

Review

Recent Developments in Lead and Lead-Free Halide Perovskite Nanostructures towards Photocatalytic CO₂ Reduction

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Abstract: Perovskite materials have been widely considered as emerging photocatalysts for CO₂ reduction due to their extraordinary physicochemical and optical properties. Perovskites offer a wide range of benefits compared to conventional semiconductors, including tunable bandgap, high surface energy, high charge carrier lifetime, and flexible crystal structure, making them ideal for high-performance photocatalytic CO₂ reduction. Notably, defect-induced perovskites, for example, crystallographic defects in perovskites, have given excellent opportunities to tune perovskites' catalytic properties. Recently, lead (Pb) halide perovskite and their composites or heterojunction with other semiconductors, metal nanoparticles (NPs), metal complexes, graphene, and metal-organic frameworks (MOFs) have been well established for CO₂ conversion. Besides, various halide perovskites have come under focus to avoid the toxicity of lead-based materials. Therefore, we reviewed the recent progress made by Pb and Pb-free halide perovskites in photo-assisted CO₂ reduction into useful chemicals. We also discussed the importance of various factors like change in solvent, structure defects, and compositions in the fabrication of halide perovskites to efficiently convert CO₂ into value-added products.

Keywords: lead halide perovskites; lead-free perovskites; CO₂ reduction; photocatalysis

1. Introduction

Photocatalytic CO₂ reduction, which transforms solar energy into usable chemical fuels, has drawn considerable attention for solving environmental pollution and global energy problems [1–11]. Many attempts have been taken to upgrade the photocatalytic CO₂ conversion process in terms of material design. In any event, the discovery of a new photocatalyst for better synergistic performance has never stopped. To date, several types of catalysts have been employed for CO₂ conversion, including metal oxides, nitrides, sulfides, selenides, chalcogenides, and perovskite materials [12–23]. These materials have made significant progress, but many of them have several drawbacks, such as high-cost synthetic approaches, lengthy/complicated synthesis process, long-term instability, and less catalytic activity. While recently, perovskites have been significantly attracted as a better replacement for traditional semiconductors for the photocatalytic CO₂ reduction process due to their extraordinary optoelectronic properties and cost-effectiveness [24,25].

Typically, perovskite materials are indicated with the chemical formula ABX₃ [26,27]; here, A site occupies large size cation (e.g., Cs⁺, Rb⁺, methylammonium), and B sites are occupied by small size cation (e.g., Pb²⁺, Sn²⁺). At the same time, X (e.g., O^{2−}, Br[−], Cl[−], I[−]) holds an anion that bonds to both A and B. According to the crystallographic perspective, the ideal perovskite structure is cubic and unbending; however, most perovskites are generally distorted. Based on the perovskite elements, the properties such as chemical stability, bandgap energies, optical stability, and crystal structure

of the catalyst can be tunable [28]. In 1978, Hemminger et al. first-time observed photosynthetic reaction using SrTiO₂ perovskite materials for the conversion of CO₂ into CH₄ in the presence of gaseous water and CO₂ [29]. The SrTiO₂ (111) crystalline phase with Pt foil was active for the CO₂ conversion. The Pt foil was responsible for the adsorption of the CO₂ on the metal faces, but the limitation was metal poisoning. In the case of SrTiO₃, the regeneration of the Ti³⁺ after the oxidation reaction in water, surface properties, and crystallite size play a key role. Afterward, SrTiO₃, Sr₂TiO₄, NaNbO₃, and H₂SrTa₂O₇ have been documented for the CO₂ reduction process [30–33]. Luo et al. observed the relationship between the surface structure of SrTiO₃ and photocatalytic activity for CO₂ photoreduction [30]. The SrTiO₃ was treated with the etching process and functionalized with the OH group. The SrO-terminated surface exhibits nucleophilicity, which allows CO₂ adsorption, and TiO₂-terminated is electrophilic. The effect of the electronic properties also differs from these two surfaces; the Sr 4d orbital conduction band level is more negative than the Ti 3d orbital. Though in the case of SrO-terminated or Sr(OH)₂-decorated allowed the highest CO₂ fixation than the Ti-rich surface, but the photoreduction activity was low. Because of the produced surface, molecules were attached to the weakly active Sr ions and exhibited lower reactivity. The Ti-rich catalyst showed the highest activity because the active Ti-edges shifted light absorption in the visible region. Therefore, these studies showed that the properties of perovskites, especially structural flexibility, will be of great interest to study as efficient materials for large-scale photocatalytic applications.

Among the various perovskite materials, halide perovskites have been successfully emerging as an efficient catalyst due to their extraordinary properties like cost-effectiveness, easy synthesis process, visible light absorption, high CO₂ adsorption surface area, surface disorders for charge trapping, and tunable structure [34–42]. There are two classes of materials in the halide perovskites: (1) Lead-based halide perovskites and (2) lead-free halide perovskites. Most of the lead halide perovskites offer a narrow bandgap as compared to traditional semiconductors. The hybrid composites of lead halide perovskites with other semiconductors/materials can efficiently enhance the yield and stability of the CO₂ conversion. Later, however, few more studies have been reported on lead-free halide perovskites to avoid toxicity. Therefore, lead and lead-free halide perovskites' recent development towards reducing CO₂ in different materials has fascinated us. This review would offer a thorough look into the recent success of optimal halide perovskites for the CO₂ photoreduction application.

2. Fundamentals of Photocatalytic CO₂ Reduction

The process of thermal catalysis is the easiest option for CO₂ reduction. Still, it is not environmentally appropriate due to an endothermic reaction so that the input energy must be high [43]. As we already knew, nature is doing the same process that converts CO₂ to hydrocarbons by the photosynthesis process. So why not artificial photosynthesis can help to solve the problem of CO₂ reduction? The process of CO₂ reduction begins after the chemisorption of the CO₂ molecules on the catalytic surface. Therefore, the CO₂ reduction process's high efficiency can be achieved by employing high surface area catalysts to maximize CO₂ molecules' adsorption on the catalyst's surface. As we know, CO₂ is a highly stable molecule, therefore to break the C-O bonding, it requires 750 kJ mol^{−1} of the bond dissociation energy, which is approximately 54% higher than C-H bond dissociation energy (411 kJ mol^{−1}). To reduce CO₂ molecules, the conduction and valence band potentials of particular catalysts should be above and below the standard redox potentials of the products, respectively. Thus, to convert the CO₂ into any product, it is necessary to cross the high energy of the activation barrier for forwarding reaction [44]. In the conversion of CO₂, a single-electron transfer is practically inconceivable to produce CO₂^{•−} due to the necessity of high redox potential of −1.90 V vs. NHE (see Table 1). Therefore, as a single electron process is practically challenging, the proton assisted CO₂ reduction process is thermodynamically feasible to form various products. Depending upon the concentration of available electrons and protons, the CO₂ reduction proceeds into the formation of various products; for instance, CO evolution can be achieved by contributing 2e[−] and 2H⁺ at the redox potential −0.53 V (pH = 7). Consequently, an increase in the reduction potential concerning the number of electrons, converting CO₂ to ethane, desires the 14e[−]

and 14H^+ . In recent days, there have been several excellent reviews based on the fundamentals of photo-reduction of CO_2 [45–50]; thus, readers may turn to these reviews for more details. Our review article focuses on the fabrication of lead and lead-free halide perovskites' and their composites, the effect of solvents, and other parameters to improve the catalytic performance towards the CO_2 conversion process.

Table 1. The catalytic pathway of CO_2 reduction towards various main products with their redox potentials (at pH = 7).

No.	Reaction	$E^0_{\text{redox Vs NHE}}$	Product
1	$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^{\bullet-}$	−1.90 V	$\text{CO}_2^{\bullet-}$
2	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	−0.53 V	Carbon monoxide
3	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	−0.61 V	Formic acid
4	$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	−0.48 V	Formaldehyde
5	$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	−0.38 V	Methanol
6	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	−0.24 V	Methane
7	$2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	−0.31 V	Acetic acid
8	$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	−0.51 V	Ethane

3. Lead Halide Perovskites for Photocatalytic CO_2 Reduction

So far, organic–inorganic lead halide perovskites (LHPs) have been well established for photovoltaic applications with high power conversion proficiency [25]. Later, they have been successfully used for various applications, including photodetector, laser, LED, thermoelectric, and piezoelectric [51,52]. Recently, Zhu et al. reported LHPs for organic synthesis that have fundamental significance in drug production [53]. The high efficiency of LHPs was mainly attributed to the properties that are very suitable for photocatalytic applications, such as high absorption coefficient, greater defect tolerance, superior photogenerated charge-carrier lifetime, and high carrier mobility [54]. In recent years, LHPs have also been used as photocatalytic materials for various applications like hydrogen evolution reaction [55,56], organic pollutant degradation [57,58], and alkylation of aldehyde [41,51]. In addition, they have been proved the best materials for oxygen evolution reactions; thus, water can be used as an electron source for the photoreduction of CO_2 by preventing the use of sacrificial agents [59]. Thus, the introduction of halide perovskites for CO_2 photoreduction has made substantial progress in the field of catalysis. These materials possess poor water stability due to the ionic nature of the LHPs. Numerous attempts have been made to boost the catalytic activity and stability of LHPs towards photocatalytic CO_2 reduction. In this contribution, Wu et al. encapsulated methylammonium lead iodide quantum dots (QDs) in iron-based metal–organic frameworks (MOFs) and successfully utilized them for CO_2 photoreduction [60]. They have used Fe-porphyrin-based MOFs to increase the water stability of perovskite. Fe act as an active catalytic site for CO_2 photoreduction, which also suppresses the charge recombination and effectively enhances the charge transportation. The optimized samples of MAPbI_3 with Fe-porphyrin MOF PCN-221(Fe_x) exhibited a total hydrocarbon yield of $1559 \mu\text{mol g}^{-1}$ combined for CO and CH_4 production. As the concentration of Fe in PCN-221 (Fe_x) increases, the improvement in CO and CH_4 formation was observed. The catalyst showed excellent stability over 80 h, which was much higher than pristine halide perovskite QDs. Remarkably, water was used as a sacrificial agent with ethyl acetate, which acts as an electron source for the CO_2 reduction reaction. The light-harvesting efficiency of MAPbI_3 and fast electron transfer from MAPbI_3 to Fe were attributed to high catalytic activity.

Apart from this exceptional research, most methylammonium halides have been documented for hydrogen production. Previous studies have shown that MAPbI_3 is unstable in humid conditions; thus, other halide perovskites have been intended for CO_2 photoreduction [61]. Subsequently, major advances have been made in the field of research with cesium lead halide perovskites as a novel and most common catalyst for CO_2 reduction in recent years. Most of the inorganic Cs-based perovskites possess suitable valence and conduction band potentials for the CO_2 reduction reaction. To this end, Hou et al. suggested a controlled synthesis of colloidal QDs of CsPbBr_3 and investigated the size-dependent CO_2 photoreduction

into CH_4 , CO , and H_2 [61]. Using less costly inorganic precursors and oleylamine/oleic acid as a surface ligand, the QDs were synthesized using a simple solution process. These colloidal QDs display the tunable particle size due to the quantum confinement effect at different temperatures, as shown in Figure 1a–d. The optical properties of CsPbBr_3 showed a significant impact on photocatalytic efficiency (Figure 1e,f). During the photocatalytic reaction, the average electron yield for CO_2 reduction was $20.9 \mu\text{mol g}^{-1}$. A Time-resolved PL study signifies that an optimized catalyst has the most extended lifetime responsible for enhanced catalytic activity (Figure 1g). The band alignment of the valence and conduction band were well matched for CO_2 reduction and water oxidation leading to the formation of CO , CH_4 , and H_2 (Figure 1h). Therefore, such QDs can be used as inexpensive catalysts for catalytic applications.

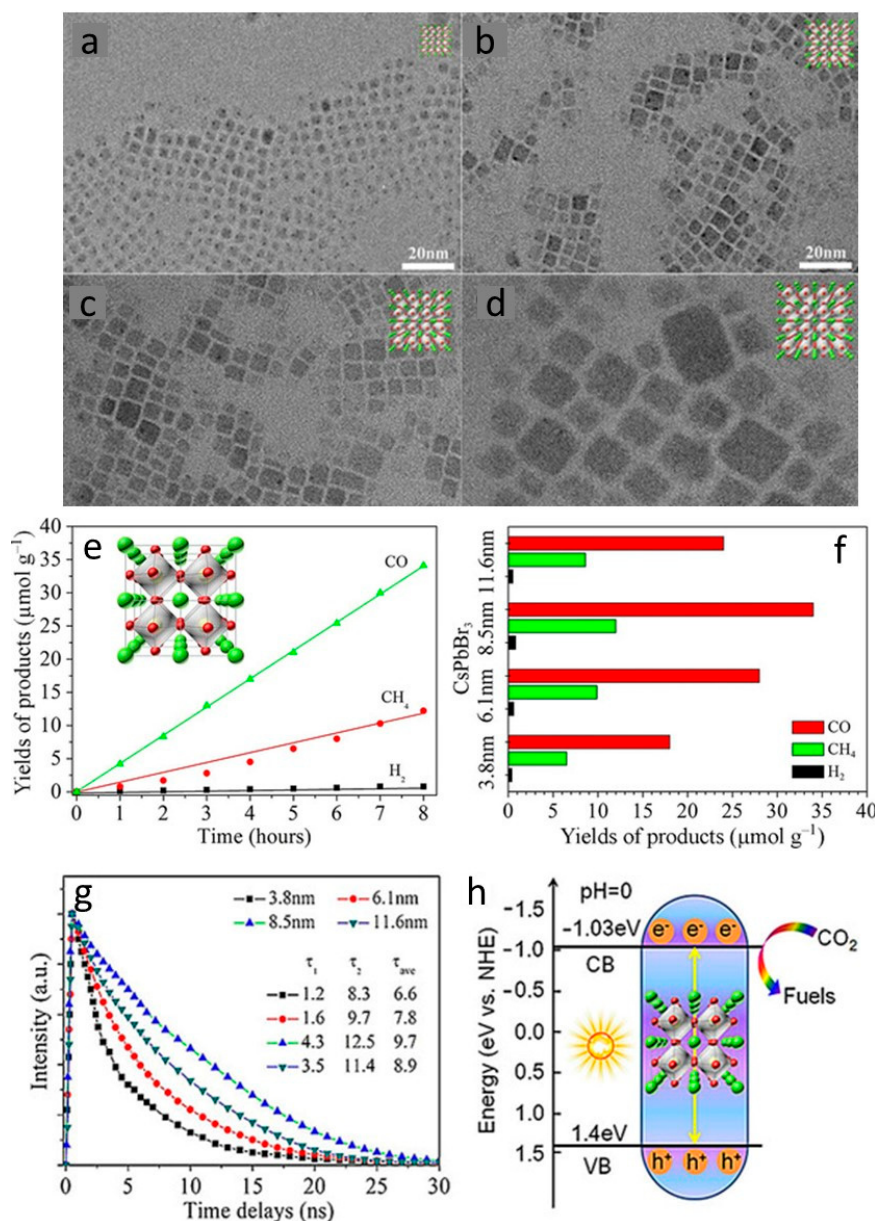


Figure 1. (a–d) CsPbBr_3 quantum dots (QDs) TEM images showing the difference in particle size, (e) photocatalytic CO_2 reduction using an optimized sample of CsPbBr_3 , (f) particle size effect on the CO_2 reduction activity, (g) Time-resolved photoluminescence (TRPL) decay of different samples, and (h) band diagram showing mechanism of CO_2 reduction to chemical fuels. Reproduced from [61], with permission from John Wiley and Sons, 2017.

Mixed halide perovskites, i.e., a mixture of the cation (MA^+ , Cs^+) and anion (Cl^- , I^- , Br^-), can further increase the efficiency of catalytic reaction towards CO_2 reduction. Tuning the halide ratio can change the structural combination of perovskites that significantly impact catalytic behavior. Thus, Su and co-workers reported a low-cost, cubic phase $\text{CsPb}(\text{Br}_{0.5}/\text{Cl}_{0.5})_3$ perovskite with varied ratios of Br and Cl and studied for photocatalytic CO_2 reduction [62]. The controlled synthesis of mixed halide perovskite was carried out by the hot injection method. Mixed halide perovskite, i.e., $\text{CsPb}(\text{Br}_x/\text{Cl}_{1-x})_3$, offers excellent absorption in the visible region ranging from 400–700 nm, relatively broader than distinctive semiconductors like TiO_2 and ZnO . The calculated band edges were quite suitable for CO_2 reduction potentials of CO and CH_4 , with the bandgap ranging from 2.33 to 2.98 eV for $\text{CsPb}(\text{Br}_x/\text{Cl}_{1-x})_3$ samples. While in the emission spectra, the gradual shifting and quenching of pristine CsPbBr_3 from 517 to 413 nm was observed as the amount of Cl increases, which is attributed to the improved electron separation. The authors performed a CO_2 reduction test in ethyl acetate. The increased CO and CH_4 formation was found with an increase in the Cl concentration, and the optimized sample achieved much higher catalytic activity than the pristine CsPbBr_3 and CsPbCl_3 perovskites. The time-dependent CO_2 reduction rate for the optimized catalyst demonstrated strong stability over the 9 h for CH_4 and CO evolution. The increased activity and stability of mixed halide perovskite were attributed to the controlled ratios of Br and Cl.

It is well known that pristine semiconductor/perovskites suffer from poor catalytic activity and stability due to the rapid recombination of photogenerated charges or lack of suitable optical absorption, or ineffective CO_2 adsorption. Therefore, several studies have been documented with metal doping for cesium halide perovskites to boost catalytic activity, stability, and selectivity. In order to attain these distinct characteristics, it is crucial to consider the mechanism of product formation and the pathway of CO_2 reduction over the catalyst. Tang et al. theoretically studied the effect of metal doping in CsPbBr_3 on product selectivity by employing DFT calculations (Figure 2) [63]. The model used for this analysis has considered the chemical potential of an electron and proton is equal to half of the hydrogen gas phase at standard pressure. The first step of CO_2 reduction formed the HCOO^* , and further adsorption of the excessive proton on the oxygen atom leads to HCO^*OH formation. The HCO^*OH is a spontaneous reaction; however, dissociation of HCO^*OH to CO and H_2O is the nonspontaneous reaction in the case of pristine- CsPbBr_3 . After Co and Fe doping, the catalytic activity was improved and showed a downhill reaction. The numerical values of Gibbs free energy indicated that Co and Fe doping increases the rate of chemical reaction approximately two times for catalytic activity than pristine- CsPbBr_3 material. Pristine CsPbBr_3 was initially examined to reduce CO_2 , and the findings of the free barrier energy showed that CsPbBr_3 is inactive for the evolution of any hydrocarbons. While Fe and Co-doped CsPbBr_3 were investigated for selective formation of CH_4 , these metals have great potential to break the O-C-O bond. The resultant activity and selectivity towards CH_4 formation were ascribed to the successful adsorption and activation of $\text{CO}_2^\bullet$ on the doped CsPbBr_3 . After this, Pradhan and co-workers practically explored Fe (II)- CsPbBr_3 for selective CH_4 evolution via CO_2 photoreduction [64]. Doping of Fe (II) replaces Pb (II) in the CsPbBr_3 lattice, and an increased CH_4 selectivity was observed over the increment of Fe (II) concentration; however, pristine CsPbBr_3 forms CO. Later, another study by Su et al. showed that Mn^{2+} substitution to perovskite could significantly improve the optical and thermal properties of halide perovskites [65]. They observed that Mn-doped cesium lead halide (Br/Cl) perovskite showed more than 14 times improvement in catalytic performance than pristine catalysts. The Mn- $\text{CsPb}(\text{Br}/\text{Cl})$ exhibited the catalytic towards CO and CH_4 formation with a yield of $1917 \mu\text{mol g}^{-1}$ and $82 \mu\text{mol g}^{-1}$, respectively. Other metals such as Fe and Co have been reported as ideal dopants with cesium perovskite, and improved water sustainability was reported [63]. For instance, Fe (II) doped CsPbBr_3 and Co-doped CsPbBr_3 have been reported for the evolution of CO and CH_4 by Pradhan et al. and Lu et al., respectively. Particularly, Fe doped CsPbBr_3 predominantly forms CH_4 while pristine nanocrystals (NCs) are selective towards CO formation [64].

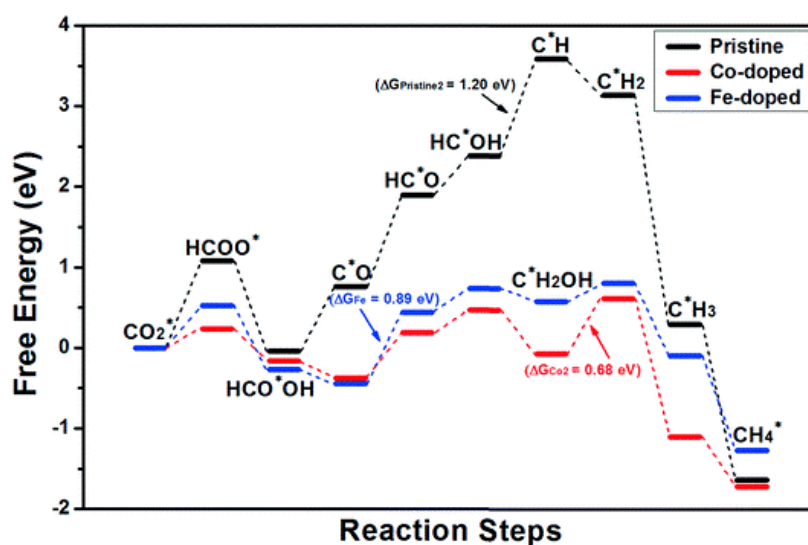


Figure 2. The free energy diagram showing the pathway of CO_2 reduction on pristine and Co/Fe doped CsPbBr_3 . Reproduced from [63], Royal Society of Chemistry, 2019.

Afterward, more outcomes of metal confined halide perovskites are reported. Lu and co-workers' study showed that Co-doped $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ combination improved catalytic performance for CH_4 and CO evolution [59]. Co doping to perovskite has two benefits; first, it produces surface trap states due to the presence of Co^{2+} and extends the lifetime of photogenerated charges. Second, it broadens the adsorption of CO_2^* intermediate to the catalytic surface. Remarkably, they have employed hexafluorobutyl methacrylate to improve NC's stability and dispersity in an aqueous medium. Then, in this class of materials, Zhang and coworkers reported Co-doped CsPbBr_3 embedded in the matrix of Cs_4PbBr_6 (a surface protector) [66]. The reason behind such protection of Cs_4PbBr_6 was to improve the stability of ligand-free CsPbBr_3 perovskite. As a result, the optimized Co-doped perovskite composite exhibited excellent CO_2 reduction towards CO formation with $1835 \mu\text{mol g}^{-1}$ in 15 h. In combination with the acetonitrile/water solution, the methanol was used as a hole scavenger to improve the catalytic activity towards CO_2 reduction. Interestingly, Cs_4PbBr_6 does not take part in the redox reaction due to its unsuitable band potentials/alignment; however, CsPbBr_3 takes part in the CO_2 reduction process and triggers the catalytic activity towards CO formation. After these reports, Pt has also been successfully used as a co-catalyst for CsPbBr_3 [67]. This study stated the solvent effect, where it was observed that acetate is the most potent solvent, which provides a stable atmosphere for perovskite to conduct the CO_2 reduction process. The optimized Pt loaded catalyst demonstrated an electron consumption rate of $5.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ in ethyl acetate. In another study of Zhu and co-workers, the water-stable CsPbCl_3 was documented with Mn and Ni doping. They illustrated the significance of the Pb-rich surface, which extends the lifetime of PL to increase the catalytic activity [68]. By interpenetrating solid-liquid, the synthesis of surface Pb enriched CsPbCl_3 was accomplished by allowing the water to drain through the CsPbCl_3 layer originating with Cs^+ and Cl^- . These Cs^+ and Cl^- inhibit the decomposition of CsPbCl_3 and increase the PL lifetime. Therefore, Ni-doped Pb-rich CsPbCl_3 QDs displayed superior CO_2 reduction behavior against CO evolution with a rate of $169.37 \mu\text{mol g}^{-1} \text{h}^{-1}$.

In addition to metal doping/deposition, perovskites are combined with supporting material to increase light absorption and charge separation. Among various materials, graphene can be a good choice as a support material for perovskites due to its well-known surface, optoelectronic, and physicochemical properties [69,70], which ultimately prolongs the electron/hole pair's lifetime and makes perovskite ideal for photocatalytic CO_2 conversion. Hence, Xu et al. fabricated CsPbBr_3 QDs/graphene oxide (GO) composite by a simple precipitation process for photoconversion of CO_2 in a nonaqueous medium [71]. The CO_2 reduction reaction was conducted in a Pyrex bottle using ethyl acetate as a solvent. The use of ethyl acetate has two benefits; (i) it stabilizes CsPbBr_3 due to its

moderate polarity; and (ii) it increases the solubility of CO₂ even more than in water. The presence of GO provides additional electron transfer from CsPbBr₃ to GO; therefore, it was found that the CsPbBr₃/GO composite exhibited improved catalytic activity compared to pristine CsPbBr₃ QDs. The catalyst displayed stability over 12 h, and no phase change of CsPbBr₃ was observed during the catalytic reaction. Excited electrons from CsPbBr₃ quickly transfer to the GO sheet, suppress the electron-hole pair's recombination, and increase catalytic activity.

Shortly after, few more studies have been reported in combination with graphene. For instance, Eslava and the group reported a surfactant-free synthesis of CsPbBr₃ NCs [72]. They have synthesized CsPbBr₃ on a gram scale by employing the simple mechanochemical process to get the different morphology of NCs, including nanorods, nanosheets, and nanospheres. To improve the catalytic efficiency, CsPbBr₃ was further combined with Cu-RGO by the mechanochemical process. The CsPbBr₃ nanosheets with Cu-RGO achieved 12.7, 0.46, and 0.27 $\mu\text{mol g}^{-1} \text{h}^{-1}$ of CH₄, CO, and H₂ evolution rates after CO₂ reduction. The catalyst composed of CsPbBr₃-Cu-RGO achieved 1.10% apparent quantum efficiency and showed excellent stability over three consecutive runs. Such an alternative method of large-scale synthesis is notable and essential for advancing the photocatalytic technology practically. Later, Wang and co-workers demonstrated the effectiveness of RGO sheets combined with Cs₄PbBr₆ for CO₂ reduction [73]. They revealed that the dual nature of the RGO is responsible for increased catalytic activity and stability, (i) the defect-induced RGO efficiently traps the electron excited by Cs₄PbBr₆, and (ii) oxygen-deficient RGO adsorbs and stimulates CO₂ molecule. In addition to these studies, Mu and co-workers described the ultrathin small-sized graphene oxide (USGO) as an electron mediator between CsPbBr₃/α-Fe₂O₃ Z-scheme photocatalyst [74]. Intense contact between CsPbBr₃/USGO through the Br-O-C bond; and USGO/α-Fe₂O₃ via the C-O-Fe bond accelerates the transfer of electrons through the Z-scheme. As a result, such a Z-scheme combination achieved 9 times greater catalytic efficiency compared to CsPbBr₃ NCs. Later on, such a Z-scheme heterojunction of CsPbBr₃ QDs was also reported with Bi₂WO₆ nanosheet [75]. Therefore, the Z-scheme combination then performs efficient charge separation across the closely connected interface and enhances the catalytic activity.

Recently, 2D materials have grabbed huge attention as the best supporting materials in many applications. A halide perovskites/2D composite materials strategy can achieve an efficient charge transfer and reduced electron-hole recombination among the perovskite-based photocatalysts. Xu et al. produced the CsPbBr₃/Pd Schottky junction in 2018 and studied the enhanced consumption rate of electrons for photoreduction of CO₂ [76]. For this analysis, CsPbBr₃ NCs were deposited on Pd nanosheets under atmospheric conditions using a simple technique on a glass substrate, and the photocatalytic reduction of CO₂ to CO/CH₄ was studied. The charge transport and charge carrier dynamics among the composite were studied by PL and fs-TAS (femtosecond transient absorption spectroscopy). The PL quenching of 0.5–8.6% in the CsPbBr₃/Pd composite was observed compared to the pristine sample (Figure 3a). Likewise, the decreased PL decay (Figure 3b) of the composite was observed in TRPL analysis with an average lifetime of 2.71–13.38 ns; however, such a decay lifetime for CsPbBr₃ was measured to be 52.03 ns. Furthermore, a similar trend was observed in the fs-TAS analysis (Figure 3c), where a large decrease in peak intensity of composite than the pristine sample was observed. These findings indicate that the recombination rate of the electron-hole in CsPbBr₃ was reduced by integrating it over Pd nanosheets, which consciously promotes the process of CO₂ reduction to form CH₄ and CO (Figure 3d). Remarkably, the Schottky contact between CsPbBr₃/Pd composite increases the electron consumption rate up to 33.80 $\mu\text{mol g}^{-1}$ (for CH₄ and CO evolution), 2.43 times higher than the pristine CsPbBr₃ with the improved quantum efficiency (Figure 3e,f). Therefore, a combination of halide perovskite with 2D materials proved to be a good strategy for the photocatalytic CO₂ reduction reaction.

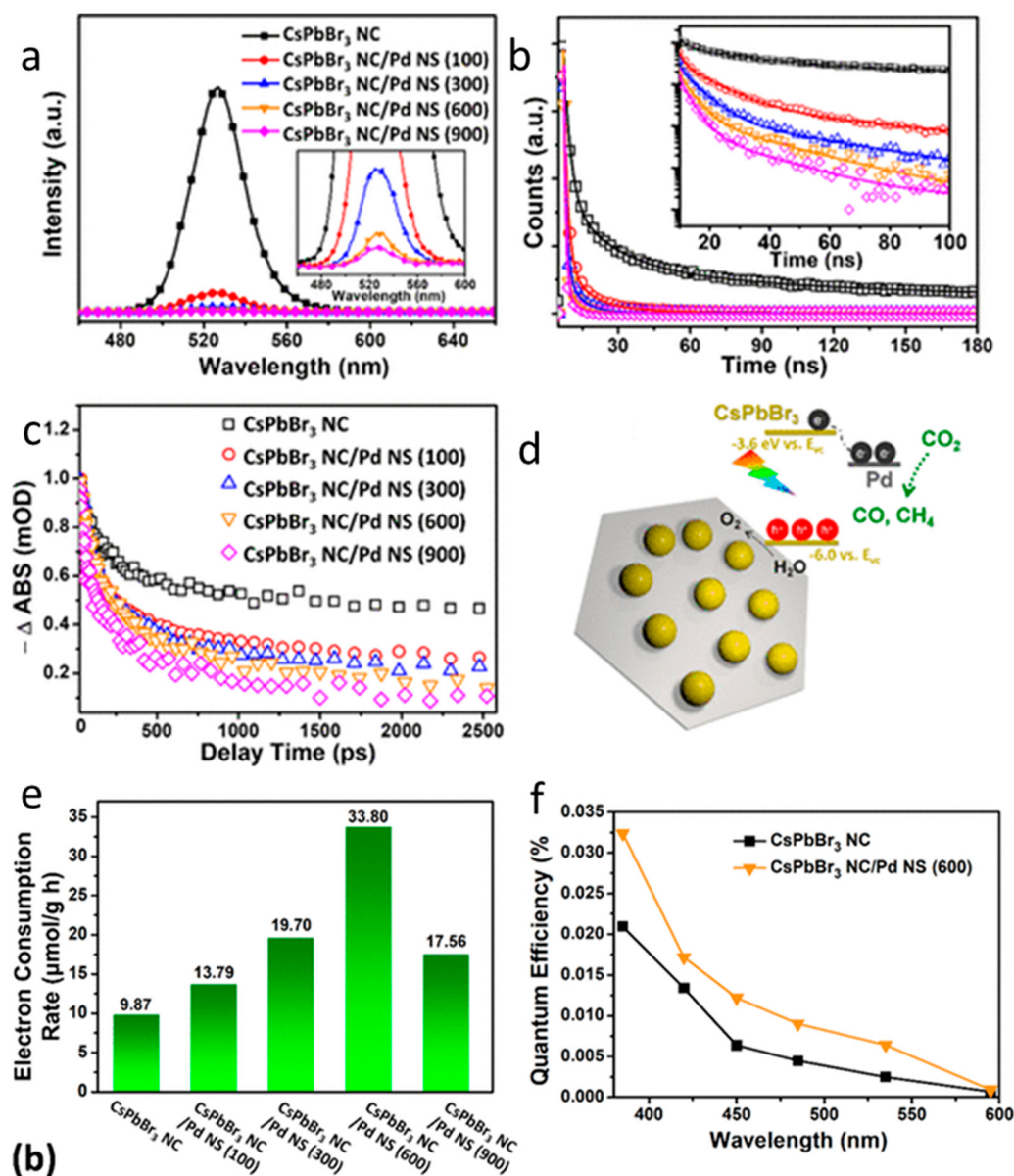


Figure 3. The comparative (a) PL spectra, (b) PL decay, (c) transient absorption kinetic plots (at an excitation wavelength of 400 nm) among CsPbBr₃ NC and composite samples, (d) schematic illustration and band alignment of CsPbBr₃/Pd composite for CO₂ reduction, (e) photocatalytic CO₂ reduction performance, and (f) quantum efficiency of different samples. Reproduced from [76], with permission from Royal Society of Chemistry, 2019.

Later on, Liu et al. introduced a functional CsPbBr₃/MXene nanocomposite for CO₂ reduction to CO and CH₄ under visible light [77]. The consistent growth of CsPbBr₃ on exfoliated MXene_{-n} (n = 10, 20, 30, 40, and 50, a different amount of MXene) nanosheet was achieved by an in-situ method, as shown in Figure 4a. The etching of Ti₃AlC₂ was carried out by using the HCl-HF solution to form a Ti₃C₂T_x nanosheet. Then, the final nanocomposite was obtained by the exfoliation of multilayered Ti₃C₂T_x and in-situ growth of CsPbBr₃ on Ti₃C₂T_x nanosheets. The dispersion of cubic CsPbBr₃ with an average size of 25 nm on MXene nanosheets was observed in the TEM images (Figure 4b–d), and the presence of Ti, Pb, Br, and Cs confirms the constant growth of perovskite NCs on MXene nanosheet (Figure 4e–i). As expected, the PL and TRPL quenching in composite compared to pristine perovskite confirm the efficient charge transfer among the interface of CsPbBr₃/MXene. The photocatalytic CO₂ reduction test was carried out under light irradiation using ethyl acetate solvent towards CO and

CH_4 formation with a rate of 26.32 and $7.25 \mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. Therefore, such perovskite/2D composites can be used as an efficient catalyst for photocatalytic applications.

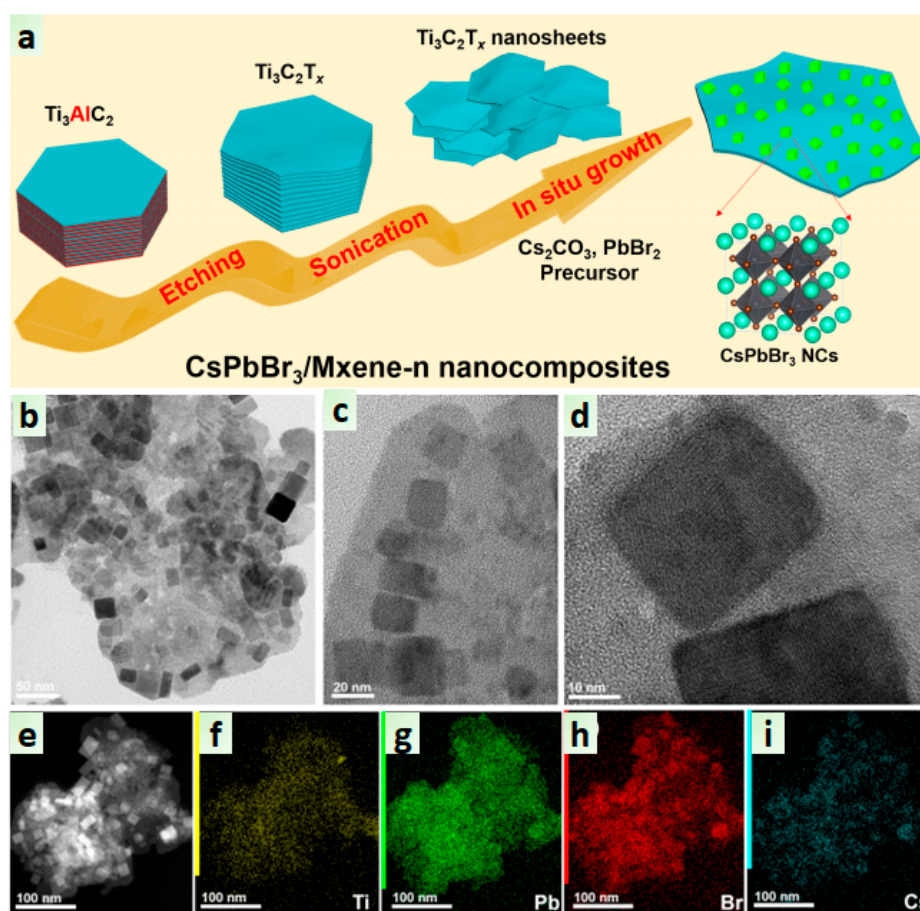


Figure 4. (a) An in-situ synthetic procedure for $\text{CsPbBr}_3/\text{MXene}$, (b–d) TEM and HR-TEM images of $\text{CsPbBr}_3/\text{MXene-20}$ composite and (e–i) EDX elemental mapping for the respective elements. Reproduced from [77], with permission from American Chemical Society, 2019.

Construction of perovskites/semiconductor heterojunction is advantageous to improve the optoelectronic or photochemical properties of catalytic systems. As well known, when two semiconductors with different band potentials combine, heterojunction forms at the interface of particular semiconductors and facilitate the charge separation process. Among various candidates, TiO_2 was proven to be an excellent semiconducting material all over the years for photocatalytic applications. In this aspect, Xu et al. in 2018 reported an amorphous TiO_2 encapsulated CsPbBr_3 composite with enhanced catalytic efficiency [78]. The improved separation of the charge between CsPbBr_3 and TiO_2 was shown by the decay of the PL and TRPL, where dramatic quenching of radiative recombination was observed. Moreover, the fs-TAS analysis revealed that the decreased electron-hole recombination improves the charge separation efficiently among the composite. As a result, the $\text{CsPbBr}_3/\text{amorphous TiO}_2$ composite demonstrated 6.5 times better photoelectron intake during the CO_2 photoreduction and stability over 30 h. The high selectivity towards CH_4 formation was attributed to the perfect combination of CsPbBr_3 and amorphous TiO_2 . The electron generated by CsPbBr_3 accumulates on TiO_2 to break the dynamic barrier and therefore fast-track the rate of CH_4 formation. Thus, such a study helps to understand the surface modification of halide perovskites for various applications.

Afterward, in 2020 Yu and co-workers developed a self-assembled CsPbBr_3 QDs/ TiO_2 nanofibers, an S-scheme heterojunction hybrid for CO_2 reduction under the irradiation of UV-Vis light [79]. The electron microscopy results revealed that CsPbBr_3 QDs were uniformly distributed on TiO_2 nanofibers.

Density functional theory (DFT) and experimental studies were combined to comprehend the interfacial charge transfer among the composite. The chemical states of pristine and composite samples were explored by in-situ and ex-situ XPS analysis. As shown in Figure 5a,b, the Ti 2p peak of Ti^{4+} ions, O 1s of lattice oxygen, and surface -OH group are present in all the samples. However, in the in-situ measurement, the binding energies (BE) of Ti 2p and O 1s peaks shifted towards higher BE than ex-situ spectra. A similar observation but opposite peak shift was observed in the Br 2d peak, mainly attributed to an electron transfer from CsPbBr_3 to TiO_2 (Figure 5c). Such electron transfer is responsible for constructing the S-scheme heterojunction among $\text{TiO}_2/\text{CsPbBr}_3$, which efficiently separates the photogenerated charges to promote CO_2 reduction. The electron transfer from CsPbBr_3 to TiO_2 was further validated by work function values calculated from the energy difference of vacuum and fermi levels, as shown in Figure 5d–f. Due to the lower Fermi level of TiO_2 than CsPbBr_3 QDs (work function (ϕ) of CsPbBr_3 , 5.79 eV and TiO_2 , 7.18 or 7.08 eV), the electron flow would be favorable from CsPbBr_3 to TiO_2 for enabling the phases at the similar Fermi level and created an internal electric field at the interface of $\text{TiO}_2/\text{CsPbBr}_3$. A similar observation was observed in DFT calculations. Therefore, such an improved electron transfer is responsible for the enhanced catalytic performance of hybrid ($9.02 \mu\text{mol g}^{-1} \text{h}^{-1}$) than the pristine CsPbBr_3 and TiO_2 (4.94 and $4.68 \mu\text{mol g}^{-1} \text{h}^{-1}$), respectively, towards CO formation. The improved CO_2 adsorption on CsPbBr_3 QDs and S-scheme heterojunction formation was ascribed to superior photocatalytic activity.

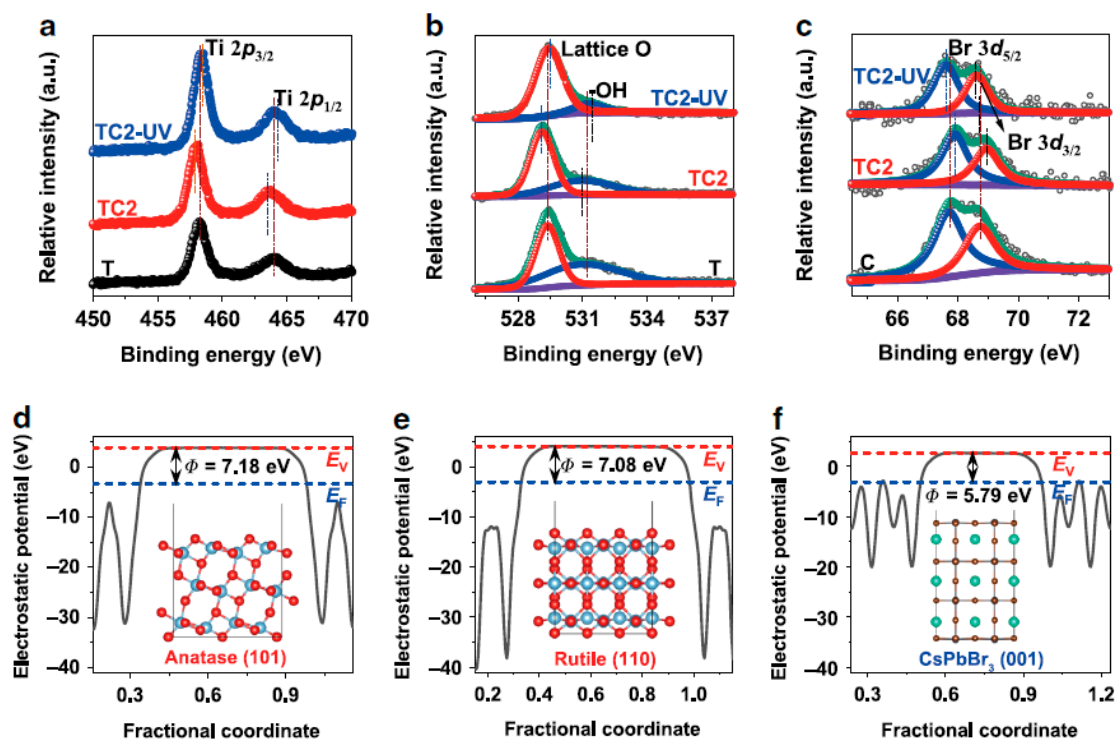


Figure 5. (a–c) Ex-situ and in-situ XPS of TiO_2 (T) and $\text{TiO}_2/\text{CsPbBr}_3$ (TC2) samples (TC2-UV is in-situ XPS under UV light irradiation), and electrostatic potentials for (d) anatase TiO_2 (101), (e) rutile TiO_2 (110) and (f) CsPbBr_3 (001) facets. Reproduced from [79], with permission from Springer Nature, 2020.

Next, 3D structures, e.g., 3D microporous graphene, exhibited possible support material for catalytic reactions [80,81]. Such a 3D network structure can provide more CO_2 reactive sites and provide fast charge transport across multidimensional networks. Kaung and co-workers fabricated the hierarchical ternary nanocomposite of CsPbBr_3 with ZnO nanowire/3D graphene through a multi-step process for photocatalytic CO_2 reduction [81]. First, in-situ 1D ZnO/2D RGO macropores with a high specific surface area were fabricated on a film. Then, as-prepared CsPbBr_3 was used for the synthesis of ternary composite through the centrifugation cast method. SEM and TEM images revealed that the CsPbBr_3 NCs are well decorated in the ZnO nanowires over RGO. Similarly, optoelectronic and surface

properties showed improved light harvesting in the visible region and improved CO₂ adsorption on the catalyst's surface, respectively. As a result, the ternary composite exhibited 52.02 $\mu\text{mol g}^{-1} \text{h}^{-1}$ of CH₄ evolution (96.7% selectivity) along with CO formation. The electron pathway for CO₂ reduction was achieved via CsPbBr₃ to 1D ZnO to 3D RGO.

Apart from metal oxides, CsPbBr₃ can also be anchored with g-C₃N₄ due to its superior properties, such as visible-light active, tunable band potentials, and rich active surface area [82,83]. The combination of CsPbBr₃ and g-C₃N₄ facilitates efficient charge transport through their closely connected interface. In this regard, Xu et al. attached CsPbBr₃ QDs to amino-functionalized g-C₃N₄ nanosheet through N-Br bonding [83]. The 20 wt.% contained QDs anchored on g-C₃N₄ achieved a superior photocatalytic CO₂ reduction towards CO formation with a rate of 149 $\mu\text{mol h}^{-1} \text{g}^{-1}$ in acetonitrile/water solvent. The surface functionalization of g-C₃N₄ with abundant NH_x was shown to help build a bridge between g-C₃N₄ and CsPbBr₃. Such N-Br bonding was confirmed by XPS analysis, which is responsible for the enhanced charge separation and decreased electron-hole recombination rate. Resulting, the composite showed 15- and 3-fold improved catalytic activity than pristine CsPbBr₃ QDs and g-C₃N₄. Later, in 2019 a similar study was reported by Zhang and co-workers for CsPbBr₃/g-C₃N₄ containing TiO species (TiO-CN) [84]. The well-defined composite of CsPbBr₃@TiO-CN was able to undergo CO₂ reduction to produce a 129 $\mu\text{mol g}^{-1}$ of CO under 10 h visible light irradiation. The interaction among CsPbBr₃ and g-C₃N₄ was established via N-Br and O-Br, reducing the recombination of the electron/hole pair. The electrons generated in the conduction band of CsPbBr₃ transfer to TiO-CN nanosheet and react with adsorbed CO₂ molecules. At the same time, water oxidation was carried out by holes accumulated at the valence band of CsPbBr₃.

The core-shell combinations have been reported as an alternative option to improve halide perovskite's stability and activity towards CO₂ reduction, where coating the surface of perovskite may also upsurge water stability. Hence, various materials, including metal oxides, polymers, silica, zeolites, and metal-organic framework (MOF), have been successfully utilized. These days, MOFs are widely employed for photocatalytic applications due to their unique properties such as high specific surface area, more catalytic active sites, and tunable structural flexibility. In this way, CsPbBr₃@ZIF (zeolitic imidazolate framework) was reported for an efficient CO₂ photoreduction [85]. In this study, CsPbBr₃ was coated with the Zn-based metal-organic system ZIF-8 and the Co-based ZIF-67 by an in-situ approach that activates the CO₂ molecule, as shown in Figure 6a. The HAADF-STEM images and elemental mapping confirmed the formation of the CsPbBr₃@ZIF core-shell structure, as shown in Figure 6b–e. It has been reported that ZIF coating increases the stability of CsPbBr₃ due to its weak hydrophobic nature. The gas-phase photocatalytic CO₂ reduction with water vapor showed CH₄ and CO evolution; and, the CH₄ formation was increased with the increase in irradiation time and achieved 100% selectivity. The increased catalytic activity was demonstrated by composite with ZIF-67 achieving 10.53 $\mu\text{mol g}^{-1}$ of CH₄ evolution (Figure 6f). The electron consumption rate for ZIF-8 and ZIF-67 composites was 15.498 and 29.630 $\mu\text{mol g}^{-1} \text{h}^{-1}$. Moreover, the CsPbBr₃@ZIF catalyst showed stability for six consecutive cycles, which proves its excellent proficiency (Figure 6g). Therefore, such studies could lead to fabricated highly stable hybrid composites of perovskite materials. Later on, few more studies have been reported on a similar class of hybrid perovskites. For instance, Wang and co-workers successfully developed CsPbBr₃ QDs/Uio-66(NH₂) nano junction and employed it for visible-light-active CO₂ reduction [86]. TEM images confirmed the construction of a nano junction between CsPbBr₃ and Uio-66(NH₂). The optimized catalyst was able to produce 98.57 $\mu\text{mol g}^{-1}$ of CO and 3.08 $\mu\text{mol g}^{-1}$ of CH₄. Interestingly, the specific surface of pristine Uio-66(NH₂) was 709.02 $\text{m}^2 \text{g}^{-1}$, which was more than the nanocomposite (465.68 $\text{m}^2 \text{g}^{-1}$); the catalyst exhibited much more catalytic activity than the bare samples. The catalyst's reusability was reported for three cycles, proving its high chemical stability and photo resistivity. The suitable VB and CB potentials of CsPbBr₃ and HOMO-LUMO of Uio-66(NH₂) were well matched for CO₂ reduction and water oxidation to generate H⁺ and O₂, resulting to form CO. The photocatalytic reactions were carried out in ethyl

acetate/H₂O combination; therefore, H₂ evolution could be possible. However, the absence of any co-catalyst restricts the H₂ evolution and selectively produces CO more efficiently along with CH₄.

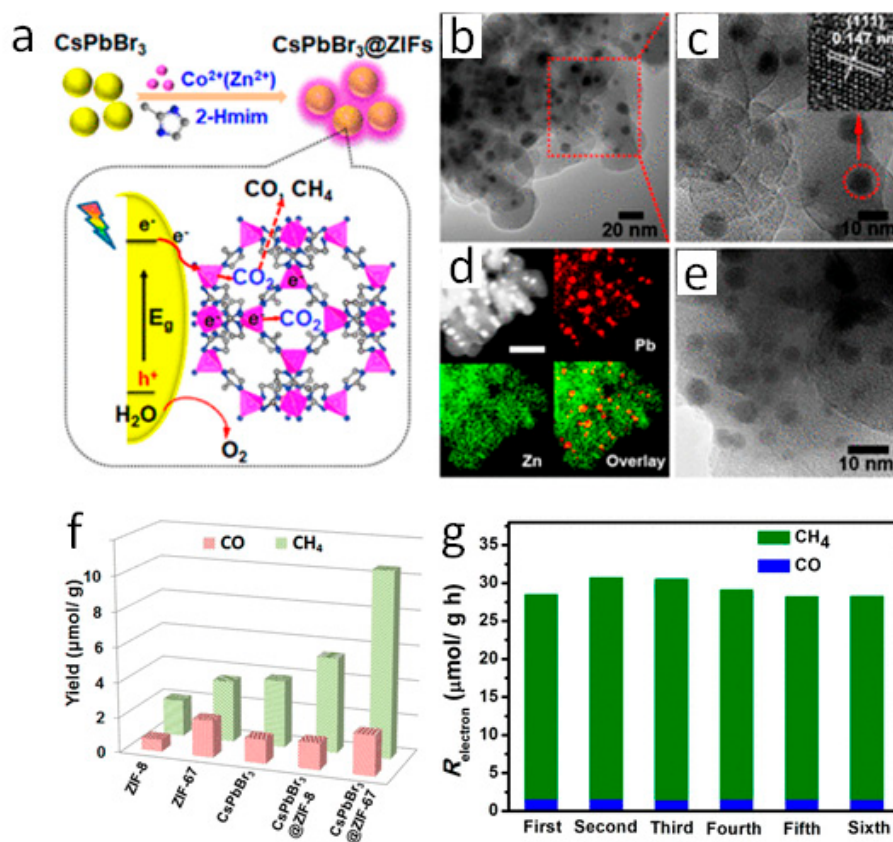


Figure 6. (a) Schematic illustration of synthesis and utilization of CsPbBr₃/ZIFs for CO₂ reduction, (b,c) TEM of CsPbBr₃@ZIF-8, (d) HAADF-STEM of CsPbBr₃@ZIF-27, (e) TEM of CsPbBr₃@ZIF-27, (f) CO₂ reduction results for pristine and composite, and (g) Stability test for CsPbBr₃@ZIF-67. Reproduced from [85], with permission from American chemical society, 2018.

Metal complexes have long been recognized for CO₂ photoreduction due to their exciting characteristics such as high selectivity and CO₂ conversion activity, and structural flexibility [87–90]. The conjugated structures of metal complexes are commonly employed as a multi-electron transporter in the catalytic process. Moreover, the structural flexibility of these materials proved beneficial for tailoring catalytic activity and product selectivity. Previously, metal complexes were employed for visible-light-driven CO₂ reduction combined with various organic photosensitizers [91]. In the study of Kaung and co-workers in 2020, similar class of material anchoring CsPbBr₃ with Re(CO)₃Br(dcbpy) (dcbpy¹_{4,4'}-dicarboxy-2,2'-bipyridine) complex has been reported [92]. The interface between Re-complex and CsPbBr₃ was established through the carboxyl group, which is responsible for the fast electron transfer to boost the catalytic activity towards CO₂ reduction. Hence, the optimized catalyst showed 23 times higher electron consumption rate than CsPbBr₃ towards CO evolution. However, arduous synthetic procedures of photosensitizer or the use of precious metals restrict them for large-scale applications. Later, the combination of CsPbBr₃ perovskite NCs with (Ni(tpy)), a hybrid transition metal complex, was developed by Gaponik et al. and cast-off for the conversion of photocatalytic CO₂ into CO/CH₄ [93]. The synthesis of the hybrid composite includes multi-steps, synthesis of (i) organic ligands of CsPbBr₃, (ii) ligand exchange, and (iii) assembly of CsPbBr₃-Ni(tpy) by immobilization. The charge transfer between the composite was confirmed by TRPL decay and transient absorption spectroscopy, where the electron transfer from CsPbBr₃ to Ni(tpy) was observed. Thus, under the light irradiation, the catalyst undergoes CO₂ reduction and achieved 1724 μmol g^{−1} of CO/CH₄ formation. The catalytic activity was

shown to be 26 times higher than the pristine CsPbBr₃ and AQE of 0.23% for CO and CH₄ evolution under monochromatic light (450 nm). Also, the catalyst showed stability over 16 h, and post catalytic analysis confirmed its high stability. Therefore, Ni(tpy) offers more catalytic sites for the CO₂ molecule and improves the catalytic performance.

After MAPbBr₃ and CsPbBr₃, Que and co-workers introduced a novel FAPbBr₃ as an alternative option for traditional perovskites [94]. The synthesis of FAPbBr₃ was carried out by a hot injection method, and the results were compared with CsPbBr₃ synthesized similarly. As shown in Figure 7a–e, the XRD patterns and optical properties of as-prepared FAPbBr₃ are almost identical to that of CsPbBr₃, and they possess identical morphology with cubic shape. Despite, FAPbBr₃ showed an enormous improvement in the CO evolution (main product) under the CO₂ photoreduction compared to CsPbBr₃, achieving 181.25 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which was ≈ 17 times greater than CsPbBr₃ (Figure 7f). The significant cyclic stability was observed in FAPbBr₃, preserving more than 165 $\mu\text{mol g}^{-1} \text{h}^{-1}$ of CO evolution after three cycles (Figure 7g). Such high catalytic efficiency in FAPbBr₃ was due to the improved lifetime of 7003 ps compared to CsPbBr₃ with 956 ps.

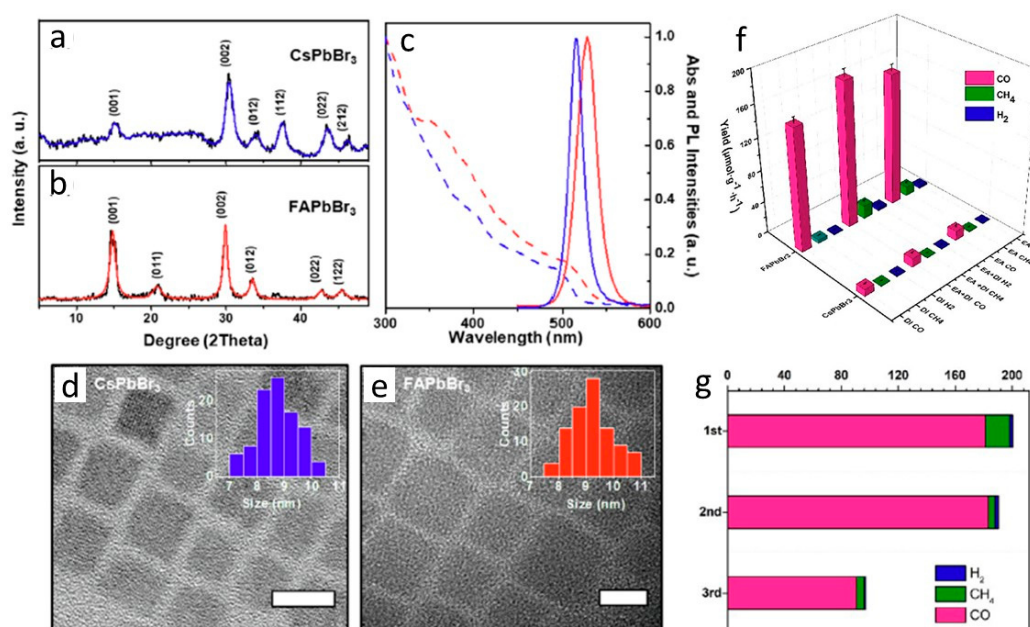


Figure 7. (a,b) The XRD patterns, (c) UV-Vis/PL spectra and (d,e) TEM images of FAPbBr₃, and CsPbBr₃, (f) Results of comparative photocatalytic CO₂ reduction in FAPbBr₃ and CsPbBr₃, and (g) reusability test of FAPbBr₃. Reproduced from [94], with permission from Elsevier, 2020.

4. Lead-Free Halide Perovskites

Throughout the years, Pb-based perovskites have been proved as the most efficient materials for photocatalytic CO₂ reduction applications due to their excellent photophysical properties. Nevertheless, Pb perovskites' high toxicity may restrict large-scale applications in the near future [95]. Li and colleagues' recent research revealed that the biological impact of Pb-perovskite is unsafe, which shows that Pb could reach the human food chain by plants from perovskites leakage into the ground [96]. Lead exposure can cause a severe problem to human health, including nausea, clumsiness, muscle weakness, and clouded consciousness [97,98]. Therefore, eliminating Pb from perovskite structure should be the primary concern to use them for long-term applications [99,100]. To this end, numerous attempts are being made to replace Pb from halide perovskite structure with other potential candidates, including Sn, Sb, Bi, Cu, In, and Pd. In this contribution, Chu et al. published a review article on lead-free halide double perovskites for various applications covering photodetector, X-ray detector, LEDs, solar cells, and photocatalysis [98].

To date, a limited number of studies were carried out on Pb-free halide perovskites for photocatalytic CO₂ reduction [101].

Recently, halide double perovskite materials have been recognized as the ideal alternative for toxic lead halide perovskites [98]. Numerous experiments have demonstrated excellent optoelectronic features of halide double perovskites, which are also suitable for photocatalytic CO₂ applications [102,103]. In 2018, Zhou et al. demonstrated a highly crystalline Cs₂AgBiBr₆ double perovskite NCs synthesized through a hot injection process [104]. To acquire the highly crystalline Cs₂AgBiBr₆, the temperature was optimized, and it was observed that 200 °C is a suitable temperature to get a pure form of double perovskite. The significant role of OLA and OA ligands towards the formation of crystalline Cs₂AgBiBr₆ was studied, where it was observed that in the absence of these ligands, bulk Cs₂AgBiBr₆ was formed. The bandgap was calculated to be 2.52 eV by Tauc's plot, and band potentials were measured by combining the results of VB-XPS and bandgap values. The enlarged band gap was observed in NCs as compared to bulk Cs₂AgBiBr₆, which was attributed to its quantum confinement effect. The stability of the NCs was studied in different solvents ranging from polar, partial polar, non-polar, and protonic solvents. Results revealed that the NCs were quickly decomposed in polar solvents like DMF or acetone and highly stable in mild/non-polar solvents for 3 weeks. The high ligand density on the surface of NCs may block electron/hole transportation and decrease the catalytic activity. Therefore, to decline the ligand density, the NCs were washed with absolute ethanol, which was supposed to improve the catalytic activity. The XPS and FTIR revealed that the surface ligands were wholly removed by the washing process (Figure 8a, b), while TGA results further confirm the removal of organic residues (Figure 8c, d). As shown in Figure 9a, b, the catalytic activity of CO₂ reduction towards CO and CH₄ evolution was much higher in the NCs washed by absolute ethanol than the Cs₂AgBiBr₆ NCs without the washed one in 6 h. The band potentials of the NCs are well suitable for the reduction of CO₂ to produce CO/CH₄, as shown in Figure 9c. The stability of catalysts was examined by post catalytic analysis using TEM, XRD, and XPS analysis. The results revealed that the catalyst's structure and the surface did not differ from those of fresh samples. The further extension for the development of the Z-scheme Cs₂AgBiBr₆@g-C₃N₄ was carried out by Wang and coworkers [105].

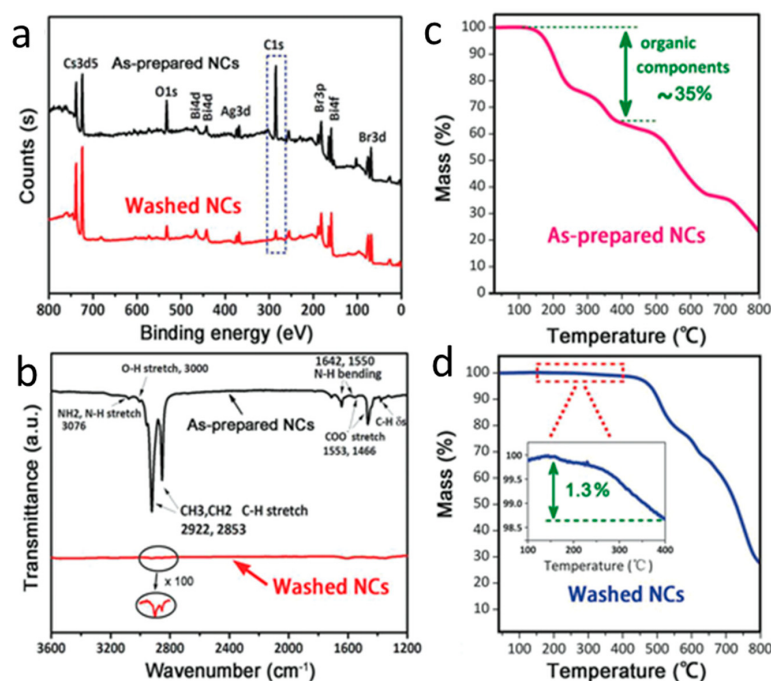


Figure 8. (a) XPS, (b) FTIR, and (c,d) TGA analysis of Cs₂AgBiBr₆ before and after the washing. Reproduced from [104], with permission from John Wiley and Sons, 2018.

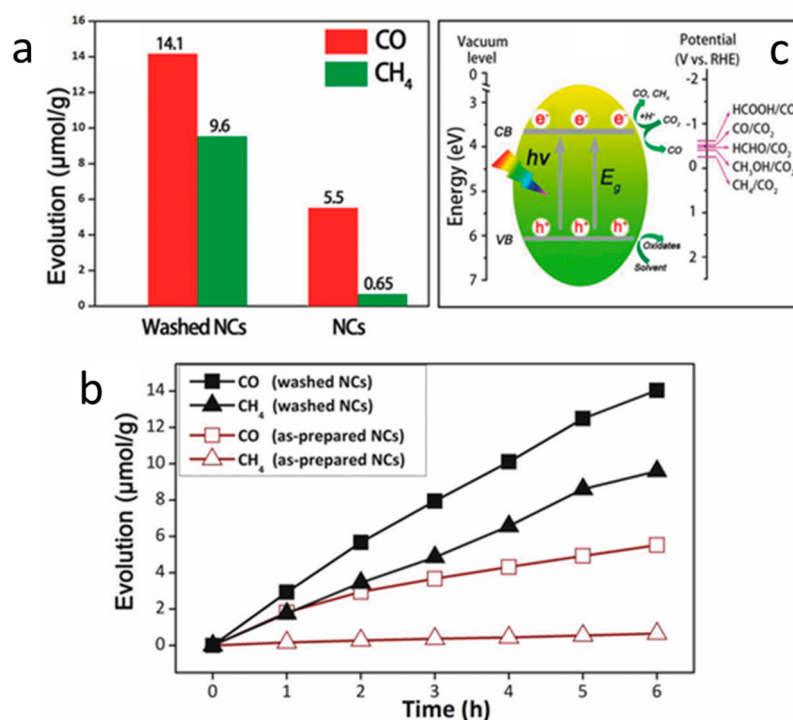


Figure 9. (a) CO and CH₄ formation, (b) times course product formation in different samples of Cs₂AgBiBr₆, and (c) Schematic illustration of CO₂ reduction on the surface of Cs₂AgBiBr₆. Reproduced from [104], with permission from John Wiley and Sons, 2018.

The Z-scheme combination was achieved by the in-situ method, mixing g-C₃N₄ precursor to Cs₂AgBiBr₆ nanoparticles in dichloromethane/toluene. The optimized catalyst achieved 2.0 μmol g⁻¹ h⁻¹ of activity for CO and CH₄ production with CH₄ selectivity over 70%. The construction of Z-scheme among perovskite and g-C₃N₄ improves the redox ability of the system. After that, Sn-based halide perovskites fell into the spotlight as Pb-free materials. Wang et al. successfully developed the novel Cs₂SnI₆/SnS₂ nanosheet combination in 2019 [106]. Such a heterojunction mixture of perovskite NCs with metal dichalcogenide (SnS₂) nanosheets greatly increases the lifetime of photogenerated electrons from 1290 to 3080 ps, observed from transient absorption measurements. DFT studies confirmed the type-II band alignment in Cs₂SnI₆/SnS₂ heterojunction, which was further supported by UPS measurement. Such a heterojunction was responsible for improved electron transportation through Cs₂SnI₆ and SnS₂ interface, and hole extraction by Cs₂SnI₆ from SnS₂, defeating the electron-hole recombination. As a result, the 5.4 times improved activity was observed in the Cs₂SnI₆(1.0)/SnS₂ sample (CH₄, 6.09 μmol g⁻¹) compared to the pristine SnS₂ and the stability of 3 cycles. No changes in the XRD pattern and UV-Vis-NIR spectra were observed in the samples tested after CO₂ reduction. Apart from Sn-based perovskites, Bi-based materials are considered the best replacement for Pb-materials [107]. In this regard, Bhosale et al. developed a system anchored series of non-toxic, Bi-based halide perovskites, such as Rb₃Bi₂I₉, Cs₃Bi₂I₉, and MA₃Bi₂I₉ by an ultrasonic, top-down method (Figure 10a). The catalyst showed 12 h of stability after seven days of aging under UV illumination, confirmed by XRD patterns. The catalytic responses were acquired at a gas-solid interface under UV irradiation. The time-dependent CH₄ evolution was measured for 10 h illumination, and increased CH₄ production was observed in all the samples (Figure 10b). The comparative catalyst activity for Bi-based perovskite was observed in the order of Cs₃Bi₂I₉ > Rb₃Bi₂I₉ > MA₃Bi₂I₉ towards CO and Rb₃Bi₂I₉ > Cs₃Bi₂I₉ > MA₃Bi₂I₉ for CH₄ evolution after 10 h UV illumination (Figure 10c).

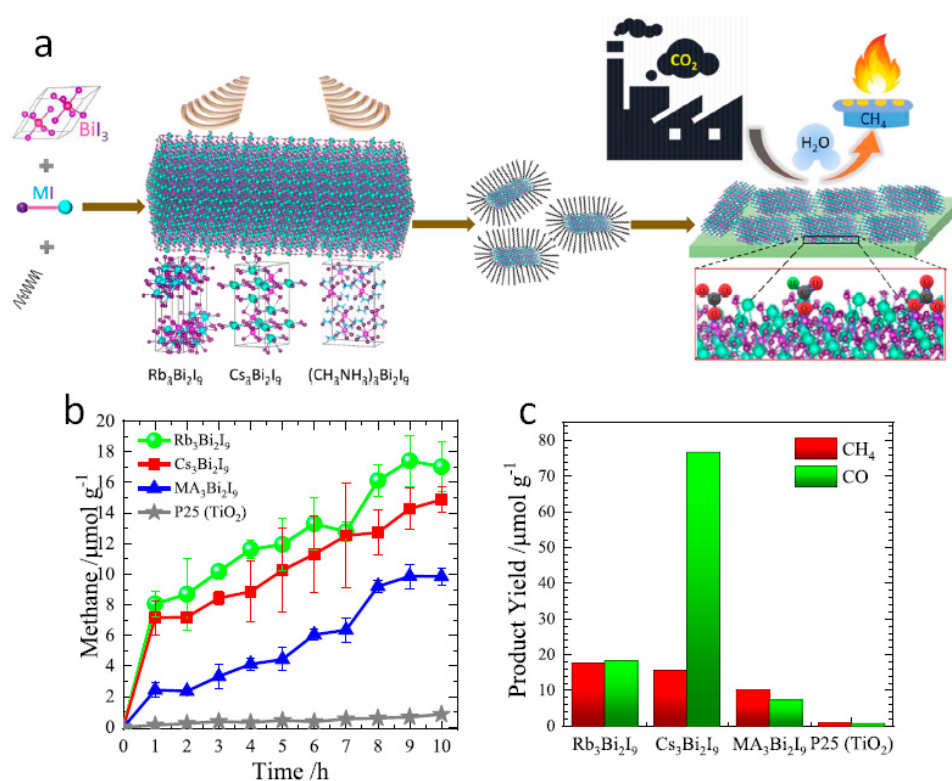


Figure 10. (a) Schematic illustration of the synthesis of Bi-based perovskites by top-down method, (b) Time-dependent CH_4 production in Bi-based perovskites, and (c) yields of CO and CH_4 production in different samples. Reproduced from [107], with permission from American Chemical Society, 2019.

Later, halide perovskite confined with Sb metal center (i.e., $\text{Cs}_3\text{Sb}_2\text{Br}_9$) was developed by Lu et al. and showed 10 times better activity than CsPbBr_3 NCs [108]. The effect of the ligand in the hot injection synthesis of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ from CsPbX_3 was studied. It was revealed that the use of saturated octanoic acid by replacing unsaturated oleic acid produces pure $\text{Cs}_3\text{Sb}_2\text{Br}_9$ NCs due to the temperature expansion up to 230°C . Moreover, these ligands were purified/removed by simple hexane/acetone washings before CO_2 reduction tests. Resulting, the photocatalytic CO_2 reduction of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ was carried out in the presence of dried octadecene solvent. The octadecene plays an important role; (i) it has low volatility and (ii) increases the solubility of CO_2 compared to typical solvents like acetonitrile or ethyl acetate. After 4 h light illumination, $\text{Cs}_3\text{Sb}_2\text{Br}_9$ generated $510 \mu\text{mol g}^{-1}$ of CO, which was over 10 times greater than various halide perovskites. The DFT calculations revealed that the sites $\text{Cs}_3\text{Sb}_2\text{Br}_9$ on the (1000) and (0001) surfaces play an essential role in forming COOH^* and CO^* intermediates. Hence, such studies may help establish a practical, large-scale, Pb-free photocatalyst for the CO_2 reduction process in the near future. The summary of all the studied catalysts has been presented in Table 2.

Table 2. The progress of Pb and Pb-free perovskites for CO_2 reduction with details including catalysts [reference], reaction medium, light source, product yield and time, and stability (*EA = ethyl acetate, MeOH = methanol, AN = acetonitrile, IPN = isopropanol, TCM = trichloromethane, OC = octadecene).

No	Catalyst	Medium	Light Source	Product, Yield, and Reaction Time	Catalytic Stability
Lead-based halide perovskites					
1	$\text{Fe/CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI ₃) QDs [60]	EA/H ₂ O	300 W Xe-lamp with standard 400 nm filter	CO + CH ₄ , 1559 $\mu\text{mol g}^{-1}$ CO (34%) and CH ₄ (66%)	80 h
2	CsPbBr_3 QDs [61]	EA/H ₂ O	300 W Xe-lamp with standard AM 1.5 filter	CO, 20.9 $\mu\text{mol g}^{-1}$ (average electron yield)	8 h

Table 2. Cont.

No	Catalyst	Medium	Light Source	Product, Yield, and Reaction Time	Catalytic Stability
3	CsPb(Br _{0.5} /Cl _{0.5}) ₃ [62]	EA	300 W Xe-lamp with AM 1.5 filter	CO, 767 $\mu\text{mol g}^{-1}$ (9 h) CH ₄ , 108 $\mu\text{mol g}^{-1}$ (9 h)	9 h
4	Co- and Fe-CsPbBr ₃ [63]	A theoretical study, DFT calculations with DMol ₃ program			
5	Fe(II)-CsPbBr ₃ [64]	EA/H ₂ O	300 W Xe-lamp (150 mW cm ⁻² light intensity)	CO, 6.1 $\mu\text{mol g}^{-1}$ h ⁻¹ (3 h) CH ₄ , 3.2 $\mu\text{mol g}^{-1}$ h ⁻¹ (3 h)	-
6	Mn/CsPb(Br/Cl) ₃ [65]	EA	300 W Xe-lamp with AM 1.5 filter	CO, 1917 $\mu\text{mol g}^{-1}$ (9 h) CH ₄ , 82 $\mu\text{mol g}^{-1}$ (9 h)	9 h
7	Co-CsPbBr ₃ /Cs ₄ PbBr ₆ [59]	H ₂ O	Xe-lamp irradiation with a 400 nm filter (100 mW cm ⁻² light intensity)	CO, 239 $\mu\text{mol g}^{-1}$ (20 h) CH ₄ , 7 $\mu\text{mol g}^{-1}$ (20 h)	-
8	Co-CsPbBr ₃ /Cs ₄ PbBr ₆ [66]	AN/H ₂ O/MeOH	300 W Xe-lamp (light intensity of 100 mW m ⁻²)	CO, 1835 $\mu\text{mol g}^{-1}$ (15 h)	-
9	Pt/CsPbBr ₃ [67]	EA	150 W Xe-lamp with 380 nm cut off filter	CO, 5.6 $\mu\text{mol g}^{-1}$ h ⁻¹	30 h
10	Ni and Mn-doped CsPbCl ₃ NCs [68]	CO ₂ / H ₂ O	300 W Xe-lamp with AM 1.5 filter	Ni = CO, 169.37 $\mu\text{mol g}^{-1}$ h ⁻¹ Mn = 152.49 $\mu\text{mol g}^{-1}$ h ⁻¹	6 h (3 runs)
11	CsPbBr ₃ QDs/GO [71]	EA	100 W Xe-lamp with AM 1.5 filter	CO, 58.7 $\mu\text{mol g}^{-1}$ (12 h) CH ₄ , 29.6 $\mu\text{mol g}^{-1}$ (12 h) H ₂ , 1.58 $\mu\text{mol g}^{-1}$ (12 h)	12 h
12	Cs ₄ PbBr ₆ /rGO [73]	EA/H ₂ O	300 W Xe-lamp with 420 nm filter (light intensity, 100 mW cm ⁻²)	CO, 11.4 $\mu\text{mol g}^{-1}$ h ⁻¹	60 h
13	Cu-RGO-CsPbBr ₃ [72]	CO ₂ /H ₂ O	Xe-lamp irradiation with a 400 nm filter	CH ₄ 12.7 $\mu\text{mol g}^{-1}$ h ⁻¹ (4 h)	12 h (3 cycles)
14	CsPbBr ₃ /USGO/ α -Fe ₂ O ₃ [74]	ACN/H ₂ O	300 W Xe-lamp with 420 nm filter (light intensity, 100 mW cm ⁻²)	CO, 73.8 $\mu\text{mol g}^{-1}$ h ⁻¹	2 cycles
15	CsPbBr ₃ /Bi ₂ WO ₆ [75]		300 W Xe-lamp with 420 nm filter (100 mW cm ⁻² light intensity)	CH ₄ /CO, 503 $\mu\text{mol g}^{-1}$	4 Runs (pristine samples)
16	CsPbBr ₃ /Pd Nanosheet [76]	H ₂ O vapor	A 150 W Xe-lamp (Zolix) equipped with an AM 1.5 G and 420 nm optical filter (100 mW cm ⁻² light intensity)	CO, 12.63 $\mu\text{mol g}^{-1}$ (3 h) CH ₄ , 10.41 $\mu\text{mol g}^{-1}$ (3 h) Electron consumption rate, 101.39 $\mu\text{mol g}^{-1}$ (3 h)	-
17	CsPbBr ₃ /MXene Nanosheets [77]	EA	300 W Xe-lamp with 420 nm cut-off filter	CO, 26.32 $\mu\text{mol g}^{-1}$ h ⁻¹ CH ₄ , 7.25 $\mu\text{mol g}^{-1}$ h ⁻¹	-
18	Amorphous-TiO ₂ /CsPbBr ₃ NCs [78]	EA/IPN	150 W Xe-lamp with an AM 1.5 G filter	CO, 11.71 $\mu\text{mol g}^{-1}$ CH ₄ , 20.15 $\mu\text{mol g}^{-1}$ H ₂ , 4.38 $\mu\text{mol g}^{-1}$	30 h
19	TiO ₂ /CsPbBr ₃ [79]	ACN/H ₂ O	300 W Xe-arc lamp	CO, 9.02 $\mu\text{mol g}^{-1}$ h ⁻¹	16 h
20	CsPbBr ₃ NCs- ZnO nanowire/graphene [81]	CO ₂ /H ₂ O	A 150 W Xe-lamp with an AM 1.5 G and 420 nm optical filter (100 mW cm ⁻² light intensity)	CH ₄ , 6.29 $\mu\text{mol g}^{-1}$ h ⁻¹ (3 h) CO, 0.8 $\mu\text{mol g}^{-1}$ h ⁻¹ (3 h) Photoelectron consumption rate, 52.02 $\mu\text{mol g}^{-1}$ h ⁻¹ (3 h)	4 cycles
21	CsPbBr ₃ QDs/g-C ₃ N ₄ [83]	ACN/H ₂ O	300 W Xe-lamp with a 420 nm cut-off filter	CO, 149 $\mu\text{mol g}^{-1}$ h ⁻¹	3 Runs
22	CsPbBr ₃ /g-C ₃ N ₄ containing TiO species [84]	EA/H ₂ O	Xe-lamp with a 400 nm cut off filter (100 mW cm ⁻² light intensity)	CO, 129 $\mu\text{mol g}^{-1}$ (10 h)	-
23	CsPbBr ₃ @Zeolitic Imidazolate [85]	CO ₂ / H ₂ O	100 W Xe-lamp with AM 1.5 G filter (light intensity was 150 mW cm ⁻²)	The electron consumption rate for CH ₄ , 29.630 $\mu\text{mol g}^{-1}$ h ⁻¹ (3 h)	6 cycles

Table 2. Cont.

No	Catalyst	Medium	Light Source	Product, Yield, and Reaction Time	Catalytic Stability	
24	CsPbBr ₃ QDs/UiO-66(NH ₂) nanojunction [86]	EA/H ₂ O	300 W Xe-lamp with a 420 nm UV-cut filter	CO, 98.57 μmol g ⁻¹ CH ₄ , 3.08 μmol g ⁻¹ (12 h)	3 cycles	
25	[Ni(terpy) ₂] ²⁺ (Ni(tpy)) CsPbBr ₃ NCs [93]	EA/H ₂ O	300 W Xe-lamp (Solaredge 700, 100 mW cm ⁻²), λ > 400 nm	CO + CH ₄ , 1724 μmol g ⁻¹ (4 h)	16 h	
26	CsPbBr ₃ -Re(CO) ₃ Br(dcbpy) (dcbpy $\frac{1}{4}$ 4,4'- dicarboxy-2,2'-bipyridine) [92]	Toluene/IPN	150 W Xe-lamp (≥420 nm)	CO, 509.14 μmol g ⁻¹ (15 h)	-	
27	FAPbBr ₃ QDs [94]	EA/H ₂ O	300 W Xe-lamp (light intensity of 100 mW cm ⁻²)	CO, 181.25 μmol g ⁻¹ h ⁻¹	-	
Lead-free halide perovskites						
28	Cs ₂ AgBiBr ₆ [104]	EA	100 W Xe-lamp with an AM 1.5 G filter	CO, 14.1 μmol g ⁻¹ (6 h) CH ₄ , 9.6 μmol g ⁻¹ (6 h)	6 h	
29	Cs ₂ AgBiBr ₆ @g-C ₃ N ₄ Z-scheme [105]	EA/MeOH	Xe-lamp (80 mW cm ⁻² light intensity)	CO + CH ₄ , 2.0 μmol g ⁻¹ h ⁻¹	12 h	
30	Cs ₂ SnI ₆ /SnS ₂ Nanosheet [106]	CO ₂ /H ₂ O/MeOH	150 mW cm ⁻² Xe-lamp with 400 nm filter	CH ₄ , 6.09 μmol g ⁻¹ (3 h)	9 h (3 cycles)	
31	Bi-based perovskite NCs [107]		32 W UV-lamp, 305 nm	Cs ₃ Bi ₂ I ₉ = CO, 77.6 μmol g ⁻¹ and CH ₄ , 14.9 μmol g ⁻¹ (10 h)	-	
	a.	Rb ₃ Bi ₂ I ₂		TCM		Rb ₃ Bi ₂ I ₉ = CO, 18.2 μmol g ⁻¹ and CH ₄ , 17.0 μmol g ⁻¹ (10 h)
	b.	Cs ₃ Bi ₂ I ₉				MA ₃ Bi ₂ I ₉ = CO, 7.2 μmol g ⁻¹ and CH ₄ , 9.8 μmol g ⁻¹ (10 h)
	c.	MA ₃ Bi ₂ T ₉				
32	Cs ₃ Sb ₂ Br ₉ [108]	Dried OC	300 W Xe-lamp with AM 1.5 irradiation	CO, 510 μmol g ⁻¹ (4 h)	9 h	

5. Summary and Outlook

Halide perovskites have been considered an advanced and high-performance material for many applications over the last few years. Their superior optoelectronic properties make them suitable for photocatalytic CO₂ reduction. Pb-halide perovskites have proven to be the finest materials for CO₂ conversion due to their high catalytic activity, high stability towards humidity, and long-term photostability. However, due to Pb's high toxicity, the research focus is shifting towards the development of non-toxic, Pb-free halide perovskites. Therefore, in this review, the Pb and Pb-free halide perovskite's recent progress towards photocatalytic CO₂ reduction has been involved. We have covered the halide perovskites and their hybrid heterostructures/composites formed with metal co-catalyst, graphene, metal complexes, MOFs, and other 0D or 2D semiconductors. Although halide perovskites achieved significant success for photoreduction of CO₂; still the catalytic efficiency is restricted in the μmol range, which keeps them away from large-scale use. Almost all the reported halide perovskites undergo CO₂ reduction to form C₁ products like CO and CH₄. Therefore, more focus should be given to generate higher hydrocarbons, which are industrially important. Therefore, understanding the reaction mechanism towards the formation of higher-ordered organic chemicals via CO₂ reduction of perovskite structure is crucial. Moreover, it is necessary to emphasize improving the structural and chemical stability of these materials. Improved catalytic efficiency and stability can be achieved by combining halide perovskite with other efficient semiconductors, improving the optical behavior, and charge separation ability. Therefore, developing sustainable, scalable, and low-cost halide perovskites will be

a tremendous challenge for real applications. We believe that the process of unlocking more perovskite materials with improved optoelectronic features should continue to make them perfect for better CO₂ reduction performance.

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