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# Engineering of photoanodes based on ordered $TiO_2$-nanotube arrays in solar photo-electrocatalytic (PECa) cells

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## HIGHLIGHTS

- $H_2$ production from water is studied without external bias and sacrificial agents.
- Undoped $TiO_2$ nanotube array films were prepared at different anodization times.
- A highly compact photo-electrocatalytic device was used to minimize overpotential.
- Charge recombination increases for thicker $TiO_2$ nanotube films.
- The optimal film thickness of the photoanode is around one micron.

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## ABSTRACT

Photoanodes based on undoped $TiO_2$ nanotube (TNT) thin films, fabricated by anodic oxidation of Ti foils modulating the anodization time (from 30 min to 5 h), were analysed and tested in a compact photo-electrocatalytic (PECa) device for $H_2$ generation by water photo-electrolysis. The vertically aligned TNT films differ only in the film thickness (i.e. the length of the nanotubes), but they show: i) similar nanotube diameter, ii) uniform thickness and clean top surface and iii) same crystallinity degree in anatase phase. The TNT film becomes thicker by increasing the anodization time (up to 5.8 μm for TNTs anodized for 5 h). All the photoactive layers are able to almost completely absorb the UV part of irradiated light, while the thicker film evidences an enhanced visible light absorption. On the contrary, the photocurrent response decreases by increasing the film thickness. The most active photo-catalyst was the TNT sample anodized for 45 min, providing a $H_2$ production rate of 22.4 μmol $h^{-1}$ $cm^{-2}$ and a *STH* efficiency as high as 2.5%. These values are among the best ever reported insofar as PECa cells use undoped $TiO_2$ photoanodes and in absence of external bias or sacrificial agents.



## 1. Introduction

An efficient use of renewable energy sources, particularly of solar energy, is the necessary path to a sustainable future [1], but this objective requires solving the issues of intermittency, storage and transport of renewable energy. For this reason, there has been an increasing research interest on the conversion of renewable electrical energy to chemical energy [2], as well as the use of photo-electrochemical (PEC) systems, whose interest is now shifting from environmental remediation [3] to solar fuel generation [4–7].

In this context, PEC devices are often indicated as photo-electrocatalytic (PECa) devices to remark the key role of catalysis in their design. The two main types of solar fuels discussed in literature are i) hydrogen, generated by water photo-electrolysis or splitting and ii) the products derived from the hydrogenation of $CO_2$, such as formic acid, methanol etc. [8]. There has been increasing R&D activity on the development of cells and related catalytic electrodes, in terms of both materials and cell configuration [9]. However, several of the literature studies utilize cells that are quite different from those that may be practically implemented. It is necessary, from this point of view, to evaluate the engineering aspects and implications that may influence the PECa performances taking into account the solar cell design. In terms of application, the most important factors are related to: i) the need to have a compact design (to minimize electrolyte volumes); ii) the separation of

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the anodic and cathodic zones (to have the electrodes at the two opposite faces of a membrane, as present in fuel cells); iii) the robustness of the cell (to operate at temperatures higher than room temperature) and iv) the continuous flow operation (for an easy recovery of products) [10]. The design of the electrodes, however, is not separated from the cell design, as the optimal characteristics of the photoanode and its nanostructure depend on all the above mentioned aspects [11,12]. Therefore, it is necessary to study and engineer the electrodes taking into account both the cell design needed for implementation, and the electrode nanostructure and film thickness, together with other aspects related to the photoanode (i.e. light harvesting and charge separation).

In general terms, a PECa device with design analogous to PEM-type (proton exchange membrane) fuel cells and based on the use of n-type semiconductors at the photoanode, consists of two distinct compartments where the products of oxidation ($O_2$) evolve separately by the products of reduction ($H_2$ or the products deriving from the hydrogenation of $CO_2$). A MEA (Membrane Electrode Assembly) is used to separate the two half-cells. For water photo-electrolysis, the MEA consists of three layers (cathode/Nafion® membrane/photoanode) assembled together and physically separating the two areas of reduction and oxidation. The two half-reactions (balanced in acidic solution) are reported as follows:

$$\text{Photoanode}: H_2O + h\nu \rightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^- \quad (1)$$

$$\text{Cathode}: 2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \quad (2)$$

Both protons $H^+$ and electrons $e^-$, combining at the cathode to generate $H_2$, come from the anode side, the protons migrating across the Nafion® proton-conductive membrane, while the electrons reaching the cathode through an external circuit that connects the two electrodes. The separation of the two zones is necessary to avoid back reactions, safety problems, costs of separation and quenching effects [9,10]. However, this configuration creates issues related to the transport of protons. The protons, in fact, should diffuse first in the photoanode layer, then through the interface with the Nafion® membrane and the membrane itself, and finally in the cathode side (through the membrane-cathode interface and on the electrode surface, up to reach the catalytic sites where can react with the electrons to generate $H_2$). Simultaneously, the photo-generated electrons should be collected at the photoanode side (avoiding recombination with protons), then transported with an external wire to the cathode, where should be uniformly distributed in all the electrode surface area, avoiding resistance that can increase the overpotential of the cell. At the same time, the photoanode should realize high efficiency in light harvesting. While many studies in literature have investigated aspects such as nanoarchitecture [13] and interfacial band-edge energetics [14] to improve the photoanode performances, only a few studies have attempted to optimize these performances in terms of the engineering aspects mentioned above [15]. Modelling and simulations in PEC water splitting have been used in improving performance of such systems, by means of theoretical calculations of light absorption, band gap/band edge, charge transport, and electrochemical reactions occurring at the electrode-electrolyte interface [16]. However, even in these cases, the problem of charge transport and of electrode/cell design to minimize the resistances as well as the charge recombination pathways, has scarcely been considered.

The scope of this work is to contribute to these aspects and in general to obtain a better understanding of the relationship between nanoarchitecture and photo-catalytic behaviour in a $TiO_2$-nanotube (TNT) array-based PECa device for producing hydrogen by water photo-electrolysis. The photoactive layer was prepared by controlled anodic oxidation of Ti foils in fluoride-based electrolytes to prepare thin films characterized by ordered arrays of vertically-aligned $TiO_2$ nanotube [11,17]. Many studies have been reported in literature discussing how to "tailor" the nanoarchitecture by modulating the synthesis parameters: applied voltage, time of anodization, type of electrolyte, pH, etc. [18–22]. However, the characteristics of these nanomaterials are often not linked to the specific needs for the design of solar PECa cells [9,23].

There are only a few studies of the effect of the anodization time in relation to the length of the nanotubes and the effect on photo-response [7,24,25], the latter aspect limited to the determination of the quantum efficiency or incident photon to current conversion efficiency (*IPCE*). Lynch et al. [24] observed that the *IPCE* of titania nanotubes does not depend on their length, for layers having a thickness of less than the electron diffusion length. However, they did not report a correlation between *IPCE* and performances in $H_2$ production by water photo-electrolysis. Sun et al. [26] observed a maximum in the $H_2$ production rate for an intermediate thickness of the TNT layer, but in a cell where the titania-based electrode was immersed in the electrolyte and not in direct contact with the membrane. This indicates how the cell design can introduce different engineering implications with respect to conventional devices where other nanostructure characteristics may determine the optimal behaviour of the TNT-based photoanode.

There are also various studies on the relation between thickness of the photoactive layers and performance in process of photo-degradation of dyes and pollutants or in other applications, such as dye-sensitized solar cells (DSSCs). Zhuang et al. [27] observed a maximum photodegradation efficiency to methyl orange (MO) when a thick $TiO_2$ nanotube layer (2.5 μm) was used. Ong et al. [28] studied theoretically the optimal thickness for DSSCs uses. Kim et al. [29] reported that solar conversion efficiency in DSSCs doubled, when TNT film thickness was increased approximately 2-fold. Liu et al. [30] observed in the degradation of phenol that a smaller TNT thickness instead has better activity, because of the reduced charge recombination. Liang and Li [31] reported that in the degradation of 2,3-dichlorophenol in aqueous solution there is an optimal length in titania nanotubes for maximum photocatalytic activity. Choi et al. [32] reported that the photocatalytic efficiency increases proportionally with the length of the nanotubes (in the range 6.5–10 μm). It is also unclear whether a TNT nanostructure is preferable over a titania-thin film layer prepared for example by sol-gel method [33,34]. There are thus apparent discordances on the concept of which nanostructure and film thickness is optimal for photocatalytic activity in PECa devices, but this derives from the fact that non-homogeneous solar cells and conditions have been compared. This aspect indicates that the issues regarding charge transport and resistance to diffusion we mentioned above, influence the overall photo-efficiency and not only aspects such as band-engineering and others that are instead typically investigated.

## 2. Materials and methods

### 2.1. Synthesis by controlled anodic oxidation

$TiO_2$-nanotube (TNT) based photoactive layers having different thicknesses 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 the presence of fluoride-based electrolytes [17,35]. The starting titanium disc (Alfa Aesar, 0.025 mm of thickness, 3.5 cm of diameter) was anodized by using a two-electrode electrochemical cell work-