

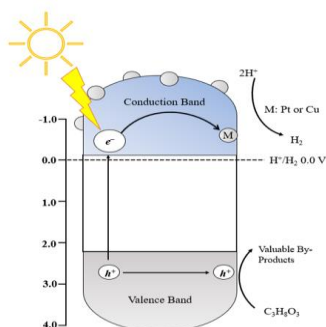
## Simple Method Immobilization of Metal Doped-TiO<sub>2</sub> for Photo-Induced Glycerol Conversion to Hydrogen

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The increase in searches for alternative energy sources has led to emerging research into Hydrogen as a promising energy source. With the present work, we sought to analyze the production of H<sub>2</sub> through the photocatalytic route using a method of immobilization of TiO<sub>2</sub>-based catalysts modified with Pt and Cu. The results show the efficiency of the impregnated material in the production of H<sub>2</sub>. TiO<sub>2</sub>@Pt had a significant production when compared to TiO<sub>2</sub>@Cu, however production using Cu has characteristics to be explored, such as the use of basic pH. The unique characteristics of each cocatalyst as well as its production, during the tests the impregnation method was satisfactory, as well as the results of TiO<sub>2</sub>@Pt which were 11 times higher than the H<sub>2</sub> production of TiO<sub>2</sub>@Cu. Further studies should be conducted in such a way as to work with minimum concentrations of dopants, leading to the economic feasibility of the photocatalytic technique without loss of efficiency.

### Introduction

The increasing demand for alternative energy sources has intensified as the race for decarbonization advances. In this scenario, hydrogen (H<sub>2</sub>) presents itself as a promising source [1]. This is due to its high heat power and the by-products of its combustion that do not carry carbon in its form of CO<sub>2</sub> or CO. Another factor that intensifies H<sub>2</sub> expectations are its low-carbon synthesis methods, such as electrolysis and photocatalysis, which have low carbon content involved in its production. Nevertheless, we also have the use of biomass as a sacrifice reagent for the production of H<sub>2</sub> by the photocatalytic pathway, with emphasis on glycerol as a by-product of biodiesel production [2]. Photocatalysis explores the photoactivation of a catalyst, usually a semiconductor oxide, resulting in the formation of the electron/spin pair (e<sup>-</sup>/h<sup>+</sup>) [3]. Photogenerated electrons can act in reactions via a reduction, such as the conversion of H<sup>+</sup> to H<sub>2</sub>. At the same time, the gaps assume oxidative characteristics, allowing the conversion of biomass directly or by means of reactive species of oxygen. For this process, titanium dioxide (TiO<sub>2</sub>) is a catalyst that presents itself as an exponent in due to its stability, low toxicity and high activity. However, it has a low interaction with visible light, which can be bypassed with the use of co-catalysts. As examples of co-catalysts in the literature as dopants for photocatalytic production of H<sub>2</sub> there are noble metals such as gold [4], silver [5] and platinum [6]. Additionally, less expensive metals have also been, such as copper [7] and iron [8]. In this sense, platinum is as an important dopant to TiO<sub>2</sub> for increasing its activity against radiation in the region

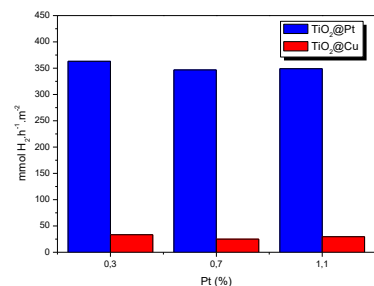
of the visible, but it has a high cost associated with its use. Alternatively, copper presents potential for application in photocatalytic production of H<sub>2</sub> when present as a co-catalyst to TiO<sub>2</sub>, having considerably lower cost than noble metals, despite a reduced activity in standard pH and temperature conditions.

### Material and Methods

The TiO<sub>2</sub> catalysts were doped with Cu and Pt using the photodeposition method. Initially, the Cu and Pt precursors were kept in balance with TiO<sub>2</sub> in a 10% methanol solution (v/v) for a period of two hours, followed by irradiation using a 300 W xenon lamp. Cu and Pt levels were varied by 0.3, 0.7 and 1.0% (m/m). The catalysts produced were impregnated in 5 cm<sup>2</sup> acrylic plates using Nafion<sup>®</sup>. The photocatalytic reactions were conducted in a glass reactor containing 25 mL of glycerol (10%, v/v) together with the plates with the catalysts. The system was irradiated for a period of 3 hours using a 300 W xenon lamp. The gas phase co-products were quantified by gas chromatography in a CG 490 (Agilent) equipped with TCD detector.

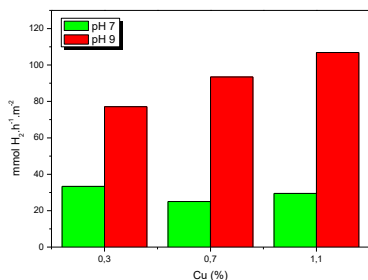
### Results and Discussion

Figure 1 highlights the results of the production of H<sub>2</sub> by the TiO<sub>2</sub>@Pt catalysts and TiO<sub>2</sub>@Cu. Both catalysts were evaluated at neutral pH and at a temperature of 40°C. In this context, TiO<sub>2</sub>@Pt had an expressive output when compared to TiO<sub>2</sub>@Cu. Despite the high output, the increase in Pt concentration did not present itself as a relevant variable, and this effect is possibly attributed to TiO<sub>2</sub> coating during platinum photodeposition. The same effect can also be attributed to the decrease in production with the increase in the concentration of Cu.



**Figure 1.** Production of H<sub>2</sub> with TiO<sub>2</sub>@M (M = Pt or Cu) and 10% glycerol.

The evolution in H<sub>2</sub> production of deviations under certain conditions and variations, in Figure 1 we can observe a gradual decline in production as the concentration increases for TiO<sub>2</sub>@Pt. This decline may be related to the coating of titanium by platinum cores, hindering the interaction of the encounter with radiation and resulting in a progressive decline with increasing co-catalytic concentration.



**Figure 2.** Production of H<sub>2</sub> with TiO<sub>2</sub>@Cu at pH 7 and 9.

## Conclusions

The method of immobilizing photocatalysts on acrylic plates proved to be satisfactory for producing H<sub>2</sub>, proposing an easy-to-execute methodology using accessible materials. TiO<sub>2</sub>@Pt demonstrated its efficiency when compared to TiO<sub>2</sub>@Cu under the conditions used in the work for the production of H<sub>2</sub>, proving the high activity attributed to the use of noble metals for photocatalytic reforming of biomass. Further studies must be conducted in order to work with minimum concentrations of dopants, leading to the economic viability of the photocatalytic technique without reducing efficiency.

## Acknowledgments

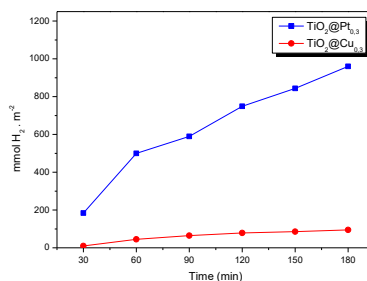
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Already with TiO<sub>2</sub>@Cu a variation in its production was detected with the change in pH (Figure 2). At pH = 9.0 the Hydrogen production values are inverted, the concentration of 1.1% of Cu that produced 29,46 mmol.h<sup>-1</sup>.m<sup>-2</sup> starts to produce 106,85 mmol.h<sup>-1</sup>.m<sup>-2</sup> of H<sub>2</sub> and becomes the ideal catalyst concentration. This result presents a change in the stability of TiO<sub>2</sub>@Cu when at basic pH, supporting literature[9] that already states the same about the catalyst. Thus, pH is a relevant variable for the use of TiO<sub>2</sub>@Cu for the production of H<sub>2</sub>.

The kinetic profiles (Figure 3) demonstrate distinct trends between the catalysts tested. In addition to the discrepancy regarding the production of H<sub>2</sub>, TiO<sub>2</sub>@Pt shows continued production of H<sub>2</sub> in a reaction time later than that experienced, while the presence of Cu denotes photocatalytic stability after 2h of reaction.



**Figure 3.** Evolution kinetics of production from H<sub>2</sub> to TiO<sub>2</sub>@Pt 0.3% and TiO<sub>2</sub>@Cu 0.3%.