Cell and Electrode Engineering in Green H_2 Production via Photo-Electro-Catalytic (PEC) Approach

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Highlights

- Clean H_2 is produced in combination with high-value carbon products by photo-electro-catalysis
- 3D meso/macro porous electrodes were designed and realized to improve mass and charge transfer
- Reaction mechanism is strongly affected by cell/electrode engineering beyond catalyst properties

1. Introduction

Hydrogen (H_2) will play an increasingly leading role in the future energy scenario to address important challenges of reducing greenhouse gas emissions. Today, H_2 is mainly produced using fossil fuels, and its use refers to refining and chemical sectors. However, green H_2 can be successfully produced by water electrolysis starting from renewable electricity and is one of the few options for storing energy for long periods. Many efforts are still needed to bring down the costs of technologies for producing and using clean H_2, such as electrolysers, fuel cells and hydrogen production with carbon capture. Alternatively, other emerging technologies enable the production of clean H_2, e.g. the photo-degradation of organics (anodic reaction) integrated with H_2 production by proton reduction (cathodic reaction) also in combination with the conversion of CO_2 to high-value products, thus improving carbon circularity and resilience [1].

In this context, the photo-electro-catalytic (PEC) approach in artificial leaf-type devices is an attractive technology to produce green H_2 [2]. While most scientists have focused on the development of active electrocatalytic materials to accelerate both the cathodic and anodic half-reactions, we believe that cell and electrode engineering is the key to boosting the electrocatalytic performance and overcoming the limitations that currently hinder the commercialization of such types of devices [3,4]. A proper chemical reaction engineering is required to increase/modulate the selectivity of CO_2 reduction towards the formation of a single carbon product (e.g. formate instead of CO) in combination with H_2. On the other hand, aqueous solutions of organic waste coming from biorefineries (e.g. bioethanol) can be oxidized/upgraded to more valuable products such as aldehydes and/or esters.

This contribution is mainly focused on the design of the anodic part of the device, including the development of the electrode for the oxidation reaction. Specifically, a 3D-type electrode based on macro/mesoporous oxide materials was developed, and processed in both liquid- and gas-phase configurations.

2. Methods

Highly ordered TiO_2 nanotube arrays (TNTs) were prepared by controlled anodic oxidation of a macroporous Ti substrate (TNTs-Ti mesh) consisting of Ti wires (0.13 mm dia.) regularly woven to form an 80 mesh (i.e. 0.18 mm) gauze with an open geometric area of ~35% [5]. The resulting substrate is a 3D-type meso/macro porous structured photo-electrode, active in the UV light region, with the mesopores formed within the TNTs and the macropores provided by the mesh (Figure 1). To enhance the photo-activity in the visible light region, different metal nanoparticles (M=Au, Pd, Ag, Cu) were

used to modify the TNTs-Ti mesh, deposited on the electrode surface by electrodeposition, pulsed electrodeposition or photo-deposition.

The as-prepared electrodes were fully characterized to study the morphological, structural and electronic structure (SEM-EDX, XRD, XPS, BET) and electrochemical properties (Linear Sweep Voltammetry, Chronoamperometry, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy –EIS–). Finally, they were tested in homemade compact electrochemical photo-reactors, designed on purpose to minimize overpotentials and reduce energy losses.

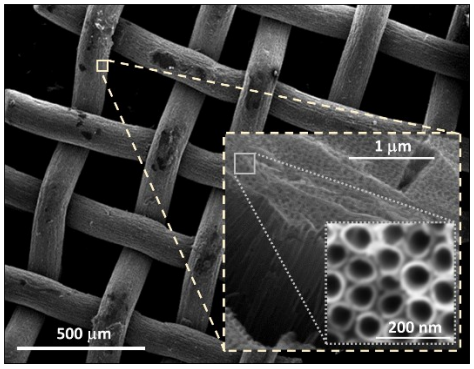

Figure 1. SEM images of the 3D nanostructured electrode based on Ti mesh covered by TiO_2 nanotube arrays.

3. Results and discussion

The 3D-type porous structure photoanodes were processed in two flow-type reactor configurations: i) liquid-phase, with the anolyte in contact with the M-doped TNTs-Ti mesh, and ii) gas-phase (also called zero-gap or electrolyte-less). In the latter configuration, the porous electrode was assembled with a proton exchange membrane (i.e. Nafion) to separate the working electrode from the catholyte. In both the systems, H_2 production was measured in the cathode part. Interestingly, zero-gap systems provided the best PEC performance, with more than 90 μmol h^{-1} cm^{-1} of H_2 production rate for Ag-doped TNTs-Ti mesh in absence of sacrificial donors. Furthermore, the photo-upgrading of bioethanol provided the formation of both acetaldehyde and acetic acid, with a close to 100% selectivity to acetaldehyde for Au-doped TNTs-Ti mesh. The zero-gap operation was preferable as it showed several advantages in terms of improved mass and charge diffusion, also confirmed by EIS measurements.

4. Conclusions

Reaction mechanism in photo-electrocatalytic processes is strongly influenced by cell and electrode design, going beyond the properties of the electrocatalyst itself. The production of green H_2 was successfully demonstrated in combination with high-value carbon products. This work opens the route towards the realization of artificial leaves/trees for the continuous production of clean H_2, using a carbon-based product (e.g. formate) to store H_2 in dark periods [1,2].

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Keywords
Green H_2; Solar fuels; Porous electrodes; PEC devices.