Nano-Engineered Electrodes for the Generation of Solar Fuels: Benefits and Drawbacks of Adopting a Photo-Electrocatalytic (PECa) Approach

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In this contribution, the advantages of adopting a photo-electrocatalytic (PECa) approach for the production of solar fuels were discussed through the analysis of the factors that can influence the performances of PECa cells. Particularly, there are some issues, conventionally not studied, that should be taken into account already at the initial stage of cell design, such as: i) light harvesting and charge separation, ii) electron conductivity and mass diffusion, iii) productivity and type of products formed. The choice of the electrodic materials and the preparation of nanostructured electrodes are of great importance to improve the above aspects, by enhancing the photo-catalytic activity and limiting the overpotential of the cell. The experimental data were obtained by preparing and testing two different types of electrodes, one based on highly ordered TiO_2 nanotube arrays (the photo-anode) and the other based on Cu nanoparticles deposited on nano-carbons (the electro-cathode). The electrodes were assembled together and located in a compact device with two separate compartments for each half-reaction. Finally, they were tested in the process of water photo-electrolysis and/or photo-reforming of organic wastes for the production of H_2, as well as in the process of CO_2 reduction to liquid fuels. Results, given in terms of H_2 evolution, solar-to-hydrogen (STH) efficiency and liquid fuel productivity, were very promising. Particularly, 195 μmol of H_2 were produced in 4 h of light irradiation without adding sacrificial donors, being over 16 % of this production due to only solar irradiation. This attractive result (if considering that non-doped TiO_2 was employed as the photo-anode) is to ascribe to the enhanced visible light absorption of TiO_2 nanotube arrays (due to their structural resonance effect) and to the reduced charge recombination (for their improved electron transfer). On the other hand, CO_2 electrocatalytic reduction allowed obtaining not only formic acid (as usually obtained in conventional cells) but also methanol, ethanol, acetic acid, isopropanol and acetone. The formation of these products is due to the catalytic sites located in the interface between the small copper particles and the carbon surface, favouring electron transfer and C-C bond formation.

1. Introduction

The photo-electrocatalytic (PECa) approach for the production of solar fuels is an attractive technology for the tomorrow's sustainable production of energy (Armaroli and Balzani, 2016). PECa systems consist of compact devices, similar to fuel cells, with separated zones for the reactions of oxidation (photo-anode) and reduction (electro-cathode) (Hisatomi et al., 2014). The small volume and the separation of the two reaction environments are both aspects of fundamental importance to enhance the photo-catalytic activity, as they i) reduce the charge recombination effects, ii) limit overpotential due to mass transport and proton diffusion, and iii) avoid safety problems and costs for the separation of products (Ampelli et al., 2016a). One of the important challenges for the future commercialization of PECa cells is the preparation of active, robust and low-cost catalysts (Li and Wu, 2015), as well as a proper design of the configuration of the cell and the related catalytic electrodes (Zhao et al., 2016). However, there are some issues that currently limit the efficiency of solar PECa

cells and that should be taken into account in designing the electrodes: i) light harvesting and band gap structure of the photo-catalysts, ii) charge separation efficiency, iii) good collection of the charges iv) catalytic activity and selectivity of the redox half-reactions and v) overall efficiency and productivity. The preparation of 3D nanostructured electrodes can highly favour all these factors, by increasing the active area and limiting the overpotential phenomena (Ampelli et al., 2016b). Recently, hierarchical tree-like TiO_2 nanostructures, showing improved electron transfer, were successfully proposed as photoanodes for photoelectrochemical water splitting (Matarrese et al., 2014).

In this context, we discuss here about our recent findings on the preparation of the electrode materials and assembling of the electrodes in our novel design PECa cells. Particularly, the electrodes are based on highly ordered TiO_2 nanotube arrays and metal nanoparticles (NPs) deposited on nano-carbons, and they were tested in the process of water photo-electrolysis and/or photo-reforming of waste organic solutions for the production of H_2, as well as in the process of CO_2 reduction to liquid fuels. The production of higher C-chain compounds (C2-C9 hydrocarbons, alcohols, oxygenates, etc.) should be preferable with respect to H_2, as liquid fuels can easily be stored and transported by using the current energy infrastructure (Ampelli et al., 2015a).

2. Experimental

2.1 Photo-anode

TiO_2 nanotube array (TNTs) photo-electrodes were prepared by controlled anodic oxidation of Ti foils. The essence of the method can be described as a reconstruction of a thin TiO_2 layer (formed initially by oxidation of a Ti foil) which occurs under the application of a constant voltage in presence of fluoride-based electrolytes (Macak et al., 2007).

The starting titanium disc (Alfa Aesar, 0.025 mm of thickness, 3.5 cm of diameter) was anodized using a two-electrode electrochemical cell working at room temperature and constant voltage (in the range 15-60 V) for times until 5 h (Ampelli et al., 2017a). The reaction bath consisted of a solution of ethylene glycol with H_2O (2 wt. %) and NaF (0.3 wt. %). Details about the geometry of the cell and the synthetic procedure were described elsewhere (Ampelli et al., 2015b).

After the preparation, the nanostructured amorphous substrates were annealed at 450 °C in air for 3 h in order to induce crystallization into the anatase phase. The thin metallic Ti layer (remained non-oxidized after the anodization) can act as the electron-collective layer during the photo-catalytic process.

2.2 Electro-cathode

Metal Cu nanoparticles (NPs) were deposited onto a nanocarbon substrate by incipient wetness impregnation method using an ethanolic solution containing the metal precursor [$Cu(NO_3)_2 \cdot 3H_2O$]. The total amount of copper loaded onto the carbon substrate was finally 10 wt. %. The nanocarbon substrate consists of commercial carbon nanotubes (CNTs, PR-24-XT-PS Pyrograf®), having an average diameter of about 100 nanometers. They were pyrolyzed at 750 °C to remove polyaromatic hydrocarbons from their surface. Due to their turbographic structure, these CNTs offer a large number of sites for functionalization of the external surface (Genovese et al., 2013). CNTs were activated by direct oxidative treatment in concentrated HNO_3, thus introducing oxygen functionalities on the carbon surface. Details about the pre-treatment of CNTs and metal deposition were reported elsewhere (Ampelli et al., 2015c). The as-prepared electrocatalyst was then deposited on a gas diffusion layer (GDL 25-BC Sigracet®).

2.3 Assembling the electrodes in PECa cell

The two electrodes (TNTs and Cu/CNTs/GDL layers) were assembled together by hot pressing with a Nafion® membrane to form a Membrane Electrode Assembly (MEA), as it is shown in Figure 1. The MEA was then located within the PECa device and tested in different processes for the production of solar fuels.

The mechanism of reaction can be described as follows: i) the irradiated light, coming from an external solar simulator (Xe-arc lamp of 300 W, Lot Oriel), reaches the photo-anode surface creating a charge separation (electrons e^- and holes h^+), ii) the holes oxidize the water to oxygen (or the waste organics to CO_2 in the case of photo-reforming), iii) protons and electrons are transferred to the cathode compartment (the protons crossing the Nafion® membrane and the electrons through an external circuit) iv) where they combine to produce H_2 (or combine with CO_2 to form liquid fuels).

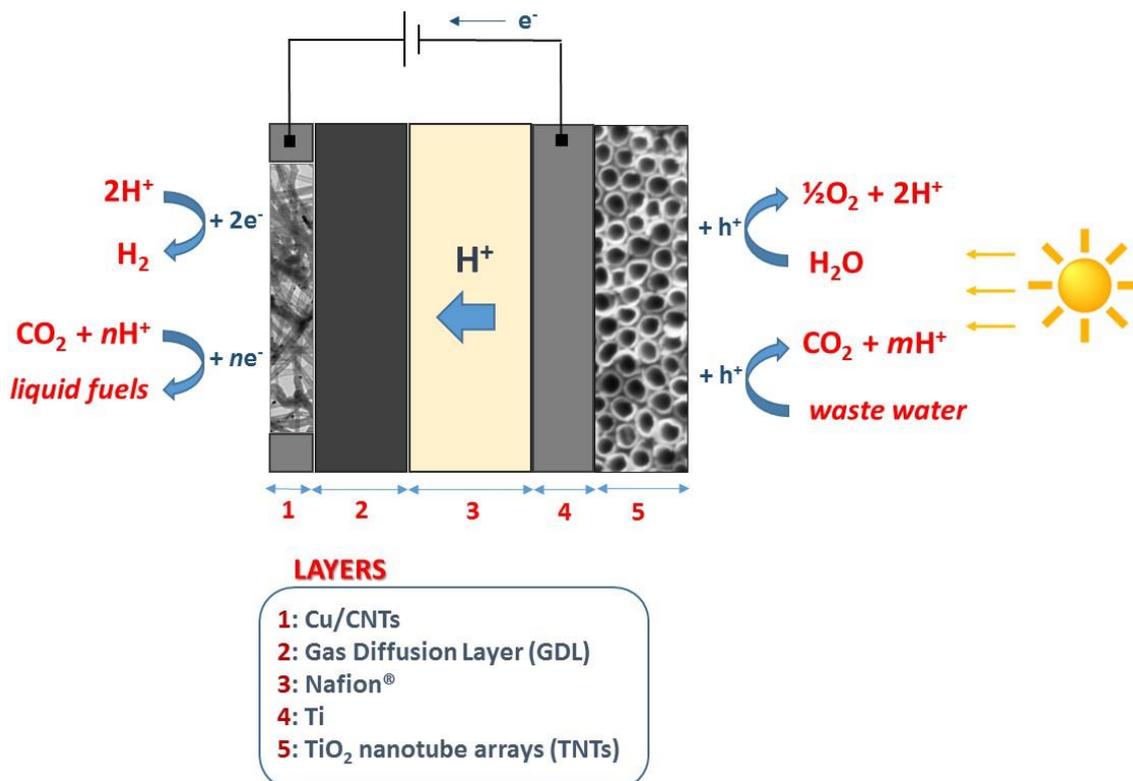The products were finally analysed by gaschromatography (GC) and mass spectrometry (MS).

Figure 1: Schematic depiction of the Membrane Electrode Assembly (MEA) in a solar PECa cell. The insert in layer 1 shows a TEM image of Cu/CNTs, while the insert in layer 5 shows a SEM top image of TiO₂ nanotube arrays prepared by anodic oxidation.

3. Results and discussion

3.1 Benefits and drawbacks of PECa cells

There are many benefits in adopting the PECa approach for the production of solar fuels. In general, even if other technologies can be used to convert solar energy into chemical energy (i.e. high temperature thermochemical approach), PECa systems are potentially more advantageous as: i) they work at room temperature (or at temperatures slightly higher than r.t., i.e. 50-60 °C, taking into account that temperature may increase during exposition to sunlight); ii) the electrolyte can fully be recycled, but we demonstrated that electrolyte-less configuration is also possible (Ampelli et al., 2016a); iii) the energy required for the process comes solely from sunlight; iv) the production of liquid fuels is performed by converting back CO_2, thus diminishing its level in the environment and closing its cycle of production/consumption (Goeppert et al., 2014).

The particular benefits of using a PECa device, instead, refer to: i) the separation of the products of oxidation (O_2) and reduction (H_2, or the products of CO_2 reduction), avoiding safety problems, costs of separation, quenching effects, ii) the continuous operation, with easy recovery of the reaction products, and iii) the compact design, easily scalable. These aspects should all be taken into account in designing the cell, because they determine the choice of the materials constituting the electrodes and their needs (Ampelli et al., 2017b).

However, there are many constrains, not accounted in general, which limit the performances of PECa cells. They are mainly related to problems of light harvesting, charge recombination, electron transport, proton diffusion, which increase the overpotential of the cell. The development of nanostructured electrodes may strongly improve the PECa performances, by limiting the above overpotential phenomena and enhancing the quantum efficiency and productivity of the cell.
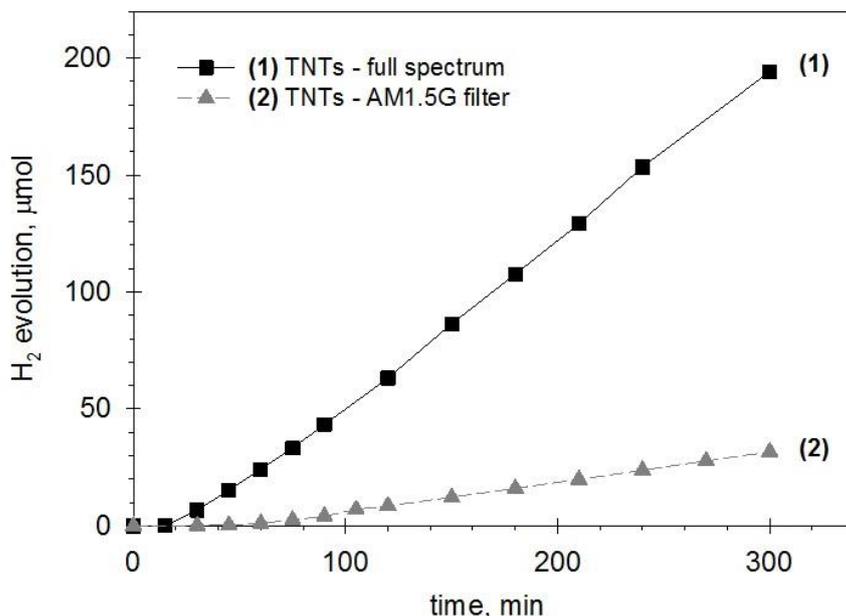
Figure 2: Hydrogen evolution as a function of time from the cathode of a PECa cell in water photo-electrolysis.

3.2 Photo-anodes for H$_2$ production

TNTs prepared by anodic oxidation were tested in the process of water photo-electrolysis. Figure 2 shows the H$_2$ production detected in the gaseous stream leaving the cathode. After an initial induction period of 10-15 min, due to establish the equilibrium in the cell, the H$_2$ evolution increased linearly with a quite constant production rate, at least in the time range investigated. We also detected O$_2$ evolution in the anode side of the PECa cell and the H$_2$:O$_2$ ratio was the expected for stoichiometric water photo-electrolysis. No H$_2$ was instead detected in the anode part. When a full spectrum of irradiated light was used, ~195 μmol of hydrogen were measured after five-hour time of irradiation.

It is well known that one of the main drawbacks of TiO$_2$ is that it works only if irradiated in the ultraviolet (UV) region. Being the UV part only a short percentage of the solar irradiation, the challenge is to shift the TiO$_2$ band gap to the visible region, thus exploiting better the entire solar spectrum. Creating a nano-architecture in TiO$_2$ can improve its visible light absorption, due to the structural resonance effect for light diffraction (Ampelli et al., 2017b).

By cutting the light irradiation using a filter AM 1.5G (this filter simulates the standard terrestrial solar irradiance distribution), the quantity of H$_2$ at the cathode decreased to ~32 μmol after five-hour time of irradiation, which is over 16 % with respect to H$_2$ productivity obtained at open spectrum. Considering that the percentage of UV light in solar spectrum is only 4 %, the result obtained by AM 1.5 G filter evidences an improved performance of TNTs in the visible region with respect to standard TiO$_2$.

If ethanol (10 vol. %) was added into the photo-anode, H$_2$ productivity increased even to ~355 μmol (not shown in the figure) with a side production of acetaldehyde (ethanol dehydrogenation). This may open the route for a new application, the treatment of waste organic solutions containing alcohols, i.e. coming from biorefineries, which are too dilute to be processed by conventional catalytic routes.

Table 1 reports the solar-to-hydrogen (STH) efficiency calculated following the Eq.(1) (Varghese and Grimes, (2008):

$$STH = \frac{R_{H2} * \Delta G^0}{Ptot * A} \tag{1}$$

where R$_{H2}$ is the rate of hydrogen production (mol·s^{-1}), ΔG^0 is the standard Gibbs energy at standard conditions (2.372 x 10^5 J·mol^{-1}), P$_{tot}$ is the light irradiance (W cm^{-2}) and A is the irradiated area of the photocatalyst (cm^2).

Table 1: Solar-to-hydrogen (STH) efficiency (%) for TNTs-based photoanode.

Process	Irradiated light	STH (%)
Water photo-electrolysis	Full spectrum	0.83
Water photo-electrolysis	AM1.5G filter	0.23
Ethanol photo-reforming	Full spectrum	1.43
Ethanol photo-reforming	AM1.5G filter	0.24

3.3 Electro-cathodes for CO_2 reduction

The Cu/CNTs/GDL electrodes were tested in the process of CO_2 electrocatalytic reduction, in presence of aqueous $KHCO_3$ (0.5 M) electrolyte and 10 mL pure CO_2 flow. In these experiments, solar light was simulated by applying a small bias (-1 V) between the two electrodes.

Table 2 summarizes the productivity of the liquid products obtained in the reduction process. Under these conditions, formic acid and acetic acid formed as the main products with similar productivity (4.25 and 4.17 μmol in 4 h, respectively), while 0.27 μmol of methanol was also produced.

Table 2: Products obtained from the electrocatalytic reduction of CO_2 in 4 h of applied potential (-1 V).

Electro-cathode	Formic acid, μmol	Acetic acid, μmol	Methanol, μmol
Cu/CNTs/GDL	4.25	4.17	0.27
CNTs/GDL	1.29	0.88	-

The analysis of the outlet gaseous stream leaving the cathode revealed the formation of H_2, with a rate of production of 0.32 μmol min^{-1}, while no CO and CH_4 were detected. The observed rates of reaction remained quite constant until 24 h, evidencing a good stability on a laboratory scale. The data obtained by the electrocatalytic test with only CNTs/GDL (the CNTs were functionalized by oxidative pre-treatment but no Cu particles were deposited) are also reported in Table 2, in order to evaluate the catalytic influence of the CNTs on the whole activity.

As it can be observed, CNTs-based electrode itself is able to convert CO_2 towards formic acid and acetic acid with a production rate of 1.29 and 0.88 μmol in 4 h, respectively, but no methanol was produced. The activity of the oxidized CNTs can be ascribed to the presence of oxygen functional groups of different kinds (ketone, carboxylic and carbonyl groups) created by the oxidative pre-treatment near defects and edges on the surface of CNTs (Ampelli et al., 2014). Their presence is necessary to anchor strongly the Cu NPs on CNTs. Consequently, these oxygen functional groups may act as electron trapping sites favouring the reduction of the adsorbed species (Wang and Su, 2014). However, Cu/CNTs/GDL electrode allowed obtaining also traces of ethanol, acetone and isopropanol. The formation of these products can be ascribed to the adsorption of the reactant species on the catalytic sites located in the interface between the small copper particles and the CNT surface, favouring electron transfer and C-C bond formation (Genovese et al., 2017).

4. Conclusions

In this work, different electrodes based on highly ordered TiO_2 nanotube arrays and Cu nanoparticles deposited on nano-carbons were tested in the process of water photo-electrolysis and/or photo-reforming of organic wastes for the production of H_2, as well as in the process of CO_2 reduction to liquid fuels. The results, which have been given in terms of H_2 production, solar-to-hydrogen (STH) efficiency and liquid productivity, are very promising.

We also discussed about the importance of the choice of materials to be used for the catalytic electrodes, which depends on several constraints such as light harvesting, charge separation, electron conductivity, proton and mass diffusion, productivity and selectivity. These issues are not usually taken into account in the engineering design of PECa cells, but are strictly related to the catalytic materials used. In general, the most important factors to consider refer to i) the need of having a compact design, ii) the separation of the anodic and cathodic zones, iii) the robustness of the cell and iv) the continuous flow operation (for an easy recovery of products). The development of nanostructured electrodes can highly favour these factors, by increasing the active area and limiting the overpotential of the cell.

In conclusion, the photo-electrocatalytic (PECa) approach has been demonstrated as an attractive technology for a future sustainable production of energy, fuels and chemicals. The PECa approach may be adopted not only for the production of solar fuels, but also for other applications, i.e the activation of small molecules, such

as the synthesis of ammonia starting from N_2 and H_2O, as we recently demonstrated (Chen et al., 2017) as a novel process using C-based electrodes without the need of doping with noble metals.

Acknowledgments

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