# Photoelectrocatalytic Hydrogen Production Supported by Ascorbic Acid

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#### Abstract

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Photoelectrochemical hydrogen production combines electrochemistry and photocatalysis, resulting in sustainable hydrogen production. The process can be improved by the addition of hole scavengers, which reduce the recombination of electrons and holes, increasing the utilisation of solar radiation. Because of its low oxidation potential, ascorbic acid (AA) is an environmentally friendly and readily available hole scavenger. The commonly studied photocatalyst TiO<sub>2</sub> makes little utilisation of solar radiation energy due to its high energy gap of 3.2 eV. The metal sulphide SnS<sub>2</sub> attracts attention due to its low energy band gap of 2.2 eV, which allows the use of the visible region of the spectrum. In this work, the electrochemical characterisation of SnS<sub>2</sub> and TiO<sub>2</sub> photoanodes in NaCl solution in the presence and absence of AA was performed. The effect of AA on the photoresponse was investigated using the linear polarisation method and monitoring the open circuit potential. The results confirmed that SnS<sub>2</sub> and TiO<sub>2</sub> electrodes are photoactive, and that AA has good hole scavenging properties. Hydrogen production was performed at constant potentials of 0.6 and 1.35 V, respectively. TiO<sub>2</sub> exhibited higher photoactivity, thus producing more hydrogen at 0.6 V. On the other hand, at a potential of 1.35 V, most of the hydrogen produced was the result of an electrochemical reaction rather than a photoelectrochemical reaction, thus, a larger amount of hydrogen was produced with the SnS<sub>2</sub> electrode. The highest amount of hydrogen produced in this work was at 1.35 V for the SnS<sub>2</sub> electrode in an argon atmosphere and it was 0.799 ml h<sup>-1</sup> cm<sup>-2</sup>.

#### Keywords

Ascorbic acid, hydrogen, hole scavenger, photoelectrochemical hydrogen production, tin(IV) sulphide, titanium(IV) oxide

## 1 Introduction

In 1972, the first report on the Fujishima-Honda effect was published, after which photoelectrochemical (PEC) generation of hydrogen and oxygen gained importance. The mentioned report showed that water splitting was possible by using light energy, with great efforts being made to develop it over time.<sup>1</sup> The PEC process combines electrochemistry and photocatalysis, resulting in a cost-effective approach for the sustainable production of green hydrogen. In the PEC process, the photoanode is subjected to light excitation leading to the separation of electron-hole pairs:

semiconductor 
$$+ hv \rightarrow h^+ + e^-$$
 (1)

Photoinduced electrons (e<sup>-</sup>) are continuously pulled from the anode into the external circuit and to the cathode, where hydrogen reduction occurs. The photogenerated holes ( $h^+$ ) created at the anode surface oxidise water and generate oxygen. Voltage application causes the bands bending, as shown in Fig. 1, resulting in efficient charge separation.<sup>2</sup> Without voltage application, the bands are nearly flat, leading to more prominent recombination. Moreover, the process can be improved by adding agents known as hole scavengers. Hole scavengers have a lower redox potential than oxygen,<sup>1,3</sup> which reduces the minimum voltage required for hydrogen production. Wellknown hole scavengers are methanol, ethylene glycol, tetraacetic acid, Na<sub>2</sub>SO<sub>3</sub> and triethanolamine.<sup>4</sup>

The photogenerated holes at the surface of the electrode can oxidise the scavengers directly (1) or indirectly by HO<sup>•</sup> radicals generated near the electrode surface (2):

$$h^+ + H_2O \rightarrow HO^{\bullet} + H^+$$
 (2)

Because of its low oxidation potential, ascorbic acid is a suitable hole scavenger, and since it occurs naturally, it can be considered an environmentally friendly and readily available agent for this purpose. In the electrochemical reaction, ascorbic acid is converted into dehydroascorbic acid (3), exchanging two protons and two electrons.



However, photoelectrocatalytic degradation of ascorbic acid can also progress to a greater extent when 2,3-dike-togulonic acid is formed, or even threonic and oxalic acid.<sup>5</sup> In previous studies, there are only a few reports of AA being an efficient hole scavenger, but it had only been used

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in photocatalytic processes.<sup>6–8</sup> There are also reports that modification of  $TiO_2$  surface with AA resulted in an improvement of photocatalytic activity upon irradiation with visible light.<sup>9–11</sup> To our knowledge, there is no report on the usage of AA as a sacrificial agent in PEC processes.



*Fig.* 1 – Illustration of photoelectrocatalytic hydrogen production supported by ascorbic acid

Slika 1 – Ilustracija fotoelektrokemijskog dobivanja vodika potpomognutog askorbinskom kiselinom

The most commonly studied photocatalyst is TiO<sub>2</sub> due to its availability, low cost, nontoxicity, high photochemical stability, and suitable band position.<sup>12</sup> However, two factors limit this photocatalytic material: its low ability to absorb visible light, and the rapid recombination of electron-hole pairs. Due to the energy gap of 3.2 eV, TiO<sub>2</sub> mainly absorbs light from the ultraviolet (UV) region of the spectrum, resulting in low utilisation of solar radiation energy.<sup>6</sup> Many strategies have been proposed to overcome these limitations, such as  $TiO_2$  dye sensitisation and  $TiO_2$  doping with metals or non-metals (N, O, S). One of the strategies is to develop new materials that are active in the visible region (metal oxides, metal sulphides, or various heterostructures). The metal sulphide SnS<sub>2</sub> has attracted much attention due to its low cost and low energy band gap of 2.2 eV, which allows the absorption of photons in the visible part of the spectrum.<sup>13-15</sup> In this work, the electrochemical characterisation of SnS<sub>2</sub> and TiO<sub>2</sub> photoanodes in NaCl solution in the presence and absence of AA was performed. The influence of AA on the photoresponse was studied using the linear polarisation method. To confirm the good properties, the studied system was also tested for photocatalytic hydrogen production.

### 2 Experimental

#### 2.1 Active material synthesis

Aeroxide P25 TiO<sub>2</sub> (TiO<sub>2</sub>-P25, Evonik, Germany) was the TiO<sub>2</sub> photocatalytic material used in this work. SnS<sub>2</sub> was prepared hydrothermally following a procedure adopted from *Zhang et al.*<sup>16</sup> SnS<sub>2</sub> synthesis starts with dissolving the precursors (2.250 g of tin(IV) chloride and 1.205 g of thioacetamide) in a 5 % v/v solution of glacial acetic acid in ethanol (total volume of 100 ml) in a Teflon reaction vessel, constantly stirring. The Teflon reaction vessel was then transferred to a stainless-steel autoclave, and treated for 12 h at 180 °C. Letting it naturally cool to room temperature, the obtained suspension was rinsed with distilled water, centrifuged (3500 rpm for 3 min), dried in a vacuum (3 h at 60 °C), and homogenised with a porcelain pestle and mortar.

#### 2.2 Photoanode preparation and characterisation by electrochemical methods

In this investigation, a three-electrode cell was used to characterise the photoactive materials. The cell contained a saturated calomel electrode (SCE) as a reference electrode, a platinum sheet (1 cm<sup>2</sup>) electrode as a counter electrode, and FTO glass covered with a layer of TiO<sub>2</sub> or SnS<sub>2</sub> (1.5–2 cm<sup>2</sup>) as a working electrode (Fig. 2). Measurements were performed at room temperature using a potentiostat/galvanostat (SP-150, Biologic, France), while data was recorded in the EC-lab program (V 11.33).

To prepare the working electrodes (TiO<sub>2</sub> electrode and SnS<sub>2</sub> electrode) for PEC measurements, photoactive materials (TiO<sub>2</sub> or SnS<sub>2</sub>) needed to be immobilised onto FTO glass slides. This was achieved using the spin coating technique (KW-4A spin coater, Chemat Technology, USA). Prior to the coating, FTO glass slides were sonicated in acetone, EtOH, and Milli-Q water, each for 10 min, and dried at room temperature. Further, for each layer, a 200  $\mu$ l aliquot of the photoactive material dispersed within the titania/silica binder was dropped onto an FTO substrate and annealed at 200 °C for 2 h in a laboratory oven (UN-55, Memmert, Germany). Further details of the procedure can be found in *Sharifi et al.*<sup>17</sup>



- Fig. 2 Working electrode covered with  $TiO_2$  layer (left) and  $SnS_2$  layer (right)
- Slika 2 Radna elektroda prekrivena TiO $_2$  slojem (lijevo) i SnS $_2$  slojem (desno)



Fig. 3 – Experimental design for hydrogen production in two compartment cells containing a)  $SnS_2$  or b) TiO<sub>2</sub> photoanode and platinum cathode

Slika 3 – Eksperimentalna postava za proizvodnju vodika u ćeliji s odvojenim anodnim i katodnim prostorom uz a) SnS<sub>2</sub> ili b) TiO<sub>2</sub> fotoanodu i platinsku katodu

The obtained electrodes were characterised by linear sweep voltammetry (LSV), while open-circuit potential (OCP) measurement was performed only for the  $SnS_2$  electrode. Measurements were performed in 0.1 mol dm<sup>-3</sup> NaCl solution and a solution containing 10 mmol dm<sup>-3</sup> ascorbic acid dissolved in 0.1 mol dm<sup>-3</sup> NaCl. The measurement was performed in dark conditions as well as under light illumination. Characterisation of TiO<sub>2</sub> electrodes was done under UV light (Pen-Ray 90-0019-01, 365 nm; UVP), and  $SnS_2$  testing under LED light (COB, 50 W, 4400 lm, 6000 K)<sup>17</sup>.

All potentials in this work are reported *versus* saturated calomel electrode (SCE). Analytical-grade chemicals purchased and used in this work were NaCl (Lach-Ner, Czech Republic) and ascorbic acid (Poljo Evelin, Croatia).

#### 2.3 Hydrogen production

The photoelectrochemical production of hydrogen using UV light and  $TiO_2$  or LED light and  $SnS_2$  was performed in a two-compartment cell, presented in Fig. 3. Although hydrogen evolution was the targeted process, the overall process rate depends on anode activity, and therefore in this work, anode response was monitored. Hydrogen production was carried out by the chronoamperometry method for 2 hours. The process was monitored using visual observation of the amount of hydrogen within the tube immersed in the cathodic compartment of the electrochemical cell (Fig. 3). The solution in the anodic compartment was stirred for the entire duration of the experiment using a magnetic stirrer.

The hydrogen production was carried out for 2 h at different voltage values of a) 1.35 V, and b) 0.6 V. The first voltage value was selected in the potential range where current peak was obtained, and the other voltage value was selected in the potential range where the contribution of peak current was low. Experiment at 1.35 V was also performed with argon purging for 10 min prior to the experiment in order to remove oxygen.

## 3 Results and discussion

#### 3.1 Characterisation of the photoanode containing SnS<sub>2</sub>

Fig. 4 shows the light and dark response of  $SnS_2$  photoanode in 0.1 mol dm<sup>-3</sup> NaCl solution in the presence and absence of 10 mmol dm<sup>-3</sup> AA. The test was performed using the potential range from -0.5 V to +1.5 V at a scan rate of 20 mV s<sup>-1</sup>.



- *Fig.* 4 Linear sweep voltammetry responses of the SnS<sub>2</sub> electrode in 0.1 mol dm<sup>-3</sup> NaCl solution in the presence and absence of 10 mmol dm<sup>-3</sup> AA, the inset represents the enlarged part of the voltammogram
- Slika 4 Odziv voltametrije linearne promjene potencijala za SnS<sub>2</sub> elektrodu u 0,1 mol dm<sup>-3</sup> NaCl uz prisutnost i bez prisutnosti 10 mmol dm<sup>-3</sup> AA, umetak prikazuje uvećani dio voltamograma

The inset of linear sweep voltammetry responses in the NaCl solution (Fig. 4) indicates that the dark characteristic of the photoanode up to 0.25 V shows currents equal to zero, while the illuminated electrode shows a current of about 20 µA. The resulting behaviour is characteristic of photoactive materials, and the obtained current is related to the photocurrent. Furthermore, in both solutions (with the presence and absence of 10 mmol dm<sup>-3</sup> AA), photocurrent increases with growing potential. This indicates a positive effect of the potential on the photocurrent response, which is a consequence of reduced electron-hole recombination.<sup>18</sup> It is also evident that the photocurrent, recorded at lower potentials for the AA solution, was almost twice the value of the photocurrent in the NaCl solution. Therefore, it can be concluded that AA behaves as a hole scavenger, which significantly increases the photocurrent response. However, it is not completely clear whether the reaction takes place through the reaction of AA and holes or AA and radicals.9,11,19

Fig. 4 also shows that the current significantly increases at potentials more positive than 0.25 V, and the current peak characteristic for the electrochemical oxidation of AA was obtained at 1.25 V. Although electrochemical oxidation is not expected when an *n*-type semiconductor electrode is used, in this investigation, it was obtained due to holes generated by an electric field.<sup>18</sup> Similar results were also obtained for the TiO<sub>2</sub> electrode in the presence of antioxidants.<sup>20</sup> A higher current peak recorded for the illuminated electrode compared to the response of the dark electrode indicates photoactivity of SnS<sub>2</sub> in a wide potential range.

Open-circuit potential (OCP) monitoring for the  $SnS_2$  photoanode was performed in chopped light irradiation in the AA and NaCl solutions, as shown in Fig. 5. A characteristic of an n-type semiconductor is a potential drop to more negative values upon illumination.<sup>17,18</sup> The OCP of the



- Fig. 5 Open-circuit potential of the  $SnS_2$  photoanode in chopped light irradiation in 0.1 mol dm<sup>-3</sup> NaCl solution in the presence and absence of 10 mmol dm<sup>-3</sup> AA
- Slika 5 Mjerenje potencijala otvorenog kruga za SnS<sub>2</sub> elektrodu u 0,1 mol dm<sup>-3</sup> NaCl uz prisutnost i bez prisutnosti 10 mmol dm<sup>-3</sup> AA

 $SnS_2$  electrode in the NaCl solution exhibits a decrease of 100 mV when illuminated, while the potential of the same electrode in ascorbic acid shows a decrease of 140 mV. The obtained behaviours indicate that a higher photoactivity was obtained in the AA solution, which additionally confirms the good hole scavenging properties of AA.

#### 3.2 Characterisation of the photoanode containing TiO<sub>2</sub>

Fig. 6 shows a linear polarisation response of the dark and illuminated  $TiO_2$  photoanode in a 0.1 mol dm<sup>-3</sup> NaCl solution in the presence and absence of 10 mmol dm<sup>-3</sup> ascorbic acid. The test was performed in the potential range from -0.5 V to +1.2 V at a scan rate of 20 mV s<sup>-1</sup>.



- Fig. 6 Linear sweep voltammetry responses of the TiO<sub>2</sub> electrode in 0.1 mol dm<sup>-3</sup> NaCl solution in the presence and absence of 10 mmol dm<sup>-3</sup> AA, the inset represents the enlarged part of the voltammogram
- Slika 6 Odziv voltametrije linearne promjene potencijala za TiO<sub>2</sub> elektrodu u 0,1 mol dm<sup>-3</sup> NaCl uz prisutnost i bez prisutnosti 10 mmol dm<sup>-3</sup> AA, umetak prikazuje uvećani dio voltamograma

The inset in Fig. 6 indicates that up to 0.2 V, the dark characteristic of the photoanode (in NaCl) shows currents approximately equal to zero, while the illuminated photoanode shows a current of 75  $\mu$ A at 0 V. It is also evident that the photocurrent in the NaCl solution increases with growing potential, just as in the case of the SnS<sub>2</sub> photoanode. With the addition of AA, the photocurrent surged to 175  $\mu$ A at 0 V, proving the good hole scavenging properties of AA.

By comparing the results obtained for  $SnS_2$  and  $TiO_2$  (Figs. 4 and 6), it is evident that the photoactivity of  $TiO_2$  in the presence of UV radiation is higher than the photoactivity of  $SnS_2$  in the presence of visible radiation. However, the activity in the visible spectrum enables a more efficient utilisation of solar radiation and is, therefore, more sustainable and acceptable for a practical application.

# 3.3 Hydrogen production with $SnS_2$ and $TiO_2$ photoanodes

After the characterisation of the electrodes, the production of hydrogen was performed at a constant potential of 0.6 V and 1.35 V. The PEC process of hydrogen generation in the case of the SnS<sub>2</sub> photoanode in 10 mmol dm<sup>-3</sup> AA solution was followed by monitoring current density, *j*, in time, *t*. Fig. 7 shows that the current dropped suddenly in the beginning and then gradually increased. It is also evident that the current density at 1.35 V was slightly higher when argon purging was applied before the experiment, and that the lowest current value was recorded at a potential of 0.6 V. The similar experiment was carried out for the TiO<sub>2</sub> photoanode (Fig. 8), and the same trend was obtained.

The currents at 1.35 V are mainly the result of an electrochemical reaction, as evident from the responses registered during the linear polarisation experiment (Figs. 4 and 6). In this case, the photocurrent contribution to the overall current response was small. For this reason, similar current values were recorded for TiO<sub>2</sub> and SnS<sub>2</sub> electrodes (1.7–1.8 mA and 1.75–2 mA) (Figs. 7 and 8). At a lower potential value (0.6 V), the photocurrent contribution was more significant, and therefore the difference between the TiO<sub>2</sub> and SnS<sub>2</sub> response was more pronounced. For the SnS<sub>2</sub> electrode, the current of 0.3 mA was recorded (Figs. 7 and 8). The obtained result indicates better photoactivity of TiO<sub>2</sub> compared to SnS<sub>2</sub>, which is in accordance with linear sweep voltammetry results (Figs. 4 and 6).

Additionally, Figs. 7 and 8 show that the current at the very beginning of the process rises suddenly and then falls. These currents are most likely a characteristic of electrochemical double-layer charging. The continuous current increase, registered after the initial drop, could be an indication of: 1) a mechanical decomposition of the electrode, which



- Fig. 7 Chronoamperometry response recorded during PEC hydrogen generation with the  $SnS_2$  photoanode in 10 mmol dm<sup>-3</sup> AA solution in 0.1 mol dm<sup>-3</sup> NaCl
- Slika 7 Kronoamperometrijski odziv zabilježen tijekom dobivanja vodika u sustavu sa SnS<sub>2</sub> fotoanodom u otopini 10 mmol dm<sup>-3</sup> AA u 0.1 mol dm<sup>-3</sup> NaCl



- *Fig. 8* Chronoamperometry response recorded during PEC hydrogen generation with the TiO<sub>2</sub> photoanode in 10 mmol dm<sup>-3</sup> AA solution in 0.1 mol dm<sup>-3</sup> NaCl
- Slika 8 Kronoamperometrijski odziv zabilježen tijekom dobivanja vodika u sustavu s TiO<sub>2</sub> fotoanodom u otopini 10 mmol dm<sup>-3</sup> AA u 0,1 mol dm<sup>-3</sup> NaCl

leads to an increase in the surface of the electrode, or 2) a decomposition products reaction.<sup>21</sup> In order to determine what exactly affected the current increase (Figs. 7 and 8), additional analysis of the electrode surface and products generated within the solution should be carried out.

- Table 1 Results related to hydrogen production with the SnS<sub>2</sub> electrode
- Tablica 1 Rezultati koji se odnose na dobivanje vodika uz SnS<sub>2</sub> elektrodu

Electrode area /cm <sup>2</sup> Površina elektrode/cm <sup>2</sup>	Voltage/V Napon/V	Argon Argon	Hydrogen evolution rate/ml h <sup>-1</sup> cm <sup>-2</sup> Brzina razvijanja vodika /ml h <sup>-1</sup> cm <sup>-2</sup>
2.31	1.35	No	0.725
1.52	0.60	No	0.016
1.44	1.35	Yes	0.799

- Table 2 Results related to hydrogen production with the TiO<sub>2</sub> electrode
- *Tablica 2 –* Rezultati koji se odnose na dobivanje vodika uz TiO<sub>2</sub> elektrodu

Electrode area /cm <sup>2</sup> Površina elektrode/cm <sup>2</sup>	Voltage/V Napon/V	Argon Argon	Hydrogen evolution rate/ml h <sup>-1</sup> cm <sup>-2</sup> Brzina razvijanja vodika /ml h <sup>-1</sup> cm <sup>-2</sup>
1.98	1.35	No	0.707
1.53	0.60	No	0.098
1.98	1.35	Yes	0.783

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Tables 1 and 2 show the amounts of produced hydrogen under the investigated conditions. The largest volume of hydrogen was produced in an argon atmosphere at a potential of 1.35 V. Under these conditions,  $0.799 \text{ ml h}^{-1} \text{ cm}^{-2}$  hydrogen was produced using the SnS<sub>2</sub> photoanode, and  $0.783 \text{ ml h}^{-1} \text{ cm}^{-2}$  hydrogen was produced using the TiO<sub>2</sub> photoanode. A slightly smaller volume was generated at a potential of 1.35 V in an oxygen atmosphere,  $0.725 \text{ ml h}^{-1} \text{ cm}^{-2}$  for SnS<sub>2</sub> photoanode, and  $0.707 \text{ ml h}^{-1} \text{ cm}^{-2}$  for TiO<sub>2</sub> photoanode. When hydrogen is produced in an oxygen atmosphere,<sup>22</sup> in addition to the hydrogen reaction, the oxygen reduction reaction also takes place. Therefore, more hydrogen will be produced in an argon atmosphere<sup>23</sup> where the oxygen reduction is prevented.

By comparing the amount of hydrogen, it is evident that, at 1.35 V, a similar amount of hydrogen was produced with both the TiO<sub>2</sub> and SnS<sub>2</sub> photoanodes. This supports the previous conclusion that the current related to the electrochemical oxidation of AA is dominant over the photocurrent at 1.35 V. Hence, the better photoactivity of TiO<sub>2</sub> did not result in a higher amount of hydrogen. At a potential of 0.6 V, the volume of hydrogen is higher for the TiO<sub>2</sub> electrode, which is in accordance with the current values recorded during the PEC process (Figs. 7 and 8). Therefore, it is obvious that, at 0.6 V, the photocurrent was dominant over electrochemical reaction.

In previous studies, 0.65–0.89 ml h<sup>-1</sup> cm<sup>-2</sup> hydrogen in 1 mol dm<sup>-3</sup> KOH solution at 1.62 V was produced using a W-doped electrode and a Cr-doped TiO<sub>2</sub> electrode with a RuO<sub>2</sub> layer.<sup>22</sup> Using a TiO<sub>2</sub>/WO<sub>3</sub> electrode in 0.5 mol dm<sup>-3</sup>  $NaClO_4$  solution with ethanol as a hole scavenger and at a potential from 0.27 to 1.37 V, the recorded amount of hydrogen ranged from 0.24 to 0.72 ml h<sup>-1</sup> cm<sup>-2</sup>.<sup>23</sup> The hydrogen obtained by photocatalysis in 1 mol dm<sup>-3</sup> solution of  $(NH_4)_2SO_3$  was 86.6 to 155.2 µmol h<sup>-1</sup> (2.08 to 3.72 ml h<sup>-1</sup>)/50 mg WP/CdS photocatalyst.<sup>25</sup> Comparing the aforementioned results with the results from this investigation, it can be concluded that hydrogen volumes obtained at the higher potentials are equal to or greater than the values previously reported.<sup>23-25</sup> However, hydrogen volumes generated at lower potentials are slightly lower than those reported in the literature. It can be concluded that the application of AA as a hole scavenger in the PEC process investigated in this work was successful and shows potential for practical application.

# 4 Conclusion

In this work, the electrochemical characterisation of  $SnS_2$  and  $TiO_2$  electrodes confirmed a good photoactivity. By using an AA solution, the LSV photocurrent response significantly increased, confirming that AA behaves as a good hole scavenger. OCP monitoring also proved the good hole scavenging properties of AA. LSV indicated that the photoactivity of  $TiO_2$  under the UV lamp was higher than the

photoactivity of SnS<sub>2</sub> under the LED light. Although TiO<sub>2</sub> photoanode showed better results, its disadvantage is the requirement of UV light. Consequently, SnS<sub>2</sub> appears to be the more suitable photoanode due to efficient solar radiation harvesting.

The photocatalytic hydrogen production was performed at a constant potential of 0.6 V and 1.35 V to prove the good applicable properties of the investigated system. Besides a photocatalytic reaction, an electrochemical reaction also took place in the range of investigated potentials, and contributed to the produced hydrogen quantity. At a 1.35 V potential, most of the produced hydrogen was the result of the electrochemical reaction, so it is not surprising that a larger quantity of hydrogen volume was provided with the SnS<sub>2</sub> electrode. At a lower potential value of 0.60 V, the contribution of the photocurrent was more significant, making the difference between the TiO<sub>2</sub> and SnS<sub>2</sub> responses more pronounced.

The higher amount of hydrogen, for both electrodes, was produced at a potential of 1.35 V in an argon atmosphere where competitive oxygen reduction reaction was prevented. It can be concluded that the application of AA as a hole scavenger in the PEC process is promising for practical applications.

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#### List of abbreviations and symbols Popis kratica i simbola

- E potential, V
- potencijal, V
- j current density, mA cm<sup>-2</sup>
  - gustoća struje, mA cm<sup>-2</sup>
- t time, s
  - vrijeme, s
- I electric current, A
  ialvast alaltična struio
- jakost elektične struje, A
- AA ascorbic acid
  - askorbinska kiselina
- FTO fluorine-doped tin oxide – fluorom dopiran kositrov oksid
- PEC photoelectrochemical – fotoelektrokemijsko
- SCE saturated calomel electrode – zasićena kalomel elektroda

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# SAŽETAK

# Fotoelektrokemijsko dobivanje vodika potpomognuto askorbinskom kiselinom

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Fotoelektrokemijski procesi kombiniraju primjenu napona i fotokatalizu, što može rezultirati održivom proizvodnjom vodika. Proces se može poboljšati dodatkom sredstva koje reagira sa šupljinama, čime se smanjuje rekombinacija elektrona i šupljina. Askorbinska kiselina (AA) smatra se ekološki i ekonomski prihvatljivim sredstvom pogodnim zbog svojeg niskog oksidacijskog potencijala. Najčešće upotrebljavani fotokatalizator, TiO<sub>2</sub>, u fotokatalitičkom procesu slabo iskorištava sunčevu svjetlost zbog velikog energetskog procjepa od 3,2 eV. Metalni sulfid, SnS<sub>2</sub>, privlači pažnju zbog malog energetskog procjepa od 2,2 eV, koji omogućava uporabu vidljivog dijela spektra. Elektrokemijska karakterizacija SnS2 i TiO2 fotoanoda provedena je u otopini NaCl uz prisutnost i bez prisutnosti AA. Utjecaj AA na fotostruje praćen je metodom linearne promjene potencijala i mjerenjem potencijala otvorenog kruga. Rezultati su potvrdili da su SnS2 i TiO2 elektrode fotoaktivne te da je AA pogodna za smanjenje rekombinacije elektrona i šupljina. Da bi se potvrdila dobra svojstva istraživanog sustava, provela se reakcija dobivanja vodika pri konstantnim potencijalima od 0,6 i 1,35 V. Pri potencijalu od 0,6 V više vodika je dobiveno uz TiO2 elektrodu, jer ona pokazuje veću fotoaktivnost. Pri 1,35 V većina proizvedenog vodika bila je rezultat elektrokemijske reakcije te je veći volumen vodika dobiven uz SnS<sub>2</sub> elektrodu. Najveća količina vodika u ovom radu, 0,799 ml h<sup>-1</sup> cm<sup>-2</sup>, proizvedena je pri 1,35 V uz SnS<sub>2</sub> elektrodu kao fotoanodu u atmosferi argona.

#### Ključne riječi

Askorbinska kiselina, vodik, sredstvo za smanjenje rekombinacije, fotoelektrokemijski proces, kositrov(IV) sulfid, titanijev(IV) oksid

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