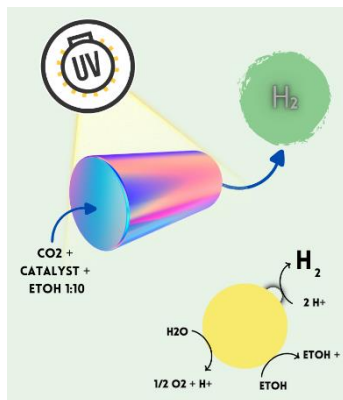


Evaluation of TiO₂/CQD/Ag photocatalytic heterostructures for H₂ generation through the water splitting process

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L. Z. Fogaça¹, L. G. Sakaguti¹, L. S. I. Omori¹, J. C. M. Vicentini², V. R. Batistela¹, M. H. N. O. Scallante¹.
(1) State University of Maringá, Colombo Avenue 5790, Maringá, Paraná, Izfogaça@gmail.com.
(2) FEITEP, Paranavaí Avenue 1164, Maringá, Paraná.



The processes of the production of hydrogen (H₂) through photocatalysis is considered environmentally friendly. Titanium dioxide (TiO₂) is one of the primary photocatalysts used, however, it exhibits a high bandgap energy and electronic recombination. This study employed the synthesis of photocatalysts using TiO₂ P25, carbon quantum dots, and silver through hydrothermal and wet impregnation methods, aiming for better photocatalytic performance and selectivity. The assays were conducted under UV-C light, in a cylindrical batch reactor, for 4 hours, without agitation, in a CO₂ atmosphere, and ethanol as sacrificial reagent. The results indicate that the photocatalysts containing silver, synthesized, via hydrothermal process, demonstrated an average production of 26.941 μmoles g⁻¹ of H₂ and no subproducts were observed, while silver-free catalysts showed no H₂ production during the 4-hour reaction.

Introduction

The production of green hydrogen arouses great due to its capability of mitigating the environmental problems caused by high CO₂ emissions. Redox reactions by photocatalysis are capable of splitting water molecules without emitting atmospheric pollutants, however, bandgap energy (E_g) limitations and electronic recombination in catalysts such as titanium dioxide (TiO₂), hinder the application of this technique in real processes^[1]. Therefore, the doping of catalysts with carbon quantum dots (CQDs) and metals such as silver (Ag) has shown to be effective in improving the presented aspects^[2,3]. Thus, the objective of the present work was to synthesize TiO₂/CQD/Ag heterostructures to evaluate the improvement of photocatalytic performance aiming for high selectivity in hydrogen production.

Material and Methods

Synthesis of photocatalysts

In this stage, four systems were developed using 2 g of TiO₂ P25 (Evonik). Two systems were added to 50 mL of deionized water, and the remaining was added to a solution of 0.01 M AgNO₃. One system with deionized water and the other two systems with AgNO₃ had the addition of 1.5% w/w of CQD, with an average size of 4.9 nm, synthesized via hydrothermal route with a precursor derived from commercial biomass. The systems with AgNO₃ were exposed to UVC light for 1 hour for the photodecomposition of AgNO₃. Subsequently, one of the systems containing Ag and the systems containing deionized water were subjected to a hydrothermal process at 160°C for 4 hours. All catalysts were dried in an oven at 60°C for 12 hours and denoted as TiO₂HT, TiO₂/CQD, TiO₂/CQD/Ag-U and TiO₂/CQD/Ag-HT. The photocatalysts were submitted to DRX, FTIR and PAS characterization.

Hydrogen Production Reaction

The assays were conducted using the module represented by Figure 1, which consists of a cylindrical quartz reactor with a volume of 108.8 mL, an 18 W mercury vapor lamp, and an anodized aluminum refractory arc. Firstly, 30 mg of catalyst were dispersed in 30 mL of a 10% v/v ethanol solution as a sacrificial reagent, resulting in a 1 g.L⁻¹ catalyst solution^[4]. Next, the reactor was purged for 10 minutes with CO₂ to remove atmospheric air and then pressurized to 1.2 bar. The reactor was maintained at 25°C for 4 hours of reaction, and aliquots were withdrawn at 1-hour intervals. The samples were analyzed by gas chromatography.

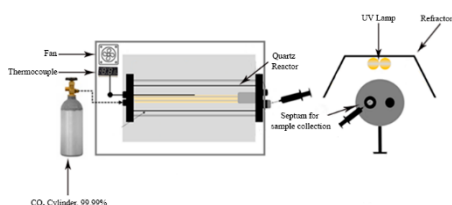


Figure 1. Photoreactor module schematic image. Adapted from: Vicentini et al., (2021)

Results and Discussion

Figure 2 illustrates the hydrogen productions over time for each catalyst, and Table 1 compiles the results concerning the last reaction time (4 h). It is observed that catalysts without the presence of silver were not capable of produce hydrogen throughout the reaction period.

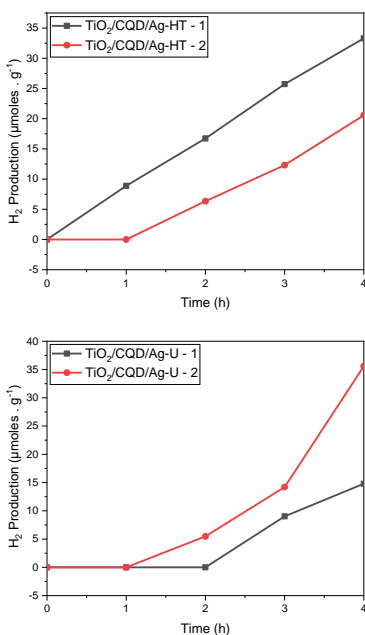


Figure 2. H₂ Production of TiO₂/CQD/Ag-HT and TiO₂/CQD/Ag-U photocatalysts.

It is noticeable that the TiO₂/CQD/Ag-HT catalyst demonstrated better hydrogen productions and higher reaction stability, showing more consistent H₂ rate. This could be attributed to the presence of silver oxide in the catalyst synthesized via the wet route (TiO₂/CQD/Ag-U) confirmed by DRX analysis,

leading to the in-situ reduction process during the photoreaction, thereby justifying the lag in production. Additionally, no by-products resulting from potential CO₂ photoreduction reactions or from the redox reactions of the sacrificial reagent, such as CO, CH₄, C₂H₂ molecules, were observed. The absence of agitation in the reaction module promotes the deposition of photocatalysts at the bottom of the quartz reactor and implies low solution homogeneity, these difficulties could reflect the lack of H₂ production with pure TiO₂. This lack of production also demonstrates the influence of silver presence as a cocatalyst in this photocatalytic system. Photoacoustic spectroscopy (Fig. 3) demonstrates a high absorption pattern throughout the irradiation interval for the catalysts containing Ag, implying significant reductions in E_g, justifying H₂ production even under the reactor's operational conditions.

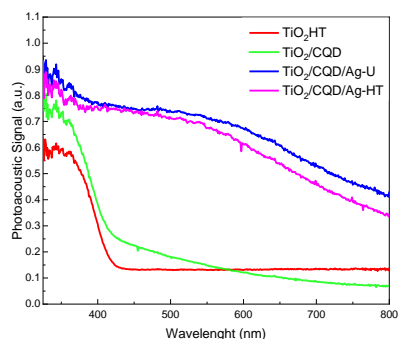


Figure 3. Photoacoustic spectroscopy of catalysts.

Table 1. Results of H₂ production in 4h experiment.

Catalyst	Synthesis Process	Experiment 1	Experiment 2	Average
		H ₂ Production (µmoles g ⁻¹)		
TiO ₂ HT	Hydrothermal	0	0	-
TiO ₂ /CQD	Hydrothermal	0	0	-
TiO ₂ /CQD/Ag-U	Wet Impregnation	14.801	35.580	25.191
TiO ₂ /CQD/Ag-HT	Hydrothermal	33.309	20.573	26.941

Conclusions

The synergy between Ag and CQD allowed the heterostructure enabled its performance, demonstrating the necessity of metals to reduce the bandgap energy, which is essential to water splitting process. Additionally, the absence of by-products from other competitive reactions demonstrates high selectivity on the part of the catalyst. Finally, the in-situ reduction of silver oxide allows for a reduction in the number of processes required for catalyst development, thereby reducing costs and the time needed for synthesis.

Acknowledgments

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