

## Intensification of photocatalytic hydrogen generation from glycerol under natural sunlight: Cocatalyst effects and solar applicability

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**Abstract:** This study focuses on intensifying photocatalytic hydrogen generation from glycerol under natural sunlight, examining the effects of cocatalysts and solar applicability. Cocatalysts are commonly employed to enhance the separation of photo-generated charges, while sacrificial agents suppress electron-hole recombination. Utilizing crude glycerol and solar light for photocatalytic hydrogen generation presents a promising avenue. The main objective was to enhance H<sub>2</sub> production from a glycerol-containing solution by selecting parameters and scaling up the process using various reactor types and research systems. The study investigated the applicability of natural sunlight for photocatalytic H<sub>2</sub> production and examined the influence of organic impurities on H<sub>2</sub> production from synthetic and real crude glycerol. Scaling up the process intensified the rate of hydrogen generation, with the highest production achieved using TiO<sub>2</sub> loaded with 0.5% Pt under visible light irradiation. It was

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concluded that H<sub>2</sub> can be generated by reducing protons from both water and glycerol, the sacrificial agent. Glycerol and water, in the presence of photodeposited Pt or Pd on TiO<sub>2</sub> and light, are converted to H<sub>2</sub> through photocatalytic water-splitting and light-induced oxidation of glycerol. The successful application of photocatalysts under natural sunlight for hydrogen production was confirmed, highlighting the potential for sustainable and scalable green hydrogen generation.

**Keywords:** hydrogen production, photocatalysis, noble metal modification, water-splitting, cocatalysts.

## 1. INTRODUCTION

Hydrogen is considered an ecological energy carrier with significant potential for reducing greenhouse gas emissions. To evaluate its potential as a fuel source, the overall energy efficiency and viability of various stages need to be considered, including production, purification, transport, storage, and use (combustion) (Dean, 1999; Ibadon and Fitzpatrick, 2013). An important parameter indicating hydrogen's viability as an energy carrier is its gross calorific value, which is very high (120–142 MJ/kg). This value is more than twice that of methane (50–55 MJ/kg), almost three times that of octane (gasoline) (47.90 MJ/kg), and over five times that of methanol (22.70 MJ/kg). This high calorific value is one of hydrogen's key advantages as a future fuel compared to other energy carriers (Dean, 1999; Bowker et al., 2009).

However, it is crucial to recognize the challenges associated with hydrogen utilization. Due to its very low molar weight, hydrogen requires compression or liquefaction to achieve a usable energy density. This process significantly increases the complexity and cost of hydrogen storage and transportation, particularly for vehicle propulsion. Compressed hydrogen storage necessitates high-pressure tanks, while liquefied hydrogen requires cryogenic temperatures, both of which present technical and economic challenges. Additionally, the energy required for these processes can offset some of the environmental benefits of hydrogen as a clean energy carrier.

The photocatalytic H<sub>2</sub> generation process is performed in the presence of semiconductors that act as photocatalysts. Titanium (IV) oxide is a well-known, non-toxic, and mostly inert photocatalytic material. However, pristine TiO<sub>2</sub> exhibits a low H<sub>2</sub> generation yield, and

several methods can be used to improve its visible light absorbance. Modifying the photocatalyst with metal ions is one of the most popular methods. Generally, the modification narrows the bandgap and enhances light absorption, which can be achieved by depositing metals or sensitized dyes that absorb visible light. When TiO<sub>2</sub> is modified with metal nanoparticles (especially noble metals such as Pt, Au, Pd, and Ag), it acts as an electron trapper and can prevent electron-hole recombination. The absorption of radiation of suitable energy (greater than or equal to the bandgap energy, e.g., 3.2 eV for TiO<sub>2</sub> anatase form) excites electrons from the valence band to the conduction band (Fujishima et al., 2000; Fujishima et al., 2007; Fan et al., 2013; Stelmachowski et al., 2014a, 2014b; Cybula et al., 2014; Bednarczyk et al., 2018; Rafique et al., 2023). Photoexcitation generates highly oxidizing holes and reduces electrons. Catalytic reactions occur at active centers, such as the corners and edges of crystals, contact points between adjacent crystals, and defects in the crystal lattice. The bandgap energy of a semiconductor may reach as much as ~2 eV (Bowker et al., 2009). In practice, pristine substances are rarely used as catalysts; the addition of active ingredients via deposition improves the structural and catalytic properties of the material, modifying the bandgap energy. P25-TiO<sub>2</sub> (pristine TiO<sub>2</sub>) is an n-type semiconductor, and the n/p transition depends on the type and concentration of the metal deposition (Dean, 1999; Ibadon and Fitzpatrick, 2013; Bednarczyk et al., 2018).

It is well known that modification of TiO<sub>2</sub>-based catalysts/carriers with noble metals increases their activity under visible light, enhances charge transfer, and creates active sites for H<sub>2</sub>, significantly increasing H<sub>2</sub> production (Daskalaki and Kondarides, 2009; Zaleska, 2008; Bednarczyk et al., 2018; Kumar et al., 2015; Lei et al., 2023). The effects of many other factors on the efficiency of photocatalytic conversion of organic compounds and water splitting processes have also been widely studied using various catalysts, although most studies focus on noble-metal modification of TiO<sub>2</sub> (Zaleska, 2008; Bowker et al., 2009; Daskalaki et al., 2011; Villachica-Llamosas et al., 2024). One of the most important factors is increasing the spectral sensitivity of TiO<sub>2</sub>-based photocatalysts to visible light (Yu et al., 2010; Yu et al., 2011; Sadandam et al., 2013). The published results are not very optimistic considering the further implementation of the required fabrication methods on a large scale. Maximum hydrogen productivity of 0.22 mmol H<sub>2</sub>/h·g<sub>cat</sub> was observed for water splitting using Cobalt-modified titanium (IV) oxide as a photocatalyst (0.1 g of catalyst suspended in 50 mL of water) under real solar radiation (Gomathisankar et al., 2013). However, our previous study demonstrates that under UV-Vis light, promising high hydrogen production

(141 mmol H<sub>2</sub>/h·g<sub>cat</sub>) can be achieved when 0.5 wt.% Pt-modified TiO<sub>2</sub> is used (Bednarczyk et al., 2018).

Replacing current hydrogen production methods requires the development of a cheap, efficient, and fast hydrogen production method. It is important to first consider the total energy balance of all stages of hydrogen production. One of the most promising processes for producing hydrogen is via photocatalytic H<sub>2</sub> generation in the presence of organic compounds (e.g., alcohols and purified glycerol from bio-ester production). Photocatalytic hydrogen (H<sub>2</sub>) generation by utilizing crude glycerol and solar light is considered a promising avenue. The present work illustrates enhanced rates of H<sub>2</sub> generation and TiO<sub>2</sub>-based catalyst behavior suspended in aqueous synthetic and real crude glycerol solution (industrial byproduct) under visible light irradiation. To the best of our knowledge, for the first time, it was shown that synthetic and industrial byproduct crude glycerol was used as a sacrificial agent to improve photocatalytic efficiency.

This study investigated the applicability of the photocatalytic process for H<sub>2</sub> production from the glycerol–water system under simulated and natural sunlight conditions. Glycerol was selected as a sacrificial agent for improving hydrogen photogeneration. There is a surplus of crude glycerol on the market; it is the main by-product of the transesterification of vegetable oils to produce biodiesel. The increasing amount of crude glycerol may be a serious barrier to the further development of this industry. Photoconversion of glycerol to hydrogen, or bioconversion into hydrogen or other products, may provide a value-added product from a waste product. Therefore, we investigate the mechanism of photocatalytic generation in the presence of crude glycerol as well.

The main goal of this study was to increase the rate of hydrogen generation. Cocatalysts were applied to improve the separation of photogenerated charges, facilitating the water oxidation or reduction reaction. To substantially suppress electron-hole recombination and increase the rate of hydrogen generation, a sacrificial agent was added. The objective of this paper is to present a strategy for photocatalytic H<sub>2</sub> generation using different types of reactors. To achieve this, we combine a detailed analysis of experimental conditions such as the light source, photoreactor, amount of catalyst, type of catalysts with different cocatalysts loading, amount and type of sacrificial reagent, configuration of lamp and photoreactor, etc. Moreover, to reinvigorate industrial interest in the technology, tests on real crude glycerol have been done. Therefore, the study aimed to investigate: (1) production of H<sub>2</sub> from a glycerol-

containing solution, selections of process parameters, and increasing the scale of the process through the use of various types of reactors and research systems; (2) applicability of natural sunlight for photocatalytic production of H<sub>2</sub>; and (3) the influence of organic impurities on H<sub>2</sub> production from synthetic and real crude glycerol.

## 2. MATERIALS AND METHODS

### 2.1. Materials

All reagents used in this work were analytical grade and were used without further purification. Glycerol (GLC;  $\geq 99\%$ ) and 4 hydroxybenzoic acid methyl ester were purchased from Sigma-Aldrich. Methanol (MeOH;  $> 99\%$ ) and 96% ethanol (EtOH) was purchased from Stanlab and ChemLand, respectively. 1-butanol (1-BuOH;  $> 99\%$ ) and 1-propanol (1-PrOH;  $> 99\%$ ) were purchased from Chempur. All solutions were prepared using deionized (DI) water from a Millipore system (Direct-Q®, Merck Millipore). Argon gas (purity  $> 99\%$ ) was purchased from Air Products.

### 2.2. Catalyst preparation

All photocatalysts were obtained by UV reduction of Pt<sup>4+</sup> or Pd<sup>2+</sup> ions in a TiO<sub>2</sub> suspension. An aqueous solution of alcohol (ethanol and isopropanol, 99.8%; Polchem) was used as a hole scavenger and contained TiO<sub>2</sub> microspheres (3 g) and metal precursor (0.1, 0.5, or 1% wt. Pt or Pd). This solution was sonicated for 10 min, stirred in the dark for 2 h, degassed with nitrogen in the dark for 1 h, and finally illuminated using a 1000-W Xe lamp (Osram) as an irradiation source. Details of this procedure are as follows. An aqueous solution of isopropanol containing H<sub>2</sub>PtCl<sub>6</sub> (99%; Sigma Aldrich) or PdCl<sub>2</sub> (5 wt.% solutions in 10 wt.% HCl; Sigma Aldrich) was degassed with nitrogen and irradiated using UV-Vis light from a 1000 W Xe lamp) for 6 h. The modified TiO<sub>2</sub> photocatalysts were rinsed with DI water, separated by centrifugation, and then dried at 65–120 °C for 12 h without calcination. The temperatures used to dry the catalysts did not modify their properties and only removed humidity from the pores. To achieve Pd doping at concentrations of 0.1 wt.%, 0.5 wt.%, and 1 wt.%, the precursor concentrations of PdCl<sub>2</sub> were  $4.02 \times 10^4$  mol/L,  $2.01 \times 10^3$  mol/L, and  $4.02 \times 10^3$  mol/L, respectively. Similarly, the precursor concentrations of H<sub>2</sub>PtCl<sub>6</sub> for Pt-doped catalysts were  $2.2 \times 10^4$  mol/L,  $1.1 \times 10^3$  mol/L, and  $2.2 \times 10^3$  mol/L for 0.1 wt.%, 0.5 wt.%, and 1 wt.%, respectively.

### 2.3. Catalyst characterization

The optoelectronic properties of the pristine TiO<sub>2</sub> and modified catalysts were evaluated by performing diffuse reflectance spectroscopy measurements (DRS-UV/Vis) in the region of 250-700 nm using an Evolution 220 spectrophotometer (Thermo Scientific, Waltham, MA, USA) applying BaSO<sub>4</sub> as the internal reflectance standard. Spectra were recorded in diffuse reflectance mode and transformed to a magnitude proportional to the extinction coefficient ( $\alpha$ ) employing the Kubelka-Munk function ( $F(R_{\infty})$ ) where  $R_{\infty}$  represents the relative percentage of reflectance of the catalyst sample with respect to the reference. The optical band gaps were analyzed using converted Tauc plot by the Kubelka–Munk method and with the application of baseline in the sub-bandgap region approach (based on formula indirect transitions gap) according to Equation (1) based on (Makula et al., 2018).

$$(F(R_{\infty}) \cdot hv)^{\frac{1}{\gamma}} = B(hv - E_g) \quad (1)$$

Where B is a constant,  $hv$  is the photon energy, and  $E_g$  is the bandgap. The  $\gamma$  factor depends on the nature of the electron transition therefore direct and indirect transition band gaps can be calculated when  $\gamma$  is equal to 1/2 or 2, respectively (Makula et al., 2018).

Details about characterization techniques methodology: BET, SEM, XRD, and XPS can be found in our previous papers (Bednarczyk et al., 2018; Borowska et al., 2019; Gomes et al., 2017; Gmurek et al., 2019).

### 2.4. Catalytic activity for hydrogen production

#### 2.4.1. Preliminary study

The experiments were carried out on a “merry-go-round” device with quartz tubes placed between two exposure panels (Luzchem). Each panel consisted of four low-pressure mercury lamps (USHIO, model G8T5 Hg (7.2 W each)) with a maximum emission of 254 nm. The photon flux rate is equal to  $1.56 \times 10^{-4}$  Einstein/m<sup>2</sup> s was previously determined using uranyl oxalate and confirmed by measuring with a radiometer (UV–vis–NIR, Ocean Optics USB4000, USA). The volume of the quartz tube was equal to 13 mL, with an average optical path length of 0.85 cm. Each quartz tube was occupied by a septa and a small hydrogen storage balloon (Fig. 1A). Additionally, the next panel with XBO lamps was used. H<sub>2</sub> was

generated and stored continuously for 2h. After experiments, H<sub>2</sub> was sampled and injected (50 μL) for analysis.

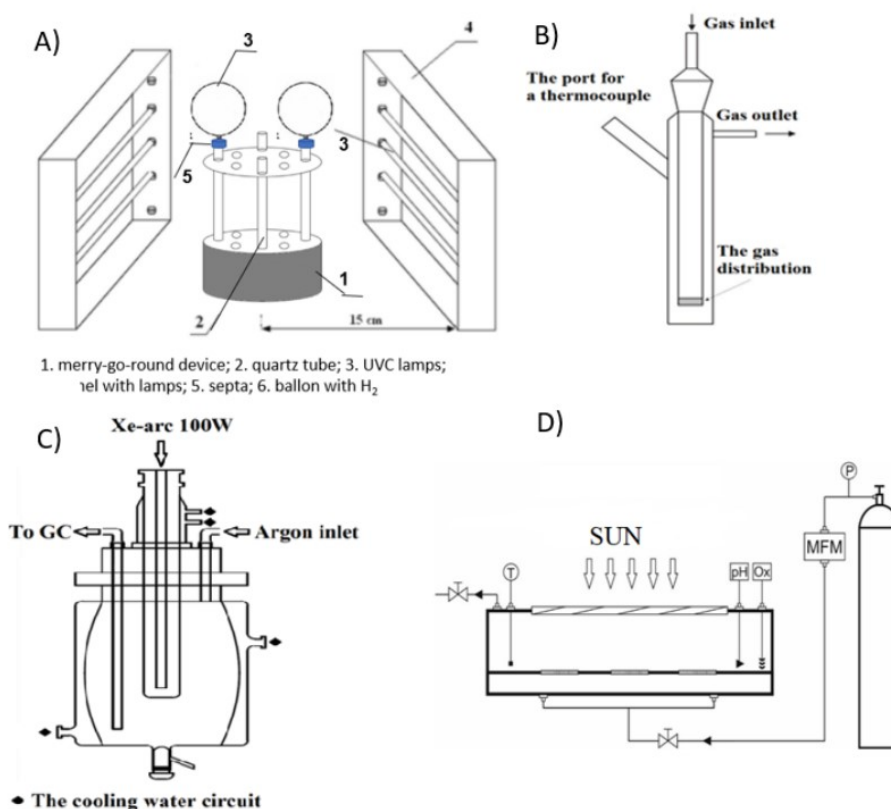


Fig. 1. Schematic diagrams of the (A) reactor for preliminary study; (B) small-lab reactor (40 mL) for H<sub>2</sub> production from synthetic and real crude glycerol solution; (C) large reactor (1200 mL) with the cooling water circuit, (D) reactor for experiments in the Sun (500 mL)

#### 2.4.2. Artificial light

Photocatalytic reaction experiments were performed in a glass semi-batch reactor (1200 mL, Fig. 1C) with a quartz immersion cooling well where the light source was placed. Additionally, the reactor was occupied with a cooling jacket and the temperature was stable at 25±5 °C. The volume of the reaction solution containing the aqueous glycerol solution and photocatalysts was 600 mL. A 100-W Xe arc lamp was used to simulate sunlight and was placed on the vertical axis of the reactor. At the start of each test, the reactor was loaded with an aqueous glycerol solution (4.5 wt.%) and/or other alcohols such as methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), and 1-butanol (1-BuOH), to which the photocatalyst was then added. Suspension of the catalyst in the reaction mixture was obtained by magnetic stirring. Argon was used as a carrier gas in all tests with a flow rate of 150 mL/min. The flux

of argon removed gases from the solution, such as dissolved oxygen, as well as oxygen, hydrogen, and carbon dioxide produced during the photocatalytic process (this stream of gaseous products was then analyzed by GC). Carbon dioxide concentration measurements were made using an LB-854 meter (LAB-EL), which was located in the discharge gas loop into the GC system. Each experiment lasted approximately 4 to 6 h.

#### 2.4.3. *Natural sunlight*

For this purpose, a specially designed reactor was applied. The reactor was made of boron glass with a special quartz glass upper layer. The total capacity of the reactor was 500 mL with a working volume of 250 mL (Fig. 1D). The bottom of the reactor was equipped with a bubble system responsible for distributing the carrier gas and mixing the solution. During the process, measurements of oxygen concentration, carbon dioxide, pH, and reaction temperature were performed. Additionally, the same setup was used for comparison with artificial XBO 100 W and 150 W. At the beginning of the process, the reaction temperature was 25 °C, which increased to 40-55 °C during the experiments, depending on the weather conditions.

#### 2.4.4. *Photocatalytic H<sub>2</sub> generation from synthetic and real crude glycerol solution*

The photocatalytic generation of H<sub>2</sub> from the synthetic and real crude glycerol solution was performed in a semi-batch quartz reactor with a volume of 40 mL (Fig. 1B). The volume of the reaction solution containing a mixture of water, the selected organic ester (4-hydroxybenzoic acid methyl ester), and the photocatalyst was 16 mL. Three external xenon lamps (Xe-arc XBO; 75 W each) were used to simulate sunlight. The reactor was loaded with an aqueous solution containing glycerol (1.5 wt.%), methanol (1 wt.%), rapeseed oil (2 wt.%), 4-hydroxybenzoic acid methyl ester (0.1% wt.%) (MP, methylparaben), and 0.083 g/L of 1 wt.% Pt/TiO<sub>2</sub>. During the experiments, the temperature was measured but not controlled. At the start of the process, the reaction temperature was 25 °C, which increased to 55 °C during the experiments. Argon with a flow rate of 30 mL/min was used as a carrier gas in all tests to remove dissolved oxygen (before the start of each run) and remove gaseous products from the reaction mixture during the experiment. Suspension of the catalyst in the reaction mixture was obtained by magnetic stirring and bubbling argon.



## 2.5. Analytical methods

A gas chromatograph (Perkin Elmer) equipped with a TCD detector was used for the analysis of the gas phase. The volume of the gas sample was 1 mL. The evolved gases were analyzed every 15 min using a silica gel-packed column (Altech 5651 PC). The chromatographic conditions were as follows: injector port temperature of 200 °C, detector temperature of 220 °C, a temperature program of 120 °C for 3.5 min, ramp up to 180 °C at 40 °C/min, and then held for 4 min.

Samples were taken from the liquid phase after the reaction was complete and analyzed using a gas chromatography/mass spectrometry system equipped with a headspace Shimadzu Ultra GCMS-QP2010. A gas chromatograph with a mass detector enables the analysis of organic compounds in both the gas and liquid phases. The mass range of the analyzed compounds:  $m/z$  was 1.5–1090. The chromatographic conditions were as follows: column temperature of 40 °C, injection temperature of 260 °C, pressure of 15.5 kPa, and column flow of 1.56 mL/min.

Carbon dioxide concentration measurements were performed using a LAB-EL LB-854 meter based on the non-dispersive infra-red (NDIR) detector method, which is now the industry standard for measuring the concentration of carbon oxides (CO and CO<sub>2</sub>). This technique is based on the measurement of the attenuation of IR radiation at a specific wavelength transmitted by the measured gas, where its suppression is dependent on the carbon content in the test gas. The NDIR method provides accurate and stable measurement results. A sensor for measuring CO<sub>2</sub> was placed inside the controller and fed with the gas stream to be analyzed, which allowed the gas to be supplied from a distant source. The measurement range of the volume content of CO<sub>2</sub> was 0–10000 ppm (0–1%), while the accuracy of CO<sub>2</sub> measurement at 22 °C was  $\pm 5\%$  of the measured value plus  $\pm 100$  ppm.

## 3. RESULTS AND DISCUSSION

### 3.1. Preliminary study - enhancement by visible light

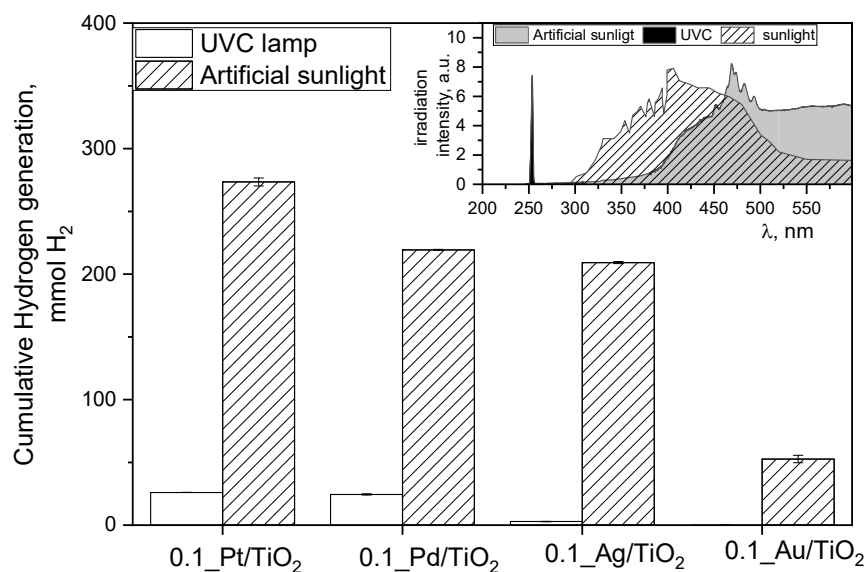


Fig. 2. Cumulative hydrogen generation after UVC and Visible light irradiation in the presence of modified catalysts. Insert: Emission spectra of different light sources (UVC, XBO, and sunlight)

A preliminary study focused on investigating the improvement of hydrogen generation under different light irradiations. Therefore, experiments have been conducted with the application of a monochromatic UVC lamp (254nm; 44.4 W / m<sup>2</sup> equals 1.56 × 10<sup>-5</sup> Einstein / m<sup>2</sup> s) as well as a polychromatic Xenon arc lamp ( $\lambda > 370\text{nm}$ ; 192.02 W/m<sup>2</sup> equals 6.76 × 10<sup>-4</sup> Einstein/m<sup>2</sup>s) used as artificial sunlight. The experiments were performed on a “merry-go-round” device with quartz tubes, each occupied by a septa and a small hydrogen storage balloon (more details in the Methods section). 13 mL of the aqueous solution of glycerol (4.5 wt.%) in the presence of 70 mg (5.38 g/L) catalyst modified by 0.1wt% of Pt, Pd, Ag, and Au. Additionally, as a baseline, pristine TiO<sub>2</sub> has been applied. Fig. 2 presents cumulative hydrogen after 1 hour of irradiation. As can be seen, H<sub>2</sub> generation is enhanced under visible light. Modification by noble metals favors photocatalytic production compared to pristine TiO<sub>2</sub> (1.18 mmol of H<sub>2</sub> and 0.02 mmol of H<sub>2</sub> under visible and UVC light, respectively). Apparent quantum yield (AQY) calculation (twice the ratio of the number of produced hydrogen molecules to the number of incident photons) is often used for photocatalytic activity description. For evaluation of photocatalytic activity following AQY was determined for the primary experiments with 0.1 wt.% modification as well as for 1 wt.% of Platinum TiO<sub>2</sub> modification for 4.5% glycerol solution.

The highest H<sub>2</sub> efficiency has been observed for Pt\_TiO<sub>2</sub> catalysts for both light sources (273.46±3.17 mmol of H<sub>2</sub> (Vis, AQY equals 14.3% for 420 nm) and 25.97±0.15 mmol of H<sub>2</sub> for (UVC, AQY equals 9.7). Interestingly, considering Pd\_TiO<sub>2</sub>, slightly lower H<sub>2</sub> efficiency was observed under UVC light (24.44±0.49 mmol of H<sub>2</sub>) compared to Pt\_TiO<sub>2</sub>. While, when XBO lamps have been used the efficiency of Pd\_TiO<sub>2</sub> was much lower and comparable to Ag\_TiO<sub>2</sub> (219.46±0.42 and 209.17±0.85 mmol of H<sub>2</sub>, respectively). Au\_TiO<sub>2</sub> seems to be the worst catalyst under visible and UVC light.

Modifying TiO<sub>2</sub> by a metal enables visible-light-activated photocatalysis and enhanced hydrogen generation efficiency by improving the separation of photo-generated charges (the Schottky barrier formation at the metal-semiconductor interface). It is known that the Fermi level of unmodified TiO<sub>2</sub> is higher than that of noble metals; therefore, modification results in the effective transfer of the photogenerated electrons from the conduction band of TiO<sub>2</sub> to the metal particles. On the basis of that electron trapping process, the electron-hole recombination rate is significantly reduced, causing stronger photocatalytic reactions. Therefore, the enhancement of photoactivity in the visible range arises from the prolongation of the lifetime of charge carriers. As mentioned, the noble metal acts as an electron trap, and the transfer of electrons from TiO<sub>2</sub> to substrates is accelerated (Janczarek and Kowalska, 2017; Grabowska et al., 2018). These photocatalysts have also used plasmonic properties to gain activity under visible-light irradiation (Zaleska, 2008; Janczarek and Kowalska, 2017; Grabowska et al., 2018). As can be concluded, an improvement in photocatalytic activity and H<sub>2</sub> generation efficiency can be observed due to minimizing electron-hole recombination that is enabled by the cocatalytic role of Pt and Pd. Given that Pt has a higher work function (5.65 eV) than Pd (5.12 eV), this resulted in a higher Schottky barrier (the lower Fermi level) that inhibits the recombination of photogenerated charges. However, according to the volcano plot of hydrogen evolution in metal catalysts, the hydrogen evolution reaction (HER) in Au is limited by its lower binding energy (metal-hydrogen bond) compared to Ag, Pd, and Pt (Greeley et al., 2006).

The visible-light activities originate from the changes in the band-gap structure of the semiconductor resulting from noble metal modification. The optical properties of the photocatalysts obtained by the photodeposition method (Pd\_TiO<sub>2</sub>, Pt\_TiO<sub>2</sub>, and Ag\_TiO<sub>2</sub>) and the sol-gel (Au\_TiO<sub>2</sub>) were investigated by diffuse reflection spectroscopy. Fig. 3 shows the UV/Vis DRS spectra for TiO<sub>2</sub> photocatalysts modified by 0.1 wt.% (A) and 0.1 wt.%, 0.5 wt.%, and 1 wt.% modification of Pd and Pt (B, C).

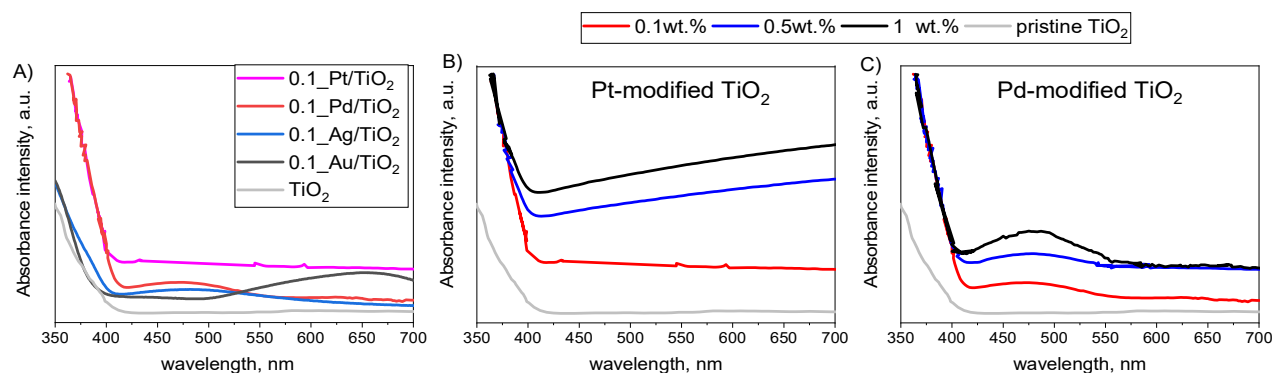


Fig. 3. UV/Vis DRS spectra of TiO<sub>2</sub> photocatalysts modified with 0.1 wt.% loading of Pt, Pd, Ag and Au (A) as well as of TiO<sub>2</sub> catalysts with Pt and Pd loadings from 0.1 to 1 wt% (B and C, respectively)

The spectrum of unmodified TiO<sub>2</sub> clearly shows an absorption onset at about 400 nm while above 400nm P25-TiO<sub>2</sub> (pristine TiO<sub>2</sub>) does not exhibit any absorption ability. Conversely, visible light absorption enhancement has been clearly shown after modification (significant for Pt and Pd loaded catalysts). As can be seen in Fig. 3A, modification by 0.1wt.% is the most sufficient for Pt\_TiO<sub>2</sub>, which confirms preliminary results. Moreover, spectra of Pt\_TiO<sub>2</sub> and Pd\_TiO<sub>2</sub> overlap in the UV region, which can explain similar H<sub>2</sub> efficiency of those catalysts under UVC light. Surprisingly, the spectra for Pd\_TiO<sub>2</sub> and Ag\_TiO<sub>2</sub> confirm similar visible light absorption ability, which was shown in the similar H<sub>2</sub> efficiency for the XBO lamp. When different loadings are considered, the highest absorption of light in the visible range is shown by the 1\_Pt/TiO<sub>2</sub> photocatalyst containing 1 wt. % of platinum. A bathochromic shift of the absorption maximum was also observed for palladium-modified photocatalysts. Undoubtedly, there is a trend of improvement in visible light absorption with increasing metal content (for Pd and Pt) when the photodeposition method is considered. In the case of the sol-gel synthesis method, the highest absorption in the visible light range is shown by the 1\_Pd/TiO<sub>2</sub> photocatalyst containing 1 wt. % palladium. However, in the case of platinum modification by the sol-gel method no differences can be observed for samples with a content of 0.5 wt. % and 0.1 wt. % (0.5\_Pt/TiO<sub>2</sub> and 0.1\_Pt/TiO<sub>2</sub>, respectively).

Several characterization techniques, including BET, SEM, XRD, and XPS, have been used for morphological and surface characterization of catalyst samples and discussed in our previous papers (Bednarczyk et al., 2018; Borowska et al., 2019; Gomes et al., 2017; Gmurek et al., 2019). Chemical composition of the noble metal decorated TiO<sub>2</sub> obtained from XPS

measurement of various modification loadings are provided in Table 1. In almost all cases the lowest loadings were below detection, only modification with Pt confirmed its presence in the structure (atomic Pt content equal to 0.08%). For silver and gold modification (0.1 wt.%), it was not possible to precisely measure the contents (data not shown). However, for 0.5 wt.% Ag/TiO<sub>2</sub> 0.47 atom% was successfully deposited on the TiO<sub>2</sub> surface, while for 0.5 wt.% Au/TiO<sub>2</sub> only 0.02 atom% of Au was detected. As discussed by Borowska et al, 2019, XPS measurements of catalyst with higher loadings (0.5 wt.% and 1 wt.%) the analyzed content of deposited metals are lower than assumed due to lower yield of the photodeposition method. But still, the highest atomic content was detected for highest loading, 0.61 atom% and 0.70 atom% for 1 wt.% Pt/TiO<sub>2</sub> and 1 wt.% Pd/TiO<sub>2</sub>, respectively (Table 1). This finding has been confirmed by SEM analysis, that can be found in (Borowska et al., 2019). The high-resolution XPS spectra for Pd3d and Pt4f and XPS survey spectra are depicted and discussed in (Borowska et al., 2019). The surface area of P25-TiO<sub>2</sub> (pristine TiO<sub>2</sub>) was shown to be 50 m<sup>2</sup>/g. For catalysts prepared by photodeposition decolorized by Pt and Pd nanoparticles method BET surface area equaled 55 m<sup>2</sup>/g (for highest loadings) and 53 m<sup>2</sup>/g for 0.5 wt.% (Borowska et al., 2019). The highest BET surface area of ~135 m<sup>2</sup>/g was analyzed for catalyst modified by sol-gel method with Au nanoparticles. X-ray diffraction (XRD) analysis showed that phase concentrations did not depend on the amount of metal modification, and the original 80% anatase and 20% rutile fraction were mostly maintained (Bednarczyk et al., 2018). With increasing Pt concentration, the crystallite size increased from 19.6 nm to 22.0 nm for anatase and decreased from 41.5 nm to 21.6 nm for rutile.

The corresponding bandgaps ( $E_g$ ) were determined from the Tauc plot of the transformed Kubelka – Munk function as it results from the estimation presented in Table 1. The bandgap results confirmed that with increasing load of nanoparticles, the bandgap decreased. For catalysts prepared by photodeposition and for sol-gel method, the lowest  $E_g$  were found to have Pt/TiO<sub>2</sub> compared to Pd/TiO<sub>2</sub>. The bandgap value for the photocatalysts obtained by the photodeposition method was lower than that obtained by the sol-gel method (data not shown). Pt and Pd modified TiO<sub>2</sub> by the photodeposition method have been selected for further investigation based on characteristic results and  $E_g$ .

Table. 1. Characterization of photocatalysts: determined bandgap, XRD analysis, specific surface area (BET), relative elemental metal concentrations obtained from XPS analysis (characteristics summarized based on our previous research (Bednarczyk et al., 2018; Borowska et al., 2019; Gomes et al., 2017; Gmurek et al., 2019))

Catalysts	E <sub>g</sub> ,	Anatase	Rutile	Crystallite size	BET	O content	Ti content	C content	Metal content
	eV	%	%	nm	m <sup>2</sup> /g	at.%	at.%	at.%	at.%
0.1_Pt/TiO <sub>2</sub>	3.054	80	20	18.4-19.6	54	48.57 ± 0.43	21.11 ± 0.17	30.25 ± 0.59	0.08 ± 0.01
0.5_Pt/TiO <sub>2</sub>	3.031	79	21	19.8-21.5	53	48.70 ± 0.55	20.73 ± 0.01	30.46 ± 0.54	0.13 ± 0.01
1_Pt/TiO <sub>2</sub>	3.017	80	20	20.0-22.0	55	46.74 ± 0.27	18.13 ± 0.04	34.23 ± 0.13	0.61 ± 0.01
0.5_Pd/TiO <sub>2</sub>	3.051	80	20	20.3-22.3	53	55.88 ± 0.05	23.66 ± 0.62	20.24 ± 0.66	0.23 ± 0.01
1_Pd/TiO <sub>2</sub>	3.033	88	12	19.1-20.6	55	54.95 ± 0.41	23.40 ± 0.32	20.95 ± 0.05	0.70 ± 0.02
0.5_TiO <sub>2</sub> -Au*	-	99	1	10-12	135	14.30 ± 0.07	76.20 ± 0.44	9.48 ± 0.37	0.02 ± 0.00
0.5_TiO <sub>2</sub> -Ag	-	80	20	45-52	34	58.63 ± 0.66	23.84 ± 0.25	17.06 ± 0.88	0.47 ± 0.04

BET for P25-TiO<sub>2</sub> (pristine TiO<sub>2</sub>)= 51 m<sup>2</sup>/g; TIP== 160 m<sup>2</sup>/g; E.g. for 0.1\_Pd/TiO<sub>2</sub> equals 3.066 and for P25-TiO<sub>2</sub> (pristine TiO<sub>2</sub>) equals 3.297; \*- prepared by sol-gel method calcined in 400 °C

### 3.2. Up-scale artificial sunlight experiments

The first part of this study involved the selection of parameters for different types of reactors. This was done from several perspectives to maximize hydrogen production, including the type of catalyst, catalyst dose, and type of organic compound dissolved in the water. The glycerol concentration was the same for all runs (4.5 wt.%). The influence of the type and concentration of metal loading was determined. An important aspect of the research was the intensification of process parameters and the scaling up of the process using various types of reactors and research systems. The process was upgraded from a 40 mL to a 1200 mL reactor (working solution 16 mL and 600 mL, respectively). Based on our previous research, where experiments were performed in the small reactor (40 mL) we assumed that water splitting and glycerol conversion into hydrogen occurred simultaneously. The highest H<sub>2</sub> production was obtained for the aqueous solution of glycerol (4.5 wt%), for Pt\_TiO<sub>2</sub> (0.5 wt.% of Pt, prepared by the photodeposition method and calcined). The average H<sub>2</sub> generation efficiency was 137.53 ± 4.31) mmol H<sub>2</sub>/h·g<sub>cat</sub> (while the maximum yield reached during the experiments was 141.84 mmol H<sub>2</sub>/h·g<sub>cat</sub>).-To investigate the scaling-up effect, the concentration of the catalyst was kept at 0.083 g/L, as in the smaller reactor. As shown in Fig. 4A, scaling up improved H<sub>2</sub> production. When P25-TiO<sub>2</sub> (pristine TiO<sub>2</sub>) was applied, the efficiency of H<sub>2</sub> generation reached ~5.6 mmol H<sub>2</sub>/h·g<sub>cat</sub> in the scaled-up system, while in the small reactor, it was by half

lower. Modified TiO<sub>2</sub> with photodeposited Pt and Pd significantly increased productivity. Moreover, the Pt-modified catalysts achieved higher hydrogen production efficiency than Pd-based catalysts. However, it should be noted that the smaller reactor worked with an external light source, while the larger reactor with an internal light source. Therefore, the next intensification and scaling up were performed using the same experimental equipment.

Based on preliminary results, Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> were selected. The increase in metal loadings had a positive impact on visible light ability, making it reasonable to investigate this parameter. As shown in Fig. 3A insert, the H<sub>2</sub> evolution rate slightly depended on noble metal loading. For three loading levels of Pt nanoparticles, we obtained 150.0±1.75 mmol H<sub>2</sub>/h·g<sub>cat</sub>, 161.48±2.10 mmol H<sub>2</sub>/h·g<sub>cat</sub>, and 147.51±1.15 mmol H<sub>2</sub>/h·g<sub>cat</sub> for 0.1, 0.5, and 1 wt.% loadings, respectively. For Pd/TiO<sub>2</sub> catalysts, the H<sub>2</sub> evolution rate was found to be almost equal across all Pd loadings (0.1 wt.% - 118.92±1.94 mmol H<sub>2</sub>/h·g<sub>cat</sub>, 0.5 wt.% - 125.52±1.57 mmol H<sub>2</sub>/h·g<sub>cat</sub>, 1 wt.% - 120.54±1.43 mmol H<sub>2</sub>/h·g<sub>cat</sub>). In both cases, insignificantly higher values were found for 0.5 wt.% loadings.

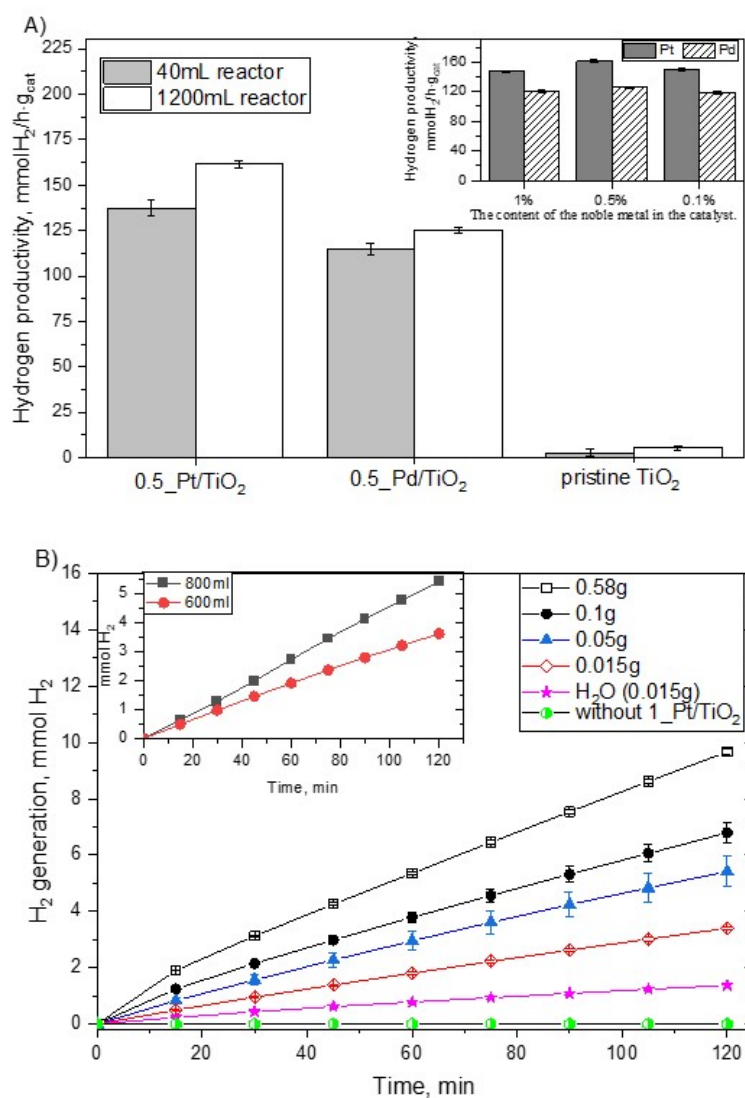


Fig. 4. A) Effect of upscaling for Pt and Pd modified catalysts loaded by 0.5 wt.%, Insert: Catalyst type and content of metal modification influence on H<sub>2</sub> generation (4.5% wt. GLC, 100 W; 0.083 g/L of catalyst). B) Catalyst dose influence on H<sub>2</sub> generation (1\_Pt/TiO<sub>2</sub>, 4.5% wt. GLC, 100 W). Insert: Increasing the reactor volume from 600mL to 800mL (1\_Pt/TiO<sub>2</sub>, 4.5% wt. GLC, 150 W for 800mL and 100W for 600mL, 0.03 g/L)

High H<sub>2</sub> productivity is the obvious goal for reaction engineering and reactor design. The H<sub>2</sub> evolution is strongly dependent on the catalyst used. Thus, the catalyst selection and its applied dose play a vital role in the success of scaling-up of this process. Therefore, a next step of investigation was to examine the influence of catalyst dose (0.015g–0.58g per 600 mL, 100 W internal light  $3.16 \times 10^{-6}$  Einstein/m<sup>2</sup> s). As mentioned above, the productivity of H<sub>2</sub> is commonly described by the rate of H<sub>2</sub> evolution (mmol H<sub>2</sub>/h.g<sub>cat</sub>). But when the catalyst dose is examined, this unit could lead to misunderstanding (due to the calculation per catalyst



dose). Here, the evolution of H<sub>2</sub> is presented as an amount of produced H<sub>2</sub> in mmol. The highest hydrogen evolution after 2h was achieved for the highest catalyst dose – 9.67±0.09 mmol of H<sub>2</sub> (Fig. 4). However, considering the cost of catalysts, the best solution has to be obtained. Based on this approach, the concentration of 0.05 g per 600 mL (0.083 g/L) could be considered an efficient one. When 0.05 g was applied (more than 10 times lower than the highest dose), the H<sub>2</sub> concentration was less than twice lower (5.41 mmol of H<sub>2</sub> compared to 9.67 mmol of H<sub>2</sub>). It should be noted that when the lowest catalyst dose was used, 3.40±0.07 mmol of H<sub>2</sub> was produced in a solution containing 4.5 wt.% GLC, while without glycerol, 1.37±0.07 mmol of H<sub>2</sub> was generated. The irradiation of solution without GLC and catalyst was not able to produce hydrogen. Upscaling to 800 mL with the application of a more powerful lamp led to significant improvement (Fig. 4: Insert).

Different organic substances (e.g., alcohols, oils, and sugars) influence hydrogen yield when dissolved in reaction water (Gombac et al., 2010; Gomathisankar et al., 2013; Jovic et al., 2013; Kumar et al., 2016; Chen et al., 2018; Hainer et al., 2018; Chen et al., 2020; Villachica-Llamosas et al., 2024;). The addition of sacrificial hole scavengers such as methanol is a commonly used practice in semiconductor photocatalysis to promote electron-hole pair separation after photoexcitation (Daskalaki and Kondarides, 2009; Gombac et al., 2010; Daskalaki et al., 2011; Kumar et al., 2016). The addition of an alcohol sacrificial agent (sacrificial electron donors) quenches electron-hole pair recombination in the semiconductor (progressively oxidized by valence band holes on the photocatalyst surface), thus accelerating the H<sub>2</sub> production efficiency of metal-modified TiO<sub>2</sub> photocatalysts under visible and UV excitation (Gombac et al., 2010; Kumar et al., 2016; Chen et al., 2018; Hainer et al., 2018; Chen et al., 2020).

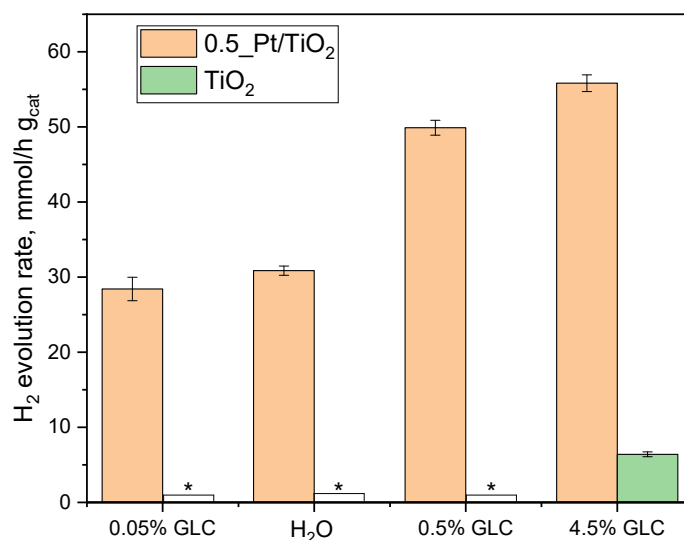


Fig. 5. Effect of glycerol addition on H<sub>2</sub> generation in the presence of Pt/TiO<sub>2</sub> catalyst loaded by 0.5 wt.% and pristine TiO<sub>2</sub> (40 mL reactor, 225 W (3 lamps); 0.93 g/L of catalyst)

Investigating the impact of glycerol on the productivity of H<sub>2</sub> in the small reactor confirmed this hypothesis (Fig. 5). The highest yield - 55.82 mmol /h·g<sub>cat</sub> was obtained for 4.5% glycerol with the addition of a metal-loaded photocatalyst. However, for the addition of pristine TiO<sub>2</sub>, the hydrogen production was 86% lower than for the platinum-modified photocatalyst. For water with a 0.5 wt. % Pt/TiO<sub>2</sub> photocatalyst, the yield was 33% lower than for the glycerol solution, while for water with the addition of pristine TiO<sub>2</sub>, no hydrogen peak was obtained. Interestingly, when Pt/TiO<sub>2</sub> was applied with a load of 0.5 wt.%, an acceleration in H<sub>2</sub> productivity was observed even after 0.5 % glycerol addition compared to water. While when pristine TiO<sub>2</sub> was used, H<sub>2</sub> was generated only in the presence of 4.5 % glycerol. In a bigger reactor, as shown in Fig. 4A, experiments performed with P25-TiO<sub>2</sub> (pristine TiO<sub>2</sub>) suspended in a water-glycerol solution showed very low hydrogen production (5.62 mmol H<sub>2</sub>/h·g<sub>cat</sub>). No H<sub>2</sub> was detected when pristine TiO<sub>2</sub> was applied to water or when the experiment was carried out without catalysts (Table 2). Moreover, for the reaction without irradiation, the efficiency of hydrogen production was also negligible. However, experiments using modified TiO<sub>2</sub> by noble metals in water showed a H<sub>2</sub> productivity of ~13 mmol H<sub>2</sub>/h·g<sub>cat</sub>. Unmodified TiO<sub>2</sub> is known to be inefficient for H<sub>2</sub> generation as a result of rapid electron-hole recombination, leading to the limitation of charge carriers available for photoreactions (Jovic, 2013). Table 2 shows the hydrogen yields when different alcohols, such as glycerol (GLC), methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH) and 1-butanol (1-BuOH) were added to the water. The following trend was observed: GLC > MeOH

> EtOH > 1-PrOH > 1-BuOH > pure water. This finding is in agreement with our previous results on a smaller scale (Bednarczyk et al., 2018). As can be seen, true water splitting in the absence of sacrificial donors (that act as hole traps) is very inefficient even when Pt\_TiO<sub>2</sub> is considered. The H<sub>2</sub> production from pure water is around 10% of the overall H<sub>2</sub> production when GLC is presented.

Table 2. Influence of sacrificial electron donor additives (4.5 wt.% ) on H<sub>2</sub> production. The concentration of the catalyst was 0.083 g/L and 1 wt.% Pt\_TiO<sub>2</sub> catalyst was used

The type of solvent	GLC C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	MeOH CH <sub>4</sub> O	EtOH C <sub>2</sub> H <sub>6</sub> O	1-PrOH C <sub>3</sub> H <sub>8</sub> O	1-BuOH C <sub>4</sub> H <sub>10</sub> O	Water H <sub>2</sub> O	WATER H <sub>2</sub> O*
Average hydrogen yield, mmol H <sub>2</sub> /h·g <sub>cat</sub>	147.52 ±1.45	124.24 ±2.34	98.65 ±1.89	72.54 ±1.45	56.31 ±1.97	13.56 ±1.68	0

\* H<sub>2</sub> was not detected in two experiments (1) without the addition of a photocatalyst and (2) with pristine TiO<sub>2</sub>

The study examined the influence of glycerol concentration on H<sub>2</sub> yield. Optimal hydrogen production occurred with glycerol concentrations between 1% and 12% (Fig. 6), with the highest rate observed at 9% glycerol concentration. The cumulative production of H<sub>2</sub> after 2 h is shown in Fig. 6 inset; these data also did not show a clear trend. Only slightly higher H<sub>2</sub> concentration was detected when using higher glycerol contents. Yet these differences were not significant. Therefore, the optimal concentration of glycerol cannot be predicted with sufficient precision. This may be because the photoconversion of glycerol into hydrogen and water splitting occurred simultaneously, making it difficult to separate these processes. If the presence of glycerol in water influences the rate and yield of the water-splitting reaction, it is very difficult to determine the effect of the concentration of glycerol on the total hydrogen production. Hence, further studies are required.

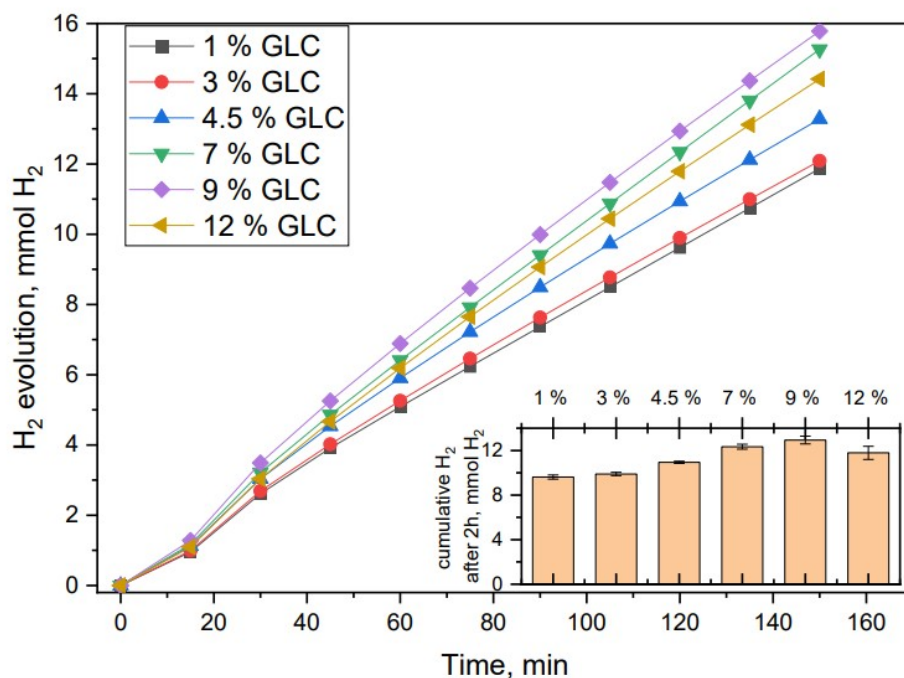


Fig. 6. Influence of glycerol concentration on the hydrogen productivity over time with a catalyst concentration of 0.083 g/L and 1 wt.% Pt/TiO<sub>2</sub> catalyst

### 3.3. Natural sunlight experiments

In small-scale experiments, the effect of lamp power - radiation intensity on the efficiency of H<sub>2</sub> production was determined (Bednarczyk et al., 2018). As expected increasing photon entry to the solution resulted in higher H<sub>2</sub> efficiency. While the natural sunlight experiments were planned, a preliminary study with a new reactor for experiments in the sun was performed. The difference was in the construction of the reactor and in the irradiation of the reaction mixture system by an external light source. The mixture was a solution of 250 mL of 4.5 wt.% GLC with the addition of a TiO<sub>2</sub> photocatalyst with the deposition of Pt or Pd metal and irradiation of the system with a xenon lamp: with a power of 100 W and 150 W. Then, for the same conditions, the photocatalytic production of H<sub>2</sub> was carried out using solar radiation (in August 2017 - experiments were performed between 10 a.m. and 2 p.m.). As can be seen in Fig. 1 insert, the emission spectrum of natural sunlight contains UVA and visible light (from 300nm), while the XBO lamp emits radiation above 370 nm.

The influence of the radiation intensity is confirmed by the use of different lamp powers for this reactor: 100 W and 150 W. For the 0.5\_Pt/TiO<sub>2</sub> photocatalyst and the 150 W lamp, the efficiency of H<sub>2</sub> production was 28.53 mmol H<sub>2</sub>/h·g<sub>cat</sub>, while for 100 W - 25.17 mmol H<sub>2</sub>/h·g<sub>cat</sub>.

Photocatalysis is one of the main approaches to producing hydrogen by utilizing solar energy. A summary of the photocatalysts and the main results is reported in Table 3. The results showed the influence of the type and power of radiation on the efficiency of H<sub>2</sub> production. It was found that under natural sunlight, higher radiation intensity resulted in higher H<sub>2</sub> productivity. The highest efficiency of H<sub>2</sub> production was obtained for the photocatalysts modified with Pt and Pd with 0.1 wt. % and 0.5 wt. %, respectively. For 0.5\_Pt/TiO<sub>2</sub>, the highest production efficiency was 66.34 mmol H<sub>2</sub>/h·g<sub>cat</sub> at irradiance greater than 450 W/m<sup>2</sup>. The measured concentration of CO<sub>2</sub> and O<sub>2</sub> in the solution increased with increasing H<sub>2</sub> production efficiency. The pH of the solution for 0.5\_Pt/TiO<sub>2</sub> decreased from the value of 5.27 to 3.25, which is the result of dissolving a part of the CO<sub>2</sub> in the solution. For these process conditions, the decomposition of GLC was small (around 1%).

Table 3. Photocatalytic H<sub>2</sub> yield under natural sunlight (4.5 wt.% GLC, photocatalyst: 0.083 g/L, Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> with different loading)

Type of photocatalyst	1_Pt/TiO <sub>2</sub>	0.5_Pt/TiO <sub>2</sub>	0.1_Pt/TiO <sub>2</sub>	1_Pd/TiO <sub>2</sub>	0.5_Pd/TiO <sub>2</sub>	0.1_Pd/TiO <sub>2</sub>
The average yield of H <sub>2</sub> production, mmol H <sub>2</sub> /h·g <sub>cat</sub>	30.1	<b>47.02</b>	45.58	28.26	41.97	41.05
The highest productivity of H <sub>2</sub> , mmol H <sub>2</sub> /h·g <sub>cat</sub>	35.45	<b>66.34</b>	58.46	31.21	45.56	43.14
The highest concentration of H <sub>2</sub> , ppm	0.232	<b>0.435</b>	0.383	0.205	0.299	0.283
Average CO <sub>2</sub> concentration, ppm	21	<b>24</b>	23	21	22	22
Average the concentration O <sub>2</sub> in solution, ppm	0.87	<b>1.75</b>	1.69	1.26	1.43	1.49
Average irradiance, W/m <sup>2</sup>	305.2	<b>337.3</b>	320.6	310.1	312.4	315.4

The reactor platform was adjusted to allow maximum illumination to sunlight and to check the activity of photocatalysts in the photocatalytic reaction of H<sub>2</sub> production depending on the intensity of the solar radiation, which was monitored by a radiometer. For 0.5\_Pt/TiO<sub>2</sub> at the highest irradiance of more than 450 W/m<sup>2</sup>, the H<sub>2</sub> production value was more than twice as high as at the lowest measurement of 205 W/m<sup>2</sup>, where the H<sub>2</sub> production efficiency was 30.61 mmol H<sub>2</sub>/h·g<sub>cat</sub>. The lower efficiency of hydrogen production was due to the lower radiation intensity and the type of reactor construction which was confirmed by the application of an artificial light source (lamps XBO). At the same process parameters under visible light lamp for Pt-modified catalysts (0.5\_Pt/TiO<sub>2</sub>) 28.53 mmol H<sub>2</sub>/h·g<sub>cat</sub> and 25.17

mmol H<sub>2</sub>/h·g<sub>cat</sub> were analyzed for 150W and 100W, respectively. It was already shown in our previous study (Bednarczyk et al., 2018) that light intensity is a very important factor in photocatalytic H<sub>2</sub> production. It was shown that a decrease in lamp power by as much as 75 W reduces the efficiency of hydrogen generation by about 25% to 30%, depending on the photocatalyst used.

### ***3.4. Mechanism consideration***

For experiments performed under natural sunlight irradiation in the gas phase, mainly hydrogen, oxygen, and small amounts of carbon dioxide were detected. During the experiments, the pH of the liquid reaction mixture was measured in addition to the concentration of CO<sub>2</sub> in the gas phase. At the beginning of the experiments, the pH was ~6.4, and after 120 min of irradiation, it decreased to about 3.9. CO<sub>2</sub> concentration measurements showed an increase from 325 to 390 ppm (by weight). The pH of the solution decreased as a result of the dissolution of carbon dioxide in the water. The liquid phase analysis showed that the reduction of glycerol concentration was small, within the error margin of 1–2%. Therefore, it was concluded that glycerol acted mostly as a sacrificial agent (hole scavenger) to enhance photocatalytic hydrogen production rates and enhance the water-splitting reaction. However, based on the liquid phase analysis in which formic acid, acetic acid, diglycerol, and 2-amino-1-1-3-propanediol have been detected, the conversion of glycerol can be considered as a small part of the mechanism of H<sub>2</sub> generation (Villachica-Llamosas et al., 2024). This suspension is confirmed by the increasing concentration of CO<sub>2</sub> in the gas phase. Only during the photocatalytic production of hydrogen with the addition of glycerin were gaseous products H<sub>2</sub> and CO<sub>2</sub> detected. Although the amount of CO<sub>2</sub> is not much due to the low degree of glycerol conversion, some CO<sub>2</sub> dissolves in water and affects the pH of the solution.

The capture of photogenerated electrons from Pt and Pd photodeposited on TiO<sub>2</sub> represses the recombination of electron-hole pairs and facilitates/accelerates the transfer of holes on the TiO<sub>2</sub> surface. The photocatalytic activity is enhanced in terms of a longer electron-hole pair separation lifetime. The appropriate Fermi level position of Pt or Pd with its high work function initiates an effective Schottky barrier preventing the undesirable migration of electrons back into the conduction band of TiO<sub>2</sub>. H<sub>2</sub> may be generated by the reduction of two protons originating from both water and glycerol, the sacrificial agent. And at the same time, glycerol and water in the presence of Pt or Pd photodeposited on TiO<sub>2</sub> and sunlight are converted to H<sub>2</sub> through photocatalytic splitting of water and light-induced oxidation of

glycerol. It is known that in alcohol photoreforming, H<sub>2</sub> production is promoted by the presence of H atoms at the  $\alpha$ -position with respect to the hydroxyl group (Villachica-Llamosas et al., 2024).

### 3.5. Photocatalytic H<sub>2</sub> generation from synthetic and real crude glycerol solution

To investigate organic impurities, influence on the generation of H<sub>2</sub> and oxidation of organic compounds, a preliminary study focused on photocatalytic oxidation was performed. Based on recent studies (Gomes et al., 2017; Bednarczyk et al., 2018; Gmurek et al., 2019) and our experimental results, we concluded that photocatalytic oxidation of various organic wastes, and even toxic organic compounds such as parabens, could be a promising and environmentally friendly method for co-producing hydrogen. The efficiency values obtained for photocatalytic oxidation of 4 hydroxybenzoic acid esters (parabens, methyl (MP), ethyl (EP), and benzylparaben (BeP)) are shown in Fig. 7.

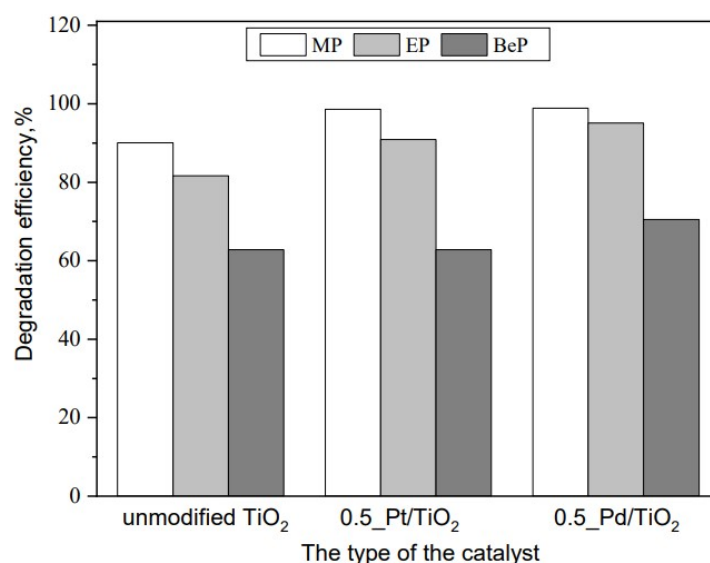


Fig. 7. Photodegradation efficiency of different parabens after 120 min for mixtures containing various catalysts (0.07 g/L)

The degradation efficiency of the organics increased when noble-metal-modified photocatalysts were used. The suitability of modified catalysts for both H<sub>2</sub> production and photocatalytic oxidation of organic esters was investigated. Therefore, the viability of both processes occurring simultaneously in solutions of synthetic and real crude glycerol was studied as well. Three experiments with different solutions that mimic synthetic crude glycerol were performed and the results were compared with those obtained for real crude

glycerol. The first experiments were carried out with water–glycerol solutions containing only 4.5 wt.% GLC. Second, synthetic crude glycerol containing 1.5 wt.% of GLC, 1 wt.% of MeOH, and 2 wt.% vegetable oil (maintaining the overall concentration of additives at 4.5 wt.%). Third, synthetic crude glycerol was prepared by adding 0.1 wt.% 4-hydroxybenzoic acid methyl ester (methylparaben, MP) to the second solution. The hydrogen yields of these solutions are shown in Fig. 8. It should be noted that during all experiments no changes in the MP concentration were observed. Hence, it was assumed that photodegradation of MP did not occur because of a lack of oxygen, and hence, limited production of reactive oxygen species. However, the addition of MP significantly increased the efficiency of hydrogen production efficiency; after 60 min, it was more than 50 mmol H<sub>2</sub>/h·g<sub>cat</sub>. Compared to experiments with synthetic crude glycerol, those using 4.5 wt.% real crude glycerol (obtained from the production of biodiesel) showed a much lower H<sub>2</sub> yield of 5.5 mmol H<sub>2</sub>/h·g<sub>cat</sub>, which was attributed to various impurities in the crude glycerol. Contaminants, such as dyes and lubricants, have a negative effect on light dispersion, decreasing the efficacy of the photocatalytic process.

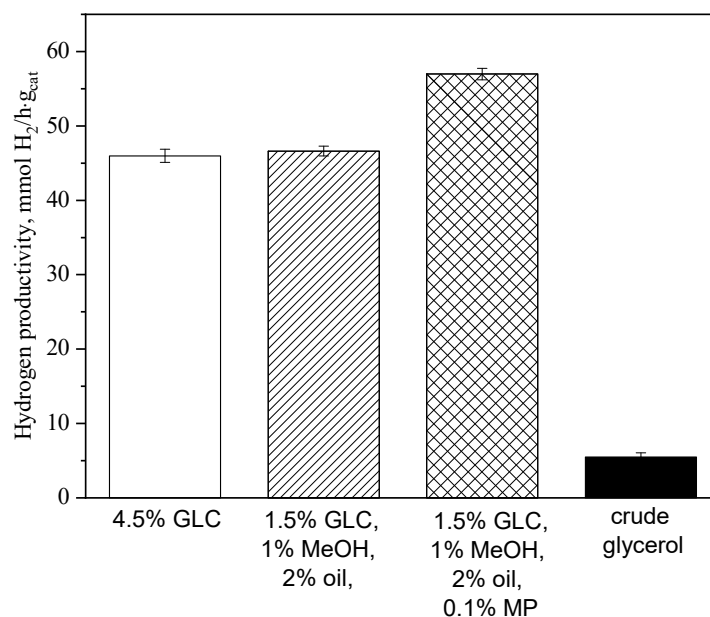


Fig. 8. Effect of the addition of methylparaben on hydrogen production with 0.083 g/L of 1 wt.% Pt/TiO<sub>2</sub>

#### 4. CONCLUSIONS

Green hydrogen energy is urgently needed and accelerating the expansion for industrial applicability is essential. This study examined the enlargement of H<sub>2</sub> photocatalytic



generation from glycerol solution, transitioning from a small laboratory setup (13 mL) to a larger setup (800 mL). Key aspects included artificial agents, reactor design, cocatalyst type, and dose. The platinum-loaded catalyst showed the highest hydrogen production rate, with an optimal platinum content of 0.5 wt.%. Hydrogen productivity depended on both the metal modification content and the total catalyst concentration. Considering catalyst costs, a concentration of 0.05 g per 600 mL (0.083 g/L) was optimal, producing 5.41 mmol of H<sub>2</sub> compared to 9.67 mmol with a 10 times higher dose (0.58 g).

The study highlighted the importance of radiation type and intensity on H<sub>2</sub> production efficiency. Using natural sunlight for photocatalytic hydrogen production proved viable, with the H<sub>2</sub> evolution rate depending on sunlight intensity and weather conditions. There was no significant difference between Pt and Pd modifications under sunlight. Sacrificial agents like glycerol, methanol, ethanol, 1-propanol, and 1-butanol accelerated H<sub>2</sub> production compared to pure water splitting, with glycerol being superior due to its OH groups.

The study confirmed that adding organic compounds can enhance photocatalytic hydrogen production compared to pure water splitting. Glycerol acted as a sacrificial agent, enhancing water-splitting reactions and H<sub>2</sub> production rates. Moreover, H<sub>2</sub> production from waste glycerol, though around ten times lower than from synthetic solutions, offers a promising approach for utilizing crude glycerol. Impurities in waste glycerol significantly reduced productivity, indicating a need for further research to identify and remove detrimental components in the purification process.

## SYMBOLS

*MP* – methyl

*EP* – ethyl

*BeP* – benzylparaben

*GLC* – glycerol

*MeOH* – methanol

*EtOH* – ethanol

*l*-BuOH - 1-butanol

*l*-PrOH - and 1-propanol

*BET* – specific surface area calculated based on the Brunauer, Emmet and Teller equation, m<sup>2</sup>/g

*GC* – gas chromatography

$\lambda$  - wavelength of light, nm

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