

# SOLAR HYDROGEN PRODUCTION FROM AQUEOUS SOLUTIONS OF ETHANOL AT NEAR AMBIENT TEMPERATURES

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## Abstract

Nanostructured semi-conductor materials based on titanium dioxide, with effective photo-catalytic properties under UV illumination, were synthesized and characterized with the objective of studying the photo-catalytic hydrogen production from water. The need to decrease the electron-hole recombination rate was accounted for by metal doping. Ethanol was used as a hole trap. Aqueous suspensions of the semiconductor powders, with noble metal loadings (Pt) were used and the effects of solution pH and temperature (20-70°C) on hydrogen production were studied, for a selected catalyst concentration. Hydrogen production was found to be linear with UV irradiation time at all tested temperature. Values were larger than published literature data.

Keywords: hydrogen production, doped-titanium dioxide, ethanol, photo-catalytic materials.

## 1. Introduction

The generation of hydrogen from water splitting using photo-catalytic surfaces of oxide materials has been recognized since the early seventies [1]. In the last decades interest in semiconductor photocatalysis has grown significantly, with works mostly referring to uses in water/air purification.

The photo-catalytic production of hydrogen by means of irradiation of a suspension of semiconductor oxides, presents attractive features over other methods with higher cost such as water electrolysis.

Some of the materials properties and requirements for solar hydrogen production include tailored electronic structure: band gap - essential for absorption of solar energy; and flat band potential - must be higher than the redox potential of the couple  $H^+/H_2$ . Furthermore, efficient charge transport is necessary since low electrical resistance is required as well as effective charge separation and prevention of electron-hole pair recombination.

Titania is the base catalyst material of choice, notwithstanding the stability and non-corrosive properties, and the environment friendliness and low cost, the actual efficiency in the production of solar hydrogen is still very low, due to electron-hole pair recombination [2-6] and also due to  $TiO_2$  band gap (~3.2 eV) which only allows utilization of UV light.

The feasibility of photo electrochemical generation of solar hydrogen requires that the energy conversion efficiency goes from current levels < 1% to levels of > 10%, with accompanying durability. In order to increase efficiency in the use of semiconductor electrodes in electrochemical

photolysis, integrated systems including semi-conductor / redox couples interfaces, deposition of metallic co-catalyst, sensitizers, etc. have been studied [2,3]. The modification of TiO<sub>2</sub> properties may contribute for a more efficient hydrogen production that may take advantage of visible light utilization [4,7,8,9]. Effective charge transfer from water molecules and the TiO<sub>2</sub> lattice requires the presence of surface active sites, associated to point defects, that can form activated complexes with water molecules.

In this work, a nanostructured semi-conductor material based on titanium dioxide, with effective photo-catalytic properties under UV illumination, was used for hydrogen production using ethanol as a sacrificial agent, with excellent results.

## 2. Experimental

A photochemical reactor with a total volume of 4.40 liters distributed between an internal (irradiated) reactor and an external reactor (fluid reservoir) was used according to need; a sensing pH electrode was allowed for as well as facilities for titration of H<sup>+</sup>, in order to adjust pH, when required. The internal reactor was contained in a black box and used a 450 W Hg immersion lamp (A.C.E. Glass Incorporated, NJ), as a radiation source. The emission spectrum of the lamp indicated that the UV radiation is mainly situated between 313 and 366 nm. Circulation between reactors, when required, was ensured by a peristaltic pump, according to the required recirculation rate. Agitation by magnetic stirrers in both reactors was also used.

In this paper, titanium dioxide Degussa P-25 was modified by photochemical deposition of Pt. Platinised TiO<sub>2</sub> catalyst (at 1.5 wt.% Pt) was prepared using hexachloroplatinic acid (Riedel-de Haen) as the precursor. A pre-determined amount of TiO<sub>2</sub> was first suspended in hot water and the hexachloroplatinic acid previously dissolved in an aliquot of fresh distilled water was added, with continuous nitrogen purging (15 min.) inside the described photo-reactor. The mixture was irradiated for 60 min, at constant temperature (30-40°C), to ensure that all the platinum in the suspension was reduced and deposited onto the surface of TiO<sub>2</sub>. The TiO<sub>2</sub> / Pt catalyst was subsequently recovered by filtration and washed repeatedly with water. Finally, the powder was dried at 70°C and stored under vacuum in a desiccator. Catalyst were heat treated at 440 °C during one hour.

After some preliminary studies a concentration of TiO<sub>2</sub> of 0.5 gL<sup>-1</sup> was selected as well as a concentration of ethanol of 5 M and an initial pH of 11[10].

Characterisation of the powders was done by X-Ray diffraction using a Rigaku, model D-Max IIIC and by scanning electron microscopy (SEM) using a Phillips model XL 30 FEG microscope coupled to EDS.

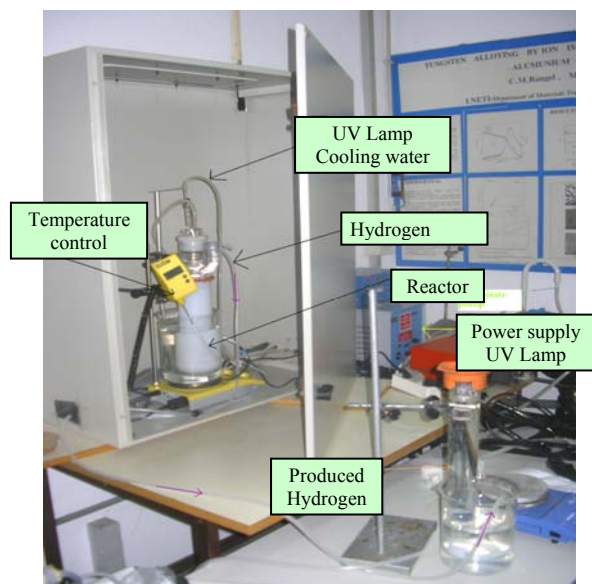


Fig. 1. Experimental set-up showing the internal reactor of the system assembled for the photo-catalytic production of hydrogen using modified  $\text{TiO}_2$  powder suspensions and ethanol as a sacrificial agent.

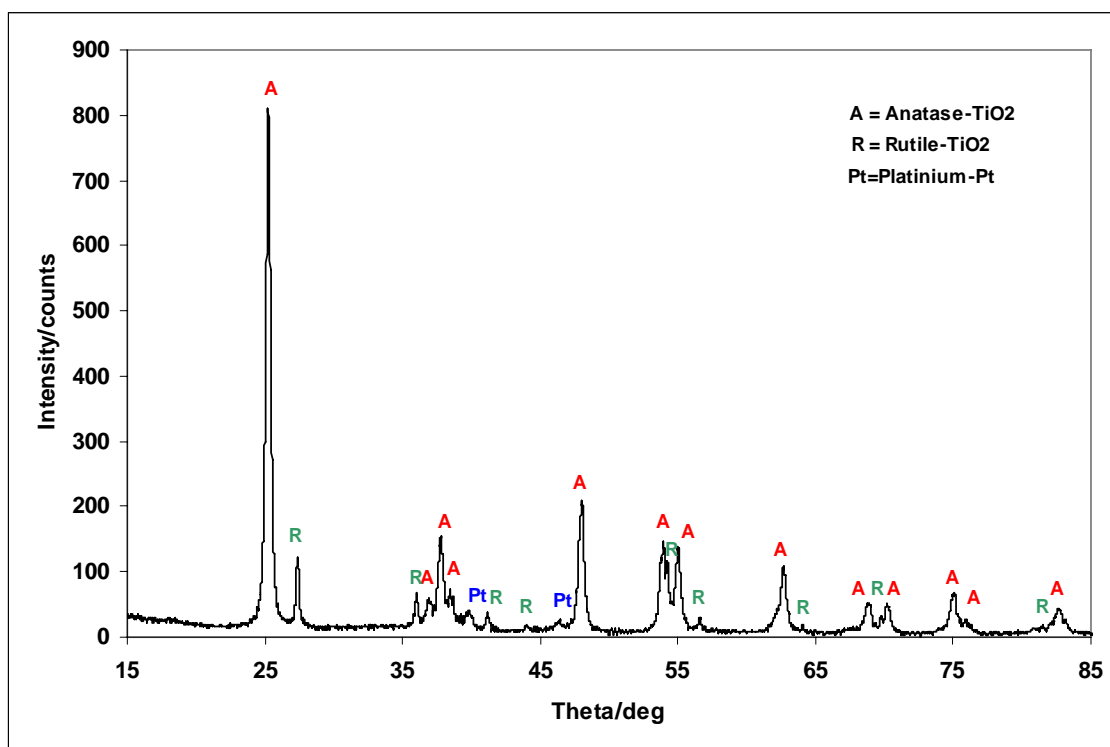
### 3. Results and Discussion

In this work, a nanostructured semi-conductor material based on titanium dioxide, with effective photo-catalytic properties under UV illumination, was synthesized. X-Ray diffraction data indicated the presence of anatase and rutile and a crystallite size of 21 nm and  $\sim 90\%$  anatase content. Typical morphology of the powder is shown in figure 2, exhibiting particle size at a nanoscale.

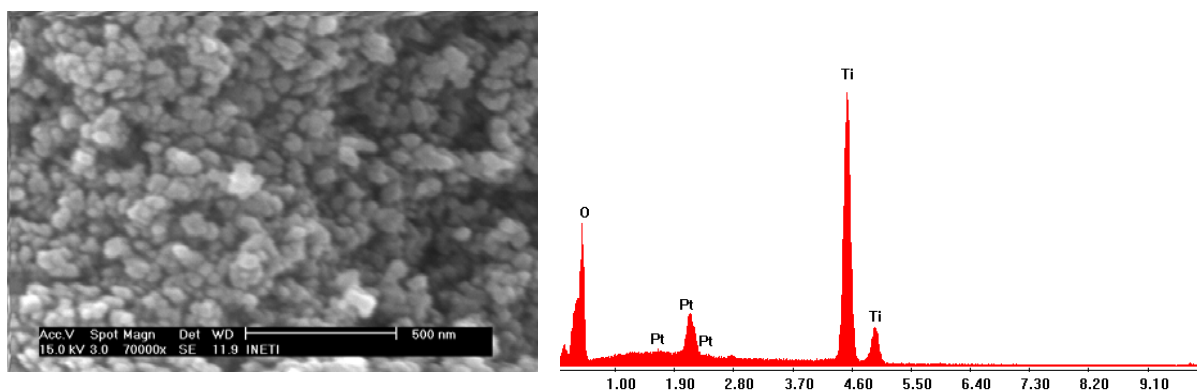
Aqueous suspensions of the semiconductor powders, with noble metal loadings (Pt) of 1.5 wt% were used and the effect of solution pH and temperature (20 - 70°C) for a 5M ethanol concentration on hydrogen production were studied, for a fixed amount of the catalyst of 0,5 g/L, value obtained after optimisation in previous work by the authors.

Typical results obtained during the photocatalytic production of hydrogen by UV illumination of the suspension of  $\text{TiO}_2$ -Pt are shown in figure 3, in terms of the number of mol per unit time of produced gases by gram of catalyst. The rate increases linearly with temperature. When compared with recent literature data [2], the values produced in this work are clearly higher by more than an order of magnitude, see figure 3.

Data obtained using gas chromatography indicated the presence of large amounts of hydrogen in the reaction products. CO<sub>2</sub> and CH<sub>4</sub> were found in smaller amounts.



(a)



(b)

Fig. 2 X-Ray spectra for synthesized Pt-TiO<sub>2</sub> (a); typical morphology as observed under the scanning electron microscope and respective EDAX spectrum (b).

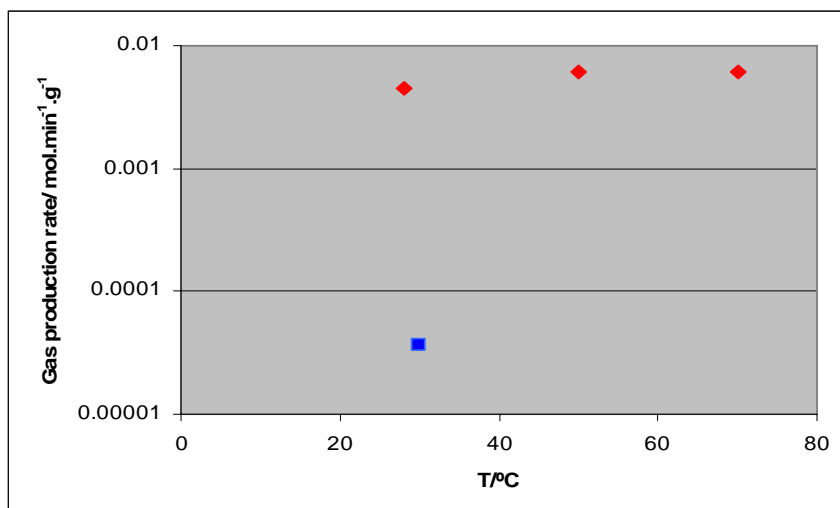
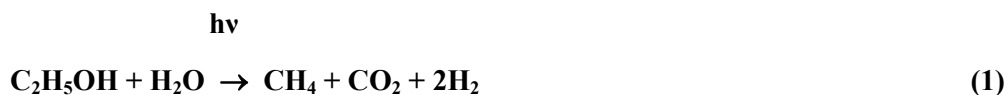


Fig. 3 Gas production rate as a function of temperature, from a 5 M aqueous solution of ethanol at pH 11, using own synthesized Pt-TiO<sub>2</sub>. Results are compared with literature data from [2] (♦ own synthesized Pt-TiO<sub>2</sub> catalyst data; ■ literature data).

The fact that the amounts of methane and CO<sub>2</sub> obtained were less than expected taking into account the stoichiometry of the reaction, led to consider that methane and CO<sub>2</sub> may be produced by decomposition of acetic acid according to reactions (4) and (5) and furthermore that in the present conditions the formed acetic acid remain in solution. A titration confirmed the presence of large amounts of acetic acid, indicating that pH variations during the reaction must be significant.

Typical pH variations with irradiation time were measured starting from the initial pH value of 11 falling to 5.1, see figure 4. It was also observed that for pH values < 5.5 the rate of hydrogen production starts to diminish. Increase in the pH back to 11 was noticed to keep the initial gas production rate.

Possible reactions are:



Where Me - Metal (Pt); h- hole

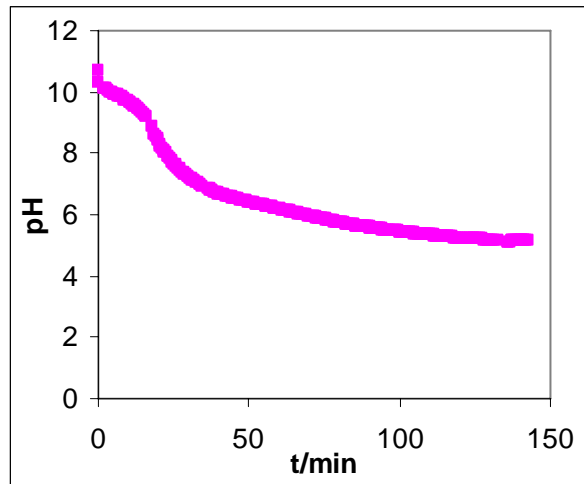


Fig. 4 pH solution variation in the photocatalytic production of hydrogen using modified TiO<sub>2</sub> powder.

Methane and CO<sub>2</sub> can be produced by the decomposition of acetic acid,



Another pathway for CH<sub>4</sub> formation may be the hydrogenation of CO<sub>2</sub> according to equation (7)



Another possible reaction pathway is the involvement of adsorbed surface hydroxyls on TiO<sub>2</sub> in the trapping of holes. The interaction of surface hydroxyl groups with holes will result in the formation of hydroxyl radicals which, in turn, will interact with C<sub>2</sub>H<sub>5</sub>OH or its intermediates adsorbed on the metal- TiO<sub>2</sub> surface or present in the vicinity to produce CO<sub>2</sub> and other side products.

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Work proceeds where results are compared with sol-gel titanium dioxide modified with Pt in the same experimental conditions. Modification of the titanium dioxide band gap is also in progress, in order to account for the advantageous use of visible light [11].

#### 4. Conclusions

Titania was used as the base catalyst material of choice for solar hydrogen production, due to its stability and non-corrosive properties, as well as environmentally friendliness and low cost. The need to decrease the electron-hole recombination rate was accounted for by platinum deposition and the addition of ethanol as a hole trap.

- Gas production rates were found to be linear with temperature in the range from room temperature up to 70°C. In the present conditions used in this work, values were found larger than published literature.
- pH variations during hydrogen production were striking changing from 11 to values as low as 5.6, this is thought to be due to the formation of acetic acid during the reaction, accounting for the lower concentration of CO<sub>2</sub> and CH<sub>4</sub> found by gas chromatography. Keeping the pH in the alkaline range ensured a constant rate of gas production for extended periods of time.

Further work is needed to identify low cost metal loading materials with acceptable enhancement for hydrogen production, as well as modified catalysts that allow effective utilization of visible light.

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