

# Nanostructured Electrodes and Devices for Converting Carbon Dioxide Back to Fuels: Advances and Perspectives

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**Abstract** The production of solar fuels from water and CO<sub>2</sub> is an efficient solution to store and use solar energy and reduce the negative effects associated with large volumes of CO<sub>2</sub> emissions. In this vision, the liquid fuels produced by recycling CO<sub>2</sub> using solar energy are an ideal energy source: easy to store/transport and providing full integration into the existing energy infrastructure. After discussing the possible option to reach this objective, the use of a novel photoelectrocatalytic (PEC) device is analyzed in a more detail. New characteristics of the photoanode and electrocatalyst are required. Some aspects related to the characteristics of nanostructured (a) TiO<sub>2</sub> thin films (based on an ordered array of titania nanotubes) and their performances as photoanodes and (b) carbon nanotube-based electrodes for the gas phase reduction of CO<sub>2</sub> to liquid fuels (mainly isopropanol) together with their application for the design of a novel photoelectrocatalytic (PEC) approach for the synthesis of solar fuels will be presented.

## 1 Introduction

Rising concerns over carbon dioxide emissions, shown at the recent United Nations Climate Change Conference (Copenhagen, December 2009) has accelerated the R&D activities on carbon dioxide sequestration and storage (CSS) [1–3].

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However, at the same time the interest in considering CO<sub>2</sub> as a value instead of a waste increased [4–6]. The increasing amounts of CO<sub>2</sub> available from current and planned CSS plants will make carbon dioxide a feedstock of zero (or even negative!) cost for conversion to fuels and chemicals. Furthermore, incentives exist, such as goodwill for companies adopting policies of CO<sub>2</sub> emissions reduction.

The other factor stimulating the interest in CO<sub>2</sub> chemical recycling is the presence of many emissions for which the CSS option is unsuitable: distance from safe sequestration sites, diluted concentration of CO<sub>2</sub> in the emission, small-medium size sources, and uncertainty on the impact on environment. Considering that at least 5–10% of the total CO<sub>2</sub> emissions (about 30 Gt worldwide in 2009 [7]) could be suitable for production of fuels and chemicals, e.g., at least one order of magnitude higher than the actual use of CO<sub>2</sub> in industry, there are large opportunities to develop new approaches for recycling [8–14]. The utilization of CO<sub>2</sub> as a raw material in the synthesis of chemicals and liquid energy carriers offers a way to mitigate the increasing CO<sub>2</sub> build-up in conjunction with economic opportunities.

The volume of CO<sub>2</sub> emissions is so large with respect to the amount which may be converted to chemicals that recycling it back to fuel using renewable sources of energy is the necessary and sustainable option to consider [15–20]. Worldwide fuel consumption is two orders of magnitude higher than that of chemicals. Therefore, the fuel market has the largest potential to utilize the products of CO<sub>2</sub> conversion. In addition, valorization of carbon dioxide emissions could be one important part of the general strategy for reducing CO<sub>2</sub> emissions and pushing the chemical and energy companies toward a more sustainable use of the resources [21, 22].

From a different perspective, it should be pointed out that in the near-term, we could forecast an increasing use of solar energy, allowing it to become predominant in a longer-term energy scenario. A massive use of solar energy would require converting light energy to forms that can be easily stored to be used when and where required. In fact, photovoltaic (PV) cells for converting solar to electrical energy can have a mismatch between the time and location of production and use. Actual methods for storing electrical energy (mainly based on potential energy) are not very efficient. The storage of electrical energy by devices such as batteries and capacitors, notwithstanding the significant developments in nanostructured materials for them [23, 24], still remains an issue for large energy amounts. Therefore, there is a strong need to develop efficient chemical energy vectors to store and easy transport energy produced from solar light.

H<sub>2</sub> is a clean energy vector that has received a large amount of attention, part of the idea to implement the “hydrogen economy” [25–27]. However, the technical limits in efficient and cost-effective hydrogen storage put serious constraints on the possibility of its use as the primary energy vector. Other alternatives, such as ammonia, have relevant limits in terms of safety and toxicity. Furthermore, huge investments are necessary to rebuild the energy infrastructure using H<sub>2</sub> or other alternative energy vectors. Liquid products such as methanol or better longer-chain alcohols or hydrocarbons are preferable options as energy vectors in terms of energy density, low toxicity, easy and safe storage/transport, and, especially,

capability of integration into the existing energy infrastructure for both mobile and stationary applications. We have thus proposed these *C-based energy vectors* as the preferable and more sustainable options toward solar fuels [28–30].

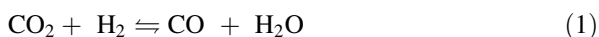
### ***1.1 Options for Converting Carbon Dioxide Back to Fuels***

In principle, there are different possibilities in converting CO<sub>2</sub> back to fuels. The most investigated area is the hydrogenation of CO<sub>2</sub> to form oxygenates and/or hydrocarbons. Methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> has been investigated up to pilot-plant stage with promising results [16]. An alternate possibility is the production of dimethyl ether (DME), a clean-burning fuel that is a potential diesel substitute. Ethanol formation, either directly or via methanol homologation, or the conversion of CO<sub>2</sub> to formic acid are also potentially interesting routes. Methanol, ethanol, and formic acid can also be used as feedstocks in fuel cells, providing a route to store energy using CO<sub>2</sub> and subsequently produce electricity. Alcohols are, in principle, preferable over hydrocarbons because their synthesis requires less hydrogen per unit of product. In fact, the key problem in this route is the availability of H<sub>2</sub>. If the latter is produced from hydrocarbons (the main current route is by steam reforming of methane) there are no real advantages in converting CO<sub>2</sub>. H<sub>2</sub> must be derived from renewable sources. The possible options are the following:

- Water electrolysis, coupled with a renewable source of electrical energy (photovoltaic cells, wind or waves, etc.). This technology is already available, but the need of multiple steps, the overpotential in the electrolyzer, and other issues limit the overall efficiency. The technology is mature with a limited degree of further possible improvements.
- Biomass conversion, preferably using waste materials and in conditions which require low energy consumption. An example is the catalytic production of H<sub>2</sub> directly in liquid phase from aqueous solutions (ethanol waste streams, for example). This option could be a way for the valorization of side waste streams from a biorefinery, but it is not an efficient method if considered alone. In fact, if we consider the whole life cycle from growing the plant, harvesting, fermentation, etc. and finally H<sub>2</sub> production (from bioethanol, for example), the overall energy consumption (and thus amount of CO<sub>2</sub> produced) is higher than the advantage in hydrogenating CO<sub>2</sub> back to fuels.
- Production of H<sub>2</sub> via biogas produced from anaerobic fermentation of biomass. Also in this case, it could be a valuable option using waste biomass, but is a quite complex process considering the whole production chain. There are also problems with the purification of biogas.
- Production of H<sub>2</sub> using cyanobacteria or green-algae. This is an interesting option, but with low productivity and still under development.

- Direct H<sub>2</sub> production by water photoelectrolysis, which suffers low productivity and, in some cases, of the need for further separation/recovery of hydrogen.

Renewable H<sub>2</sub>, after the eventual compression and heating to the requisite reaction temperature, may then be used for the hydrogenation of CO<sub>2</sub>. The first step is the reversible reaction of reverse water gas shift (RWGS), a mildly endothermic reaction with enthalpy and free energy changes of  $\Delta H_{298\text{K}} = 41.2$  kJ/mol and  $\Delta G_{298\text{K}} = 28.6$  kJ/mol:



Carbon monoxide and hydrogen, also called syngas, may then be converted to methanol and/or DME, or Fischer–Tropsch products (hydrocarbons, mainly) by known catalytic processes. These processes may also be combined into a single process with the RWGS reaction, but the formation of water in the latter is an issue in syngas transformation.

If we consider H<sub>2</sub> produced at 10% efficiency by a combination of PV + electrolyzer cell, the need of three H<sub>2</sub> molecules for converting CO<sub>2</sub> to methanol is shown by:



and the energy associated with the whole process chain (including the separation, etc.) in a complete life cycle assessment (LCA), it is possible to calculate the effective energy efficiency (EEE) of the process (the ratio between energy content of the product (methanol) and the total energy input necessary for the whole chain) and the CO<sub>2</sub> recycle effectiveness (CRE) [the ratio between CO<sub>2</sub> recycled and CO<sub>2</sub> emitted due energy consumption (due to the use of fossil fuels in producing and running the various devices)].

A few LCA studies exist on the use of CO<sub>2</sub>, H<sub>2</sub> production, PV cells, methanol production, etc. [31–38] and they are not specific to the above case or its analogous paths. It is therefore not possible to make conclusions, but it can be estimated that EEE is significant below 1% and the CRE is only slightly negative. The routes using H<sub>2</sub> produced via biomass have significantly lower EEEs and positive CRE values. In other words, specific studies are necessary to evaluate the effective sustainability of CO<sub>2</sub> hydrogenation routes. This technology is nearly viable, although some further improvement is necessary. The overall complexity (multi-stage process) makes the overall efficiency low, with a limited degree of possible improvement. Therefore, it is not a long-term, sustainable option for converting CO<sub>2</sub> back to fuels.

Dry reformation of methane with CO<sub>2</sub> is an alternative possibility to produce syngas:



This is a strong endothermic reaction that suffers from fast deactivation due to carbon formation. The coupling of the reaction of steam reforming of methane and partial methane combustion (the tri-reforming process) reduces the issue of

deactivation and allows autothermic operations. The process is interesting and has been developed to pilot-scale operations. However, the CO<sub>2</sub> recycle effectiveness is probably low, even if specific LCA studies are not present in the literature.

There are other routes and options in converting CO<sub>2</sub> to fuels, but it is not our aim to discuss them in detail here. More specific aspects are reported elsewhere [1, 15–17, 39–46]. The above discussion highlights the concept that when complex and multi-stage processes are necessary, the final effectiveness is low, as is the effective potential in reducing CO<sub>2</sub> emissions. It is necessary to explore direct routes for producing fuels from carbon oxides using solar energy. Although all of these routes are still at an early stage of development, they have the potential to be more effective and more economical. They are therefore the necessary direction for research, although in a medium to long-term perspective.

## ***1.2 Solar Fuels Based on Carbon Dioxide Recycle***

There are essentially three main routes for solar fuels based on carbon dioxide recycling:

- Bio-route, based on plants, algae, bacteria, etc.
- Concentrated solar energy, where the solar radiation is concentrated using mirrors, providing the required heat to perform endothermic reactions or suitable thermodynamic cycles
- Low-temperature conversions using semiconductors, where the light absorption is used to generate electrons and holes by charge separation, which subsequently react with water and CO<sub>2</sub>.

Photosynthesis in green plants is the best known example of solar energy used for the conversion of CO<sub>2</sub>, but its efficiency is relative low (around 1%) and the CO<sub>2</sub> is converted (in a slow process) to carbohydrates, lipids, etc. Producing fuels from biomass is possible and the research interest is growing, especially on biomass conversion to liquid fuels (the BtL process) [47, 48]. Many steps are necessary, from plant growth to harvesting, treatment, transport, and finally conversion in typically multi-step processes before producing biofuels. This is only a feasible short-term solution but, in our opinion, not in the long-term perspective of sustainable energy.

Using algae, the efficiency in using solar light is higher (around 10%) and CO<sub>2</sub> (from power plants) can be even fed directly to the photobioreactors or open ponds [49, 50]. However, the process of producing biofuels from (micro)algae is quite complex and critical problems are the controlled growth of the algae and cost. Biofuels from microalgae are considered third generation biofuels, after the second generation processes based on biofuels produced from lignocellulosic materials [50]. However, from a conceptual point of view, direct routes of solar energy use for conversion of CO<sub>2</sub> to fuels that do not pass through the phase of

complex molecules (cellulose, hemicellulose, lignine, starch, lipides, oils, etc.) are preferable. A life cycle assessment of biodiesel production confirms the necessity to decrease the energy and fertilizer consumed by the process [51].

Some algae and cyanobacteria can use light directly to produce fuels [45, 52, 53], but only hydrogen can be produced. It could be possible to genetically manipulate enzymes, fungi, or bacteria to convert  $\text{CO}_2$  directly to biofuels, but it is difficult to predict if this will ever be realized. Bio-routes for the production of solar fuels by recycling  $\text{CO}_2$  suffer the intrinsic limitation to go “uphill” in energy by creating complex molecules that are then decomposed (“downhill” in energy) to produce fuels. It is evident that it is preferable to preserve this complexity to make chemicals instead of fuels and that a direct route to use solar energy that directly (or at least in fewer steps) converts  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to liquid fuels and  $\text{O}_2$  is the energetically preferable route. In addition, biomaterials (algae, cyanobacteria, etc.) are typically quite sensitive to the environment and it is necessary to have sophisticated control of the reaction conditions, which in turn demand higher costs.

Concentrated solar radiation (in solar high-temperature furnaces) can be used to produce  $\text{H}_2$  (and  $\text{O}_2$ ) from water or  $\text{CO}$  (and  $\text{O}_2$ ) from  $\text{CO}_2$  [1, 43, 54–56]. Thermochemical cycles are necessary to lower the temperatures required. An example is the use of a metal oxide that spontaneously reduces at high temperature and is then reoxidized by interaction with  $\text{H}_2\text{O}$  to form  $\text{H}_2$  or alternatively with  $\text{CO}_2$  to produce  $\text{CO}$ . Nevertheless, temperatures above 1200–1400°C are necessary. This creates a number of issues in terms of materials, stability, cost-effectiveness, and output. The syngas ( $\text{CO}/\text{H}_2$ ) should then be catalytically upgraded to fuels (e.g., methanol and FT hydrocarbons). This approach is essentially suitable for solar plants, while it may be difficult to adapt to a delocalized production of solar fuels. In addition, scaling problems are likely.

A variation of the concept is to use this solar concentrators and reactors to drive  $\text{CO}_2$  reforming with methane (solar dry reforming of methane) to produce syngas, which can be then converted to methanol and Fischer–Tropsch products. The advantage is the possibility of continuous operations, instead of cyclic, while the disadvantage is the need of a methane feed. Solar illumination provides the heat necessary for the endothermic, dry reforming of methane with  $\text{CO}_2$ . Also in this case, there are issues related to the difficulty of maintaining a homogeneous temperature in the monolith, materials stability, and carbon formation. Scaling of the solar system to larger production of solar fuels remains an issue.

Possible alternatives are the solar, wet reforming of methane (e.g., feeding water instead of  $\text{CO}_2$ ) and the solar decomposition of methane to carbon and hydrogen. All of these reactions are endothermic and the sun provides the heat of reaction. However, in the wet reforming of methane, the water to methane ratio should be greater than three in order to avoid excessive build-up of carbon over the catalyst. In the conventional catalytic process, with an external heat supply, this dilution is not critical, but in solar reformers, where the uniformly heated zone is limited, the productivity and cost-effectiveness is significantly affected. The reaction is controlled by the heat transfer rate and the parameters to improve the reaction rate are therefore very limited. In solar decomposition of methane,

the production of a solid (carbon) is a clear issue, particularly for larger-scale applications. Solar dry reforming of methane with  $\text{CO}_2$  appears the preferable choice between these three options, although in all cases the problem of catalyst stability (due to inhomogeneities in the heating) is a big issue.

Therefore, although the potential gain in energy efficiency of solar reformers over the conventional catalytic process to generate syngas or  $\text{H}_2$  is attractive, the low productivity and limited scale of economy are the main issues, not to forget the problem of the materials. The feasibility of concentrated solar power (CSP) for producing solar fuels was proven, but not its stability of operations or its economic value. The expansion of the market for CSP (mainly to produce electrical energy) provides incentive to further explore this technology.

Delocalization of energy production is also an important aspect for better integration, reduction of eco-impact, and of the fuel transport costs. Low-temperature approaches in producing solar fuels present advantages in this respect.

In the low-temperature approach, solar energy is used by a suitable semiconductor to generate electrons and holes by charge separations, which react with water and  $\text{CO}_2$ . The reduction of the latter can be a two-step approach (e.g., generation of electricity and then using the electrons to reduce electrochemically/catalytically  $\text{CO}_2$  in a physically separate cell) [57]. Alternatively, a one-step approach is possible by coupling the two processes in a single unit, a photoelectrochemical/catalytic approach [18, 28, 29, 58–60]. The physical separation of the two reactions of water oxidation and  $\text{CO}_2$  reduction, in a photoanode and electrocathode, respectively, is necessary to increase the efficiency of the two reactions and limit charge recombination. The same device can also be used for the production of physically separated flows of  $\text{H}_2$  and  $\text{O}_2$  during water photoelectrolysis.

Many studies have been dedicated to water splitting on semiconductor catalysts under solar irradiation. Recent developments have been reviewed in detail by various research groups [61–63]. Remarkable progress has been made since the pioneering work by Fujishima and Honda in 1972, but the development of photocatalysts with improved efficiencies for hydrogen production from water using solar energy still faces major challenges. Most of the recent efforts focus in the search for active and efficient photocatalysts, for example through new materials and synthesis methods. While good quantum efficiencies (>50%) have been obtained with ultraviolet light, the use of visible light still poses major problems. While in principle the same materials could be used also for the photocatalytic reduction of  $\text{CO}_2$  to fuels, the progresses in this field has been much more limited.

There are several basic problems in the photocatalytic reduction of  $\text{CO}_2$  to fuels. The addition of one electron to  $\text{CO}_2$  leads to the formation of the corresponding anion radical  $\bullet\text{CO}_2^-$ , which is easily transformed to acids (formic and oxalic acids) in water solution. These are the main products of reaction, but their recovery from the water solution is energetically very expensive. While they could be used in fuel cells in principle, the concentration that can be achieved by the photocatalytic reduction of  $\text{CO}_2$  is too small to be used without a further treatment. Moreover, another relevant problem is the low solubility of  $\text{CO}_2$  in water and the abundance of quenching reactions present, which lower the quantum efficiency.

Although the photocatalytic reduction of  $\text{CO}_2$  to gaseous fuels such as  $\text{CH}_4$  has been reported [64, 65], the amounts produced are very limited. In addition,  $\text{O}_2$  forms simultaneously and must be separated from methane. Also, potential safety issues are created. Alcohols such as methanol can also be obtained by photocatalytic reduction of  $\text{CO}_2$  on  $\text{Ag}/\text{TiO}_2$  [66]. A maximum methanol yield of  $4.12 \mu\text{mole}/\text{g}_{\text{cat}} \text{ h}$  was observed, while using  $\text{TiO}_2\text{-SiO}_2$  doped with Cu and Fe, hydrocarbons (methane and ethylene) were formed. It is possible to form alcohols or hydrocarbons by photocatalytic reduction of  $\text{CO}_2$  using different doped photomaterials, but the problems mentioned above are not solved. When liquid products form, their recovery from solution is energetically too expensive. When gaseous hydrocarbons form, they are not separated from the oxygen derived from the simultaneous reaction of water oxidation. In addition, these gaseous products have exactly the same problems of storage/transport discussed previously for  $\text{H}_2$ .

Although the direct photocatalytic reduction of  $\text{CO}_2$  to fuels is potentially attractive, we suggest that it will be not practically feasible and the approach should be based on the physical separation of the water photo-oxidation reaction from the electrocatalytic reduction of  $\text{CO}_2$ , i.e., the photoelectrocatalytic (PEC) approach.

## 2 PEC Approach

The photoelectrocatalytic or photoelectrochemical (PEC) approach involves the separation of the oxidation and reduction processes into two half-cell reactions [59]. Three approaches are possible: the use of (i) photovoltaic (PV) cells, (ii) semiconductor-liquid junctions (SCLJ), or (iii) a combination of the two (PV/SCLJ). The approach based on solid-state photovoltaics is to couple a PV cell and electrolyzer into a single system. Semiconductor layers are connected in series to form a single monolithic device capable of generating the potential needed to split water. These tandem cells or multi-junction cells are modified with, or connected to,  $\text{H}_2$  and  $\text{O}_2$  producing electrodes, like Pt and  $\text{RuO}_2$ -modified Pt acting as cathode and anode, respectively.

An example of recent achievement in this area is a flexible, thin film Cu (In,Ga)Se<sub>2</sub> solar cell deposited on a titanium foil which was combined with a  $\text{TiO}_2$  photocatalyst layer and modified by a niobium-doped titanium oxide front electrode to function as a photoelectrochemical tandem cell/membrane to facilitate the direct, light-driven hydrogen evolution from aqueous solution [67]. Under illumination with UV/visible light, the system produced up to  $0.052 \mu\text{L}_{\text{H}_2}/\text{s cm}^2$  (i.e., the hydrogen formation rate was about  $7250 \mu\text{mol}/\text{h g}$  relative to the amount of  $\text{TiO}_2$  used). Several aspects of the operating principles of the photoelectrochemical devices, the materials requirements, main bottlenecks, and the various device concepts (in relation to  $\text{H}_2$  production) were discussed in a chapter of a recent book on sustainable energy technologies [68]. However, this approach may be adapted



with difficulty to the reduction of  $\text{CO}_2$ , and to date, the attempts in this direction have been quite limited.

In the semiconductor—liquid junction approach, the water splitting occurs at the semiconductor—liquid interface. In 1972, Fujishima and Honda first reported the sunlight-assisted electrolysis of water using crystalline  $\text{TiO}_2$  photoelectrodes [69]. The photoelectrochemical cell consisted of  $\text{TiO}_2$  (rutile) as a photoanode and platinum as a cathode. Illumination of the  $\text{TiO}_2$  electrode led to  $\text{O}_2$  evolution on the anode and  $\text{H}_2$  evolution on the cathode. The quantum efficiency increased with an increase in alkalinity in the  $\text{TiO}_2$  photoanode compartment and in the acidity of the Pt cathode compartment. This means that the thermodynamic potential of 1.23 V required for water splitting was substantially decreased due to the presence of a large pH gradient between the compartments ( $\Delta\text{pH} \sim 13$ , chemical bias  $\sim 0.77$  V).

A photoelectrolysis cell based on two illuminated semiconductor—liquid junctions is another possibility. An *n*-type semiconductor is used for the evolution of  $\text{O}_2$  and a *p*-type semiconductor for the evolution of  $\text{H}_2$ . By separating the oxidation and reduction processes into half-cell reactions, the optimization of each reaction is possible, in addition to reducing recombination. Besides, two semiconductors with smaller band gaps can be utilized since each needs only to provide part of the water-splitting potential. These smaller band gaps mean more absorption in the visible region of the solar spectrum where the sun has a greater photon flux. As a result, the maximum theoretical efficiency is considerably higher.

In the PV/SCLJ approach for overall water splitting, a PV cell is directly combined with a semiconductor that is in direct contact with the electrolyte to form a single integrated unit. The PV cell can be combined either with a reduction (photocathode) or an oxidation (photoanode) photocatalyst.

Using these approaches, good efficiencies in separate  $\text{H}_2$  and  $\text{O}_2$  production are possible even with visible light, although in several cases stability was a major issue, in addition to complexity and cost. These systems may be adapted with difficulty for the solar conversion of  $\text{CO}_2$  to fuels. In general, there is a need to develop robust and cost-effective systems that can be scaled and are suitable for small to medium-sized installations. The key issue for applicability is an approach that intrinsically solves the problem of recovering the fuels produced from  $\text{CO}_2$  and at the same time allows the production of liquid fuels to be used directly in the energy infrastructure.

The feasibility of  $\text{CO}_2$  conversion depends on the ability to form liquid fuels under solventless conditions; such liquid fuels include long-chain hydrocarbons and/or alcohols, which can be easily collected without the need to distill from liquid solutions (a very energy intensive process). There are very few studies based on this novel approach, which will be discussed in more detail in the following section. The need to recycle carbon dioxide to liquid fuels (methanol and dimethyl ether) has been addressed in the perspective paper of Nobel Laureate Olah and co-workers [20], which summarizes the more extensive discussion made in the recent 2nd edition of their famous book on the methanol economy [70].

## 2.1 Novel PEC Solar Cells

For practical use of PEC solar cells, the design of the cells should be quite different from what is used commonly in the literature: devices based essentially on slightly modified conventional electrochemical cells operating in the liquid phase.

The cathode and anode in the PEC device should take the form of thin films separated by a proton-conducting membrane (Nafion<sup>®</sup> for example, but other membranes could be used) and deposited over a porous conductive substrate that allows efficient collection/transport of the electrons over the entire film as well the diffusion of protons to/from the membrane. It is also necessary to allow an efficient evolution of the gas. The reactor geometry and the spatial relation between the reactor and light source are also important, as is the efficient control of the temperature to avoid overheating during operations. It is necessary to have different types of nanostructured electrodes (both at the photoanode and at the cathode).

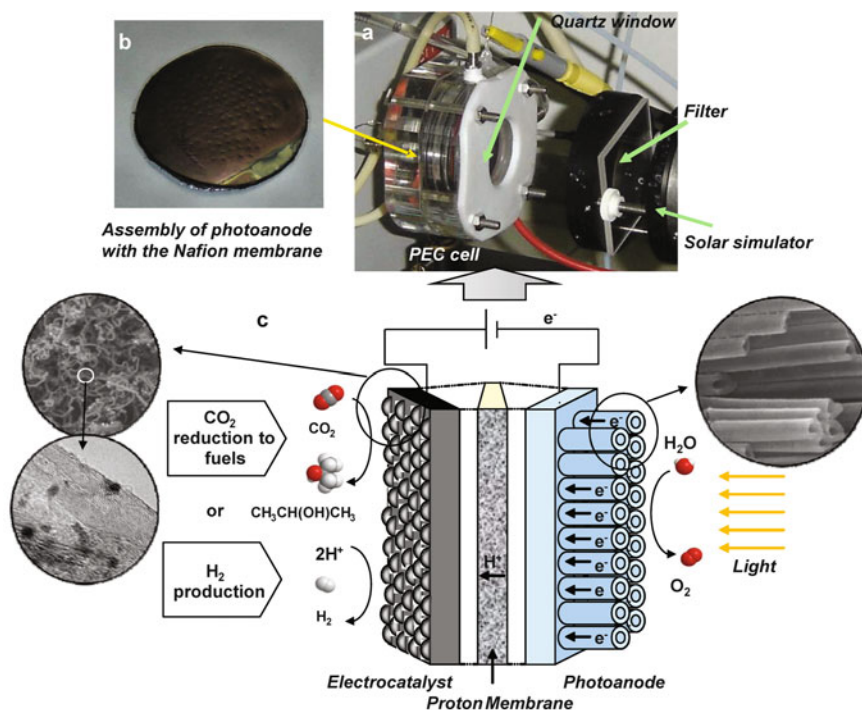
On the cathode side, gas phase operation is necessary for CO<sub>2</sub> reduction to avoid the problem of forming a gas cap over the electrode, CO<sub>2</sub>'s limited solubility in solution and change the type of products formed. Note, the electrocatalytic reduction of CO<sub>2</sub> in gas phase is essentially a new area of development; most of studies focus on liquid phase CO<sub>2</sub> reduction. This would also require new approaches in the type of electrodes to be used.

Electrochemical utilization of CO<sub>2</sub> (in liquid phase) has been studied for many years, as recently reviewed [71, 72]. There are two main approaches, depending whether the conversion of CO<sub>2</sub> is studied in aqueous or non-aqueous solutions. Formic acid is the main reaction product in the electrolysis of aqueous solutions of CO<sub>2</sub> because the carbon dioxide anion radical forms easily by addition of one electron to CO<sub>2</sub> on the electrode surface. Desorption of this product is faster than its consecutive reduction. In addition, a problem in the utilization of CO<sub>2</sub> in aqueous solution derives from its low solubility in water at standard temperature and pressure. Higher pressures are necessary to increase the CO<sub>2</sub> concentration in the liquid phase, but electrode stability in these conditions is limited [73].

Solvents with high solubility for CO<sub>2</sub> are used in the non-aqueous electrochemical reduction. However, high CO<sub>2</sub> solubility requires larger current density, but low electrolytic conductivity leads to high Ohmic losses. High current densities are also necessary to maximize the formation of hydrocarbons. Also, a fast deactivation can occur under these conditions [74].

A solventless electrocatalytic reduction of CO<sub>2</sub> would overcome these problems and can form more valuable products (liquid fuels) as it will be discussed later. A novel design for the PEC solar cell is necessary for this scope. An example is presented in Fig. 1. The apparatus for the photocatalytic experiments consists of a solar illuminator source, a photo-reactor and gas chromatographs for on-line analysis. The lamp housing is furnished with a Xe-arc lamp (ORIEL, 300 W), a set of lenses for light collection and focusing, and a water filter, to eliminate the infrared radiation.

The PEC solar cell consists of three layers: a nanostructured TiO<sub>2</sub> thin film supported on Ti prepared by anodization, a Nafion<sup>®</sup> membrane for electrical



**Fig. 1** **a** View of the lab-scale PEC device. **b** Image of the assembly of the photoanode with the Nafion<sup>®</sup> membrane and the electrocatalyst (*on the back*). **c** Scheme of the PEC device for CO<sub>2</sub> reduction to fuels and H<sub>2</sub> production. In the inset, SEM images of the photoanode and the electrocatalyst. Adapted from Ampelli et al. [29]

insulation and proton transport, and an electrocatalyst (Fig. 1). This PEC device can be used either for water photo-splitting/-electrolysis with separate evolution of O<sub>2</sub> and H<sub>2</sub>, or for the CO<sub>2</sub> reduction to liquid fuels using solar energy. In the H<sub>2</sub> photoproduction configuration, the electrocatalyst is a carbon cloth (E-tek<sup>®</sup>) with a high platinum dispersion (20%). For CO<sub>2</sub> reduction, the electrocatalyst is the electrode prepared by the deposition of Fe/CNT or Pt/CNT (carbon nanotubes) on carbon cloth, described later. The assembly of the disc was performed by hot-pressing at 120°C under a pressure of 20 kg/cm<sup>2</sup>.

## 2.2 Photoanode and Role of Titania Thin-Film Nanostructure

The photoanode in a PEC solar cell, as introduced before, should be in the form of a porous thin film allowing good light harvesting, fast transport of the protons and electrons produced during the water oxidation, and good contact with both the

electron-collector substrate and the proton-conductor membrane. There is a need to have a specific nanostructure in the photoanode.

The use of an array of 1D aligned nanostructures (nanorods, nanotubes, etc.) improves light harvesting and limits charge recombination at the grain boundaries with respect to an assembly of nanoparticles, while maintaining a high surface area necessary to improve the photoresponse [23, 75–77]. An optimal contact/interface with the  $H^+$ -membrane is also necessary.

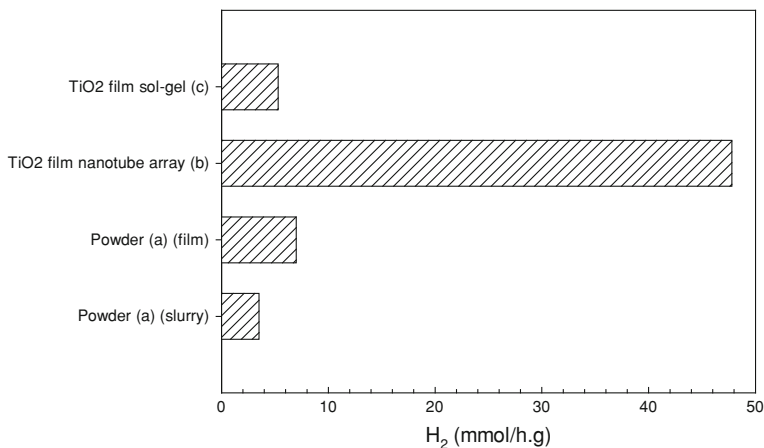
A further general issue is the need of a preparation method to produce the photoanode that (i) is cost-effective, (ii) allows a good control of the nanostructure in terms of 1D-array characteristics (vertical alignment, density, and thickness), and (iii) can be easily scaled to large films (at least  $10 \times 10$  cm). The choice of suitable preparation methods having all of these characteristics is quite restricted [75, 76]. We have therefore focused our attention on the anodic oxidation of titanium thin foils [76, 78, 79] to synthesize 1D nanostructured titania arrays to be used as photoanode in PEC solar cells.

These  $TiO_2$  materials show excellent properties in the preparation of solar cells and photoelectrodes [80–82]. We limit discussion here to not doped titania films, but their reactivity properties, which can be further promoted by doping or creating of heterostructures. Such structures promote visible-light absorption and effective transfer of electrons from the valence to the conduction band of titania.

A critical question is whether clear proofs exist that the use of a specific nanostructure has advantages in terms of photo-performances. In fact, notwithstanding the fast-growing literature on the subject (discussed in detail in the cited reviews and books [76, 78, 79]), often a clear comparison with conventional titania films (under comparable conditions) is not made.

An example of such a comparison is shown in Fig. 2 [29], which reports the performances in ethanol photoreforming for  $H_2$  production of three different titania films: (a) produced by pressing commercial P25 Degussa  $TiO_2$ , (b) prepared by anodic oxidation of Ti foils, and (c) prepared by sol–gel dip-coating method. For comparison, the results obtained with P25 Degussa using a slurry-type well-mixed reactor are also reported. All of these titania samples were loaded with 0.5 wt% Pt by wet impregnation because without Pt all the samples show very low activity in photoreforming [83]. The data in Fig. 2 demonstrate that the specific photoreforming activity (per amount of titania) considerably depends on both the reactor geometry and the nanostructure of the titania thin film.

P25  $TiO_2$  Degussa is a classical reference material in photocatalysis. Under the tested reaction condition this material shows about twice the specific activity when used in the form of a thin film than as a suspended powder (slurry reactor), due to reduced light scattering. The sample prepared by sol–gel dip-coating, also a conventional method to prepare titania thin films, shows performances quite similar to those of the thin film prepared by compacting the P25  $TiO_2$  nanoparticles. On the contrary, the thin film in the form of an ordered array of vertically aligned  $TiO_2$  nanotubes (produced by anodic oxidation) shows higher activity than the other samples. It is evident that the nanostructure of  $TiO_2$  has a large effect. There are several reasons for this improvement: better light harvesting, lower rate

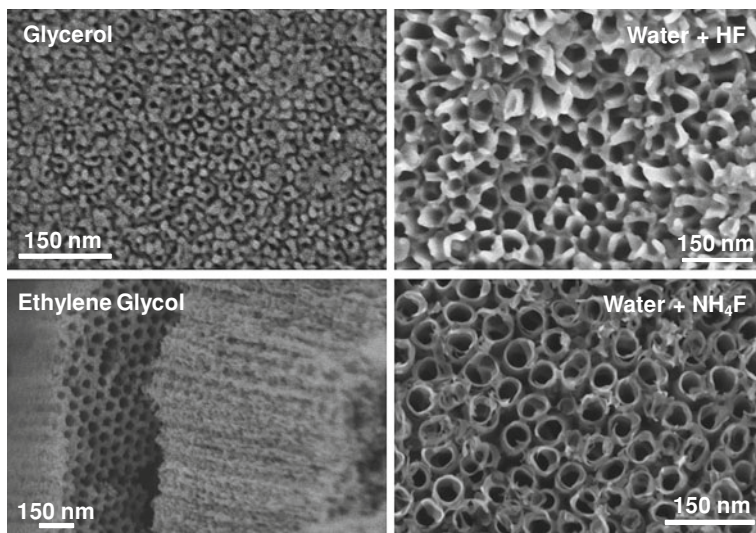


**Fig. 2** Hydrogen evolution rate for different kinds of TiO<sub>2</sub> samples during photoreforming of 10% ethanol in water. **a** Degussa P-25 TiO<sub>2</sub> powder; **b** ordered array of TiO<sub>2</sub> nanotubes prepared by anodization on Ti foil; **c** TiO<sub>2</sub> dense film prepared by sol-gel dip-coating. In all samples 0.5 wt% Pt was added by wet impregnation. Adapted from Ampelli et al. [29]

of recombination at the grain boundaries, reduced effects related to formation of a H<sub>2</sub> cap, faster electron transport and charge separation, and a nanostructure that increases the absorption of visible-light components. The result of these effects is that the specific activity of the TiO<sub>2</sub> nanotube array thin film has significant higher activity in H<sub>2</sub> photoreforming.

Similar observations have been made in water photoelectrolysis (splitting), although the activity in hydrogen production is lower than in the photoreforming of ethanol [29]. A parallel trend for the photocurrent generated during the reaction and the amount of H<sub>2</sub> formed was also demonstrated [29]. This is a general observation that is in accordance with the indication that the reaction of H<sub>2</sub> production from water on semiconductors such as titania is effectively a photoelectrolysis rather than a photocatalytic splitting as often described. In other words, the semiconductor generates an electric current by adsorbing solar light and these promoted electrons are responsible for the electrolysis of water at short-circuited nanoelectrodes. The latter are associated with the metal nanoparticles (Pt, for example).

The process of anodic anodization used to prepare the nanostructured titania thin films can be summarized, by analogy with the formation of porous alumina by anodization [84], as follows. When the Ti foil, after the preliminary cleaning treatment, is immersed in the electrolyte for the anodization process, a fast surface oxidation occurs with formation of a thin TiO<sub>2</sub> layer. This process can be monitored by a fast decrease of the current, since the TiO<sub>2</sub> layer is not conductive. Due to the presence of an aqueous solution of HF as electrolyte, the solubilization of Ti<sup>4+</sup> ions and/or of small TiO<sub>2</sub> particles starts simultaneously with the formation of the oxide layer. These processes lead to the formation of holes,



**Fig. 3** Role of the electrolyte on the nanostructure of titania films produced by anodic oxidation. SEM images (*top view*, apart cross-section in the case of ethylene glycol) of titania nanotube arrays prepared by anodic oxidation under different conditions: (i) in glycerol + 0.5 wt%  $\text{NH}_4\text{F}$  at pH 6 applying a 20 V potential for 45 min. (ii) in water + 0.5 wt% HF at pH 0 applying a 15 V potential for 45 min. (iii) in ethylene glycol + 0.3 wt%  $\text{NH}_4\text{F}$  and 2 vol%  $\text{H}_2\text{O}$  applying a 50 V potential for 6 h. (iv) in water + 0.5 wt% HF at pH 4 (adjusted with  $\text{NH}_4\text{OH}$ ) applying a 20 V potential for 45 min

which locally modify the electric field and induce from one-side the acceleration of the process of dissolution, due to field-enhanced effects, and from the other side the oriented growing of a 1D structure (nanotubes, nanorods, etc.). All of these processes are strongly influenced by the reaction conditions, which, in turn, determine the characteristics of the different nanostructures.

The electrolyte and conditions of anodization influence the film characteristics (thickness, type of nanostructure, specific features on 1D nano-objects, etc.). An example is given in Fig. 3 which reports the scanning electron microscopy (SEM) images for two cases using organic electrolytes and two different anodization conditions in an aqueous medium in the presence of fluoride ions. All these titania nanostructured films give very different performances in terms of photocurrent generation upon irradiation and photocatalytic activity.

The film thickness increases with the time of anodization with a consequent increase of the photocurrent. While minor differences are observed using either water or glycerol as the solvent, a very large difference is observed using ethylene glycol as the solvent. In this case, a photocurrent density of about an order of magnitude higher is observed, particularly for the longer anodization times. Using ethylene glycol, very regular straight  $\text{TiO}_2$  nanotubes with thick walls are obtained (see Fig. 3). At longer times of anodization, the presence of an amorphous titania deposit on the surface is observed, but this debris can be removed from the surface

by sonication. The photocurrent generated during irradiation could be measured in situ also during the catalytic reaction using the apparatus schematized in Fig. 1.

### 2.3 Nanostructured Electrodes for CO<sub>2</sub> Gas-Phase Reduction

In the liquid phase, electrochemical reduction of carbon dioxide Cu-based foils as electrode materials gives the best results to form hydrocarbons [71, 72]. High current densities are necessary to maximize the formation of hydrocarbons. Hori et al. [74], using immobilized CuCl on a Cu-mesh electrode, reported a Faradaic efficiency of about 70% to C<sub>2</sub>H<sub>4</sub>, although the electrode quickly deactivates. In addition, corrosive media (high pressure, metal halides) are used because they are necessary to promote a high surface concentration of CO<sub>2</sub> at the electrode. Also of note, Cu is the only metal, which gives appreciable amounts of C<sub>2</sub> hydrocarbons. Several critical aspects determine the performance, such as (a) the gas evolution in the electrochemical cells, which reduces electrolyte conductivity and increases Ohmic resistance, (b) the pH and reaction temperature, which negatively influence the solubility of CO<sub>2</sub> and selectivity to C<sub>2</sub> products [85], and (c) the porosity of the electrodes. Using TiO<sub>2</sub> nanotube composite electrodes for the electrochemical reduction of CO<sub>2</sub> to methanol [86], current efficiencies over 60% were reported.

The reaction network in the CO<sub>2</sub> electrocatalytic reduction on Cu-electrodes involves an initial stage of formation of carbon dioxide anion radicals  $\bullet\text{CO}_2^-$ , which shows why metal halides are necessary to promote the reaction. The next step leads to the formation of adsorbed carbon monoxide (CO) which can react with protons and electrons (in the presence hydroxide anions) to give water and chemisorbed methylene (:CH<sub>2</sub>). The latter may be further hydrogenated to CH<sub>4</sub> or react with another methylene intermediate following a Fischer–Tropsch like chain growth mechanism.

Alkanes and alkenes up to C<sub>6</sub> hydrocarbons were recently reported by Shibata et al. [87] using a Cu-electrode that was not pre-treated by electropolishing. The product distribution follows the Schultz–Flory distribution and, depending on the applied potential, the chain growth probability ( $\alpha$ ) ranges from 0.23 to 0.31, values lower than those obtained in Fischer–Tropsch synthesis over heterogeneous Co- or Fe-based catalysts. When the same electrode material was pre-treated by electropolishing it behaved like a pure Cu-electrode, yielding mainly methane and ethene.

These results show that the electrode's specific nanostructure affects the performances and type of products formed. In these tests, flat-type electrodes have been used, as typically made for electrochemical studies. However, as discussed before, the feasibility of CO<sub>2</sub> conversion to fuels depends on the formation of long-chain hydrocarbons and/or alcohols and the use of solventless reaction conditions. This suggests using different types of electrodes.

The PEC solar cell reported in Fig. 1 is analogous to proton-exchange membrane (PEM) fuel cells, where the reaction of O<sub>2</sub> reduction is also made in the gas phase. The commercial electrodes for PEM fuel cells typically use a

tissue of carbon macrofibers (carbon cloth—CC) as a substrate, which has the function of electron transport and allows a homogeneous dispersion of the electrocatalyst and good diffusion of the gases. On CC, the electrocatalyst is deposited on the side in contact with the proton-conducting membrane (Nafion<sup>®</sup> 112, for example).

On the anode side, Pt (20 wt%) deposited on carbon black (for example, Vulcan XC-72 carbon black) is used as the electrocatalyst. The typical size of noble metal particles is around 2 nm. On the cathode side (O<sub>2</sub> reduction) Pt-Ru bimetallic electrocatalysts also deposited on carbon black are used. Moreover, on the sides of the CC, which are in contact with the gas phase, a hydrophobic porous layer is created (for example, by deposition of a Teflon solution), in order to avoid the dehydration of the proton-conducting membrane. This structure is called the gas diffusion electrode (GDE). The anode and cathode GDE are then hot pressed with the Nafion to realize the final composite known as membrane-electrode assembly (MEA) to be used in the PEMFC.

For the electrocatalytic reduction of CO<sub>2</sub> commercial-type electrodes for PEM fuel cells were used [87, 88] (e.g., a carbon cloth/Pt on carbon black/Nafion assembled electrode). The electrocatalyst is Pt supported on carbon black, which is then deposited on a conductive carbon cloth to allow the electrical contact and the diffusion of gas-phase CO<sub>2</sub> to the electrocatalyst. The Pt particles are in contact with Nafion, through which protons diffuse.

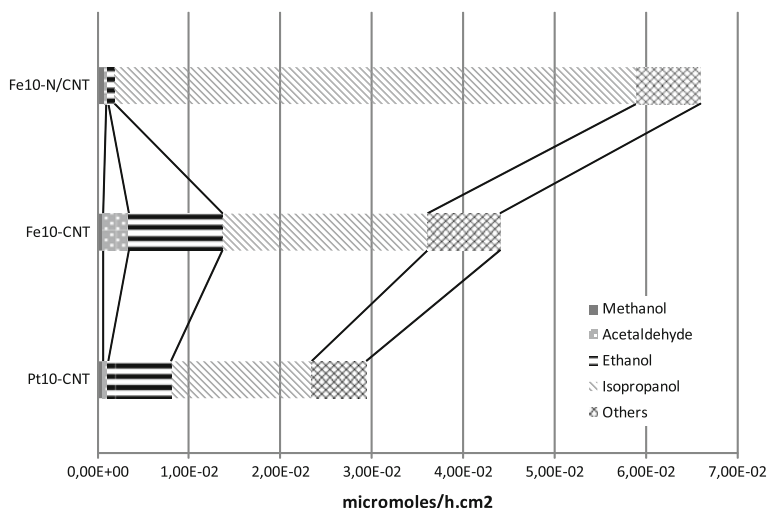
On the Pt nanoparticles, gas-phase CO<sub>2</sub> reacts with electrons and protons to be reduced to long-chain hydrocarbons and alcohols, with relative distributions dependant upon the reaction temperature. At room temperature, long-chain hydrocarbons (up to C<sub>9</sub>) were formed, but with low productivities [88, 89]. At 60°C and atmospheric pressure, acetone was found to be the major product of conversion.

Flat-type carbon electrodes (i.e., glassy carbon) were not effective. Due to the active carbon's high porosity, the Pt nanoparticles were mainly located inside nanopores. To realize an efficient reduction of CO<sub>2</sub>, it is necessary to optimize the three-phase reaction at the catalyst surface between the protons diffusing through the Nafion membrane, the electrons necessary for the carbon dioxide reduction, and the CO<sub>2</sub> from the gas phase. Furthermore, the formation of C–C bonds should be enhanced when CO<sub>2</sub> (and its products of conversion) remains confined over the electrocatalyst surface. Thus, nanoporosity (nanoconfinement concept) should have a role in forming products with longer C-chains from CO<sub>2</sub>.

However, it is equally important to guarantee fast diffusion of the protons and electrons to the electrocatalytic nanoparticles. The latter should be in good contact with a conductive (graphitic) carbon support. For this reason, carbon nanotubes should be used as the substrate instead of active carbon because they combine good electron conductivity with a specific nanostructure, thereby optimizing the nanoconfinement.

Using a similar GDE configuration, but with carbon nanotubes as the substrate for the electrocatalyst nanoparticles, it is possible to form isopropanol as the main reaction product [90, 91] (Fig. 4). This figure also shows that the electrocatalyst





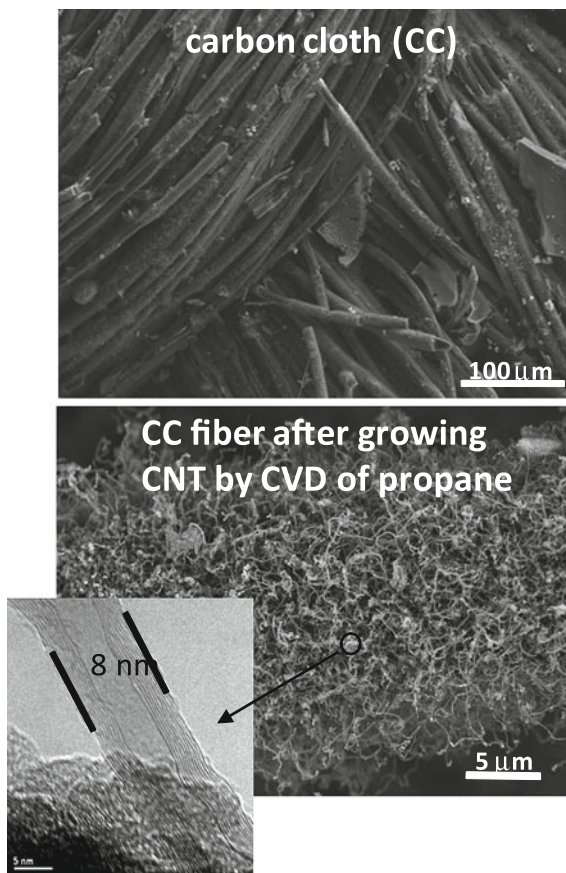
**Fig. 4** Products distribution at 60°C in the electrocatalytic reduction of carbon dioxide in gas phase over Nafion 117/(Pt or Fe(10%)/CNT)20%/carbon cloth GDM (gas diffusion membrane) electrode. Tests in a semi-batch cell, using a 0.5  $\text{KHCO}_3$  electrolyte on the anode side and operating the cathode in the gas phase with a continuous feed of 50%  $\text{CO}_2$  in humidified nitrogen. Adapted from Centi and Perathoner [90] and Gangeri et al. [91]

can be based on iron nanoparticles instead of a noble metal. In any case, the Pt-based electrodes show better stability on carbon nanotubes. In addition, it is shown that the use of N-doped carbon nanotubes (N/CNT) allows a further improvement in the productivity of isopropanol. This is related to two concepts. The first is a better dispersion and stabilization of the metal particles, due to the creation of nitrogen moieties, which anchor the nanoparticles. The nature and amount of these nitrogen species (which depends on the modalities adopted to dope the carbon nanotubes with nitrogen sources, and the thermal treatment after this doping procedure) influences the performances. The second is a modification of the hydrophilic properties of the carbon nanotubes which influences the contact interface with the Nafion<sup>®</sup> and the diffusivity of the protons.

In general, the doping and creation of surface defect sites in carbon nanotubes, increasing the number of surface functional groups on each CNT, influences various aspects: (i) the efficiency of the three-phase boundary and the transport of protons to or from the active metal particles, (ii) the resistance of electron transfer, and (iii) the intrinsic reactivity properties of the metal nanoparticles. Many aspects determine the final properties.

There are other aspects to consider in the optimization of the performance of nanostructured electrodes for  $\text{CO}_2$  gas-phase reduction, such as the presence of a suitable 3D organization to maximize the contact with the Nafion, promotion of an efficient diffusion of  $\text{CO}_2$  and back-diffusion of the reaction products, and limited dehydration of Nafion, which negatively affects the transport properties of the

**Fig. 5** Top image: electron microscopy images of carbon cloth used as substrate to create the necessary flexible grid to allow electron transport and good diffusion of the gases. *Bottom image:* carbon nanotubes covering a carbon macrofiber; the CNTs were obtained by propane CVD after deposition on the carbon cloth of a suitable catalyst (Fe, Co nanoparticles); in the inset a higher resolution image of one CNT growing from the catalyst [90]



membrane and proton diffusion. For this objective, the use of a hierarchically organized structures by growing carbon nanotubes over carbon macro fibres (CC) has been proposed [90, 92].

Figure 5 shows an example of these materials prepared by deposition of a Co-Fe/SBA-15 catalyst onto carbon cloth and the use of these catalysts to grow CNT by the propane CVD method [90]. It was observed that the CNTs uniformly cover the carbon macrofibres. This allows for the improvement of the surface area of carbon while avoiding the need to use the carbon black as the support for Pt. The use of hierarchically organized structures provides a better 3D geometry for contact with the Nafion. However, the properties of these materials are not optimal in terms of wettability by the Nafion and transport of protons. Thus modification is necessary to optimize the performances. Also tuning the conductivity properties by annealing in an inert atmosphere is necessary. There are therefore many aspects that must be controlled and optimized to prepare the optimal electrocatalysts for the CO<sub>2</sub> conversion to fuels.

### 3 Conclusions

The interest in the use of solar energy is quickly growing, as is the need to find efficient solutions to reduce the negative effects associated with large volumes of CO<sub>2</sub> emissions. We have discussed here an approach to combine these two aspects by producing solar fuels from water and CO<sub>2</sub>. In this vision, liquid fuels produced by recycling CO<sub>2</sub> using solar energy are ideal energy vectors, easy to store/transport and fully integratable with the existing energy infrastructure.

The approach discussed to reach this objective is based on a novel photoelectrocatalytic (PEC) device, which solves some of the potential issues in the photoelectrochemical or photocatalytic approaches to convert carbon dioxide. This device needs some specific new characteristics in the photoanode and electrocatalyst, which were briefly discussed. In particular, some aspects related to the characteristics of nanostructured (a) TiO<sub>2</sub> thin films (based on an ordered array of titania nanotubes) and their performances as photoanodes, and (b) carbon-nanotube-based electrodes for the gas phase reduction of CO<sub>2</sub> to liquid fuels (mainly isopropanol) was presented. Finally, their application to the design of a novel photoelectrocatalytic (PEC) approach for the synthesis of solar fuels has been analyzed.

This is an area currently under fast development worldwide and significant progress is expected in the near future. We feel that the PEC reactor design discussed here is a good attempt toward the practical implementation of solar fuels, even if the passage from the proof-of-the-concept (actual state) to the practical implementation still requires significant research.

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