Prospects of Z-Scheme Photocatalytic Systems
Based on Metal Halide Perovskites

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KEYWORDS: Metal halide perovskites; photocatalysis; Z-scheme; heterostructure
ABSTRACT

Considering the attractive optoelectronic properties of metal halide perovskites (MHPs), their introduction to the field of photocatalysis was only a matter of time. Thus far, MHPs have been explored for the photocatalytic generation of hydrogen, carbon dioxide reduction, organic synthesis, and pollutant degradation applications. Of growing research interest and possible applied significance are the currently emerging developments of MHP-based Z-scheme heterostructures, which can potentially enable efficient photocatalysis of highly energy-demanding redox processes. In this Perspective, we discuss the advantages and limitations of MHPs compared to traditional semiconductor materials for applications as photocatalysts and describe emerging examples in the construction of MHP-based Z-scheme systems. We discuss the principles and material properties that are required for a rational design and development of such Z-scheme heterostructure photocatalysts, and consider the ongoing challenges and opportunities in this emerging field.
The tremendous current interest in metal halide perovskites (MHPs) is evident from the global research efforts in which they feature. Although research has been dominated by studies on photovoltaics and light-emitting devices, accompanying fundamental investigations have convinced the scientific community that the properties of MHPs are versatile and unique to the extent that their applications can and should be much broader. Metal halide perovskites possess a generalized chemical formula of ABX$_3$, where A$^+$ (e.g., MA$^+$, FA$^+$, Cs$^+$), B$^{2+}$ (Pb$^{2+}$, Sn$^{2+}$), and X$^-$ (Cl$^-$, Br$^-$, I$^-$) form corner sharing [BX$_6$]$^{4-}$ octahedra surrounding a large A$^+$ cation with 12-fold coordination (Figure 1a).$^1$ A distinct feature of the high-performing MHPs over conventional tetrahedrally bonded semiconductors, such as GaAs, is the antibonding B-site ($p$) and hybridized X ($p$) - B (s) orbital characteristics of their valence and conduction bands.$^2$ As a result, the optical properties of these MHPs are largely dictated by the B$^{2+}$ and X$^-$ ions in the lattice, whose variation enables broad spectral tunability of the optical features across the visible and near-infrared (NIR) regions through direct composition engineering$^3$ or postsynthetic ion exchange processes (Figure 1b).$^4,5$ Moreover, this electronic structure supports shallow gap states within the bandgap, making MHPs highly defect tolerant$^6$ and enabling near unity photoluminescence quantum yields$^7$ along with $\mu$m scale carrier diffusion lengths.$^8$ These advantageous properties are achievable through technologically simple solution- and/or vacuum-based processing methods, which further enable MHPs with a diverse structural portfolio, ranging from nanocrystals to thin-films and bulk single crystals (Figure 1c,d). This diversity presents many opportunities for their use in prospective applications beyond photovoltaics, with MHP photocatalysts representing a relatively young yet rapidly emerging area.$^9$
**Figure 1.** Metal halide perovskites (MHPs). (a) Archetypal perovskite structure. (b) Tunability of the MHP optoelectronic properties through anion exchange exemplified for the CsPbX$_3$ system. Adapted with permission from ref 5. Copyright 2020 Royal Society of Chemistry. (c-e) General synthetic/deposition approaches used to obtain MHP materials as (c) nanocrystals (CsPbI$_3$), (d) thin-films (MAPbI$_3$), and (e) single-crystals (MAPbBr$_3$). The single crystals shown in Figure 1e were adapted with permission from ref 10. Copyright 2018 Elsevier Ltd.

The progenitor and the current benchmark of contemporary photochemistry is titanium (IV) oxide (TiO$_2$).$^{11,12}$ Although TiO$_2$ was the first reported semiconductor to demonstrate all the necessary functions to split water under ultraviolet (UV) irradiation, its large bandgap of ca 3.2
eV inherently limits the utilizable solar photons to the high energy tail of the solar spectrum (~8% of the total available irradiance). The search for alternative semiconductors with improved photoconversion efficiencies has unveiled a wide range of oxide-, chalcogenide- and nitride-based binary, ternary, and quaternary semiconductors as suitable photocatalysts. The ABO₃ and AB₂O₄ semiconductors commonly exhibit a wide bandgap, which can theoretically sustain a wide range of redox reactions but, similarly to TiO₂, also limits their activity to the UV spectral region. Meanwhile, ABO₄, ABO₂, and aurivillius oxides and ternary chalcogenides are photoactive in the visible spectral range, but often do not present appropriate band edge energy levels to catalyze many important reactions, such as water splitting or CO₂ reduction.

This natural trade-off between visible light activity and a photocatalyst’s capacity to sustain redox reactions over a wide range of potentials is one of the major limitations of any photocatalytic system based on a single semiconductor, regardless of composition. This limitation is depicted in Figure 2, where the relationship between the total absorption from the AM1.5G solar spectrum and a photocatalyst’s photochemical potential upper limit is shown. A promising strategy designed to overcome this limitation is based on the combination of photocatalysts within a so-called Z-scheme heterostructure. This architecture requires multiphoton absorption and selective recombination of low-energy photocarriers to permit high redox potentials without the compromise of light absorption (vide infra). As such, the direct Z-scheme heterojunction is a novel and powerful strategy to suppress charge carrier recombination and to promote efficient charge separation in photocatalysts.
Figure 2. The solar spectrum absorption limit of different photocatalysts versus their photochemical potential limits as defined by their optical bandgaps. Included are indicators of the thermodynamic potential for water splitting ($E_{H_2O}^{0} = 1.23$ V at 298 K) and what is deemed a standard photochemical cell potential when accounting for overpotentials ($E_{H_2O} \approx 1.70$ V). For this reaction, single photocatalysts (PC) and those in type-II heterojunctions exhibit a practical solar spectrum absorption limit of ca 55%. Owing to its selective low-energy carrier recombination at the heterojunction, the Z-scheme architecture enables lower bandgap materials to be harnessed without compromising the photochemical potential limit, thus providing the prospect to go beyond this absorption limit.

Heterostructure photocatalysts employing this concept have been investigated utilizing a number of traditional semiconductors for different photochemical reactions, including CO₂ reduction,¹⁵ water splitting,¹⁶,¹⁷ and degradation of organics.¹⁶,¹⁷ For example, Low et al. identified a recyclable direct Z-scheme TiO₂/CdS composite film fabricated by the deposition-precipitation method.¹⁸ In this system, the highest photocatalytic conversion rate of CO₂ to CH₄ reached ca 12 mmol h⁻¹ m⁻², which was approximately 3.5 and 5.4 times larger than pure TiO₂ and CdS, respectively. Researchers have also explored two-dimensional (2D) layered materials, in
particular the three-dimensional (3D)-SiC/2D-MoS$_2$ heterojunction system within a direct Z-scheme. This composite exhibits a high charge carrier mobility due to its marigold flower-like morphology, which enables effective Z-scheme charge transfer and enhances charge separation characteristics.

When tested for the photocatalytic CO$_2$ reduction coupled to H$_2$O oxidation, 3D-SiC/2D-MoS$_2$ sustained CH$_4$ and O$_2$ evolution at the rates of ca 7.9 and 15 mmol g$^{-1}$ h$^{-1}$, respectively. Under continuous reaction conditions, the CH$_4$ yield rate was further enhanced up to 62 mmol g$^{-1}$ h$^{-1}$, with stable operation during cycling over a 40 h period.

Importantly, the materials pairing plays critical roles in defining the nature of the heterojunction and these performance characteristics. For example, the combination of 2D/2D Co$_3$(PO$_4$)$_2$/g-C$_3$N$_4$ forms a type-II heterojunction with a photocatalytic H$_2$ generation rate of ca 0.38 mmol g$^{-1}$ h$^{-1}$. This rate is significantly lower than those of g-C$_3$N$_4$-based direct Z-scheme systems such as g-C$_3$N$_4$/W$_{18}$O$_{49}$ (ca 8.6 mmol g$^{-1}$ h$^{-1}$) and g-C$_3$N$_4$/WO$_3$ (ca 3.1 mmol g$^{-1}$ h$^{-1}$). Thus, careful material selection to support appropriate pairing is critical for the successful formation of a direct Z-scheme type heterojunction.

These considerations bring MHPs into the picture as a potentially highly useful class of semiconductors that provides the necessary optical tunability across the visible spectrum and electronic properties to satisfy the requirements of an efficient photocatalytic system. In this Perspective, we explore the use of MHPs as photocatalysts, in particular focusing on the emerging Z-scheme architecture. Although Z-schemes can be achieved using spatially separated semiconductors with a suitable redox shuttle completing the charge-transfer or can present two semiconductors that are intimately connected through a heterojunction, in this Perspective, we
predominantly focus on the latter “direct” Z-scheme. We first provide a brief overview of the general principles of a Z-scheme and analyze material requirements in terms of a basic charge-management model. Further, we summarize recent developments in the construction of MHP-based Z-scheme systems. Finally, we provide our comments and outlook on the most promising application domains and future developments in the field.

PHOTOCATALYTIC SYSTEMS
The key functions of any photocatalytic system are light absorption, photoinduced charge separation, photocarrier transport, and interfacial charge transfer/reaction.22 Stand-alone photocatalysts undergo these processes within the bulk of a single material (Figure 3a). While offering simplicity, such systems do not provide intrinsic mechanisms for the suppression of the recombination of photogenerated charges and offer limited control over the spatial separation of the oxidative and reductive half-reactions. Meanwhile, heterostructured photocatalytic systems enable the mediation of the redox reaction pathway through effective separation of photogenerated carriers across two different semiconductors, each supporting only one of the half-reactions.

The nature of the heterostructure is fundamentally dictated by the degree of charge transfer across the interface, which, in turn, dictates the extent of interfacial band bending and the relative energy level alignment. Traditional photocatalytic systems have utilized a type-II offset heterojunction (Figure 3b). This electronic structure supports photogenerated electrons and holes with high relative energy to transfer across the heterojunction to lower energy levels. Although this structure inherently reduces the rate of recombination, its major limitation is significant energy loss (Figure 3b). This loss in the available photovoltage compared to a stand-
alone photocatalyst limits the achievable redox potentials and the applicability of these heterostructures for photocatalytic processes with a high $\Delta G$ in excess of 2.0 eV, such as CO$_2$ reduction coupled to the oxidation of water or organic molecules.

To drive such energetically demanding photocatalytic processes, Z-scheme heterojunctions have been designed.$^{14}$ These photocatalytic architectures provide a mechanism for the selective interfacial recombination ($v_z$) of low relative energy photogenerated carriers at the junction (Figure 3c). Through this approach, the high energy carriers that are sustained within the conduction bands ($v_{CB}$) or valence bands ($v_{VB}$) of the individual semiconductors can support a redox process with $\Delta G$ that is significantly higher than that defined by the individual bandgaps of each semiconductor. Thus, the Z-scheme heterostructure both increases the internal potential to drive the photochemical reactions and provides a mechanism to separate photogenerated charges spatially. The broader operating considerations for optimal Z-scheme systems require enhancing the rates of the desired redox reactions ($v_{ox}$, $v_{red}$) and the absorption of light in both semiconductors ($v_{hv1}$, $v_{hv2}$) while decreasing the rates of the undesirable radiative charge recombination inside the individual semiconductor components ($v_{SC1}$, $v_{SC2}$) and charge transfer of high energy carriers across the junction between conduction bands ($v_{CB}$) and valence bands ($v_{VB}$). Underlying these considerations are several essential criteria that need to be achieved:

1. Balanced generation of photocarriers in both semiconductors ($v_{hv1} = v_{hv2}$).
2. Diffusion lengths ($L_D$) of the photogenerated charge carriers need to be sufficiently high to enable these carriers to reach both the heterojunction and the reaction surface (resulting in lower $v_{SC1}$, $v_{SC2}$).
3. Sufficiently long charge carrier lifetime and/or an efficient catalytic surface to facilitate half-reactions at the photocatalyst surfaces ($v_{ox}$, $v_{red} >> v_{SC1}$, $v_{SC2}$).
4. Heterojunction between the two semiconductors that supports selective recombination of low energy charge carriers across the junction ($v_Z \gg v_{CB}, v_{VB}$).

![Figure 3: Simplified generic energy level diagrams of a photocatalytic process sustained by a (a) single semiconductor (SC), (b) traditional type-II heterojunction system, and (c) direct Z-scheme heterojunction system. Red arrows indicate radiative recombination, while black and blue arrows show electron and hole transfer pathways, respectively. Dotted line indicates junction.](image)

In Figure 4, we include an idealized schematic of a direct Z-scheme architecture. Evidently, appropriate selection of complementary materials that are integrated within a heterostructure with appropriate length scales to achieve all of the above conditions predicates successful Z-scheme operation. Specifically, the optimal dimensions of each semiconductor should not exceed corresponding $L_D$ values to minimize losses in efficiency. Therein lies the challenge and opportunity for exploring new material combinations that support photocatalytic processes driven by parts of the electromagnetic spectrum which are not accessible to single semiconductor photocatalysts or heterojunction systems other than Z-scheme.
**Figure 4.** Schematic depiction of a direct Z-scheme photocatalytic system. In the process, light is absorbed within both semiconductor I (SC I) and semiconductor II (SC II) to form electron (e⁻) and hole (h+) carriers that diffuse to the recombination or redox active interfaces.

**OPTOELECTRONIC PROPERTIES OF PHOTOCATALYSTS**

The absorption properties, energy levels, and diffusion lengths of some common photocatalytic materials that have successfully been used in Z-scheme architectures are schematically compared with those of several traditional MHPs in **Figure 5** and summarized in **Table S1**. From **Figure 5a**, we observe that existing candidates typically have optical bandgaps ($E_g$) of more than 2.5 eV, with some exceptions being MoS$_2$ crystals, a prominent layered material, and CdSe ($E_g \sim 1.7$ eV; not shown). This trend is consistent with the fact that most photocatalytic systems have been focused on single semiconductors or type-II heterojunctions, thus requiring high bandgaps to support any useful redox reactions. Furthermore, the absorption coefficients ($\alpha$) of most candidates are $>10^5$ cm$^{-1}$ above their direct $E_g$, which results in their absorption lengths ($1/\alpha$) being $\sim$100 nm or less. Graphitized carbon nitride (g-C$_3$N$_4$) in this regard is the exception, with very low $\alpha$ of less than $10^4$ cm$^{-1}$ across the visible region.$^{23}$ As can be seen, traditional MHPs are
also good absorbers, with direct optical bandgaps being heavily dependent on the halide selection. Notably, for the lower bandgap MHPs, such as MAPbI$_3$ and FAPbI$_3$, $\alpha$ is reduced to $\sim 10^4$ cm$^{-1}$ at the absorption band-edge, thus requiring larger absorption lengths of $\sim 1000$ nm compared to their Br and Cl derivatives at $\sim 100$–200 nm.

The suitability of these material candidates for targeted photochemical reactions is further dictated by how their valence and conduction band edge positions straddle the relevant reduction and oxidation redox potentials. Figure 5b presents a comparative overview of the relevant energy levels of the common photocatalysts and MHPs depicted in Figure 5a, together with selected redox processes of academic and applied interest. Given that the photocatalyst’s energy levels in an operating photochemical system are dependent on numerous parameters, including solvent, pH, light intensity, processing conditions, etc.,$^{24}$ we have included herein values derived for single crystals or thin films only as a high level benchmark. It is noted that even for a single material under comparable preparation methods, such as MAPbI$_3$, reported ionization energies range between 5.1 and 6.6 eV,$^{25}$ with X-ray photoelectron techniques always yielding much higher values than measurements undertaken under ambient conditions using electrochemical techniques or photoelectron spectroscopy in air. As such, making a direct comparison should be done with care. Nonetheless, the trends indicate that many of the successfully used photocatalysts have deep valence bands, which inherently makes them $n$-type,$^{26}$ and enables their use in a variety of energetically demanding oxidation reactions, including that of H$_2$O or alcohols, while being less favorable for energetically demanding reduction processes, such as that of CO$_2$, O$_2$, and H$^+$. However, exceptions exist, with g-C$_3$N$_4$ being a highly prospective candidate for these latter reaction types.$^{27}$
In comparison, the electronic levels offered by MHPs provide broad tunability, with the valence and conduction bands being dictated by the hybridization of the lead and halide lattice ions.\textsuperscript{2} Subtle changes are noted for variations to the $A^+$ cations, with these arising from modifications to the lattice volume and structural distortion rather than direct bonding contributions.\textsuperscript{28} These bonding characteristics entail bromide and chloride MHP derivatives exhibiting conduction band levels of between -3 to -4 eV \textit{versus} vacuum. These conduction band levels make them lucrative alternatives to g-C\textsubscript{3}N\textsubscript{4}, which, while exhibiting good stability and electronic levels, suffers from unfavourable absorption characteristics.

Following absorption, a key aspect of the operation of a Z-scheme architecture is that photogenerated carriers reach the surface and heterojunction before recombining (Figure 4). To contextualize the practical limitation of carrier diffusion lengths, we consider that the average diffusion length of an electron or hole carrier in a semiconductor is determined from $L_D = \sqrt{D\tau}$, where $\tau$ is the recombination lifetime of the neat material and $D$ is the diffusion coefficient of the carrier.\textsuperscript{29} Under low carrier concentrations relative to the band-edge density of states, the diffusion coefficient can be approximated through the classical Einstein relation, $D = \frac{\mu_e/k_B T}{q}$, where $\mu_{e/h}$ is the electron (e) / hole (h) mobility, $k_B$ is the Boltzmann constant and $T$ is temperature. Alternatively, $D$ can also be extrapolated directly from photoluminescence quenching experiments.\textsuperscript{8} We have collated literature values of $\mu$, $\tau$, and/or $D$ to summarize the $L_D$ of the various photocatalysts and MHPs shown in Figure 5.
Figure 5. (a) Absorption coefficients, (b) energy levels, and (c) carrier diffusion lengths of various semiconductors that have been used in Z-scheme photocatalytic schemes, including TiO$_2$, BiVO$_4$, SrTiO$_3$, α-Fe$_2$O$_3$, WO$_3$, MoS$_2$, CdS, and g-C$_3$N$_4$ and selected lead halide perovskite materials, including MAPbCl$_3$, MAPbBr$_3$, FAPbBr$_3$, CsPbBr$_3$, MAPbI$_3$, FAPbI$_3$, and MAPbBr$_3$. These values are all tabulated in Table S1. As a compendium to (b) are a list of various reduction (r) and oxidation (o) reactions for electrochemical processes that are considered important. These reactions are tabulated in Table S2.

Where possible, we have considered these values for single crystals. We note that enhanced defects due to disorder and impurities will reduce these values in typical catalytic systems. This
arises because the (minority carrier) recombination lifetime for a semiconductor can be related directly to the defect density, \(N_t\), through \(\tau \propto 1/N_t \sigma\), where \(\sigma\) is the capture cross-section of the defect.\(^\text{29}\) Evidently, materials with low defect capture cross-sections and defect concentrations afford the longest carrier recombination lifetimes. A qualitative comparison of these defect characteristics can be evidenced from the band-edge absorption gradient, which defines the Urbach energy.\(^\text{30}\) The Urbach energy for MHPs is significantly lower (~15–30 meV) than that of most of the existing photocatalysts (>30 meV), which is indicative of the enhanced structural quality and more optically benign nature of defects in the halide perovskites.\(^\text{31}\)

In photocatalytic systems, the minority carrier diffusion length limits the photocurrent in absorption regions away from interfaces where band banding is limited. As such, for most of the studied metal oxide photocatalysts, the distinctly low hole diffusion lengths of ~10\(^2\) nm or less provide practical limitations to the physical dimensions of these materials candidates. These limitations arise from the difficulty in controlling oxygen levels, which inherently introduce localized impurity states that trap photogenerated carriers and increase recombination,\(^\text{32}\) and the localization of carriers as small polaron, which dramatically lowers their carrier mobilities to less than 1 cm\(^2\) V\(^{-1}\).\(^\text{33}\) Therefore, although many traditional oxide systems are attractive due to their potential chemical stability, these electronic limitations make alternative candidates, such as MoS\(_2\), CdS, and g-C\(_3\)N\(_4\) prospective. In comparison, the nearly equivalent carrier mobilities and long carrier recombination lifetimes of traditional MHPs translate to exceptional \(L_D\) of both the electrons and holes being more than 1 \(\mu\)m (see Table S1).\(^\text{34}\) Such long \(L_D\) are reflective of the low defect concentrations in single crystals of 10\(^{10}\)–10\(^{12}\) cm\(^{-3}\) compared to >10\(^{14}\) cm\(^{-3}\) for thin films.\(^\text{35}\) Nonetheless, through the use of appropriate additives during processing, carrier diffusion
lengths approaching 1 µm have been reported for low-temperature and solution-processed MHP coatings.\textsuperscript{8} This finding highlights that traditional MHPs possess among the best carrier transport properties of any known photocatalytic material system to date.

**METAL HALIDE PEROVSKITE Z-SCHEME PHOTOCATALYSIS**

To date, the advantageous optoelectronic properties of MHPs highlighted above have been harnessed within a range of photocatalytic applications,\textsuperscript{74} including several examples of the Z-scheme systems that have largely been applied to redox processes that couple the reduction of CO\textsubscript{2} with either water oxidation to oxygen or oxidation of organic compounds. Operational stability is one parameter that requires special attention in the design of the MHP-based photocatalysts. Water is often present in photocatalytic processes, either as a solvent, reactant, or adventitious admixture, and it is notoriously damaging to traditional MHPs.\textsuperscript{75} One strategy to increase MHP stability in aqueous solutions is to use the concept of dynamic equilibrium in aqueous HX solutions.\textsuperscript{75} Alternatively, and arguably more promising, is the operation of heterostructured MHP-based photocatalysts in organic\textsuperscript{62,76} and mixed aqueous-organic solvents.\textsuperscript{77} Highlighting the latter strategy, Wang \textit{et al.} used only a small fraction of water (2 vol.\%), which did not induce stability issues, presumably because H\textsubscript{2}O was consumed by photocatalytic oxidation to oxygen.\textsuperscript{77} To avoid negative effects of water completely, oxidation of organic compounds, such as isopropyl alcohol\textsuperscript{76}, benzyl alcohol,\textsuperscript{62} and ethyl acetate,\textsuperscript{78} in non-aqueous media can be introduced as an oxidative half-reaction.

A summary of the major works that have used MHPs in Z-scheme configurations compared to the performance of the corresponding individual components is given in \textbf{Table 1}. These reports focus on cesium or formamidinium (FA\textsuperscript{+}) lead bromides, which fulfilled the role of the reductive
semiconductors in the heterostructured systems. The choice of CsPbBr$_3$ and FAPbBr$_3$ against other archetypal MHPs provides a reasonable compromise between stability and optoelectronic properties. From a stability perspective, both materials are thermally, chemically, and/or structurally more robust than methylammonium-, tin-, or iodide-based MHPs, for example.$^{79,80}$ Meanwhile, CsPbBr$_3$ and FAPbBr$_3$ have $E_g$ values of 2.4 eV and 2.2 eV, respectively, which enable reasonable absorption across visible parts of the solar spectrum (Figure 2). Finally, these materials possess a sufficiently negative conduction band energy level to sustain the CO$_2$ reduction half-reaction and a reasonably positive valence band energy level to enable efficient Z-scheme coupling to a semiconductor that would fulfill the oxidative function (Figure 5b).

Complementing the CsPbBr$_3$ and FAPbBr$_3$ MHPs within the reported Z-schemes are the n-type semiconductors Bi$_2$WO$_6$ for direct Z-scheme and α-Fe$_2$O$_3$ (hematite) for all-solid-state Z-scheme, both of which have been intensively studied as components for heterostructured photocatalysts.$^{81,82}$ Wang et al. reported the formation of seamless heterojunctions between CsPbBr$_3$ “zero-dimensional” (0D) nanocrystals immobilized on Bi$_2$WO$_6$ 2D nanosheets through simple stirring and ultrasonication of a mixture of the pre-synthesized semiconductors (Figure 6a,b).$^{77}$ This spontaneous assembly was attributed to the formation of bismuth–bromine chemical bonds between surface Br$^-$ ions of CsPbBr$_3$ and Bi$^{3+}$ cations in Bi$_2$WO$_6$. Localization of the reduction half-reaction to the CsPbBr$_3$ rather than Bi$_2$WO$_6$ surface by selective photodeposition of Pt nanoparticles revealed the electron transfer route in the heterojunction and suggested the Z-scheme operation.$^{83,84}$ This mode enabled an order-of-magnitude higher photocatalytic activity toward the reduction of CO$_2$ to CO coupled to the H$_2$ oxidation in ethyl acetate/water solution for the CsPbBr$_3$/Bi$_2$WO$_6$ heterojunction as compared to the MHP alone.
(Table 1 and Figure 6c). Although photocatalytic durability tests of four 2 h cycles showed a performance decrease of more than 20% for pristine CsPbBr$_3$, the combined heterostructure was much more stable, with a performance decrease of only 5%. The stability enhancement was considered to arise from a reduced photocorrosion of CsPbBr$_3$ due to the rapid extraction and subsequent recombination of photogenerated holes across the heterojunction with electrons from Bi$_2$WO$_6$.

Figure 6. (a) Schematic illustration and (b) transmission electron micrograph of CsPbBr$_3$ “zero-dimensional” (0D) nanocrystals immobilized on Bi$_2$WO$_6$ two-dimensional (2D) nanosheets; yellow dashed circles highlight CsPbBr$_3$ nanocrystals. (c) CO and CH$_4$ yield rates during the CO$_2$ photoreduction / H$_2$O photooxidation over 0D/2D CsPbBr$_3$/Bi$_2$WO$_6$ and its individual...
components. Inset shows qualitative band energy diagram of the Z-scheme. (a–c) Adapted from ref 77. Copyright 2020 American Chemical Society. (d) Elemental mapping of the 2D/2D CsPbBr3/Bi2WO4 Z-scheme photocatalyst. (e) Atomic force microscopy image and (f) surface potential across the interface between the CsPbBr3 and Bi2WO4 nanosheets. (g) Hypothesized diagram of the charge carrier dynamics at the heterojunction of the 2D/2D CsPbBr3/Bi2WO4 system and qualitative energy diagram of the Z-scheme. (h) Product yield rates during photocatalytic CO2 reduction / isopropanol oxidation over the 2D/2D CsPbBr3/Bi2WO4 system and its individual components. (i) Stability of the 2D/2D CsPbBr3/Bi2WO4 system over five 6 h operation cycles. (d–i) Adapted with permission from ref 76. Copyright 2020 Wiley-VCH GmbH.

The possibility of combining Bi2WO6 and CsPbBr3 in a Z-scheme system was corroborated by Jiang et al.,76 who also demonstrated enhanced photocatalytic CO2 reduction, although now coupled to the oxidation of isopropanol in a fully organic mixed solvent. Arguably, the most distinct feature of their study was the implementation of stacked layers of the two semiconductors as very thin sheets (Figure 6d). Electron migration from CsPbBr3 to Bi2WO6 upon hybridization was suggested based on the analysis of binding energies from X-ray photoelectron spectroscopy. The use of electron paramagnetic resonance analysis to explore the electron transfer direction extended insights into the CsPbBr3/Bi2WO6 heterojunction and supported the Z-scheme charge transfer route in the system. Further evidence was provided using photo-assisted Kelvin probe force microscopy to study the surface potential distribution at the interface of both nanosheet components (Figure 6e). An increase in the surface potential across this interface under illumination was observed (Figure 6f). This finding presents an appealing photocatalytic heterojunction configuration utilizing the Z-scheme as it maximizes the surface areas of the heterojunction and catalytically active interfaces (Figure 6g). The latter was verified with the CO2 conversion yield being shown to increase 5-fold for the hybrid as compared to
pristine CsPbBr$_3$ nanosheets. Notably, the performance was further increased to 12-fold in conjunction with a Pt catalyst, which was selectively photodeposited on the CsPbBr$_3$ surface (Figure 6h). The latter was demonstrated to be stable during five 6 h cycles (Figure 6i). A direct performance comparison between the reported 2D/2D and 0D/2D CsPbBr$_3$/Bi$_2$WO$_4$ systems is complicated by the different media and oxidative half-reactions used by Jiang et al.\textsuperscript{76} and Wang et al.\textsuperscript{77}

Table 1. Summary of reported metal halide perovskite (MHP)-based Z-scheme photocatalytic systems, all of which were designed for the CO$_2$ reduction.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Semiconductor System</th>
<th>Irradiation</th>
<th>Medium</th>
<th>Photo-electron consumption rate $\mu$mol g$^{-1}$ h$^{-1}$</th>
<th>CO $\mu$mol g$^{-1}$ h$^{-1}$</th>
<th>CH$_4$ $\mu$mol g$^{-1}$ h$^{-1}$</th>
<th>H$_2$ $\mu$mol g$^{-1}$ h$^{-1}$</th>
<th>Oxidation half reaction</th>
<th>Stability</th>
<th>Ref</th>
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<tbody>
<tr>
<td>CsPbBr$_3$ QD/ Bi$_2$WO$_6$</td>
<td>Direct Z-scheme</td>
<td>300 W Xe, 400 nm filter</td>
<td>Ethyl acetate/H$_2$O</td>
<td>114.4</td>
<td>48</td>
<td>2.3</td>
<td>-</td>
<td>Water oxidation</td>
<td>95% After 4 × 2 h</td>
<td>77</td>
</tr>
<tr>
<td>CsPbBr$_3$ QD</td>
<td>Single semiconductor</td>
<td>300 W Xe, 400 nm filter</td>
<td>Ethyl acetate/H$_2$O</td>
<td>12.3</td>
<td>4.3</td>
<td>0.5</td>
<td>-</td>
<td>Water oxidation</td>
<td>&lt;80% After 4 × 2 h</td>
<td>77</td>
</tr>
<tr>
<td>Bi$_2$WO$_6$</td>
<td>Single semiconductor</td>
<td>300 W Xe, 400 nm filter</td>
<td>Ethyl acetate/H$_2$O</td>
<td>30.4</td>
<td>0</td>
<td>3.8</td>
<td>-</td>
<td>Water oxidation</td>
<td>-</td>
<td>77</td>
</tr>
<tr>
<td>Pt-CsPbBr$_3$ NS/ Bi$_2$WO$_6$</td>
<td>Direct Z-scheme</td>
<td>150 W Xe, AM 1.5G</td>
<td>Ethyl acetate/isopropanol</td>
<td>324.0</td>
<td>17.2</td>
<td>34.4</td>
<td>7.4</td>
<td>IPA oxidation</td>
<td>&gt;95% After 5 × 6 h</td>
<td>76</td>
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<tr>
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<td>Direct Z-scheme</td>
<td>150 W Xe, AM 1.5G</td>
<td>Ethyl acetate/isopropanol</td>
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<td>9.4</td>
<td>14.3</td>
<td>1.8</td>
<td>IPA oxidation</td>
<td>-</td>
<td>76</td>
</tr>
<tr>
<td>CsPbBr$_3$ NS</td>
<td>Single semiconductor</td>
<td>150 W Xe, AM 1.5G</td>
<td>Ethyl acetate/isopropanol</td>
<td>26.6</td>
<td>4.6</td>
<td>2.0</td>
<td>1.0</td>
<td>IPA oxidation</td>
<td>-</td>
<td>76</td>
</tr>
<tr>
<td>FAPbBr$_3$ Bi$_2$WO$_6$</td>
<td>Direct Z-scheme</td>
<td>150 W Xe, AM 1.5G</td>
<td>Trifluorotoluene</td>
<td>340</td>
<td>170</td>
<td>-</td>
<td>-</td>
<td>Benzyl alcohol oxidation</td>
<td>&gt;80% After 5 × 4 h</td>
<td>62</td>
</tr>
</tbody>
</table>
The use of an organo–lead halide perovskite, viz. FAPbBr$_3$, in a Z-scheme photocatalytic system was recently reported by Huang et al. in the December issue of *ACS Nano*, again using Bi$_2$WO$_6$. The morphology of the designed photocatalyst can be described as 0D/2D, similar to the work by Wang et al., while the solvent and oxidative half-reaction were organic-based, similar to the work by Jiang et al. Huang et al. fabricated the FAPbBr$_3$/Bi$_2$WO$_6$ heterostructure by directly growing the perovskite on the bismuth tungstate surface through an antisolvent precipitation method, forming a semi-coherent heterointerface spanning over several unit cells (Figure 4d). X-ray photoelectron spectroscopic measurements suggested chemical and electronic interactions between the two components, with decreased and increased electron density in the FAPbBr$_3$ and Bi$_2$WO$_6$ components at the heterojunction, respectively. This interpretation is consistent with the findings of Jiang et al. for the CsPbBr$_3$-based material, and again supports the formation of an internal electric field that promotes electron transfer from Bi$_2$WO$_6$ to
FAPbBr$_3$ to facilitate the direct Z-scheme operation. The latter was supported by ultrafast transient infrared absorption studies employing selective excitation. The Z-scheme operation was confirmed through very low activity of the individual semiconductors for the target photocatalytic process as opposed to the measurable rates of the CO$_2$ reduction and oxidation of benzylalcohol to benzyladehyde, which was used as a sacrificial source of electrons (Table 1). The increase of the photocatalytic activity was suggested to be facilitated by the epitaxial heterojunction between Bi$_2$WO$_6$ and FAPbBr$_3$. However, in contrast to Wang et al. and Jiang et al., Huang et al. observed notable instability in their system, decreasing the photocatalytic performance by approximately 20% after five 5 h cycles. This instability was linked to the decomposition of the FAPbBr$_3$ exposed to the generated benzaldehyde, water, and irradiation. Particularly insightful was the investigation of the yield of the photocatalytic process as a function of the FAPbBr$_3$ to Bi$_2$WO$_6$ ratio in the composite photocatalyst. An increase of the perovskite fraction up to 12.5 wt.% improved the performance, but higher FAPbBr$_3$ loadings deteriorated the rate of the reaction. The authors ascribe this finding to excessive injection of charge, disrupted balance between internal electric fields, Coulomb repulsion, and potential difference at the interface, which together promoted the operation of the FAPbBr$_3$/Bi$_2$WO$_4$ as a classical “type-II” heterojunction photocatalyst (Figure 2c) rather than a Z-scheme system.

To promote the Z-scheme mode of operation, the interface between the two semiconductors can be improved through the inclusion of an additional component that might theoretically support the recombination of the relevant photogenerated charges. To date, this strategy has been tested for photocatalysts based on CsPbBr$_3$ and α-Fe$_2$O$_3$ combined with graphene-oxide-based materials as conductive supports connecting the two semiconductors. In their report on CsPbBr$_3$
nanocrystals and hematite rods immobilized on graphene oxide (GO) nanosheets, Mu et al.\textsuperscript{78} suggested that the simultaneous contact of both semiconductors to the conductive support promotes the migration of electrons from the surface of the perovskite to the oxide. It was suggested that this supports Femi energy level equilibration of the system and results in a built-in electric field at the CsPbBr\textsubscript{3}|GO|α-Fe\textsubscript{2}O\textsubscript{3} interface. The CsPbBr\textsubscript{3} to α-Fe\textsubscript{2}O\textsubscript{3} orientation of the built-in electric field might facilitate the photogenerated electron transfer through a Z-scheme pathway. A similar hypothesis was put forward for the amine-functionalized reduced GO that was used as the charge mediator between the same semiconductors.\textsuperscript{85} The critical role of the solid GO-based charge transfer/recombination component was circumstantially supported through significant improvements in the photocatalytic CO\textsubscript{2}-conversion yields with respect to individual semiconductors and the mixture of CsPbBr\textsubscript{3} and α-Fe\textsubscript{2}O\textsubscript{3} devoid of GO (Table 1).

Overall, the studies briefly surveyed above indicate the possibility of the integration of MHPs as components of the heterostructured photocatalysts operating in a Z-scheme mode. Among these studies, the formation of an epitaxial direct Z-scheme heterojunction showed the largest increase in performance as compared to the respective single MHP photocatalysts. Notably, all of these studies were published in 2020, reflecting the embryonic stage of the field and numerous possibilities for further improvements.

**PERSPECTIVES**

*Chemical Reactions of Interest*

In an ideal photocatalytic process, both oxidation and reduction half-reactions (Figure 3) would efficiently and durably sustain the formation of valuable products from an abundant and cheap feedstock. Systems that produce one high-value product with the counter half-reaction yielding a
harmless by-product are also useful. Systems that do not achieve these goals are of limited applied significance but instead can provide fundamentally important knowledge on the photocatalytic mechanisms through studies of model reactions. Such systems should not be discouraged, but accurately acknowledged for their particular contributions. Within this context, we look at the previously investigated photocatalytic reactions with MHPs and discuss possible applications where the Z-scheme architecture may be particularly beneficial.

**Reductive half-reactions.** Among the reductive processes, the conversion of carbon dioxide currently attracts significant attention due to its topical ecological significance, including in studies on the MHP-based Z-scheme (Table 1), as well as single semiconductor and traditional type-II (Table S3) photocatalysts. Subject to the availability of significant amounts of concentrated carbon dioxide, CO\(_2\) photoreduction can produce valuable products such as CH\(_4\) and other hydrocarbons or C\(_2\) compounds, all being more advantageous than the frequently observed CO (Tables 1 and S3).\(^8^6\) One approach to tune the selectivity and activity of MHP-based photocatalysts favorably is to change their chemical composition. For example, the distinctive feature of the FAPbBr\(_3\)/Bi\(_2\)WO\(_6\) Z-scheme system is the preferential selectivity of the CO\(_2\) reduction toward CO in contrast to the increased formation of more valuable CH\(_4\) when the CsPbBr\(_3\)/Bi\(_2\)WO\(_6\) system is employed (Table 1).

Studies on the individual and type-II MHP-based photocatalysts also reveal tentative trends in the activity and selectivity as a function of composition (Table S3). For example, the CO\(_2\) photoconversion yield rate increases upon partial anionic substitution of Br\(^-\) with Cl\(^-\), while doping of CsPbBr\(_{3-x}\)Cl\(_x\) by manganese (II) provides an even more significant improvement, although CO
production dominates in both cases. Apart from changing the chemical composition of the semiconductor itself, its surface can be modified with catalysts that have been specifically designed to promote the reaction of interest—an approach ubiquitously employed in classical photocatalytic and photoelectrocatalytic research. Indeed, aside from platinum, the modification of CsPbBr₃ with the CO₂-reduction catalysts Re(CO)₅Br(dcbpy) (dcbpy = 4,4′-dicarboxy2,2′-bipyridine) and Ni(tpy) (nickel complex with 2,2′:6′,2″-terpyridine, [Ni(terpy)₂]²⁺) provided a more than 20-fold increase in the conversion rate. An intriguing possibility that is yet to be investigated is the modification of perovskite semiconductors with simpler, inorganic CO₂ reduction catalysts, e.g. those based on copper, which are known to provide the best selectivity and yields toward the most valuable products.

From a practical perspective, the direct photoreduction of CO₂ in air without initial expensive capture and concentration processes presents another challenge due to the low concentration of the reactant and the presence of other compounds, whose reduction is much more thermodynamically and often kinetically favorable, i.e. O₂ and NOₓ. High-concentration CO₂ environments, such as gas exhausts, offer a more economical environment for operation, although present an obvious challenge in terms of light required for the photocatalyst operation. In contrast, high-performance electrochemical CO₂ reduction devices, which have recently been demonstrated to operate at high rates and are on the edge of commercialization, appear much better placed to be used at stationary flue gas exhausts to capture and to refine the concentrated CO₂. Theoretically, direct photochemical approaches may provide cost benefits owing to potential lower capital investments. To become long-term viable alternatives, their current low productivity and instability have to be resolved, while also
addressing the system design challenges around illumination within a waste gas environment, whether it be from an artificial or natural source.\textsuperscript{102}

Another commonly studied photocatalytic reductive process is the generation of H\textsubscript{2} from water. This process has been demonstrated to be possible with methylammonium lead iodide and bromide perovskites when high concentrations of HI or HBr are present to help stabilize the material (\textbf{Figure 7a, Table S4}).\textsuperscript{75,103–105} Operation in such solutions also means that the dominant oxidation reaction is I\textsuperscript{-}/Br\textsuperscript{-} to I\textsubscript{3}\textsuperscript{-}/Br\textsubscript{3}\textsuperscript{-}, which necessitates a nonabundant feedstock. Despite these demonstrations, hydrogen generation is simpler to achieve through electrolysis, operates at much higher rates with conventional photocatalysts and electrochemical processes, and is an extensively commercialized process. Given the issues above, MHP photocatalytic H\textsubscript{2} evolution is a prime example where fundamental insights are the main outcome given that its practical applicability is low.

The oxygen reduction reaction (ORR) is an important reaction in organic synthesis with generated superoxide ions O\textsubscript{2}\textsuperscript{-} able to function as bases, nucleophiles, oxidants, reductants, electron transfer shuttles, and free radicals.\textsuperscript{106} The ORR is usually coupled with equally important oxidation reactions in organic synthesis and will be discussed in more detail below. Beyond the reductive synthesis, other useful processes primarily belong to the domain of environmental remediation and include conversion of NO\textsubscript{x} to N\textsubscript{2}, highly toxic chromium(VI) to chromium(III), 4-nitrophenol to 4-aminophenol, and other related reactions. All of these reactions can be coupled to corresponding oxidative half-reactions that are also focused on remediation, some of which are discussed in the following subsection.
Figure 7. (a) Schematic illustration of MAPbI$_3$ in dynamic equilibrium with a saturated HI solution. Dotted lines represent dissolution and precipitation of MAPbI$_3$ crystal and ions. Adapted with permission from ref 75. Copyright 2020 Springer Nature Limited. (b) Schematic representation of the photocatalytic degradation mechanism of methylene blue by $\gamma$-CsPbI$_3$ nanocrystals and $\gamma$-CsPbI$_3$ nanocrystals with WS$_2$ nanoplates/sheets. Adapted from ref 107. Copyright 2020 American Chemical Society. (c) Scope of photocatalytic $\alpha$-alkylation of aldehydes by a hybrid (Cs$_x$MA$_y$)PbBr$_3$ photocatalyst. Adapted from ref 108. Copyright 2020 American Chemical Society.
**Oxidative half-reactions.** In traditional photo/electrosynthesis of fuels and chemicals, the oxygen evolution reaction (OER) is a common oxidation counter process to the desired reductive processes, such as H₂ evolution, CO₂ reduction, and, most recently, N₂ reduction.⁹⁹,¹⁰⁰ Although the OER enables the use of the cheap and abundant H₂O feedstock as a convenient source of electrons and protons, given the difficulties involving MHP stability in aqueous media mentioned above, and the applications where O₂ is only a by-product, it might be more beneficial to design systems that synthesize a more valuable commodity through the oxidation half-reaction.

One important application might be the degradation of pollutants, which is becoming increasingly important due to expanding industrialization, antibiotic treatments in health, and fertilizer use in agriculture. Photo/electrooxidative degradation of relevant organic pollutants usually occurs through the activation of oxygen, which then reacts with the target compound.¹¹¹,¹¹² This oxygen can be either in the form of chemisorbed O* on the surface of catalytic materials, such as Pt/Ru, or physisorbed O₂ on more inert surfaces, generated by the oxidation of water in both cases. In other words, these processes are inherently based on the OER, which is problematic for the photocatalytic systems based on the MHPs. An alternative is the degradation of pollutants in organic solvents, where promising results have been achieved using individual MHP photocatalysts (*Figure 7b, Table S5*).¹¹³⁻¹¹⁵ However, the overall concept of pollutant degradation in organic media is questionable, as this would require an additional step of extraction of the compounds to be oxidized from wastewaters, something that is unlikely to be technologically and economically feasible at this stage.
Even though material engineering might eventually enable stable operation of MHPs in aqueous environments, the intrinsic high toxicity of the best-performing (lead) halide perovskites will remain a critical counter argument. In essence, the utilization of such photocatalysts, which will always be prone to at least partial dissolution, would impose risks of further pollution of water streams with heavy toxic metals such as lead.\textsuperscript{116} Hence, it is important to develop and to improve nontoxic MHPs with high stability in aqueous environments for this application. This need seems to have already been recognized by some researchers who have focused on investigating less toxic, bismuth-based halide perovskite photocatalysts operating in aqueous solutions.\textsuperscript{117} It is noteworthy that researchers have succeeded in the integration of the Cs\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9} perovskite into a type-II heterojunction structure with TiO\textsubscript{2} to achieve significant enhancement in performance for the degradation of methylene blue in water under visible light irradiation (\textbf{Table S5}). This achievement might be the first step toward the creation of a Z-scheme system based on similar MHPs that will additionally enable the formation of a more useful product in the reductive half-reaction.

\textbf{Photocatalytic organic synthesis reactions.} Arguably, one of the most attractive photocatalytic prospects building upon the unique physicochemical properties of MHPs and their good stability in organic media is visible-light-induced organic photosynthesis.\textsuperscript{118} The intrinsic redox properties, as well as sharp absorption and emissions bands of MHPs can enable the targeted and specific photochemical interaction with reactive centers of organic molecules to induce a specific transformation selectively. To date, MHPs have been demonstrated to activate small molecules, such as CO, CH\textsubscript{4}, and NO, as well as to induce organic bond formation, oxidation, polymerization and dimerization under irradiation (\textbf{Table S6}).\textsuperscript{118}
One interesting example of halide perovskite use in organic synthesis reactions is the $\alpha$-alkylation of aldehydes (Figure 7c),\textsuperscript{108} a class of reactions established by the combination of organocatalysis and photocatalysis.\textsuperscript{119,120} In this case, the conventional process involves molecular noble metal (Ru or Ir)-based complexes for photocatalysis, whereas the use of much simpler and cheaper CsPbBr$_3$ enables a 3-orders of magnitude higher catalytic turnover number. Within this reaction class, MHPs show further advantages, such as minimal synthetic effort of production, ease of processability, and the possibility to activate a broader scope of organic compounds due to facile band edge-tuning.

In the example highlighted above, the photocatalytic reaction is essential; hence, the role and advantages of MHPs are clear. In other cases, such as the oxidation of toluene to benzaldehyde, both industrial and other nonphotocatalytic processes exist. Specifically, the industrial synthesis of benzaldehyde proceeds with the liquid phase air oxidation of toluene at elevated temperature (136–160 °C) and pressure (2–7 atm) using a soluble cobalt catalyst.\textsuperscript{121} Research is ongoing to improve on these nonideal conditions, for example, by the use of MnWO$_3$ catalysts that enable the reaction to proceed at a lower temperature (80 °C) but only when using H$_2$O$_2$ as an oxidant.\textsuperscript{122} In an alternative photocatalytic process, a MHP-based catalyst can support light-driven in situ reduction of O$_2$ to superoxide (O$_2^-$) and efficiently oxidize toluene to benzaldehyde under ambient conditions.\textsuperscript{123} This photocatalytic process provides a clear advantage over the traditional industrial process or the alternative MnWO$_3$-catalyzed reaction with expensive H$_2$O$_2$.

Although the studies above highlight justified selection of reactions for the development of useful photocatalytic processes promoted by MHPs, some other organic transformations investigated in
this context cannot be considered as value adding. Considering benzaldehyde as an example again, we note that it is widely used in organic synthesis as a raw material for a large number of products and its single largest use is in the production of benzylalcohol via hydrogenation. As such, photocatalytic systems that convert benzylalcohol to benzaldehyde, as some of those listed in Table 1 and Table S6, appear to be counterproductive.

The key message is that not all synthetic organic reactions are equally important and, thus, should ideally be selected where useful and where MHPs have a competitive advantage. This evaluation rule includes the alkylation and toluene oxidation examples above, as well as industrially relevant photooxidation of alcohols (other than benzylalcohol) to corresponding aldehydes, ketones, or carboxylic acids; decarboxylation; dehydrogenation; and other photocatalytic reactions, for example the oxidative valorization of biomass. Implementation of the photocatalytic process provides some key advantages from the perspective of green chemistry principles, in the first place through the replacement of the conventional oxidants with green alternatives such as O₂. However, for the reactions where equivalent/competing industrial processes are in place, it is important to consider and to benchmark these in terms of efficiency, selectivity, stability, and other relevant metrics, including a robust way to compare conventional and photocatalytic approaches.

In summary, based on the considerations discussed above, we envisage that the most significant prospects for MHP photocatalysis exist in the organic synthesis domain. As one possible and highly desirable outcome, we envisage the development of the MHP-based Z-scheme systems with appropriately aligned energy levels to sustain processes that bring together selective CO₂ reduction
and organics oxidation to enable robust and efficient synthesis of useful products through both half-reactions.

**MHP Z-Scheme Design**

The ability of the Z-scheme to support high energy redox reactions while utilizing a significant portion of the visible spectrum has already been demonstrated experimentally for several MHP-based systems (Table 1 and Figure 6). However, one of the challenges in the design of the Z architecture is that the charge transfer across the junction may not be equivalent, thus lending itself to the potential of a quasi-type-II behavior (Figure 3b). Huang et al. showed that such an unfavorable scenario may apply for the FAPbBr$_3$/Bi$_2$WO$_3$ Z-scheme system, when the relative amounts of the two semiconductors are not optimal (vide supra). Controlling the heterojunction properties to minimize/prevent high energy carrier transfer presents a major opportunity going forward. At a high level, this manipulation requires the judicious control of energy and Fermi level alignment. The former can be readily accommodated in MHPs through simple compositional tuning (e.g., halide modification). Meanwhile, tuning the Fermi level of MHPs is more complicated owing to their defect-tolerant nature, although extrinsic doping mechanisms through the incorporation of suitable ions, such as Na$^+$, Rb$^+$, Sb$^{3+}$, and Bi$^{3+}$ can enable both $n$- and $p$-type characteristics.

Interfacing these perovskite materials to suitable semiconductors in a Z-scheme lends itself to the next main challenge. Metal halide perovskites can exhibit substantial interface defect concentrations of $\sim 10^{16} - 10^{17}$ cm$^{-3}$, which necessitates the implementation of appropriate surface passivation to reduce interfacial recombination effects. This reduction can be achieved directly through surface ligand interactions, which has become common practice in photovoltaics, but is
yet to be well explored in photocatalytic applications. deQuilettes et al. showed that pyridine exposure of MAPbI$_3$(Cl) films can significantly impact their local carrier lifetimes, for example (Figure 8a–b). The use of bifunctional ligands, such as symmetric alkyl diammonium salts or more tailored ligand chemistries, might provide a good strategy to achieve passivation of the MHPs and chemical adhesion across the interface. An alternative approach is to control the synthetic conditions and structural material parameters to achieve epitaxial interfaces. Such interfaces have been demonstrated in 3D/2D MHPs structures, which have been shown to provide interfacial passivation of the bulk (i.e., 3D) MHPs, while also assisting in carrier extraction within solar cells and dramatically enhancing their stability. Meanwhile, semi-epitaxial formation between FAPbBr$_3$ and Bi$_2$WO$_3$ has been demonstrated in the above-mentioned Z-scheme system, albeit in a microstructurally uncontrolled manner (Figure 8c–f). While promising, developing a greater understanding into the requirements for and mechanism of epitaxially interfacing to MHPs is required to bridge interfacial quality, recombination dynamics, and photocatalytic activity of the heterostructure.
Figure 8. (a–b) Fluorescence images of a MAPbI$_3$(Cl) film (a) before and (b) after exposure to pyridine. The significant enhancement in light emission intensity following pyridine exposure arises from its surface passivation effects. Adapted with permission from ref 126. Copyright 2020 American Association for the Advancement of Science. (c) Transmission electron microscopy (TEM) of FAPbBr$_3$/Bi$_2$WO$_6$ direct Z-scheme photocatalyst particles with 12.5% FA/Bi ratio. (d) Structural scheme of the semi-coherent interface formed between FAPbBr$_3$ (red) and Bi$_2$WO$_6$ (blue). (e) High-resolution TEM image of the interface between FAPbBr$_3$ and Bi$_2$WO$_6$, as well as (f) the semi-epitaxial interface with the corresponding fast Fourier transfer pattern shown in the inset.$^{62,126}$ Adapted from ref 62. Copyright 2020 American Chemical Society.

As a final point on MHP Z-scheme design, many of the prominent studies to date have used pre-synthesized MHP nanocrystals or nanosheets that have been directly precipitated or adsorbed on complimentary Z-scheme photocatalysts with little in the way of precise structural control. Given the large diffusion lengths presented by traditional MHPs, there is an opportunity to harness larger
perovskite structures with dimensions of >100 nm without compromising the photocatalytic properties of the system. This possibility should be considered in parallel with controlled assembly of such MHP structures to achieve balanced absorption and reaction rates across both semiconductors forming the heterojunction. Achieving these goals requires more detailed investigations into the synthetic pathways of MHPs, likely departing from traditional homogeneous growth approaches, to those that are reliant on a heterogeneous mechanism in which low-defect MHP can be deposited with controllable size and spatial distribution on suitable supporting photoconductors. The structure and dimensions of the latter should also be optimized to ensure the most efficient generation and separation of the photogenerated charge carriers.

_Beyond Lead-Halide Metal Halide Perovskites_

General instability issues remain the Achilles’ heel for many applications harnessing traditional lead-halide MHPs. Toxicity concerns are also prominent, although likely less so for smaller scale specialized synthetic applications. Significant efforts have been made over the past several years to investigate nonlead alternatives to the traditional Pb-based MHPs, with numerous excellent reviews covering these topics in detail. In general, broad substitution approaches of the B-site using Sn(II), Ge(II), Sn(IV), Cu(II), Bi(III), and Sb(III) have been explored to yield a diverse range of optical properties (**Figure 9a**). Of these, Sn(II) and Ge(II) candidates, such as MASnX₃, FASnX₃, CsSnX₃, and CsGeX₃, have been shown to exhibit visible-to-NIR absorption with high absorption coefficients of >10⁵ cm⁻¹ and good transport characteristics. However, these materials are sensitive to moisture and oxygen, in part due to the oxidation of the B-site ion from a +2 to +4 valence state, which ultimately renders them unlikely substituents to lead-based MHPs for photocatalytic applications. Meanwhile, Sn(IV) perovskites, such as Cs₂SnX₆, present a more stable material class that adopts an antifluorite structure, where half the Sn are removed.
compared to CsSnX₃ to result in a 0D perovskite featuring isolated [SnI₆]⁺ octahedra (see Figure 9b). Although providing spectral tunability across the visible spectrum, this structural configuration modifies the main defect energies to reside within the band gap,¹³⁴ degrading optoelectronic properties compared to more traditional MHPs in which the dominant defects energy levels are in the valence band.²

Bi and Sb perovskites also typically exhibit 0D structures that take the chemical form of A₃Bi₂X₉ and A₃Sb₂X₉, respectively (Figure 9b). As a result, such material classes exhibit much larger Wannier-Mott exciton binding energies compared to their lead counterparts, as well as larger relative optical bandgaps (Figure 9c).¹²⁹ Nonetheless, numerous candidates can be identified that possess optical band gaps of ~2.0–2.2 eV, such as Cs₃Bi₂I₉, Rb₃Bi₂I₉, and MA₃Sb₂I₉, which are attractive for photocatalytic applications.¹³¹ Compositional and reaction engineering further provide the opportunity to tune the structural characteristics of such materials to achieve 2D or 3D perovskites structures, such as the 2D layered Cs₃Bi₂I₉¹³⁵ and AgBi₂I₇,¹³⁶ respectively. A compositionally related family of promising photoactive materials are silver–bismuth halides, which, while different from the perovskite structure, present many possibilities for tailored energy level tuning.¹³⁷,¹³⁸ This structural flexibility is attractive for achieving optimized redox and recombination interfaces in Z-scheme photocatalytic systems, for example, through the design of large interfacial and reactive surface areas provided by 2D materials.
Figure 9. (a) Summary of various bandgaps of lead and lead-free perovskite materials. Adapted with permission from ref 131. Copyright 2020 Springer Nature Limited. (b) Structure of a number of Cs-based lead-free perovskite candidates and relevant structural transition. CsSnI$_3$ and Cs$_2$SnI$_6$ adapted with permission from ref 134. Copyright 2020 Royal Society of Chemistry. Cs$_3$Bi$_2$I$_9$ and Cs$_2$AgBi(ClBr)$_6$ adapted with permission from ref 131. Copyright 2020 Springer Nature Limited. (c) Comparison of the absorption coefficients for different bismuth-based perovskites (top) and
the normalized absorptance and photoluminescence of \((\text{CH}_3\text{NH}_3)_2\text{Sb}_2\text{I}_9\) (bottom). Adapted from ref 139. Copyright 2016 American Chemical Society.

Double perovskites form the other material pathway to achieving lead-free perovskites, harnessing two nonequivalent \([\text{BX}_6]\) octahedra alternating in the 3D perovskite structure (Figure 9b).\textsuperscript{140,141} Studies on bi-perovskite systems, such as those based on \(\text{Cs}_2\text{B}^+\text{B}^{3+}\text{X}_6\) with \(\text{B}^+ = \text{Cu}^+, \text{Ag}^+\) and \(\text{Au}^+, \text{B}^{3+} = \text{Sb}^{3+}\) and \(\text{Bi}^{3}\), have shown broad spectrum tunability across the NIR and visible spectrum, making them attractive for photocatalytic applications.\textsuperscript{142} Among the most promising of such candidates to date is \(\text{Cs}_2\text{AgBiBr}_6\), which has a (defect-dependent) band gap between \(\sim1.7\) eV and \(2.2\) eV.\textsuperscript{143} Single crystal measurements have shown it to possess carrier mobilities of \(>11\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) with recombination lifetimes of up to \(660\) ns, yielding carrier diffusion lengths in excess of \(4\) \(\mu\)m.\textsuperscript{144} Despite these findings, detailed work in thin films has yielded electron diffusion lengths of only \(\sim30\) nm and hole diffusion lengths of \(>150\) nm.\textsuperscript{145} Thus, controlling the impact of \(\text{AgBi}\) and \(\text{Bi}_{\text{Ag}}\) antisites, which are considered deep defects in such systems,\textsuperscript{146} remains a major synthetic obstacle to the practical application of such materials.

Comparisons across all of these emerging perovskite candidates highlight a multitude of opportunities that exist for their application in Z-scheme photocatalytic systems. A notable caveat across these material classes is that they tend to exhibit higher Urbach energies (\(>30\) meV) compared to lead halide analogues due to their greater structural disorder (Figure 9c). This higher Urbach energy is reflective of their less benign defect structures, which detrimentally affect their electronic properties. Although such electronic deficiencies plague the application of most lead-free perovskites in photovoltaics,\textsuperscript{131} these effects are likely to be mitigated through well-designed photocatalytic systems harnessing nanostructuring. Moreover, the valence and conduction band
energies of such lead-free MHPs are generally displaced toward the vacuum; Cs$_3$Bi$_2$I$_9$ has a bandgap of $\sim$2.1 eV and exhibits the valence and conduction band energies relative to vacuum of -5.6 and -3.5 eV,$^{135}$ respectively, thus favorably providing greater reduction potential within Z-scheme architectures. Given that little has been done in applying such lead-free perovskites to photocatalytic systems, major opportunities exist for those that dare to explore.

**CONCLUSIONS AND PROSPECTS**

Photosynthesis is a globally scalable, sustainable, and low-cost route to selective and rapid chemical transformations. Its mere existence highlights the immense opportunities that photochemical systems can provide in our global decarbonization efforts and across the chemical sector, provided that significant developments around improved photochemical efficiency, stability, and reaction selectivity continue to be made. In this regard, the Z-scheme heterojunction has emerged as a photocatalytic system that stands out in its ability to support a broader range of redox potentials and to harness lower optical bandgap materials that can absorb more of the solar spectrum, compared to the more traditional single semiconductor and type-II photocatalytic systems.

In this Perspective, we provide an overview of the application of MHPs to the Z-scheme architecture. Although such perovskites have made indelible marks on optoelectronic devices due to their often remarkable properties, they are comparatively new in terms of applications in photocatalysis. The few examples reported of Z-schemes have solely been applied to CO$_2$ reduction coupled with water or organic compound oxidation. Significant scope exists to broaden this reaction base while also considering the need for more structurally and compositionally controlled MHP materials, as well as more idealized Z-scheme heterojunction interfaces. Moving beyond lead halide perovskites to ensure high stability and low toxicity of the designed
photocatalysts is a key future challenge. But given the immense efforts across the next-generation MHPs within photovoltaics, significant learnings can be borrowed. By doing so, the stage is set for what will certainly be an exciting next phase in the application of metal halide perovskites within photocatalytic systems, particularly those that harness the Z-scheme architecture.
ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supplementary tables (PDF)

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Notes: Views expressed in this Perspective are those of the author and not necessarily the views of the ACS.

Funding Sources

The research leading to these results has been funded by the Australian Government through the Australian Research Council Grants CE170100026, CE140100012 and FT200100317. E.M.A.
acknowledges funding by the Alexander von Humboldt Foundation through a Feodor Lynen Research Fellowship.
REFERENCES


(101) Pinaud, B. A.; Benck, J. D.; Seitz, L. C.; Forman, A. J.; Chen, Z.; Deutsch, T. G.; James, B. D.; Baum, K. N.; Baum, G. N.; Ardo, S.; Wang, H.; Miller, E.; Jaramillo, T. F. Technical and


(123) Zhang, Z.; Yang, Y.; Wang, Y.; Yang, L.; Li, Q.; Chen, L.; Xu, D. Revealing the A-Site Effect of Lead-Free A\textsubscript{3}Sb\textsubscript{2}Br\textsubscript{9} Perovskite in Photocatalytic C(sp\textsubscript{3})-H Bond Activation. Angew. Chem. Int. Ed. 2020, 59, 18136–18139. DOI: 10.1002/anie.202005495.


Christensen, C. K.; Etter, M.; Ederth, T.; Sun, L.; Simak, S. I.; Abrikosov, I. A.; Gao, F. Lead-
Free Halide Double Perovskite Cs$_2$AgBiBr$_6$ with Decreased Band Gap. Angew. Chem. Int. Ed.
2020. DOI: 10.1002/anie.202005568.
(144) Pan, W.; Wu, H.; Luo, J.; Deng, Z.; Ge, C.; Chen, C.; Jiang, X.; Yin, W.-J.; Niu, G.; Zhu,
Detectors with a Low Detection Limit. Nat. Photon. 2017, 11, 726–732. DOI: 10.1038/s41566-
017-0012-4.
(145) Longo, G.; Mahesh, S.; Buizza, L. R. V.; Wright, A. D.; Ramadan, A. J.; Abdi-Jalebi, M.;
Nayak, P. K.; Herz, L. M.; Snaith, H. J. Understanding the Performance-Limiting Factors of
Cs$_2$AgBiBr$_6$ Double-Perovskite Solar Cells. ACS Energy Lett. 2020, 5, 2200–2207. DOI:
10.1021/acsenergylett.0c01020.
(146) Xiao, Z.; Meng, W.; Wang, J.; Yan, Y. Thermodynamic Stability and Defect Chemistry of
Bismuth-Based Lead-Free Double Perovskites. ChemSusChem 2016, 9, 2628–2633. DOI:
10.1002/cssc.201600771.
Metal halide perovskites photocatalysts represent a relatively young yet rapidly emerging area.

The direct Z-scheme heterojunction is a novel and powerful strategy to suppress charge carrier recombination and to promote efficient charge separation in photocatalysts.

Following absorption, a key aspect of the operation of a Z-scheme architecture is that photogenerated carriers reach the surface and heterojunction before recombining.

Traditional metal halide perovskites possess among the best carrier transport properties of any known photocatalytic material system to date.

Arguably, one of the most attractive photocatalytic prospects building upon the unique physicochemical properties of metal halide perovskites and their good stability in organic media is visible-light-induced organic photosynthesis.

Not all synthetic organic reactions are equally important and, thus, should ideally be selected where useful and where metal halide perovskites have a competitive advantage.