A novel gas-phase approach to control selectivity in ethanol photo-oxidation on metal-doped TiO_2/Ti gauze photoanodes

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Significance and Relevance

Artificial leaf-type systems are small-scale electrochemical devices designed for the distributed production of chemical and fuels using renewable energy sources, e.g. solar power.[1] The cathodic reaction is the electrocatalytic reduction of abundant small molecules, like carbon dioxide (CO_2) and dinitrogen (N_2), while the counter half-reaction is typically the Oxygen Evolution Reaction (OER), which takes place at the anodic part. However, the OER is quite challenging due to its large overpotential, being the rate-limiting step in water-splitting electrolysers. Additionally, although water oxidation generates protons needed for the cathodic reduction reactions, the evolved oxygen (O_2) is unsuitable for distributed industrial applications due to the lack of efficient end-users for dilute oxygen streams. In this work, we explored alternative anodic reactions for artificial leaf devices and water electrolysers to address these limitations, aiming to reduce overpotential and lower power requirements for driving the electrocatalytic reduction. We introduced (bio)ethanol into the anode, where it was oxidized to acetaldehyde and acetic acid. The influence of different metals (Ag or Pd) used to decorate TiO_2/Ti gauze-based photo-anodes was investigated, and unconventional gas phase conditions were compared with the common use of a liquid electrolyte. Results showed a shifted selectivity to acetic acid in gas-phase operation, while only acetaldehyde was observed in conventional liquid phase configuration.

Preferred and 2nd choice for the topic: Photocatalysis and photo-electrocatalytic approaches, solar energy utilization – Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred or Short Oral / Poster

Introduction and Motivations

Artificial photosynthesis to directly convert CO_2 (and/or N_2) and water into valuable industrial chemicals is one of today's major challenges to address growing energy demands and mitigate climate change. This reaction can be performed in advanced photo electro-chemical (PEC) devices,[2] where a photoactive anode is irradiated by sunlight to generate protons for the reduction reaction. Typically, the protons migrate through an ion-exchange membrane to the cathode side, while O_2 evolves from the anodic compartment. In general, the limited production rates and profit margins of PEC devices explored so far have hindered strong interest from the industry. In this work, we present a novel PEC compact flow device designed to minimize energy losses caused by overpotential. We focused on the development and behaviour of the photoanode, which can operate both in presence of a liquid electrolyte or under unconventional gas-phase (electrolyte-less) conditions. The photo-anode consists of highly ordered TiO_2 nanotube arrays grown on Ti gauze (then decorated with metal nanoparticles), specifically designed to improve light harvesting and enhance mass and charge transfer processes. We studied the role of the gas-phase configuration in addressing selectivity of (bio)ethanol oxidation to acetaldehyde and/or acetic acid, considering the effect of different deposited metals.

Materials and Methods

TiO_2 nanotubes were synthesized on Ti gauze via controlled anodic oxidation.[3] Prior to anodization, the metallic supports were cleaned by sonication in isopropanol for 30 min, followed by drying in air at 100 °C. The clean substrate was then placed in a two-electrode electrochemical cell, using an electrolyte containing 2 wt% H_2O and 0.33 wt% NH_4F in ethylene glycol, under a constant voltage of 50

V for 60 min. After anodization, the samples were annealed at 450 °C for 3 h to induce the crystalline anatase phase. Silver (Ag) or palladium (Pd) nanoparticles were then deposited onto the TiO_2/Ti gauze surface using the photo-deposition technique. The PEC cell, made of Plexiglas, consists of two separate chambers for cathodic and anodic reactions, as shown in Figure 1a. In the liquid-phase configuration, the device is connected to two storage tanks for electrolyte circulation. In the gas-phase configuration, an external hot plate pre-heats a 20 vol% ethanol solution, while an inert gas flow moves the vapours directly into the anode chamber.

Results and Discussion

Figure 1b shows a picture and two SEM images of Ti/TiO_2 electrode. Vertically aligned TiO_2 nanotubes with a circular shape were formed on the round surface of the Ti gauze, exhibiting an opening diameter of around 52 nm. The final electrode shows two types of porosity: a mesoporosity due to the TiO_2 nanotubes, and a macroporosity due to the mesh structure of the Ti gauze. Photo-electrocatalytic tests were conducted by irradiating the photoanode with a solar simulator (300 W, Xe arc lamp, 1 sun). The photoanode (i.e. metal-doped TiO_2/Ti gauze) was coupled with a Nafion membrane to form a MEA (Membrane Electrode Assembly), effectively reducing overpotential. In gas-phase configuration, no liquid electrolyte was introduced into the cathode compartment. Results showed acetaldehyde as the only oxidation product observed under conventional liquid-phase configuration. Contrarily, in gas-phase configuration, the selectivity shifted partially to acetic acid formation, with Faradaic efficiency of 1.6% and 3.6% for Pd and Ag-doped TiO_2-Ti gauze, respectively, highlighting the advantages of operating without a liquid electrolyte to boost the oxidation process.

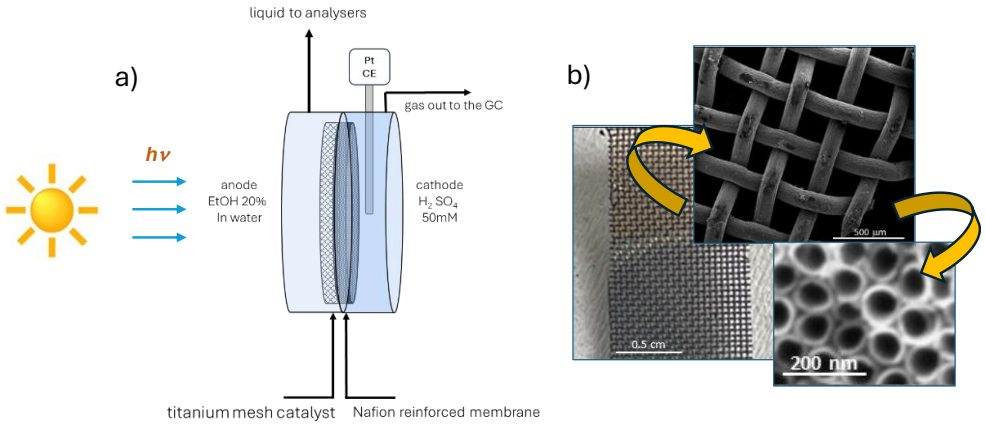

Figure 1: a) Schematic representation of the compact photo-electrocatalytic device working under unconventional gas-phase conditions; b) pictures and SEM images of the Ti/TiO_2 gauze electrode.

References

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