

# AN EXPERIMENTAL STUDY OF THE PHOTOCATALYTIC HYDROGEN PRODUCTION IN THE LABORATORY-SCALE SET-UP DEPENDING ON THE PROCESS CONDITIONS

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## ABSTRACT

Concern for the environment and the use of renewable energy sources are the two main priorities of energy policy combined with an environmental policy that is based on the principles of sustainable development. Many aspects should be taken into account in the case of energy production based on biomass/biofuels, in particular, the possibility of the formation of additional by-products. Glycerol is the main by-product during the trans-esterification of vegetable oils to biodiesel. The photocatalytic hydrogen production from the glycerol-water solution is less energy consuming reaction in comparison (for example) with its steam reforming or bio-conversion because it can be processed under mild conditions and low temperature. The paper presents the experimental results of the application process of photocatalytic hydrogen production from an aqueous solution of glycerol, with the use of TiO<sub>2</sub> doped with noble metals (platinum, palladium, silver) as a photocatalyst under solar-like light irradiation. The aim was to compare the hydrogen productivity depending on the catalyst concentration, the kind of the doped metal and the amount of the metal in the catalyst. The reaction (glycerol-water with suspended catalyst) mixture was irradiated by Xe-arc lamps (100 W). The influence of the doped metal on the hydrogen yield was studied for the photocatalysts prepared by the sol-gel and photodeposition method. The photocatalysts have been studied using scanning electron microscopy (SEM) with EDX (Quanta FEI 200F, Oxford Instruments X-Max50), X-ray powder diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS). It was proved, that glycerol is a good and efficient substance for the photocatalytic hydrogen production. The prepared and studied photocatalysts are characterized by high stability and very high yield under used process conditions. The experiments were performed in the quartz reactor with volume 1200 cm<sup>3</sup>. The volume of the reaction solution containing aqueous glycerol solution was 600 cm<sup>3</sup>. The maximum hydrogen production was about  $269.13 \cdot 10^{-3}$  [mole H<sub>2</sub>/(h·gcat)] and it was observed for TiO<sub>2</sub> doped by platinum (1% by weight; prepared by photodeposition) for 4.5% aqueous solution of glycerol.

*Keywords: photocatalytic, conversion, photocatalyst, hydrogen, glycerol.*

## 1 INTRODUCTION

Various by-products are generated during the production of bio-diesel from plant oils. The most important one, obtained during oil transesterification, is crude glycerol. The increase of the production of biodiesel and the resulting excessive amount of glycerol produced by the transesterification of oils have led to considerable lower market prices of glycerol [1]. This will also decrease the profitability of the production of bioesters unless new glycerol utilizations are found. The literature data indicate that the (aqueous/steam) reforming of glycerol, photocatalytic conversion as well bio-conversion may prove to be the best processes for the utilization of glycerol from an economic and environmental point of view. In our opinion, photocatalytic conversion of it and simultaneously carried out water splitting is the best way to produce hydrogen. Glycerol and/or other alcohols are often used as sacrificial agents in the hydrogen process production, because can react irreversibly with the photoinduced holes, to achieve higher efficiency [2]–[4]. The rate of hydrogen production



from glycerol depends on: the type of the catalyst, its amount in the solution, glycerol concentration and the intensity of irradiation [1], [2], [5], [6].

## 2 MATERIAL AND METHODS

### 2.1 Materials

All reagents used in this work were of analytical grade and were used without any further purification. Glycerol ( $\geq 99\%$ ) was purchased from Sigma-Aldrich. All solutions were prepared using water from a Millipore system (Direct-Q® Water Purification System- Merck Millipore). Argon (Ar- gas: purity  $> 99\%$ ) was purchased from Air Products.

### 2.2 Catalysts preparation

#### 2.2.1 Reagents

Titanium (IV) isopropoxide (TIP) (97%) was purchased from Aldrich Chem. And used as a titanium source for the preparation of TiO<sub>2</sub> nanoparticles. A commercial form of TiO<sub>2</sub> (P25, crystalline composition: 80% anatase, 20% rutile, surface area 50 g/m<sup>2</sup>) was from Evonik, Germany. PdCl<sub>2</sub> (5 wt.% solution in 10 wt. % HCl), NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O (reagent grade 50–60%), H<sub>2</sub>PtCl<sub>6</sub> (99%) and AgNO<sub>3</sub> (99%) from Sigma Aldrich were used as metal source in the preparation procedure. Ethanol (99,8%) was purchased from POLCHEM (Poland). The photocatalysts based on TiO<sub>2</sub> were obtained by two methods:

1. a) sol-gel method (titania doped with transition metals).
2. b) photodeposition of noble metals at the surface of P25.

#### 2.2.2 The photodeposition method

All the photocatalysts were obtained by UV-reduction of Pt<sup>4+</sup>, Pd<sup>2+</sup>, Ag ions in the TiO<sub>2</sub> suspension. 70 cm<sup>3</sup> of ethanolic solution- containing TiO<sub>2</sub> nanosheets (2g) and metal precursor (0.1; 0.5; 1% (m/m) was sonicated for 10 min, stirring in dark for 2h, degassed with nitrogen in dark for 1 h and finally illuminated by 1000W Xe lamp. An aqueous solution of isopropanol containing H<sub>2</sub>PtCl<sub>6</sub> (0.5 wt. %) or PdCl<sub>2</sub> (0.5 wt. %) was degassed with nitrogen and irradiated by UV-Vis light (1000 W Xe lamp) for 6 h. An aqueous solution of ethanol containing AgNO<sub>3</sub> (0,1; 0,5; 1 wt. %) was degassed with nitrogen and irradiated by UV-Vis light (1000 W Xe lamp) for 100 min. The modified TiO<sub>2</sub> photocatalysts were separated by centrifugation and dried at 65–120°C for 12 h.

Metal ion concentration [M]:

1. dla Ag 0.1%, 0.5%, 1% ( $3,98 \times 10^{-4}$ ,  $1,99 \times 10^{-3}$ ,  $3,98 \times 10^{-3}$ )
2. dla Pd 0.1%, 0.5%, 1% ( $4,02 \times 10^{-4}$ ,  $2,01 \times 10^{-3}$ ,  $4,02 \times 10^{-3}$ )
3. dla Pt 0.1%, 0.5%, 1% ( $2,2 \times 10^{-4}$ ,  $1,1 \times 10^{-3}$ ,  $2,2 \times 10^{-3}$ )

#### 2.2.3 The sol-gel method

Au – modified TiO<sub>2</sub> was prepared from titanium (IV) isopropoxide, known to be the titanium source origin for the anatase-type TiO<sub>2</sub>. Anatase titanium dioxide nanoparticles were prepared by the hydrolysis reaction of TIP with water. 35 ml of titanium (IV) isopropoxide was added to 35 ml of ethanol and next metal precursor - (0.1%; 0.5%) KAuCl<sub>4</sub> (m/m) and the mixture was stirred for 5 min using a magnetic stirrer operating at 500 rpm. Next, 11.63 ml of distilled water was added to the mixture and was stirred for 1 h. After stirring, distilled water and hydrazine were added to the mixture and thick precipitate was formed which



gradually peptized for 2 h to form a clear sol, followed by a 24 hour thermal treatment (45°C) and calcination at 400°C for 2h.

### 2.3 Catalysts characterization

The structure of the photocatalyst was characterized by XRD (X-ray diffraction). The measurement of the powder X-ray diffraction was performed on X-ray diffractometer Philips X 'Pert Pro MPD equipped with a copper X-ray tube,  $\lambda$  (Cu K $\alpha$ ) = 1.54 Å. The resulting diffraction patterns were then analyzed using HighScore Plus. The surface area of catalysts, Brunauer-Emmet-Teller (SBET) was analyzed using nitrogen (-196°C) with an accelerated surface area and porosimetry analyzer CASAP 2000, Micrometrics.

The XPS (X-ray photoelectron spectroscopy) analyses were carried out with a Kratos AXIS Ultra spectrometer using monochromatic Al K $\alpha$  X-Rays source of excitation energy equal to 1486.6 eV. The spectra were obtained using an analysis area of 300  $\mu\text{m}$  x 700  $\mu\text{m}$ . The power of the anode was set at 150 W and the hemispherical electron energy analyzer was operated at a pass energy of 20 eV for all high-resolution measurements. The use of a charge neutralizer during spectra collecting was necessary due to the insulating character of the samples. Reproducibility was ensured by taking more than three measurements per analyzed sample.

The microstructural analysis of the surface and particles average diameter was performed using a TESCAN VEGA 3 SBH – Easy Probe Scanning Electron Microscopy (SEM) with a tungsten heated cathode and SEM+EDX (Quanta FEI 200F, Oxford Instruments X-Max50).

The BET (Brunauer-Emmet-Teller ( $S_{\text{BET}}$ )) specific surface area of the catalysts were analyzed using nitrogen (-196°C) with an accelerated surface area and porosimetry analyzer (ASAP 2000, Micrometrics).

### 2.4 The experimental procedures of the performed photocatalytic tests

All the experiments of the process of photocatalytic conversion of glycerol into hydrogen were carried out in the quartz reactor with the volume 1200cm<sup>3</sup> that was cooled by water. The volume of the aqueous solution of glycerol with suspended photocatalyst was 600cm<sup>3</sup>. The Xe-arc lamp (100 W) was placed in the vertical axis of the reactor. The lamp was used as a source of energy and to simulate sunlight. The temperature of the reaction mixture at the beginning of the runs was 25°C and during the experiments increased up to 30°C. Argon with the flow rate equal to 150 (cm<sup>3</sup>/min) was used as a carrier gas in all tests. The suspension of the catalyst in the reaction mixture was obtained by stirring (magnetic stirrer), as well as through the (bubbling) flow of argon. The stream of flowing argon enabled also the removal of the dissolved oxygen (that was present in the system before the start the experiments and that was produced in the simultaneous water splitting) as well the removal of hydrogen and carbon dioxide produced in the process of glycerol conversion. The scheme of the laboratory set-up is shown in Fig. 1. Each of the experiments lasted approximately 4–6 hours. The process conditions of the carried out test runs are presented in Table 1.



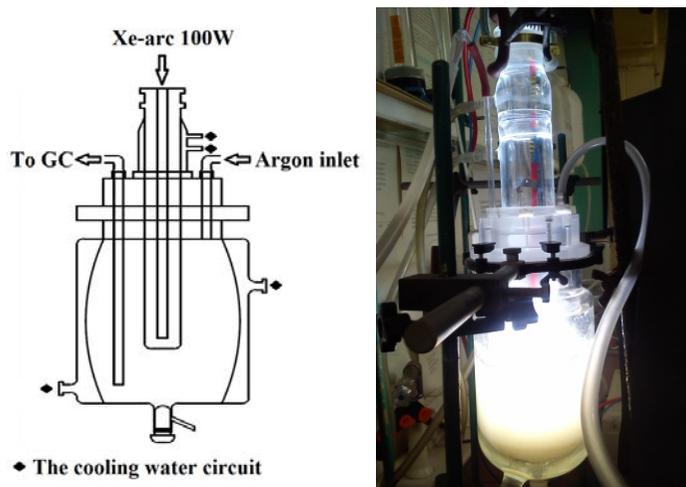


Figure 1: The scheme and the photo of the quartz reactor with cooling and the lamp placed in the vertical axis of the reactor.

Table 1: Process conditions for the process of hydrogen from glycerol.

The volume of the reactor (cm <sup>3</sup> )	The volume of the reaction solution (cm <sup>3</sup> )	Glycerol initial concentration (wt. %)	Power the light source (W)	The temperature of the reaction mixture (°C)	Argon flow rate (cm <sup>3</sup> /min)
1200	600	4.5	100	25-30	150

## 2.5 The analytical methods

The gas chromatograph (Perkin Elmer) equipped with a TCD detector was used for the analysis of the gas phase (on line). The injection volume of the gas sample was 1 cm<sup>3</sup>. The evolved gases were analysed every 15 minutes using a gas chromatograph (using an Altech silica gel Packed Columns 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.

## 3 RESULTS AND DISCUSSION

### 3.1 Catalysts characterization

#### 3.1.1 Determination of the surface of the catalyst

The SEM + EDX electron microscope (Quanta FEI 200F, Oxford Instruments X-Max50) was used to determine the nature of the surface of the catalyst test sample. The microscope resolution is 1.2 nm and allows accurate imaging of objects ranging in size from tens of nm. The EDX adapter allows you to determine the composition of the element of the test material and to determine the topography of the decomposition of the elements on the surface of the sample.

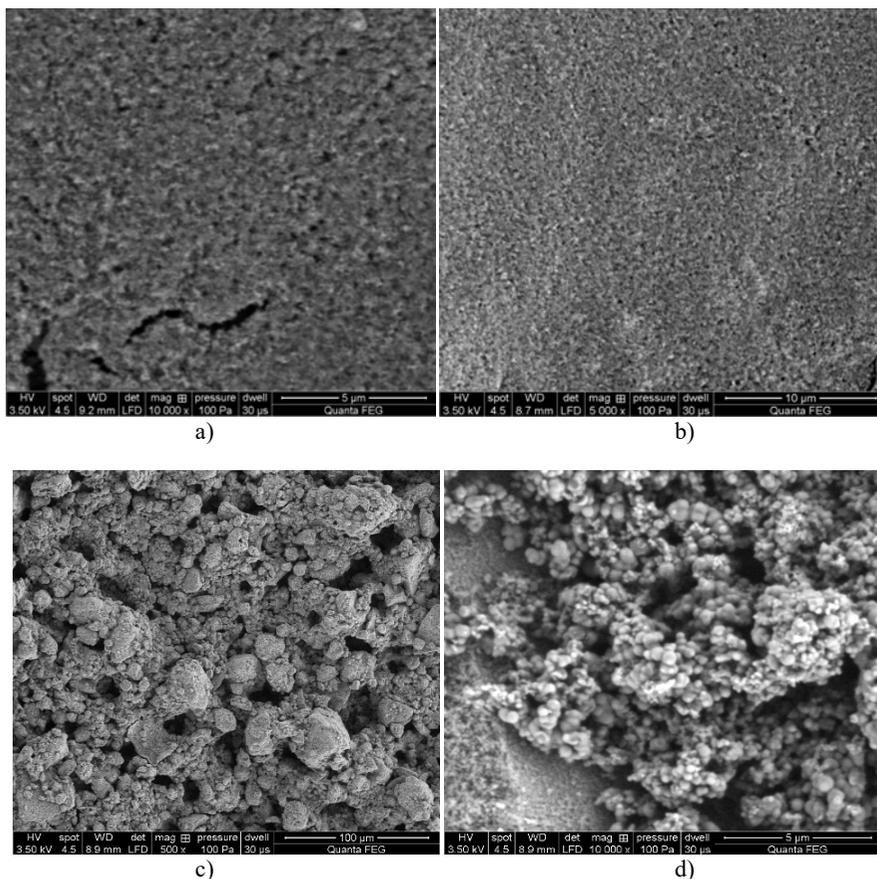


Figure 2: SEM images of different catalyst materials. (a)  $-0.5 \text{ Pt/TiO}_2$ ; (b)  $-0.5 \text{ Pd/TiO}_2$ ; (c)  $-0.5 \text{ Ag/TiO}_2$  – all prepared by the photodeposition method and (d)  $-0.5 \text{ Pt/TiO}_2$  – prepared by the sol-gel method.

The basic principle of operation of the microscope to obtain an image is to subject the analyzed sample to scanning by means of a directed electron stream. For a given test material a signal is generated which is emitted and recorded by suitable detectors and then processed into the image. Microsphere cluster formation (rounded crystalline forms of irregular size) was observed. The photocatalyst is characterized by the uneven distribution of metal particles, which create places of high density. SEM images are presented in Fig. 2.

### 3.1.2 The XRD analysis of the catalysts

The XRD patterns of the photocatalyst doped with platinum and palladium (0.1 wt. %, 0.5 wt. %) prepared by photodeposition are presented in Fig. 3. For all samples, two phases (anatase and rutile) of  $\text{TiO}_2$  were observed. The percentages of the phases did not depend on the amount of dopant and are composed of 80 wt. % (anatase) and 20 wt. % (rutile). The strongest reflexes for rutile were observed at  $27.5 \text{ deg.}$  (marked by # - in Fig. 3).

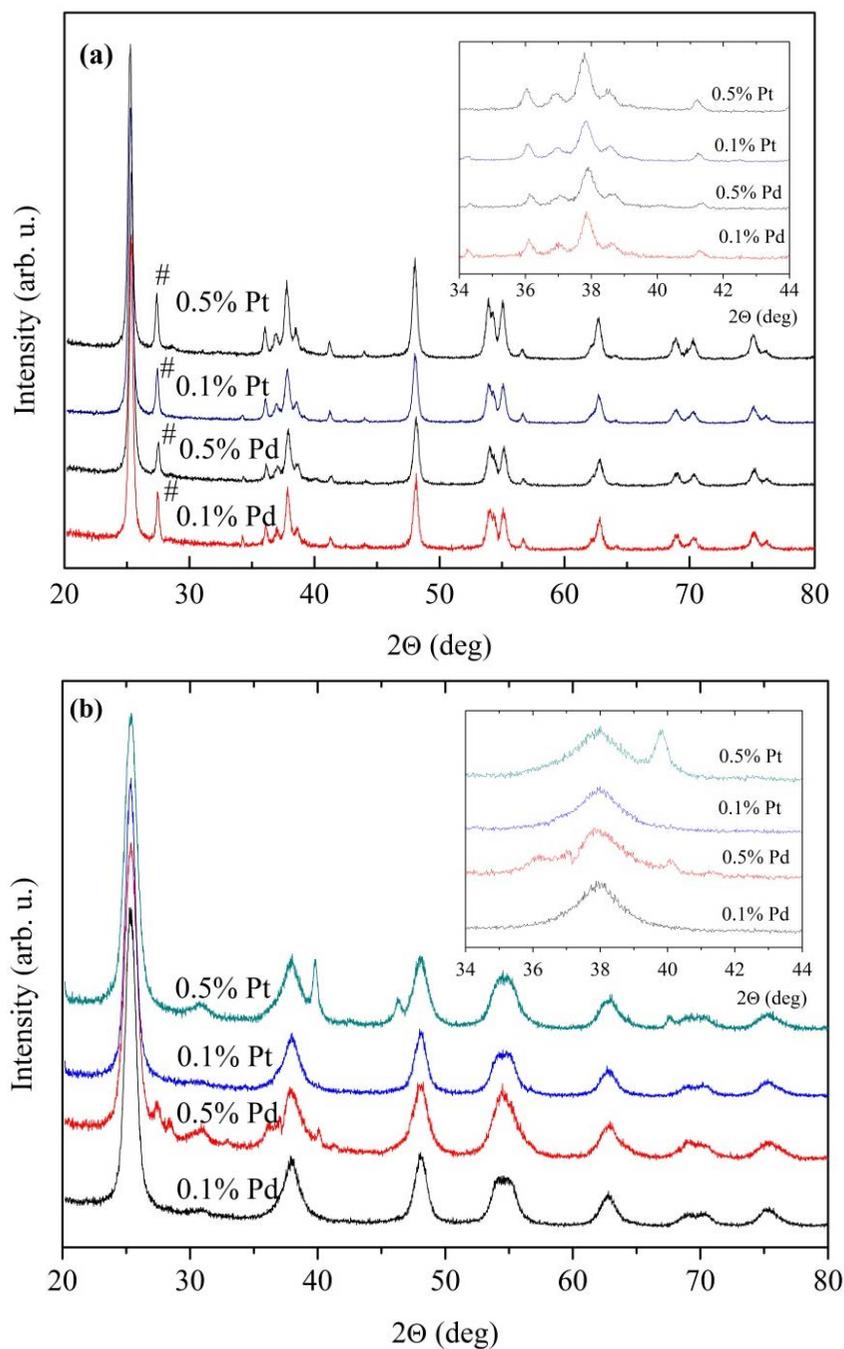


Figure 3: XRD analysis for Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> catalysts prepared by: (a) photodeposition method; (b) sol-gel method.

Table 2: Relative elemental concentrations obtained from the XPS composition analysis.

Catalysts Me/TiO <sub>2</sub>	O (wt. %)	Ti (wt. %)	C (wt. %)	Me content (wt. %)
0.1 Pt/TiO <sub>2</sub>	48.57±0.43	21.11±0.17	30.25±0.59	0.08±0.01
0.5 Pt/TiO <sub>2</sub> PD	48.70±0.55	20.73±0.01	30.46±0.54	0.13±0.01
0.5 Pd/TiO <sub>2</sub> PD	55.88±0.05	23.66±0.62	20.24±0.66	0.23±0.01
0.5 Ag/TiO <sub>2</sub> PD	58.63±0.66	23.84±0.25	17.06±0.88	0.47±0.04
0.1 Pt/TiO <sub>2</sub> sol-gel	47.85±0.39	20.19±0.04	31.89±0.36	0.09±0.01
0.5 Pt/TiO <sub>2</sub> sol-gel	48.70±0.55	20.73±0.01	30.46±0.54	0.13±0.01

With increasing concentration of the Pt, the crystallite size appears to be increasing (from 196 nm to 220 nm) for the anatase form and decreasing (from 415 nm to 216 nm) for the rutile form. Test samples contain anatase, but brookite is present in place of rutile, which is the dominant phase for sample 25 (0.5% Pt). Brookite crystallizes in the orthorhombic structure with low symmetry (spatial group 61), resulting in many diffraction reflections. The most intense reflections almost coincide with the strongest anatase reflection (about 25.3 deg.), which complicates LeBail's analysis.

### 3.2 A methodology for identifying the chemical composition of the surface analysis by XPS

Relative concentrations of elements in modified of catalysts are presented in Table 2. Morphological and surface characterization of the sample (Pt/TiO<sub>2</sub>, Pd/TiO<sub>2</sub> and Ag/TiO<sub>2</sub>) were studied earlier and published in our previous papers [7], [8].

### 3.3 The photocatalytic hydrogen production tests

The comparison of the influence of kind of the doped metal and its amount in the catalyst (TiO<sub>2</sub>) on H<sub>2</sub> productivity in the glycerol solution (4.5 wt. %) was studied for the photocatalysts prepared by the both methods: the photodeposition as well as the sol-gel method. The hydrogen productivity in the performed runs for different catalysts is presented in Fig. 4. As it can be noticed, the productivity of hydrogen in the system with pure TiO<sub>2</sub> is very small while for the catalysts doped by the noble metals the productivity was essential higher. It also can be seen that the obtained effect for of the catalysts prepared by the photodeposition method were significantly better.



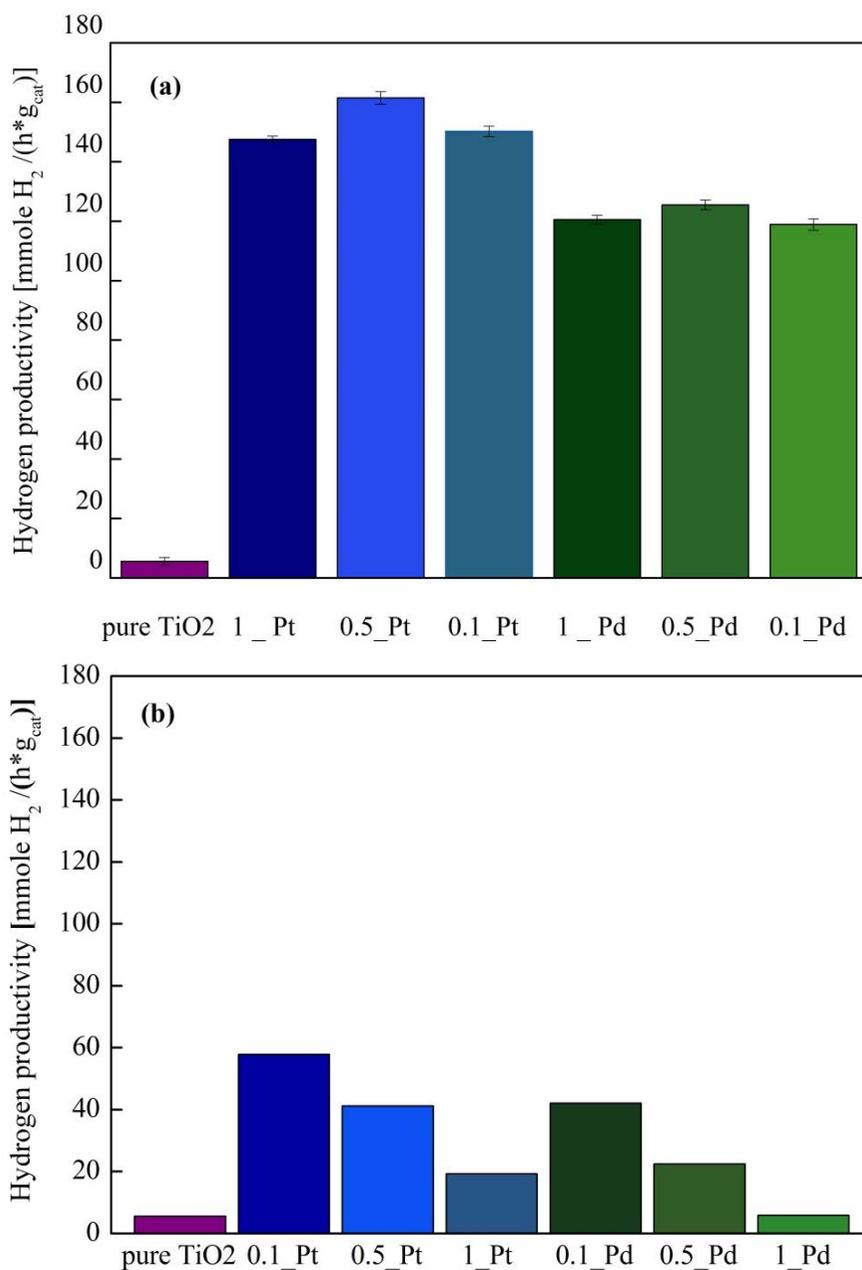


Figure 4: Hydrogen productivity for different of catalyst prepared by the photodeposition method. (a) and by the sol-gel method (b); Concentration of the catalyst in the glycerol solution was equal to 0.083 g/L and concentration of glycerol was 4.5 wt. % in the all cases.

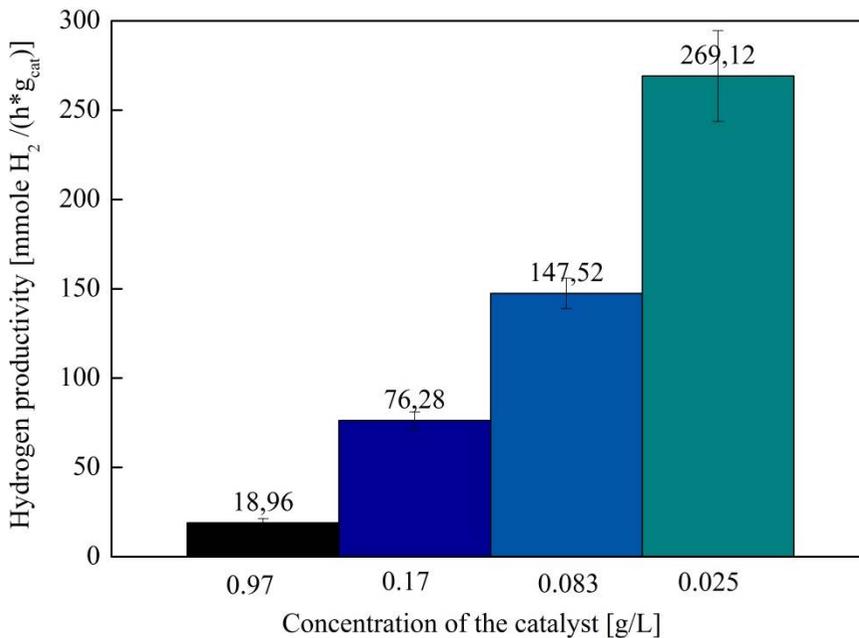


Figure 5: The productivity of hydrogen for different concentrations of the catalyst; the reaction solution: 4.5 wt. % of glycerol); catalyst: Pt/TiO<sub>2</sub> (1 wt. %) prepared by the photodeposition method.

The influence of the amount of photocatalyst (the concentration of the catalyst in the reaction mixture) added to the solution was also studied. The volume of the reaction mixture was equal to 600 cm<sup>3</sup>. The distribution of light dispersion depends on the amount of the photocatalyst and has a large impact on the performance of hydrogen production. In our opinion, already a very small amount of the catalyst in the solution may be enough to reach the high hydrogen productivity. As we can see in Fig. 5, the highest productivity of H<sub>2</sub> was obtained for the lowest concentration of the catalyst that was possible to prepare by us.

The influence of the intensity of the lamps was also studied and analysed for the Pt/TiO<sub>2</sub> obtained by photodeposition. The obtained results, that the intensity of radiation has an essential influence on the efficiency of hydrogen production. The study and results are in progress and they will be presented in our future papers.

#### 4 CONCLUSIONS

- The preparation method has a significant effect on the catalytic properties of the material used as a catalyst. The obtained results favour the use of the photodeposition method.
- In the investigated process, consisting of two simultaneous reactions: photocatalytic conversion of glycerin to hydrogen and photocatalytic cleavage of water, an optimum content of doped metal (to TiO<sub>2</sub>) may be observed. Experiments show that in the case of platinum it is about 0.5 percent by weight.
- Experiments have also shown that the preferred metal added to TiO<sub>2</sub> is platinum.



- The XRD analysis shows that for the catalyst produced by photodeposition there are two crystalline forms of TiO<sub>2</sub> in the studied material: anatase and rutile in a ratio of about 4:1. For the catalyst prepared by the sol-gel method, the brookite form is also observed in the catalyst. It was not possible to determine the detailed ratio of these different forms of TiO<sub>2</sub> for studied catalysts. No regularity was found.

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