# Perovskites for $CO_2$ Reduction

Subjects: Electrochemistry

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Due to their outstanding operational and compositional properties, perovskite-based structures have already been studied as an important class of solid-state components for electrochemical (EC), photoelectrochemical (PEC), and photovoltaic–electrochemical (PV-EC) $CO_2$ reduction, showing great potential in their catalytic activity and device stability and with a promising window for further technological developments.

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## 1. Introduction

Anthropogenic $CO_2$ emissions have increased significantly as a result of the extensive use of fossil fuels for energy generation. The International Energy Agency estimates that around 81% of the world's energy consumption is met by fossil fuels. The entire energy demand is anticipated to increase to 24–26 TW by 2040, with $CO_2$ emissions averaging 37–44 Gt annually [1]. It is critical to close the carbon cycle because this is one of the biggest issues facing our civilization. Global warming, glacier melting, and ocean acidification are just a few of the environmental issues brought on by an excessive amount of $CO_2$ in the atmosphere. These issues have a long-term negative impact on both humans' wellbeing and the health of the planet's ecosystem [2][3]. As a result of these serious problems, developing progressive technologies for $CO_2$ capture, utilization, and storage (CCUS) is becoming increasingly necessary in the twenty-first century. Accordingly, we need to focus more on renewable energy sources and relevant transition technologies. Renewable energy systems such as solar and wind power can be considered the main sources of electricity supply, and the rates of electrical energy produced from them is estimated to be comparable to conventional coal generation [4][5]. As essential operational resources for the exploitation and storing of renewable energy, electrocatalytic carbon dioxide reduction reactions can be performed to capture and activate stable $CO_2$ molecules via electrochemical (EC), photovoltaic–electrochemical (PV-EC), or photoelectrochemical (PEC) catalysis, resulting in the creation of a number of products such as methane, methanol, ethanol, carbon monoxide, formic acid, and so on [6][7]. Electrocatalysis is a catalytic process that involves the conversion of electrical energy into chemical energy through the use of electricity [8]. PV-EC consists of an integration between photovoltaic (PV) and electrochemical (EC) systems due to the capture of the incident photon and the use of the generated photovoltage for synthesizing the necessary carbon-based chemicals when fed with $CO_2$. Meanwhile, the photoelectrochemical (PEC) technique, which uses a semiconductor light collector and is integrated with an electrochemical catalyst in a device stack, is an outstanding method for $CO_2$ reduction, using sunlight as an energy supply [9][10]. Compared with conventional high-temperature thermal conversion, electrochemical $CO_2$ reduction using sustainable energy sources is more favorable because of its mild functional

situations [11]. Electro-$CO_2$ reduction ($CO_2$ER) offers an attractive way to convert $CO_2$ into additional chemicals under standard ambient atmospheric temperature and pressure (SATP) conditions, and it can be simply joined with renewable energy sources like wind and solar power, providing a “green” path to carbon recycling [12]. However, because of the slow reaction mechanism of inert $CO_2$ molecules, which initiates a competitive process (hydrogen evolution reaction; HER) and leads to low faradaic efficiency in aqueous solutions, the practical application of direct $CO_2$ER has been seriously delayed [13]. In addition, due to the multiple proton–electron transfer mechanisms, $CO_2$ER products are usually very complex, leading to excessive costs for separation and purification [14].

As for $CO_2$ER, while many metallic (e.g., Ag, Au, Pd, Cu, Co, Sn) and non-metallic (e.g., N-doped graphene, carbon nanotubes) catalysts have been investigated and shown to have significant catalytic activity, their performance is much lower than expected [15]. For example, Sn derivatives have received a lot of attention because of the selectivity of their formed products, but they usually suffer from limited reaction selectivity and activity [13]. Therefore, using efficient catalysts with selectivity and acceptable activity is important but also challenging.

In recent decades, perovskites with the general formula $ABX_3$ have been devoted significant consideration owing to their flexible compositions and diverse properties, and they have found broad applications in the fields of electronics, photonics, photovoltaics, magnetism, and catalysis [16][17][18][19][20][21], showing a promising potential to reach the best sustainable solution based on the results of their life-cycle assessment (LCA) [22]. Previous studies have shown that the metal–oxygen bonds in the perovskite form the basis for the regulation of its electronic properties, which further affects the surface binding energy [23]. In addition, B ($BO_5$) surface sites with an asymmetric coordination environment also induce special surface properties for perovskites. The high flexibility in the arrangement and crystal structure of perovskites lead to their tunable electronic structure, with well-defined physical and chemical properties, making them ideal candidates as electrocatalysts for $CO_2$ reduction [24][25].

# 2. Structure of Perovskites

Depending on their ability to occupy different cationic and anionic sites, perovskites can present in various forms, including as oxides, sulfides, nitrides, and metal–halides [26]. Perovskites have four dimensionalities, namely 0-D, 1-D, 2-D, and 3-D, which exist in various forms; for example, (a) $ABX_3$ perovskites (e.g., $CH_3NH_3PbI_3$, $CaTiO_3$), (b) $A_2BX_4$ layered perovskites (e.g., $Cs_2PbI_4$), (c) $A_2BB'X_6$ double perovskites (e.g., $Sr_2FeMoO_6$, $Ba_2TiRuO_6$), and (d) $A_2A'B_2B'X_9$ triple perovskites (e.g., $La_2SrCo_2FeO_9$) [27]. A variety of cation/anion combinations can be employed to create different shapes while maintaining charge neutrality.

## 2.1. Perovskite Oxides

Several transition metal oxides with the basic chemical formula of $ABO_3$ belong to the perovskite oxide family, where the 12-fold O-coordinated A-sites and the 6-fold O-coordinated B-sites are occupied by the larger alkali metals or rare-earth cations and the smaller transition metal cations, respectively. The A- and B-sites of perovskite oxides could be substituted by almost 90% of the elements in the periodic table. A common approach to expanding

the perovskite family and adjusting its properties is doping new cations at A and B sites that possibly will lead to a random or well-organized arrangement. These oxides typically are in a cubic structure, but it is possible to display transitions to hexagonal, tetrahedral, orthorhombic, and rhombohedral structures [28]. Structural variations in perovskite oxides can lead to the realization of different magnetic orderings [29]. The appropriate substitution of anions/cations or the doping of these perovskites can create a variety of piezoelectric, ferroelectric, superconducting, catalytic, metallic, and magnetic properties [30]. This wide range of properties allows perovskite oxides to be used in various electronic devices, piezoelectric devices, biosensors, transducers, and actuators [31][32][33]. Owing to their structure flexibility, high stability, distinctive arrangement, ionic conductivity, as well as their electron mobility and redox behavior, perovskite oxides are also used as electrocatalysts in different reactions. In particular, the application of these perovskites in electrocatalysis have following advantages: (1) more stoichiometric regulation and homogeneity are provided at a low cost and in an easy synthetic procedure; (2) modulation of perovskite oxide properties lead to the use of a wide range of substituting components. Despite the extensive use of perovskite oxides in various fields, these compounds face serious challenges. For example, at high temperature, perovskite oxides can easily decompose or react with other materials. This can limit their use in high-temperature processes.

### 2.2. Metal–Halide Perovskites

Owing to their favorable features such as efficient optoelectronic properties, low cost, and simple synthesis method, metal–halide perovskites can be considered a notable material for next-generation devices [34][35][36]. Metal–halide perovskites have a general formula of ABX3, where A is a monovalent organic or inorganic cation (e.g., $CH_3NH_3^+$, $Cs^+$), B is a divalent metal cation (e.g., $Pb^{2+}$), and X is a halide ion. Depending on the cations in the A-site of the perovskite structure, these compounds are divided into organometallic halide perovskites (OHPs) and inorganic halide perovskites (IHPs) [37][38][39][40][41][42]. Metal–halide perovskites display high absorption coefficients and high exciton emission and tunable energy bands at ambient temperature. Also, these perovskites are described as favorite direct-bandgap semiconductor compounds [43][44]. $MAPbI_3$ and $FAPbI_3$ are the main types of these perovskites and are the most widely applied materials in photovoltaic applications due to their high absorption coefficient and high electron and hole mobility [45]. In particular, these classes of hybrid metal–halide perovskites are well developed for various scalable solution-based deposition techniques, with a promising pathway toward the sustainable generation of renewable energies [16][46][47][48][49][50]. In spite of their outstanding features, the metal–halide perovskites have serious problems in practical applications because of their lack of stability.

## 3. Fundamentals of $CO_2$ Reduction

The electrochemical reduction of $CO_2$ is a promising and outstanding method that leads to diminishing greenhouse gas emissions by allowing renewable energy storage in different chemical forms. This procedure presents exceptional benefits; for instance, the EC method can employ some environmentally friendly energy sources like solar energy, and it can be carried out at atmospheric temperature and pressure. Meanwhile, through altering the electrolyte and applied voltage, the reaction conditions and products can be controlled [51]. Nevertheless, $CO_2$ is a

stable and inert linear molecule that requires an appropriate electrocatalyst to assist in breaking the C=O bond. The EC process can yield a diversity of products, including formic acid, formate, oxalic acid or oxalate, carbon monoxide, formaldehyde, methanol, methane, ethanol, ethylene, and other products. Solid-oxide fuel cells (SOFCs) and organic- or inorganic-materials-based electrodes collected with typical electrochemical cells are usually utilized for $CO_2$ conversion in high-temperature and low-temperature methods, respectively.

SOFC systems reveal a higher selectivity, whereas low-temperature $CO_2$-reduction reactions usually provide a wide range of products. In addition, low-temperature $CO_2$-reduction systems involve large overpotentials and, thus, great power requests. In electrochemical $CO_2$RR, two, four, six, or eight electrons can be transferred.

Nowadays, in order to reduce the disadvantages and promote the benefits of electrochemical and photocatalytic techniques for efficient $CO_2$ reduction, the combination of both technologies is being investigated. In the photoelectrochemical technique (PEC), which is also known as artificial photosynthesis because it imitates nature's energy cycle, $CO_2$ reduces into various products at ambient pressure and temperature by harvesting light energy. The PEC $CO_2$ reduction offers many advantages such as environmental compatibility, great selectivity, economic viability, and the use of solar as a renewable energy source. In PEC systems, photocathodes and anodes are p-type and n-type semiconductors, respectively. Whenever light is illuminated, electrons are formed at the conduction band (CB) and holes are generated at the valence band (VB), leading to band bending at the connection point of the p-type and n-type electrodes. To improve the $CO_2$ reduction efficiency, band bending is crucial to create discrete electrons and holes at the electrodes and the electrolyte interface [9]. In the PEC $CO_2$RR process in aqueous solution (pH = 7), various intermediates are produced. The reactions below show the creation of electrons and protons that lead to the formation of various products [52].

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \; E^{\circ}_{OX}{}^{\circ} = -1.23 \text{ V}$$

$$CO_2(aq) + e^- \rightarrow CO_2^{-}(aq) \; E^{\circ}_{red} = -1.65 \text{ V}$$

Reaction of water and holes:

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+$$

$$2H_2O + 2h+ \rightarrow H_2O_2 + 2H+$$

$$2H_2O + 4h+ \rightarrow 4H+ + O_2$$

Formation of hydrogen radicals:

$$H+ + e- \rightarrow \bullet H$$

Construction of $CO_2$ anion radicals:

$$CO_2 + e^- \rightarrow {}^{\bullet}CO_2^- \; E° = -1.9 \text{ V}$$

In the photoelectrochemical procedure, $CO_2$ can be transformed into different products, such as formaldehyde, carbon monoxide, formic acid, methane, methanol, ethanol, isopropanol, etc.

# 4. Perovskites for $CO_2$ Reduction

## 4.1. Direct Electrochemical $CO_2$ Reduction

An active and selective $CO_2$ reduction reaction ($CO_2$RR) is an important step in recycling excess $CO_2$ into renewable forms of carbon and building an energy-efficient society. Direct electrochemical $CO_2$RRs can proceed under ambient conditions and have been extensively studied to understand the fundamentals of catalysis and to develop efficient catalysts for practical applications [53]. Li et al. showed, for the first time, that a $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) ceramic fuel-reforming electrode with a cubic perovskite structure can be used as an electrocatalyst to electrolyze pure $CO_2$ and convert it into CO without using syn-gases such as $H_2$ and CO in solid-oxide electrolysis cells [54]. Higher electrochemical efficiencies are demonstrated for single SFM cathodes using pure $CO_2$ as the feed gas compared with those reported for simple oxide–ceramic electrodes. The electrocatalytic properties of the SFM cathode for $CO_2$RR in solid-oxide electrolysis cells were tested by supported cells based on the double-layer electrolyte, containing an LSGM ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$) electrolyte and an LDC ($La_{0.4}Ce_{0.6}O_{2-\delta}$) barrier layer with a thickness of ~230 μm and 5 μm, respectively. Owing to the improved conductivity and greater electrocatalytic activity at raised temperatures, higher current densities and faster $CO_2$RR rates were obtained by increasing the operational temperature. Applied temperatures of 650, 700, 750, and 800 °C under a voltage of 1.5 V led to current densities of 0.26, 0.33, 0.49, and 0.71 A·cm$^{-2}$, respectively. The achieved current density of 0.71 A·cm$^{-2}$ was greater than almost all of the reported results for electrolyzing $CO_2$ using stable oxide electrodes at 800 °C. For $CO_2$ electrolysis under harsh conditions of pure $CO_2$ without a shielding gas, a relatively stable efficiency was obtained, and the current density reached above 1 A cm$^{-2}$; furthermore, the faradaic efficiency (FE) was above 95%, which was hardly ever attained in the literature but very desirable for commercial use. By using a SFM−$Sm_{0.2}Ce_{0.8}O_{2-\delta}$ composite cathode in 1.5 V and different temperatures of 650, 700, 750, and 800 °C, current densities of 0.40, 0.54, 0.75, and 1.09 A cm$^{-2}$ were attained, respectively. Using the SFM−$Sm_{0.2}Ce_{0.8}O_{2-\delta}$ composite cathode, the electrocatalytic activity was considerably developed, and the current density showed a growth of about 53.5% in a practical voltage of 1.5 V at 800 °C. These results signified that the SFM ceramics are favorable catalysts for $CO_2$ electroreduction.

$SrSnO_3$ nanowires (NWs) with a single 1D nanostructure and cubic perovskite phase have been reported by Pi et al. [55]. An adapted setup of a gas-tight two-chamber with a proton-exchange membrane (PEM) as the separator was designed for electrochemical investigation. An Ag/AgCl electrode, carbon-fiber-paper-modified $SrSnO_3$ nanowires in the cathodic chamber, and a Pt wire in the anodic chamber were used as the reference electrode (RE), working electrode (WE), and counter electrode (CE), respectively. When applied to $CO_2$ER catalysis, these prepared perovskite NWs show outstanding selectivity and catalytic activity in formate production, with a high FE (~80%) and remarkable current density over a wide potential range, making them outstanding electrocatalysts for

the $CO_2$ electroreduction to formate. Consequently, great selectivity (~80%), a large current density (21.6 mA $cm^{-2}$), and a notable durability of at least 10 h were obtained, making a new class of perovskite NWs with potential applications for $CO_2$ER and beyond. In comparison, bulk $SrSnO_3$ and $SnO_2$ nanoparticles (NPs) show very low activity and/or selectivity for $CO_2$ER.

Various nanostructures based on transition-metal nitrides have been examined for electroreduction reactions; however, a very limited number of these materials have been verified for $CO_2$ reduction reactions. For instance, $Ni_3N$ was employed for the $CO_2$ reduction to CO [56]. Yin et al. prepared perovskites based on copper (I) nitride ($Cu_3N$) nanocubes as a new catalyst for the selective $CO_2$ reduction to ethylene ($C_2H_4$) under ambient conditions [57]. These samples were synthesized by the nitridation of copper (II) hydroxide nanowires and were converted into multigrain nanowires to prove their great $CO_2$ reduction selectivity toward $C_2$ products, possibly due to the semiconductor properties of $Cu_3N$. These samples, with perovskite-related $ReO_3$ structures, can convert $CO_2$ into ethylene with a faradaic efficiency of about 60% and a Cu mass activity of around 34 A/g in a 0.1 M $KHCO_3$ electrolyte solution at −1.6 V compared with a reversible hydrogen electrode (RHE). Notably, in the products of the gas phase with a molar ratio of >2000 for $C_2H_4/CH_4$, the $Cu_3N$ catalyst suspends $CH_4$ formation, and the highest selectivity is realized for $CO_2$RR by Cu-based catalysis.

Two bismuth-based halide perovskite composites, $Cs_3Bi_2Br_9$/C and $Cs_2AgBiBr_6$/C, were prepared for electrochemical $CO_2$ reduction to HCOOH by Wang et al. [58]. They carried out the electrochemical analyses in acidic media (pH = 2.5) and could directly convert intermediates to formic acid instead of formate. In acidic electrolysis, the two $Cs_3Bi_2Br_9$/C and $Cs_2AgBiBr_6$/C composites can successfully inhibit structural degradation. A great FE of 92% at −0.95 V vs. RHE with a current density ($j_{HCOOH}$) of 133.7 $mAcm^{-2}$ was obtained by $Cs_3Bi_2Br_9$/C, while the $Cs_2AgBiBr_6$/C show a lower FE (68%) at −1.15 V vs. RHE. More investigation and analyses confirm that the existence of more Bi atoms in $Cs_3Bi_2Br_9$ is a crucial factor to more favorably generate OCHO* intermediates than $Cs_2AgBiBr_6$/C, accelerating the fabrication of HCOOH. Moreover, at −0.95 V over 20 h of electrolysis, for $Cs_3Bi_2Br_9$/C, the current density and FE (~92%) showed no evident decline, while the FE of HCOOH in $Cs_2AgBiBr_6$/C clearly deteriorated from 68% to 50% at −1.15 V after 10 h. The difference in stability between the two composites could be due to the faster charge transfer and faster increase in the $CO_2$ conversion ratio for $Cs_3Bi_2Br_9$ than $Cs_2AgBiBr_6$, leading to a reduction in the degradation effect and an enhancement in durability in an aqueous electrolyte.

A nanosized $LaInO_3$ perovskite electrocatalyst was effectively prepared by a simple hydrothermal–calcination method and applied in the electrocatalytic reduction of $CO_2$ to formate by Zhu et al. [59]. This synthesized electrocatalyst displayed superb activity and excellent selectivity in the $CO_2$RR. In an aqueous electrolyte solution, $CO_2$ has low solubility, so its reduction reaction is rigorously restricted in the H-cell, and the current density was very low. So, the flow cell was applied to carry out the $CO_2$RR. Thus, to solve the problem of solubility and the inadequate mass transfer of $CO_2$ in an aqueous solution, a suitable setup was designed by the $CO_2$ diffusion and electrolyte flow-channel-flanked gas-diffusion electrode. The results showed that the current density and faradaic efficiency of $LaInO_3$ in the flow cell was higher than in the H-cell. Electrochemical tests showed that the FE of

formate reached up 91.4% (−1.1 V vs. RHE) and the current density of formate was 116.8 mA $cm^{-2}$ (−1.1 V vs. RHE).

## 4.2. Photoelectrochemical $CO_2$ Reduction

Making advances in electrocatalysts and photoelectrocatalytic systems for the selective and efficient production of a target product is a substantial challenge [60][61][62]. Indeed, perovskite structures with interesting photoconversion and redox properties are always interesting for photoelectrochemical concepts. An $In_{0.4}Bi_{0.6}$ alloy-coated $CH_3NH_3PbI_3$-based photocathode has been demonstrated to produce selective $CO_2$ reduction with nearly 100% faradaic efficiency (FE) for formic acid production in aqueous solution by Chen et al. [63]. Their examinations revealed that $In_{0.4}Bi_{0.6}$ and $In_{0.6}Bi_{0.2}Sn_{0.2}$ alloys led to more electrocatalytic activity for the selective production of HCOOH as a result of the presence of the $In_5Bi_3$ phases. The HCOO*, as the intermediate in this procedure, was better stabilized on the $In_5Bi_3$ phases than on other alloys. At an applied voltage of −1.2 to −1.3 V versus RHE, the highest FE (95−98%) for the production of HCOOH was achieved by the $In_{0.6}Bi_{0.2}Sn_{0.2}$ and $In_{0.4}Bi_{0.6}$ alloys. Next, a favorable method that included coating the perovskite halide with an $In_{0.4}Bi_{0.6}$ alloy was used. With the $In_{0.4}Bi_{0.6}/CH_3NH_3PbI_3$ photocathode, at a low applied potential of −0.52 V vs. RHE under AM 1.5G irradiation, almost 100% FE for formic acid formation could be attained, signifying a 680 mV positive shift relative to the potential detected for the $In_{0.4}Bi_{0.6}$ electrode. At −0.6 V vs. RHE, the faradaic efficiency remained at nearly 100% for at least 1.5 h, and a photo-assisted electrocatalysis efficiency of 7.2% was determined. This photoelectrocatalyst showed a high selectivity for $CO_2$ reduction to HCOOH.

LSV analysis was applied to examine the samples for their PEC performances in a cell containing propylene carbonate solution saturated with $CO_2$ in 0.1 M tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$). Compared with the $CH_3NH_3PbBr_3$ quantum dots, $GO/CH_3NH_3PbBr_3$ showed an increase in photocurrents for the photoelectrochemical $CO_2$ reduction, as the maximum variation of photocurrent was observed at ca. −0.6 V. The photocurrent response of the as-synthesized samples was investigated at −0.6 V. This voltage was selected from the LSV results. An increase in the photocurrent response was observed for $GO/CH_3NH_3PbBr_3$, while $CH_3NH_3PbBr_3$ showed a decaying photocurrent, suggesting that graphene oxide acts as a stabilizer to preserve $CH_3NH_3PbBr_3$ QDs. Graphene oxide can protect $CH_3NH_3PbBr_3$ quantum dots against degradation by organic solvents and can also act as a charge-transfer intermediate to efficiently distinguish generated electrons and holes. The as-prepared catalyst exhibits an outstanding yield for $CO_2$ conversion to CO (1.05 μmol $cm^{-2}$ $h^{-1}$). The chronoamperometric analysis was applied to examine the effect of GO on the stability of $CH_3NH_3PbBr_3$. The photocurrent of $CH_3NH_3PbBr_3$ remained stable for about 1800 s. After introducing GO, the photocathode produced a long photocurrent for about 6000 s because of the protective effect of GO.

A PEC system based on a Au-decorated ZnO@ZnTe@CdTe photocathode and $CH_3NH_3PbI_3$ perovskite tandem cell has been verified by Jang et al. as an unbiased solar-driven $CO_2$ reduction to CO [64]. The designed cell disclosed a stable efficiency of solar-to-CO of above 0.35% with a faradaic efficiency of over 80% and a solar-to-fuel efficiency of more than 0.43%, with $H_2$ as a byproduct. This PEC cell showed the selective CO creation from $CO_2$ reduction using an operative photocathode−perovskite tandem device working in sunlight without an exterior

bias. The overpotential was decreased by the ternary photocathode, and the $CH_3NH_3PbI_3$ perovskite generated a voltage that is sufficient to initiate the reduction of $CO_2$ without an exterior bias.

### 4.3. Photovoltaic–Electrochemical $CO_2$ Reduction

Artificial photosynthesis, a technological device that uses solar irradiation as an energy source and water as an electron source to convert carbon dioxide into energy-dense organic compounds (fuels or other carbons for the chemical industry), is attractive in specific contexts [65]. This can be achieved in an integrated cell by using photovoltaic (PV) cells to supply photoelectrons and holes to be used in an electrochemical cell (EC) to oxidize water at the anode and to reduce carbon dioxide at the cathode, creating a PV-EC reference system to reduce $CO_2$ to fuels. The PV-EC systems can be classified into two general configurations, namely monolithic and polylithic. In a monolithic configuration, the junction terminals of the photovoltaic cell is directly connected to the anode and cathode of the EC unit, and the direct-circuit (DC) photogenerated power is designed to be used in the electrocatalytic process without any external electrical connections and/or inversion, while in a polylithic configuration, the PV and EC cells work separately, and the electrical power of the PV cell can be used in the electrochemical cell usually after a DC/DC inversion. Generally, the polylithic PV-EC has significantly better controllability of product selectivity, e.g., increasing the applied voltage via the series connection of PV modules and easier matching of the operating current by using certain ratios of the PV and EC areas.

Huan et al. provided a new catalyst for $CO_2$ conversion to hydrocarbons, which exhibited a faradaic yield of 62% in product generation [66]. This three-layer catalyst contains a metal Cu core protected by layers of CuO and $Cu_2O$. Remarkably, over a 60 min electrolysis at −0.95 V versus RHE, the structure of the CuO cathode changed. When joined with an advanced, low-cost perovskite photovoltaic minimodule, this PV-EC device achieves a solar-to-fuel value of 2.3% by combining it with a mini-module perovskite photovoltaic device recognized using two sequences of three perovskite photovoltaics with an active area of 0.25 $cm^2$ coupled in parallel, offering a yardstick for PV-EC systems that includes plentiful earth-abundant elements. To examine the $CO_2$-reduction performance on this system, current–voltage measurements of the modules were applied, which exposed a high photo-to-current efficiency (17.5%) at 2.45 V and 10.0 mA. A constant current of 6.0 ± 0.2 mA with a current density of ~18 $mA{\cdot}cm^{-2}$ and a potential of 2.8 ± 0.02 (V) were proved by the connection of both systems. Over a 50 min electrolysis by using the gas chromatography (GC) technique and analyzing the reduction products, it was shown that the PV-EC catalyst generates a steady current.

## 5. Conclusions

The conversion of $CO_2$ to added-value chemicals or fuels is an attractive strategy for storing such a renewable source of energy into the form of chemical energy. The catalysis technology has received more and more attention for such a concept. Therefore, in parallel to more developed systems for electrochemical water splitting, the utility of innovative and advanced catalysts to develop critical performance factors, e.g., durability, conversion efficiency, and energy/power densities, must be explored in the specific concept of the $CO_2$RR. To achieve this purpose, the scientific community has been working on the construction of new materials that allow the design of advanced

electrode systems for efficient $CO_2$ capture and reduction. Recently, perovskite-based catalysts have drawn a growing interest in various sectors from renewable energy to environmental processes. Perovskite oxides have shown more potential in EC $CO_2$RRs because of their oxygen vacancy sites and lattice distortions, which create more active sites for electrochemical $CO_2$ reduction. Moreover, perovskite oxides have more stability under harsh conditions like high temperature and can be used for solid-oxide fuel cells. Due to the presence of halide ions, halide perovskites show higher absorption coefficients and have more carrier mobilities, which make them more suitable for PEC and PV-EC $CO_2$ reduction [67][68]. To achieve outstanding perovskite-based electrocatalysts, there are various strategies available, including developing the intrinsic activity and increasing available active sites by defect engineering on the perovskite surface, crystal structure regulation, tuning the electrical conductivity and synthesis process, and surface modification. High electron transfer of perovskites leads to the reduction of ohmic losses and the evolution of active sites, developing electrocatalytic performance. To increase electronic conductivity, some strategies such as using electrically conductive materials and doping agents are beneficial.

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