materials and co-catalysts can expedite the process. Employing LHPs for splitting hydroiodic acids marked an innovative solution for generating H_2 while circumventing their instability under OWS conditions. While some progress has been made in boosting activity, this requires the use of Pt, which is not a scalable option. Using single-atom Pt has allowed a reduction in the loading required by $\approx 95\%$ (from an average of 2–3 wt% to 0.12 wt%), but efficiency remains low. Furthermore, a highly corrosive environment is required to stabilize the perovskite ($pH < -0.5$ in the case of MAPI).^[47] This raises the question of the long-term stability of the materials, especially with regard to moving away from corrosion-resistant noble metal cocatalysts. Lastly, photocatalytic HX splitting involves the added input of HX and H_3PO_2 as feedstocks, the latter having to be continuously supplied to replenish H^+ and re-generate X^- , which increases the cost of H_2 produced.^[197]

While recent work circumvents the requirement of H_3PO_2 ,^[191] finding a system that can perform OWS efficiently and cost-effectively is the holy grail of the field. No harsh conditions are involved, nor added reactants other than water, but the reaction itself is extremely difficult due to the sluggish and not-yet-well-understood OER. In fact, CO_2 reduction in the gas phase is commonly performed using water oxidation as the second half of the redox process.^[56,290,406] However, little attention is given to (i) understanding the feasibility and mechanism of OER on halide perovskites, especially in the absence of OER co-catalysts, and (ii) whether or not H_2O_2 formation is competing with O_2 .

6.2. CO_2 Reduction

Various studies have been reported regarding the improvement of the activity of halide perovskites toward CO_2 reduction. These studies include structural engineering, heterostructure formation for interfacial charge transfer, metal ion doping, encapsulation with different MOFs or using conducting substrates, and surface modification. The performance of the perovskite-based photocatalysts towards CO_2 reduction is summarized in Table 3. Despite considerable research advances in CO_2 reduction using halide perovskite photocatalysts, fundamental studies are yet to be fully addressed, including the kinetic problem in multi-electron reduction processes, poor reduction selectivity, and low quantum yield of the photocatalysts. These issues should be addressed through extensive research on improving the performance of perovskite-based photocatalysts and employing them on an industrial scale. Here, we summarize some of the possible directions and associated challenges that we believe are worthy to investigate soon.

- 1) Among all ABX_3 ($A = Cs^+$, Rb^+ , and $CH_3NH_3^+$; $X = Cl^-$, Br^- and I^-) perovskites, $CsPbBr_3$ has been widely explored as a photocatalyst for CO_2 reduction,^[38,282,81] it would be interesting to explore other compositions of A, B, and X to expand the scope of potential catalysts and identify materials with superior performance.
- 2) Although the mechanism of CO_2 reduction has been studied,^[111,312] the main focus has been on single-electron systems, while the specific redox pathways for both reduction and counter oxidation have remained unexplored. A thorough understanding of the redox species involved in the catalytic process would help optimize catalyst design and performance.
- 3) In most reported studies, the reduction products were attributed to CO_2 reduction only, with the control experiments supporting the essential role of nanocrystals in enhancing the evolution of these products. However, it is noted that other species like water, carbon content materials, and polar solvent are also present in the reaction system. Therefore, to strengthen the claim of exclusive reduction of CO_2 in the catalysis process, more solid evidence is needed for each case of such reactions. This suggests the importance of carefully characterizing and analyzing reaction products to confirm their origin and ensure that they are indeed exclusively derived from CO_2 reduction.
- 4) The facets of nanocrystals play a crucial role in promoting the adsorption and desorption of reactants and products and thus influence the rate of catalysis. Therefore, it is essential to extend the study of nanocrystal catalysis to include different facet nanocrystals and investigate their specific impacts on the rate of CO_2 reduction. Researchers can thus gain insights into structure-function relationships and identify optimal catalyst configurations for enhancing catalytic activity, selectivity, and efficiency in CO_2 reduction.
- 5) Doping refers to intentionally introducing impurities into a material to alter its properties, and in the case of perovskite nanomaterials, this can significantly influence their catalytic activity. However, the selection of a suitable metal ion is cru-

cial for potential improvement of the catalytic efficiency of the reaction and also for the enhanced stability of the catalyst.

- 6) Another significant issue is the toxicity of lead (Pb) that should be addressed for eco-friendly nature of photocatalyst by testing the activity of Pb-free perovskites with the substitution of Pb with other transition metals like Sn, Sb, and Bi.
- 7) While most attention has been photocatalytic CO₂ reduction with perovskites, more studies could be focused on photoelectrochemical reduction of CO₂ by coating the perovskite layer with a protective layer that can transport charges.
- 8) Many recent studies focused on achieving a higher conversion rate of CO₂, in which the typical products are single carbon atom compounds such as carbon monoxide, methane, formic acid, etc. Nevertheless, few studies have demonstrated the selective production of compounds with two or more carbon atoms (C₂+), such as ethanol, ethane, acetic acid, etc. This shift towards focusing on (C₂+) products is driven by the desire to produce higher value-added chemicals that can serve as feedstocks for various industrial processes. However, further investigations are required to optimize the product selectivity of these (C₂+) compounds and to explore the potential for generating even more valuable compounds such as alkenes, aromatic hydrocarbons, and higher alcohols.

6.3. Organic Synthesis

We discussed various photocatalytic organic transformations and strategies involving MHP photocatalysts. It highlights that many reactions targeted using MHPs involve substrates with passivating functional groups such as amine, carboxylic acid, thiol, *etc.*, facilitating their interaction with catalysts. In addition, the use of substrates containing C–X bonds is noted to be crucial for numerous reactions, as these are anticipated to interact with the surface via halide vacancies. In most cases, it was observed that hole-driven reactions involve quenching electrons with oxygen to form superoxide radicals, whereas electron-driven reactions usually quench holes using nitrogen-containing compounds like DIPEA. We also discussed chemical transformation in water, achieved using bola-amphiphilic ligand stabilized NCs. Furthermore, MHP-chromophore composite systems are also explored, where electrons and holes are extracted to the perovskite surface, aiding in photocatalytic transformations, and increasing reaction turnover numbers. Additionally, the review delves into catalysis using energy transfer composites, showcasing a [2+2]-cycloaddition reaction achieved on MHP NC surfaces. These discussions underlined the versatility and potential of MHPs in various catalytic and transformational processes, including those in non-polar solvents and water-based environments. Despite their versatility, MHPs have a few major drawbacks that hinder efficient catalytic organic transformations, requiring the attention of the community to be addressed; i) synthesis of robust MHP NCs that survive under harsh environments, ii) exploring a wide range of MHP-chromophore composite, iii) employing lead-free perovskites, iv) ligand engineering to achieve optimum charge transport.

In general, NC catalysts stand out due to their ability to adjust both the redox potential and the catalyst-substrate interface. This involves tailoring the size and composition to control redox potentials and managing catalyst-substrate interaction through

surface termination control and ligand shell design. Moreover, the colloidal nature of NCs enhances their interactions with the substrate and simplifies the removal of the catalysts, bringing together the benefits of homogeneous and heterogeneous catalysts. Additionally, NCs exhibit a large extinction coefficient, wide absorption spectrum, and large surface-to-volume ratio.^[407] Despite the numerous advantages they offer, conventionally synthesized MHP NCs are not exclusively employed in photocatalysis due to their poor photostability and compositional instability when exposed to moisture and air. Instead, polydisperse MHP NCs ranging from 2 to 100 nm are commonly used and are relatively more efficient because they are robust against moisture, air, and light. Although a few attempts have been made to tackle this issue by utilizing halide passivated NCs, which have shown greater efficiency in oxidative aromatization, significant efforts are still needed to develop new strategies applicable across a wide range of reactions.

Since the lifetime of photoinduced charge carriers in MHP NCs is typically on the order of nanoseconds, substrates lacking the anchoring groups that enable binding with the NC surface are less likely to get activated. It has been evident in the literature that most of the substrates used thus far have anchoring groups in some way or another. Extensive studies were conducted with similar aims, focusing on investigating MHP-chromophore composites and establishing their ability to extract charge carriers onto the MHP surface over an extended period. While these composites have demonstrated potential in photovoltaics, they require the attention of the community for their applications in photocatalysis. This is because these systems offer a broader scope for substrates, expanding their utility and impact. It is likely that these composites might help in enhancing reaction yield and selectivity by adjusting ligands and chromophore molecules.

The toxicity of lead is a major issue for LHP-based materials to be used in real-world applications. Despite efforts to create lead-free perovskites, their performance still lags behind LHPs, limiting their practical use. Pb can be replaced with Sn, Ge, Sb, and Bi in ABX₃ structures, such as CsSnI₃, FASnBr₃, MAgE₃, Cs₂Sb₃I₉, Cs₂Bi₃I₉, and other materials that are chemically, structurally or electronically analogous.^[408] While Sn-based perovskites show promise as an alternative to LHPs, their stability is a concern due to the oxidation of Sn²⁺ to Sn⁴⁺.^[409] However, the solutions developed to tackle the stability issues of LHPs can also benefit Sn-based perovskites, making them a more environmentally friendly choice for applications in photocatalysis. The stability of the perovskite surface in various chemical environments and its photoluminescence quantum yield often depend on the long-chain ligands. However, the long hydrocarbon chains impede charge transport, necessitating significant efforts to overcome stability and passivation challenges using shorter or conductive long-chain ligands. Recently, ethanol was showcased as an effective stabilizing ligand, offering the potential for enhanced photocatalytic applications.^[404] Alternatively, conjugated long-chain hydrocarbon ligands can improve charge transport properties while maintaining the robustness of perovskites. Despite great progress in the field of halide perovskite photocatalysts, the commercial viability of these materials in comparison with catalysts that are being used at the industrial scale is yet to be explored. The study by Yan and co-workers demonstrates that the cost of halide perovskite photocatalysts is two orders

of magnitude lower than Ir/Ru-based catalysts for photocatalytic α -alkylation of aldehydes.^[349]

As outlined in this review, there are a myriad of strategies that can be explored to advance the field of perovskites for photocatalysis, not least of which is the vast chemical space of these materials. As such, we propose the following strategies as most promising towards achieving progress:

- 1) AI-driven exploration of new photocatalysts and catalytic reaction mechanisms will undeniably play a key role in advancing the field. This is evidenced by a growing number of papers in this area, which thus far have focused on oxide-based photocatalysts,^[153,410] organic semiconductors,^[411,412] and more recently on halide perovskites.^[413–417] Further advances in this area, namely fine-tuning language models and integration with experiment, will expedite discovery of new high-performing catalysts and improve mechanistic understanding of the desired reactions.
- 2) It is evident that heterojunction composites are the way forward in terms of suspension systems.^[418] Combining all necessary requirements of bandgap, extinction coefficient, charge transport, catalytic sites and stability in a single photocatalyst is impossible. Despite some progress having been achieved with perovskite/inorganic composites, heterojunctions relying on organic semiconductors, such as 1D polymers or 2D covalent organic frameworks (COFs), remain poorly explored, with few LHP/organic composite examples beyond the more traditional rGO and $g\text{-C}_3\text{N}_4$.^[418–420] Such materials offer advantages relative to their inorganic counterparts, especially in terms of extinction coefficient, bandgap, and charge transport. Furthermore, they can not only perform the role of photocatalyst for one of the two redox reactions of interest, but also confer stability to the perovskite,^[421] avoiding the need for ligand incorporation. Further evidence of the potential of such composites lies in the increasing interest in COFs as interlayers in perovskite solar cells to address issues related to stability, morphology, and charge dynamics in the bulk and at interfaces.^[422–424] Furthermore, heteroatoms on the conjugated polymer can act as binding sites for cocatalysts,^[425] further simplifying the requirements surrounding the perovskite component.
- 3) Despite some advantages of a particulate system in terms of simplicity relative to a PEC system, we suggest that integrated PV-PEC devices constitute an equally promising route. As mentioned in (1), the perovskite chemical space is already vast; the added requirement of a composite, as outlined in 2., complicates reaching a particulate photocatalyst system that achieves rapid significant improvements in activity and stability. In contrast, perovskite solar cells have already achieved great progress in terms of stability and performance. The same can also be said of organic solar cells. We thus propose that an equal amount of focus be placed on PEC devices, where stability concerns are mitigated via encapsulation, as evidenced by the works discussed in this review. The next steps in this approach should be PEC devices relying solely on a perovskite photo-anode(cathode) combined with an organic photo-cathode(anode) to enhance light absorption relative to the traditional BiVO_4 photoanode.^[426]

- 4) Halide perovskite PEC has great promises for hydrogen production at the commercial level. However, current performance is far from the $<\$2\text{ kg}^{-1}$ target. For more details on the technoeconomics of pathways for reaching $\$2\text{ kg}^{-1}$ cost using halide perovskite PECs, readers are referred to the perspective by Mohite and co-workers.^[206]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CO_2 reduction, halide perovskites, photocatalysis, solar-to-fuel production, water splitting

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