

## Photocatalytic Hydrogen Production: Water Splitting and Reforming of Biomass

**KEYWORDS:** Hydrogen / Water Splitting / Biomass derivatives / TiO<sub>2</sub>/ Carbon Nanotubes/ Graphitic Carbon Nitride

The future requires clean energy solutions using sustainable resources to face increasing demand and the depletion of fossil fuels. Photocatalytic technology was implemented as an effective strategy to produce renewable and sustainable hydrogen (H<sub>2</sub>) by visible-driven water splitting and photocatalytic biomass reforming.

### Introduction

Due to the growing energy demands, energy crisis, and environmental concerns, the pursuit of sustainable and efficient energy sources has increased drastically. Among the various alternatives, hydrogen (H<sub>2</sub>) has emerged as a promising candidate owing to its high energy content and the potential for clean combustion.

Photocatalytic water splitting and photocatalytic reforming of biomass are promising alternatives to generate H<sub>2</sub>. The later has advantages since H<sub>2</sub> is produced with concomitant (photocatalytic) degradation of organic molecules present in water at mild conditions, which may also contribute to the treatment of industrial waters. If other natural renewable resources (like solar energy, widely abundant in south-European countries (e.g., Portugal) are used, then the process becomes even more attractive.

Taking advantage of the increasing advances and knowledge of photochemical technologies, the main objective of our study was to explore strategies to revitalize H<sub>2</sub> production from water splitting and photocatalytic reforming of biomass as an alternative to steam-methane reforming.

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was combined with different materials (e.g., porphyrins, metalloporphyrins, β-cyclodextrin and carbon nanotubes) [1-3] to construct efficient electronically coupled highly stable visible-light-active nanohybrid catalysts, capable of achieving water splitting with minimum possible consumption of energy. The innovative step was to combine the visible light harvesting capabilities of porphyrins with the unique electronic, optical and mechanical properties of carbon-based materials, when acting as supporting substrates, in order to extend charge separation lifetimes by enhancing the intermolecular donor-acceptor electron transfer process between the porphyrin and the semiconductor, a key step in the overall water splitting process.

In addition, the efficiency of the photocatalytic process lies in the combination of effective low-cost photocatalysts with innovative devices, working in continuous mode, enabling

reusability and mass transfer limitation commonly associated with the use of powdered materials.

### Current Development

#### H<sub>2</sub> generation via visible-driven water splitting

We successfully prepared a series of stable and active hybrid photocatalysts composed of g-C<sub>3</sub>N<sub>4</sub> and free-base porphyrins, containing meso-phenyl groups (TPP) and meso-phenyl groups bearing meta- and para-carboxy substituents (mTCPP and pTCPP, respectively). These porphyrins were easily hybridised with g-C<sub>3</sub>N<sub>4</sub> through π-π stacking interactions while maintaining the electronic properties of the g-C<sub>3</sub>N<sub>4</sub>. Their photocatalytic activity was tested for H<sub>2</sub> in water using Pt as co-catalyst and EDTA as sacrificial electron donor. The three hybrids (TPP/g-C<sub>3</sub>N<sub>4</sub>, mTCPP/g-C<sub>3</sub>N<sub>4</sub> and pTCPP/g-C<sub>3</sub>N<sub>4</sub>) show higher performance for photocatalytic H<sub>2</sub> production than that of pure g-C<sub>3</sub>N<sub>4</sub>. The mechanism of H<sub>2</sub> generation involves electron transfer from the excited state of the porphyrin to the conduction band of g-C<sub>3</sub>N<sub>4</sub>, facilitating therefore the separation and transport of the photogenerated charge carriers, thus enhancing the photocatalytic H<sub>2</sub> production activity. This work demonstrates the promising application of graphitic carbon nitride prepared with dye porphyrins for the visible photocatalytic H<sub>2</sub> production from water.

In another study [3], we reported a novel, straightforward, ecofriendly and scalable route towards the simultaneous synthesis of holey carbon-doped g-C<sub>3</sub>N<sub>4</sub> nanosheets with a distorted structure. In this approach, β-cyclodextrin (βCD), a natural macrocyclic oligosaccharide that contains seven d-(+)-glucopyranosyl units connected through α-1,4-glucosidic bonds, was used to induce physicochemical modifications in the electronic structure of the optical semiconductor, because βCD can condense with the precursors of carbon nitrides through H-

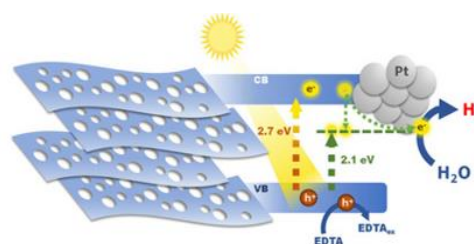


Fig 2. Schematic diagram of charge separation/transportation for the photocatalyst βCD/g-C<sub>3</sub>N<sub>4</sub>. The energies 2.7 eV and 2.1 eV refers to the band gap and midgap states, respectively [2].

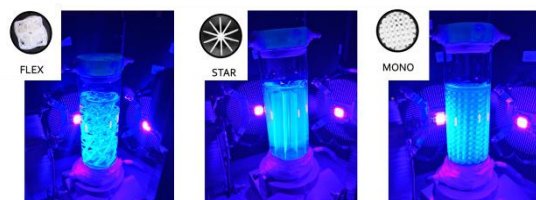


Fig 1. Experimental set-up for H<sub>2</sub> production using the different immobilised photocatalyst structures.

process intensification for H<sub>2</sub> production. Thus, selected catalysts were immobilised in different supports with distinct configurations using additive manufacturing (Fig 1), aiming to eliminate the separation steps, catalyst recovery,

bond formation or can be incorporated in carbon nitride layers. Therefore, considering its chemical structure and properties, βCD was selected to polymerize with dicyandiamide (DCDA) to obtain a modified carbon nitride material. In a simple synthesis, βCD and DCDA in water were thermally heated to dryness, followed by a calcination step. The prepared catalyst not only showed an efficient enhancement in the separation and mobility of the photogenerated charge carriers, but also extended the absorption into the visible region and increased the surface area, showing intriguing structural-distortion-dependent photocatalytic activity. Compared to bulk g-C<sub>3</sub>N<sub>4</sub>, our material increased the H<sub>2</sub> generation from photocatalytic water splitting using EDTA as electron donor by visible light. This work demonstrates a useful strategy for the design and fabrication of highly efficient visible-light carbon nitride photocatalysts with improved texture and electronic properties. Both studies were

carried out in collaboration with multidisciplinary research groups from University of Lisboa and University of Aveiro.

g-C<sub>3</sub>N<sub>4</sub> has also been combined with few-layer graphene (FLG) to develop novel 2D/2D heterostructures that have been used for photocatalytic water splitting [3] in collaboration with the University Abdelmalek Essaadi (Tangier, Morocco) and the University of Toulouse (France). The improved photoactivity was ascribed to a synergistic effect between GCN and FLG, owing to: i) efficient charge separation of photoinduced electron-hole pairs through electron transfer from GCN to FLG, ii) increased surface area, and iii) enhanced visible light absorption. CuAl-layered double hydroxide has also been combined with g-C<sub>3</sub>N<sub>4</sub> to form 2D/2D heterostructures in a collaboration with the Technische Universität Wien (Austria) [4]. The best-performing material exhibited an increased number of active sites and showed a trade-off between charge separation efficiency and light shading, resulting in a 32-fold increase in the amount of evolved H<sub>2</sub> compared with g-C<sub>3</sub>N<sub>4</sub>.

#### Photocatalytic reforming of biomass for H<sub>2</sub> production

Hybrid photocatalysts containing different amounts of carbon nanotubes (CNTs) and Titanium dioxide (TiO<sub>2</sub>) were synthesized by a one-pot oxidation/hydrothermal route and used for H<sub>2</sub> production from aqueous solutions of methanol and glycerol under UV-LED irradiation (Fig 3). Platinum nanoparticles were loaded on the hybrid photocatalyst as co-catalysts [5].

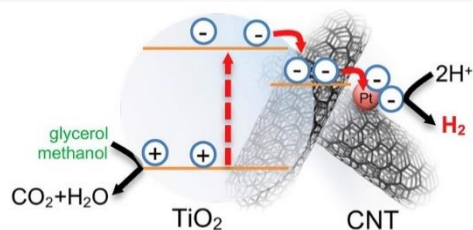


Fig 3. Schematic photocatalytic mechanism using CNT-Pt/TiO<sub>2</sub> hybrids for H<sub>2</sub> production [3].

Overall results revealed that the presence of CNTs promotes an increase in the photoefficiency of the process compared with the neat Pt/TiO<sub>2</sub>, clearly indicate the beneficial effect of CNTs on the

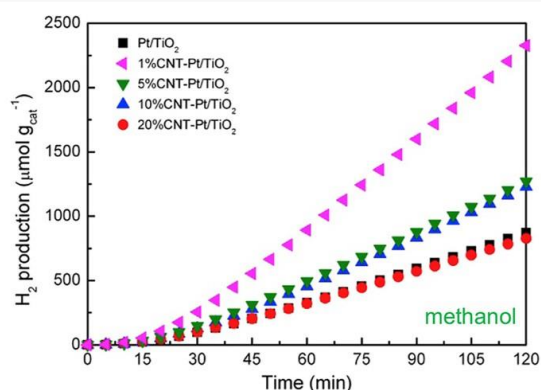


Fig 4. Hydrogen production at 120 min of irradiation from the aqueous solutions of methanol using Pt/TiO<sub>2</sub> and CNT-Pt/TiO<sub>2</sub> materials.

photocatalytic performance of CNT-TiO<sub>2</sub> hybrids for H<sub>2</sub> production. Among the materials tested, the composite containing the lowest CNT content (1 wt%) was the most effective for H<sub>2</sub> generation, with 2327 μmol g<sup>-1</sup> of this gas being formed after 120 min of irradiation using aqueous solutions of methanol

(Fig 4) [5]. Similar results were obtained with glycerol aqueous solutions. This study resulted from a collaboration with the University of Sousse (Tunisia), with a PhD candidate being received at LSRE-LCM.

In another study we have focused on exploring alternative technologies based on H<sub>2</sub> photogeneration from water and biomass using immobilised based photocatalysts. The first approach in the experimental work was to develop a photocatalytic H<sub>2</sub> production system where the photocatalyst was immobilized using additive manufacturing. This method enables highly complex configurations, essential in the photocatalysis field, to maximize the irradiated area.

Two distinct photocatalysts were used for this process, TiO<sub>2</sub> and exfoliated g-C<sub>3</sub>N<sub>4</sub> both loaded with Pt as cocatalyst. The two types of photocatalysts were synthesised, characterised, and later immobilised into the designed structures. Three organic compounds were also studied as sacrificial reagents: methanol, glycerol, and glucose. The photocatalytic experiments were conducted by several evaluation steps concerning the photocatalyst immobilisation method, the structure's configuration, and the sacrificial reagent used for the reaction, firstly with Pt/TiO<sub>2</sub> photocatalyst. For the immobilisation method, the higher performance was achieved with the process consisting of 3D printing of the support structure followed by the immobilisation of the photocatalyst by dip coating. It was concluded that among the tested geometries, the best-performing configuration was the one that potentially allowed a larger irradiated area (FLEX geometry, Fig 1). Among the polyhydroxy compounds tested, the highest concentration of H<sub>2</sub> was achieved using glucose.

#### Future Work

The possibility of immobilising the photocatalysts in various fixed supports is a challenge that has been continuously explored. This approach will avoid the time-consuming and added cost of catalyst separation. In addition, we have been exploring the possibility of using actual waters (seawater and wastewaters) as water sources instead using freshwater.

#### Related Sustainable Development Goals



#### Outputs

##### PhD Theses

Hanane Boumeriame, Development of a novel family of 2D photocatalysts for water splitting in solar applications, PDEQB, FEUP, 2021.

##### Master Dissertations

Hélder Filipe Verdade da Silva Fontes, Synthesis and characterization of doped 2D materials, MIEQ, FEUP, 2019.

Maria Ana Ribeiro de Oliveira e Silva, Structured Photocatalysts Manufactured by 3D Printing for Green Hydrogen Generation, MIEQ, FEUP, 2021.

##### Selected Publications

- [1] E.S. Da Silva et al., ChemSusChem, 11(16), 2681-2694 (2018).
- [2] E.S. Da Silva et al., Appl. Catal. B: Environm., 221, 56-69 (2018).
- [3] H. Boumeriame et al., Int. J. Hydrogen Energy 47, 25555-25570 (2022).
- [4] H. Boumeriame et al., J. Colloid Interface Sci. 652, 2147-2158 (2023).
- [5] N. Naffati et al., Mater. Sci. Semicond. Process. 115, 105098 (2020).

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