Solar carbon fuel via photoelectrochemistry

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ABSTRACT

A promising strategy to mitigate both energy shortage and global warming is the conversion of CO_2 into chemicals that can be used as fuels (chemical fuels) by utilizing renewable energy sources. Up to date, solar-driven CO_2 reduction has been achieved with photochemical (PC) and photoelectrochemical (PEC) systems or electrochemical cells combined with a photovoltaic system (PV-EC). This study is intended to compare and highlight the state-of-the-art PEC systems for CO_2 reduction and show the limitation factors that still hinder their widespread utilization. The review starts with a description of semiconducting photocatalyst properties and fundamental understanding of PEC CO_2 reduction process. Then, the most significant performance metrics used for evaluation of PEC systems are explained in details. In addition, recent progress in PEC CO_2 reduction systems is summarized and classified in different categories according to the chemical product. Different strategies such as doping, combination of two or more semiconductors, synthesis of nanostructured materials, passivation layers and co-catalysts that enhance light absorption, chemical stability, charge transfer and reduce ohmic losses and overpotentials of photoactive materials are reviewed. Besides the improvement of photocatalysts, research progress on the front of PEC reactor design, combined with the development of advanced modelling tools and characterization techniques are expected to bring PEC CO_2 reduction a step closer to commercialization.

1. Introduction

Human civilization heavily relies on non-renewable hydrocarbon fuel sources such as crude oil, coal and natural gas for energy supply. However, overdependence of fossil fuels due to large population growth and economic expansion not only leads to energy shortage, but also causes global warming. Specifically, global climate change, one of the most pressing environmental issues of the 21st century, is mainly caused by rising anthropogenic greenhouse gases emissions, with carbon dioxide(CO_2) being the most important [1,2].

The concentration of CO_2 in the atmosphere has increased steadily over recent decades due to fossil fuel combustion. Furthermore, it has been proven that the global increase of CO_2 levels in the atmosphere is the major contributor to global warming [3]. Consequently, to address this issue, it is urgent to develop technologies in order to decrease the concentration of atmospheric CO_2 [4]. In addition to reducing anthropogenic emissions of CO_2, a large variety of strategies are investigated, ranging from converting atmospheric CO_2 to chemicals or fuels to capturing and storing it underground [5–7].

In general, CO_2 can be converted into high value products by several technologies through biological [8,9], thermochemical [10],

electrochemical [11–13], photochemical [14–17] and photoelectrochemical [17–20] processes. Apart from the latter two options, other conversion processes have several drawbacks including high temperature or pressure, unsustainability, high-operative cost and limitations of raw materials. Methods of solar-driven CO_2 conversion to fuels have recently attracted considerable attention, as they could open up the possibility of controlling and maintaining an anthropogenic carbon cycle for a sustainable future [21]. Therefore, artificial systems that mimic natural photosynthesis are considered to be an ideal route for CO_2 transformation into clean and storable fuels. Additionally, the energy carriers (especially methanol) [22] produced in this way are easier to be handled, transported and stored compared to hydrogen as they also take advantage of an existing huge infrastructure network.

The increasing research interest in the field of sunlight-assisted CO_2 reduction to several chemicals or fuels has driven the development of several methods. These methods can be categorized into three groups: photochemical reduction by photocatalysts (PC), electrochemical reduction by an electrolyzer supplied with electrical energy by a typical photovoltaic cell (PV-EC) [19,23] and photoelectrochemical reduction by semiconducting photoelectrodes (PEC).

PC conversion of CO_2 can be achieved using either homogeneous or

heterogeneous systems. A typical homogeneous system consists of a molecular catalyst, a photosensitizer, a sacrificial electron donor and/or an electron relay [17]. While promising, this method requires rare and expensive metals, still uses a sacrificial agent and suffers from poor performance and instability issues. In the heterogeneous approach, a large variety of semiconductors have been explored extensively over the last four decades. The semiconductor must have a suitable band gap not only large enough to offer electrons but also small enough to enable efficient visible light absorption. Moreover, the potential of the conduction band must be more negative than the CO_2 reduction potential, while the valence band must be more positive than the water oxidation potential [18]. These requirements minimize the number of the semiconductors that can be used as photocatalysts for the conversion of CO_2.

Another approach for light-assisted CO_2 reduction is the utilization of a photovoltaic junction in order to provide external potential to an electrochemical (PV-EC) [24] or a photoelectrochemical (PV-PEC) [25,26] set-up. However, although there are several cases where PV-EC and PV-PEC approaches have been used for water splitting and hydrogen production, there is limited research reported using this type of systems for CO_2 transformation into chemical fuels. These systems have achieved very high efficiencies, but the expensive metal electrodes combined with the cost of the peripherals (cables, wires, converters etc.) are significant drawbacks for the commercialization of this technology.

Heterogeneous PEC devices for direct CO_2 transformation seem a more promising approach to obtain chemical fuels. In these devices, there is an interface of a semiconducting photoelectrode and a liquid electrolyte that offers a direct and efficient way of light-to-chemical fuels conversion. In particular, a photoelectrode, an electrode coated with a light-sensitive semiconductor, interacts with a liquid electrolyte when exposed to light. Electron-hole pairs are photogenerated and drive reduction-oxidation reactions for chemical fuel production. Consequently, photoelectrodes are considered as the most significant parts of PEC devices for solar fuels production. A large number of studies has been reported since Halmann [27] in 1978 developed the first PEC cell based on a p-type gallium phosphide photocathode through which bubbled CO_2 was converted into methanol, formic acid and formaldehyde. To date, three different types of PEC systems for CO_2 conversion have been used: photocathode-driven PEC cells, photoanode-driven PEC cells and photoanode-photocathode-driven (Z-scheme) PEC cells.

This review article illustrates all the up-to-date developments of the PEC systems for direct solar CO_2 reduction. An overview of theoretical and fundamental aspects of heterogeneous CO_2 photoreduction will be presented first. In addition, the most well-known performance indicators of either a particular part or the entire PEC device for CO_2 reduction will be demonstrated and explained. It also provides a summary on the fuels and valuable products that can be generated by PEC systems. Specifically, the most efficient PEC systems so far will be highlighted for the production of HCOOH, CH_3OH, C_2H_5OH, CO and CH_4. Due to the fact that PEC conversion of CO_2 into fuels is a very complex process, most PEC systems suffer from either low selectivity or efficiency. Thus, a significant part of the review is intended to demonstrate a lot of examples of the recent literature emphasizing the challenges of this field and showing the large variety of possible chemical products.

2. Principles of PEC CO_2 reduction

PEC CO_2 reduction cells consist of a semiconducting photoactive electrode, photoelectrode, electrolyte, a metal-based electrocatalyst or a second photoelectrode and in most cases a separation membrane. In this Section, fundamentals of photoelectrodes and thermodynamics of PEC CO_2 reduction systems will be reviewed, followed by a description of all the aforementioned components. Finally, proposed mechanisms and pathways of PEC CO_2 reduction process will be discussed.

Table 1
Standard potentials related to CO_2 reduction and water oxidation with reference to Normal Hydrogen Electrode (NHE) at pH = 0 [28,29].

Reaction	E^0 vs. NHE at pH = 0	Equation number
$2H^+ + 2e^- \rightarrow H_2$	0 V	(1)
$2H_2O \rightarrow O_2 + 4e^- + 4H^+$	-1.23 V	(2)
$CO_2 + e^- \rightarrow CO_2 \cdot^-$	-1.90 V	(3)
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.20 V	(4)
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.11 V	(5)
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.07 V	(6)
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	0.03 V	(7)
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 3H_2O$	0.08 V	(8)
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	0.08 V	(9)
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 2H_2O$	0.14 V	(10)
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	0.17 V	(11)

2.1. Thermodynamics and fundamentals of PEC cells for CO_2 reduction

The conversion of CO_2 into fuels is an energetically uphill reaction. The spontaneity of CO_2 conversion into several fuels is indicated by the reduction potential (E^0) of each reaction, as given in Table 1. Therefore, energy must be supplied to a CO_2 reduction system in order to overcome the negative potentials and generate valuable chemicals or fuels.

In photocatalytic systems, a photocatalyst harvests light offering the required energy input for reduction-oxidation reactions. Specifically, a semiconductor has the ability to convert incident photons with energy equal to or greater than the width of its bandgap to electron-hole pairs. (Fig. 1a, b) According to the band theory, bandgap represents a zone of forbidden energy-states between the highest energy-state filled with electrons in the valence band and the lowest unfilled energy-state in the conduction band. Electrical mobility of semiconductors can be enhanced by promoting electrons from the valence band to the conduction band under irradiation with photons of sufficiently high energy. Electrons promoted to the conduction band leave empty positions (holes) for electrons in the valence band. The photo-excited pairs of electron and holes can be utilized to drive oxidation and reduction reactions [30,31]. Alternatively, the combination of two different semiconductors with suitable band gaps, as given in the schematic energy-band diagram (Fig. 1c), can allow the performance of water oxidation and reduction of CO_2 at different sites. The two-step CO_2 photo-reduction systems are also known as Z-scheme because they replicate the electron excitation and transfer processes of natural photosynthesis in green plants.

Although PEC cells mainly rely on light harvesting, application of an external electrical bias can significantly lower the energy needed for oxidation-reduction reactions. Thus, in PEC systems, a larger variety of semiconductors can be theoretically used in comparison with photocatalytic systems. However, in photocatalytic applications the photocatalyst is suspended in the reaction solution and there is no need for charge transfer between the semiconductor particles, while this process is crucial in PEC systems. In other words, photocatalysts with low charge transportation cannot be used for efficient PEC CO_2 reduction. In the following subsections, it will be presented the fundamental aspects of the three different types of PEC systems for CO_2 conversion: photocathode-driven PEC cells, photoanode-driven PEC cells and photoanode-photocathode-driven (Z-scheme) PEC cells.

2.1.1. P-type semiconductors in PEC cells for CO_2 reduction

Semiconductors doped with impurities that accept electrons from the valence band creating an excess of holes in the lattice are known as p-type semiconductors. When a p-type semiconducting electrode placed in an electrolyte with a redox potential within the semiconductor energy gap and different from its Fermi level, electrons will move from the electrolyte solution to the semiconductor increasing the Fermi level energy until an electronic equilibrium is established [35]. The flow of
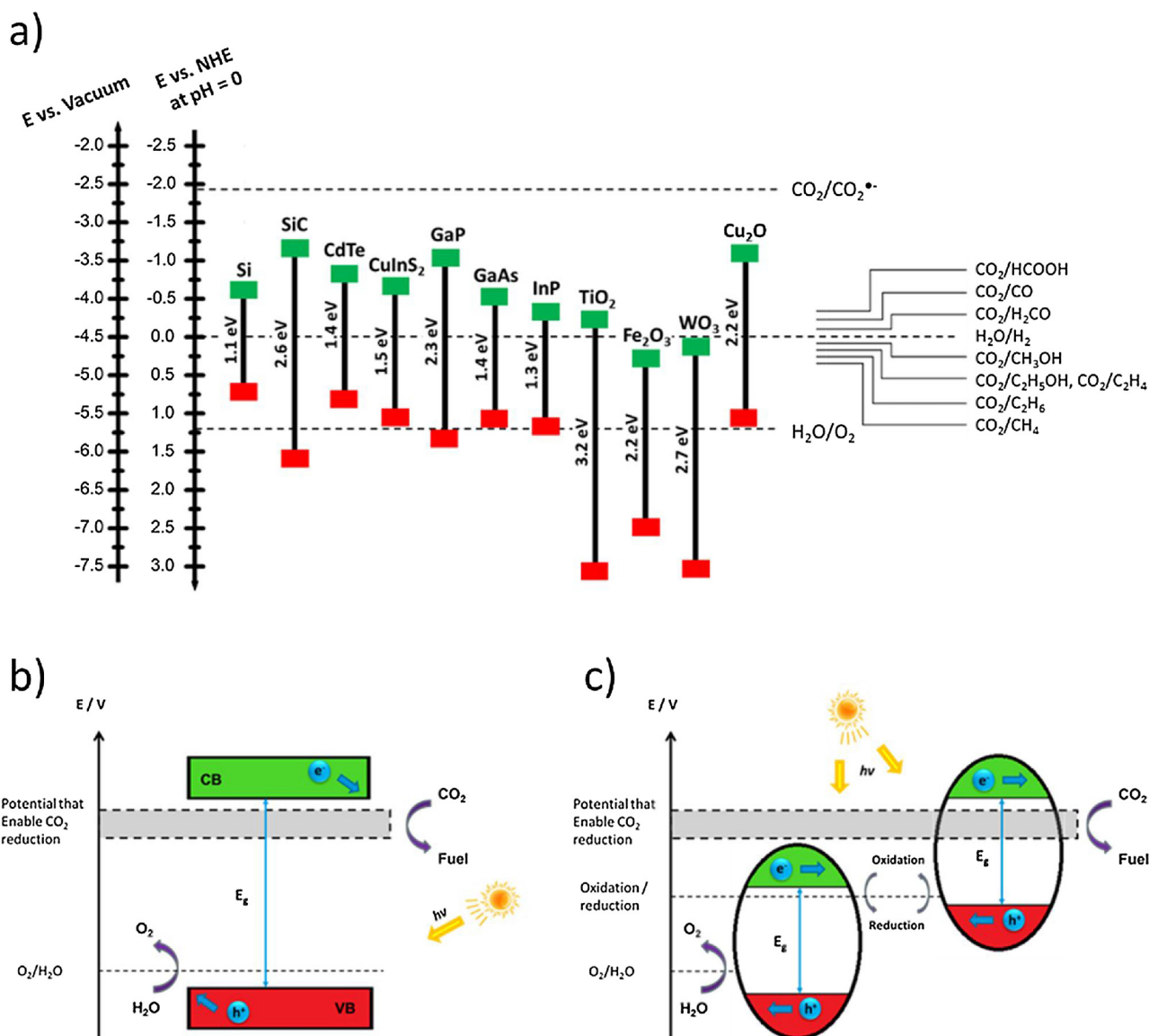
Fig. 1. a) Conduction band (green rectangles) and valence band (red rectangles) positions of some typical semiconducting materials in photoelectrocatalytic processes with respect to the reduction-oxidation potentials of CO_2 reduction and water splitting versus NHE at pH = 0. Band edges for TiO_2, WO_3, Si, GaP, GaAs, InP found in reference [32], for Cu_2O, Fe_2O_3, CdTe, $CuInS_2$ found in reference [33] and for SiC found in reference [34]. b) Schematic illustration of one step CO_2 photoreduction and c) a system with two semiconductors in contact (Z-scheme). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

charge carriers form a space-charge region near to each side of the semiconductor-electrolyte interface where the electron and hole distribution is different compared to bulk material. On the semiconductor side, this region is known as the depletion layer, while on the electrolyte side is the Helmholtz layer that consists of charged ions absorbed on the semiconductor surface [30,31]. This also results in an upward bending of the valence and conduction band near the interface known as band bending effect [30]. However, this effect is not equal to the difference between the Fermi level and the redox potential due to the formation of Helmholtz layer.

Apart from band bending properties, a p-type semiconductor utilized for the photocathode for CO_2 reduction should also have resistance to chemical degradation and a suitable band gap for CO_2 reduction reactions [18]. Particularly, an ideal p-type semiconductor for CO_2 reduction must absorb visible light wavelengths that fall in the visible solar spectrum (E_g between 1.8–3.0 eV) and at the same time, the potential of its conduction band edge should be more negative than the CO_2 reduction potential [36]. Additionally, a p-type semiconductor

with a relatively negative conduction band edge can assist in overcoming the challenge of slow kinetics. Consequently, researchers should take into consideration all the factors that affect the efficiency of a semiconducting photocathode in order to develop new materials or optimize the performance of the explored p-type semiconductors.

Typically, a Photocathode-driven PEC cell for CO_2 reduction (Fig. 2) consists of a photocathode, a p-type semiconducting photocatalyst coated on a conductive substrate, and a counter electrode bearing an electrocatalyst. This configuration has been studied extensively since Halmann [27] in late 1970′s reported for the first time a PEC cell that relied on a photocathode in order to convert CO_2 directly into fuels. Semiconducting photocathodes are the most crucial components for the performance of this type of cells. The most well studied materials for this purpose are semiconductors such as III–V, IV, II–VI and more recently a few metal oxides. Briefly, photocathodes harvest incident photons creating electron-hole pairs (excitons). Band bending occurring near the semiconductor-electrolyte interface is responsible for the formation of an electric field inside the semiconductor strong enough to
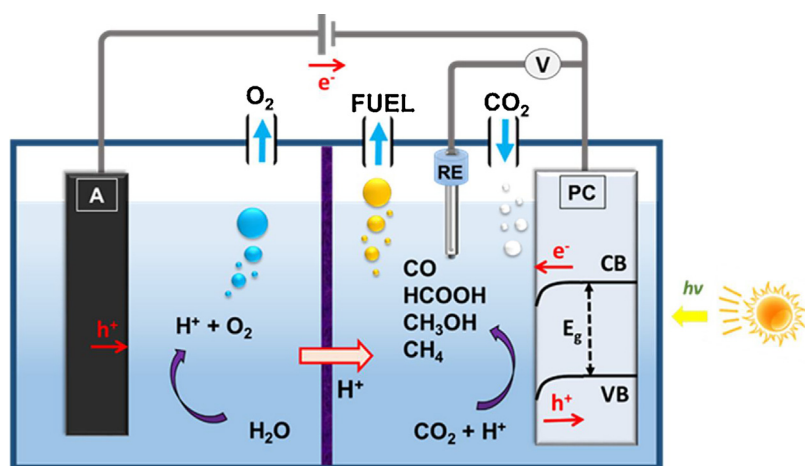
Fig. 2. Schematic illustration of a three-electrode configuration of a photoelectrochemical cell for CO_2 reduction separated into two compartments by a proton-exchange membrane with an anode (A), an illuminated photocathode (PC) and a reference electrode (RE). Band bending at the semiconductor-electrolyte interface and flow of photogenerated carriers and protons are also indicated.

break the electron-hole pairs. In addition, the application of an external potential can further improve the charge separation due to an increase on the band bending [30]. The aforementioned charge separation mechanism provides photoexcited electrons to the CO_2 reduction process at the photoelectrode-electrolyte interface, and drives photogenerated holes to a counter electrode. Then, photogenerated holes accumulate on the electrocatalyst-electrolyte interface and participate in oxidation reactions. However, only some of the separated photogenerated charge carriers will be extracted successfully in CO_2 reduction process, while the rest will recombine, producing heat or radiation. The main reason for charge carrier recombination in semiconducting photocatalysts is related to the presence of defects or impurities that can act as electron and hole traps.

2.1.2. N-type semiconductors in PEC cells for CO$_2$ reduction

Semiconductors doped with impurities that donate an excess of electrons to the conduction band are known as n-type semiconductors. Due to the presence of electrons in the conduction band the Fermi-level in n-type semiconductors is located close to the conduction band. When an n-type semiconductor is immersed in an electrolyte with a redox potential close to its energy levels, some electrons will be transferred from the semiconductor to the electrolyte solution in order to equilibrate their Fermi levels. This electron migration leads to a decrease in the Fermi energy level and forms a downward band bending that push valence band holes toward the semiconductor surface. Generally, n-type semiconductors are employed in photo-oxidation reactions because holes flow from the valence band to the semiconductor-electrolyte interface (Fig. 3).

Ogura and co-workers [37] first investigated the utilization of n-type semiconductors as photoanodes in photoelectrochemical CO_2

reduction in 1986. However, most of the reported studies that investigate photoanode-driven PEC cells focus on water-splitting processes. Briefly, in this kind of system, the semiconducting photoanode absorbs incident light when the energy of photons is equal to or higher than the band gap energy, generating electron-hole pairs. Photogenerated holes on the surface of the semiconductor allow the oxidation of a solution species such as water, while electrons reach the cathode through an external circuit and participate in reduction reactions.

A photoanode-driven PEC system for CO_2 reduction is composed of a semiconducting photoanode, an electrocatalyst which serve as cathode and usually a proton exchange membrane (Fig. 3). In contrast with photocathode-driven systems for CO_2 reduction, the overall performance of photoanode-driven cells rely on both photoanode and cathode. In other words, the semiconducting photoanode can harvest solar light and lower the external bias needed for CO_2 reduction process allowing the utilization of a large variety of electrocatalysts as cathode that can improve the overall efficiency of the PEC cell and control the chemical products.

2.1.3. Photoanode-Photocathode PEC cells for CO$_2$ reduction

Recently, the combination of both photoanode and photocathode in a single system [38] has opened a new avenue in photoelectrochemical CO_2 reduction systems [39]. These integrated systems that mimic photosynthetic mechanism of plants have not been fully developed enough yet, although they seem very promising because coupling of photoanodic and photocathodic reaction can lead to CO_2 reduction even without external applied potential. The most straightforward way to build a Z-scheme cell is to connect through ohmic contacts a p-type photocathode and an n-type photoanode (Fig. 4). In this case, both illuminated photoelectrodes absorb light generating electron-hole pairs
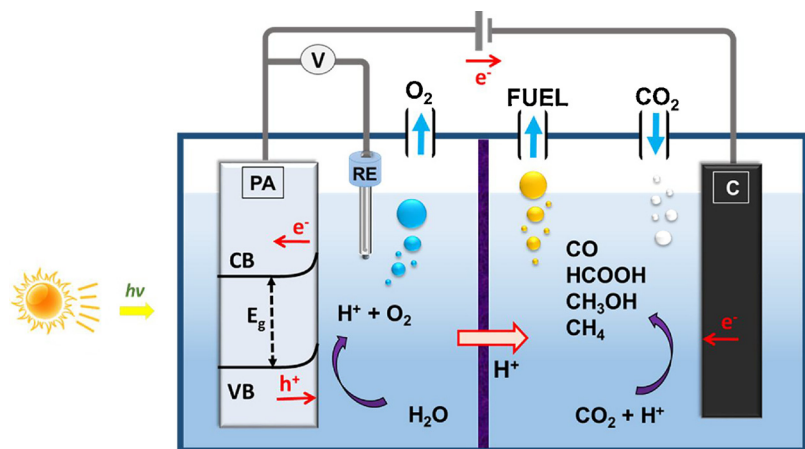

Fig. 3. Schematic illustration of a three-electrode configuration of a PEC cell for CO_2 reduction separated into two compartments by a proton-exchange membrane with an illuminated photoanode (PA), a cathode (C) and a reference electrode (RE). Band bending at the semiconductor-electrolyte interface and flow of photogenerated carriers and protons are also indicated.

Fig. 4. Schematic illustration of a three-electrode configuration of a PEC cell for CO_2 reduction separated into two compartments by a proton-exchange membrane with photoanode (PA) and photo-cathode under illumination (C) and a reference electrode (RE). Band bending at the semiconductor-electrolyte interface and flow of photogenerated carriers and protons are also indicated.
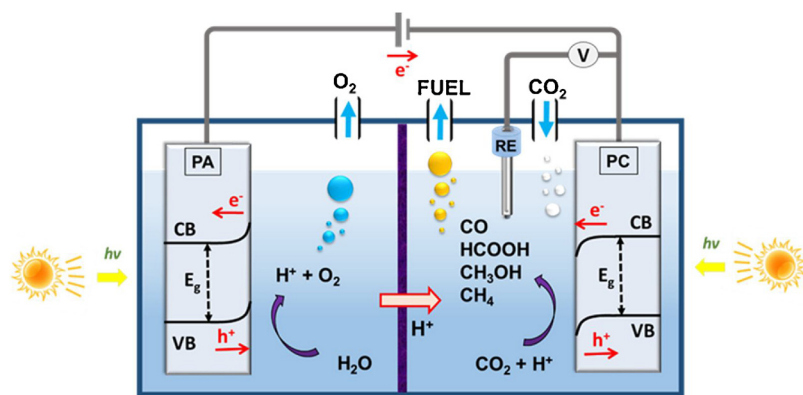
simultaneously. The majority of the charge carriers are recombined at the ohmic contacts while the minority of the charge carriers drive the reactions of water oxidation and CO_2 reduction on photoanode and photocathode respectively.

2.2. Reactor design of PEC CO_2 reduction cells

An undeveloped field in PEC CO_2 reduction cells is the reactor design. An efficient reactor design should meet the following criteria: i) molecular separation of anodic and cathodic compartments, ii) minimum resistive losses between electrodes, iii) minimum optical losses, and iv) minimum mass transfer limitations. The most common type of reactor used in PEC CO_2 reduction process so far is two-compartment reactor separated with a proton exchange membrane. Apart from proton exchange membrane, glass frit has also been used in PEC cells to physically separate the chemical reactions of water oxidation and CO_2 reduction [19].

The presence of membrane is crucial because it can act as a molecular barrier while it allows the migration of protons from the anodic compartment to react with CO_2 on the cathodic compartment. Therefore, it can protect the system from cross-over which can lead to back reactions and significant decrease the overall efficiency. Moreover, the presence of a molecular barrier in PEC CO_2 reduction systems can eliminate the formation of dangerous and flammable mixtures from the CO_2 reduction such as oxygen and fuel. In addition, these membranes allow the utilization of different types of electrolytes in the anodic and the cathodic compartments of the cell [40], which can also increase the efficiency of photoelectrochemical system due to formation of chemical bias. Needless to say, there is a balance between the enhancement of molecular barrier function and the decrease of proton conductivity [41].

Elimination of mass transfer limitations is another key element for the design of efficient PEC CO_2 conversion reactors. Up to date, only one study reported the utilization of a continuous flow PEC microreactor for CO_2 reduction showing significant enhancement of current density compared to common batch reactors [42]. The utilization of continuous flow microreactor led to the production of longer chain alcohols such as ethanol and isopropanol, making this technology an even more attractive choice. Such significant improvement is mainly related to high mass transfer of CO_2 and high surface area to volume ratio [42].

2.3. Possible mechanism and pathways for PEC CO_2 reduction

CO_2 is a linear and chemically very stable molecule, so its conversion to fuels needs a substantial input of energy. Much attention has been paid to the investigation of the reaction mechanism behind CO_2 reduction. However, the majority of research efforts have focused on systems based on homogeneous [17] or metal-based electrocatalysts [13]. The first mechanism for CO_2 reduction in PEC systems, proposed

by Halmann [27], was similar to the mechanism based on studies conducted on metallic electrodes for electrochemical CO_2 reduction [13,43]. In this mechanistic route, it was proposed that the formation of an intermediate carbon dioxide anion radical ($CO_2 \cdot^-$) by a single electron reduction of carbon dioxide is the initial and the rate-determining step as given by Eq. (3) in Table 1.

The initial step is followed by a second electron and a water-mediated proton in $CO_2 \cdot^-$ forming $HCOO^-$ [27,44–49], while an alternative pathway of this mechanism is the formation of CO in which another electron transfer and a CO_2 molecule are involved [44,49,50]. It has been further suggested that in the presence of Cu particles, $CO_2 \cdot^-$ can be converted into methane or ethene by several electronation/protonation steps [49]. Furthermore, according to a more recent study, Li et al. [51] speculated a pathway in which $CO_2 \cdot^-$ was converted into methanol by several consecutive electronation/protonation steps. However, single-electron reduction of CO_2 to $CO_2 \cdot^-$ is questionable due to the fact that they reported production of carbon fuels in electrochemical systems without applying external potentials as negative as the $CO_2/CO_2 \cdot^-$ redox potential. Additionally, from a thermodynamic point of view, the initial step can be achieved on a photocatalyst only if its conduction band edge is more negative than the $CO_2/CO_2 \cdot^-$ redox potential, while at the same time, its valence band edge is located lower than the standard redox potential of water oxidation to O_2. Nevertheless, it can be clearly seen from Fig. 5 that single electron reduction of CO_2 is questionable because the most common semiconductors in photocatalytic and photoelectrocatalytic systems do not satisfy these criteria [18,52]. Therefore, further investigations are needed to provide enough evidence for the clarification of the aforementioned mechanism and especially for the first step.

Another plausible scenario for the PEC CO_2 reduction, in which the formation of $CO_2 \cdot^-$ can be sidestepped through a series of proton and electron transfers, was firstly proposed by Inoue et al. in 1979. This mechanism involves a succession of multiple proton-coupled electron transfers recently known as PCET [53,54]. Specifically, the transfer of a proton with an electron not only assists in the prevention of large activation barriers that derived from high reorganization energies but also reduces the formation of unstable intermediates. However, it should be mentioned that the kinetics of PCET processes highly depend on the properties of the redox species, the temperature, the pH and the over-potential of the system [55].

Finally, an alternative approach, originated from a photocatalytic mechanistic model [56], was proposed by Peng et al. [40] to explain the PEC CO_2 conversion into carbon based fuels and hydrogen in a two-compartment reactor separated with a cation-exchange membrane. In this approach, oxidation of water occurred at the photoanodic chamber forming oxygen, protons and electrons (Eq. (2)), while hydrogen radicals were formed in the cathodic chamber. Then, hydrogen radicals can either recombine, forming hydrogen, or they can react with CO_2 to produce formaldehyde, methanol and methane in series.

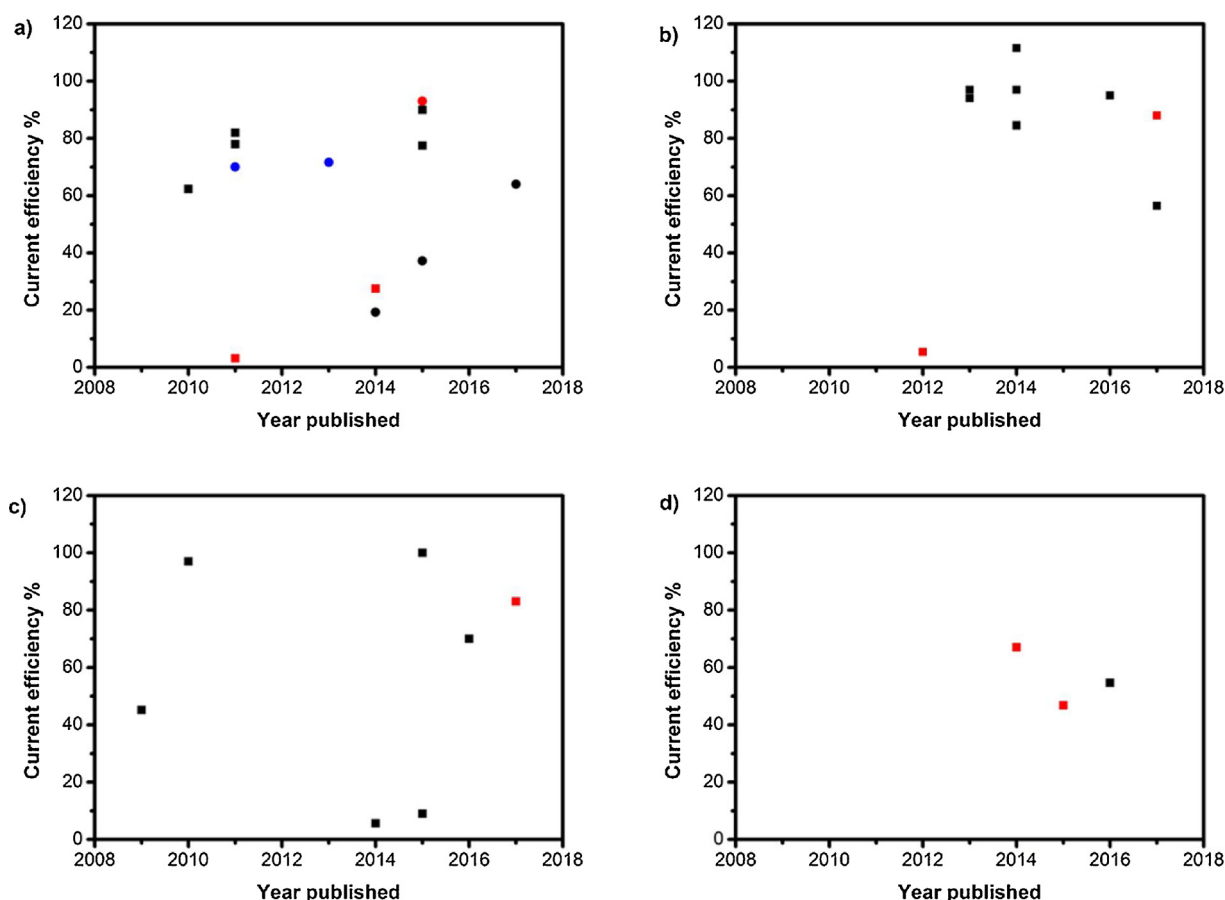Although a large number of studies have reported PEC CO_2

Fig. 5. Current efficiency vs. year of publication for different fuels produced in PEC cells for CO_2 reduction: a) Formic acid (squares) or Formate (circles), b) Methanol, c) Carbon monoxide and d) Methane. Three different types of PEC systems were utilized for CO_2 conversion: Photocathode-driven cells (black symbols), Photoanode-driven cells (red symbols) and Photoanode-Photocathode systems (blue symbols) [40,44,46,47,49,51,58–90]. (For additional details see supplementary information). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conversion, only a few of them dealt with the mechanistic routes, pathways and kinetics. Furthermore, a large variety of PEC systems has been utilized in CO_2 reduction to produce several gas and liquid products, which further complicate the understanding of the pathways [18]. Moreover, the adsorptive and catalytic processes on semiconductor surfaces are still not very clear. Adsorption of CO_2 on the surface of the photocatalyst is the initial step of CO_2 photocatalytic reduction. Therefore, it is a critical challenge to understand the adsorption mechanism because it has a great effect on the overall efficiency of heterogeneous photocatalytic CO_2 reduction systems. Consequently, the PEC reduction of CO_2 is a very complex process and there still remain a lot of uncertainties that hamper the progress on clarification of a universally recognised mechanism.

3. Performance metrics

3.1. Efficiency

Currently, there are several performance indicators that can be utilized to measure the efficiency of either a particular part or the entire PEC device for CO_2 reduction. Solar-to-fuel efficiency (STF) is the most well-known figure of merit of a whole PEC cell. STF expresses the overall conversion efficiency of PEC systems illuminated by a light source (AM 1.5G) under zero applied voltage between the working and the counter electrode. This means that light irradiation is the only energy input. It should also be mentioned that if the working and the counter electrode are immersed in different electrolytes with different pH, STF cannot be measured correctly due to the existence of chemical

bias between the two compartments [57]. Apart from that, sacrificial agents such as CH_3OH should not be involved in the electrolyte because they are not sustainable and they can be oxidized more easily than water. STF describes the total chemical energy produced divided by the energy input from light irradiation that reaches the photoactive area of a PEC cell and can be expressed by the following equation:[57]

$$STF = \frac{r_{fuel}(mmol\,of\,fuel/s) \times \Delta G^0 (kJ/mol)}{P_{solar}(mW/cm^2) \times Area(cm^2)} \quad (12)$$

where r_{fuel} is the amount of chemical fuel produced per second, ΔG^0 is the Gibbs free energy for conversion of gaseous CO_2 into fuel, P_{solar} is the power density of the light source (AM 1.5G) and Area is the irradiated photoelectrode area of the PEC system. For example, in the case of CO_2 conversion into formic acid, ΔG^0_{HCOOH} represents the Gibbs free energy for conversion of gaseous CO_2 into liquid formic acid based on the following chemical reaction:

$$CO_2\,(g) + H_2O\,(l) \rightarrow HCOOH\,(l) + \tfrac{1}{2}O_2\,(g) \quad (13)$$
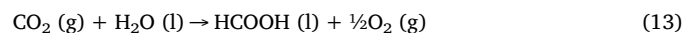
As an alternative, STF can be defined by another equation [24]:

$$STF = \frac{J_{sc}(mA/cm^2) \times \Delta E^0 (V) \times FE}{P_{solar}(mW/cm^2)} \quad (14)$$

In this equation, J_{sc} is the observed short circuit photocurrent density, ΔE^0 is the thermodynamic energy stored in the CO_2-chemical fuel couple at 25 °C (E^0 values as shown in Table 1), FE is the Faradaic or current efficiency and P_{solar} is the incident illumination power density (AM 1.5G). FE for CO_2 PEC reduction is defined as a ratio of the current contributing to CO_2 conversion into chemical fuels to the

observed current and can be calculated as follows: [58]

$$FE = \frac{e_{output}}{e_{input}} \times 100\% = \frac{n(mol) \times y}{\frac{Q(Coulomb)}{F(Coulomb/mol)}} \times 100\% \tag{15}$$

where n is the amount of moles of formed product, y is the number of electrons required to reduce CO_2 into a specific product (Table 1), F is the Faraday constant (96485C/mol) and Q is the measured charge. (Q can also be calculated using electrolysis laws of Faraday: $Q = I \times t$). Thus, if all the aforementioned criteria can be obtained, then it is possible to estimate the amount of current density that was consumed in order to produce the desired oxidation and reduction reactions or wasted to other processes such as photocorrosion of the catalyst or undesired side reactions and back reactions.

FE values for PEC CO_2 conversion into several fuels are represented in Fig. 5. It can be noticed that an increasing interest in PEC CO_2 reduction the last decade which generally led to higher levels of faradaic efficiencies. Although one of the main purposes of PEC CO_2 reduction is the achievement of high FE, there are some research groups that focus on the development of cheaper and more stable materials for PEC cells. Consequently, this is the main reason why there are still studies in which low FE is reported. However, according to the same figure, there is a general upward trend in the levels of FE towards chemical products from PEC CO_2 conversion systems over the last 8 years especially in cases of fuels such as methanol, formic acid and methane. In the end of last decade, there was a rise on the number of research groups that worked in the development of new photoactive materials for PEC water splitting applications. The transfer of knowledge from PEC water splitting research area combined with the increase of interest for CO_2 reduction systems led to more publications with higher FE.

If an applied voltage between the working and the counter electrode is necessary to obtain CO_2 conversion, another efficiency indicator is utilized instead of STF efficiency. This additional tool called 'Applied Bias Photon-to-current Efficiency' (ABPE) describes how STF efficiency of a CO_2 reduction PEC system changes by applying an external applied bias. Hence, ABPE can be defined from the following equation [30]:

$$ABPE = \frac{J_{ph}(mA/cm^2) \times [\Delta E^0(V) - V_{bias}(V)] \times FE}{P_{solar}(mW/cm^2)} \tag{16}$$

where V_{bias} is the applied voltage between the working and the counter electrode in a two electrode configuration and J_{ph} is the photocurrent observed under that V_{bias}. Both STF and ABPE can provide information about the total efficiency of a PEC cell utilizing a two-electrode configuration. On the other hand, three-electrode configurations can be very useful in the evaluation of new photoactive materials for PEC CO_2 reduction systems. Generally, a three-electrode set up consists of a working electrode (photoelectrode), a reference electrode and a counter electrode. It should be mentioned that it is very complicated to indirectly estimate the total efficiency of a PEC device from a three-electrode set up due to the fact that the working electrode potential is reported relative to the potential of the reference electrode.

One of the most useful performance tool that utilizes a three-electrode configuration is the Incident Photon-to-Current Efficiency (IPCE). The IPCE method measures how efficient the incident photons are converted into photocurrent as a function of the irradiation wavelength. It can also describe the maximum chemical conversion efficiency of a particular photoelectrode by integrating the IPCE measurements over the whole solar spectrum. It is one of the most important diagnostic tools because it can provide useful information in both two-electrode and three-electrode modes with or without any applied bias. The IPCE as a function of illumination wavelength can be described by the following equation [57]:

$$IPCE(\lambda) = \frac{hc}{e} \frac{J_{ph}}{P_{mono} \times \lambda} = \frac{J_{ph}(mA/cm^2) \times 1239.8(V \times nm)]}{P_{mono}(mW/cm^2) \times \lambda(nm)} \tag{17}$$

where h is Planck's constant, c is the speed of light, e is the electron

charge, P_{mono} is the power density of the monochromated illumination and λ is the wavelength of this monochromatic light. In the concept of PEC CO_2 reduction, the IPCE represents the maximum possible conversion efficiency of incident photons to chemical fuels assuming that all the excited electrons are used only for this electrochemical reaction (FE = 100%).

Another useful diagnostic tool is the absorbed photon-to-current conversion efficiency (APCE). This tool describes only the efficiency of the absorbed photons, while the transmittance and reflection losses are subtracted. The APCE can be calculated as follows [30]:

$$APCE(\lambda) = \frac{IPCE(\lambda)}{A(\lambda)} = \frac{IPCE(\lambda)}{1 - R - T} \tag{18}$$

$A(\lambda)$, R and T are the absorbance, the reflectance and the transmittance respectively. The importance of this parameter is that allows the evaluation of the recombination of photogenerated charge carriers within the semiconductor. In other words, APCE provides useful information about the optimal thickness, purity and the defect density of a semiconductor-based material. Values of the best PEC CO_2 reduction systems for efficiency and others performance indicators are presented in details in Section 4 (Table 3).

3.2. Current density and production rate of fuels in PEC systems

The most common practice to evaluate the performance of a

Table 3
Best values observed of figures of merit for several fuels produced in CO_2 reduction PEC systems.

Liquid phase Products

Figures of Merit	Formic Acid or Formate		Methanol		Ethanol	
	Best value measured	Ref.	Best value measured	Ref.	Best value measured	Ref.
Faradaic efficiency (F.E.) %	90	[58]	111.58	[51]	52	[42]
Current Density C. D. (mA/cm²)	4.20	[92]	6.97	[78]	20	[42]
External Applied Voltage (V)	0	[62]	–	–	–	–
Production Rate (mmol/ L h cm²)	1.49*	[62]	2.52*	[48]	7.5	[42]
Stability (h)	168	[58]	11	[110]	5	[42]
Solar to Fuel efficiency (STF) %	1.2	[58]	–	–	–	–

Gas Phase products

Figures of Merit	Carbon Monoxide		Methane	
	Best value measured	Ref.	Best value measured	Ref.
Faradaic efficiency (F.E.) %	100	[67]	67	[67]
Current Density C. D. (mA/cm²)	1.6	[67]	0.40	[67]
External Applied Voltage (V)	–	[67]	1.19	[67]
Production Rate (μmol/ h cm²)	0.024*	[67]	1.333*	[67]
Stability (h)	5.5	[81]	2	[81]
Solar to Fuel efficiency (STF) %	–	–	–	–

The * symbol indicates that the values were calculated from the data provided by the cited publication.

photoelectrode is the measurement of current density under 1 sun AM 1.5G illumination in a three-electrode configuration. Generally, current density is defined as the charge flow (Amperes) divided by the projected area of the photoelectrode (cm^2). It should be noted that the aforementioned area is completely different from the actual surface area. For the determination of actual surface area, all the nanostructured or microstructured features and defects are taken into account. Linear sweep and cyclic voltammetry modes are used in PEC cells in order to measure the photocurrent density versus the applied voltage. These measurements should be carried out not only under illumination, but also in the dark to identify how much of the measured current derives from sunlight conversion [91]. Thus, photocurrent in PEC systems is the flow of electric current that stems from the photoresponse of their photoelectrodes. An alternative way to measure the photocurrent is to place a light chopper between the photoelectrode and the light source. In this way, the current density with and without illumination can be measured in a potensiodynamic sweep. Apart from photocurrent density, these measurements can also indicate the flatband potential and the fill factor of PEC devices. Flatband potential is defined as the electrochemical potential that have to be applied to a semiconductor in order to reduce band bending to zero and fill factor is the ratio of available power at the maximum point to the product of open circuit voltage and short circuit current. A high fill factor means high efficiency.

The main goal of PEC cells for CO_2 reduction is the production of chemical fuels. Generally, in electrochemical and photoelectrochemical devices for CO_2 reduction, low current densities result in slow production rates of fuels. On the other hand, high current densities do not necessarily lead to high production rates of carbon-based fuels due to the fact that the FE also plays a significant role. Specifically, a substantial part of the produced photocurrent can originate from catalyst corrosion or other undesired reactions such as water splitting or back reactions. Thus, analysis of results based on photocurrent should always be accompanied by static tests and product detection and quantification measurements.

Nevertheless, production rate is highly related to current densities. In other words, if an increased photocurrent density of a PEC system does not affect negatively the FE, the rate of the reaction will also increase. In order to study the production of fuels in these systems, a two-electrode configuration is usually used. The presence of a membrane as mentioned in Section 2.1.2 is very important because it can separate the products from water oxidation and CO_2 reduction reactions. The products of PEC CO_2 reduction can be either in liquid or gas form. Several methods and devices are used in each case to detect and measure the products from the experimental apparatus. Particularly in PEC experiments, gas products such as CO, H_2 and CH_4 are mainly detected and measured by using Gas Chromatography (GC) techniques [67]. On the other hand, for the detection and analysis of liquid products, apart from some gas chromatography techniques, High-Performance Liquid Chromatography (HPLC), spectroscopy (NMR) can also be used. Ion exchange Chromatography and Nuclear Magnetic Resonance are additional useful techniques [58,61]. In PEC literature there are generally two possible ways to report the production of fuels as a function of time. The first way (Fig. 6a) is to measure the amount of chemical products and divide it by the surface of the illuminated photoelectrode which is in contact with the electrolyte. To obtain the production rate this value should be plotted versus the time of the reaction. Alternatively, the production rate of fuels can be determined by measuring their concentration in the electrolyte (Fig. 6b) over time.

Both ways of calculating the production rate are presented in Fig. 6, showing that the number of publications has steadily risen through the years. Besides that, there is a considerable increase in production rate of chemical fuels which is mainly attributed to the development of new materials for photoelectrodes. This figure aims to display these trends and not to highlight the best PEC systems for CO_2 reduction. In other words, it is not possible to make a fair comparison between them

because of the utilization of different reactors and electrolytes as well as due to the fact that most of the studies were conducted under different conditions (applied voltage etc.). For example, the highest production rate of methanol was obtained in a study that used an aqueous electrolyte containing 10% methyldiethanolamine (MDEA) [48], so, further investigation is required to understand if the presence of MDEA in the electrolyte solution is responsible for the high production rate of methanol. Consequently, it is very difficult to evaluate the efficiency of a PEC system by taking into account only the production rate.

3.3. Durability in PEC CO_2 reduction systems

Although the fabrication of stable and durable photoelectrodes is one of the biggest challenges in the field of PEC CO_2 reduction. A semiconducting photoelectrode that is resistant to decomposition should be thermodynamically stable. To avoid photocorrosion effects on the semiconductor, the redox potential of the oxidative decomposition reaction should lie below its valence band edge and at the same time the redox potential of the reductive decomposition reaction should be more negative than its conduction band [30]. Photocorrossion occurs commonly in semiconductors due to the fact that one of the aforementioned oxidation and reduction decomposition potentials usually lies within the band gap. Generally, newly developed materials should be evaluated under experimental conditions because it is very hard to predict photocorrosive processes. Experimentally, the stability of a photoelectrode can be tested by chronoamperometry measurements under illumination. Chronoamperometry in PEC devices is a technique where a fixed potential is applied and the photocurrent density is obtained as a function of time [91]. Typically, the photocurrent density decreases in cases of unstable photoelectrodes whereas it remains constant for several hours in cases of stable photoelectrodes. In PEC systems for CO_2 reduction the most stable photoelectode so far, a combination of $CuFeO_2/CuO$ [58], has managed to operate under experimental conditions for seven days. However, the majority of studies report undesired catalyst degradation after several hours, resulting in significant decrease of current densities. One way to address the corrosion of semiconducting photoelectrodes is the use of thin passivation layers. Several studies have been used this technique and they described in more detail in Section 4.2.

3.4. Other useful evaluation tools

Aside from the aforementioned diagnostic tools and figure of merits, some other important parameters are used in electrochemical and photocatalytic CO_2 reduction studies and more rarely in photoelectrocatalysis. Nevertheless, the following parameters can assist in the evaluation of the performance of the materials that are utilized in photoelectrodes.

Quantum yield, Φ, is one of the key parameters to characterize the performance of a photocatalytic system. Specifically in CO_2 reduction systems, it is defined as the ratio of moles of products formed to absorbed photons multiplied by the number of electrons required for the conversion [17].

$$\Phi = \left(\frac{\textit{moles of products formed}}{\textit{absorbed photons}} \right) \times \left(\begin{array}{c} \textit{number of electrons} \\ \textit{needed for } CO_2 \textit{ conversion} \end{array} \right) \tag{19}$$

Another commonly used figure of merit in catalysis is the turnover frequency (TOF) which can assess the catalytic activity and stability of a material [96]. TOF can be calculated by the following equation:

$$TOF = \frac{TON}{reaction\ time} = \frac{\left(\frac{moles\ of\ reaction\ product\ formed}{moles\ of\ catalyticsites} \right)}{reaction\ time} \tag{20}$$

where TON is known as turnover number [19]. In addition, selectivity is another figure that allows to evaluate the ability of a catalyst to
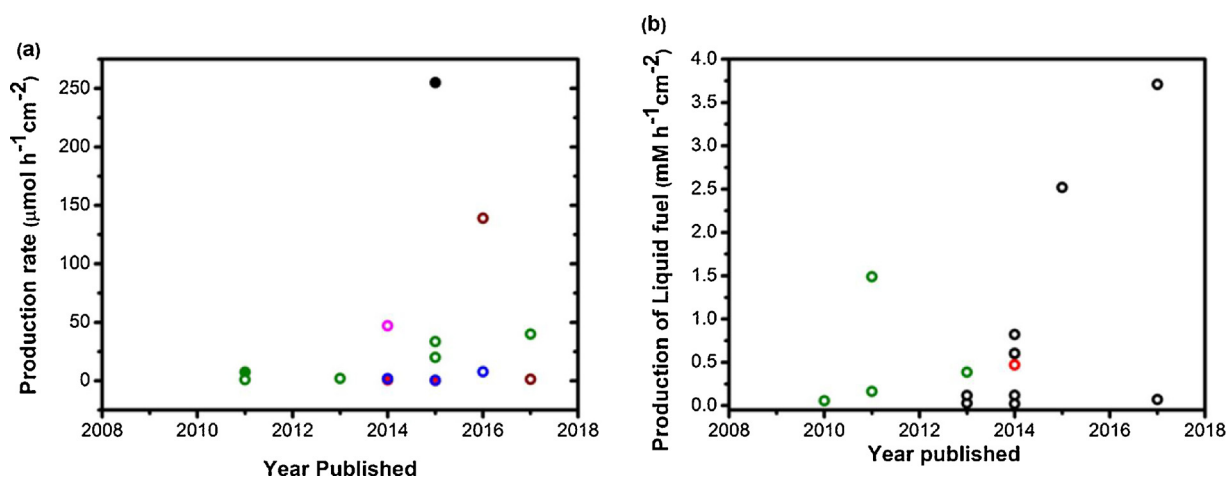
Fig. 6. Production rate for selected fuels produced in PEC cells for CO_2 reduction vs. year of publication. The most common products are displayed: formic acid (red circles), formate (green circles), methanol (black circles) and methane (blue circles). Two different ways to evaluate liquid chemical fuel production are represented: a) Measuring the amount of converted chemical fuels in μmoles per square cm of photoelectrode surface per hour, b) Measuring the concentration of fuels in the electrolyte in millimolar per square cm of photoelectrode surface per hour. Closed circles indicate values found in literature while open circles show calculated values from the literature. In all cases were used aqueous electrolytes and light sources that emitted a spectrum of light close to that of sunlight and intensity of approximately 100 mW/cm². [48,51,58,61–63,65–76,92–95] (For additional details see supplementary information). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

convert CO_2 into a preferred chemical or fuel [17].

$$Catalytic\ Selectivity = \frac{moles\ of\ reaction\ product\ formed}{moles\ of\ all\ the\ different\ products\ formed} \quad (21)$$

In other words, high selectivity means that a catalyst can direct a particular reaction to yield a specific product. However, the community of electrochemical and PEC CO_2 reduction researchers mainly utilizes FE to verify the selectivity of a system. Generally, although TOF, Φ and catalytic selectivity can assist in the development of new improved photocatalysts, they are not used widely in PEC CO_2 reduction studies. The main reasons that these indicators are not used very often are: i) the complexity of CO_2 reduction reaction which lead to the formation of a large number of chemicals and ii) the difficulty in measuring the number of catalytic sites or the number of absorbed photons.

Finally, overpotential is one of the most important indicators of energy efficiency in systems related to electrochemical CO_2 reduction. Due to the fact that CO_2 is a highly stable molecule ($\Delta G_f^{\circ} = -394.4\ kJ\ mol^{-1}$), a significant energy input is required for its chemical conversion. In addition, all electrochemical systems in practice involve several losses such as ohmic and mass transport losses or losses caused by slow reaction kinetics. Overpotential of an electrochemical system is defined as the additional amount of energy that is required to overcome the aforementioned losses and drive the redox reactions at the desired rate. This means that development of materials that require low overpotential for CO_2 reduction can increase the total efficiency of an electrochemical cell. This figure of merit is also used in PEC systems for CO_2 reduction, but not to the same extent. However, it should be mentioned that in some PEC studies the energy gained from light conversion is large enough to allow CO_2 conversion at potentials lower than the theoretical redox potentials. Sometimes, in these cases the term underpotential it is used instead of overpotential [97].

4. Chemical fuels obtained in PEC CO_2 reduction systems

Generally, CO_2 conversion can be classified in two categories [98]: i) Low-energy processes producing chemical products such as urea, salicylic acid, polymeric materials and inorganic carbonates. ii) High-energy processes in which carbon oxidation state is reduced from +4 to +2 or lower giving chemical products such as HCOOH, CO, CH_3OH, CH_4 or other hydrocarbons.

Conversion of CO_2 into fuels by electrochemical or photocatalytic

means is clearly considered as a high-energy and complex process. A large number of different chemicals and fuels have been reported as products from CO_2 reduction systems. To understand the complexity of this process, Jaramillo et al. observed 16 different CO_2 electro-reduction products on copper electrodes [99]. In this study, it was also showed that the chemical products highly depend on the overpotential of the electrochemical CO_2 reduction system. In PEC systems, however, the variety of chemical products is significantly smaller due to stability issues of photoelectrodes at high overpotentials. Some of the most common liquid fuels produced by PEC CO_2 reduction devices are formic acid, methanol and ethanol while CO and methane are the most common gas products. In Table 2 the following table, the market price and volume of the desired products are presented.

Among liquid fuels, methanol has the biggest market volume and considerably high price due to its wide range of applications. Methanol is mainly produced from petrochemicals and only a small part of the global methanol production is used as fuel. In contrast, ethanol is considered as a 'green' energy carrier and it is mainly produced from biomass. Ethanol is primarily used as fuel in modified engines for vehicles. Thus, a huge advantage of ethanol at the moment is the developed technology and infrastructures in several countries such as Brazil.

Natural gas which is the most abundant gas fuel in our planet is mainly consist of methane. Nowadays, natural gas is used in heating, cooking and production of electricity or as fuel in transportations. Therefore, methane production through renewable sources is a very ambitious and attractive idea which can lead to a sustainable world.

Table 2
Market value and volume for some of the most common products of PEC CO_2 reduction.

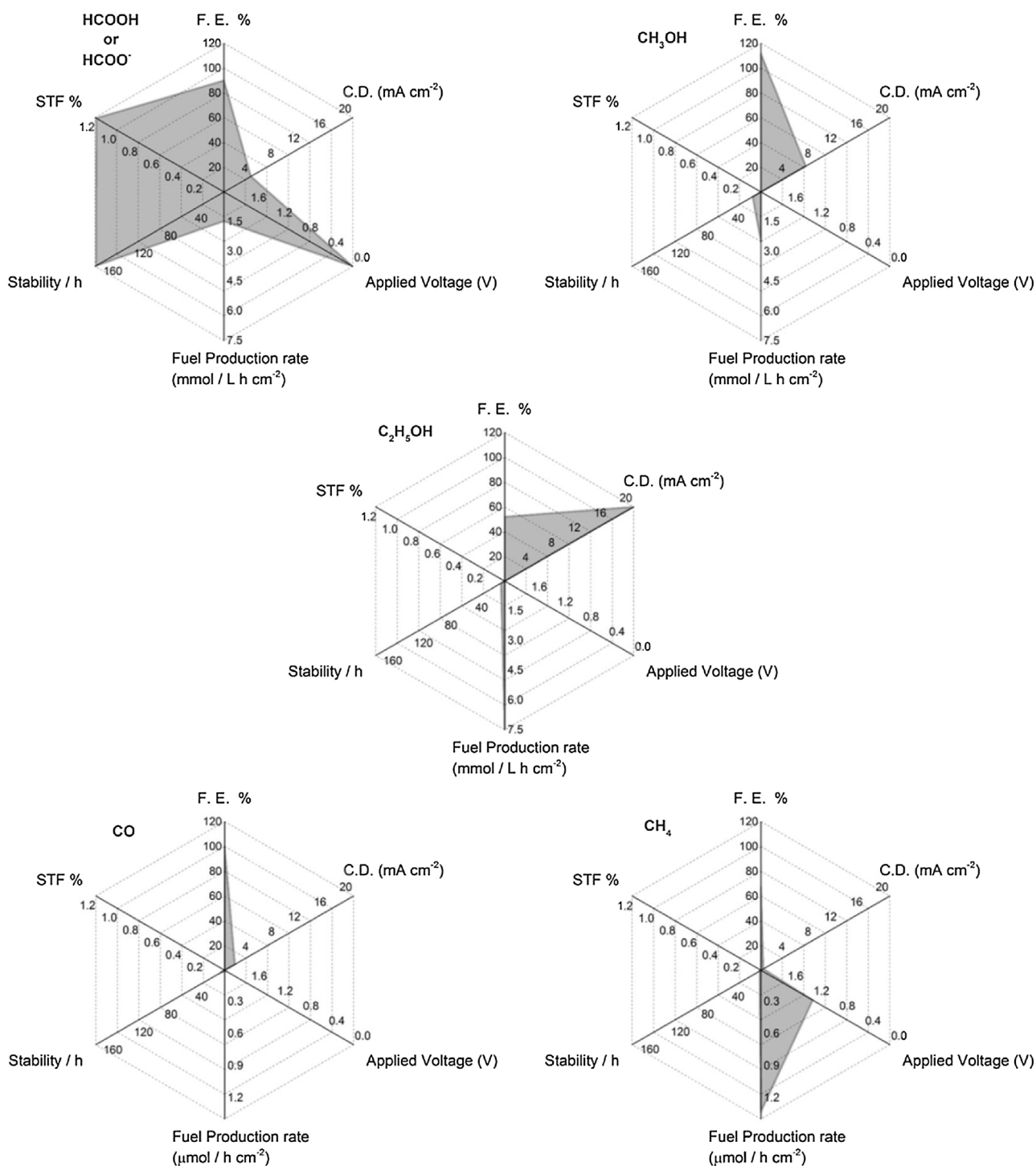|	Liquid products			Gas products	
	Formic acid [100]	Methanol [101,102]	Ethanol [103–105]	Carbon monoxide [106,107]	Methane/Natural gas [108,109]
Market value	(85% purity) 770 $/ton	409 $/ton	690 $/ton	1200 $/ton	0.11 $/m³
Market volume	7.6×10^5 tonnes per year	1.1×10^8 tonnes per year	7.9×10^7 tonnes per year	1.9×10^7 tonnes per year	$3.4 \times 10^{12}\ m^3$

Fig. 7. Illustration of hexagonal radar charts for selected fuels reporting the best value for each figure of merit. The values found in literature among similar reports and they analytically presented in Table 3. In all cases were used aqueous electrolytes and light sources that emitted a spectrum of light close to that of sunlight and intensity of approximately 100 mW/cm^2. (For additional details see supplementary information).

Currently, the efficient production of stable fuels with high energy density is the main goal of this research field.

Best performance values of state-of-the-art PEC systems for CO_2 conversion into typical products such as HCOOH or HCOO$^-$, CH_3OH, C_2H_5OH, CO and CH_4 are highlighted in Table 3. These values were used in radar charts of Fig. 7 showing the current status of the field. In this way, not only the best PEC CO_2 reduction systems can be spotted, but also the areas that need much more attention and significant improvements can be easily revealed. For each figure of merit, the best

value found in literature was plotted. In addition, each axis of the radar ends at the highest value found among all selected fuels. In other words, if all the values reported for the production of a certain fuel are the highest among the selected fuels, then the entire hexagonal area of the radar chart will be covered.

4.1. Formate or formic acid

Formic acid is considered as a valuable chemical product due to its

wide range of applications, for instance, in pharmaceuticals, food industry and agriculture uses, and it is a starting material in production of several chemicals. Nowadays, although it can be synthesized from biomass and CO_2 hydrogenation processes, it is mainly produced from petrochemical industry such as naphtha and methanol. However, formic acid has attracted increasing attention from the scientific community because it can be used as a fuel in direct formic acid fuel cells (DFAFC) [111] and it is has also been proposed as a possible hydrogen storage material [112]. In addition, it can be easily stored and transported because it is liquid at room temperature. Thus, formic acid could serve as a potential fuel for future applications such as portable devices and vehicles.

So far, a large number of PEC CO_2 reduction studies report production of formic acid or formate as a primary or a side product. The radar chart of formic acid and formate (Fig. 7) presents the highest values recorded for each figure of merit. To the best of our knowledge, Kang et al. has fabricated a photocathode-driven cell for PEC CO_2 conversion into formate that achieved the highest STF to-date (up to 1.2%) [58]. In addition, over 90% FE was observed for more than one week due to the fact that the CuFeO₂/CuO photocathodes showed very high stability under experimental conditions. The combination of these two semiconductors with narrow band gaps is the main reason for the high efficiency and selectivity of this device.

In another study, Sato et al. reported CO_2 conversion to formate utilizing a Z-scheme configuration without any external voltage [62]. In this case, STF reached 0.04% while the selectivity for formate production was over 70%. Later, the same research group reported an improved system in which TiO_2/Pt photoanode was replaced by $SrTiO_3$, while the photocathode remained the same [65]. As a result, STF efficiency increased to 0.14% indicating that an enlarged difference in the band energy position between the photoanode and the photocathode can improve the performance of the system.

Apart from the adaption of a Z-scheme for CO_2 reduction, another innovative approach was developed from this group that allowed solar-driven CO_2 conversion into formate with very low external electrical bias. Firstly, the surface of Zn-doped p-InP photocathodes was modified with a ruthenium-complex electrocatalyst [61]. Then, the modified photocathode was further improved by introducing an anchor ligand to a Ru-complex electrocatalyst [62]. In this way, electron transfer from the semiconductor to the metal-complex electrocatalyst was enhanced significantly. Thus, very high production rate of formate, 7.46 μmol h^{-1} cm^{-2} (or calculated value of 1.49 mM h^{-1}cm^{-2} as showed in Fig. 7), was observed in a photocathode-driven configuration comprising the previous photocathode and a glassy carbon counter electrode [62]. The same approach was also applied on Cu_2ZnSnS_4 (CZTS) p-type semiconductors [63]. Particularly, more than 80% selectivity for PEC CO_2 transformation to formate in water was obtained by combining a semiconductor much cheaper than InP and a metal-complex co-catalyst.

One of the highest current densities, 4.20 mA/cm^2 (Fig. 7) [92], was observed for a photocathode-driven PEC cell that used p-CdTe as a photocatalyst in the presence of pyridine. In addition, this study showed that a concentration of 10 mM pyridine in the electrolyte can increase the current density and the faradaic efficiency of the system proving that further investigation of the synergistic effect between pyridine catalysis and PEC CO_2 reduction is needed. However, the pyridine effect will be discussed in more detail in Section 4.2 due to the fact that PEC systems with electrolyte containing pyridine mainly converted CO_2 into methanol.

Generally, p-GaP is the most popular material for PEC CO_2conversion to formic acid or formate due to their relatively suitable band gap. GaP and GaAs were the first materials that were ever used for this purpose by Halmann in late 1970′s [27]. However, in this study, in addition to formic acid, methanol and formaldehyde were also observed, showing that poor selectivity would be one of the major disadvantages of this approach. In 1982, Taniguchi and co-workers also

investigated p-GaP photoelectrodes in an electrolyte of Li_2CO_3 with and without crown ether and they observed the same products as the previous report [113]. In particular, 44% current efficiency for CO_2 conversion into formic acid was reported in the presence of crown ether. Nevertheless, the role of this substance and the reduction mechanism were not explained extensively. While most of the research groups until 1984 reported the formation of several chemical products from CO_2 reduction on p-GaP photocathodes, Ikeda et al. suggested that apart from formic acid all the other products were formed due to the photolysis that occurred in the presence of epoxy resin that was utilized in the construction of the cell [114]. A few years later, the same author and co-workers investigated the effect of light on the conversion of CO_2 to formate on p-GaP photocathodes. FE of 70%was reported at about 320 mW cm^{-2}, while further increase of light density led to lower levels of FE due to hydrogen evolution [115].

Another p-type semiconductor of III–V group that has been extensively investigated as photocathode for PEC CO_2 reduction is p-InP. In a study of Yoneyama and co-workers, p-InP semiconductors were used as photocathodes for CO_2 conversion into formic acid in a carbonate-based electrolyte environment [50]. The same PEC device, in the presence of several electrolyte solutions (e.g. sulfates, perchlorates, tetraethylammonium perchlorate), produced CO instead of formic acid indicating that the electrolyte environment has a crucial role to the production of a desired fuel. Another material that has been widely used in solar applications is silicon. An example of a p-Si photocathode utilized in a photo-driven cell for CO_2 conversion into formic acid was reported from Junfu and Baozhu [59]. More specific, monocrystalline p$^+$-Si with 10 μm epitaxial layer of p-Si converted CO_2 into formic acid and displayed its highest Faradaic efficiency, 65.6%, at −1.2 V vs SCE.

Various metal electrocatalysts such as Cu, Au and Ag have been proposed for efficient CO_2 reduction [13,116]. Combining semiconducting photoelectrodes with these metals, higher stability and catalytic activity can be achieved. However, in order to avoid a decrease of photovoltage metals should be coated on semiconductors in the form of small crystallites. Early studies indicate the use of Pt particles on photoelectrodes for solar-driven PEC cells [117,118]. The same approach has been also applied to many PEC CO_2 reduction systems. Ikeda and co-workers were firstly reported PEC reduction of CO_2 on metal coated p-GaP photoelectrodes in aqueous electrolytes [119]. In this report, among several metals, Pb and Zn coatings favored formic acid and hydrogen production. Similar results were observed for the case of p-InP photoelectrodes coated with Pb. Coating of Pb particles on these photoelectrodes was showed to favor formic acid production that reached 28% FE.

In a later study, Flaisher et al. also presented photoelectrochemical CO_2 reduction on p-GaP photocathodes [120]. Although a significant improvement of 15% in photocathodic current (pH 7 phosphate buffer electrolyte) was obtained when the Ar bubbling was replaced by CO_2 bubbling, no further details about the FE or production rate were reported. Furthermore, a copper or ruthenium pretreatment procedure was applied to the p-GaP photoelectrodes that increased their photoresponse. As a result, the presence of Cu or Ru particles on the surface of p-GaP photocathodes enhanced the efficiency of the PEC cell.

Beside the semiconductors of group III–V, p-CdTe was also modified with various metals, with Pd and Zn showing the highest FE towards formate. However, the levels of FE for hydrogen production were higher than that of formate indicating that hydrogen was the primary product in this case [46]. More recently, Won et al. proposed another similar semiconducting photoelectrode for PEC CO_2 reduction to formic acid [68]. Photocathodes of ZnTe were coated with polypyrrole in order to reach 37.2% FE, while the efficiency of bare photoelectrodes was significantly lower. According to the authors, decoration of polypyrrole on the surface of the semiconductor can enhance electron transfer by reducing the recombination rate of photogenerated charge-carriers and minimize the resistance of CO_2reduction reaction. Iron pyrite was also proposed as a new photoactive semiconductor for the production of

formic acid [121]. However, very low levels of FE were obtained for this system under high-intensity illumination (890 mW cm^{-2}).

Besides metal coatings, alternative materials has been deposited onto photocathodes in order to improve the performance in PEC CO_2 conversion. Bockris and co-workers in 1983 deposited a thin film of polyaniline on the surface of a p-Si photocathode by electro-polymerization of aniline.[122] In this study, the main product of the light-assisted CO_2 reduction in aqueous electrolyte was formic acid obtaining a FE of 21.2% at a potential −1.9 V vs SCE.

More recently, metal oxides, such as Co_3O_4 and $CuFeO_2$, have been also utilized for formic acid production in PEC CO_2 reduction systems. Co_3O_4 photoelectrodeswere fabricated by Zhao's research group [123] and in a later study, they successfully decorated them with metallic Cu nanoparticles using a pulsed electrodeposition method [47]. According to these studies, the sophisticated metal photocathodes gave higher yields and higher selectivity of formate than the undecorated electrodes. Mg-doped $CuFeO_2$ photocathodes were also employed in PEC systems for transformation of CO_2 to formate [124]. However, these photoelectrodes presented low FE of 10%. Cuprous and cupric oxides are also considered as promising materials for this use. Woo and co-workers fabricated Cu_2O/CuO photoelectrodes and decorated them with a large variety of metals [66]. The metals with the highest FE towards formic acid were Au and Pd. Nevertheless, the selectivity remained low due to the production of other chemical products such as methanol and CO.

High pressure, a method adapted from electrochemical cells, was utilized to enhance the overall performance of PEC CO_2 reduction cells. Aurian-Blajeni et al. first investigated the influence of high pressure of CO_2 on current-potential behavior, selectivity and stability of these systems [45]. More specifically, they presented the conversion of CO_2 in formic acid, formaldehyde and methanol on illuminated p-Gap and p-GaAs semiconducting photocathodes under varying CO_2 pressure below 10 atm. Increased photocurrent and FE under pressures were attributed to strong interactions between the surface of the semiconductor and the dissolved CO_2.

On the other hand, only a few photoanode-driven systems reported production of formic acid. A PEC cell consisted of a WO_3 photoanode and Sn/SnO_x cathode was fabricated by Magesh and co-workers achieving a FE of 27.5% [67]. However, the primary product of this cell was hydrogen with higher FE. In a later study, the effect of Sn-doping on WO_3 thin films was investigated by Yang et al. [93]. They synthesized in situ Sn-doped WO_3 nanostructured films via a hydrothermal method achieving enhanced PEC CO_2 reduction in comparison with undoped photoanodes. Increased separation of photogenerated electron-hole pairs, electrical conductivity, electron lifetime and photostability were attributed to the presence of Sn atoms in the WO_3 lattice and the formation of a passivation layer of SnO_2 on the surface.

The only flow PEC reactor for efficient CO_2 conversion into formate was reported recently by Irtem and co-workers [70]. More specific, a typical design of electrochemical flow cell was adapted to fabricate a PEC cell consisting of a photoanode of TiO_2 nanorods instead of a metal-based anode and a cathode of electrodeposited Sn on carbon fibres (gas diffusion electrode-GDE). This flow PEC cell operating under continuous flow of CO_2 and liquid electrolyte achieved 0.24% solar-to-fuel efficiency and reached 65% FE at 1.2 V applied bias potential.

4.2. Methanol

The largest amount of methanol worldwide is produced from fossil fuels via synthesis gas methods [125]. Nowadays, it is mainly used as a feedstock in the chemical industry for the production of a wide variety of chemical products including formaldehyde and acetic acid and materials such as paints, resins and polymers. Currently, methanol is not used as a fuel due to its low volumetric energy density (15.8 MJ/l) compared to gasoline (32.2 MJ/l) and other hydrocarbons. However, it is considered as an energy carrier for future power needs mainly due to

the fact that it can be produced using renewable energy sources and its characteristics including high octane number, "flame speed" and high latent heat of vaporization. In addition, it can be easily integrated into the existing liquid fuels infrastructures and technologies. Lately, several ways are being developed for the production of renewable methanol from industrial and municipal waste, biomass and CO_2. Replacing fossil fuels with renewable methanol produced via CO_2 reduction can maintain the cycling of anthropogenic carbon which is the basis of the methanol economy idea [125].

PEC CO_2 reduction is one of the most attractive ways to produce renewable methanol. For this reason PEC CO_2 conversion into methanol has been studied widely since 1978. Some of the earliest studies [27,45,113,126] mentioned the production of methanol but this was attributed to the photolysis that was caused by epoxy resins used in PEC cells [119]. The first PEC study for CO_2 conversion into methanol with high faradaic efficiency was reported by Barton et al. in 2008 [127]. In particular, p-GaP electrodes were used in a photocathode-driven system in aqueous electrolyte. However, methanol formation was observed only in the presence of pyridine in the electrolyte solution showing a catalytic interaction between the pyridinium ion and the CO_2. The highest values of faradaic efficiency towards methanol were observed to be 96% and 90% under 365 nm and 465 nm illumination respectively.

Several semiconductors including p-GaP, p-InP and Cu_2O suffer from severe photocorrosion. One approach to deal with this problem is the deposition of TiO_2 thin surface layers. Passivation layers of TiO_2 can be applied very easily by several methods such as atomic layer deposition (ALD) and sputtering and they can be coated on photoelectrodes with high surface area. The thickness of these layers can be varied from less than 1 nm to more than 100 nm. Although this method has been used extensively in photoelectrodes for various PEC applications, only a few studies [77,87,128–130] investigated the benefits of this method for solar-driven CO_2 reduction.

Cronin and co-workers managed to deposit TiO_2 passivation layer by ALD on p-GaP electrode [130]. The utilization of this photocathode in the presence of pyridine led to a FE of 55% towards methanol under green laser (532 nm) illumination. TiO_2 passivation layers not only protected the semiconducting electrodes against photocorrosion, but also improved the PEC CO_2 conversion through the formation of a carrier separating *p-n* region, which minimize the rate of electron-hole recombination and downshift the overpotential required to drive the reaction for CO_2 reduction to methanol. Similarly, analogous thin TiO_2 surface layers have been coated by ALD in p-InP nanopillars by the same research group [128]. The authors also reported enhanced efficiency of PEC CO_2 conversion to methanol and increased methanol yields. Taking into account all the previous studies, several p-type semiconductors dramatically increased their lifetime in electrolytes under illumination and improved their photoelectrocatalytic performance, thanks to the TiO_2 passivation layers . Lee et al. deposited a similar type of protective overlayers of Cu^+-incorporated TiO_2 on Cu_2O nanowire photocathodes [77]. The presence of Cu^+ further improved the stability of the photoelectrodes and the FE of PEC CO_2 conversion into methanol by increasing charge transfer and creating active sites favorable to CO_2 reduction.

CuO and Cu_2O have generally attracted much attention in the field of PEC CO_2 reduction due to the fact that their band gap matches the solar spectrum. Rajeshwar and co-workers studied the PEC transformation of CO_2 into methanol on hybrid CuO/Cu_2O nanorod arrays [72]. In this research work, high FE efficiency of 96% was measured towards methanol at very low potential (-0.2 V vs SCE) which was attributed to the high surface area of nanostructured photocathode and the combination of band edges of the two oxides. The groups of Rajeshwar and Janáky also investigated the PEC behavior of Cu_2O nanoparticles on ultra-long carbon nanotubes (CNT) [131]. In general, the presence of CNT offered stability and increased photocurrent due to faster transport of photogenerated holes from the Cu_2O crystallites to the supporting

electrode.

In another study, wedged N-doped CuO photocathodes were prepared in order to produce methanol by CO_2 reduction [74]. This material was picked due to its excellent photocatalytic and electrocatalytic properties that led to a high current efficiency of 84.4%. However, the main conclusion of this study was the illustration of a strong synergistic effect between electrochemical and photochemical CO_2 reduction of wedged N-doped CuO electrodes. In other words, the methanol yield of PEC CO_2 reduction was higher than the simple sum of electrochemical and photochemical CO_2 reduction.

The same effect was observed on Cu_2O/Fe_2O_3 nanostructured electrodes [73]. In this study, very high current density (1.90 mA cm^{-2}) was measured at −1.3 V vs SCE while the production rate of methanol and FE reached 0.823 mM h^{-1} cm^{-2} and 93%, respectively. The good performance of this system was ascribed to the conjunction of the two semiconductors, Fe_2O_3 that possess a narrow band gap that matches the photocatalytic CO_2 reduction requirements and the Cu_2O electrocatalyst that offers high selectivity to methanol and great conductive ability. In another study, hematite nanotubes were combined with one-dimensional ribbon cobalt phthalocyanine for CO_2 conversion to methanol displaying the same synergistic effect [75].

A similar approach was also used by Li et al. in which MoS_2-rods/TiO_2-nanotubes served as photoelectrodes showing that their combination can improve the methanol yield [51]. Therefore, extremely high FE (111.58%) was attained which was the highest recorded value among all studies for PEC CO_2 conversion into methanol. A heterojunction of graphitic carbon nitride (g-C_3N_4) and SnS_2 was successfully used as photoelectrode for CO_2 conversion into methanol via a PEC cell [132].

Another semiconductor utilized in photocathode-driven systems for CO_2 conversion into methanol is chalcopyrite p-$CuInS_2$ [71,76,94,133]. The performance of this material was explored by Yuan et al. in a PEC configuration and achieved production of methanol with very high FE of 97% at −0.54 V vs SCE in electrolyte containing 10 mM pyridine. In addition, this photocathode-driven system showed remarkable stability over 11 h. The same research group also investigated the effect of pyridine at p-$CuInS_2$ photocathodes in PEC CO_2 reduction to methanol. Specifically, the authors suggested that pyridine acts as co-catalyst in these systems decreasing the required overpotential of CO_2 reduction and constrain hydrogen evolution which is inevitable in an aqueous electrolyte. However, the relatively low production rate of methanol (0.12 mM h^{-1} cm^{-2}) was attributed to the formation of a pyridine adsorption layer on the surface of p-$CuInS_2$ photoelectrodes [94]. Furthermore, the modification of $CuInS_2$ thin films with graphene can further increase the CO_2 reduction to methanol by 40% [76].

Alternatively, there are several studies that reported adequate methanol production using photoanode-driven PEC CO_2 reduction cells. Ogura and co-workers were the first who reported a photoanode-driven PEC system consisted of n-CdS [37] and n-TiO_2 [134] photoanodes and a Pt plate coated with Everitt's Salt serving as cathode. In the case of n-CdS, CO_2 was converted to methanol in the presence of a metal complex and a primary alcohol, while in the case of n-TiO_2 the presence of a homogeneous catalyst was needed. More recently, Cu-RGO–TiO_2 photoanodes were used for PEC conversion of CO_2 to methanol and formic acid in the presence of 10% MDEA [48]. The utilization of reduced graphene oxide (RGO) into the composite can lead to a decrease of the band gap into the visible region compared to pure TiO_2 and expands the electron-hole recombination time. Apart from that, the addition of MDEA in the electrolyte can significantly increase the solubility of CO_2. Consequently, in this study, the highest production rate of methanol was measured as shown in Fig. 7 (2.52 mM h^{-1} cm^{-2}). The modification of TiO_2 photoanodes with a narrow band gap semiconductor is another great way to improve their PEC performance. Wei et al. fabricated photoanodes of TiO_2 nanotubes combined with CdSeTe nanoparticles (1.24 eV) that led to a very high current density of 6.97 mA cm^{-2} (Fig. 7) at −1.2 V [78]. An even more creative approach

was proposed by Stülp and co-workers in which a copper (II) aspirinate complex was deposited on TiO_2 nanotubes [95]. Selective PEC CO_2 reduction to methanol was achieved because the complex acted as an electron mediator.

4.3. Carbon monoxide

CO is produced either naturally by photochemical reactions in the troposphere and volcanos or artificially by incomplete combustion of various fuels. Nowadays, it is used in a wide range of industrial applications such as in the production of chemicals and pharmaceuticals, metal purification in metallurgy and catalyst regeneration. In addition, mixtures of CO with hydrogen (syngas) can be used to synthesize fuels, although it cannot be burnt directly. There are several commercially available processes in which products such as fertilizers, fuels and other industrial gases are generated from syngas. For instance, it can be converted to more valuable fuels and chemicals by using Fischer-Tropsch processes. However, its production mainly relies on fossil fuels including natural gas, coal and other petrochemicals.

An alternative and attractive process is the employment of PEC systems for CO_2 reduction to CO, especially if combined with water reduction to hydrogen. Generally, several aqueous and non-aqueous solvents such as methanol, acetonitrile, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) have been also used in PEC CO_2 conversion to CO on p-type semiconductors. The main difference between them is that the solubility of CO_2 in water is 7–8 times lower compared to other non-aqueous solvents [17].

In early studies, the addition of water to non-aqueous electrolytes was believed to negatively affect the efficiency of CO_2 conversion into CO [135]. Furthermore, Taniguchi et al. investigated the behavior of p-GaP, p-InP, p-Si and p-CdTe photocathodes in DMF electrolyte solutions containing 5% of water and 0.1 tetrabutylammoniumperchlorate TBAP [136]. The highest value of FE towards CO was 78.3% for photocathodes in this electrolyte. However, further increase of water quantity in the electrolyte solution led to lower FE due to dominant hydrogen evolution. Generally, CO and H_2 were the only products detected in all cases.

Later, Hirota and co-workers employed high-pressure PEC systems to convert efficiently CO_2 into CO [85]. The investigation of p-Si, p-GaP and p-InP photoelectrodes illustrated that high CO_2 pressure can improve the performance of PEC CO_2 reduction. It can offer an increase in current density due to the high concentration of CO_2 in the methanol-based electrolyte and high FE for CO_2 conversion to CO, 93%. More specifically, it was proposed the formation of an absorbed layer of $(CO_2)_2$·$^-$ that blocked the surface of the semiconductor and the high stability of the photocathodes were mainly attributed to this layer.

Another way to improve PEC reduction of CO_2 to CO is the deposition of small metallic particles on a photocathode. This approach was utilized by Nakato's research group on p-Si photocathodes [80]. This study is an excellent example for showing the role of deposited metals in PEC CO_2 reduction processes. Photogenerated electrons on the surface of the semiconductor can be transferred to the metallic particles which assist CO_2 reduction. Therefore, metal particles act as electrocatalysts and can improve the selectivity of a chemical product. It was claimed that the photoelectrocatalytic behavior of the photoelectrodes coated with metal highly depend on the size of metallic particles. Several studies have shown that the nature of the metal can favor CO_2 reduction into particular products due to different electrocatalytic properties of each metal.

Kaneco et al. explored the effect of metal modification of p-InP photoelectrodes on the FE of products [60]. Among them Ag, Au, Pd showed increased selectivity for CO_2 conversion to CO. The best FE of 80.4% was measured for Ag-coated p-InP photocathodes in 0.08 M LiOH in methanol. The same group investigated the effect of the external potential on the performance of PEC CO_2 reduction system. It was found that the best current efficiency for CO formation on bare p-

InP photocathodes was 41.5% at -2.4 V versus Ag/AgCl. Therefore, it was proved that applied potential highly effects the current efficiency and selectivity of a PEC system similar to CO_2 electro-reduction systems. Another study in which the deposition of metals on semiconducting photoelectrodes improved the performance of PEC CO_2 reduction was reported by Ikeda and co-workers [135]. Specifically, Zn, In and Au coated on the surface of p-GaP photoelectrodes via sputtering and electroplating method led to higher current efficiencies of CO_2 conversion into CO than bare p-GaP photoelectrodes. In addition, the presence of Ru on the surface of p-CdTe photocathodes showed an increase from 92% to 102% for PEC CO_2 conversion into CO under monochromatic (560 nm) illumination [46]. In this study, beside metal deposition, CoPc was also paired with p-CdTe photoelectrodes obtaining 104% FE.

More recently, a more promising and relatively inexpensive material, $Cu_3Nb_2O_8$, was used as photocathode for CO_2 conversion to CO [137]. Although this metal oxide presented very low FE of 9% at -0.20 V vs Ag/AgCl, the evolution rate of CO (Fig. 7) was one of the highest in comparison with reports related to PEC reduction of CO_2 to CO. Most of the aforementioned studies reported low CO production rate. This means that the approach of PEC CO_2 reduction into CO needs significant improvements to become competitive with the reduction into other gaseous products such as methane. Strategies such as passivation layers, combination of different photocatalysts and utilization of molecular catalysts that have been used so far to enhance PEC CO_2 conversion rates into CO are described below.

As already mentioned in Section 4.2, deposition of passivation layers of TiO_2 on semiconducting photoelectrodes is another effective method to improve their durability and efficiency. This method was also adapted by Cronin and co-workers in order to improve p-type photocathodes utilized for CO_2 conversion to CO [129]. Specifically, they used p-InP nanopillars with and without coated Pt nanoparticles and TiO_2 passivation layers of different thickness in a non-aqueous electrolyte solution consisting of an ionic liquid dissolved in acetonitrile. A FE of 99% towards CO was measured at 0.77 V vs. NHE under laser (532 nm) illumination in the case that the thickness of TiO_2 layers was only 1 nm. The main factors for the high FE were the non-aqueous ionic liquid solution which favor production of CO instead of hydrogen, Pt co-catalyst that decrease the probability of charge carrier recombination attributed to electron extraction from the semiconductor and the creation of a charge separation pn-region due to p-InP and n-TiO_2 semiconductors.

Another research group used thick nanosheets (300–500 nm) of ZnO decorated with Cu in order to increase the PEC performance of GaN/n^+-p-Si photocathode for syngas production (CO + H_2) [89]. By tuning the applied voltage a wide range of CO/H_2 can be obtained. This monolithic photocathode demonstrated 70% FE at a low underpotential of 180 mV combining the light absorption of *p-n* junction Si, the excellent electron extraction properties of GaN with the photostability and the fast surface kinetics of Cu-ZnO co-catalyst.

In another study, Schreier et al. followed a similar approach in which they illustrated that Cu_2O based photoelectrodes coated with TiO_2 overlayers can operate efficiently over several hours for CO_2 reduction to CO [87]. In contrast, bare photocathodes lost their photoelectrocatalytic activity into a few minutes of direct contact with the electrolyte under illumination. In this case, TiO_2 passivation layers besides chemical stability provided higher selectivity to CO. Another key factor of this study was the utilization of a rhenium-based molecular catalyst in combination with a protic additive that enable PEC CO_2 reduction to CO with 100% FE under simulated sunlight illumination. The authors suggested that the presence of a protic additive such as methanol facilitates charge transfer from the semiconductor to the molecular catalyst. Therefore, the utilization of molecular co-catalysts is another promising strategy to improve the PEC behavior of photocathodes for CO_2 reduction.

Much research has been done on the integration of p-type

semiconductors and molecular catalysts in order to improve the overall performance of PEC CO_2 reduction. Bradley and co-workers investigated for the first time in 1982 a combined system of several tetraazomacrocyclic metal complexes and a p-Si photocathode [138]. In this system, tetraazomacrocyclic metal complexes were used as solution redox reagents. They showed that reduction of CO_2 under illumination can be performed on p-Si electrodes at less negative potentials compared to Pt and Hg electrodes. In a later study, they reported 95% FE for CO production when using a similar system [139]. Unfortunately, although high FE and high selectivity were observed in systems where molecular catalysts are dissolved in the electrolyte, several drawbacks have been noticed including instability, difficult separation of products from molecular catalysts, deposition of molecular catalysts on the electrodes or the reactor and electron transfer losses due to the fact that there is no linkage between the semiconductor and the molecular catalyst. The aforementioned drawbacks can be eliminated by anchoring molecular catalysts on the surface of semiconducting photocathodes [65].

Cabrera et al. also used a molecular catalyst, [Re(CO)$_3$(4-vinyl,4'-methyl-2,2′-bipyridine)Cl]$_4$, coated into p-Si and p-WSe$_2$ by electropolymerization techniques [140]. It was reported that PEC CO_2 conversion to CO on these photocathodes was much more efficient in comparison to a Pt electrode modified with the same molecular catalyst. Furthermore, Tinnemans et al. also used a series of tetraazomacrocyclicmetal complexes as an electron relay in combination with p-GaP or p-GaAs photocathodes [141]. Illuminated p-GaP phoelectrodes were unstable while in the case of p-GaAs there was no photovoltage. Likewise, Kumar et al. observed CO_2 conversion into CO on hydrogen terminated p-Si photocathodes in the presence of Re(bipy-tBu)(CO)$_3$Cl as the electrocatalyst [86]. It was found that the required potential for CO_2 conversion was much lower than those needed in the case of a Pt electrode, and the quantum efficiency of light-to-chemical energy conversion exceeded 61%.

A different metal complex catalyst, Ni(cyclam)$^{2+}$, combined with p-GaP and p-GaAs semiconducting photoelectrodes for selective reduction of CO_2 to CO was investigated by Petit and co-workers [83,142]. Much higher selectivity was achieved in the presence of Ni(cyclam)$^{2+}$ in the electrolyte due to the suppression of water reduction reaction. However, the system based on p-GaP photocathode illustrated higher efficiency and CO selectivity than p-GaAs system due to the amplitude in band bending and the different surface characteristics. A significant decrease in the efficiency and selectivity of the system was observed after several hours of photoelectrocatalysis because of the carbon deposition on to the semiconducting photocathodes blocking the active catalytic sites.

To the best of our knowledge only two studies reported CO as the primary product when utilizing photoanode-driven PEC CO_2 reduction. Hatano et al. studied the performance of a 3C-SiC photoanode combined with Ag and Pt counter electrodes in aqueous electrolytes. It was illustrated that the utilization of Ag electrodes as cathodes increased the production rate of CO compared to Pt cathodes [143]. In contrast, measurements of hydrogen evolution indicated that Pt anodes enable 4 times higher production of hydrogen. Therefore, it is claimed that the ratio of the products of such a system can be tuned by changing the cathode.

Another photoanode-driven cell for selective PEC CO_2 conversion into CO consisted of surface modified $BiVO_4$ photoanode and a cobalt chlorin complex adsorbed on multiwall carbon nanotubes was reported by Aoi and co-workers [90]. Chlorin complex increased the selective electrocatalytic CO_2 reduction into CO, while the modification of photoanode with FeO(OH) offers higher photocurrent and stability leading to a FE of 83% at -1.3 V.

4.4. Methane

Besides CO, methane is another gas that can be produced by PEC

CO_2 reduction systems. It is the simplest alkane consisting of a single carbon atom connected with four hydrogen atoms by single bonds, CH_4. Since methane is the major component of natural and shale gas, it is widely available and relatively cheap. Nowadays, it is mainly used in the form of natural gas either as an energy source for fueling vehicles and generating electricity or as a feedstock in the chemical industry for the synthesis of syngas and other valuable products [144]. Methane is considered as a potential future energy-carrier because it can be produced from renewable energy sources. This concept is known as the methane economy and offers an alternative to a hydrogen or methanol economy. Therefore, the coupling of solar energy harvesting with CO_2 reduction to methane is a very attractive strategy.

Photoanode-driven systems have mainly been used to achieve PEC CO_2 reduction. The first study that reported methane as a primary product from a PEC CO_2 reduction cell was conducted by Ichikawa et al. in 1996 [79]. Particularly, TiO_2 photoanode was combined with a Cu cathode in a single unit PEC system and hydrogen and methane production was observed. To increase the selectivity towards methane and avoid the deactivation of the Cu electrocatalyst, small islands of ZnO were deposited on the surface of the Cu electrode. Apart from that, pulsed bias instead of constant bias was applied which, according to the authors, improved the stability and FE of the cell. After these modifications, a FE of 44% towards methane was observed followed by ethylene and hydrogen production with FE of 24% and 18% respectively. When the pulsed bias technique was used, an increase of 82% of CO_2 conversion was observed and the conversion rate was stable for more than 24 h while the system that operated under constant bias illustrated a significant decrease of CO_2 conversion after 2 h.

TiO_2 photoanodes for methane production through PEC CO_2 reduction were also reported by Chang and co-workers [82]. This research work focused on the evaluation of the performance of Cu_2O as dark cathode. In other words, the photoanode side was illuminated with 100 mW cm^2 AM 1.5G light while the Cu_2O cathode was shadowed. FE towards methane production reached 54.6% for bare Cu_2O and FE for all carbonaceous products and hydrogen was 94.4%. It is a simple but very creative idea which shows a significantly negative effect of photogenerated holes on the stability of Cu_2O as photocathode. In contrast, the oxidative holes were hardly present under dark conditions and the performance Cu_2O cathodes were almost stable.

Recently, Magesh et al. introduced a metal oxide, WO_3, serving as a photoanode due to its stability in aqueous media, low toxicity and abundance on earth [67]. As already mentioned, the performance and the selectivity of a photoanode-driven PEC system is highly dependent on both photoelectrode and counter electrode whereas the overall and the faradaic efficiency of a photocathode-driven PEC cells are almost exclusively related to the photoelectrode's performance. Therefore, in this study a Cu electrode was used as cathode in order to produce methane. A 67% FE towards methane was observed at relatively low external bias of 1.19 V between working and counter electrode which remained stable for 3 h. The same research group attempted to prepare an even better photoanode by depositing a thin $BiVO_4$ film over a WO_3 layer [81]. In addition, an oxygen evolution electrocatalyst, cobalt bicarbonate, was added on the surface of the semiconducting photoelectrode to further improve the performance of the photoanode. Although the deposition of this electrocatalyst led to enhanced photocurrent density and increased FE towards methane, the production rate and the selectivity that was obtained in bare WO_3 photoanode-driven PEC CO_2 reduction of the previous study was higher than that of Co-Ci/$BiVO_4$/WO_3. Higher photocurrent density does not necessarily mean higher fuel production, due to the fact that photocorrosion or other undesired reactions such as water splitting, parasitic side reactions or back reactions may take place.

Graphene oxide, a material with some outstanding properties such as large specific surface area, high electrical conductivity and electron mobility, has attracted considerable attention in photocatalysis and photoelectrocatalysis. Benedetti et al. illustrated a quaternary

nanocomposite consisting of TiO_2, CdS, reduced graphene oxide and Pt which used in PEC experiments as a working electrode [145]. The anodic photocurrent indicated that this electrode acts as a photoanode. Chronoamperometry measurements verified that the photoelectrocatalytic behavior of the material was improved in the presence of reduced GO. Nevertheless, although it was reported efficient photocatalytic CO_2 reduction to methane, no data were presented about the amount of PEC methane production.

On the other hand, studies that utilized photocathode-driven PEC systems reported production of methane as a by-product with low FE values. Each of these studies is discussed in the Section on the fuel that was reported as the primary product of CO_2 reduction.

4.5. Ethanol

Ethanol also called ethyl alcohol is considered as a promising carbon-neutral and renewable fuel because it is commonly made from plants such as corn, sugarcane and cellulosic biomass. Today, it is produced in large quantities in US and Brazil and mainly used as a substitute or partial replacement of transportation fuels including gasoline and diesel. Therefore, the technology for its utilization as a fuel already exists and the infrastructure of gasoline and diesel can be easily modified for its storage and transportation. Furthermore, the use of ethanol is even more promising when paired with the low polluting technology of fuel cells [146]. However, direct ethanol fuel cells (DEFC) are still at a premature stage of development, even though they seem very attractive. Generally, ethanol is a strong competitor of methanol not only in fuel cells, but also as a transportation fuel due to its high energy density and availability as a biofuel.

PEC CO_2 reduction is an even more attractive way to produce ethanol from an environmental perspective. Nevertheless, only a few studies have managed to obtain ethanol with this approach. Reduction of CO_2 to ethanol is much more complicated and difficult in comparison with previous fuels because it requires a larger number of steps.

There are only a few studies that produced ethanol as a primary product. Among them, Homayoni et al. fabricated hybrid p-type CuO/Cu_2O semiconductor nanorod arrays that served as a photocathode [42]. The main innovation of this study that led to ethanol formation was the use of a two-compartment continuous flow PEC reactor (CFPR) with microchannels instead of a conventional batch-type two-compartment PEC reactor. In particular, ethanol with maximum FE of 55% was observed only in experiments that were conducted in a CFPR showing the significant importance of the photoreactor design. The value of FE was not very high due to the formation of other alcohols, methanol and isopropanol. On the other hand, only methanol was formed in the batch reactor. Furthermore, the photocurrent density in the CFPR were about 5 times higher compared to that measured in a conventional batch reactor. This enhancement was attributed to the high surface area-to-volume ratio due to the microchannels and the increased CO_2 mass transfer. In addition, they proposed a chemical route for the formation of ethanol and other by-products which involved consecutive 2-electron uptake and protonation steps or interaction between intermediates like formate and products such as methanol.

The combination of Cu_2O with highly conductive carbon nanostructures seems an attractive route for PEC CO_2 reduction. For this reason, Kecsenovity et al. studied several hybrids consisting of Cuprous Oxide and graphene [147]. Generally, carbon nanostructures provide a substrate with very high surface area and a highly conductive network that ease the electron/hole transport and exciton dissociation. In addition, interconnected structured materials have an extra advantage that there are not plenty of carbon/carbon interfaces. Thus, all the hybrid photoelectrodes tested in this study outperformed the bare Cu_2O photoelectrodes. Among them, 3-D graphene combined with Cu_2O showed the best PEC behavior for CO_2 conversion into ethanol due to its organized and uniform structure with less carbon/carbon interfaces.

Sagara et al. synthesized p-type semiconducting photoelectrodes made of non-doped and B-doped g-C_3N_4 thin films [148]. B-doped photocathodes successfully converted CO_2 into ethanol with a maximum FE of 78%. In the same research work, B-doped g-C_3N_4 films were decorated with Ag, Rh and Au. Although Au decorated films showed lower FE of CO_2 to ethanol conversion than that of non-decorated photoanodes, the amount of produced ethanol was significantly higher.

Beside these studies, ethanol production was also reported in photoanode-driven PEC cells [149–153]. However, in these studies hydrogen was by far the main chemical product, while the FE for the photoelectroreduction of CO_2 ethanol and other hydrocarbons was very low.

4.6. Other valuable chemical products

As already noted, reduction of CO_2 is a multistep and complicated process leading to a large number of different products. Besides the aforementioned chemicals, PEC CO_2 reduction studies reported the production of several other chemical products including formaldehyde (CH_2O), ethylene (C_2H_4), ethane (C_2H_6), acetic acid (CH_3COOH) or acetate (CH_3COO^-), acetaldehyde (CH_3CHO), oxalic acid ($C_2H_2O_4$) and isopropanol (C_3H_7OH). Today, these chemicals are mainly manufactured industrially from fossil fuels. Thus, the utilization of solar energy to synthesize these valuable chemicals from CO_2 is a promising strategy that can diversify their present production from crude oil and natural gas. However, the majority of PEC CO_2 reduction studies reported the production of these chemicals with low selectivity and not as major products.

4.6.1. Ethylene

PEC CO_2 reduction to higher hydrocarbons than CH_4 was reported by Ba and co-workers with relatively high current efficiency (32.69%) [154]. In this case, CO_2 was mainly converted to ethylene under blue (435–450 nm) light irradiation. The production of ethylene was mainly attributed to the utilization of nanostructured Cu/Cu_2O photoelectrodes. It was also demonstrated that the specific surface area of the photoelectrodes affects the performance of the entire system. Another possible factor that played an important role in the selectivity of CO_2 conversion into ethylene was the utilization of monochromatic light source. Monochromatic irradiation probably photogenerates electrons with a centered reduction energy that favors the production of a specific chemical product, whereas a light source with a wide range of wavelengths may promote the production of several chemical products [155]. Other possible evidence for this conclusion may be the high faradaic efficiencies observed in most of PEC CO_2 reduction studies that used an illumination source with a narrow range of wavelengths of the solar spectrum. However, further investigation is needed in order to understand this effect in PEC systems.

Apart from this study, ethylene has been also detected as a minor product in several studies of PEC CO_2 reduction. A common factor in most of these studies is the presence of Cu in the PEC systems which probably favors the formation of higher order hydrocarbons due to its unique catalytic properties. For instance, Ichikawa et al. studied a PEC system consisting of an n-TiO_2 photoanode a Cu/ZnO cathode in which ethylene was produced with a FE of 24%, although the main product was methane [156]. In addition, Lee and co-workers reported minor production of C_2H_4 via PEC CO_2 reduction systems combining WO_3-based photoanodes and Cu cathodes.[67,81] However, ethylene traces were not detected when they used Sn/SnO_x electrodes as cathodes indicating that Cu plays an important role. Deguchi et al. reported ethylene formation in the presence of Cu cathodes. Photoanodes based on AlGaN/GaN in association with Cu plates were able to convert CO_2 mainly into formic acid, hydrogen, CO, ethanol and ethylene [157]. Specifically, ethylene was a minor product reaching a FE of approximately 2.5%.

Another study that illustrated the effect of Cu particles on CO_2

conversion was reported by La Tempa and co-workers [39]. In this study, they proposed a Z-scheme PEC cell based on p-Si photocathode modified with Cu nanoparticles and TiO_2 photoanode for CO_2 reduction. Several products were also observed such as hydrogen, CO, CH_4, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}. However, the presence of Cu improved the selectivity of the system. Specifically, an increase in the amount of Cu particles deposited on p-Si photoelectrodes led to higher CO, ethylene and methane production rates but hydrogen remained the main product by far [39].

A Cu electrocatalyst was paired with n-TiO_2 in a monolithic device in which CO_2 successfully converted into hydrogen, CO, methane and ethylene. The combination of Cu electrocatalyst with Ag increased the production of ethylene, while methane production was decreased [158]. This is an indication showing that the presence of Ag in combination with Cu affects the selectivity of PEC CO_2 reduction process and favors the ethylene production over methane. Another possible way to obtain methane and ethylene, introduced by Kaneco et al., is the addition of Cu particles in the electrolyte solution [49]. In particular, Kaneco and co-workers used p-InP semiconducting electrodes as photocathodes in a methanol-based electrolyte containing copper particles. In this system, although CO was the primary chemical product, formic acid and small amounts of methane and ethylene were also detected. However, in the absence of copper particles from the catholyte, methane and ethylene were not observed at all.

4.6.2. Formaldehyde

Formaldehyde, CH_2O, is another chemical product that was detected in some early PEC CO_2 reduction studies [27,113,122,159]. Specifically, it was reported that in photocathode-driven systems CO_2 could partially converted into formaldehyde with low FE. However, Ikeda and co-workers attributed the formation of chemical products such as formaldehyde to the presence of epoxy resins in the electrolyte as already mentioned in Section 4.1 [114].

In a later study, formaldehyde was also detected in a photoanode-driven system [40]. A low FE of 1.04% toward formaldehyde was achieved after 1 h, but a significant decrease was observed in this value over time due to the prevalence of hydrogen evolution and further reduction of formaldehyde to other chemical products such as methane.

4.6.3. Less common products

To the best of our knowledge there is only one case so far that a high value product such as acetate is the primary product of PEC CO_2 reduction [160]. It was reported that a photocathode consisting of mixed $CuFeO_2$ and CuO showed a remarkable FE of 80% at −0.4 V vs Ag/AgCl. In addition, by tuning the atomic ratio of Fe:Cu of the mixed-phase photocathodes it was possible to change the selectivity of CO_2 reduction. This research work showed that earth-abundant and low-cost semiconducting materials not only can enable C−C bond coupling through PEC CO_2 reduction but also it can be tunable to a certain extent.

Acetic acid has been also produced by a photocathode-driven system with high pressure CO_2-methanol-TBAP electrolyte. However, in this case CO was the main product with FE of 93% at −1.4 V vs. Ag/AgCl followed by acetic acid with 11% FE. Additionally, Cheng et al. conducted a series of studies in which the same product was detected utilizing several monolithic photoanode-driven PEC CO_2 reduction cells [149–153]. Photoanodes based on TiO_2 nanotubes in conjunction with Pt-modified reduced graphene oxide electrocatalysts enabled CO_2 conversion into several products including acetic acid, isopropanol and propionic acid. The presence of Ni and Cu foam affect positively the formation of higher order hydrocarbons due to their excellent mechanical and electrical properties. Isopropanol was also produced with 48% FE after 5 h in a continuous flow PEC CO_2 reduction system consisting of a CuO/Cu_2O working electrode and a Pt counter electrode [42]. Finally, there is one study that reported oxalic acid formation on metal decorated p-GaP photocathodes [135]. The best FE towards

oxalic acid was obtained when p-GaP photoelectrodes were modified with Pb. The utilization of proper electrocatalysts can increase both the selectivity and the efficiency of PEC CO_2 reduction cells, so their choice should be done carefully in order to lead to the production of the desired product.

5. Perspective

A plethora of experimental demonstrations of PEC CO_2 reduction systems have been overviewed. In this Section, the main bottlenecks and potential solutions for future development and deployment of PEC CO_2 reduction technology are discussed.

The most critical component of PEC CO_2 reduction systems is the photo-responsive material. Early research efforts focused on finding a good solar absorber for PEC CO_2 reduction, but this field has not been developed enough yet. A large variety of strategies such as doping, combination of two or more semiconductors, synthesis of nanostructured materials, passivation layers and co-catalysts have been used so far to increase the efficiency and stability of photoactive materials. Among them, multijunction PEC cells seem one of the most promising strategies because they can absorb photons from a wider region of solar spectrum and still match the potentials of CO_2 reduction and H_2O oxidation. The highest efficiencies can be achieved with a multijunction configuration, in which each photocatalyst absorbs a different part of the solar spectrum. Computational studies and development of modelling tools in PEC CO_2 reduction field can reveal the most efficient combination of photocatalysts for the formation of each fuel [161,162]. Additionally, theoretical studies can also unveil the ideal multijunction cell for PEC CO_2 conversion into higher order hydrocarbons, which remains the "Holy Grail" of solar fuel technologies.

The next important challenge in PEC CO_2 reduction systems is the development of advanced PEC reactors. Although a large amount of experimental demonstrations has been reported, only a few of them studied the reactor design and scale up. Scaling up can significantly affect the efficiency of a PEC cell due to mass transport and ion limitations. An array of small-scale reactors instead of a big batch reactor can minimize the mass transport limitations. However, the overall complexity and cost of the PEC system will be increased due to the utilization of more materials and peripherals such as pipes.

As already discussed in Section 2.2, membrane is an important component of PEC CO_2 reduction cells which acts as molecular barrier while it allows the migration of protons from the anodic compartment to react with CO_2 on the cathodic compartment. However, the presence of membrane within the PEC cell significantly increases the cost and the ohmic losses. For this reason, membrane-less flow PEC reactors, in which hydrodynamic flow alone separates the two compartments, have attracted considerable attention recently[163]. Taking into consideration the aforementioned reactor design and scale-up issues, more research efforts and engineering innovations are needed.

Development of advanced PEC CO_2 reduction devices requires the improvement of procedures that can provide trustworthy benchmarking of efficiency and stability. Although a large variety of figure of merits are widely used in PEC studies as discussed in Section 3, laboratories or facilities that can certify the efficiency of PEC CO_2 reduction or water splitting similar to that of PV field do not exist yet. This mainly happens because PEC CO_2 reduction devices are much more complicated devices than PV consisting of several components such as photoelectrodes, membranes, different containers for liquids and gases. However, an alternative way to facilitate a fair comparison between different PEC CO_2 reduction devices is the development of a standard evaluation procedure with standard criteria, experimental set ups and conditions. The establishment of a standard benchmarking protocol will minimize discrepancies in PEC CO_2 reduction efficiency and stability between different groups. Finally, a universally accepted chart, similar to that of National Renewable Energy Laboratory (NREL) on record PV efficiencies [164], will show the progress of solar fuel devices over time

and will give guidance for potential commercialization of the state-of-the-art systems.

6. Conclusions

This review illustrated the early achievements, the general progress and the current state of PEC CO_2 reduction cells. It was also highlighted the studies with the highest values of several figure of merits including, FE, current density, production rate, durability, applied voltage and STF efficiency for each chemical fuel. Formic acid and methanol were the most common liquid fuels while CO and CH_4 were the most common gas products. Generally, most of the studies utilized photo-cathode-driven systems following the example of the first study of PEC CO_2 reduction [27]. Although a large number of semiconductors and electrocatalysts have been utilized in PEC cells, most of them are very expensive and rare. On the other hand, photoanode-driven PEC cells consisting of more abundant materials, are also able to reduce CO_2. Although these systems presented a wide range of products, most of them showed low selectivity. Recently, systems with photocathodes combined with photoanodes (Z-scheme) opened a new promising pathway because they can convert CO_2 into fuels without any external bias.

The production of several fuels and chemicals utilizing CO_2 as a feedstock and solar light as an energy source holds considerable promise, but many issues such as low production rates, durability and efficiency still remain unsolved. In order to overcome these drawbacks and apply this technology for practical use, even on a small scale, significant improvements should be made on several fronts. One way to improve the efficiency of PEC CO_2 reduction cells is the development of new photoactive materials with excellent absorption, stability, improved charge transfer and reduced ohmic losses and overpotentials. One approach to enhance electron and hole transport is the preparation of nanostructured photocatalysts with high-surface area and high crystallinity which mainly depends on the method of material synthesis. In addition, doping of semiconductors can improve their charge carrier transport or their spectral response. Coating of co-catalysts on the surface of photoelectrodes can enhance their photoelectrocatalytic activity because they can act as light harvesters while at the same time they can provide active reduction or oxidation reaction sites. It has been also observed that the deposition of electrocatalysts on the surface of semiconducting photoelectrodes can lower the required overpotential by lowering the activation energy of the water oxidation reaction. Additionally, the presence of co-catalyst can improve the photochemical stability of photocalysts due to the fact that punctual consumption of photogenerated electrons and holes inhibits photocorrosion. Utilization of metals such as Cu and Ni with great electrocatalytic properties as co-catalysts showed enhanced production of higher order hydrocarbons and improved selectivity of PEC CO_2 reduction. Apart from co-catalysts, passivation layers can also deposited on the surface of photoelectrodes in order to protect them from photocorrosion. In this way, unstable photoanodes and photocathodes can show high resistance under harsh oxidative conditions.

Although a large number of CO_2 reduction studies has been dedicated to the clarification of mechanism and pathways of CO_2 reduction, it still remains unclear. However, the development of advanced in situ characterization techniques and modelling tools can assist in deeper understanding of this process in the future. The knowledge of rate-determining reaction steps and barriers will enable the elaboration and design of more effective PEC systems. In conclusion, more attention should be paid to the development of advanced and stable photoactive materials, the understanding of PEC CO_2 reduction pathways and mechanism, the design of more efficient PEC reactors and establishment of a universally accepted benchmarking protocol in order to prepare solid bases for the next step forward.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cattod.2018.02.045.

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