

## Review Article

# Integration of Solar Chemistry and Biotechnology for Building-up an Effective Man-Made C-Cycle that May Complement the Natural C-Cycle

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**Abstract**

The need to cut the CO<sub>2</sub> immission into the atmosphere is pushing scientists and technologists to discover and implement new strategies that may be effective for controlling the CO<sub>2</sub> atmospheric level (and its putative effects on Climate Change-CC). One option is the capture of CO<sub>2</sub> (from power plants flue gases or other industrial processes) for avoiding that it can enter the atmosphere. The captured CO<sub>2</sub> can be either disposed in natural fields (geological cavities, spent gas or oil wells, coal beads, aquifers; even oceans have been proposed) or used as source of carbon in synthetic processes.

In this paper we present the options for CO<sub>2</sub> utilization driven by solar energy and make an analysis of a variety of solutions for the conversion of large volumes of CO<sub>2</sub> by either combining it with H<sub>2</sub> that must be generated from water, or by directly converting it into fuels by electrolysis in water, or else by integrating catalysis and biotechnology for an effective conversion of CO<sub>2</sub>. A CO<sub>2</sub>-H<sub>2</sub> based economy may address the issue of reducing the environmental burden of energy production, also saving fossil carbon for next generations. The enhanced growth of aquatic biomass is not discussed in this paper.

**INTRODUCTION**

The reduction of the emission of CO<sub>2</sub> generated in burning fossil-C (coal, oil, and natural gas) has been the objective of international agreement programmes since the Kyoto Protocol in 1997 and the Doha Amendment to it signed in 2012. Altogether, a reduction of *ca.* 20% of the emission with respect to 1990 was planned by 2020. As a matter of fact, in 2018 fossil-C contributed 81.2+% of the total energy used and it was 81.12% in 1990 [1]. Only the increment of energy used worldwide was covered by renewables (biomass) and perennial sources (Solar-, Wind, Hydro-, Geothermal-power, SWHG). There is an objective difficulty in replacing fossil-C derived fuels essentially for two reasons: i. they are the most concentrated energy vectors (Table 1); ii. They can be shipped everywhere in the world. Hydrogen would require building up new infrastructures in addition to rising safety issues in a distributed use (transport) and high construction costs due to the risk of handling liquid hydrogen, most effective than compressed hydrogen as energy carrier.

The use of fuel-cells may represent a possible solution to the use of hydrogen aboard light and heavy carriers, but still the safety issues will continue to exist. The direct use of PV-electricity rises problems of intensity for its application in industries.

PV cannot be used for direct use in cars, and batteries, due to their low-density energy (which is close to that of compressed hydrogen), the short autonomy and future availability of materials (Li) for a global electrification of cars, buses and trucks, is not a solution. It is obvious that more than searching for a single solution to all applications, a bunch of technologies must be used for the various fields of application. However, for the short term, shifting from fossil-C to biomass, renewable form of carbon, has been considered a way to reduce the emission of CO<sub>2</sub> without any major changes of existing infrastructures. Biomass is made from atmospheric CO<sub>2</sub> and gives off CO<sub>2</sub> upon burning: Nature cycle's carbon in the form of CO<sub>2</sub>, then CO<sub>2</sub> must be considered as renewable-C. This concept has been at the basis of our attitude to consider carbon dioxide not yet as a waste but as a "source of carbon", [2] which has led us to our most recent book "An economy based on Carbon dioxide and water" [3a]. Is, thus, possible to build-up a strategy for a large-scale CO<sub>2</sub> utilization as source of carbon, supplanting fossil-C and implementing the "circular economy" concept? At what extent is possible to recycle carbon through the CO<sub>2</sub>-utilization as building block for making chemicals and materials or source of carbon for fuels? In this paper we shall make an analysis of possibilities and conditions for the exploitation of CO<sub>2</sub>. We shall not discuss in this paper the

**Table 1:** Energy density of various vectors.

Vector	Diesel	Gasoline	Coke	Brown coal	Methanol	Bio-oil from algae	H <sub>2,l</sub>	Methane	H <sub>2,g</sub> (20MPa)
GJ m <sup>-3</sup>	36	34	30	18	17	13	9	8	2

enhanced growth of land or aquatic (micro- and macro-algae, see ref. 3b) biomass that represents a quite different approach.

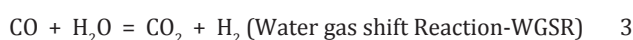
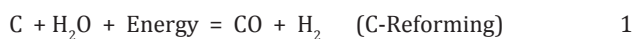
### Possible uses of CO<sub>2</sub>

CO<sub>2</sub> can be converted into a variety of products with different properties. The reactions [4] can be categorized in three main classes.

- Reactions in which the carbon atom forms a bond with more electronegative atoms (e.g., N, O), maintaining the oxidation state of +4. The formation of moieties such as HCO<sub>3</sub><sup>-</sup> (hydrogencarbonate), CO<sub>3</sub><sup>2-</sup> (inorganic carbonates), (RO)<sub>2</sub>CO (organic carbonates), RR'N-CO<sub>2</sub>R (carbamates or urethanes if R=R'=H) are examples of such reactions.
- Reactions in which the formation of a C-C bond takes place (HO<sub>2</sub>C-CO<sub>2</sub>H, oxalic acid), R-CO<sub>2</sub>H (carboxylic acids) and any other molecule in which the -C-CO<sub>2</sub>- moiety exist.
- Reactions in which CO<sub>2</sub> is reduced to CO or forms a number of C-H bonds like in CH<sub>3</sub>OH or CH<sub>4</sub>.

The energetics of such reactions is shown in Figure 1.

The reactions which convert CO<sub>2</sub> into energy products (CO, CH<sub>3</sub>OH, CH<sub>4</sub>, long chain hydrocarbons) require energy and hydrogen, as shown in Figure 1. Such hydrogen is today formed (> 85%) by reacting fossil-C (coal, methane) with water at high temperature.



The strongly endo-ergonic processes in Equation 1-3, emit large volumes of CO<sub>2</sub> if fed with fossil-C.

For these reasons, being our energy system mostly based on fossil-C (81.2 % at 2018), had no sense so far to develop the

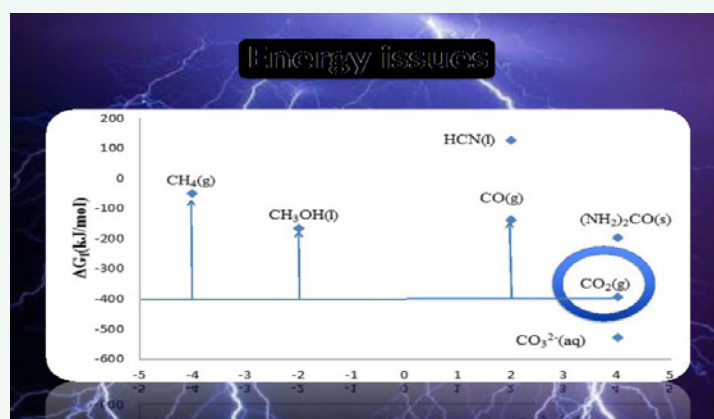
conversion of CO<sub>2</sub> into energy products (which market is 15 times that of chemicals), while the use of CO<sub>2</sub> for making chemicals such as those mentioned before had a meaning.

Since the development of efficient (20 % conversion of solar energy into electrons), affordable and robust (timespan of several years) PV-systems, [4b] that will become even more efficient (40%) cheap and resistant (decade) in future, the hydrogenation of CO<sub>2</sub> makes sense. The different ways to use solar light will be discussed in following paragraphs.

### From Solar Energy to Hydrogen (StH) and E-Fuels (StF)

Today, there are several demo plants around the world that demonstrate the feasibility of conversion of solar energy into hydrogen by PV-driven water electrolysis. Hydrogen is then reacted with CO<sub>2</sub> to form methanol or methane through a thermal exo-ergonic reaction. For a large-scale implementation, such process needs large capacity electrolyzers, robust (stable electrodes) and cheap (avoiding noble metals). Although water electrolysis for the production of H<sub>2</sub> and O<sub>2</sub> is a technology known and practised since long time (100+ y), nevertheless substantial changes are necessary for up scaling such processes to the level required for a significant CO<sub>2</sub> conversion into fuels and lowering the production price of H<sub>2</sub>. Moreover, as PV is discontinuous, a back option must be developed for a continuous (day and night) production of H<sub>2</sub>. This could be the use of molten salts as solar energy storage (above 400-500 °C) that could be used during dark periods for making pressurized-high temperature steam used for spinning an alternator and producing electricity, or any other solution such as the use of excess energy at night, or innovative technologies today not on the market. In any case, when dealing with PV an integrated technology is necessary.

This option would necessarily include hydrogen collection and pressurization to the utilization process requirements (usually 3.0-6.0 MPa) or even storage, unless the production and



**Figure 1** Energetics of some selected CO<sub>2</sub> reactions. The blue circle includes the formation of carbonates and carbamates. Only the formation of inorganic carbonates, and some organic carbonates and carbamates, are exothermic. All others are endothermic and require hydrogen.

consumption of hydrogen will be synchronized. An interesting option would be the production of  $H_2$  under pressure that would be directly fed to the utilizer, a new technology.

### Direct use of solar energy in $CO_2$ -water coprocessing

An alternative to the production of hydrogen is the direct *coprocessing of  $CO_2$  and water* (or waste organic proton-donors) to final energy products. Such system steps away from “water splitting”, a process that is not “natural”. In general in Nature, if  $H_2$  is produced from water, oxygen is fixed into organic substrates, conversely when  $O_2$  is produced, the “ $H^+ + e^-$ ”-couple is used in the reduction a substrate without making  $H_2$ .

An approach which is under investigation since long time is the *PV-driven electrocatalytic reduction of  $CO_2$  in water*. In this case, the water oxidation (to oxygen) and  $CO_2$  reduction (to a variety of products, depending on electrodes/electrocatalysts, Table 2) occur separated in space (at the two electrodes) and the potential negative effect of  $O_2$  mixing with organic products is eliminated. There are several bottlenecks to this technology, mainly represented by the long-term stability of electrodes, selective production of  $CO_2$  reduced forms, and their separation from water.

The ideal case would be that the product is a gas or liquid not miscible with water so that it could spontaneously separate and be easily collected with low energy expenditure. Example of a useful gaseous product is ethene ( $CH_2=CH_2$ ) that can be produced with interesting selectivity (> 30%) using a Cu-cathode. Liquid hydrocarbons are not miscible with water, therefore making products which chains longer than C4, is an interesting option. Hydrocarbons are lighter than water and would spontaneously accumulate on its surface.

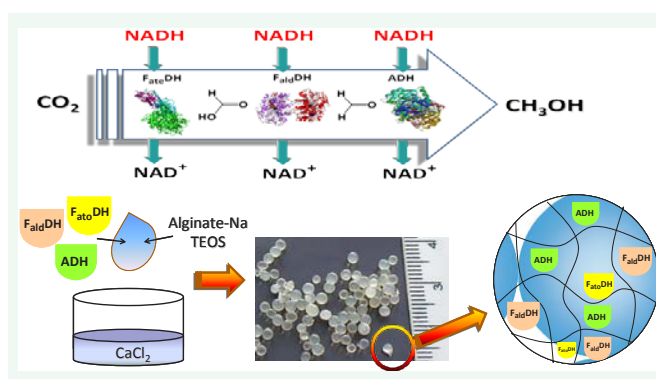
An evolution of this technology is the *photoelectrochemical conversion of  $CO_2$  in water*. In this case, the external PV system would not be necessary. In fact, solar light would be directly shade on electrodes made of semiconductors that would generate a charge separation ( $e^- + h^+$ ) that would drive the oxidation and reduction process. Such electrodes could also be covered with catalysts (including bio-systems, see next paragraph) that would drive the reactions. This system is the most-close to a natural one, as it uses solar light, water and  $CO_2$  and delivers  $O_2$  and organic products without producing  $H_2$ , but using the “proton coupled to electron transfer-PCET” strategy, mimicking Nature.

### Integration of biotechnology and catalysis

An advanced and integrated system is the use of enzymes for  $CO_2$  reduction. An example is given by the direct  $CO_2$  conversion to methanol in water (at room temperature) by a system of three co-encapsulated enzymes [5] that use NADH (3 mol, 6e<sup>-</sup> per  $CH_3OH$ ) as cofactor (Figure 2). Such Process, although interesting, is not economically viable unless  $NAD^+$  is back-converted to NADH. We have used either chemicals (that affect the enzymes) or semiconductors in such reduction (Figure 3) The drawback of such system is that the rate of utilization of NADH by enzymes is much higher than that of reduction of  $NAD^+$  to NADH. Being the two rates not-synchronous an excess of NADH is necessary so to have a reserve of reducing power.

**Table 2: Electrodes and products of reduction of  $CO_2$  in water.**

Electrodes	Products
Cu	$C_2H_4$ (32-80%) $C_nH_{2n+2}$
Zn, Au, Ag, p-InP, p-GaAs, Pt-Pd-Rh	CO CO + HCOOH
RuOx on conductive diamond, B-doped-C	MeOH, EtOH, $C_nH_{2n+1}OH$



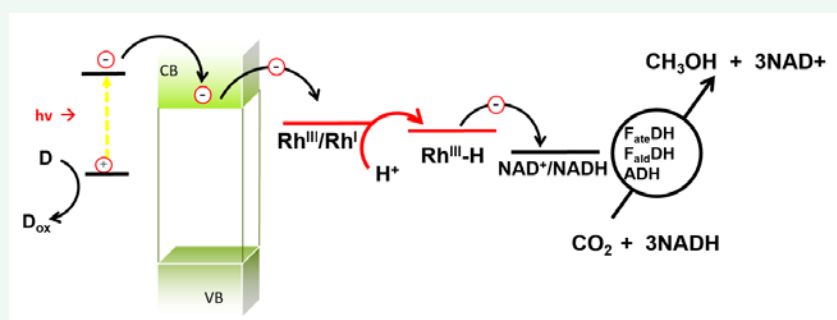
**Figure 2** Coupling of enzymes for  $CO_2$  reduction in water.

This not yet economic, even if a net progress is made in terms of mol of methanol produced per each NADH, jumping from 3 NADH per methanol mole of Figure 2 to over 100 methanol per NADH of Fig. 3. A further step forward was made by supporting microorganisms (or enzymes) on an electrode coupled to a photochemical system for generating electrons for  $NAD^+$  reduction [6]

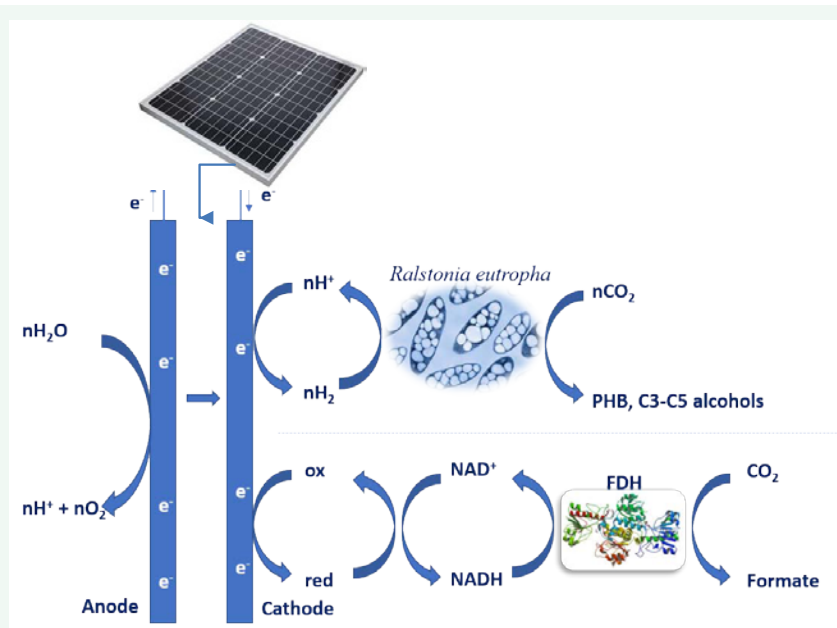
As well interesting is the case in which electrons coupled to protons are transferred to microorganisms or enzymes for the reduction of  $CO_2$  to formate that can originate acetate. The latter can be used by a number of microorganisms to build Cn moieties such as hydrocarbons or hydroxo-acids.

Figure 4 shows a hybrid system obtained by coupling a microbial electrosynthesis (MES) reactor with solid-state photovoltaics (PVs) able to convert  $CO_2$  with high efficiency and productivity [7,8].

Figure 4 shows that a MES system can be used for the production of polyhydroxybutyrate (PHB) and short chain alcohols (C3–C5) from  $CO_2$  by using a metal cobalt inorganic-phosphate ( $CoP_i$ ) anode and a cobalt-phosphorus (Co-P) alloy cathode coupled to a microorganism, (*Ralstonia eutropha*) [9]. *R. eutropha* uses  $H_2$  generated at the cathode for reducing  $CO_2$  with a solar energy-to-chemicals conversion efficiency of 7.6% for PHB and 7.1% for C3–C5 alcohols.  $CO_2$  can be reduced into formate [10–12] by a formate dehydrogenase via NADH (Fig 4 lower part). Recently Zhiguang Zhu [13] reported a hybrid  $CO_2$  electroreduction system, in which  $CO_2$  is reduced to formate by using a Cu nanoparticle (CuNPs) for enzyme immobilization and cofactor regeneration with a faraday efficiency of 22.8%. In order to realize a highly efficient  $CO_2$  fixation system, a mesoporous material (based on NU-1006) was used to encapsulate FDH. The system was coupled with a pre-installed Rh-based electron mediator to allow solar energy to regenerate



**Figure 3** Photoreduction of NAD<sup>+</sup> to NADH and integration in CO<sub>2</sub> reduction.



**Figure 4** PV-driven MES.

the coenzyme. Under such conditions FDH was able to convert CO<sub>2</sub> to formic acid selectively with a TON of about 865 h<sup>-1</sup> during 24 hours [14]. Another application is shown in Figure 5: a hybrid system is built-up with solid-state PVs connected to an electrolyser in order to produce H<sub>2</sub> for a gas fermentation reactor where CO<sub>2</sub> reduction occurs [15]. In general, these systems use proton-exchange membrane (PEM) with energetic efficiency range of 65-70% [16]. Such kind of electrolyzers can be used to reduce CO<sub>2</sub> into CO with efficiencies greater than 80% [17].

More recent systems are the photobioelectrochemical cells (PBECS) where absorbers immersed in the electrolytes are able to capture solar energy that is used for water splitting generating reducing equivalents (Figure 6) [18].

PBECS using living cells as biocatalysts are characterized by low productivity and solar energy-to-chemical conversion efficiency. Sakimoto et al. report the use of thermophilic *Moorella thermoacetica* as microbial catalyst able to reduce CO<sub>2</sub> into acetate and to acquire electrons from a cathode [18] with not very high production of acetic acid. Although coupling photocatalyst nanoparticles with microbial catalysts do not appear to be very

productive, this technology is still in progress, and needs to be improved in productivity and efficiency: it could become more cost effective than competing approaches since it requires only a single bioreactor without electrodes, PV cells, or electrolyzers.

### Perspectives: System integration

Nature is systemic. Nature does not produce waste. We have to learn from it. The success of shifting from the *linear* to the *circular* economy lays in our capacity of moving from a disseminated localization of "isolated" plants to *clustering chemical processes and integrating chemistry and biotechnology*. Clustering processes allows optimizing the materials utilization through a cascade of applications that would allow that residuals of a process are used as raw material for others without exiting the industrial site, reducing risks by eliminating road-transport, and converting actual waste into useful materials. Integration allows chemistry and biotechnology to work together, making the necessary, significant jump from two separate in space and time processes to integrated processes and even to a single hybrid device that incorporates both actors. This is a very attracting challenge and the power of such hybrid systems must

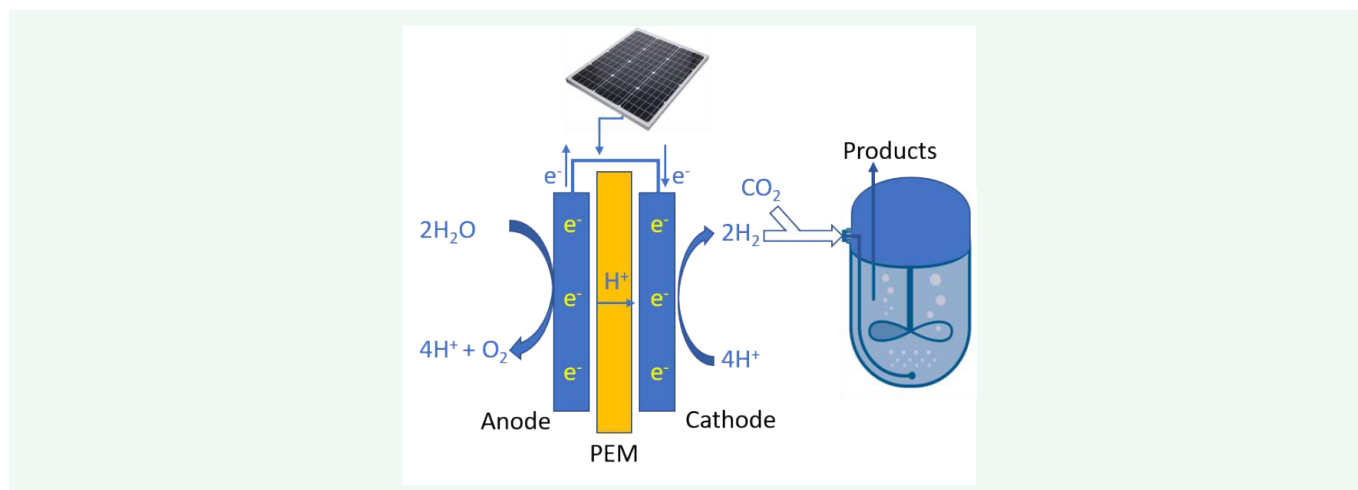


Figure 5 PV driven electrolyzer.

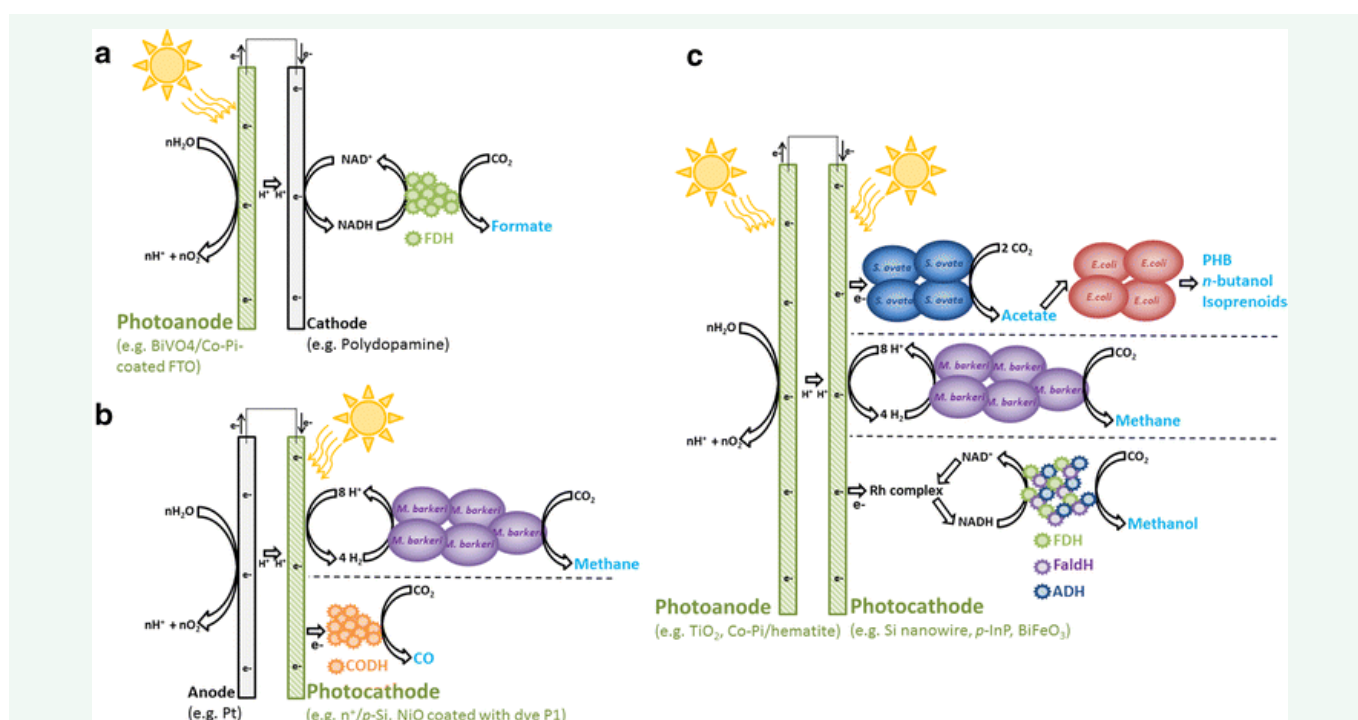


Figure 6 Photobioelectrochemical cells (PBECS). a PBECS with a photoanode. b PBECS with a photocathode. c PBECS with a photoelectrodes tandem.

be demonstrated. The use of the integrated systems as MES or PBECS can be considered very attractive within the circular economy perspective as their products ( $H_2$ ,  $CH_4$ , acetate/short chain fatty acids and alcohols) can be useful for making valuable chemicals, materials and energy products [19]. For application at industrial level the  $CO_2$  conversion rate must further be improved and optimized. Besides, the discovery of active photocatalysts [20] for selective solar-driven  $CO_2$  reduction to a single energy product is also a field of great interest. The two strategies can be integrated into a single device.

A variety of solar-driven systems for converting  $CO_2$  into chemicals and fuels with the implication of bio-systems (microorganisms or enzymes) exist that are worth of

demonstration of their real power, and new ones will be invented, that will allow to build a man-made cycle for recycling-C through the conversion of  $CO_2$  that will complement the natural C-cycle, accelerating the  $CO_2$  conversion, reducing its accumulation in the atmosphere and avoiding extraction of fossil-C.

However, BES and PBES rise great expectation for their potential. Nevertheless, several drawbacks and bottlenecks exist to their exploitation, such as high CAPEX and OPEX, the intrinsic kinetics of biosystems, lifetime of enzymes and devices, need of continuous energy feed that mismatches the discontinuous availability of solar energy. Discovering new low-cost photo-materials, engineering faster enzymes, developing hybrid biotechnologies are key steps to a better use of such interesting

option. A clever engineering of energy supply with best mix of different primary sources or stored energies is also essential for a continuous run of the new technologies [3]. Our future is in CO<sub>2</sub> conversion.

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