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Photocatalytic Reduction of CO$_2$ by Halide Perovskite: Recent Advances and Future Perspectives

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ABSTRACT

Photocatalytic CO$_2$ reduction to generate energy-riching fuels through solar energy provides an attractive route to alleviate the global energy crisis and environmental concerns. Searching for various photocatalysts with high catalytic activity and selectivity for the transformation of CO$_2$ is the key strategy to accomplish this goal. Halide perovskite nanomaterials, with the advancements of facile synthesis, excellent light-harvesting, efficient exciton generation, long carrier diffusion length, and abundant surface sites, have great potentials in solar energy conversion. In this review, the fundamental photocatalytic mechanism for CO$_2$ reduction is firstly highlighted and the impact of the structural properties of halide perovskite is presented. Then, recent advancements of the reaction medium, halide perovskites (e.g., ABX$_3$ structure, A$_2$B'B"X$_6$ structure), and their composites (e.g., oxide, sulfide, carbide, metal-organic framework, noble metal, and carbon derivative) as photocatalysts, are described and analyzed. Finally, potential research approaches and future perspectives for the improvement of halide perovskite-based photocatalysts toward efficient CO$_2$ reduction are briefly discussed. This review sheds light on the coming innovative photocatalysts for CO$_2$ reduction into high value-added products.
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1. INTRODUCTION

Tremendous natural environmental changes have made people around the world increase crisis awareness when we are facing unprecedented nature. Great attention has been plunged into the depletion of natural resources and the impact of the emission of greenhouse gases on the environment due to the burning of fossil fuels.\(^1-4\) Solar-driven carbon dioxide (CO\(_2\)) conversion is an encouraging strategy to alleviate the negative effect of greenhouse gases,\(^5,6\) which uses artificial photosynthesis and photocatalysis of solar energy for carbon feedbacks and is also a straightforward and flexible pathway of CO\(_2\) valorization.\(^7,8\)

Since the landmark breakthrough in 1972, the pioneering work on ultraviolet (UV) driven photocatalytic production of hydrogen by TiO\(_2\) \(^9\) has spurred enormous interest and motivated decades of scientific research and progress, which are of particular importance for energy transformation (e.g., reduction of CO\(_2\) and water splitting), chemical transformations, and the decontamination of organic pollutants.\(^10\) During recent years, the rapid increase in CO\(_2\) concentration in the environment has drawn widespread concern.\(^11\) Extensive efforts have been devoted into stabilizing and controlling the concentration of CO\(_2\) in the environment, leading to CO\(_2\) capture and renewable energy production. Particularly, the state-of-the-art photocatalytic reduction of CO\(_2\) has been considered as one of the most promising ways.\(^12\)

From the perspective of long-term development, it is essential to explore the cost-efficient photocatalysts with outstanding properties and performances. An ideal photocatalytic material should possess wide-range and superior light absorption, effective charge separation, excellent stability as well as proper redox ability.\(^13\) Upon illumination, the photogenerated charge carriers are produced in the conduction band (CB) and valence band (VB) in semiconductors, respectively. When the energy structure of these semiconductors straddles the redox potentials, their photogenerated charge carriers would involve the surface
redox reaction. However, most pure semiconductors (g-C$_3$N$_4$, TiO$_2$, Cu$_2$O) as photocatalysts are far from the ideal state yet, because of various limitations, e.g., quick recombination of photo-generated charge carriers, large bandgap, and poor photoreduction potential. Hence, there is still huge demand to explore the low-cost, stable, and effective artificial photocatalysts for CO$_2$ fixation.

Recently, halide perovskites have drawn enormous attention in virtue of their excellent photoelectric properties, for example, long charge carrier diffusion length, adjustable bandgap, high absorption coefficient, and excellent external quantum efficiency.\textsuperscript{17-21} Due to these impressive characteristics and attractive properties, halide perovskites have been extensively employed in the fields of photoelectrical conversion,\textsuperscript{22} reduction reaction of CO$_2$, and hydrogen evolution reaction.\textsuperscript{23-27} These successful applications also encourage more applications in other traditional fields.\textsuperscript{28} Recent developments in the synthesis methods (e.g., hot-injection, ligand-assisted reprecipitation scheme, ultrasonic method, solvothermal method, microwave assistant, and ball milling)\textsuperscript{29-35}, have promoted halide perovskites marching to practical usage.\textsuperscript{36} Through controlling the production method, reaction temperature, capping ligand, and the additional reaction conditions, halide perovskites with variable chemical components (e.g., inorganic, organic, and inorganic hybrid), dimensions, sizes, and morphologies can be obtained.\textsuperscript{37-41} These efforts are expected to bring new opportunities for halide perovskite in the application of photocatalysis.

Halide perovskites has recently attracted great attention towards the reduction of CO$_2$ into high value-added products, from basic and theoretical researches to applied science.\textsuperscript{42-52} Shown in Figure 1 is a timeline of the development of halide perovskites as photocatalyst for CO$_2$ reduction.
Figure 1. The development of halide perovskites as photocatalyst for CO\textsubscript{2} reduction.

Up to now, there have been some review works of halide perovskites as photocatalyst focusing on the stability issues, or modification strategies through structural engineering and interfacial modulations.\textsuperscript{53-57} However, a timely and comprehensive review is still in demand concerning the photoreduction mechanism, reductants and products, the structure and photocatalytic performances, and the exploration efforts of halide perovskites and their composites for further improvements. In this review, we start with the basic mechanism of the photoreduction of CO\textsubscript{2}, and the reductants and products. After that, the fundamental photoelectrical properties of halide perovskites are described collectively, including their crystal structure, defect tolerance toxicity, luminescence properties, and photostability issues. Insights into the molecular calculations of halide based perovskites concerning their unique electronic structure and physio-chemical properties are also included. Then, we summarize the existing exploration efforts of halide perovskites and their composites in tuning the photocatalytic reduction of CO\textsubscript{2} selectivity as well as increasing the active sites. Finally, we
present the outlook for upcoming directions and the great potentials of halide perovskites toward photocatalytic CO$_2$ reduction.

2. PHOTOCATALYTIC MECHANISM FOR CO$_2$ REDUCTION

In the process of photocatalysis, the abundantly available solar energy is transformed into electrical/chemical/thermal energies through semiconductor materials.$^{13, 58-61}$ In general, the photocatalysis process for CO$_2$ reduction mainly consists of three critical synergistic steps, as illustrated in Figure 2. In the first step, photon absorption occurs to create electron-hole pairs. During this catalytic reaction, incident light induces the transition of electrons from the valence band (VB) to the conduction band (CB), leaving an equal number of holes in VB. Suitable band structure of photocatalyst is required to reduce CO$_2$ or oxidize water. While in the second step, a large number of fractions of photogenerated electron-hole pairs may be consumed by recombination. The recombination is dominant over charge separation or vice versa, depending on the relative time scale among the rate of recombination and photogenerated carriers. This issue can be resolved via a very complex interaction among dimension, surface properties, material crystallinity, and several other structural factors. The design of balanced active sites was utilized to facilitate charge separation. The final step is the CO$_2$ adsorption. This redox reaction involves the transfer of electrons from photocatalyst to CO$_2$ molecule. In general, larger surface area of the photocatalyst can lead to higher rate of CO$_2$ adsorption thanks to more active sites.$^{62-64}$ The photocatalytic activity is generally associated with two main conditions: (i) The bandgap energy ($E_g$) of the photocatalyst should be lower than the energy of the incident light ($h\nu$; the absorption energy). (ii) The reduction potential of the reacting species should be positioned between the CB and VB values of the photocatalyst material. The former condition specifies a narrower bandgap that can help the effective utilization of incident photon. Conversely, the later condition reveals that a higher value of CB potential and a lower value of VB potential are thermodynamically advantageous.
toward the reduction as well as oxidation reactions of the reacting species, respectively. Therefore, it is inevitable to seek the balance point owing to the existence of the noticeable inconsistency as discussed in the above conditions. However, this is quite a challenging task to obtain both broad light absorption and robust redox capability simultaneously for pure component semiconductor materials. Moreover, the photogenerated electrons in CB can easily recombine with holes, or be trapped in the defect state, or easily come back to the VB for a pure-component material, which would decrease the efficiency of solar energy utilization. Hence, designing a suitable heterogeneous photocatalyst is an effective approach to overcome the above-mentioned issues. Generally, there are four vital rules played by cocatalysts: (i) Enhancing the separation and transfer of charge, (ii) Boosting the performance, and the selectivity photoreduction of CO$_2$ reduction. (iii) Improving the durability of photocatalysts in the peculiar environment (e.g. high humidity and high temperature). (iv) Overwhelming the adverse reactions (e.g., H$_2$ reduction).

Figure 2. Schematic diagram of photocatalytic CO$_2$ reduction mechanism.

Photocatalytic reduction of CO$_2$ with semiconductor-based cocatalyst is affected by many aspects, for example, photocatalyst loading, particle size, structure, composition, dispersion, crystal facets, alloy phase, morphology, and valence states. In a photocatalyst system, the maximum photocatalytic performance is accomplished at an optimum loading of
cocatalysts. An additional loading of the cocatalyst may lead to deterioration of catalytic activity owing to the following factors. (i) Too much cocatalyst can hinder the incident light and reduce the light absorption ability, hence decrease the photogenerated electron-hole pairs. (ii) Excessive cocatalyst percentage could in turn shield the active sites on the surface of photocatalyst, therefore lessen the contact with H$_2$O and CO$_2$ molecules. (iii) Excessive loading may cause the irregular dispersion and formation of bigger particles, consequently reducing the catalytic performance.

A closed gas circulating reactor is usually used for photoreduction of CO$_2$, where the responded CO$_2$ decreased in the existence of semiconductors under continuous illumination.$^{66-71}$ Since the Gibbs free-energy ($\Delta G$) value for the reduction reaction of CO$_2$ to produce carbon monoxide (CO) is $\sim$258.95 kJ/mol, the bandgap of no less than 1.35 eV is needed. Then rapid separation and transfer of the photogenerated charge carriers to the particular catalytic active sites of the photocatalysts triggers the electrochemical reaction, resulting in chemical fuel. For photocatalytic reduction of CO$_2$ in the existence of water, the CB must be negatively paralleled to the reduction potential of CO$_2$ (-1.07 V vs. normal hydrogen electrode (NHE) for CO$_2$ reduction to CO at pH=0. Simultaneously, the VB should be larger than the oxidation potential of water (1.23 V vs. NHE at pH 0) to procedure O$_2$. Figure 3 displays the schematic presentation of the bandgap and band position of reported typical halide perovskite materials and CO$_2$ reduction potential.
Photocatalytic CO$_2$ reduction reaction is a high energy-driven process, because of the carbon-based compound that has a thermodynamically stable and high bond energy of C=O (750 kJ/mol). Therefore, the photocatalytic reduction reaction of CO$_2$ also needs prior activation. The process of mass transfer of reactants, CO$_2$ adsorption and creation of active sites for CO$_2$ reduction can be improved by increasing surface area of a photocatalyst. A large number of nanostructured materials for photocatalyst were developed to achieve larger surface areas, including zero dimensional (0D) nanoparticles, one dimensional (1D) nanowires/nanotubes, two dimensional (2D) nanosheets, and three dimensional (3D) hierarchical nanostructures. Furthermore, various porous and hollow materials were extensively studied for CO$_2$ conversion because of their increased surface area and porosity. The adsorption and activation of CO$_2$ can also be facilitated by tuning surface defects of photocatalysts, which can be quite helpful in improving the reactivity and photochemical properties of the photocatalytic processes. Strongly negative reduction potential is required for the activation of CO$_2$, which occurs on the surface of photocatalysts by chemisorption method to convert a linear molecule to bend carbonate anion radical (CO$_2$•–) via mono- or bi-dentate coordination. Hence, this reactive carbonate anion is the critical
factor for various photoreduction of CO$_2$. To create chains of hydrocarbons, more reactive CO$_2$• – species can promote reactions via two different ways (carbene and formaldehyde), as illustrated in Table 1. However, the obtained products are methane (CH$_4$) and the formation of some additional products (C$_1$-C$_3$ hydrocarbons) in the photocatalytic reduction of CO$_2$. Hori et al. suggested the conversion tracking of CO$_2$ to CO by reactive CO$_2$• –, subsequently the reaction with a proton. For the photocatalytic CO$_2$ reduction reaction, the selectivity of product formation is still challenging and relies on several factors, such as reaction intermediate, and active sites of the photocatalysts. The release of proton initiates these reactions in the presence of water vapor, H$_2$, or in both cases. These above-mentioned protons form different reduction products after reacting with CO$_2$ in the existence of photogenerated electrons. The efficiency of photoreduction of the CO$_2$ process can be manifested in terms of product formation rate and the conversion rate of CO$_2$. CO$_2$ reduction initiates with the formation of new carbon bonds by the cleavage of the O=C=O bond. Photocatalytic reduction of CO$_2$ is a proton-assisted multielectron reduction process that comprises various intermediate steps as shown in Table 1, for obtaining high-value products (e.g., CO, formic acid, methane, and methanol).

| Equation | Product | $E^0$ (V) |
|----------|---------|-----------|
| CO$_2$ + 1e$^-$ = CO$_2$• – | Carbonate anion radical | -1.90 |
| CO$_2$ + 2H$^+$ + 2e$^-$ = HCOOH (aq) | Formic acid | -0.61 |
| CO$_2$ + 2H$^+$ + 2e$^-$ = CO (g) + H$_2$O | Carbon monoxide | -0.53 |
| CO$_2$ + 4H$^+$ + 4e$^-$ = HCHO (aq) + H$_2$O | Formaldehyde | -0.48 |
| CO$_2$ + 6H$^+$ + 6e$^-$ = CH$_3$OH (aq) + H$_2$O | Methanol | -0.38 |
| CO$_2$ + 8H$^+$ + 8e$^-$ = CH$_4$ (g) + H$_2$O | Methane | -0.24 |
3. CRYSTAL STRUCTURE PROPERTY OF HALIDE PEROVSKITE

3.1. ABX₃ structure

Halide perovskites employed by photocatalytic CO₂ reduction facilitate band alignment with CB position and hinder the photogenerated charge carrier from undergoing recombination. For achieving the higher productivity and selectivity of halide perovskite nanocrystals (NCs) for photoreduction of CO₂, fundamental understandings of the relationships between the structure (chemical composition as well as morphology) and CO₂ selectivity need to be determined.⁸⁹ In this section, the impact stemming of halide perovskites from the unit cell will be reviewed. The unit cell is the simplest and smallest volume of a material. The properties of materials derive from special characteristics of the unit cell, e.g., the bond angle, bond length, and symmetry. Moreover, the diffusion lengths and lifetimes of charge carriers in optoelectronic materials are more affected by crystal boundaries and crystal defects.

One of the main chemical formulas of halide perovskites can be symbolized as ABX₃, where A and B represent two different kinds of cations and X represents halide anion (i.e., Cl, Br, and I). Cation B restricts at the median of the octahedron body composed of six halide anions (Figure 4a).⁹⁰-⁹² Conventionally, A and B are cations with 12- and 6-fold coordination with X anions at the corner in ABX₃ halide perovskites (Figure 4a), respectively.⁹³-⁹⁵ Recently, various high-performing perovskite materials were developed with A being formamidinium (FA), methylammonium (MA), or Cs; B being Pb, Bi, or Sn; and X being Cl, Br or I.⁹³-¹⁰⁶

When A site is employed with higher organic cations, low-dimensional halide perovskite structures may form, where the inorganic network connectivity has degenerated to 2D sheets, 1D chains, or 0D clusters (Figure 4b).¹⁰⁷ Conversely, the crystal symmetry will reduce and the cubic structure is distorted. In bulk lead halide perovskites, three polymorphs are usually
noticed: cubic, tetragonal, and orthorhombic phases in the order of decreasing symmetry (Figure 4a). At higher temperatures, the more stable phase is the cubic phase, and the temperature of phase transitions is clearly defined. For NCs, surface effects may regulate the relative stabilities of several polymorphs, which gains limited attention. All as-synthesized lead halide perovskite NCs crystallize into three-dimensional (3D) phases as follows: MAPbI$_3$ NC is tetragonal; FAPbBr$_3$, FAPbI$_3$, and MAPbBr$_3$ NCs are pseudocubic; and CsPbI$_3$ and CsPbBr$_3$ NCs are orthorhombic at room temperature. One of the most significant features of halide perovskites is their higher tolerance for defects. The nature of halide perovskites is defect-tolerant generally owing to their electronic band structure, where VB maximum is mostly composed of anti-bonding orbital, and the CB minimum becomes stabilized via the strongest spin-orbit coupling. Suchlike defect tolerance behavior involves the conservation of a pristine $E_g$ upon the formation of typical defects, due to their defect energy levels residing entirely in either VB or CB, rather than within the $E_g$ itself. The large hollow between octahedral (A-site) is preoccupied through one or a combination of three big cations (CH(NH$_2$)$_2^{2+}$, CH$_3$NH$_3^+$, or Cs$^+$), yielding generally the structure of ABX$_3$. The tolerance factor calculated by $t = (R_A + R_X) / \sqrt{2}(R_B + R_X)$ where $R_A$, $R_B$, and $R_X$ are the ionic radii of the corresponding ions, should be near to 1 to keep a higher symmetry cubical structure of the perovskite. Figure 4c presents the tolerance factors for the best widespread Pb or Sn halide perovskites. Due to the larger numbers of Pb or Sn atoms occupying the B sites of halide perovskites, the A site must be larger enough to placate the tolerance factor.
3.2. Luminescence properties

Halide perovskite NCs have excellent luminescence without advance electronic surface passivation. Protesescu et al. presented nearly ideal photoluminescence efficiency from colloidal CsPbBr$_3$ NCs.$^{32}$ The composition of lead halide perovskite NCs can be appropriately adjusted through cation or anion exchange, as shown in Figure 5a.$^{38}$ The photoluminescence spectra of lead halide perovskite NCs spans the whole visible light range and their peak positions are tunable through modifying the composition (Figure 5b), size, and shape.$^{92}$ Higher photoluminescence quantum yield with tunable emission, low cost, and simple synthesis of halide perovskite NCs makes them appealing in practical applications. However, the toxicity of lead, sensitivity to atmosphere condition (humidity, oxygen,
daylight, and temperature), and limited yield, still hamper further photocatalysis application of lead-based halide perovskite NCs. Halide perovskites have great photophysical properties, including high absorption coefficients, low trap densities, long charge diffusion lengths, and broadly tunable bandgaps. These properties allow light-harvesting from ultra-visible to the near inferred spectral range.\textsuperscript{46,112} Besides, the band positions of halide perovskites mostly fulfill the thermodynamic requirements for photocatalytic reduction of CO\textsubscript{2}.\textsuperscript{113}

**Figure 5.** (a) Schematic of the halide anion-exchange process. Reproduced with permission from ref. \textsuperscript{38} at https://pubs.acs.org/doi/abs/10.1021/acs.nanolett.5b02404, further permissions are directed to the ACS. (b) Photoluminescence spectra and the corresponding photographs (under varied daylight and UV excitation) of colloid composition-tuned APbX\textsubscript{3} NCs. From ref. \textsuperscript{92}, reprinted with permission from AAAS.

### 3.3. Other structure

The lead halide perovskite-based NCs with 3D APbX\textsubscript{3} crystal structure and composition have become the focus of much research interest up to now. However, the inherent toxicity and overall reactivity of these halide perovskites have also motivated the scientist to investigate it in various research directions. Firstly, the structural instability and higher ionicity of LHP NCs could usually be taken as a positive aspect, as APbX\textsubscript{3} lattice could be easily rationalized into other phases. This has motivated the researcher to investigate NCs more extensively by exploring their composition and structural characteristics that are defined as “perovskite-related structures”, for example Cs\textsubscript{4}PbX\textsubscript{6} and CsPb\textsubscript{2}X\textsubscript{5} (often called as zero-dimensional (0D) and two dimensional (2D) structures, respectively). Whereas, the
characterization of 3D APbX$_3$ structure was observed to have corner-sharing [PbX$_6$]$^{4-}$ octahedra with the A$^+$ cations filling the holes formed by four neighboring PbX$_6$$^{4-}$ octahedra ensuing in a cubic or pseudo-cubic structure (Figure 6a). The PbX$_6$$^{4-}$ octahedra in A$_4$PbX$_6$ structures are dissociated in all extents and the halide ions are no longer shared between them (Figure 6b). Layered perovskites have recently been under a lot of scrutinization process. Similar to that of layered double hydroxides containing alternating Cs$^+$ and [Pb$_2$X$_5$]$^-$ polyhedron layers, the CsPb$_2$X$_5$ has emerged as a 2D version of lead halide perovskite materials with a tetragonal phase (Figure 6c). Another type that is containing an alternating layer of corner-sharing [PbX$_6$]$^{4-}$ octahedra and bulky cations is known as the 2D perovskites A$_2$PbX$_4$ phase (Figure 6d).

Figure 6. Schematic illustration of different halide structures: (a) pseudocubic ABX$_3$ (3D) and (b) A$_4$BX$_6$, (c) AB$_2$X$_5$ (2D), (d) A$_2$BX$_4$, (e) A$_2$BX$_6$ (0D), (f) A$_2$B$^{+}$B$^{3+}$X$_6$ (3D), (g) A$_3$B$_2$X$_9$ (2D).
In APbX₃ NC systems, the lead toxicity and its bioaccumulation in the ecosystem are known as a key drawback, which in turn motivate the researcher to find out alternative materials with similar optoelectronic characteristics, such as Cs₂SnI₆ NCs.¹¹⁹-¹²¹ To date, there has been very little success. Cs₂SnI₆ crystallizes in the face-centered cubic structure. Four [SnI₆]²⁻ octahedra at the corners and face centers, and eight Cs⁺ cations at the tetragonal interstitials, make up the unit cell (Figure 6e). A Cs₂SnI₆ structure is a perovskite derivative that is made by removing half of the Sn atoms at regular intervals from each center of the [SnI₆] octahedron.¹²⁰ Because of this, the structure is also known as a "vacancy ordered double perovskite." Two primary techniques are now being explored in the search for lead-free metal halide compounds: a "simple" substitution of Pb²⁺ cations with other less toxic divalent metal ions from the same group IV, such as Sn or Ge; and a "complex" substitution of Pb²⁺ cations with other less toxic divalent metal ions from the same group IV,¹²² such as Sn or Ge or a substitution of one monovalent M⁺ and one trivalent M³⁺ cation for every two divalent Pb²⁺ ions (i.e., 2Pb²⁺ → B⁺ + B³⁺), resulting in quaternary A₂B⁺B³⁺X₆ systems also known as "double perovskites" in Figure 6f.¹²³ Other transition or post-transition metals, like Fe³⁺ and Bi³⁺, were used to examine the diversity of halide compounds associated to LHPs.¹²⁴-¹²⁷ Cs₃M₂X₉ (M = Fe³⁺, Bi³⁺) crystallizes in the hexagonal space group P6₃/mmc. This is made up of isolated clusters, each of which is made up of two face-sharing octahedra and has the M₂Br₉⁺ formula, with Cs⁺ acting as a bridging ion between the clusters. Antimony-based halide compounds, on the other hand, form in a layered shape with each Sb₂Br₉⁺ cluster sharing corners with three octahedra (Figure 6g).¹²¹
4. PERFORMANCE OF PHOTOCATALYTIC CO₂ REDUCTION

4.1. Reaction medium

Solvent plays a critical role in photocatalytic reactions. Halide perovskites are unstable in a polar solvent, therefore extensive researches have been accomplished to find a suitable medium for photocatalytic reduction of CO₂. Low-polar ethyl acetate was utilized as the solvent due to its higher solubility of CO₂, which guarantees durable stability for CsPbBr₃ NCs.⁴² Thereafter, various groups reported the boost in the selectivity of CO₂ conversion (99%) with the suppression production of H₂, with the addition of a small amount of water (˂ 50 µl) in ethyl acetate medium.⁴⁵, ¹⁰⁰, ¹⁰¹, ¹¹³ However, employing acetonitrile/water (0.3 vol. %) mixture showed a photocatalytic reduction of CO₂ with a high conversion rate (149 μmol g⁻¹ h⁻¹) of CO₂ to CO, compared to the ethyl acetate/water (0.3 vol. %) mixture upon light irradiation by using CsPbBr₃ NCs combined with porous g-C₃N₄. Moreover, enhanced selectivity, as well as productivity of the photocatalytic reduction of CO₂ was obtained with a high content of diluted water (1.2 vol. %).¹²⁸

Owing to several polarities, dielectric constant, and CO₂ solubility, the selection of solvent can exert a higher effect on the reaction rate and selectivity. The pairing of a robust co-catalyst is the key feature for enhancing the performance of photocatalysis. Meanwhile, it can not only separate the photogenerated electrons by the creation of Schottky junction within co-catalyst and photocatalyst to hinder the charge recombination, but also lower the kinetic bottlenecks in the activation of CO₂.¹²⁹, ¹³⁰ In the present case, the best nonaqueous solvent was ethyl acetate, which resulted in the reduction reaction of CO₂ with an electron yield rate of 2.74 μmol g⁻¹ h⁻¹ along with 95.2% of the selectivity. Furthermore, a photo-deposition of Pt co-catalyst boost the electron yield rate to 5.66 μmol g⁻¹ h⁻¹.¹³¹ Numerous additional solvents such as toluene, benzene, etc., were also explored for photocatalytic reduction of CO₂ as photocatalysis medium in halide perovskite NCs.¹⁰¹ Besides, owing to
reducing the formation of less active CO$_2$, higher hydration products and selectivity. Solid-vapor CO$_2$ reduction systems also remain very attractive. Mu et al. utilized hexafluorobutyl methacrylate to protect cobalt-doped CsPbBr$_3$/Cs$_4$PbBr$_6$ NCs for the photoreduction of CO$_2$ in the aqueous medium. They adopted pure water as a solvent, where water was used as a sacrificial reductant and electron sources. The content of 2% Co on the surface of the NCs (2%Co@CsPbBr$_3$/Cs$_4$PbBr$_6$) was employed to enhance the activity for photocatalytic reduction of CO$_2$. They proposed that Co$^{2+}$ acted as an active center to promote CO$_2$ absorption and accrued two electrons from CsPbBr$_3$/Cs$_4$PbBr$_6$, on account that that Co$^{2+}$ center formed Co-CO$_2$ complex and reacted with H$^+$ to facilitate the formation of CO.

4.2. Halide perovskite

4.2.1. ABX$_3$ structure

The conventional ABX$_3$ structure halide perovskites have various phases suchlike cubic,$^{132}$ monoclinic,$^{42}$ orthorhombic,$^{45}$ hexagonal,$^{98}$ etc. Recently, Xu et al. theoretically proved that CsPbBr$_3$ with cubic phase is an active catalyst for photocatalytic reduction of CO$_2$ in presence of benzene.$^{100}$ The usage of organic solvents makes it challenging to find out the product source. Meanwhile, organic solvents may have smaller molecules that support the final product. Research should be focused on the synthesis of water-stable CsPbX$_3$ NCs that can be utilized for catalytic reactions in water or other polar solvents. The water-resistance of CsPbX$_3$ will also encourage their application in various fields. Most of the reported photocatalytic reduction of CO$_2$ into CO and CH$_4$ were performed in the non-aqueous system employing orthorhombic-CsPbBr$_3$ NCs as photocatalysts. Guo et al. reported that CsPbBr$_3$ with cubic phase was more active than that for the orthorhombic ones because the phase transformation affects the efficiency of photocatalytic reduction of CO$_2$.$^{97}$ Recently, some perovskite materials with uniform cubic shape, such as FAPbBr$_3$ QD, have attracted much
consideration with long carrier recombination, along with the remarkable thermal, moisture, and illumination stabilities.\textsuperscript{133, 134} Que et al. developed FAPbBr\textsubscript{3} QDs with higher crystallinity as well as cubic shape by a hot injection method, which demonstrated high stability and the optimal yield of CO in the mixed solvent of ethyl acetate/deionized water. The results showed that FAPbBr\textsubscript{3} QD, as an alternative to halide perovskites, was a better reduction and capturing agent for CO\textsubscript{2} (Figure 7 a-c).\textsuperscript{51} Bandgap and band position are the major parameters for efficient photocatalysts. Therefore, tuning the bandgap energy of halide perovskites could also improve the catalytic activity. Hou et al. reported that, from the view of the different quantum sizes of CsPbBr\textsubscript{3}, 8.5 nm CsPbBr\textsubscript{3} NCs (~8.5 nm) reached the optimal yields of CO, CH\textsubscript{4}, and H\textsubscript{2} after 8 h of daylight illumination in ethyl acetate/water medium.\textsuperscript{135} For catalysis application, active facets for recanting species or products as well as the reduction of electron-hole recombination were facilitated to the efficient adsorption/desorption process. The highest production rate of CH\textsubscript{4} and CO was 7.6 and 16.4 \(\mu\text{mol g}^{-1}\), respectively, for the CsPbBr\textsubscript{3} cubic shaped NCs, which matched well with the previously reported literature.\textsuperscript{43, 99, 135} Conversely, the maximum activity was found to be higher for the hexapod nanostructures. The optimum yields of CH\textsubscript{4} and CO attained for hexapod NCs were 38.4 and 79.5 \(\mu\text{mol g}^{-1}\), respectively, as compared to 58.8 and 130.7 \(\mu\text{mol g}^{-1}\) for non-cubic NCs. The above-mentioned performance further demonstrated that poorly emitting non-cubic NCs that keep new facets showed a better photocatalytic activity as compared to the usual six-faceted cube nanostructures, as shown in Figure 7 d-f.\textsuperscript{136}
Figure 7. (a) Crystal structure of cubic FAPbBr$_3$ perovskite and (b) schematic band diagram of photocatalytic CO$_2$ reduction into chemical fuels for FAPbBr$_3$ QDs. Reprinted from ref. 51, Copyright 2021, with permission from Elsevier. (c) CO$_2$ reduction reaction by FAPbBr$_3$ QDs in DI, DI/EA, and EA system (data from ref. 51). (d) TEM and HRTEM images of non-cubes, hexapods, and cube-shaped nanostructures. (e) Schematic representation of the conduction and valance band position of CsPbBr$_3$ catalyst with the relative potential of CO$_2$ reduction. (d-e) Reprinted with permission from ref. 136, Copyright 2020 American Chemical Society. (f) Formation of CO and CH$_4$ from CO$_2$ reduction reactions using noncubes, polyhedrons, or hexapods photocatalyst (data from ref. 136).

4.2.2. Other structures

Lead-based halide perovskites are developing as the best encouraging type of materials for new-generation solar conversion energy. The metal-based halide perovskite (MHP) NCs is estimated to solve the problem affected via the usage of organic photosensitizers, and to form highly effective photocatalytic systems. Despite the considerable success, the key problems of stability and toxicity are yet to be fixed. The photostability of metal-based halide perovskites is usually low in the presence of molecular oxygen (O$_2$). The soft nature of MHPs crystal lattice renders their surfaces prone to structural modification and degradation. Previous research has indicated that a partial or complete replacement of A site organic cations with Cs$^+$ can result in many new MHPs compositions (all-inorganic chemical structure), which significantly promotes the photo- and humidity- stability. Some studies have shown that the ionization energy can be used to predict the stability of perovskite.
ionization energy difference between cesium and methylammonium provides stability to all-inorganic HPs. For example, CsPbBr$_3$ nanocrystals are more stable in polar solvents, which is promising for a wide range of photo-redox catalysis reactions.$^{143}$

Several approaches have been reported and applied to deal with the instability issues of MHPs. Examples include (i) replacing organic cations MA or FA with inorganic cations (e.g., Cs$^+$);$^{144,145}$ (ii) creating heterostructures to spatially separate photogenerated excitons;$^{99}$ and (iii) encapsulating halide perovskites to minimize direct contact with the highly polar environments.$^{45,93}$ In this context, the incident light absorption range for metallic complexes can be extended by coupling with halide perovskite NCs. Meantime, these metallic complexes are expected to be responsible for catalytic sites designed for halide perovskite NCs and capture exciting electrons from halide perovskite NCs for selective photoreduction of CO$_2$. Lead-free inorganic halide double perovskites were based on antimony or bismuth and noble metals.$^{33}$ Most halide double perovskites have been described to own a cubic face-centered structure, which has the space group Fm$\overline{3}$m and with a lattice parameter ranging from approximately 10-12 Å.$^{123,146}$ This new-type perovskite consists of B'Cl$_6$ and B"Cl$_6$ octahedral alternating in a rock-salt face-centered cubic structure. George Volonakis et al.$^{147}$ used first-principle calculations to observe the patterns in the electronic and optical properties in the whole family of double halide perovskites, A$_2$B'B"X$_6$ with A = Cs; B" = Bi, Sb; B' = Cu, Ag, Au; and X = Cl, Br, I. Their calculations showed highly tunable carrier effective masses as well as optical gaps across the visible-light range of the electromagnetic spectra.

Moving away from lead-based metal halide perovskites toward lead-free halide perovskites, Zhou et al. proved the photocatalytic reduction of CO$_2$ over double halide perovskite Cs$_2$AgBiBr$_6$ NCs in the presence of light in ethyl acetate.$^{44,148}$ The crystal structure of cubic Cs$_2$AgBiBr$_6$ NCs as well as constant advancement of CH$_4$ and CO on double halide perovskite Cs$_2$AgBiBr$_6$ NCs in the presence of solar light radiation is illustrated in Figure
Lu et al. reported that substitution of unsaturated oleic acid with saturated octanoic acid was hazardous to synthesize pure Cs$_3$Sb$_2$Br$_9$ NCs without the CsBr contamination as shown in Figure 8c.\textsuperscript{48} Cs$_3$Sb$_2$Br$_9$ NCs showed much higher efficiency of photocatalytic reduction reaction of CO$_2$, compared to Pb-based CsPbBr$_3$ NCs. For photocatalytic reduction of CO$_2$, a bound state is observed for COOH* on the surface of Cs$_3$Sb$_2$Br$_9$ NCs in which a Br ion is partially replaced to allow Sb–C bond formation as shown in Figure 8d.\textsuperscript{48} Dai et al. reported that the mesoporous silica-supported Cs$_3$Bi$_2$Br$_9$ NCs were developed. They observed that the Cs$_3$Bi$_2$Br$_9$ revealed outstanding photocatalytic properties in selective aromatic as well as non-aromatic C–H bond activation in the presence of sunlight.\textsuperscript{149} Moreover, several environmentally friendly MHPs, such as Cs$_2$InAgCl$_6$,\textsuperscript{150} CsSnI$_3$,\textsuperscript{151} Cs$_3$Sb$_2$I$_9$,\textsuperscript{152} and Cs$_3$Sb$_2$Br$_9$\textsuperscript{121} have been successfully produced. These metal-based HPs showed great optoelectronic properties for photocatalytic applications.

\textbf{Figure 8.} (a) Crystal structure of cubic Cs$_2$AgBiBr$_6$. (b) Schematic diagram of the CO$_2$ photoreduction on the surface of Cs$_2$AgBiBr$_6$ NCs. (a, b) Reproduced with permission from ref. \textsuperscript{44}, Copyright 2018 WILEY. (c) SEM image of Cs$_3$Sb$_2$Br$_9$ NCs. Inset shows the yellow color and high transparency of the solution. (d) CO$_2$ reduction mechanism by Cs$_3$Sb$_2$Br$_9$ NCs. (c, d) Republished (adapted) with permission from Royal Society of Chemistry from ref. \textsuperscript{48}; permission conveyed through Copyright Clearance Center, Inc.
4.3. Semiconductor with halide perovskite

4.3.1. Oxide with halide perovskite

Inspired by the earth-abundant and nontoxic, TiO$_2$ has a potential application for CO$_2$ photoreduction. Hence, it is of significance to design a TiO$_2$ and perovskite-based heterojunction to enhance the photocatalytic reduction of CO$_2$. Xu et al. developed an S-scheme TiO$_2$/CsPbBr$_3$ heterojunction as photocatalysis and showed a higher activity for photocatalytic reduction of CO$_2$ into solar energies under UV-light radiation Figure 9 a-h.$^{153}$ Xu et al. demonstrated a novel amorphous-TiO$_2$-encapsulated CsPbBr$_3$ NCs for a higher photocatalytic reduction of CO$_2$. The amorphous TiO$_2$ encapsulation has been witnessed as a critical driving force for excellent photocatalytic performance through increasing the efficiency of extraction and separation of the photoinduced charges. Such effects finally enhanced the consumption of photoelectron from 25.7 to 193.3 μmol g$^{-1}$ as shown in Figure 9 c-d. Moreover, the adsorption and activation of CO$_2$ were also boosted. Based on these synergetic effects, almost 6.5 times improvement on the consumption of the photoelectrons were attained through the photocatalytic CO$_2$ reduction reactions.$^{43}$
Figure 9. (a) Band structure of TiO$_2$/CsPbBr$_3$ composite photocatalyst. (b) Photocatalytic activities of CO$_2$ reduction for TiO$_2$, CsPbBr$_3$ QDs, and TiO$_2$/CsPbBr$_3$ composite, respectively. (a, b) Reproduced from ref. 153, under the Creative Commons CC BY license (http://creativecommons.org/licenses/by/4.0/). (c) A schematic illustration of CO$_2$ fixation and conversion in TiO$_2$-encapsulated CsPbBr$_3$ NCs, and (d) photocatalytic CO$_2$ reduction test results. (c-d) Reproduced with permission from ref. 43, Copyright 2018 WILEY.

When developing the stronger reduction potential of CsPbBr$_3$ to produce a Z-scheme heterojunction photocatalyst, it is best to search for a suitable oxidative semiconductor. Moreover, the oxidative semiconductor has the following properties: (i) strong interactions with CsPbBr$_3$; (ii) visible-light response; (iii) high catalytic activity for the oxidation reaction; and (iv) compatible band structure with CsPbBr$_3$. Bismuth tungsten oxide (Bi$_2$WO$_6$) is a unique oxide with visible-light response, which contains perovskite-type [WO$_4$]$^{2-}$ layers and alternating [Bi$_2$O$_2$]$^{2+}$. For oxidative reactions, Bi$_2$WO$_6$ also has an oxygen-deficient surface that detects on abundant active sites, and it is preferred as an ideal photocatalyst for O$_2$ evolution. Notably, the band structures among CsPbBr$_3$ and Bi$_2$WO$_6$ were well-matched, and in principle, they can also be incorporated into a Z-scheme heterojunction. Wang et al. developed a 0D/2D heterojunction of CsPbBr$_3$ QDs/Bi$_2$WO$_6$ nanosheet (CPB/BWO) photocatalyst for photocatalytic reduction of CO$_2$. The larger surface area of 2D Bi$_2$WO$_6$ effectively decorated 0D CsPbBr$_3$ on its surface. The close contact between Bi$_2$WO$_6$ and CsPbBr$_3$ permitted an excellent interface for the charge transfer and separation. The advanced CPB/BWO heterojunction photocatalyst exhibited higher activities for photocatalytic reduction of CO$_2$ as compared to the Bi$_2$WO$_6$ nanosheets and pristine CsPbBr$_3$ QDs (Figure 10 a-c), respectively. The separated holes and electrons in CsPbBr$_3$ QDs and Bi$_2$WO$_6$ nanosheets can be proficiently used for photocatalytic reduction of CO$_2$. The yield of CPB/BWO is 503 $\mu$molg$^{-1}$, which is 9.5 folds that of CsPbBr$_3$.

Besides, two-dimensional (2D) 2D/2D heterojunction is considered as the most promising approach to manipulate the photoreduction efficiency of semiconductor catalysts. Recently, a lot of struggles have been devoted to preparing 2D/2D heterostructures.
This is because that the large surface area of 2D ultrathin nanosheets, rich active sites, special electronic structure, and short charge transport distance, are useful for the catalytic reaction.\textsuperscript{164-166} Recently, Jiang et al. designed a lead halide perovskite-based 2D/2D direct Z scheme heterojunction by assembling ultrathin Bi\textsubscript{2}WO\textsubscript{6} nanosheets on the surface of CsPbBr\textsubscript{3} nanosheets through an electrostatic self-assembly process (Figure 10 d-f).\textsuperscript{167} Bi\textsubscript{2}WO\textsubscript{6} has been identified as one of the best visible-light oxidation photocatalysts, which have a higher oxidation ability, low manufacturing cost as well as controlled synthesis.\textsuperscript{168, 169} The CsPbBr\textsubscript{3}/Bi\textsubscript{2}WO\textsubscript{6} heterostructure provided higher photocatalytic performance for CO\textsubscript{2} reduction activity. The yield of the 2D/2D CsPbBr\textsubscript{3}/Bi\textsubscript{2}WO\textsubscript{6} hybrid was 153.0 \(\mu\)mol g\textsuperscript{-1} (10.9 \(\mu\)mol g\textsuperscript{-1} for H\textsubscript{2}, 56.4 \(\mu\)mol g\textsuperscript{-1} for CO, and 86.0 \(\mu\)mol g\textsuperscript{-1} for CH\textsubscript{4}).\textsuperscript{167}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{(a) Z-scheme photocatalytic diagram of 0D/2D CsPbBr\textsubscript{3}/Bi\textsubscript{2}WO\textsubscript{6} composite for CO\textsubscript{2} Reduction. (b) Schematic illustration of Z-scheme of the energy band structure of CsPbBr\textsubscript{3}/Bi\textsubscript{2}WO\textsubscript{6} composite. (c) Gases yields in ethyl acetate/water system over various catalysts. (a-c) Reprinted with permission from ref. \textsuperscript{159}, Copyright 2020 American Chemical Society. (d) Schematic diagram of 2D/2D CsPbBr\textsubscript{3}/Bi\textsubscript{2}WO\textsubscript{6} heterojunction for CO\textsubscript{2} reduction. (e) Schematic diagram of the energy band structure of 2D/2D CsPbBr\textsubscript{3}/Bi\textsubscript{2}WO\textsubscript{6} heterojunction. (f) Photocatalytic activity of different samples. (d-f) Reproduced with permission from ref. \textsuperscript{167}. Copyright 2020 WILEY.}
\end{figure}
4.3.2. Sulfide with halide perovskite

A high-quality interface is strongly desired in heterojunctions for effectively separating electron-hole pairs both temporarily and spatially. Co-sharing of atoms by two different materials in a heterojunction system could increase the charge separation and boost the carrier lifetime, facilitating the catalytic reaction. Recently, Wang et al. reported that 0D Cs$_2$SnI$_6$ QDs anchored on flower-like 2D SnS$_2$ nanosheet by co-sharing of Sn atoms can improve the photochemical CO$_2$ reduction rate. All-inorganic Cs$_2$SnI$_6$ is favored for its outstanding conductivity and strong chemical stability. For example, Cs$_2$SnI$_6$ thinner films own high hole mobility of $3.82 \times 10^2$ cm$^2$ V$^{-1}$ s$^{-1}$, much larger than that of Si single crystals and MAPbBr$_3$ as a hole transport material. Especially, the incorporation of Cs$_2$SnI$_6$ boosted the catalytic activity of SnS$_2$ owing to the facilitated charge separation. A flower-like Cs$_2$SnI$_6$/SnS$_2$ heterostructure was synthesized by dispersing the hydrothermally produced SnS$_2$ nanosheets in hydroiodic acid and ethanol alcohol (HI/EtOH) solution containing CsI, as shown in Figure 11. Joint research with DFT calculations, transient absorption, and kelvin probe force microscopy characterizations proved a Cs$_2$SnI$_6$/SnS$_2$ hybrid owning an intimate contact interface, which indicated that holes transferred from SnS$_2$ to Cs$_2$SnI$_6$ and electrons transferred from Cs$_2$SnI$_6$ to SnS$_2$. As a proof-of-concept application, photocatalytic reduction of CO$_2$ and photo-electrochemical experiments were conducted to demonstrate that the longer lifetime of accumulated electrons in SnS$_2$ boosted the performance by 5.4 times and 10.6 times than pristine SnS$_2$.46

![Figure 11](image-url)
reduction activities of SnS$_2$, Cs$_2$SnI$_6$(0.5)/SnS$_2$, Cs$_2$SnI$_6$(1.0)/SnS$_2$, and Cs$_2$SnI$_6$(2.0)/SnS$_2$. Reprinted with permission from ref. 46, Copyright 2019 American Chemical Society.

4.3.3 Carbide with halide perovskite

Recently, carbon-based photocatalysts have aroused great concerns and became more prevalent in photocatalytic reduction of CO$_2$ owing to their exceptional physicochemical and photo-/electrochemical properties. Various carbon materials (e.g. GO, g-C$_3$N$_4$) used as support for many photocatalysts is greatly promising as carbon can regulate photocatalytic reduction of CO$_2$ performance in the visible light region and extract photogenerated electrons from the surface of semiconductors because of its admirable electrical conductivity.

Figure 12 a-c shows the presentation of the CsPbBr$_3$ QDs/GO composite photocatalyst and its corresponding TEM image. It was noted that, in ethyl acetate, the pure CsPbBr$_3$ QDs catalyzed the photocatalytic reduction of CO$_2$ with an electron consumption rate of 23.75 μmol g$^{-1}$ h$^{-1}$ over 99.2% selectivity. Through the combination of highly conducting materials, such as GO, which has charge extraction abilities, the charge recombination was suppressed. CsPbBr$_3$ NCs/GO composite enhanced the electron consumption rate from 23.75 to 29.82 μmol g$^{-1}$ h$^{-1}$ with 99.15% selectivity.

Ou et al. described that anchoring of CsPbBr$_3$ QDs over porous g-C$_3$N$_4$ (PCN) also improved the performance of photocatalytic reduction of CO$_2$ in acetonitrile/water or ethyl acetate/water solution. With 20 wt.% CsPbBr$_3$ QDs (CPB) on NH$_x$-rich porous g-C$_3$N$_4$ nanosheets (CPB-PCN), CsPbBr$_3$ QDs were linked with PCN by N-Br bond which boosted the photogenerated charge carrier separation, as shown in Figure 12 d-f. The above-mentioned strategy helped to achieve the maximum rate of CO formation in acetonitrile/water mixture compared with bare CsPbBr$_3$ QDs.

Based on the above-mentioned composite structure, Guo et al. functionalized CsPbBr$_3$ NCs with graphitic carbon nitride, which had a titanium-oxide species (TiO-CN) through N-
Br and O-Br bonding, and developed an effective catalyst system for photocatalytic reduction of CO\textsubscript{2} utilizing water as the source of the electron\textsuperscript{98}. The introduction of TiO-CN could improve the number of catalytic active sites, along with a rapid interfacial charge separation between CsPbBr\textsubscript{3} and TiO-CN owing to their promising energy-offsets as well as chemical bonding performances (Figure 12 g-i). They also reported that the CsPbBr\textsubscript{3}@TiO-CN composite increased the separation of photogenerated charge and improved the number of catalytic active sites that led to the formation of CO after 10 hours of irradiation, which was 3 times higher than pure CsPbBr\textsubscript{3}\textsuperscript{98}.

Figure 12. Heterostructure of CsPbBr\textsubscript{3}/GO composite photocatalysts for enhanced CO\textsubscript{2} reduction. (a) Schematic model, (b) TEM image, and (c) Histogram of different products in presence and absence of GO with CsPbBr\textsubscript{3} QDs. (a-c) Reprinted with permission from ref. \textsuperscript{42}, Copyright 2017 American Chemical Society. (d) Amino-assisted anchoring of CsPbBr\textsubscript{3} QDs on porous g-C\textsubscript{3}N\textsubscript{4} for photocatalytic CO\textsubscript{2} reduction. (e) TEM image of CsPbBr\textsubscript{3}-PCN. (f) Generation of CO in acetonitrile/water and ethyl acetate/water system over various photocatalysts. (d-f) Reproduced with permission from ref. \textsuperscript{182}, Copyright 2018 WILEY. (g) Photocatalytic CO\textsubscript{2} reduction by CsPbBr\textsubscript{3} nanocrystals with graphitic carbon nitride nanosheets, containing titanium-oxide composite. (h) TEM images of TiO-CN without
and with CsPbBr$_3$ nanocrystal. (i) The yield of CO generation from photocatalytic CO$_2$ reduction reactions with TiO-CN, CsPbBr$_3$, CsPbBr$_3$@g-C$_3$N$_4$, and CsPbBr$_3$@TiO-CN. (g-i) Republished with permission of Royal Society of Chemistry, from ref. 98; permission conveyed through Copyright Clearance Center, Inc.

4.3.4 Metal-Organic Framework with halide perovskite

With unique structural architecture and admirable chemical and physical properties, metal-organic framework (MOFs) has recently attracted remarkable consideration regarding encapsulation of halide perovskites owing to their distinctive characteristics, such as tunable structure, higher surface areas, and flexibility.$^{184}$ Besides, zeolitic imidazolate framework (ZIF) based MOFs have shown a great potential to capture CO$_2$, and cobalt possessing ZIFs can be co-catalysts to stimulate CO$_2$ activation and conversion.$^{185-187}$ Kong et al. described that core@shell CsPbBr$_3$ NCs@ZIFs heterostructure boosted the yield of photocatalytic reduction of CO$_2$.$^{102}$ The maximum quantity of CO$_2$ reduction yield was attained for CsPbBr$_3$ NCs@ZIF-67 composite with the highest electron consumption rate of 29.6 μmol g$^{-1}$ h$^{-1}$, which was a 2.65 times increase compared to bare CsPbBr$_3$ NCs as shown in Figure 13 a-b. It was started that CsPbBr$_3$ NCs covered by ZIFs shell can enhance the moister stability and the CH$_4$ formation instead of CO as the main product.$^{102}$ Wan et al. developed CsPbBr$_3$ NCs/UiO-66(NH$_2$) composite toward the reduction of CO$_2$ in water/ethyl acetate with volume ratio (1/300) solution.$^{113}$ The highest conversion of CO$_2$ was accomplished for 15%-CsPbBr$_3$ QDs/UiO-66(NH$_2$) heterostructure.$^{113}$ The formation of CO was up to 98.5 μmol g$^{-1}$, which was higher as compared to the individual CsPbBr$_3$ QDs and UiO-66(NH$_2$) photocatalysts, as shown in Figure 13 c-d. The enhanced catalytic activity toward the reduction of CO$_2$ for CsPbBr$_3$ QDs/UiO-66(NH$_2$) composite was mainly ascribed to the creation of an appropriate band alignment of UiO-66(NH$_2$), which favored fast photogenerated electron transfer from the CsPbBr$_3$ QDs and repressed the charge recombination.$^{188-190}$ Lu and co-workers also demonstrated another promising application of MOFs encapsulation, where Fe-porphyrin-based MOFs(PCN221(Fe$_x$)) secured CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskite NCs in a reaction
medium containing the maximum amount of H_2O (1.2 vol.%) in ethyl acetate.\textsuperscript{45} Figure 13 displays that MAPbI_3@PCN-221(Fe) composite photocatalyst shows the close contact of NCs and Fe photocatalytic site in the MOFs, favoring the rapid transfer of photogenerated electrons to the Fe catalytic sites and improving the performance of photoreduction.\textsuperscript{102, 42} The maximum yield of 1559 \mu mol g\(^{-1}\) was reported for MAPbI_3@PCN-221(Fe0.2) composite toward the photocatalytic reduction of CO_2 to CO (34.5%) and CH_4 (65.5%), where H_2O was used as an electron source.\textsuperscript{45}

Figure 13. (a) Schematic illustration of the fabrication process and CO_2 photoreduction process of CsPbBr_3/ZIFs. (b) The product yield after 3 h of photocatalytic reaction. (a-b) Reprinted with permission from ref. \textsuperscript{102}, Copyright 2018 American Chemical Society. (c) Schematic illustration of a possible mechanism of photocatalytic CO_2 reduction. (d) Photocatalytic CO_2 reduction performance for CsPbBr_3 QDs and x%CsPbBr_3 QDs/UiO-66(NH_2) nanocomposite. (c-d) Reprinted from ref. \textsuperscript{113}, Copyright (2019), with permission from Elsevier. (e) Schematic presentation for the synthesis of (PCN-221(Fe)) MOF and MAPbI_3@PCN221(Fe) composite photocatalysts for stable and product selective CO_2 reduction. (f) Histogram of product formation using (PCN-221(Fe)) and MAPbI_3@PCN-221(Fe). (e-f) Reproduced with permission from ref. \textsuperscript{45}, Copyright 2019 WILEY.
4.4. Conductor with halide perovskite

4.4.1. Noble Metal with halide perovskite

Recently the plasmon-exciton exchange dynamic method has been broadly suggested in metal-semiconductor systems. With the help from the famous localized surface plasmon resonance (LSPR) impact, noble metal Au nanoparticles (NP) was demonstrated by introducing light extinction into visible and even near-infrared zone.\textsuperscript{191, 192} CsPbBr\textsubscript{3}-Au nanocomposite was successfully produced through the in-situ reduction of AuCl\textsubscript{3} by the surface-bound oleylamine ligand, while the obtained Au NP size is too small to form the LSPR effect.\textsuperscript{193, 194}

Xiao and co-workers examined the energy conversion in the Ag-CsPbBr\textsubscript{3} system as well as dynamics of plasmon-induced hot electron, which showed a significant hot-electron transfer efficiency near 50%.\textsuperscript{195} The studies about plasmon-exciton interaction for the hybrid method of plasmonic Au NPs over halide perovskite NCs is still at a nascent development.

CsPbBr\textsubscript{3}-Au nanocomposite was used as photocatalyst for artificial photoreduction of CO\textsubscript{2} by two different types of light sources ($\lambda > 420$ nm and $\lambda > 580$ nm). Based on the Kelvin probe force microscopy (KPFM) results and the spectroscopic characterizations, two-dimensional interaction processes for CsPbBr\textsubscript{3}-Au nanocomposite were shown in Figure 14.\textsuperscript{194} Even though there is a significant difference between the Fermi level ($E_F$) of CsPbBr\textsubscript{3} and the work function ($W_F$) of Au, energy level alignment can be obtained with their close contact (Figure 14 a-b). Consequently, photogenerated electrons would mostly accumulate in CB of CsPbBr\textsubscript{3}, which raises its $E_F$ negatively, and thermodynamically supports the electron to transfer into the Au.\textsuperscript{196, 197} The electrons accumulated in Au consequently contribute to the photoreduction reaction of CO\textsubscript{2}, as demonstrated in Figure 14c. Only the Au nanoparticle-based photo-responsive absorption occurred under the light condition of $\lambda >580$ nm, while CsPbBr\textsubscript{3} based photo-responsive absorption was started at wavelength $\lambda >530$ nm. To initiate
CO₂ reduction more efficiently, the LSPR-induced hot electrons encompassing higher energy potential in plasmonic Au nanoparticles could be further transferred rapidly to CsPbBr₃. Hence, such kind of plasmon-exciton exchange process makes the CsPbBr₃-Au nanocomposite to work well over the longer wavelength in turn as shown in Figure 14d.

![Figure 14](https://via.placeholder.com/150.png)

**Figure 14.** (a) Band structure of CsPbBr₃ nanocrystal and Au nanoparticle before contact. (b) Fermi level alignment after their close contact in dark. Schematic diagram of excitation wavelength-dependent two charge separation mechanisms in CsPbBr₃-Au nanocomposite under light irradiation with (c) λ >420 nm or (d) λ >580 nm. (a-d) Reprinted from ref. 194, Copyright 2021, with permission from Elsevier.

Xu et al. described an innovative 0D CsPbBr₃ nanocrystal (CsPbBr₃ NC)/2D Pd nanosheet (Pd-NS) composite photocatalyst for the effective and stable photocatalytic reduction of CO₂ under sunlight in the existence of water vapor. The Pd-NS not only played an important role for an electron collector to rapidly separate the electron-hole pairs in CsPbBr₃ NC and controlled the unwanted radiative charge recombination, but also modified the kinetics of catalytic reduction of CO₂ reaction. Therefore, the addition of Pd-NS increased the consumption rate of photoelectron from 9.85 μmol g⁻¹ h⁻¹ to 33.7 μmol g⁻¹ h⁻¹ under visible light (>420 nm). Especially, the incorporation of 2D metallic semiconductor not
only formed a Schottky junction at the interface to increase the electrons transfer from semiconductors to metal, but also presented photocatalytic reaction sites to promote the transfer of electrons and increased the resulting chemical reactions \(^{164, 198}\), as presented in Figure 15 a-c.

**Figure 15.** (a) Diagram of CsPbBr\(_3\) NC/Pd-NC composite. (b) The sketch of the composite material (CsPbBr\(_3\) NC)/(Pd-NC) and their band alignments. (c) Photocatalytic CO\(_2\) reduction performance. (a-c) Reprinted (adapted) with permission from ref. \(^{100}\), Copyright 2018 American Chemical Society.

### 4.4.2. Carbon Derivative with halide perovskite

Recently, 2D ultrathin carbon-based materials, such as carbon nanotubes (CNTs), graphene, and graphitic carbon nitride (g-C\(_3\)N\(_4\)), have drawn great attention toward photo/electrocatalytic applications. These materials possess the advantages of great metallic conductivity, strong volumetric capacitance, flexible interlayered regulation, hydrophilic surfaces,\(^{199-203}\) tunable electronic structure, high surface area, excellent thermal/chemical stability, and environmental friendliness.\(^{204, 205}\) These properties have endorsed these materials to be employed in various applications, such as gas separation, cell imaging, catalysts, energy storage, and conversion.\(^{206-208}\) Currently, some novel functional heterostructure for CO\(_2\) reduction was prepared via in situ development of CsPbBr\(_3\) perovskite NCs on 2D MXene nanosheets to further improve the charge transfer, separation, and effective photoexciton. The rapid charge transfer efficiency also encouraged the CsPbBr\(_3\)/MXene as an active catalyst towards the CO\(_2\) conversion to CO and CH\(_4\).\(^{209}\) The low conduction band (1.5 eV) value among the CsPbBr\(_3\) NCs and MXene can efficiently help the separation of the exciton in CsPbBr\(_3\) NCs and electrons transfer to MXene nanosheets.
Photo-exciton will be shifted from a high energy level to a lower one, therefore sustaining the charge at a stable state. In this way, electrons are moved to the surface of the photocatalyst, which offers a comparatively negative position based on the band arrangement.

Pan and co-workers demonstrated that the incorporation of MXenens to CsPbBr$_3$ (CsPbBr$_3$ NCs/MXene-20) increased the yields of CO and CH$_4$ linearly. The maximum CH$_4$ and CO yield rate was 7.25 and 26.32 μmol g$^{-1}$ h$^{-1}$, respectively (Figure 16 a-b),$^{47}$ which was superior or at least comparable to the MXene free CsPbBr$_3$ NCs (<4.42 μmol g$^{-1}$ h$^{-1}$) or other state-of-the-art CsPbBr$_3$ NCs-based heterostructure photocatalysts.$^{42, 43, 102, 112, 135, 183}$ Que and co-workers successfully synthesized FAPbBr$_3$ QDs/MXene nanosheets heterostructure via a facile process. Under visible-light irradiation, the as-prepared FAPbBr$_3$ QDs/MXene composite exhibited a remarkable photocatalytic activity in the presence of water. To stimulate the quick separation of excitons, the nanosheets of MXene played a role as an electron acceptor and facilitated a large number of active sites. The optimized performance with the higher electron consumption rate of 717.18 μmol g$^{-1}$ h$^{-1}$ was achieved via FAPbBr$_3$ QDs/MXene composite (Figure 16 c-d), which showed a 2.08 times better performance as compared to the pure FAPbBr$_3$ QDs.$^{210}$
5. MOLECULAR COMPUTATION

Halide based perovskites have been extensively studied through theoretical/computational analysis concerning their unique electronic structure and physiochemical properties. Their photo-conversion efficiency greatly depends on the balance electron, bandgap, absorption coefficient, hole mobility and intrinsic recombination rates. Changes (element or molecular ion) in the structure of halide perovskites could significantly alter the optoelectronic properties. In many cases, replacing cations or anions in HPs may cause different Coulomb interaction which results in the shifting of conduction and valance band position according to their Fermi level energy. Bandgap is considered as one of the critical properties of a photocatalyst. To extend the light absorption to visible region, the bandgap required for photocatalytic reaction is ~2.00 eV. However, the position of conduction band minimum (CBM) should be lower than −0.52 eV (vs. NHE PH = 0, the
energy barriers of reducing CO$_2$ to CO) for CO$_2$ reduction reaction, which is thermodynamically more feasible for the reduction reaction.

Liu and co-worker$^{217}$ conducted density functional theory (DFT) calculations of lead-free perovskites to investigate the values of band gaps of CsGeI$_3$, MAGeI$_3$, and FAGeI$_3$ using exchange-correlation functionals. Some commonly used exchange-correlation functionals are Generalized Gradient Approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) which were found to be consistent with experimental values. The same group also performed hybrid functional Heyd-Scuseria-Ernzerhof-06 (HSE06) calculations to obtain more precise values of band gaps, which were very close to experimental values. The optimized structures, calculated band structure, and density of states (DOS) of MAGeI$_3$ are shown in Figure 17 a-c. HSE06 and PBE functionals were used to calculate the bandgap of ABX$_3$ HPs, with and without Spin orbit coupling (SOC) calculations.$^{218}$ Tang et al. elucidated the catalytic ability of pure CsPbBr$_3$ perovskite and doped CsPbBr$_3$ perovskites with different metals (Co., Fe, Ni, etc.) by density functional theory calculations.$^{139}$ It was shown that methane is formed with higher selectivity and the smaller band gap between Co-doped and Fe-doped perovskites improved the efficiency of photocatalyst as shown in Figure 17f. The adsorption free energy of intermediates was found to be much lower than pure perovskite (Figure 17 f). Besides, the calculations also showed that Co and Fe doped catalyst can enhance the catalytic activity of CsPbBr$_3$ towards CO$_2$ reduction. When dopants (Co or Fe) were introduced into CsPbBr$_3$, the band-edge states were created by Co-d and Fe-d orbitals as they contributed more actively to CB. The formed band-edge states reduced the bandgap from 2.32 eV to 1.79 and 1.71 eV for Co-doped for Fe-doped cases, respectively. The reduced bandgap not only improved light absorption in the visible spectrum but also promoted effective charge separation and transfer efficiency.$^{139, 219}$ Density of states was calculated in Figure 17 d-e for the Co-doped and the Fe-doped cases respectively. The electron-donating ability of Co and Fe is...
greater than Pb, leading to improved reduction performance of doped HPs. Besides, calculation results showed that the C=O double bond becomes weaker for the Co-doped and Fe-doped structures and CO$_2^*$ is activated to produce HCOO*.  

**Figure 17.** (a) Optimized structure, (b) calculated band structure, and (c) DOS of MAGeI$_3$. Reprinted with permission from ref. 217, Copyright 2019 American Chemical Society. (d) Calculated density of state diagrams of Co-doped CsPbBr$_3$, (e) calculated density of state diagrams of Fe-doped CsPbBr$_3$, and (f) free-energy diagrams of the most favored paths of CO$_2$ reduction by pristine, Co-doped and Fe-doped CsPbBr$_3$. Republished with permission of Royal Society of Chemistry, from ref. 139; permission conveyed through Copyright Clearance Center, Inc.

6. CONCLUSION AND FUTURE OUTLOOK

In this review, we summarize the recent progress achieved in exploring perovskite nanomaterials in terms of photocatalysts for CO$_2$ reduction. Improvement methods in this field are discussed systematically including utilizing newly emerging halide perovskite nanomaterials along with their modifications in terms of structural engineering, interfacial modulation through the formation of the heterostructure, metal ion doping, surface modification, encapsulation with several types of co-catalyst, or using the conducting substrates. **Table 2** displays the performance of recent perovskite-based photocatalysts. Significant advances have been made to the conversion of CO$_2$ into useful energy-bearing
hydrocarbons by many attractive approaches, while significant research effort is still needed for improvement in the field to accelerate practical implementation. Moreover, some fundamental studies are highly required to resolve the bottleneck problems, including the kinetic problem in multi-electron reduction processes, water oxidation reaction, poor reduction selectivity, and low quantum yield of the photocatalysts. These issues should be extensively examined and studied for future improvements to be employed at an industrial scale.

Promising research directions on halide perovskite-based photocatalysts for future exploration are forecasted including: (i) Application of halide perovskites with various modulation strategies, such as employing interface engineering, fabricating 3D hierarchical architectures, exploiting ultrathin 2D nanosheets, using the surface fluorination effects, preparing surface over layers, creating surface vacancies, etc. (ii) Accomplish higher light-harvesting ability and enhance charge separation efficiency via rational design of novel halide perovskite-based heterostructure. (iii) It's well known that solvent/electrolyte plays a significant role in any catalytic reaction. Since the halide perovskites are unstable in polar solvents, and a wide range of research efforts has been devoted towards the exploration of a more suitable medium for efficient photocatalytic CO₂ reduction. Owing to the high solubility of CO₂, the use of low-polar ethyl acetate was preferred as a better solvent. (iv) The utilization of co-catalysts in the photocatalytic process has been proved to be an environmentally benign method with high performance. Some efforts could be devoted towards the development of an innovative noble-metal-free co-catalyst. (v) Despite achieving enormous research interest in the efficient photoreduction of CO₂, the use of halide perovskites, is still restricted on the industrial scale owing to their low scale (µmol range). For artificial photosynthesis, the up to date solar-to-fuel efficiency value is ~1.1%, which is ~10 times that of natural photosynthesis, but is still very low for industrial applications.
Given that solar energy conversion efficiency is >20% in solar photovoltaics, the value required for the feasible artificial photosynthesis should be 10% or above. The commercialization of CO\textsubscript{2} photoreduction reaction is currently obstructed by the poor stability, low selectivity and high cost. One promising way to address the challenge is combining the halide perovskite with other efficient semiconductors for improving charge separation capacity and optical behaviors, so as to enhance the catalytic efficiency and stability. Therefore, the development of long-lasting, cost-effective, and potentially scalable halide perovskites is highly prerequisite for a sustainable future. (vi) Doping over proper metal ions and altering the reaction system for obtaining multiple doped halide perovskites, should also be proposed for the possible improvement of the photocatalytic performance and their stability for reduction reaction of CO\textsubscript{2}. (vii) Another issue which should be addressed is the toxic nature of halide perovskites that hinders their commercial applications. In order to get environmentally friendly halide perovskites, substitution of lead (Pb) with other transition metals such as Sn, Sb and Bi is necessary. However, these transition metal substituted HPs have relatively poor stability as compared to Pb-based halide perovskites. Any further development of Pb-free HPs should address the limitations related to stability. (viii) In recent years, there has been an increasing amount of literature on photocatalytic reduction of CO\textsubscript{2} which focus mainly on higher conversion rate of CO\textsubscript{2}. The typical products of this photocatalytic reaction are single carbon atom compounds such as methane, carbon monoxide, formic acid, etc. However, current research in photocatalytic CO\textsubscript{2} reduction by halide perovskites has emphasized on the productivity as well as selectivity of compounds with two or more carbons (C\textsubscript{2}+), for example, ethanol, ethane, acetic acid, etc.\textsuperscript{87} Further researches are required to investigate the productivity and selectivity of these C\textsubscript{2}+ products via photocatalytic reduction of CO\textsubscript{2} by halide perovskites to valuable products such as alkenes, aromatic hydrocarbons and alcohols, rather than less valuable products. These
challenges we are facing could provide countless opportunities for further improvement in photocatalytic activity. We hope that the readers can get more new insights into the recent advancements and future directions toward the energy conversion applications of halide perovskites in the field of photocatalysis.
Table 2. Photocatalytic and CO$_2$ reduction performance using halide perovskites.

| Photocatalyst                  | Medium                        | Light Source                     | Products              | Yield (μmol g$^{-1}$ h$^{-1}$) | Highest Efficiency (%) | Stability (h) | Reference |
|--------------------------------|-------------------------------|----------------------------------|-----------------------|-------------------------------|------------------------|-----------------|-----------|
| CsPbBr$_3$ QDs                | Ethyl acetate/water           | 300W Xe lamp (AM 1.5G)           | CO+CH$_4$+H$_2$       | 4.3+1.5+0.1                  | /                      | >8              | 135       |
| CsPbBr$_3$@g-C$_3$N$_4$        | Ethyl acetate                 | 450W Xe lamp AM1.5G              | CO+CH$_4$             | 2.1+22.8                     | /                      | >12             | 220       |
| CsPb(Br$_{0.5}$/Cl$_{0.5}$) NCs| Ethyl acetate                 | 300W Xe lamp (AM 1.5G)           | CO+CH$_4$             | 85.2+12.0                    | /                      | >9              | 97        |
| CsPbBr$_3$ QD/GO              | Ethyl acetate                 | 150 mW/cm$^2$ (AM 1.5G)          | CO+CH$_4$+H$_2$       | 4.9+2.5+0.1                  | 0.025%                 | >12             | 42        |
| CsPbBr$_3$@TiO-CN             | Ethyl acetate/water           | 300W Xe lamp (≥400 nm)           | CO                    | 12.9                          | /                      | >10             | 98        |
| CsPbBr$_3$ NCs/MXene          | Ethyl acetate                 | 300W Xe lamp (≥420 nm)           | CO+CH$_4$             | 26.3+7.3                     | /                      | >9              | 47        |
| CsPbBr$_3$ NCs/BZNW/MRGO      | (CO$_2$+ water vapor)         | 150W Xe lamp (AM 1.5G)           | CO+CH$_4$             | 0.9+6.3                      | /                      | >3              | 99        |
| CsPbBr$_3$ NCs/Pd NS          | (CO$_2$+ water vapor)         | 150W Xe lamp (≥420 nm)           | CO+CH$_4$+H$_2$       | 1.9+3.5+1.1                  | 0.035%                 | >3              | 100       |
| CsPbBr$_3$-Re(600)            | Toluene/isopropanol           | 150W Xe lamp (≥420 nm)           | CO+H$_2$              | 104.4+5.6                    | /                      | >3              | 101       |
| CsPbBr$_3$ NCs/a-TiO$_2$      | Ethyl acetate/isopropanol     | 150W Xe lamp (AM 1.5G)           | CO+CH$_4$+H$_2$       | 3.9+6.7+1.5                  | /                      | >3              | 43        |
| 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%                 | >3              | 102       |
| CsPbBr$_3$ NCs@ZIF-8          | (CO$_2$+ water vapor)         | 100W Xe lamp (AM 1.5G)           | CO+CH$_4$             | 0.7+2.0                      | /                      | >3              | 102       |
| CsPbBr$_3$ QDs/UiO66(NH$_3$)  | Ethyl acetate/water           | 300-W Xe lamp (≥420 nm)          | CO+CH$_4$             | 8.2+0.3                      | /                      | >12             | 113       |
| MAPbI$_3$@PCN221(Fe$_x$)      | Ethyl acetate/water           | 300-W Xe lamp (≥400 nm) 100 mW/cm$^2$ | CO+CH$_4$             | 4.2+13.0                     | /                      | 25              | 45        |
| Material System | Medium | Reaction Conditions | Product | Yield | Notes |
|-----------------|--------|---------------------|---------|-------|-------|
| Fe: CsPbBr<sub>3</sub> NCs | Ethyl acetate/water | 450 W Xe lamp 150 mW/cm<sup>2</sup> | CO+CH<sub>4</sub> | 3.2+6.1 | / | >3 |
| FAPbBr<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> | Benzyl alcohol | 150 W Xe lamp AM1.5G 100 mW/cm<sup>2</sup> | CO+Benzaldehyde | 170.0+250.0 | / | -- |
| FAPbBr<sub>3</sub> QDs | Ethyl acetate/water | 300 W Xe lamp 100 mW/cm<sup>2</sup> | CO+CH<sub>4</sub>+H<sub>2</sub> | 181.3+16.9+2.37 | / | >3 |
| CsPbBr<sub>3</sub> QDs/Bi<sub>2</sub>WO<sub>6</sub> | Ethyl acetate/water | 100 mW/cm<sup>2</sup> >400 nm | CO+CH<sub>4</sub> | totally 50.3 | / | >10 |
| Cs<sub>2</sub>SnI<sub>4</sub>/SnS<sub>2</sub> NCs | (CH<sub>3</sub>OH+CO<sub>2</sub>+water vapor) | 150 mW/cm<sup>2</sup> (≥400 nm) | CH<sub>4</sub> | 6.1 | / | >3 |
| Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> | Octadecene | 300 W Xe lamp 100 mW/cm<sup>2</sup> | CO | 127.2 | / | >6 |
| α-Fe<sub>2</sub>O<sub>3</sub>/Amine-RGO/CsPbBr<sub>3</sub> | (CO<sub>2</sub>+ water vapor) | 150 W Xe lamp AM1.5G, > 400 nm | CO+CH<sub>4</sub>+H<sub>2</sub> | 2.4+9.5+0.3 | / | >15 |
| CsPbBr<sub>3</sub>-Ni(tpy) | Ethyl acetate/water | 300 W Xe lamp >400 nm 100 mW/cm<sup>2</sup> | CO+CH<sub>4</sub> | 431.0+48.8 | 0.23% | >4 |
| Cs<sub>2</sub>AgBiBr<sub>6</sub> NCs | Ethyl acetate | 150 mW/cm<sup>2</sup> (AM 1.5G) | CO+CH<sub>4</sub> | 2.4+1.6 | 0.028% | >6 |
| Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> | (CO<sub>2</sub>+ water vapor) | 80.38 μW/cm<sup>2</sup> (AM 1.5G) | CO+CH<sub>4</sub> | 7.7+1.5 | / | >10 |
| Co<sub>2</sub>/CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> | Water | 300 W Xe lamp 100 mW/cm<sup>2</sup> | CO+CH<sub>4</sub> | 12.0+1.8 | / | >20 |
| Mn/CsPb(Br/Cl)<sub>6</sub> | Ethyl acetate 300WXe-lamp with AM 1.5 filter | CO, CH<sub>4</sub> | 213, 9.1 | / | 9 |
| Co-CsPbBr<sub>3</sub> /Cs<sub>4</sub>PbBr<sub>6</sub> | Acetonitrile/water/Methanol | 300 W Xe lamp 100 mW/cm<sup>2</sup> | CO | 122 | / | 15 |
| Pt/CsPbBr<sub>3</sub> | Ethyl acetate 150WXe-lamp with 380 nm cut o filter | CO | 5.6 | 0.012% | 30 |
| Ni and Mn-doped CsPbCl<sub>3</sub> NCs | (CO<sub>2</sub>+ water vapor) 300WXe-lamp with AM 1.5 filter | Ni = CO | 169.37, 152.49 | / | 6 |
| Cs<sub>3</sub>PbBr<sub>6</sub>/rGO | Ethyl acetate/water 300WXe-lamp with | CO | 11.4 | / | 60 |
| Material/Condition | Reaction Medium | Light Source | Product | Yield | Time (h) | Reference |
|--------------------|-----------------|--------------|---------|-------|---------|------------|
| Cu-RGO-CsPbBr$_3$  | (CO$_2$/water vapor) | Xe-lamp irradiation with a 400 nm filter | CH$_4$ | 12.7 | (1.1±0.15)% | 12 | 49 |
| TiO$_2$/CsPbBr$_3$ | Acetonitrile/water | 300WXe-arc lamp | CO | 9.02 | / | 16 | 153 |
| Cs$_2$AgBiBr$_6$@g-C$_3$N$_4$ | Ethyl acetate/ Methanol | Xe-lamp (80 mW/cm$^2$ light intensity) | CO, CH$_4$ | 2 | / | 12 | 52 |
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Notes

The authors declare no competing financial interest.

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REFERENCES

1. X. Duan, J. Xu, Z. Wei, J. Ma, S. Guo, S. Wang, H. Liu and S. Dou, Adv. Mater., 2017, 29, 1701784.
2. H. He, M. Zhong, D. Konkolewicz, K. Yacatto, T. Rappold, G. Sugar, N. E. David, J. Gelb, N. Kotwal and A. Merkle, Adv. Funct. Mater., 2013, 23, 4720-4728.
3. Y. He, L. Zhang, B. Teng and M. Fan, Environ. Sci. Technol., 2015, 49, 649-656.
4. W. Zhang, A. R. Mohamed and W.-J. Ong, Angew. Chem., 2020, 59, 22894-22915.
5. J. H. Montoya, L. C. Seitz, P. Chakraborty, A. Vojvodic, T. F. Jaramillo and J. K. Nørskov, Nat. Mater., 2017, 16, 70-81.
6. J. L. White, M. F. Baruch, J. E. Pander III, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu and Y. Yan, Chem. Rev., 2015, 115, 12888-12935.
7. D. Kim, K. K. Sakimoto, D. Hong and P. Yang, Angew. Chem. Int. Ed., 2015, 54, 3259-3266.
8. P. V. Kamat, J. Phys. Chem. C, 2007, 111, 2834-2860.
9. P. V. Kamat, *ACS Energy Lett.*, 2017, **2**, 1586-1587.

10. Ş. Neațu, J. A. Maciá-Agulló, P. Concepción and H. Garcia, *J. Am. Chem. Soc.*, 2014, **136**, 15969-15976.

11. T. Masson-Delmotte, P. Zhai, H. Pörtner, D. Roberts, J. Skea, P. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan and R. Pidcock, *World Meteorological Organization, Geneva, Tech. Rep.*, 2018.

12. E. Karamian and S. Sharifnia, *J. CO₂ Util.*, 2016, **16**, 194-203.

13. H. Zhou, Y. Qu, T. Zeid and X. Duan, *Energy Environ. Sci.*, 2012, **5**, 6732-6743.

14. J. Wen, J. Xie, X. Chen and X. Li, *Appl. Surf. Sci.*, 2017, **391**, 72-123.

15. M. Ge, Q. Li, C. Cao, J. Huang, S. Li, S. Zhang, Z. Chen, K. Zhang, S. S. Al-Deyab and Y. Lai, *Adv. Sci.*, 2017, **4**, 1600152.

16. K. Li, A. D. Handoko, M. Khraisheh and J. Tang, *Nanoscale*, 2014, **6**, 9767-9773.

17. Q. A. Akkerman, G. Rainò, M. V. Kovalenko and L. Manna, *Nat. Mater.*, 2018, **17**, 394-405.

18. Z. Shi, S. Li, Y. Li, H. Ji, X. Li, D. Wu, T. Xu, Y. Chen, Y. Tian, Y. Zhang, C. Shan and G. Du, *ACS Nano*, 2018, **12**, 1462-1472.

19. H. Zai, C. Zhu, H. Xie, Y. Zhao, C. Shi, Z. Chen, X. Ke, M. Sui, C. Chen, J. Hu, Q. Zhang, Y. Gao, H. Zhou, Y. Li and Q. Chen, *ACS Energy Lett.*, 2018, **3**, 30-38.

20. F. Cao, D. Yu, X. Li, Y. Zhu, Z. Sun, Y. Shen, Y. Wu, Y. Wei and H. Zeng, *J. Mater. Chem. C*, 2017, **5**, 7441-7445.

21. Q. Chen, H. Zhou, Y. Fang, A. Z. Stieg, T.-B. Song, H.-H. Wang, X. Xu, Y. Liu, S. Lu, J. You, P. Sun, J. McKay, M. S. Goorsky and Y. Yang, *Nat. Commun.*, 2015, **6**, 7269.

22. K. Chen, X. Deng, G. Dodekatos and H. Tüysüz, *J. Am. Chem. Soc.*, 2017, **139**, 12267-12273.

23. Y. Wu, P. Wang, X. Zhu, Q. Zhang, Z. Wang, Y. Liu, G. Zou, Y. Dai, M. H. Whangbo and B. Huang, *Adv. Mater.*, 2018, **30**, 1704342.

24. G. Do Park, C. W. Lee and K. T. Nam, *Curr. Opin. Electrochem.*, 2018, **11**, 98-104.

25. X. Song, G. Wei, J. Sun, C. Peng, J. Yin, X. Zhang, Y. Jiang and H. Fei, *Nat. Catal.*, 2020, **3**, 1027-1033.

26. L.-F. Gao, W.-J. Luo, Y.-F. Yao and Z.-G. Zou, *Chem. Commun.*, 2018, **54**, 11459-11462.

27. A. Guerrero and J. Bisquert, *Curr. Opin. Electrochem.*, 2017, **2**, 144-147.

28. X. Li, J. Yu, M. Jaroniec and X. Chen, *Chem. Rev.*, 2019, **119**, 3962-4179.
29. E. A. Tsiwah, Y. Ding, Z. Li, Z. Zhao, M. Wang, C. Hu, X. Liu, C. Sun, X. Zhao and Y. Xie, *CrystEngComm.*, 2017, **19**, 7041-7049.
30. D. M. Jang, D. H. Kim, K. Park, J. Park, J. W. Lee and J. K. Song, *J. Mater. Chem. C*, 2016, **4**, 10625-10629.
31. Z. Long, H. Ren, J. Sun, J. Ouyang and N. Na, *Chem. Commun.*, 2017, **53**, 9914-9917.
32. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.
33. F. Zhang, H. Zhong, C. Chen, X. Wu, X. Hu, H. Huang, J. Han, B. Zou and Y. Dong, *ACS Nano*, 2015, **9**, 4533-4542.
34. L. Protesescu, S. Yakunin, O. Nazarenko, D. N. Dirin and M. V. Kovalenko, *ACS Appl. Nano Mater.*, 2018, **1**, 1300-1308.
35. J. Wang, J. Liu, Z. Du and Z. Li, *J. Energy Chem.*, 2021, **54**, 770-785.
36. C. Zhang, B. Wang, W. Li, S. Huang, L. Kong, Z. Li and L. Li, *Nat. Commun.*, 2017, **8**, 1138.
37. P. Fu, Q. Shan, Y. Shang, J. Song, H. Zeng, Z. Ning and J. Gong, *Sci. Bull.*, 2017, **62**, 369-380.
38. G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent and M. V. Kovalenko, *Nano letters*, 2015, **15**, 5635-5640.
39. D. Yang, M. Cao, Q. Zhong, P. Li, X. Zhang and Q. Zhang, *J. Mater. Chem. C*, 2019, **7**, 757-789.
40. Y. Chen, M. He, J. Peng, Y. Sun and Z. Liang, *Adv. Sci.*, 2016, **3**, 1500392.
41. S. Bonabi Naghadeh, B. Luo, G. Abdelmageed, Y.-C. Pu, C. Zhang and J. Z. Zhang, *J. Phys. Chem. C*, 2018, **122**, 15799-15818.
42. Y.-F. Xu, M.-Z. Yang, B.-X. Chen, X.-D. Wang, H.-Y. Chen, D.-B. Kuang and C.-Y. Su, *J. Am. Chem. Soc.*, 2017, **139**, 5660-5663.
43. Y. F. Xu, X. D. Wang, J. F. Liao, B. X. Chen, H. Y. Chen and D. B. Kuang, *Adv. Mater. Interfaces*, 2018, **5**, 1801015.
44. L. Zhou, Y. F. Xu, B. X. Chen, D. B. Kuang and C. Y. Su, *Small*, 2018, **14**, 1703762.
45. L. Y. Wu, Y. F. Mu, X. X. Guo, W. Zhang, Z. M. Zhang, M. Zhang and T. B. Lu, *Angew. Chem. Int. Ed.*, 2019, **58**, 9491-9495.
46. X.-D. Wang, Y.-H. Huang, J.-F. Liao, Y. Jiang, L. Zhou, X.-Y. Zhang, H.-Y. Chen and D.-B. Kuang, *J. Am. Chem. Soc.*, 2019, **141**, 13434-13441.
47. A. Pan, X. Ma, S. Huang, Y. Wu, M. Jia, Y. Shi, Y. Liu, P. Wangyang, L. He and Y. Liu, *J. Phys. Chem. Lett.*, 2019, **10**, 6590-6597.
48. C. Lu, D. S. Itanze, A. G. Aragon, X. Ma, H. Li, K. B. Ucer, C. Hewitt, D. L. Carroll, R. T. Williams and Y. Qiu, *Nanoscale*, 2020, **12**, 2987-2991.

49. S. Kumar, M. Regue, M. A. Isaacs, E. Freeman and S. Eslava, *ACS Appl. Energy Mater.*, 2020, **3**, 4509-4522.

50. Z. Chen, Y. Hu, J. Wang, Q. Shen, Y. Zhang, C. Ding, Y. Bai, G. Jiang, Z. Li and N. Gaponik, *Chem. Mater.*, 2020, **32**, 1517-1525.

51. M. Que, Y. Zhao, L. Pan, Y. Yang, Z. He, H. Yuan, J. Chen and G. Zhu, *Mater. Lett.*, 2021, **282**, 128695.

52. Y. Wang, H. Huang, Z. Zhang, C. Wang, Y. Yang, Q. Li and D. Xu, *Appl. Catal. B-Environ.*, 2021, **282**, 119570.

53. H. Huang, B. Pradhan, J. Hofkens, M. B. J. Roeffaers and J. A. Steele, *ACS Energy Lett.*, 2020, **5**, 1107-1123.

54. J. Luo, W. Zhang, H. Yang, Q. Fan, F. Xiong, S. Liu, D.-S. Li and B. Liu, *EcoMat*, 2021, **3**, e12079.

55. C. B. Hiragond, N. S. Powar and S.-I. In, *Nanomaterials*, 2020, **10**, 2569.

56. S. Shyamal and N. Pradhan, *J. Phys. Chem. Lett.*, 2020, **11**, 6921-6934.

57. Y. Xu, M. Cao and S. Huang, *Nano Res.*, 2021, DOI: 10.1007/s12274-021-3362-7.

58. L. Li and M. Wang, *Advanced Catalytic Materials - Photocatalysis and Other Current Trends*, 2016, DOI: 10.5772/62206.

59. S. Linic, P. Christopher and D. B. Ingram, *Nat. Mater.*, 2011, **10**, 911-921.

60. F. Wang, Q. Li and D. Xu, *Adv. Energy Mater.*, 2017, **7**, 1700529.

61. L. Ran, J. Hou, S. Cao, Z. Li, Y. Zhang, Y. Wu, B. Zhang, P. Zhai and L. Sun, *Sol. RRL*, 2020, **4**, 2070045.

62. J. M. Elward and A. Chakraborty, *J. Chem. Theory Comput.*, 2013, **9**, 4351-4359.

63. F. Le Formal, S. R. Pendlebury, M. Cornuz, S. D. Tilley, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2014, **136**, 2564-2574.

64. P. Zhou, J. Yu and M. Jaroniec, *Adv. Mater.*, 2014, **26**, 4920-4935.

65. H. Du, Y.-N. Liu, C.-C. Shen and A.-W. Xu, *Chinese J. Catal.*, 2017, **38**, 1295-1306.

66. M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X. Zheng, C. T. Dinh, F. Fan, C. Cao, F. P. G. de Arquer, T. S. Safaei, A. Mepham, A. Klinkova, E. Kumacheva, T. Filleter, D. Sinton, S. O. Kelley and E. H. Sargent, *Nature*, 2016, **537**, 382-386.

67. X. Chen, S. Shen, L. Guo and S. S. Mao, *Chem. Rev.*, 2010, **110**, 6503-6570.

68. K. Sivula and R. van de Krol, *Nat. Rev. Mater.*, 2016, **1**, 15010.
69. W. Tu, Y. Zhou and Z. Zou, *Adv. Mater.*, 2014, **26**, 4607-4626.

70. Z. Li, J. Feng, S. Yan and Z. Zou, *Nano Today*, 2015, **10**, 468-486.

71. K. Li, X. An, K. H. Park, M. Khraisheh and J. Tang, *Catal. Today*, 2014, **224**, 3-12.

72. K. Li, B. Peng and T. Peng, *ACS Catal.*, 2016, **6**, 7485-7527.

73. J. H. Zejian Wang, Sue-Faye Ng, Wen Liu, Junjie Huang, Pengfei Chen, Wee-Jun Ong, *Acta Phys. Chim. Sin.*, 2021, **37**, 2011033.

74. J. Y. Choi, C. K. Lim, B. Park, M. Kim, A. Jamal and H. Song, *J. Mater. Chem. A*, 2019, **7**, 15068-15072.

75. Z. He, J. Zhang, X. Li, S. Guan, M. Dai and S. Wang, *Small*, 2020, **16**, 2005051.

76. W. Chen, B. Han, C. Tian, X. Liu, S. Liang, H. Deng and Z. Lin, *Appl. Catal. B-Environ.*, 2019, **244**, 996-1003.

77. Z. Sun, Q. Fan, M. Zhang, S. Liu, H. Tao and J. Texter, *Adv. Sci.*, 2019, **6**, 1901084.

78. Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao and P. K. Wong, *Adv. Mater.*, 2018, **30**, 1706108.

79. Y. Wang, S. Wang and X. W. D. Lou, *Angew. Chem. Int. Ed.*, 2019, **58**, 17236-17240.

80. H. Shen, T. Peppel, J. Strunk and Z. Sun, *Solar RRL*, 2020, **4**, 1900546.

81. Y. Hori, H. Wakebe, T. Tsukamoto and O. Koga, *Electrochim. Acta*, 1994, **39**, 1833-1839.

82. Z. Sun, N. Talreja, H. Tao, J. Texter, M. Muhler, J. Strunk and J. Chen, *Angew. Chem. Int. Ed.*, 2018, **57**, 7610-7627.

83. R. Shi, G. I. Waterhouse and T. Zhang, *Sol. RRL*, 2017, **1**, 1700126.

84. X. Chang, T. Wang and J. Gong, *Energy Environ. Sci.*, 2016, **9**, 2177-2196.

85. S. C. Roy, O. K. Varghese, M. Paulose and C. A. Grimes, *ACS Nano*, 2010, **4**, 1259-1278.

86. J. Albero, Y. Peng and H. García, *ACS Catal.*, 2020, **10**, 5734-5749.

87. J. Wu, Y. Huang, W. Ye and Y. Li, *Adv. Sci.*, 2017, **4**, 1700194.

88. S. Wang, B. Y. Guan and X. W. D. Lou, *J. Am. Chem. Soc.*, 2018, **140**, 5037-5040.

89. Z. Fan, K. Sun and J. Wang, *J. Mater. Chem. A*, 2015, **3**, 18809-18828.

90. Y. Zhao and K. Zhu, *Chem. Soc. Rev.*, 2016, **45**, 655-689.

91. M. V. Kovalenko, L. Protesescu and M. I. Bodnarchuk, *Science*, 2017, **358**, 745-750.

92. Y. F. Mu, W. Zhang, X. X. Guo, G. X. Dong, M. Zhang and T. B. Lu, *ChemSusChem.*, 2019, **12**, 4769-4774.
94. J. S. Manser, J. A. Christians and P. V. Kamat, *Chem. Rev.*, 2016, **116**, 12956-13008.
95. B. Saparov and D. B. Mitzi, *Chem. Rev.*, 2016, **116**, 4558-4596.
96. D. Weber, *Z. Naturforsch. B*, 1978, **33**, 1443-1445.
97. S.-H. Guo, J. Zhou, X. Zhao, C.-Y. Sun, S.-Q. You, X.-L. Wang and Z.-M. Su, *J. Catal.*, 2019, **369**, 201-208.
98. X.-X. Guo, S.-F. Tang, Y.-F. Mu, L.-Y. Wu, G.-X. Dong and M. Zhang, *RSC Adv.*, 2019, **9**, 34342-34348.
99. Y. Jiang, J.-F. Liao, Y.-F. Xu, H.-Y. Chen, X.-D. Wang and D.-B. Kuang, *J. Mater. Chem. A*, 2019, **7**, 13762-13769.
100. Y.-F. Xu, M.-Z. Yang, H.-Y. Chen, J.-F. Liao, X.-D. Wang and D.-B. Kuang, *ACS Appl. Energy Mater.*, 2018, **1**, 5083-5089.
101. Z.-C. Kong, H.-H. Zhang, J.-F. Liao, Y.-J. Dong, Y. Jiang, H.-Y. Chen and D.-B. Kuang, *Sol. RRL*, 2020, **4**, 1900365.
102. Z.-C. Kong, J.-F. Liao, Y.-J. Dong, Y.-F. Xu, H.-Y. Chen, D.-B. Kuang and C.-Y. Su, *ACS Energy Lett.*, 2018, **3**, 2656-2662.
103. J. Chen, J. Yin, X. Zheng, H. Ait Ahsaine, Y. Zhou, C. Dong, O. F. Mohammed, K. Takanabe and O. M. Bakr, *ACS Energy Lett.*, 2019, **4**, 1279-1286.
104. Q. Wang, L. Tao, X. Jiang, M. Wang and Y. Shen, *Appl. Surf. Sci.*, 2019, **465**, 607-613.
105. S. S. Bhosale, A. K. Kharade, E. Jokar, A. Fathi, S.-m. Chang and E. W.-G. Diau, *J. Am. Chem. Soc.*, 2019, **141**, 20434-20442.
106. M.-Z. Yang, Y.-F. Xu, J.-F. Liao, X.-D. Wang, H.-Y. Chen and D.-B. Kuang, *J. Mater. Chem. A*, 2019, **7**, 5409-5415.
107. M. I. Saidaminov, O. F. Mohammed and O. M. Bakr, *ACS Energy Lett.*, 2017, **2**, 889-896.
108. V. K. Ravi, G. B. Markad and A. Nag, *ACS Energy Lett.*, 2016, **1**, 665-671.
109. S. Yakunin, L. Protesescu, F. Krieg, M. I. Bodnaruchuk, G. Nedelcu, M. Humer, G. De Luca, M. Fiebig, W. Heiss and M. V. Kovalenko, *Nat. Commun.*, 2015, **6**, 8515.
110. A. Filippetti and A. Mattoni, *Phys. Rev. B*, 2014, **89**, 125203.
111. Z. Zhu, Q. Sun, Z. Zhang, J. Dai, G. Xing, S. Li, X. Huang and W. Huang, *J. Mater. Chem. C*, 2018, **6**, 10121-10137.
112. D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger and K. Katsiev, *Science*, 2015, **347**, 519-522.
113. S. Wan, M. Ou, Q. Zhong and X. Wang, *Chem. Eng. J.*, 2019, **358**, 1287-1295.
114. Q. A. Akkerman, A. L. Abdelhady and L. Manna, *J. Phys. Chem. Lett.*, 2018, **9**, 2326-2337.

115. Q. A. Akkerman, S. Park, E. Radicchi, F. Nunzi, E. Mosconi, F. De Angelis, R. Brescia, P. Rastogi, M. Prato and L. Manna, *Nano Lett.*, 2017, **17**, 1924-1930.

116. F. Iyikanat, E. Sari and H. Sahin, *Phys. Rev. B*, 2017, **96**, 155442.

117. K. A. Huynh, D. L. T. Nguyen, V.-H. Nguyen, D.-V. N. Vo, Q. T. Trinh, T. P. Nguyen, S. Y. Kim and Q. V. Le, *J. Chem. Technol. Biotechnol.*, 2020, **95**, 2579-2596.

118. L. Dou, A. B. Wong, Y. Yu, M. Lai, N. Kornienko, S. W. Eaton, A. Fu, C. G. Bischak, J. Ma, T. Ding, N. S. Ginsberg, L. W. Wang, A. P. Alivisatos and P. Yang, *Science (New York, N.Y.)*, 2015, **349**, 1518-1521.

119. Y. Fu, H. Zhu, C. C. Stoumpos, Q. Ding, J. Wang, M. G. Kanatzidis, X. Zhu and S. Jin, *ACS Nano*, 2016, **10**, 7963-7972.

120. M. Faizan, K. C. Bhamu, G. Murtaza, X. He, N. Kulhari, M. M. Al-Anazy and S. H. Khan, *Sci. Rep.*, 2021, **11**, 6965.

121. J. Zhang, Y. Yang, H. Deng, U. Farooq, X. Yang, J. Khan, J. Tang and H. Song, *ACS Nano*, 2017, **11**, 9294-9302.

122. T. C. Jellicoe, J. M. Richter, H. F. J. Glass, M. Tabachnyk, R. Brady, S. E. Dutton, A. Rao, R. H. Friend, D. Credgington, N. C. Greenham and M. L. Böhm, *J. Am. Chem. Soc.*, 2016, **138**, 2941-2944.

123. E. T. McClure, M. R. Ball, W. Windl and P. M. Woodward, *Chem. Mater.*, 2016, **28**, 1348-1354.

124. F. Wei, F. Brivio, Y. Wu, S. Sun, P. D. Bristowe and A. K. Cheetham, *J. Mater. Chem. C*, 2018, **6**, 3573-3577.

125. Y. Zhang, J. Yin, M. R. Parida, G. H. Ahmed, J. Pan, O. M. Bakr, J.-L. Brédas and O. F. Mohammed, *J. Phys. Chem. Lett.*, 2017, **8**, 3173-3177.

126. B. Yang, J. Chen, F. Hong, X. Mao, K. Zheng, S. Yang, Y. Li, T. Pullerits, W. Deng and K. Han, *Angew. Chem. Int. Ed.*, 2017, **56**, 12471-12475.

127. Y. Hu, S. Zhang, X. Miao, L. Su, F. Bai, T. Qiu, J. Liu and G. Yuan, *Adv. Mater. Interfaces*, 2017, **4**, 1700131.

128. M. Ou, W. Tu, S. Yin, W. Xing, S. Wu, H. Wang, S. Wan, Q. Zhong, R. Xu, *Angew. Chem. Int. Ed.* 2018, **57**, 13570.

129. W. Tu, Y. Xu, J. Wang, B. Zhang, T. Zhou, S. Yin, S. Wu, C. Li, Y. Huang and Y. Zhou, *ACS Sustain. Chem. Eng.*, 2017, **5**, 7260-7268.
130. J. Fu, K. Jiang, X. Qiu, J. Yu and M. Liu, *Mater. Today*, 2020, **32**, 222-243.
131. Y.-X. Chen, Y.-F. Xu, X.-D. Wang, H.-Y. Chen and D.-B. Kuang, *Sustain. Energy Fuels*, 2020, **4**, 2249-2255.
132. S. Thapa, K. Bhardwaj, S. Basel, S. Pradhan, C. J. Eling, A. M. Adawi, J.-S. G. Bouillard, G. J. Stasiuk, P. Reiss and A. Pariyar, *Nanoscale Adv.*, 2019, **1**, 3388-3391.
133. L. Protgescru, S. Yakunin, M. I. Bodnarchuk, F. Bertolotti, N. Masciocchi, A. Guagliardi and M. V. Kovalenko, *J. Am. Chem. Soc.*, 2016, **138**, 14202-14205.
134. I. Lignos, L. Protgescru, D. B. r. Emirgolu, R. Maceiczyk, S. Schneider, M. V. Kovalenko and A. J. deMello, *Nano Lett.*, 2018, **18**, 1246-1252.
135. J. Hou, S. Cao, Y. Wu, Z. Gao, F. Liang, Y. Sun, Z. Lin and L. Sun, *Chem. Eur. J.*, 2017, **23**, 9481-9485.
136. S. Shyamal, S. K. Dutta, T. Das, S. Sen, S. Chakraborty and N. Pradhan, *J. Phys. Chem. Lett.*, 2020, **11**, 3608-3614.
137. S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum and C. Ballif, *J. Phys. Chem. Lett.*, 2014, **5**, 1035-1039.
138. Y. Fu, H. Zhu, J. Chen, M. P. Hautzinger, X.-Y. Zhu and S. Jin, *Nat. Rev. Mater.*, 2019, **4**, 169-188.
139. C. Tang, C. Chen, W. Xu and L. Xu, *J. Mater. Chem. A*, 2019, **7**, 6911-6919.
140. G. Abdelmageed, L. Jewell, K. Helllier, L. Seymour, B. Luo, F. Bridges, J. Z. Zhang and S. Carter, *Appl. Phys. Lett.*, 2016, **109**, 233905.
141. N. Aristidou, C. Eames, I. Sanchez-Molina, X. Bu, J. Kosco, M. S. Islam and S. A. Haque, *Nat. Commun.*, 2017, **8**, 15218.
142. J.-W. Lee, D.-H. Kim, H.-S. Kim, S.-W. Seo, S. M. Cho and N.-G. Park, *Adv. Energy Mater.*, 2015, **5**, 1501310.
143. Y. Kim, E. Yassitepe, O. Voznyy, R. Comin, G. Walters, X. Gong, P. Kanjanaboos, A. F. Nogueira and E. H. Sargent, *ACS Appl. Mater. Interfaces*, 2015, **7**, 25007-25013.
144. S. You, S. Guo, X. Zhao, M. Sun, C. Sun, Z. Su and X. Wang, *Dalton Trans.*, 2019, **48**, 14115-14121.
145. J. Jiang, J.-F. Liao, H.-Y. Chen, H.-H. Zhang, J.-Y. Li, X.-D. Wang and D.-B. Kuang, *Chem*, 2020, **6**, 766-780.
146. A. H. Slavney, T. Hu, A. M. Lindenberg and H. I. Karunadasa, *J. Am. Chem. Soc.*, 2016, **138**, 2138-2141.
147. G. Volonakis, M. Filip, A.-A. Haghighirad, N. Sakai, B. Wenger, H. Snaith and F. Giustino, *J. Phys. Chem. Lett.*, 2016, **7**, 1254-1259.
148. Z. Liu, H. Yang, J. Wang, Y. Yuan, K. Hills-Kimball, T. Cai, P. Wang, A. Tang and O. Chen, *Nano Letters*, 2021, **21**, 1620-1627.

149. Y. Dai, C. Poidevin, C. Ochoa-Hernández, A. A. Auer and H. Tüysüz, *Angew. Chem. Int. Ed.*, 2020, **59**, 5788-5796.

150. G. Volonakis, A. A. Haghighirad, R. L. Milot, W. H. Sio, M. R. Filip, B. Wenger, M. B. Johnston, L. M. Herz, H. J. Snaith and F. Giustino, *J. Phys. Chem. Lett.*, 2017, **8**, 772-778.

151. I. Chung, J.-H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T. Kenney and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2012, **134**, 8579-8587.

152. J. Pal, S. Manna, A. Mondal, S. Das, K. V. Adarsh and A. Nag, *Angew. Chem. Int. Ed.*, 2017, **56**, 14187-14191.

153. F. Xu, K. Meng, B. Cheng, S. Wang, J. Xu and J. Yu, *Nat. Commun.*, 2020, **11**, 4613.

154. X.-F. Cao, L. Zhang, X.-T. Chen and Z.-L. Xue, *CrystEngComm.*, 2011, **13**, 306-311.

155. H. Huang, R. Cao, S. Yu, K. Xu, W. Hao, Y. Wang, F. Dong, T. Zhang and Y. Zhang, *Appl. Catal. B-Environ.*, 2017, **219**, 526-537.

156. C. Zhang and Y. Zhu, *Chem. Mater.*, 2005, **17**, 3537-3545.

157. Y. Zhou, Y. Zhang, M. Lin, J. Long, Z. Zhang, H. Lin, J. C.-S. Wu and X. Wang, *Nat. Commun.*, 2015, **6**, 8340.

158. J. Hu, D. Chen, Z. Mo, N. Li, Q. Xu, H. Li, J. He, H. Xu and J. Lu, *Angew. Chem. Int. Ed.*, 2019, **58**, 2073-2077.

159. J. Wang, J. Wang, N. Li, X. Du, J. Ma, C. He and Z. Li, *ACS Appl. Mater. Interfaces*, 2020, **12**, 31477-31485.

160. Q. Lu, Y. Yu, Q. Ma, B. Chen and H. Zhang, *Adv. Mater.*, 2016, **28**, 1917-1933.

161. D. Deng, K. Novoselov, Q. Fu, N. Zheng, Z. Tian and X. Bao, *Nat. Nanotechnol.*, 2016, **11**, 218-230.

162. J. Li, Y. Zhao, M. Xia, H. An, H. Bai, J. Wei, B. Yang and G. Yang, *Appl. Catal. B-Environ.*, 2020, **261**, 118244.

163. Z. Xing, J. Hu, M. Ma, H. Lin, Y. An, Z. Liu, Y. Zhang, J. Li and S. Yang, *J. Am. Chem. Soc.*, 2019, **141**, 19715-19727.

164. C. Tan, X. Cao, X.-J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han and G.-H. Nam, *Chem. Rev.*, 2017, **117**, 6225-6331.

165. Y. Zhao, S. Zhang, R. Shi, G. I. Waterhouse, J. Tang and T. Zhang, *Mater. Today*, 2020, **34**, 78-91.

166. W. Wang, W. Zhao, H. Zhang, X. Dou and H. Shi, *Chinese J. Catal.*, 2020, **42**, 97-106.
167. Y. Jiang, H. Y. Chen, J. Y. Li, J. F. Liao, H. H. Zhang, X. D. Wang and D. B. Kuang, *Adv. Funct. Mater.*, 2020, 2004293.

168. N. Zhang, R. Ciriminna, M. Pagliaro and Y.-J. Xu, *Chem. Soc. Rev.*, 2014, 43, 5276-5287.

169. H. Huang, C. Zhou, X. Jiao, H. Yuan, J. Zhao, C. He, J. Hofkens, M. B. Roelfs, J. Long and J. A. Steele, *ACS Catal.*, 2019, 10, 1439-1443.

170. P. Schulz, D. Cahen and A. Kahn, *Chem. Rev.*, 2019, 119, 3349-3417.

171. G. Kapil, T. Ohta, T. Koyanagi, M. Vigneshwaran, Y. Zhang, Y. Ogomi, S. S. Pandey, K. Yoshino, Q. Shen and T. Toyoda, *J. Phys. Chem. C*, 2017, 121, 13092-13100.

172. H. S. Rao, W. G. Li, B. X. Chen, D. B. Kuang and C. Y. Su, *Adv. Mater.*, 2017, 29, 1602639.

173. Z. Chen, Q. Dong, Y. Liu, C. Bao, Y. Fang, Y. Lin, S. Tang, Q. Wang, X. Xiao and Y. Bai, *Nat. Commun.*, 2017, 8, 1-7.

174. Y. Liu, J. Sun, Z. Yang, D. Yang, X. Ren, H. Xu, Z. Yang and S. Liu, *Adv. Opt. Mater.*, 2016, 4, 1829-1837.

175. A. Kaltzoglou, M. Antoniadou, A. G. Kontos, C. C. Stoumpos, D. Perganti, E. Siranidi, V. Raptis, K. Trohidou, V. Psycharis and M. G. Kanatzidis, *J. Phys. Chem. C*, 2016, 120, 11777-11785.

176. B. Lee, C. C. Stoumpos, N. Zhou, F. Hao, C. Mallikas, C.-Y. Yeh, T. J. Marks, M. G. Kanatzidis and R. P. Chang, *J. Am. Chem. Soc.*, 2014, 136, 15379-15385.

177. X. Jiao, X. Li, X. Jin, Y. Sun, J. Xu, L. Liang, H. Ju, J. Zhu, Y. Pan, W. Yan, Y. Lin and Y. Xie, *J. Am. Chem. Soc.*, 2017, 139, 18044-18051.

178. M. M. Kandy, *Sustain. Energy Fuels*, 2020, 4, 469-484.

179. S. Zhang, Z. He, S. Xu, X. Li, J. Zhang, X. Zhan, M. Dai and S. Wang, *Solar RRL*, 2021, 5, 2100233.

180. J. Low, B. Cheng, J. Yu and M. Jaroniec, *Energy Stor. Mater.*, 2016, 3, 24-35.

181. S. Kaniyankandy, S. Rawalekar and H. N. Ghosh, *J. Phys. Chem. C*, 2012, 116, 16271-16275.

182. M. Ou, W. Tu, S. Yin, W. Xing, S. Wu, H. Wang, S. Wan, Q. Zhong and R. Xu, *Angew. Chem.*, 2018, 130, 13758-13762.

183. C. Li, Y. Du, D. Wang, S. Yin, W. Tu, Z. Chen, M. Kraft, G. Chen and R. Xu, *Adv. Funct. Mater.*, 2017, 27, 1604328.

184. C. Cao, D.-D. Ma, J.-F. Gu, X. Xie, G. Zeng, X. Li, S.-G. Han, Q.-L. Zhu, X.-T. Wu and Q. Xu, *Angew. Chem. Int. Ed.*, 2020, 59, 15014-15020.
185. S. Wang, W. Yao, J. Lin, Z. Ding and X. Wang, *Angew. Chem. Int. Ed.*, 2014, **126**, 1052-1056.
186. J. Qin, S. Wang and X. Wang, *Appl. Catal. B-Environ.*, 2017, **209**, 476-482.
187. S. Yan, S. Ouyang, H. Xu, M. Zhao, X. Zhang and J. Ye, *J. Mater. Chem. A*, 2016, **4**, 15126-15133.
188. L. Shen, S. Liang, W. Wu, R. Liang and L. Wu, *J. Mater. Chem. A*, 2013, **1**, 11473-11482.
189. G. Gao, Q. Xi, H. Zhou, Y. Zhao, C. Wu, L. Wang, P. Guo and J. Xu, *Nanoscale*, 2017, **9**, 12032-12038.
190. M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632-6640.
191. A. A. Zhumekenov, M. I. Saidaminov, M. A. Haque, E. Alarousu, S. P. Sarmah, B. Murali, I. Dursun, X.-H. Miao, A. L. Abdelhady and T. Wu, *ACS Energy Lett.*, 2016, **1**, 32-37.
192. G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344-347.
193. J. Shamsi, A. S. Urban, M. Imran, L. De Trizio and L. Manna, *Chem. Rev.*, 2019, **119**, 3296-3348.
194. J.-F. Liao, Y.-T. Cai, J.-Y. Li, Y. Jiang, X.-D. Wang, H.-Y. Chen and D.-B. Kuang, *J. Energy Chem.*, 2021, **53**, 309-315.
195. X. Huang, H. Li, C. Zhang, S. Tan, Z. Chen, L. Chen, Z. Lu, X. Wang and M. Xiao, *Nat. Commun.*, 2019, **10**, 1163.
196. K. Wu, G. Liang, Q. Shang, Y. Ren, D. Kong and T. Lian, *J. Am. Chem. Soc.*, 2015, **137**, 12792-12795.
197. F. Liu, Y. Zhang, C. Ding, T. Toyoda, Y. Ogomi, T. S. Ripolles, S. Hayase, T. Minemoto, K. Yoshino, S. Dai and Q. Shen, *J. Phys. Chem. Lett.*, 2018, **9**, 294-297.
198. Z. Fan, X. Huang, C. Tan and H. Zhang, *Chem. Sci.*, 2015, **6**, 95-111.
199. M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, *Adv. Mater.*, 2011, **23**, 4207-4207.
200. B. Anasori, M. R. Lukatskaya and Y. Gogotsi, *Nat. Rev. Mater.*, 2017, **2**, 1-17.
201. S. Zhang, Z. He, X. Li, J. Zhang, Q. Zang and S. Wang, *Nanoscale Adv.*, 2020, **2**, 3610-3623.
202. R. Meng, J. Huang, Y. Feng, L. Zu, C. Peng, L. Zheng, L. Zheng, Z. Chen, G. Liu and B. Chen, *Adv. Energy Mater.*, 2018, **8**, 1801514.
203. H. Tao, Q. Fan, T. Ma, S. Liu, H. Gysling, J. Texter, F. Guo and Z. Sun, Prog. Mater. Sci., 2020, 111, 100637.
204. M. Arif, G. Yasin, M. Shakeel, M. A. Mushtaq, W. Ye, X. Fang, S. Ji and D. Yan, J. Energy Chem., 2021, 58, 237-246.
205. T. P. Nguyen, D. M. Tuan Nguyen, D. L. Tran, H. K. Le, D.-V. N. Vo, S. S. Lam, R. S. Varma, M. Shokouhimehr, C. C. Nguyen and Q. V. Le, Mol. Catal., 2020, 486, 110850.
206. Q. Xue, H. Zhang, M. Zhu, Z. Pei, H. Li, Z. Wang, Y. Huang, Y. Huang, Q. Deng and J. Zhou, Adv. Mater., 2017, 29, 1604847.
207. L. Ding, Y. Wei, L. Li, T. Zhang, H. Wang, J. Xue, L.-X. Ding, S. Wang, J. Caro and Y. Gogotsi, Nat. Commun., 2018, 9, 1-7.
208. M. Alhabeb, K. Maleski, T. S. Mathis, A. Sarycheva, C. B. Hatter, S. Uzun, A. Levitt and Y. Gogotsi, Angew. Chem. Int. Ed., 2018, 130, 5542-5546.
209. C. B. Hiragond, N. S. Powar and S.-I. In, Nanomaterials, 2020, 10, 2569.
210. M. Que, Y. Zhao, Y. Yang, L. Pan, W. Lei, W. Cai, H. Yuan, J. Chen and G. Zhu, ACS Appl. Mater. Interfaces, 2021, 13, 6180-6187.
211. X. Mao, L. Sun, T. Wu, T. Chu, W. Deng and K. Han, J. Phys. Chem. C, 2018, 122, 7670-7675.
212. W.-J. Yin, J.-H. Yang, J. Kang, Y. Yan and S.-H. Wei, J. Mater. Chem. A, 2015, 3, 8926-8942.
213. Y. Park and B. Park, Results in Phys., 2018, 11, 302-305.
214. M. Irfan, S. Azam, S. Hussain, S. A. Khan, M. Sohail, M. Makhdoom, Z. Ali, I. V. Kityk, S. Muhammad and A. G. Al-Sehemi, J. Alloys Compd., 2018, 766, 536-545.
215. P. Kanhere and Z. Chen, Molecules (Basel, Switzerland), 2014, 19, 19995-20022.
216. J. Schneider, H. Jia, J. T. Muckerman and E. Fujita, Chem. Soc. Rev., 2012, 41, 2036-2051.
217. D. Liu, Q. Li, H. Jing and K. Wu, J. Phys. Chem. C, 2019, 123, 3795-3800.
218. S. T. A. G. Melissen, F. Labat, P. Sautet and T. Le Bahers, Phys. Chem. Chem. Phys., 2015, 17, 2199-2209.
219. X. Liu, J. Fan and C. Huang, Frontiers in Nanotechnology, 2021, 3.
220. S. You, S. Guo, X. Zhao, M. Sun, C. Sun, Z. Su and X. Wang, Dalton Trans., 2019, 48, 14115-14121.
221. S. Shyamal, S. K. Dutta and N. Pradhan, J. Phys. Chem. Lett., 2019, 10, 7965-7969.
222. H. Huang, J. Zhao, Y. Du, C. Zhou, M. Zhang, Z. Wang, Y. Weng, J. Long, J. Hofkens and J. A. Steele, *ACS Nano*, 2020, **14**, 16689-16697.

223. Y. Jiang, J.-F. Liao, H.-Y. Chen, H.-H. Zhang, J.-Y. Li, X.-D. Wang and D.-B. Kuang, *Chem*, 2020, **6**, 766-780.

224. S. S. Bhosale, A. K. Kharade, E. Jokar, A. Fathi, S.-m. Chang and E. W.-G. Diau, *J. Am. Chem. Soc.*, 2019, **141**, 20434-20442.

225. Y.-F. Mu, W. Zhang, X.-X. Guo, G.-X. Dong, M. Zhang and T.-B. Lu, *ChemSusChem*, 2019, **12**, 4769-4774.

226. Y.-W. Liu, S.-H. Guo, S.-Q. You, C.-Y. Sun, X.-L. Wang, L. Zhao and Z.-M. Su, *Nanotechnology*, 2020, **31**, 215605.

227. G.-X. Dong, W. Zhang, Y.-F. Mu, K. Su, M. Zhang and T.-B. Lu, *Chem. Commun.*, 2020, **56**, 4664-4667.

228. J. Zhu, Y. Zhu, J. Huang, L. Hou, J. Shen and C. Li, *Nanoscale*, 2020, **12**, 11842-11846.

229. X. Wang, K. Li, J. He, J. Yang, F. Dong, W. Mai and M. Zhu, *Nano Energy*, 2020, **78**, 105388.

230. Z. Wang, H. Kim and H. N. Alshareef, *Adv. Mater.*, 2018, **30**, 1706656.

231. J. Song, L. Xu, J. Li, J. Xue, Y. Dong, X. Li and H. Zeng, *Adv. Mater.*, 2016, **28**, 4861-4869.

232. H. Huang, J. Li, Y. Yi, J. Wang, Y. Kang, P. K. Chu, H. Ong and X.-F. Yu, *Chem. Commun.*, 2018, **54**, 2365-2368.

233. R. Begum, M. R. Parida, A. L. Abdelhady, B. Murali, N. M. Alyami, G. H. Ahmed, M. N. Hedhili, O. M. Bakr and O. F. Mohammed, *J. Am. Chem. Soc.*, 2017, **139**, 731-737.

234. W. Deng, H. Huang, H. Jin, W. Li, X. Chu, D. Xiong, W. Yan, F. Chun, M. Xie and C. Luo, *Adv. Opt. Mater.*, 2019, **7**, 1801521.

235. Y. Shiraishi, T. Hagi, M. Matsumoto, S. Tanaka, S. Ichikawa and T. Hirai, *Commun. Chem.*, 2020, **3**, 169.