



# A gas-phase reactor powered by solar energy and ethanol for H<sub>2</sub> production



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## HIGHLIGHTS

- A gas-phase photoreactor for H<sub>2</sub> production by ethanol dehydrogenation was developed.
- The photocatalytic behaviours of Au and Cu metal-doped TiO<sub>2</sub> thin layers are compared.
- Benefits of operating in gas phase with respect to a slurry reactor are presented.
- Gas phase conditions and use of not-noble metals are the best economic solution.

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## ABSTRACT

In the view of H<sub>2</sub> as the future energy vector, we presented here the development of a homemade photo-reactor working in gas phase and easily interfacing with fuel cell devices, for H<sub>2</sub> production by ethanol dehydrogenation. The process generates acetaldehyde as the main co-product, which is more economically advantageous with respect to the low valuable CO<sub>2</sub> produced in the alternative pathway of ethanol photoreforming. The materials adopted as photocatalysts are based on TiO<sub>2</sub> substrates but properly modified with noble (Au) and not-noble (Cu) metals to enhance light harvesting in the visible region. The samples were characterized by BET surface area analysis, Transmission Electron Microscopy (TEM) and UV–visible Diffusive Reflectance Spectroscopy, and finally tested in our homemade photo-reactor by simulated solar irradiation. We discussed about the benefits of operating in gas phase with respect to a conventional slurry photo-reactor (minimization of scattering phenomena, no metal leaching, easy product recovery, etc.). Results showed that high H<sub>2</sub> productivity can be obtained in gas phase conditions, also irradiating titania photocatalysts doped with not-noble metals.

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## 1. Introduction

The development of the global economy and the unavoidable depletion of fossil fuels have opened a broad debate within the scientific and political communities about the strategies to adopt for sustaining the growing world energy demand and to manage the transition towards the exploitation of alternative and clean energy resources [1].

In this context, hydrogen (H<sub>2</sub>) has received increasing attention as the ideal energy vector for the future [2]. The technologies for energy production from H<sub>2</sub> (e.g. fuel cells) are already mature to be

brought onto the market and H<sub>2</sub> can also be used as a raw material for making products like fertilisers and plastics [3]. Unfortunately, most of the current H<sub>2</sub> still comes from non-renewable resources, mainly by two different routes: the most important is the steam reforming of methane, which requires heat to be performed and needs the combustion of fossil fuels for the generation of heat; the second one is the electrolysis, which separates H<sub>2</sub> from water through the use of electricity. Therefore, H<sub>2</sub> production is an energy intensive process, with serious concerns about CO<sub>2</sub> emissions in the environment [4].

Producing H<sub>2</sub> by water splitting is, instead, an extremely promising and environmentally friendly route for the direct conversion of solar energy into fuels [5]. However, its industrial applicability is still a long way off, due to issues related to i) the need to synthesize a photo-active material capable to absorb

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efficiently sunlight and catalyse the reaction of water splitting and ii) the very fast back reaction to re-generate water, which occurs too facile on the same catalytic sites active for its dissociation [6]. All the papers about water splitting refer to the pioneering work by Fujishima and Honda (1972) [7] who first observed water photolysis on TiO<sub>2</sub> semiconductor electrodes. From then on, many efforts have been made to improve TiO<sub>2</sub> performances in H<sub>2</sub> generation by i) doping the crystalline lattice with heteroatoms [8], ii) decorating the surface with metal particles (generally noble metals) or tailoring the structure on a nano-scale level [9], with the aim to move the band gap to the visible region [10]. Nonetheless, photocatalytic water splitting is far from an actual implementation and yet we have to wait a long time to use solar cell devices based on water as the sole input.

Contrarily, the addition of organic compounds, even in small concentrations (mM), may give rise to H<sub>2</sub> productivity [11]. The photo-reforming of organics may represent a good opportunity to recover waste streams coming from biomass processing (agro-food or agro-chemical) which are too dilute to be processed by conventional catalytic routes, i.e. as feed to produce H<sub>2</sub> by catalytic processes or methane by anaerobic digestion, or to be used as feed in the new generation of fuel cells [12]. From a practical perspective, it would also be interesting the possibility of co-producing, together with H<sub>2</sub>, valuable chemicals rather than carbon dioxide, in order to have better process economics. A good example could be the photocatalytic dehydrogenation of ethanol to H<sub>2</sub> and acetaldehyde, as alternative to the ethanol photoreforming. In terms of product value at current costs (assuming 100% selectivity in both the reactions), photo-dehydrogenation has an economic value about 3.0–3.5 times higher than photoreforming [13].

The aim of this work is to explore the various possibilities to produce clean H<sub>2</sub> from dilute aqueous organic waste solutions starting from conventional TiO<sub>2</sub> photocatalysts and modifying them with noble or not-noble metal, and to evaluate the issues concerning the applicability of the photo-process and its potential implementation in the future energy supply system. Particular emphasis has been given to the gas-phase conditions, which seems more suited to be coupled with fuel cell devices. It is to mention, in fact, that fuel cell technologies are now addressing to high temperature conditions, mainly for reasons related to the heated feeding streams coming from the current processes of H<sub>2</sub> production [14]. The development of Photo-ElectroChemical (PEC) systems for H<sub>2</sub> production may take advantages of fuel cell technologies, in terms of both operating conditions and materials used [15]. Therefore, it is important exploring performances of H<sub>2</sub> production in the range between room temperature and 80–100 °C, which is the required temperature operation range for Proton Exchange Membrane (PEM) fuel cells [16]. These temperatures can easily be reached by using concentrated solar power systems, which are able to concentrate a large area of sunlight onto a small area through mirrors or lenses [17].

Specifically, we have investigated the reaction of ethanol photo-dehydrogenation using metal-doped TiO<sub>2</sub> nanocomposites as photocatalysts. The focus of the investigation was the use of the photocatalyst in the form of thin film for the conversion of ethanol in an inert (N<sub>2</sub>) gas stream and, in particular, ethanol was generated directly in situ from the bottom of the photo-reactor where an aqueous ethanol solution was maintaining in evaporation, as described below in the experimental section.

The potential advantages of operating in gas phase with respect to the traditional slurry photo-chemical reactors are multiple: (i) minimization of scattering phenomena, (ii) good pattern of irradiation, (iii) ability to transfer the power coming from sunlight to a conductive substrate, (iv) easier scale-up, (v) elimination of problems associated to metal-leaching and (vi) easier product recovery

[18]. A metal-doped TiO<sub>2</sub> substrate in the form of a thin layer may also be used as an electrochemical sensor for safety and control detection devices [19].

The same photocatalytic samples were also tested in a conventional liquid photo-reactor, in the form of a powder suspended in an aqueous ethanol solution. Gas and liquid phase operations in the photo-production of H<sub>2</sub> were compared in terms of H<sub>2</sub> production and selectivity. Two different metals were used to dope TiO<sub>2</sub> photocatalysts: gold (Au) and copper (Cu). The metals were deposited by photo-reduction method that allowed obtaining a very small size of metal particles. We also discussed the differences of using noble and not-noble metals.

## 2. Experimental

### 2.1. Preparation

All the reagents were of analytical grade and were used without further purification. Bidistilled water was used in all the procedures. We started from TiO<sub>2</sub> P25 Degussa (commercial) and deposited on its surface metal (M) nanoparticles of Au or Cu by photo-deposition technique. Usually 1 g of TiO<sub>2</sub> P25 Degussa was suspended in a water/ethanol 1:1 by volume solution containing the metal precursor (copper nitrate or chloroauric acid, supplied by Sigma Aldrich). The amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O or HAuCl<sub>4</sub> was chosen in order to obtain the desired metal loading of 0.5 wt%, which is the optimal value from our previous studies [20]. After stirring for 30 min, the suspension was irradiated with a 300 W Xe-arc lamp for 2 h. The samples were finally filtered and dried.

In order to obtain a thin film of photoactive substrate, a paste was prepared by mixing 1 g of M/TiO<sub>2</sub> (M = Au or Cu, 0.5 wt%) with 10 mL of a solution consisting of water (H<sub>2</sub>O, 51 wt%), absolute ethanol (EtOH, 47 wt%) and polyethylene glycol (PEG 2000, 2 wt%). The paste was then deposited on a conductive glass substrate (ITO glass, 8–12 Ω/sq) by doctor-blade technique. After deposition, the substrate was annealed at 200 °C to eliminate all the organic. The final photocatalyst film area was about 10 cm<sup>2</sup>, with a thickness of about 50 μm, and a total photocatalyst loading of about 100 mg.

### 2.2. Characterization

The materials were characterized by nitrogen adsorption–desorption isotherms according to the conventional Brunauer–Emmett and Teller (BET) surface area analysis, using a Micromeritic ASAP 2010 after degassing the samples overnight at 350 °C. Ultra-violet–visible diffuse reflectance spectra were recorded by a Jasco V570 spectrometer equipped with an integrating sphere for solid samples using BaSO<sub>4</sub> as reference and in air. Transmission electron microscopy (TEM) images were acquired by using a Philips CM12 microscope (resolution 0.2 nm) with an accelerating voltage of 120 kV, while the elemental analysis was investigated by using a Philips XL-30-FEG scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) analyzer.

### 2.3. Testing

The photo-active thin films were tested in H<sub>2</sub> production by simulated solar irradiation. The apparatus for the photocatalytic experiments consists of i) a solar illuminator source, ii) a photo-reactor and iii) a gas chromatograph (GC). The light source is a Xe-arc lamp (ORIEL, 300 W), installed within a lamp housing with a set of lenses for light collection and focussing and a water filter to eliminate the infrared radiation. Moreover, the possibility to use filters to select the wavelength band allows to simulate sunlight under standard terrestrial solar spectral irradiance distributions

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