PHOTOANODE DEVELOPMENT FOR PHOTOELECTROCHEMICAL WATER

SPLITTING

by

Miguel Angel Leon

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Photoanode development for photoelectrochemical water splitting

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Abstract

Abundant materials, cheap synthesis methods and high efficiencies are required for photoelectrodes materials to enable commercial water splitting through photoelectrochemical processes. In this work, the synthesis and improvement through an electrochemical modification of the n-type semiconductor BiVO₄ for oxygen evolution is presented. The modification consisted on a dynamic polarization in a three-electrode cell. The pristine and modified BiVO₄ were evaluated through electrochemical and photoelectrochemical methods. The modification was found to increase the photocurrent by 80% compared to pristine BiVO₄ at 1.23 V vs RHE and increase in the incident photon-electron conversion efficiency (IPCE) by up to 20% at 400 nm. A photocathode for hydrogen evolution was synthetized and tested along with the BiVO₄ photoanode in a two electrode photoelectrochemical cell. Water splitting was obtained without external bias and an improvement of 33% in the solar to hydrogen (STH) efficiency was obtained with the modified material. Based on results gathered through electrochemical, photoelectrochemical and physical-chemical characterization, the modification causes the insertion of hydrogen into the lattice and distorts the crystal structure. Moreover, the amount of V⁴⁺ in the photoanode increases and there is OH adsorption in the surface. These results provide evidence for improved overall performance.

Lay summary

Among green technologies for energy production, hydrogen obtained by photoelectrochemical methods is a promising option because solar energy can be stored as hydrogen fuel directly. Inexpensive materials and simple improvement methodologies are necessary to develop catalysts to make the process affordable. The present work applies an electrochemical technique to improve the conversion of sunlight and water into oxygen and hydrogen. It uses an abundant material (BiVO₄) which can be used for large-scale hydrogen production.

Preface

This work benefited from experimental techniques and concurrent efforts led by Prof. Walter Mérida, Dr. Jesús (XPS and XRD measurements), Dr. Thomas Holm, and Dr. Marta Moreno (BiVO₄ SEM measurement). The projects and research led by these individuals provided an effective training environment for me to learn and apply these techniques and knowledge. The original conception of the idea of electrochemical modification on the BiVO₄ photoanode for its improvement was made by the MeridaLabs group at the University of British Columbia. Input and revision of the thesis is by Prof. Walter Mérida, Dr. Thomas Holm and Dr. Omar Herrera.

This thesis consists of four chapters. The first Chapter situates this thesis project in a general context. It emphasizes the advantages of the photoelectrochemical methods by comparing them with similar technologies. Also it provides an overview of the fundamental processes behind solar fuel production by photoelectrochemistry. The use of BiVO4 as photoanode is introduced with some of characteristics and the challenges for its improvement. Finally, some general aspects about the photocathode used in this work are presented. Chapter 2 describes the methodology used in this work for synthesis and characterization of the photoanodes and photocathodes. Chapter 3 shows the results of the thesis starting from the exploratory experiments for bismuth electrodeposition, followed by the individual characterization, performance evaluation and finally the results of the photoelectrochemical cell for water splitting. Parts of the results in this chapter are in the publication:

Miguel Ángel León-Luna, Jesús Adrián Díaz-Real, Thomas Holm, Marta Moreno-González and Walter Mérida, "Toward Solar to Hydrogen: Unassisted photoelectrochemical *water splitting with electrochemically modified BiVO*₄", (Recently submitted to *Electrochimica Acta*). The paper was written by me with input from the co-authors.

My contribution in each part of the thesis and paper is as follows:

On the synthesis, the methods employed for the $BiVO_4$ and CuO, Cu_xS and Cu_xS/TiO_2 including the experimental design, optimization, and experimental work were conducted by me.

On the BiVO₄ modification, the optimization and experimental work and design were carried out by me.

Electrochemical, Photoelectrochemical, and Spectroscopic techniques for characterization and data analysis were carried out by me. CuO SEM images were performed by me.

Discussion of results shown in Chapter 3 and on the paper was carried out by me with input from co-authors.

Microscopy measurements were carried out at CHTP, UBC.

Table of contents

Abstract		
Lay sumn	naryiv	
Preface	V	
Table of c	ontents vii	
List of Ta	blesix	
List of fig	uresX	
List of abl	previationsx	
Acknowle	dgementsxv	
Chapte	r 1: Introduction 1	
1.1	Photoelectrochemical hydrogen production2	
1.2	Photoanodes	
1.3	BiVO ₄ Photoanodes enhancement	
1.4	Photocathodes materials for the hydrogen evolution reaction (HER) 11	
Chapte	Chapter 2: Methodology13	
2.1	CuO Photocathode synthesis	
2.2	BiVO ₄ photoanode synthesis	
2.3	Electrochemical modification	
2.4	Band gap estimation	
2.5	Conduction/valence band estimation: Mott-Schottky17	

2.6	Photoelectrochemical evaluation	9
2.7	Unassisted water splitting	2
2.8	XRD and XPS	4
Chapter	3: Results and discussion	5
3.1	Bismuth vanadate synthesis	5
3.2	BiVO ₄ and modified BiVO ₄ (e-BiVO ₄)	9
3.3	Discussion about the BiVO ₄ modification	5
3.4	Copper oxide photocathode: synthesis and characterization	7
3.5	Unassisted photoelectrochemical water splitting	2
Chapter 4: Conclusions		
4.1	Future work7	1
References		5
Appendix A: 2019 Young Electrochemist Symposium poster		

List of Tables

Table 1. Comparison of BiVO ₄ improvements in terms of IPCE at 365, 400 and 450 nm	n. a=hole
scavenger is used, b=it is not used	
Table 2. Solar-To-Hydrogen (STH) efficiency from recent literature	67

List of figures

Figure 9. The left-hand side shows the current collector (FTO), the bulk of the semiconductor and the electrolyte interface when a potential E_{app} is applied and the semiconductor is being irradiated. The right-hand-side shows a hypothetical polarization curve comparing two

Figure 10. a) Average photocurrent of photodiode being irradiated each 10 nm,
b)photosensitivity spectra of photodiode employed for calibration, and c) power output of
Xe source employed for IPCE and spectral current experiments (Tauc plot)

- Figure 12. Cathodic inversion potentials at 100 mV s⁻¹ of 20 mM Bi(NO₃)₂ + 1 M HNO₃ on FTO electrode in ethylene glycol a) and voltammogram of Bi at different sweep rates. C) shows
- Figure 13. Cathodic inversion potentials of Bi(NO₃)₃ in ethylene glycol on FTO electrode at 100 mVs-¹ in ethylene glycol. The numbers at the top of each anodic peak indicates its Figure 14. BiVO₄ film voltammogram during electrochemical treatment at 100 mV s⁻¹ in 0.1 M

Figure 15. Cathodic inversion potentials of BiVO₄ before and after the electrochemical

Figure 16. Cyclic voltammetry of BiVO₄ before and after the electrochemical polarization at 100

- Figure 17. Linear sweep voltammetry from cathodic to anodic potentials at 10 mV s⁻¹ with
- Figure 18. Transient photoresponse of photoanodes applying 1000 mV vs Ag/AgCl (KClsat).... 36

Figure 19. Incident Photon-to-electron Efficiency (IPCE) a) and Tauc plot b) comparing between
pristine (BiVO ₄) and modified (e-BiVO ₄) materials measured at a constant E_{app} =500 mV vs
Ag AgCl (KCl _{sat}) under 0.1 M KClO ₄ . c) density of states diagram representing the band
gap electronic transition and the transitions attributed solely between vanadium species 43
Figure 20. Absorbance spectra of BiVO ₄ films before and after the electrochemical modification
(e-BiVO ₄)
Figure 21. a) Inverse of the square of the space-charge capacitance (C_s) at different frequencies
over a range of potentials of $BiVO_4$ film on FTO. b) flat-band potential of $BiVO_4$ and
eBiVO ₄ comparison as a function of the logarithm of the frequency determined plot. c)
Inverse of the square of C_s vs Potential comparison of both materials at 10 Hz. Flat band
potential as a function of the logarithm of the frequency
Figure 22. Polarization curves of BiVO ₄ in dark, under light irradiation and interrupted light
using 0.1M K ₂ SO ₄ and 0.1M Na ₂ SO ₄ electrolytes recorded at 10 mV s ⁻¹ 47
Figure 23. Cathodic inversion potentials at 100 mV \cdot s ⁻¹ of pristine BiVO ₄ using different
electrolytes
Figure 24. Cyclic voltammetry of BiVO ₄ at 100 mV s ⁻¹ before and after electrochemical
treatment using different electrolytes
Figure 25. Top-view SEM images of the: a) pristine BiVO ₄ and b) electrochemically treated
BiVO ₄
Figure 26. High-resolution XPS spectra of both materials: c) V 2p, d) Bi 4f, and e) O 1s 53
Figure 27. XRD patterns of BiVO4 and e-BiVO4. Monoclinic phase of BiVO4 (m - BiVO4)
(JCPDS 75 – 1867) and tetragonal SnO ₂ (JCPDS 77 - 0452) from the FTO substrate 55

Figure 28. Band diagram of BiVO ₄ before and after the treatment. The trap states on BiVO ₄
serve as recombination centers, thus there are fewer h^+ available for water reduction. When
the states are filled by either hydrogen insertion, the trap states are filled and performance is
increased
Figure 29. Cyclic voltammogram of 5 mM CuSO ₄ in aqueous solution on FTO electrode at 100
mVs ⁻¹
Figure 30. Linear sweep voltammetry from positive to negative potentials at 10 mVs ⁻¹ under 0.1
M KClO ₄ and interrumpted light of different photocathodes
Figure 31. High-resolution XPS spectra of a) Cu 2p, b) O 1s and SEM c) of CuO film 60
Figure 32. CuO film on FTO Mott-Schottky plot for the flat-band determination Flat band values
as a function of the frequency for CuO film on FTO sample
Figure 33. IPCE a) and Tauc plot b) of CuO film measured under 0.1 M KClO ₄ at -0.25 mV
irradiating from the back of the film
Figure 34. Band diagrams of BiVO ₄ materials and Cu based materials photocathodes
Figure 35. Transient photoresponse of photoelectrochemical cell at $E_{app}=0.0$ V vs photoanode of
BiVO ₄ as photoanode and CuO as photocathode a) and e-BiVO ₄ as photoanode and CuO as
photocathode. From t = 60 s to t=690 s the light was chopped in intervals of 5 s. After t=750
s the light was irradiating continuously until t=2500 s65
Figure 36. Comparison between the photoelectrochemical cell presented in this work with
photovoltaic (PV)+Electrolysis process for hydrogen production

List of abbreviations

Eg	Band Gap
PEC	Photoelectrochemical cell
MT	Mott-Schottky
IPCE	Incident photo-conversion efficiency
СВ	Conduction band
VB	Valence band
STH	Solar to hydrogen
CV	Cyclic voltammetry
FTO	Fluorine doped tin oxide
LSV	Linear sweep voltammetry
SEM	Scanning electron microscope
XRD	X-Ray Diffraction
XPS	X-ray photoelectron spectroscopy
WS	Water splitting
FTO	Tin oxide doped with Fluor conductive glass
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction

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Chapter 1: Introduction

One of the most important aspects to sustain life is energy supply. Its generation and storage are an economic indicator of a developed country. Products of the utilization of some of the energy resources, such as coal, natural gas and oil have led to environmental problems and disequilibrium in ecosystems. It is projected that by 2050 the energy demand will be of 28 TW and is estimated that 600 TW of solar energy can be potentially used [1]. Thus, only 0.5% of the solar energy is needed to cover the global energy demand [2]. Solar energy can be used in two forms: heat and light, that is, two regions of the electromagnetic wave spectrum from the sun. With solar-thermal technologies, the heat is concentrated and collected either for distributed heating systems or thermal power plants. In contrast, photovoltaic cells use sunlight to generate electricity. One remarkable difference between solar-thermal and photovoltaic technologies is the type of materials used for these purposes. Heat absorbent materials are needed for solar-thermal technologies, whereas photovoltaic generation exploits the UV-visible light spectrum to produce electricity. Photosensitive semiconductors connected to an external circuit are able to produce current when light is irradiated on them. Nevertheless, due to the daily and annual variations, it is convenient to store solar electricity either by charging batteries, electrochemical pseudocapacitors, etc., or by converting electricity into chemicals. The common approach for the latter case is to store the solar energy as hydrogen or low-chain hydrocarbons obtained from CO₂ through photocatalysis and photoelectrochemistry.

The production of hydrogen molecules as a source of fuel has drawn particular attention as the reaction involves less steps, is energetically less demanding, and no by-products are produced. Photoelectrochemical hydrogen production uses solar light to assist or completely carry out electrolytic water splitting. As the water is separated into its basic components i.e. hydrogen and oxygen, hydrogen production involves the oxygen evolution as a counter reaction. Photocatalysis achieve the same results but with the important difference that photocatalysis produce hydrogen and oxygen on the surface (particle or film), while photoelectrochemical methods form the products on different interfaces, making it possible to inherently separate the products.

Compared to other solar technologies, the efficiencies on photoelectrochemical water splitting are poor. Common solid-state photovoltaic devices such as amorphous and crystalline silicon have achieved between 14% and 19% efficiencies [3]. Photovoltaic regenerative cells employ a semiconductor or electrolyte to convert sunlight to electricity without chemical changes. This technology has achieved approximately 20% efficiency [4] whereas the reported efficiency in dye-sensitized solar cells (DSCs) is approximately 12% [1]. Finally, the leading proton exchange membrane (PEM) water electrolysis process has achieved an efficiency of 60-80% [5]. According to the US Department of Energy, the ultimate target for solar to hydrogen (STH) production is 25 % and photoanodes lifetime of 90 000 h [6]. Despite many improvements and advances of photoelectrode performance since the first water photolysis report in 1972 [7], performances are still low for commercial deployment (maximum STH reported of 8.2 % [8]). In order to significantly improve the low performances, the development of new synthesis and postsynthetic methods to overcome low efficiencies and achieve long-term stabilities.

1.1 Photoelectrochemical hydrogen production

Photocatalysis and electrocatalysis are intimately related to photoelectrochemistry. Thus, the mechanism of photocatalysis and electrocatalysis are briefly explained here. This also provides the aspects to consider for a good photoanode development in its use on a photoelectrochemical cell for unassisted water-splitting.

Hydrogen production from water entails the formation of oxygen and hydrogen. The separation of the water molecule into its components requires thermodynamically an amount of 236 kcal mol⁻¹ (at standard temperature and pressure). When it comes to electrolysis, the energy is provided by electricity and the following two reactions are carried out on each side of the cell [9]:

Anode reaction:
$$2H_2O(l) \to 4H^+(aq) + O_2(g) + e^-(E^0 = 1.23 V vs NHE)$$
 (1)

Cathode reaction:
$$4H^+(aq) + 4e^- \rightarrow + 2H_2(g) \ (E^0 = 0.00 \ V \ vs \ NHE)$$
 (2)

In addition to the thermodynamic demands, reactions do not proceed with 100% efficiency and kinetic losses due to slow reactions, diffusion or resistance in the system are common. Therefore, a large effort has gone into identifying and developing efficient electrocatalysts for this reaction.

The electrical energy required to carry out reduction and oxidation reactions is expected to diminish with photoelectrochemical methods by using sunlight. Figure 1 shows a schematic representation of the comparison in terms of energy with the electrochemical water splitting and the use of light for the same process. The electrical energy required to complete the energy demand for the reactions to occur can be provided by renewable resources (assisted water splitting) such as photovoltaic cells, wind power, etc. In the best-case scenario, the light will provide all the energy required to obtain the desirable products (unassisted water splitting). If all the light is supplied by light, two approaches can be used, photocatalytic and unassisted photoelectrochemical water splitting.



Figure 1. Schematic representation of the use of photoelectrochemical methods to reduce electrical energy demand to produce solar fuels

As it can be noticed, in order to make use of solar energy for electrolysis, electrodes must be photoresponsive. Semiconductors are commonly employed as photoelectrodes for these purposes. The reactions occurring are similar for photocatalysis and photoelectrochemistry. Semiconductor materials are used for both photocatalysis and photoelectrochemistry. However, the overall differences between the systems, such as the need to supply the whole energy in one particle in the case of photocatalysis, means that necessary characteristics in terms of porosity, crystallinity and particle size are very different [10].

The photocatalytic water splitting process is a heterogeneous reaction as it typically consists on a solid (photocatalyst) immerse in a solution (either gas or liquid) where the reaction occurs.

The solids employed are semiconductors materials which with certain energy some amount of positive and negative charges are generated. Positive charges are used to oxidize water, producing oxygen O_2 while the negative ones to produce H_2 . The positive and negative chargepair generation consists on the light irradiating upon the semiconductor, making the electrons to be promoted from a ground to an excited state. The energy of the ground state is commonly called valence band (VB) and the excited state is called conduction band (CB). The electrons, by being on the conduction band under certain conditions, they can have some mobility in the semiconductor. The positive charges are formed due to the space left by the electrons when they are promoted to the conduction band. For this reason, they are called "holes" (h⁺) and for practical purposes it is considered a particle as well and, hence, properties such as mass and velocity are given to them.

Analogous to the electrolysis case aforementioned, the processes occurring on the surface of the photocatalyst can be represented by the following equations:

$$2H_2O(l) + 4h^+ \to 4H^+(aq) + O_2 \tag{3}$$

$$4H^+(aq) + 4e^- \to + 2H_2(aq) \tag{4}$$

Which in total the overall process is the water splitting:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \tag{5}$$

Notably here, the positive charges are the charge carrier particles for oxygen evolution. The photocatalytic process for water splitting is represented in Figure 2.



Figure 2. Hydrogen and oxygen production by photocatalytic process. Semiconductor nanoparticle in solution is irradiated and an electron-hole pair is formed. Afterwards, both charges migrate to the surface of the nanoparticle. Electron on conduction band is transferred from semiconductor to water to carry out hydrogen production and the hole receives an electron from the water Notably, from Figure 2, the process is accomplished in one particle, which means that hydrogen and oxygen are produced in the same volume. Moreover, once an electron is excited in the material, the charges need to move to the surface of the material to carry out the reactions. However, this process is not fast, and the excited electrons are prone to recombine due to electrostatic forces (indicated in red arrows Figure 2). The recombination of the two charges diminishes the efficiency of energy conversion.

The minimum required energy (236 kcal mol⁻¹ or 1.23 eV) corresponds to a wavelength of 600 nm, and the semiconductor material must be able to absorb this energy to carry out the water splitting process. Moreover, the valence and conduction bands must straddle the H_2/H_2O and H_2O/O_2 energetic positions, respectively (dashed lines in Figure 2). The maximum solar emission power lies between 375 and 700 nm. Therefore, the photocatalysts must absorb mainly in this region to take advantage of solar energy.

As previously mentioned, a key point that differentiates photocatalysis from photoelectrochemical water splitting is that the latter carries out the hydrogen and oxygen production on different surfaces. Similar to those used in electrochemical water splitting, the two electrodes are connected through an external circuit. As a consequence, each electrode used during photoelectrochemical water splitting is composed of a semiconductor that absorbs the light and a current collector. An unassisted photoelectrochemical water splitting process is schematically shown in Figure 3.



Figure 3. Schematic representation of an unassisted water splitting in a photoelectrochemical cell

From Eq. (3), four holes are necessary to create one oxygen molecule, and these have to be generated at the photoanode. At the photocathode, water will be reduced, and four electrons are required in the conduction bands create two hydrogen molecules (Eq. (4)). As it is shown in Figure 3, the conduction band of the photoanode lies above the valence band of the photocathode. Hence, the holes generated at the photocathode react with water, while the electrons migrate towards the current collector and into the photocathode where they are recombined with holes in the valence band of the photocathode. In this way, the circuit is closed and unassisted water splitting can be carried out. The reactions take place on different surfaces making product separation easier. Hydrogen production entails the oxygen evolution reaction (OER). This reaction is known to be hard to catalyze and is a limiting factor in the overall efficiency. Thus, improvements on the photoanode design are required to enable affordable, large-scale H₂ production with PEC [11].

1.2 Photoanodes

The most common n-type semiconductors used for oxygen evolution reaction (OER) include TiO₂ [12] and ZnO [13]. These materials provide stability over a broad pH ranges, and high photocurrents. The main problem with both Ti and Zn oxides is that they have a band gap of approximately 3.2 eV which means that ultraviolet energy is required for electron promotion [14], and therefore, they cannot take advantage of the full solar spectrum. Some researchers have made great efforts to modify these materials enable absorption within the visible region while preserving stability [15]. Other materials with smaller band gaps such as hematite (α -Fe₂O₃) have also been employed as photoanode materials due to their stability, great abundance, and absorbance in the visible region of the spectrum (2.2 eV). However, the reported photocurrents are low [16]–[18]. Other alternatives include binary oxides (iron, tungsten, zinc) and ternary oxides whose band gaps are in the visible region (BiVO₄, CuWO₄, Bi₂WO₄) [19], [20].

BiVO₄ has attracted a lot of interest the last years due to its large, theoretical photocurrent (7.9 mA cm⁻² under solar simulator [21]). In recent years, it has been reported that this material may provide suitable band energy positions, absorption in the visible region and long term stability in aqueous solutions [22].

1.3 BiVO₄ Photoanodes enhancement

In order to improve BiVO₄ efficiency, synthetic and post-synthetic methods have been developed (e.g, nanostructured film deposition). The addition of precious metals (Pt, Au and Ag), rare-earth and transition compounds (e.g., RuO₂) [6], [23]–[25], can enhance the charge transfer once the photogenerated species have been generated in the BiVO₄ film. However, the photoelectrodes are not stable for long time operation due to photocorrosion [23], [26], [27] and the precious metals add substantial cost to the system. Another post-synthetic method is the

addition of layers on BiVO₄ photoanodes. The idea is that the added film contains both valence and conduction bands at higher energies than BiVO₄, thus providing energetic states for the holes to migrate to the surface while blocking electron movement. The latter process is represented schematically in Figure 4. Typically, the layer also improves the kinetics of the charge-transfer reaction and reduces or blocks hole accumulation at the surfaces and improving the stability for long-term operation [28], [29]. An example of such a system is the addition of FeOOH demonstrated in the work by Seabold et al. [30]. The addition of an extra layer implies the use of more synthetic steps as well as reagents, which adds cost and complexity to the overall process.



Figure 4. Process of electron charge kinetics when BiVO₄ electrode is irradiated to carry out water oxidation with a catalyst layer with favorable band position to allow the hole movement to the interface and blocks electrons

Another approach to improve efficiency is to dope the material with W and Mo. The W/Mo on the BiVO₄ surface creates a potential gradient which helps to increase the carriers diffusion length and leads to an enhancement in the electron-hole separation [31]. Structurally, it has been found that both W and Mo ions exchange position with V in the BiVO₄ lattice. The synthesis method involves the preparation of the precursors added to the mixture of typical BiVO₄ solutions [32]–[34].

Hydrogen, annealing is another possibility to improve efficiency as demonstrated in recent work [35]. This method involves fewer reagents and demonstrated similar improvement to W doping [36]. Generally, the method consists of annealing the material up to 10 h in a low pressure hydrogen atmosphere (3.3 mPa) and at temperatures from 100 to 400 °C [35]. The improvement by this method is highly dependent on the conditions used [35]–[38]. The modification promotes H insertion in two positions: at interstitial sites, and next to an oxygen, forming OH [37]. Some authors argue that the annealing process reduces the amount of V and Bi defects within the material [36]. It has been observed that the consequence of the treatment is the filling of deep states and that the density of charge carriers is increased. Such states inhibit the electrons and holes mobility, and work as recombination centers as illustrated in Figure 5.





Another option to improve the photoanode efficiency involves electrochemical treatments. This approach has recently been demonstrated to yield substantial improvements in efficiency for TiO₂ [39], [40] and BiVO₄ [41]. Electrochemical treatment has been carried out by applying a constant potential where hydrogen evolution occurs [41]. As the electrochemical treatment involves hydrogen evolution, it is expected that the mechanism is analogous to hydrogen annealing in that some hydrogen enters the material [40]. Compared to the other modification methods, electrochemical treatment uses mild conditions and inexpensive solvents. Thus, electrochemical treatment is the simplest method to implement, and if it can yield similar improvement to the other methods, it constitutes a very promising pathway towards higher efficiencies. Despite this promise, the effectiveness of electrochemical treatments to enable unassisted photoelectrochemical splitting has not been demonstrated.

1.4 Photocathodes materials for the hydrogen evolution reaction (HER)

Although it is outside of the scope of this thesis, hydrogen evolution catalysts have to be mentioned. A HER catalyst is required to carry out the PEC water splitting, and the materials that are typically used only for hydrogen evolution include p-type semiconductors. Metal oxides and chalcogenides such as CdS, PbS and Cu_xS (x=0.2, 0.5, 1, 2), selenides (CdSe) and oxides (Cu_xO) are among the most common compounds used for HER purposes. Many p-type semiconductors suffer from photocorrosion and stability issues [42]. Among the earth-abundant materials, CuO has demonstrated reasonable stability and was chosen in this work to demonstrate overall water splitting. CuO also has conduction and valence band position that combines well with the BiVO₄ making the coupling of the two theoretically able to do unassisted water splitting.

In this work, the synthesis of $BiVO_4$ on FTO (conductive glass) was developed and optimized for its use as photoanode. $BiVO_4$ films were characterized and further improvement on its performance for oxygen evolution was achieved. The improvement was made by a postsynthetic method through dynamic electrochemical treatment. The dynamic polarization was investigated as a pathway to improve the performance of BiVO₄ photoanode for water splitting.

Optoelectronic properties and performance of modified $BiVO_4$ were evaluated by electrochemical and photoelectrochemical methods. Furthermore, structural changes were analyzed by XPS, XRD and SEM. Photoanodes of copper-based materials (CuO, Cu_xS and Cu_xS/TiO₂) were also developed and characterized as potential candidates for using in a photoelectrochemical cell for water splitting. Finally, unassisted water splitting was achieved in a photoelectrochemical cell. The improvement of $BiVO_4$ through dynamic polarization was also preserved during the photoelectrochemical unassisted water splitting.

Chapter 2: Methodology

All chemicals were of analytical grade and were used as purchased without further purification. Deionized water (18.25 M Ω cm) for the experiments was obtained from a Molecular Lab Water Purifier. FTO conductive glass was cleaned using an ultrasonic bath with ethanol, isopropanol and purified water for 20 min each in sequence. Electrical contacts for the electrochemical experiments were made by attaching a copper strip to the edge of FTO glass using a Kapton[®] tape.

For the photoelectrochemical measurements, the cell was equipped with a quartz window to prevent the reflection or absorption. The experiments were always performed in a Faraday cage. A 175 W Xe lamp (Spectral products, AST-XE-175EX) was utilized for irradiation. A Bio-Logic potentiostat (SP-150) equipped with a low current board was used for both electrochemical and photoelectrochemical measurements. The typical irradiation power (P_0) was estimated as 3.75 mW cm⁻².

2.1 CuO Photocathode synthesis

An aqueous electrolyte solution containing 5 mM CuSO₄, 1 M Na₂SO₄ and 0.5 M H₃BO₄ was used for copper electrodeposition in a conventional three-electrode electrochemical cell as reported by Hong [43]. FTO glass of 0.41 cm², Ag|AgCl (KCl_{sat}) and platinum wire were used as working, reference and counter electrodes, respectively. The cyclic voltammetry of copper was recorded prior to the electrodeposition and is presented in Chapter 3 (Figure 29). Based on Miguel [44], the copper electrodeposition process consisted of 20 ms of cathodic pulse at -0.4 V vs Ag/AgCl KCl_{sat} and 10 ms of anodic pulse at 0.05 V vs Ag|AgCl (KCl_{sat}), right before the

maximum value of the anodic peak. The electrodeposition was carried out for 12 000 cycles. After the copper electrodeposition, the FTO/Cu electrode was annealed at 400 °C for 1 h in air.

2.1.1 Cu_xS and Cu_xS/TiO₂ photocathodes synthesis

As a test, Cu_xS and Cu_xS/TiO_2 photocathodes were also synthetized to try water splitting. Their synthesis consisted of the electrodeposition of Cu as described in section 2.1. Afterwards, the Cu films were immersed in a polysulfide solution (1 M Na₂S and 1 M S) for 1 h [45]. TiO₂ (nanopowder 21 nm) was suspended in isopropanol (0.1 M TiO₂) under a sonic bath. The suspension was added to the Cu_xS film by spin coating. The conditions of the film were optimized and thus, the final parameters for the deposition were 2 mL at 2000 rpm for 30 seconds.

2.2 BiVO₄ photoanode synthesis

The first step for the BiVO₄ synthesis was the electrochemical deposition of a Bi film on FTO. A preliminary study to detect the Bi oxidation and reduction potentials was carried out under ethylene glycol and HNO₃ as the supporting electrolyte. The results are briefly presented in Chapter 3:. The final perturbation for the pulse electrodeposition applied -2.0 V vs Ag|AgCl (KCl_{sat}) for 200 ms and 1.0 V vs Ag|AgCl (KCl_{sat}) for 100 ms until 2400 cycles in 20 mM Bi(NO₃)₃ in ethylene glycol solution were completed in a three-electrode cell. Ag|AgCl (KCl_{sat}) and a platinum wire were used as reference and counter electrodes, respectively. The reference electrode was placed in front of the FTO working electrode and the platinum wire next to it. A copper strip was used to connect the FTO electrode. The resulting deposited BiVO₄ film formed a circle with a total area of 0.41 cm², which is the value used to normalize the current in this work. The Bi reduction and oxidation potentials were determined by cyclic voltammetry prior to electrodeposition. After the electrodeposition, a drop of 150 mM VO(acac)₂ in DMSO was placed

on top of the Bi surface and annealed at 450° C in a furnace for 2 h. As a side reaction, V₂O₅ was obtained on the BiVO₄ surface [46]. Thus, the films were further immersed in 1 M NaOH solution on a petri dish and placed in an ultrasonic bath for 20 min.

2.3 Electrochemical modification

After BiVO₄ synthesis and cleaning with NaOH, the FTO glass with the BiVO₄ film was immersed in 0.1 M KClO₄ aqueous solution. Dynamic polarization via cyclic voltammetry was carried out by scanning 100 cycles at 100 mV/s between -1.0 and 0.0 V (vs Ag|AgCl KCl_{sat}). A platinum wire was used as counter electrode. The cyclic voltammetry remained constant after 100 cycles. At this point, the modification was assumed complete.

2.4 Band gap estimation

Using spectroscopic techniques such as UV-vis absorption or diffuse reflectance, the excitation of electrons is evaluated. However, the current response of photoelectrodes as a function of the light wavelength can be more useful as it shows the wavelengths that contribute to the water oxidation (photoanode case). The determination of the band gap of BiVO₄ materials and CuO was carried out in 0.1 M KClO₄ aqueous electrolyte in a three-electrode cell using Ag|AgCl (KCl_{sat}) and Pt wire as reference and counter electrodes, respectively. A light source and monochromatic light were used to irradiate the material. The setup is schematically shown in Figure 6.



Figure 6. Experimental setup used for the photoelectrochemical evaluations. On the left is the schematic representation of the cell. On the right, a picture of the actual light source, the monochromator and the cell

A Tauc plot is made by plotting $(j_{PH} E)^{1/n}$ vs (*E*). Here j_{PH} stands for the photocurrent and *E* is the energy of the incident photon.

The band gap is estimated according to the following equation:

$$(\mathbf{j}_{\rm PH} \mathbf{E}) = k(\mathbf{E} - \mathbf{E}_{a})^{n} \tag{6}$$

where *E* and *E*_g are the photon energy and band gap energy, respectively and *k* is a proportionality constant. The *E*_g value can be estimated by extrapolating the straight portion of the $(\alpha h v)^{1/n}$ vs (hv) plot, i.e. when the absorption is equal to zero.

The energy of the photons can be calculated by using E=hv. Here, *h* is the Planck constant and *v* is the frequency of the incident photon. The value of *n* in Eq. (6) depends on the type of electronic transition that the electron carries out when the photon strikes on the material. Transitions can be either allowed or forbidden. Phonons can be involved in the transitions as they can be either absorbed or emitted, corresponding to indirect transitions. Thus, four possibilities for the electron excitation can occur (four different values for *n*): direct forbidden/allowed or indirect forbidden/allowed. In Figure 7, a diagram of the momentum (\tilde{k}) vs the Energy (*E*) of the orbitals and the aforementioned transitions is shown. BiVO₄ has a band gap indirect allowed transition (n=2) [35].



Figure 7. Types of electron transitions of a hypothetical semiconductor. The momentum and the energy of the phonon is represented by \tilde{q}_{phonon} and $\hbar \omega_{phonon}$, respectively

2.5 Conduction/valence band estimation: Mott-Schottky

The highest electron populated energy state in a solid is the Fermi energy level. The Fermi energy value gives an estimation of the conduction band value for n-type semiconductors as the energy levels of populated electrons are found closer to the conduction band.

The conduction band (n-type) can be estimated by measuring the capacitance of the spacecharge region (C_{SC}) formed in the interface of the semiconductor at different potentials as shown in Figure 8. As shown, both valence and conduction bands bend at the interface. The bending forms the space charge region which can be described as a capacitance element (C_{SC}). The band bending can be controlled by applying an external potential.

The Mott-Schottky equation [47], [48], describes the relationship between the capacitance of the space charge region and the applied potential :

$$\frac{1}{C_{\rm sc}^2} = \left(\frac{2}{\epsilon\epsilon_0 q N_d}\right) \left(E_{\rm app} - E_{\rm FB} - \frac{kT}{q}\right) \tag{7}$$

Where E_{app} is the applied potential, k is the Boltzmann constant (1.38×10⁻²³ JK⁻¹), T the temperature (K), q the electron charge (1.602×10⁻¹⁹ C) and finally ε and ε_0 the material (150 F cm⁻¹ for BiVO₄ [49]) and void permittivity (8.85×10⁻¹⁴ F cm⁻¹), respectively. At infinite capacitance, i.e., when the left-hand side of the equation is zero, the flat band potential (E_{FB}) can be found and approximated to the Fermi energy level which can be taken as the conduction band value (Figure 8). The last term of Equation 9 is negligible at room temperature and was not considered in this work.



Figure 8. Band energy representation of the electrode/electrolyte interface of an n-type semiconductor. For the experiment the potential applied goes from lower energies (positive potentials) to higher energies until there is no band bending on the interface

Once the band gap (E_g) value is estimated by Tauc (or other methods), and the position of the Fermi level through Mott-Schottky analysis, representing an approximation of the conduction band (E_{CB}) position in BiVO₄, the valence band (E_{VB}) position can be found from Eq. 10.:

$$E_g = E_{CB} - E_{VB} \tag{8}$$

For the flat band determination, the capacitance value of the space-charge region was determined at frequencies from 1000 to 1 Hz at potentials from 0.8 V vs Ag|AgCl (KCl_{sat}) to 0.0 Ag|AgCl (KCl_{sat}) for the case of BiVO₄. The capacitance was obtained by adjusting the impedance spectrum using a Randles circuit. The impedance fitting was done directly by the software (Biologic EC-lab 11.30). The extrapolation of the linear region of the slope is the value of the flat band at each frequency. It was plotted against the logarithm of the frequency to find the region in which the flat band is independent of the frequency used. The average of this region is the conduction band of the BiVO₄ materials and the valence band for the case of the photocathodes.

The potential values in Volts obtained by Eq. 9 were converted to an absolute energy scale. The conversion used to transform from potential values to absolute scale was the following: $E/absolute scale = -(E_{fb} + 0.199 + 4.44)$ where E_{fb} is the Fermi energy band value in V vs Ag/AgCl KCl_{sat}. The last two stems from the reference electrode potential (Ag/AgCl KCl_{sat} vs SHE) and the absolute potential (SHE vs absolute scale), respectively.

2.6 Photoelectrochemical evaluation

2.6.1 Current-potential curves

Current-potential curves were recorded at a scan rate of 10 mV/s between -100 mV and 1000 mV vs Ag|AgCl (KCl_{sat}) in darkness, light, and under chopped light. At high potentials, only oxygen evolution is possible and the faradaic efficiency towards water oxidation is assumed to be

100%. The cell used for this work is shown in Figure 6. All the characterizations were done using 0.1 M KClO₄, 0.1 M K₂SO₄, or 0.1 M Na₂SO₄. A schematic of the electrode during these measurements is shown in Figure 9. The left-hand side of Figure 9 shows an n-type semiconductor being irradiated. When a potential is applied on the semiconductor, the electron-hole pairs formed can be extracted. The electrons move towards the current collector and the hole takes electrons from the water. The right-hand-side in Figure 9 shows a hypothetical polarization curve comparing two photoanode materials under irradiation. The dashed blue line represents a photoelectrode with better catalytic activity than the solid line since less energy is required for it to produce current (onset displaced) and higher photocurrents are produced.



Figure 9. The left-hand side shows the current collector (FTO), the bulk of the semiconductor and the electrolyte interface when a potential E_{app} is applied and the semiconductor is being irradiated. The right-hand-side shows a hypothetical polarization curve comparing two photoanodes materials under irradiation
2.6.2 Incident photon-to-current conversion efficiency (IPCE)

The incident photon-to-current conversion efficiency (IPCE) measures the efficiency of converting individual photon energy to current [15], [16]. This is given by the following formula:

$$IPCE \ [\%] = \frac{electron \ flux \ (\frac{mol}{s})}{photon \ flux \ (\frac{mol}{s})} = \frac{j_{sc} \left[\frac{mA}{cm^2}\right] * hc[Vm]}{P_{\lambda} \left[\frac{mW}{cm^2}\right] \lambda[nm]} * \ 100$$
(9)

Where j_{ph} is the photocurrent density, *h* is Plank's constant, *c* is the speed of light, P_{λ} is the power of light at a particular wavelength, and λ is the wavelength of irradiation. The IPCE spectra was obtained by measuring the current density as a function of the wavelength of the incident monochromatic light according to Equation 11. The product of the *h* and *c* constant was taken as 1240 eV*nm. A schematic of the test cell is shown in Figure 6.

To measure the IPCE, it is required calibration to know the power of light at certain wavelength (P_{λ}). The latter is because the Xe light irradiates photons with different intensities. The calibration was carried out by irradiating a calibrated photodiode at different wavelengths from 1100 to 350 nm each 10 nm and registering the current produced during 15 seconds. The average current is calculated from the 15 seconds. In Figure 10a the average current of the photodiode is plotted against the wavelength. The photocurrent ($_j$) from the photodiode is divided by the photosensitivity response (Figure 10b) to obtain the power output of the photons at each wavelength (Figure 10c).



Figure 10. a) Average photocurrent of photodiode being irradiated each 10 nm, b)photosensitivity spectra of photodiode employed for calibration, and c) power output of Xe source employed for IPCE and spectral current experiments (Tauc plot)

2.7 Unassisted water splitting

Unassisted water-splitting evaluation was carried out in a two-electrode cell in a tandem arrangement, where the BiVO₄ photoanode was irradiated from the front and CuO was irradiated from the back (See Figure 11).



Figure 11. Photoelectrochemical cell representation for unassisted water splitting test

2.7.1 Solar to hydrogen (STH)

The Solar to hydrogen parameter is an efficiency determination that takes into account the current produced with the irradiated light (j_{PH}) and the amount of product generated [50], [51],. It is described by the following equation:

STH [%] =
$$\frac{P_{\text{out}}}{P_{\text{in}}} = \frac{j_{\text{ph}} \, [\text{mA cm}^{-2}] \, 1.23 \, [\text{V}]^* \, \eta_{\text{f}}}{P_{\text{light}} \, [\text{mW} \cdot \text{cm}^{-2}]} * 100$$
 (10)

This is the ratio of the power of light irradiated P_{in} and the electric power generated P_{out} . The electric power is the product $P=I^*V$ and this value is multiplied by the faradic efficiency (η_f). In the case of unassisted photoelectrochemical water splitting, the E=1.23 V. The faradic efficiency (η_f) is the portion of the overall current going to the desired reaction, i.e., oxygen evolution. The faradaic efficiency was assumed to be 100%. Unlike IPCE mentioned above, STH takes into account the whole range of the light spectrum, that is, photon energy from the whole range of

wavelengths. The power of the light (P_{light}) was obtained by the integration of the power output spectrum shown in Figure 10c.

2.8 XRD and XPS

X-ray diffraction (XRD) was performed using a Bruker AXS (model D8 Advance) diffractometer with Cu K_{α} radiation ($\lambda = 1.5406$ Å), Bragg–Brentano geometry and a step size of 0.035°. X-ray photoelectron spectroscopy (XPS) was used to support the information of the surface chemistry with a Thermo Scientific instrument (model K-Alpha + surface analysis). The peaks of the XPS were analyzed and deconvoluted using the software OriginPro 2020.

Chapter 3: Results and discussion

3.1 Bismuth vanadate synthesis

Contact between the electrocatalyst and the current collector (FTO) is a factor that may influence the photoelectrochemical performance [52]. Electrodeposition is an option to improve the adherence, control the film thickness, its morphology and structure [53]. Therefore, as a first step of the synthesis, bismuth was deposited on FTO conductive glass. Bismuth (III) salts are soluble in water only at high pH. However, elemental bismuth films lose adherence in water without cathodic protection [54], [55]. Thus, the bismuth electrodeposition was carried out using ethylene glycol as a solvent. As a first try, the solution utilized consisted of 20 mM Bi(NO₃)₃ salt with 1 M of HNO₃ as an ion transport carrier to increase the conductivity in ethylene glycol. Cyclic voltammograms ranging from 0.1 V to 1 V and -1 V to 1 V vs Ag|AgCl are shown in Figure 12a.

The 0.1 V steps were selected to have an estimation of the anodic peaks with their correspondent and cathodic peak. As it is shown in Figure 12a, the cathodic inversion potentials show dependence between the peaks at 200 mV and -300 mV. The crossover potential between - 200 and 0.0 mV vs Ag|AgCl (KCl_{sat}) shows that the interface is changing. Visual inspection of the FTO electrode confirmed that a layer of Bi with the characteristic dull black colour was formed at potentials below the crossover potential. As the potential reaches -900 mV, there is an anodic peak at -500 mV usually attributed to the formation of a different Bi morphology [54]. The respective cathodic and anodic waves observed at -300 mV and 200 mV are attributed to the reduction of Bi³⁺ to Bi⁰ and its corresponding oxidation. Sweep rates (*r*) on the region of the two firsts peaks appear (900 mV and -500 mV vs Ag/AgCl) were carried out to study the reversibility and have a further insight of the film formation (Figure 10b). The peak to peak difference (Δ V) is 0.062 V which deviates with the expected 0.059 V for chemical and electrochemical reversibility of the 25

Bi/Bi³⁺ redox reaction. The current of the peak (*i*) at -200 mV adjust to an i vs r^{-1/2} plot according Randles-Sevcik equation to with a slight deviation (Figure 12c). The latter indicates that the reduction process of Bi³⁺ is carried out by diffusion from the bulk to the FTO surface [56]. Contrary, the anodic peak at 100 mV barely changes with the sweep rate. As it is observed, the potential of the peak changes with the sweep rate. The peak potential deviation with increasing *r* of the *i* vs $r^{-1/2}$ plot indicates electrochemical quasi-reversibility behaviour [56].

As a first trial, continuous electrodeposition was carried out by applying a potential lower than the crossover potential (200 mV > E_{app}) at different electrodeposition times (30 sec, 1 min, 3 min and 6 min). Although the films seemed stable, uniform and thick in solution, after the electrodeposition, they detached easily from the FTO after being removed from the solution. This observation was attributed to the acidity of the media. For this reason, the electrodeposition was later tested in ethylene glycol using only 20 mM Bi(NO₃)₃.



Figure 12. Cathodic inversion potentials at 100 mV s⁻¹ of 20 mM Bi(NO₃)₂ + 1 M HNO₃ on FTO electrode in ethylene glycol a) and voltammogram of Bi at different sweep rates. C) shows the dependence of the anodic peak current on the $r^{1/2}$

In Figure 13, the cyclic voltammetry of bismuth is presented. The peaks correspondent to Bi^{3+}/Bi^{0} reduction and oxidation are observed as well as the crossover is seen as in the case of the HNO₃ electrolyte solution (Figure 12a and b), confirming the film formation on FTO surface below -250 mV vs Ag/AgCl (KCl_{sat}). As is expected, the peaks are more separated due to the low conductivity and high viscosity of the ethylene glycol solvent and low concentration of Bi(NO₃)₃. Based on the cyclic voltammogram in Figure 13, the parameters for continuous and pulsed electrodeposition of Bi film were selected. The voltammogram showed in Figure 13 served as a footprint of the Bi. Thus, before each electrodeposition, a CV was recorded to corroborate that the

solution was not contaminated and the FTO surface was clean. Tests for electrodeposition were carried out by setting a cathodic potential from -250 mV to -2000 mV vs Ag/AgCl (KCl_{sat}). Since the diffusion is sluggish due to the high resistivity in comparison to the experiments using HNO₃, the electrodeposition times tested were doubled i.e. 1 min, 2 min, 6 min, and 12 min. By visual comparison of both electrodeposition methods, pulsed electrodeposition gave better adherence and more uniform films. The final perturbation program after optimization of parameters consisted of the application of a cathodic potential of -2.0 V and the anodic pulse 0.0 V vs Ag|AgCl (KCl_{sat}). It was noted that BiVO₄ films that were immediately dried after the electrodeposition yielded a more uniform film. After the deposition of Bi, the VO(acac)₂ in DMSO solution was added and then the film was annealed. A light green colour film was observed after the calcination which corresponds to the formation of V₂O₃ [20]. To remove the V₂O₃, the films were immersed in NaOH 0.1 M solution, the green colour disappeared and a yellow colour film was obtained as expected for BiVO₄ [57].



Figure 13. Cathodic inversion potentials of Bi(NO₃)₃ in ethylene glycol on FTO electrode at 100 mVs⁻¹ in ethylene glycol. The numbers at the top of each anodic peak indicates its respective cathodic limit

3.2 BiVO₄ and modified BiVO₄ (e-BiVO₄)

3.2.1 Dynamic polarization modification on BiVO₄

After obtaining BiVO₄ films, they were placed as a working electrode in a three-electrode cell using 0.1 M KClO₄ in an aqueous solution. Dynamic polarization tests were started from the open circuit potential (OCV) to the cathodic limit. Based on the perturbation program of TiO₂, 100 cycles and 100 mV/s were set as a benchmark [40]. In a test applying 50 cycles, the photoresponse of BiVO₄ did not show any change whereas at 200 cycles the photocurrent did not show further improvement. 100 was selected as the optimal number of cycles for the dynamic polarization. For each of the latter tests, a new BiVO₄ film was employed. The dynamic polarization current response during the electrochemical treatment is shown in Figure 14. From the voltammogram, it can be observed that the shape reaches a point where it remains constant when the cycles approach $\frac{29}{29}$

100 cycles. The latter indicates that no further change is occurring, which explains why the photocurrent does not improve when 200 cycles are applied. The voltammogram (Figure 14) suggests that exists a dependence between the anodic peak at -500 mV and the cathodic limit (-1000 mV vs Ag/AgCl KCl_{sat}) since both regions are mostly affected. On the other hand, the region between -300 mV and 0.0 mV vs Ag/AgCl remain practically constant throughout the experiment. Since hydrogen evolution is the cathodic limit, suggestible, the peak at -500 mV may be related to hydrogen desorption. Similar observations related to the hydrogen absorption/desorption process have been reported for the case of palladium [58]. The anodic peak at -500 mV increases with the number of cycles until the current superimposes for subsequent cycles after 100 cycles. The first cycles are not superimposable, indicating that an irreversible change in the material is occurring. This irreversibility may be related to V^{5+}/V^{4+} reduction as it has been suggested that it occurs at about -900 mV [59]. Some of this statements will be discussed in further detail later supported by XPS and spectroscopy results.



Figure 14. BiVO₄ film voltammogram during electrochemical treatment at 100 mV s⁻¹ in 0.1 M KClO₄

3.2.2 Electrochemical/photoelectrochemical evaluation

The electrochemical response of the BiVO₄ was studied under a large range of potentials (Figure 15a. In the region between 1000 and -250 mV, no reaction seems to occur as there are no peaks, this indicates that no change in the material is occurring. As the potential decreases (below -250 mV) the current is not superimposable in the case of pristine BiVO₄. An irreversible process occurs as the material does not go back to its original state. According to the cyclic voltammetry (Figure 15), the reduction current occurring at -900 mV is related to the oxidation peak at -500 mV and the small shoulder at -200 mV. Wenju et al. [59] suggest that the reduction at around -900 mV is due to a reduction occurring in BiVO₄. Thus, further reduction (below -900 mV) can be

attributed to water reduction. The comparison of the BiVO₄ after the electrochemical treatment shows a more superimposable current at potentials below -250 mV (Figure 15b). This suggests that the e-BiVO₄ reached stability since no further changes are occurring. Comparing to the pristine material, the cathodic current at -1000 mV is less and the shoulder at -200 mV seems to disappear. The shape of the voltammogram is narrower and the water reduction potential current at -1000 mV is less in the e-BiVO₄ sample.



Figure 15. Cathodic inversion potentials of BiVO₄ before and after the electrochemical polarization at 100 mV s⁻¹ in 0.1 M KClO₄

Figure 16 shows the cyclic voltammetry for a range between -100 mV and 1000 mV, the potentials most relevant for light response in subsequent experiments. The voltammograms presented are recorded after 100 cycles at 100 mVs⁻¹. Since the voltammograms remain stable, it

is assumed that both materials do not change significantly in this potential window. As shown in Figure 15, the oxidation and reduction waves found around 0 mV and 200 mV vs Ag|AgCl (KCl_{sat}), respectively, are correlated. The signals can be related to trap states (e.g., surface states), showing an asymmetrical kinetic behaviour for the anodic and cathodic response as usually observed for semiconductor materials [60]. The cathodic and anodic waves disappear after the electrochemical treatment (Figure 16). Therefore, these waves can be interpreted as the filling of trap states. A similar response was observed when the electrodes were modified by hydrogen annealing [36]. Notably, the anodic current at 1000 mV is higher for the treated material, indicating that the modified material has better catalytic activity than the pristine material.



Figure 16. Cyclic voltammetry of BiVO₄ before and after the electrochemical polarization at 100 mV $\rm s^{-1}$ in 0.1

M KClO₄

The study of linear polarization current response was carried out from negative to positive values under dark, constant and intermittent light conditions (Figure 17). An increase in photocurrent for the case of the modified BiVO₄ is observed in the whole potential range. Nevertheless, the increase is clearer between 500 and 1000 mV vs Ag|AgCl (KCl_{sat}). At the highest potential, 1000 mV, the modified BiVO₄ has an 80% higher current than the pristine material.

During intermittent light, the modified material has sharp peaks between 0 and 200 mV. These peaks exhibit capacitive behaviour that can be attributed to overshoot currents. These overshoots are due to kinetic limitations when charge accumulates on the surface without driving the oxidation reaction [61], [62]. As higher potential is applied, overshoots disappear since the charges are more easily extracted from the material. The accumulation of charges in the material can be caused by OH species adsorption on the BiVO₄ electrode surface. The latter statement will be discussed later (Section 3.3).



Figure 17. Linear sweep voltammetry from cathodic to anodic potentials at 10 mV s⁻¹ with continuous light, dark and interrupted light of pristine BiVO₄ and e-BiVO₄

To test the stability during long-term operation, the materials were held under light at 1000 mV for 2200s (Figure 18). A similar current value is observed at this potential during the linear polarization experiment (Figure 17). Both materials show a similar decay over time, about 16% after 2200 s, indicating a similar decay process that is independent of the electrochemical modification. This observation suggests that similar processes occur in both versions of the material.



Figure 18. Transient photoresponse of photoanodes applying 1000 mV vs Ag/AgCl (KClsat)

3.2.3 IPCE, Band gap determination and conduction band estimation

The electronic excitation is mostly observed by typical spectroscopic techniques such as diffuse reflectance, absorbance or transmittance spectroscopy. Information about the electron delocalization and charge injection can also be obtained by measuring the current during the light irradiation. Hence, the spectral current measurement provides a correlation between the energy of the photons and the electrons that are not solely excited but also delocalized and transferred. Therefore, the spectral current determination provides more relevant information for photoelectrochemical applications [12]. To study the efficiency of energy conversion, incident photo-electron conversion efficiency (IPCE) measurements were carried out for both materials

(Figure 19a). It is often employed a hole scavenger for IPCE measurements to evaluate catalytic improvement [63]. The hole scavenger increases the IPCE values as it facilitated the charge injection. However, those are not typical conditions for water splitting. For the latter reason in this thesis work, the measures hereby presented were carried out without hole scavenger. This measurement also provides information about kinetics[64]. It takes into account the rate at which the photons reach the surface of the material and the rate at which the electrons that are excited are injected and collected through the external circuit [65]. IPCE was recorded in a three-electrode cell using the BiVO₄ as a working electrode. The illumination of the BiVO₄ film was from the front using the cell schematically shown in Figure 6. As it was shown during the linear and dynamic polarization (Figure 16 and Figure 17), no relevant electron transfer reactions are observed without illumination. Thus, the currents observed when light is irradiated are solely due to the direct photo-oxygen production as water is the only species capable of donating electrons in the medium employed. For the measurement, the current response was recorded when a potential of 500 mV was applied and the current under darkness was subtracted to overcome recombination effects. Pristine BiVO₄ shows a maximum efficiency of approximately 47% (at 450 nm) without the use of a hole scavenger. This is higher than the typical values for $BiVO_4$ obtained as a powder and then deposited, or by continuous electrodeposition [41], [66]. The reason for this behaviour might be explained in terms of the adherence to the FTO substrate, and Bi formation during the pulsed electrodeposition. The influence of the addition of the catalyst has been previously proposed for other photoelectrocatalysts [44], [52]. The IPCE traces (Figure 19a) show similar shapes for both materials with a broad low-intensity peak between 500 to 900 nm and the highest efficiency value in the region between 300 and 500 nm. In both regions, the efficiency increases by ~20% after the electrochemical treatment. Most of the reported post-synthetic methods on

BiVO₄ shows an IPCE enhancement within the region between 300 and 500 nm [29], [30], [35], [41]. Only the Bi₂S₃ nanostructures [67] and WO₃/BiVO₄ heterojunction [28] are the only synthetic treatments that show an increase in IPCE far above 520 nm. The IPCE improvement is compared with other modification methods from the last two decades (Table 1). Three different wavelengths were selected to compare the methodology hereby employed: 375 nm, 400 nm, and 425 nm. The applied potential (E_{app}) at which the IPCE measurement was made is included since it influences the IPCE result [68]. e-BiVO₄ shows a higher maximum IPCE value than the doping modifications at 375 nm and 450 nm. Apart from NiFeOx [68], TiO₂/FeOOH [69], and CoPi [70] catalytic layers, the modified BiVO₄ of this thesis work has one of the highest IPCE values at the wavelengths presented. However, the electrochemical modification was carried out in less steps than the required for adding the catalytic layers. The N₂ annealing process yields a higher IPCE% than e-BiVO₄, nonetheless, the percentage increase (% increase) is higher in the latter. In comparison to H₂ annealing, IPCE values of e-BiVO₄ values are higher in difference (Δ IPCE) and increase. The difference in IPCE (Δ IPCE) and percentage increase (% increase) were taken by comparing the reference materials obtained for each of the cases. The difference in IPCE of e-BiVO₄ is smaller than some of the other methods, but the IPCE of the starting material is among the highest while still showing significant improvement compared to doping, the addition of catalyst layer and annealing with H₂ or N₂.

Overall, compared with other $BiVO_4$ treatments, the maximum IPCE value hereby achieved is one of the highest at 450 nm after the modification. This result indicates that dynamic polarization can potentially replace the aforementioned methods since comparable results are obtained but the process steps are significantly reduced. Moreover, the use of toxic or explosive compounds and higher temperatures-such as the H₂ annealing process- are avoided.

$ \begin{array}{ c c c c c c c } \hline \text{Doping} & 0.6\% \text{ Mo/BiVO4} & 1.2^b & 375 & 16\% & N/A & N/A & 2013 & [32] \\ \hline 400 & 17\% & 450 & 8\% & 450 & 80\% & 2011 & [71] \\ \hline 3\% \text{ Mo-BiVO4} & 0.8^b & 375 & 45\% & 35\% & 350\% & 450 & 450 & 35\% & 350\% & 450 & 450 & 35\% & 350\% & 450 & 450 & 450 & 40\% & 20\% & 80\% & 450 & 40\% & 13\% & 48\% & 450 & 40\% & 13\% & 48\% & 450 & 40\% & 13\% & 48\% & 450 & 40\% & 13\% & 48\% & 450 & 40\% & 13\% & 48\% & 450 & 40\% & 13\% & 48\% & 450 & 40\% & 80\% & 450 & 80\% & 450 & 80\% & 450 & 80\% & 450 & 80\% & 450 & 80\% & 450 & 80\% & 450 & 80\% & 450 & 80\% & 450 & 80\% & 450 & 90\% & 55\% & 157\% & 10\% & 10\% & 2019 & [69] & 400 & 60\% & 40\% & 200\% & 450 & 90\% & 55\% & 157\% & 10\% & 10\% & 2014 & [73] & 60\% & 450 & 90\% & 55\% & 157\% & 10\% & 10\% & 2015 & [70] & 60\% & 450 & 90\% & 450 & 10\% & 2014 & [73] & 10\% & 250\% & 2014 & [74] & 40\% & 52\% & 48\% & 120\% & 450 & 35\% & 31\% & 775\% & 450 & 44\% & 20\% & 450 & 6\% & 44\% & 20\% & 450 & 6\% & 44\% & 20\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 6\% & 450 & 9\% & 2014 & [29] & 400 & 11\% & 8\% & 267\% & 450 & 10\% & 20\% & 450 & 10\% & 20\% & 450 & 10\% & 10\% & 25\% & 2014 & [29] & 400 & 11\% & 8\% & 267\% & 450 & 6\% & 44\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 45\% & 20\% & 2$		Photoanode BiVO4 based material	E $_{app}$ / V $_{SHE}$	λ	% IPCE	∆ IPCE	% increase	year	Ref
$ \begin{array}{ c c c c c } & 400 & 17\% \\ \hline 450 & 8\% \\ \hline 3\% \ Mo- \ BiVO_4 & 0.8^b & 375 & 45\% & 20\% & 80\% \\ \hline 450 & 35\% & 35\% & 35\% \\ \hline 450 & 35\% & 30\% & 600\% \\ \hline 2\% \ W, 6\% \ Mo- \\ BiVO_4 & 1.2^b & 375 & 47\% & 20\% & 74\% \\ \hline 2\% \ W, 6\% \ Mo- \\ BiVO_4 & 1.2^b & 375 & 47\% & 20\% & 74\% \\ \hline 400 & 45\% & 20\% & 80\% \\ \hline 450 & 40\% & 13\% & 48\% \\ \hline 100 & 80\% & 13\% & 48\% \\ \hline 100 & 80\% & 13\% & 48\% \\ \hline 100 & 80\% & 13\% & 48\% \\ \hline 100 & 80\% & 13\% & 12\% & 10\% & 10\% \\ \hline 100 & 60\% & 40\% & 200\% & 10\% & 10\% \\ \hline 100 \ 60\% & 40\% & 200\% & 10\% & 10\% & 10\% & 10\% \\ \hline 100 \ Mov $	Doping	0.6% Mo/BiVO ₄	1.2 ^b	375	16%	N/A	N/A	2013	[32]
$ \begin{array}{ c c c c c c } \hline \\ & 450 & 8\% \\ \hline \\ $				400	17%				
$ \frac{3\% \ {\rm Mo- BiVO_4}}{2\% \ {\rm Mo- BiVO_4}} = 0.8^{\rm h} \\ 375 \ 45\% \ 35\% \ 35\% \ 350\% \ 60\% \ 60\% $				450	8%				
$ \begin{array}{ c c c c c } & 400 & 45\% & 35\% & 35\% & 35\% & 600\% \\ \hline & 450 & 35\% & 30\% & 600\% \\ \hline & 2\% \ W, 6\% \ Mo- \\ Bi VO_4 & 1.2^b & 375 & 47\% & 20\% & 74\% & 2014 & [72] \\ \hline & 400 & 45\% & 20\% & 80\% & 450 & 48\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 40\% & 55\% & 157\% & 45\% & 40\% & 20\% & 450 & 40\% & 20\% & 450 & 60\% & 60\% $		3% Mo- BiVO ₄	0.8 ^b	375	45%	20%	80%	2011	[71]
$ \begin{array}{ c c c c c } \hline \begin{tabular}{ c c c c c c } \hline \begin{tabular}{ c c c c c c c } \hline \begin{tabular}{ c c c c c c c } \hline \begin{tabular}{ c c c c c c c } \hline \begin{tabular}{ c c c c c c c } \hline \begin{tabular}{ c c c c c c c } \hline \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$				400	45%	35%	350%		
$ \frac{2\% \text{ W}, 6\% \text{ Mo-} \\ \text{BiVO}_4}{\text{BiVO}_4} \frac{1.2^b}{400} \frac{375}{45\%} \frac{47\%}{20\%} \frac{20\%}{74\%}{20\%} \frac{2014}{80\%} [72] \\ \frac{400}{45\%} \frac{45\%}{20\%} \frac{20\%}{80\%} \frac{80\%}{450} \frac{45\%}{40\%} \frac{40\%}{13\%} \frac{48\%}{48\%} \frac{100\%}{13\%} \frac{48\%}{10\%} \frac{100\%}{10\%} \frac{10\%}{10\%} \frac{10\%}{10\%}$				450	35%	30%	600%		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		2% W, 6% Mo- BiVO ₄	1.2 ^b	375	47%	20%	74%	2014	[72]
$ \begin{array}{ c c c c c c } \hline \\ Catalytic \\ Layer \\ \hline \\ Catalytic \\ Layer \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $				400	45%	20%	80%		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $				450	40%	13%	48%		
$ \begin{array}{ c c c c c } Layer & 400 & 80\% \\ \hline 450 & 80\% \\ \hline 450 & 80\% \\ \hline BiVO_4 - COPi & 0.8^a & 375 & 45\% & 25\% & 125\% & 2019 & [69] \\ \hline TiO_2 / FeOOH & 0.8^a & 375 & 45\% & 25\% & 157\% \\ \hline MO_2 / FeOOH & 0.6^a & 375 & N/A & N/A & N/A & 2014 & [73] \\ \hline BiVO_4 / FeOOH & 0.6^a & 375 & 90\% & 450 & 60\% \\ \hline MO_3 / BiVO_4 - & 1.2^b & 375 & 90\% & 450 & 90\% \\ \hline MO_3 / BiVO_4 - & 1.2^b & 375 & 90\% & 42\% & 1400\% & 2015 & [70] \\ \hline MO_3 / FeOOH & 0.8^b & 375 & 45\% & 42\% & 1400\% & 2012 & [30] \\ \hline BiVO_4 / FeOOH & 0.8^b & 375 & 45\% & 42\% & 1400\% & 2012 & [30] \\ \hline BiVO_4 / FeOOH & 0.8^b & 375 & 14\% & 10\% & 250\% & 2014 & [29] \\ \hline BiVO_4 / FeOOH & 0.8^b & 375 & 14\% & 10\% & 250\% & 2014 & [29] \\ \hline BiVO_4 / FeOOP & 0.8^b & 375 & 38\% & 33\% & 660\% & 2019 & [74] \\ \hline BiVO_4 - FeCOP & 0.8^b & 375 & 38\% & 33\% & 660\% & 2019 & [74] \\ \hline A00 & 44\% & 39\% & 780\% & 45\% & 40\% & 35\% & 700\% & 45\% & 40\% & 35\% & 700\% \\ \hline \end{array}$	Catalytic	BiVO ₄ /NiFeOx	0.6ª	375	80%	N/A	N/A N/A	2015	[68]
$ \begin{array}{ c c c c c } \hline $450 & 80\% \\ \hline $BiVO_4-$ 0.8^a & $375 & $45\% & $25\% & $125\% & $2019 & [69] \\ $400 & 60\% & $40\% & $200\% \\ \hline $450 & $90\% & $55\% & $157\% \\ \hline $157\% & $1.7\% & 1.2^b & $375 & $N/A & $N/A & $N/A & $N/A & $2014 & [73] \\ $0OH & $450 & 60\% & $157\% & 1.16^b & 1.2^b & 1.12^b & $$	Layer			400	80%				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$				450	80%				
$\begin{array}{c c c c c c c } TiO_{2}/FeOOH & 400 & 60\% & 40\% & 200\% \\ \hline 450 & 90\% & 55\% & 157\% \\ \hline BiVO_{4}/FeOOH/N & 0.6^{a} & 375 & N/A & N/A & N/A & 2014 & [73] \\ \hline 0OH & 400 & 60\% & & & & & & & & & & & & & & & & & & &$		BiVO ₄ -	0.8 ^a	375	45%	25%	125%	2019	[69]
$ \begin{array}{ c c c c c c } \hline \begin{tabular}{ c c c c } \hline & 450 & 90\% & 55\% & 157\% \\ \hline BiVO_4/FeOOH/N & 0.6^a & 375 & N/A & N/A & N/A & 2014 & [73] \\ \hline & 400 & 60\% & & & & & & & & & & & & & & & & & & &$		TiO ₂ /FeOOH		400	60%	40%	200%		
$ \begin{array}{ c c c c c c } \hline BiVO_4/FeOOH/N & 0.6^a & 375 & N/A & N/A & N/A & 2014 & [73] \\ \hline OOH & 400 & 60\% & & & & & & & & & & & & & & & & & & &$				450	90%	55%	157%		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		BiVO4/FeOOH/N iOOH	0.6ª	375	N/A	N/A	N/A	2014	[73]
$ \frac{450 60\%}{WO_3 \ BiVO_4 \ CoPi} 1.2^b 375 90\% N/A N/A 2015 [70] 400 90\% 450 90\% 1400\% 2012 [30] 400 52\% 48\% 1200\% 1400\% 2012 [30] 400 52\% 48\% 1200\% 10\% 250\% 2014 [29] 400 11\% 8\% 267\% 14\% 10\% 250\% 2014 [29] 400 11\% 8\% 267\% 14\% 10\% 250\% 2014 [29] 400 11\% 8\% 267\% 14\% 10\% 250\% 2014 [29] 400 11\% 8\% 267\% 14\% 10\% 250\% 2014 [29] 12\% 11\% 8\% 267\% 14\% 10\% 250\% 2014 [29] 12\% 11\% 10\% 250\% 2014 [29] 12\% 11\% 10\% 250\% 2014 [29] 12\% 11\% 10\% 25\% 14\% 10\% 25\% 10\% $				400	60%				
$ \begin{array}{ c c c c c c } WO_3/ BiVO_4-\\ CoPi & 1.2^b & 375 & 90\% & 400 & 90\% & 400 & 90\% & 400 & 90\% & 400 & 90\% & 400 & 90\% & 400 & 90\% & 450 & 90\% & 4100\% & 2012 & [30] & 400 & 52\% & 48\% & 1200\% & 450 & 35\% & 31\% & 775\% & 45\% & 42\% & 1400\% & 2012 & [30] & 400 & 52\% & 48\% & 1200\% & 450 & 35\% & 31\% & 775\% & 45\% & 41\% & 10\% & 250\% & 2014 & [29] & 400 & 11\% & 8\% & 267\% & 450 & 6\% & 4\% & 200\% & 450 & 6\% & 4\% & 200\% & 450 & 6\% & 4\% & 200\% & 450 & 6\% & 4\% & 200\% & 450 & 6\% & 4\% & 200\% & 450 & 6\% & 4\% & 200\% & 450 & 6\% & 4\% & 200\% & 450 & 6\% & 4\% & 200\% & 450 & 40\% & 35\% & 780\% & 450 & 40\% & 35\% & 700\% & 40$				450	60%				
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		WO ₃ / BiVO ₄ - CoPi	1.2 ^b	375	90%	N/A	N/A	2015	[70]
$ \begin{array}{ c c c c c c } \hline $450 & 90\%$ \\ \hline $BiVO_4/FeOOH & 0.8^b$ & $375 & 45% & 42% & 1400% & 2012 [30] \\ \hline $400 & 52% & 48% & 1200% \\ \hline $450 & 35% & 31% & 775% \\ \hline $BiVO_4/TiO_2$ & 1.2^b & 375 & 14% & 10% & 250% & 2014 [29] \\ \hline $450 & 6% & 4% & 200% \\ \hline $BiVO_4-FeCoP$ & 0.8^b & 375 & 38% & 33% & 660% & 2019 [74] \\ \hline $400 & 44% & 39% & 780% \\ \hline $450 & 40% & 35% & 700% \\ \hline \end{tabular}$				400	90%				
$ \begin{array}{ c c c c c c c } BiVO_4/FeOOH & 0.8^b & 375 & 45\% & 42\% & 1400\% & 2012 & [30] \\ \hline 400 & 52\% & 48\% & 1200\% \\ \hline 450 & 35\% & 31\% & 775\% \\ \hline BiVO_4/TiO_2 & 1.2^b & 375 & 14\% & 10\% & 250\% & 2014 & [29] \\ \hline 400 & 11\% & 8\% & 267\% & \\ \hline 450 & 6\% & 4\% & 200\% & \\ \hline BiVO_4-FeCoP & 0.8^b & 375 & 38\% & 33\% & 660\% & 2019 & [74] \\ \hline 400 & 44\% & 39\% & 780\% & \\ \hline 450 & 40\% & 35\% & 700\% & \\ \hline \end{array} $				450	90%				
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		BiVO ₄ /FeOOH	0.8 ^b	375	45%	42%	1400%	2012	[30]
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$				400	52%	48%	1200%		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$				450	35%	31%	775%		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		BiVO ₄ /TiO ₂	1.2 ^b	375	14%	10%	250%	2014	[29]
$ \begin{array}{ c c c c c c c c } \hline & 450 & 6\% & 4\% & 200\% \\ \hline & BiVO_4-FeCoP & 0.8^b & 375 & 38\% & 33\% & 660\% & 2019 & [74] \\ \hline & 400 & 44\% & 39\% & 780\% & \\ \hline & 450 & 40\% & 35\% & 700\% & \end{array} $				400	11%	8%	267%		
BiVO ₄ -FeCoP 0.8 ^b 375 38% 33% 660% 2019 [74] 400 44% 39% 780% 450 40% 35% 700% 100%				450	6%	4%	200%		
40044%39%780%45040%35%700%		BiVO ₄ -FeCoP	0.8 ^b	375	38%	33%	660%	2019	[74]
450 40% 35% 700%				400	44%	39%	780%		
				450	40%	35%	700%		

Table 1. Comparison of BiVO₄ improvements in terms of IPCE at 365, 400 and 450 nm. a=hole scavenger is

used, b=it is not used

	Photoanode BiVO4 based material	E app / VSHE	λ	% IPCE	Δ ΙΡϹΕ	% increase	year	Ref
Catalytic	BiVO ₄ -Ag ₂ PO ₄	0.8 ^b	375	38%	32%	582%	2018	[75]
Layer			400	35%	30%	600%		
			450	30%	27%	900%		
	CoAl-LDH- BiVO ₄	N/A ^b	375	43%	25%	139%	2018	[76]
			400	37%	28%	311%		
			450	23%	10%	77%		
	3-Fe ₂ O ₃ / BiVO ₄	0.8 ^b	375	27%	9%	50%	2017	[77]
			400	27%	18%	196%		
			450	27%	22%	391%		
	Bi ₂ S ₃ / BiVO ₄	-0.2 ^b	375	20%	8%	67%	2015	[67]
			400	18%	6%	50%		
			450	16%	6%	60%		
	WO ₃ / BiVO ₄	0.8 ^b	375	25%	18%	257%	2017	[28]
			400	25%	20%	400%		
			450	23%	18%	360%		
H_2 and N_2 annealing	N ₂ - BiVO4/FeOOH/N iOOH	0.6^{a}	375	56%	2%	4%	2015	[78]
			400	60%	12%	25%		
			450	60%	5%	9%		
	H- BiVO ₄	1.2 ^b	375	33%	30%	1200%	2013	[38]
	300 °C		400	33%	30%	1200%		
			450	20%	18%	700%		
Electroche	Continuous polarization	0.15 _b	375	25%	20%	400%	2017	[41]
mical modificati ons			400	18%	14%	350%		
			450	30%	27%	900%		
	Dynamic polarization e-BiVO ₄	0.7 ^b	375	51%	13%	34%	2020	This thesis work
			400	38%	18%	90%		
			450	57%	20%	54%		

Table 1. (continued)

Similarly to the IPCE measurement, the photocurrent (j_{PH}) of irradiated BiVO₄ is recorded at different wavelengths. Nevertheless, a mathematical equation is applied to the photocurrent value measured to obtained the Tauc plot (for more details see Chapter 3). According to Tauc, the band gap energy can be obtained by the extrapolation of the linear region from the plot of the square of the current response multiplied by the energy of the photons vs the energy of the photons. The factor 2 indicates a direct electronic transition, which is the type of transition that is carried out by the BiVO₄ [79]. It is assumed that the same transition occurs for e-BiVO₄. This direct transition means that no phonon assistance is required for the electrons to be promoted from the valence to the conduction band. The Tauc plot is shown in Figure 19b where it can be seen that both pristine and modified BiVO₄ materials require the same amount of energy to promote electrons from the valence to conduction band around 2.5 eV = 496 nm (blue)). The same spectral pattern is observed for both photoelectrodes, indicating that the same type of electronic transition occurs.

The broad absorption between 350 and 500 nm is in agreement with UV-vis absorption and diffuse spectra according to refs [20], [80] and shown in Figure 20. The band gap value is given mainly due to non-bonding O 2p valence band orbitals to V 3d electron transfer which is the onset of the spectrum (Figure 19c) [81]. A broad absorption and a small peak at 1.25 and 2.5 eV is observed in other BiVO₄ UV-vis spectra [82]. As observed in the polarization curves under dark conditions (Figure 17), no significant reactions are occurring at 500 mV vs Ag/AgCl (KCl_{sat}). Therefore, only water oxidation is occurring in the near-infrared region of light (above 500 nm).

The absorption in this energy region is attributed to d-d transitions of V ions in the absorbance spectra of BiVO₄ according to Jason et al. [37]. Higher values of absorption in this

region are also observed in the absorbance spectra (Figure 20) for the e-BiVO₄ case. The increase in absorbance (Figure 20) and photocurrent measurements (Figure 19 a and b) around 1.5 eV indicates that excited states correspondent to V d-d transitions are delocalized (Figure 19c). These excited states are also contributing to the oxygen evolution reaction under irradiation (Figure 17). This result is likely to have also an impact on the solar to hydrogen efficiency as it will be shown below.



Figure 19. Incident Photon-to-electron Efficiency (IPCE) a) and Tauc plot b) comparing between pristine (BiVO₄) and modified (e-BiVO₄) materials measured at a constant *E*_{app}=500 mV vs Ag|AgCl (KCl_{sat}) under 0.1 M KClO₄. c) density of states diagram representing the band gap electronic transition and the transitions attributed solely between vanadium species



Figure 20. Absorbance spectra of BiVO₄ films before and after the electrochemical modification (e-BiVO₄)

The conduction band for both materials was determined in a three-electrode cell without irradiation. The experiment consisted of measuring the capacitance of the space-charge region of the photoanodes at different potentials and plotting the inverse of the square of this value as a function of the potential at different frequencies. According to the Mott-Schottky equation, the flat band potential can be found by extrapolation (as shown in Eq. 9) and explained in the experimental section). This value can be approximated to the conduction band energy level [83]. Different values of the flat band potential are obtained depending on the frequency [84]. An example of this is shown in Figure 21a for the case of the pristine BiVO₄. For simplicity, only a few frequencies are shown, nevertheless, the scan was made from 1 to 10 000 Hz. Since many processes can influence 44

the flat band determination (such as surface states) and they can be observed at different frequencies, it is necessary to determine the region in which the flat band is independent of the frequency. The region in which the flat band is independent of the frequency can be estimated by plotting the potential values vs the logarithm of the frequency, as shown in Figure 21b for both photoelectrodes. An average potential of the flat band was measured in the frequency-independent region at $0.443 \pm 4x10^{-3}$ V and $0.3211 \pm 7x10^{-4}$ V for the pristine and modified BiVO₄, respectively. The flat band potential decrease indicates an increase in electron energy. The postsynthetic method by hydrogen annealing also increases the flat band potential [36].

A comparison of the slope at one single frequency is shown in Figure 21c. By taking the slope of the linear region, the carrier density (N_D) is obtained according to Equation 9 [83]. The N_D obtained for BiVO₄ was 5.78x10³⁰ cm⁻³ and 2.31x10³¹ cm⁻³ for e-BiVO₄. This confirms that the electrochemical treatment is increasing the charge carrier density similar to the hydrogen annealing post-synthetic treatment [37]. Therefore, from the band gap value and conduction band estimation, it can be concluded that both valence and conduction bands have higher energy levels, but the energy required for this electronic transition is the same. The latter will have an impact in the unassisted water splitting test when the materials are coupled with CuO as it will be shown below.



Figure 21. a) Inverse of the square of the space-charge capacitance (*C*_s) at different frequencies over a range of potentials of BiVO₄ film on FTO. b) flat-band potential of BiVO₄ and eBiVO₄ comparison as a function of the logarithm of the frequency determined plot. c) Inverse of the square of *C*_s vs Potential comparison of both materials at 10 Hz. Flat band potential as a function of the logarithm of the frequency

3.2.4 Electrolyte study

The influence of the electrolyte on the photoelectrochemical response was studied under $0.1 \text{ K}_2\text{SO}_4$ and $0.1 \text{ N}a_2\text{SO}_4$ electrolytes. For each of these tests, a new BiVO₄ film was synthesized. As shown in Figure 22, no significant difference in performance was observed on pristine BiVO₄ light to current response with both K₂SO₄ and Na₂SO₄ electrolytes.



Figure 22. Polarization curves of BiVO₄ in dark, under light irradiation and interrupted light using 0.1M

K₂SO₄ and 0.1M Na₂SO₄ electrolytes recorded at 10 mV s⁻¹

Cyclic voltammetry of BiVO₄ was carried out to investigate the influence of the electrolyte on electrochemical response. The comparison at a large window potential of 0.1M Na₂SO₄ and 0.1M K₂SO₄ is shown in Figure 23. For the experiments the anodic limit was maintained at 1000 mV vs Ag|AgCl (KCl_{sat}) and the cathodic limit was varied in steps starting from -10 mV up to -1000 mV. The last cycle was repeated once for each test. Both responses in Na₂SO₄ and K₂SO₄ have an anodic peak at around -500 mV which is related to the reduction occurring at the cathodic limit. Since the same signal is observed with the case of 1M KClO₄ (Figure 23), meaning that there is electrolyte independence, it is concluded that this feature is a change of the BiVO₄. Similar observations were made by Wenjun et al [59]. For the K₂SO₄ case, there is an additional peak at 0.0 mV related to the cathodic limit when very low cathodic potentials were used. The reduction is about double for the case of Na₂SO₄ as compared to K₂SO₄. This observation seems to be related to a suppression of the water reduction process since an additional process seemed to be occurring at -700 mV as a wave is observed for the Na₂SO₄ case. All the scans are superimposable until - 500 mV scans are reached, indicating an irreversible change at the electrode approximately at this potential. Therefore, it is concluded that the use of sodium cation favours the reduction of water whereas by using potassium (as in K_2SO_4 and $KClO_4$), there is a combination of electrode changes with water reduction.



Figure 23. Cathodic inversion potentials at 100 mV·s⁻¹ of pristine BiVO₄ using different electrolytes A CV between -100 mV and 1000 mV of the BiVO₄ film was recorded after one cycle of dynamic polarization between 0.0 and -1.0 V in K₂SO₄ and Na₂SO₄ (Figure 24). As it is observed, there is a suppression of the peaks at around -200 mV. The suppression of these peaks is related to

the filling of trap states [60]. Since the hydrogen evolution is less in Na_2SO_4 , the signals can be therefore due to a change in the electronic structure solely on the BiVO₄ electrode. The decrease in the K_2SO_4 signals is less remarkable than the case of Na_2SO_4 and KClO₄, indicating a higher concentration of filled states.



Figure 24. Cyclic voltammetry of BiVO₄ at 100 mV s⁻¹ before and after electrochemical treatment using different electrolytes

3.2.5 Physical-chemical characterization (SEM, XPS, XRD)

Scanning electron microscopy images from BiVO₄ are shown in Figure 25a. The image shows a surface of columnar shapes agglomerated and evenly distributed along the FTO surface.

The morphology obtained for the pristine BiVO₄ is similar to what is observed by other electrochemical electrodepositions where a BiOI film precursor is formed before the VO(acac)₂ addition [32], [33]. The morphology obtained is attributed to the use of pulsed electrodeposition according to the parameters established in the previous section. However, the BiVO₄ hereby obtained is a slightly more agglomerated material with smaller structures (less than 500 nm) compared to previously reported methods (around 2 μ m) [32], [33]. Unlike flat surfaces, nanostructures allows light scattering, increasing the penetration and enhancing photoinduced charges [73]. The shape of the columnar structures seems unaltered after the modification, although an irregular surface is observed (Figure 25b). The irregularity on the surface helps the electrolyte to penetrate the material [12], which may have a favourable impact on mass transport and ion conductivity. Some studies report that by having high-surface-area nanopourus BiVO₄ [73]. Here, both materials show enough porosity for the light to be scattered and improving the photoelectrochemical performance [85].

Although it is out of the scope of this work, an important aspect to be considered in the synthesis of BiVO₄, is the optimization of the film thickness. This parameter can be controlled by optimizing the electrodeposition time (Section 2.2). Some reports suggest that the optimal thickness is less than 200 nm [31], [86], [87]. However, this value results in low absorption in the visible region of light. In contrast, thick films imply a larger diffusion of photogenerated charges which is prone to recombination [73].

Other parameters that could be optimized include the morphology of the film. The cathodic potential and the time of the pulse influence the nucleation centers formed on the substrate yielding a variety of morphologies [19]. The anodic pulse employed in this work was intended to relax the interface. However, by applying an anodic potential above the oxidation peak, unstable nucleation

centers oxidize and redissolve, leaving only the most stable and uniform nucleation centers distributed on the substrate. This process could lead to a more defined structured film [88].



Figure 25. Top-view SEM images of the: a) pristine BiVO₄ and b) electrochemically treated BiVO₄

To identify the original composition and the changes after the treatment, high-resolution XPS was conducted on Bi, V and O ions for BiVO₄ photoanodes (Figure 26). Spin-orbit coupling of V $2p_{3/2}$ and $2p_{1/2}$, Bi $4f_{7/2}$ and $4f_{5/2}$ peaks and the O 1s signal were found in both samples. The identification of the signals was made according to other reports [26], [89], [90]. The presence of Bi³⁺ was confirmed by the $4f_{7/2}$ and $4f_{5/2}$ signals of the pristine sample that were located at 158.9 eV and 164.2 eV, respectively. Similar to the results presented using other electrochemical [89] and non-electrochemical BiVO₄ synthesis methods [91], [92]. Wang et al. observed that both Bi³⁺ signals are shifted to lower energies by applying a constant cathodic potential [41] and argued that the shifting towards lower energies is due to the partial reduction of Bi³⁺ and V⁵⁺[41]. The dynamic polarization performed in this work shifted both signals to higher energies after the treatment by 0.1 eV. According to other reports on Bi₂MoO [93] and BiPO₄ [94], the shifting of Bi to higher energies can be explained by the existence of oxygen vacancies.

Duan also observed that for the case of V^{5+} in BiVO₄ for chain-like structures, the original signals of 2p_{3/2} at 516.6 eV and 2p_{1/2} at 524.2 eV can also be found at higher energies due to the presence of oxygen vacancies [23], [31]. Three O 1s peaks associated with oxygen O²⁻ were adjusted to the measured XPS signal for both samples. The peak at 529.8 eV assigned to oxygen in the lattice (O_L) is a similar type of peak and value found by other authors [23], [89], [95]. A peak at 531.4 eV (O_H) is close in energy to what corresponds to vacancies and defects of oxygen [95]. This signal has also been assigned to OH groups bonded to the metal cations [35]. The peak at 531.4 eV could represent the oxygen-vanadium interaction. Aadesh et al. observed the same value and attributed this signal to an increased density of hydroxyl groups on the surface after hydrogenation of BiVO₄ [96].

Finally, the peak at 532.4 eV (O_c) could be assigned to be chemisorbed, dissociated or adsorbed oxygen species [23] such as water or the formation of hydroxyl groups on the surface. After the electrochemical treatment, the relative intensity of the peak at 529.8 eV (O_L) changes with respect to the other two. This change might be an indication of the consumption of O from the lattice (O_L). The previous statement can be observed from the relative intensity of the Bi 4f signal and the V 2p signals, compared to the O 1s at 529.8 eV. The relative intensities of O_v and O_c signals increase, indicating an increase in oxygen vacancies and availability of the OH groups adsorbed at the surface after the treatment. The OH adsorption is also observed to increase for the case of the electrochemical treatment by dynamic polarization of TiO₂ [40]. It has been shown [97] that the insertion or formation of OH within the lattice can occur at a controlled potential which is likely to be occurring in this case. The adsorption and formation of OH by the insertion of H can be further supported by the observed electrochemical response as will be shown later. The existence of the three peaks observed on O 1s XPS spectra in addition to the shift of Bi³⁺ and V⁵⁺ signals towards higher energies may also confirm the presence and increase in the concentration of oxygen vacancies at the surface of the modified material after the electrochemical treatment [23], [80].



Figure 26. High-resolution XPS spectra of both materials: c) V 2p, d) Bi 4f, and e) O 1s

The crystal structure of BiVO₄ is highly dependent on the synthesis method and conditions employed [80]. The BiVO₄ peaks observed in the diffractograms (Figure 27) can be assigned mainly to monoclinic (JCPDS 75 – 1867, space group I2/b) phase according to the reflection planes (011), (112), (004), (202), (204) and (024). This suggests that the preparation method by pulsed electrodeposition is selective to this phase. FTO substrate corresponding peaks to SnO₂ tetragonal phase are present (JCPDS 77 – 0452, space group P42/mnm). The SEM images show complete coverage of FTO with BiVO₄ which means that the XRD beam passes through the BIVO₄ to reach the FTO suggesting a thin film.

e-BiVO₄ presents similar peaks as the pristine BiVO₄, but with less intensity indicating a loss in crystallinity possibly caused by an increase in defects of the lattice (Figure 27) [98], [99]. The peaks at 18.5°, 35°, and 46° for e-BiVO₄ present more peaks than for the pristine BiVO₄. Tokunaga et al. reported these peaks when studying synthesis conditions and their effect in crystalline phases of BiVO₄ [80]. The splitting of the peaks is attributed to a change in the monoclinic and tetragonal scheelite phases, where the non-split peaks correspond to the monoclinic phase and peak splitting corresponds to the tetragonal phase [26], [80], [100]. It is observed a slight contribution of the tetragonal phase present after the dynamic polarization [100]. Although it is known that the monoclinic BiVO₄ phase has greater photocatalytic activity towards O₂ production performance [80], the small presence of tetragonal phase in e-BiVO₄ is insignificant for photoelectrochemical purposes as the photoelectrochemical results showed (Figure 17). The insignificant changes in lattice structure suggest the stability of the crystalline phase under the studied conditions It is worth to mention that the same monoclinic structure can be obtained by other electrochemical methods, but these processes imply the use of more steps and reagents during the process [80]. Thus, the pulsed electrodeposition hereby employed may be an option for avoiding the aforementioned additional steps, making the synthesis process of this BiVO₄ photoanode for oxygen evolution more sustainable.



Figure 27. XRD patterns of BiVO₄ and e-BiVO₄. Monoclinic phase of BiVO₄ (m - BiVO₄) (JCPDS 75 – 1867) and tetragonal SnO₂ (JCPDS 77 - 0452) from the FTO substrate

3.3 Discussion about the BiVO₄ modification

Intrinsically, oxygen vacancies are defects in the curse of BiVO₄ synthesis during the annealing process [37]. Consequently, oxygen absence leads to an electron transfer. The receptor of the electrons left by the oxygen is the adjacent vanadium in the form of V^{4+} [101]. This process is responsible for the n-type semiconductor character of the BiVO₄ as the V⁴⁺ acts as a shallow donor [102], [103].

The vanadate reduction reported by Wenjun et al. [59] was around -900 mV. The voltammogram in Figure 14 suggests that the hydrogen evolution is occurring at the same time as the vanadium reduction since both processes are within the same potential window during the dynamic polarization. Hence, the formation of hydrogen, its absorption and insertion are feasible. The concentration increase of V⁴⁺ is supported by IPCE results (Figure 19) and absorbance measurements (Figure 20) where the absorption in the visible region is increased for the case of e-BiVO₄.

It is suggested that the number of defects due to oxygen vacancies increase and therefore V^{4+} formation enhances the carrier density, thus improving the charge-separation efficiency (η_{sep}) and charge-transfer efficiency (η_{trans}) [102]. However, recent spectroscopic and electrochemical studies demonstrate that these oxygen vacancies do not have direct catalytic activity towards water oxidation [101]. On the contrary, the electrons that lie on the V⁴⁺ occupied sub-band recombine with the holes photogenerated on the valence band. Therefore, there are fewer holes available as receptors of H₂O electrons to form oxygen.

Hydrogen insertion can be accompanied by the formation of OH groups as has been previously reported by other methods [37] within the bulk of the electrode. It is proposed that hydrogen loading leads to improved photoresponse by filling the electronic traps, leading to an increase in carrier diffusion length [97] and decreasing the space-layer length (*Wsc*) (Figure 21). Furthermore, the filling of the electronic traps is also supported by cyclic voltammetry (Figure 16), where small peaks at around 100 mV and 200 mV disappear during treatment. Moreover, hydrogen insertion provides higher carrier density [37], which is observed in the Mott-Schottky experiments (Figure 21c). The filling of the interband trap states and its consequence is schematically represented in Figure 28.
In conclusion, during the dynamic polarization, the hydrogen is introduced forming OH as shown in XPS (Figure 26) until no further reachable oxygen in the lattice (O_L) is left, leading to no change in the current. Consequently, the hydrogen insertion provokes a rearrangement of the Bi and V ions that leads to a slight change in the lattice structure (Figure 27).



Figure 28. Band diagram of BiVO₄ before and after the treatment. The trap states on BiVO₄ serve as recombination centers, thus there are fewer h^+ available for water reduction. When the states are filled by either hydrogen insertion, the trap states are filled and performance is increased

3.4 Copper oxide photocathode: synthesis and characterization

Prior to the electrodeposition of copper on FTO, cyclic voltammetry was recorded to identify the respective anodic and cathodic peaks. Figure 29 shows the voltammogram of copper where the reduction peak is observed at -250 mV and the oxidation peak at 100 mV. Since Cu^{2+} is in solution, the deposition is a two-electron process. The crossover at around 0.0 mV indicates the change in the surface due to the formation of the copper film on the FTO surface. Before each 57

electrodeposition, a cyclic voltammetry was recorded to make sure that the FTO surface was properly clean.



Figure 29. Cyclic voltammogram of 5 mM CuSO₄ in aqueous solution on FTO electrode at 100 mVs⁻¹

After the calcination of the copper film at 400 °C for 1 h, CuO was obtained. Cu_xS has similar properties to CuO to be used as a photocathode and it has been used for water splitting [104]. Moreover, recently it was shown reported an improvement in efficiency and stability by adding a TiO₂ film [44]. Thus, a Cu_xS and Cu_xS/TiO₂ were synthesized and tested (for details of the synthesis, see Chapter 3). The photocathodes were tested in a three-electrode cell as shown in Figure 6. Contrary to the BiVO₄ photoanodes, the photocathodes were irradiated from the back. The linear sweep voltammetry in Figure 30 shows the comparison between the three photocathodes under interrupted light. The photocurrent is more negative as the light is irradiated as it is characteristic of photocathodes. Cu_xS shows higher photocurrents in the interval of 0.0 to -450 mV, whereas the CuO photocurrent is higher above -450 mV. The Cu_xS/TiO₂ photocathode barely shows photocurrent which is likely due to the thickness of the TiO_2 film. The TiO_2 might be blocking the light or sluggish the electrons excited of Cu_xS . The CuO was further characterized and used for the STH test because the Cu_xS was decomposed after a few linear sweep voltammetries. On the other hand, CuO showed more stability.



Figure 30. Linear sweep voltammetry from positive to negative potentials at 10 mVs⁻¹ under 0.1 M KClO₄ and interrumpted light of different photocathodes

The formation of CuO was confirmed by XPS (Figure 31a and b). From the Cu 2p XPS (Figure 31a), the peaks at 953.4 eV and 933.5 corresponds to Cu $2p_{1/2}$ and Cu $2p_{3/2}$, respectively [105]. The two satellites at 963 and ~942 eV are characteristic of the Cu²⁺ oxidation state [106]. The XPS of oxygen O 1s in Figure 31b shows a peak at 529.7 eV that has been reported in CuO

[106]. The peak at 531.7 eV has not been identified. The SEM (Figure 31c) shows a total coverage of CuO film on FTO. The morphology of the film observed is similar to other reports [107].



Figure 31. High-resolution XPS spectra of a) Cu 2p, b) O 1s and SEM c) of CuO film

The space charge capacitance was determined through electrochemical impedance spectroscopy in a three-electrode cell using the CuO as a working electrode under dark conditions. The Mott-Schottky plots of CuO are shown in Figure 32a. It is observed a straight line with a negative slope between 25 and 100 mV. The negative slope is characteristic of p-type semiconductors near the flat band value. By extrapolating the straight line to the x-axis, the flat band (E_f) is estimated at each frequency. The E_f as a function of the frequency is plotted in Figure 32b. From the region where the flat band value is independent of the frequencies (around 1 to 10

Hz) the conduction band value was estimated by taking the average. The averaged valence band value obtained was 0.1 V vs Ag/AgCl (-4.1 eV). This value will be relevant later for the photoelectrochemical water splitting as it will be shown.



Figure 32. CuO film on FTO Mott-Schottky plot for the flat-band determination Flat band values as a function of the frequency for CuO film on FTO sample

IPCE of CuO photocathode was recorded in a cell as shown in Figure 6 irradiating from the front. Figure 33 shows an IPCE value above 100% below 500 nm likely due to a side reaction involving the copper reduction that was occurring at the potential employed for the measurement. There is a current response above 500 nm which corresponds to the visible region of light. The absorption of the light in the visible region is also confirmed by the band gap estimated by the Tauc plot (Figure 33) which yields a value of 1.7 eV close to what has been reported previously [108].



Figure 33. IPCE a) and Tauc plot b) of CuO film measured under 0.1 M KClO₄ at -0.25 mV irradiating from the back of the film

3.5 Unassisted photoelectrochemical water splitting

With the information gathered from the individual evaluation of the BiVO₄ photoanode, CuO, Cu_xS and Cu_xS/TiO₂ photocathodes a band diagram was constructed (Figure 34). Cu_xS and Cu_xS/TiO₂ photocathodes band gap and valence band were determined in the same fashion as CuO (Section 3.4). BiVO₄ undergoes a band shifting to higher energies without changing its band gap value after the modification (e-BiVO₄). This shifting allows a better overlap of the conduction band of e-BiVO₄ and CuO valence band. This overlap band between the photoanode and the photocathode, reducing the energy required to transfer the electrons from the photoanode to the photocathode. For this reason among the synthesized photocathodes, CuO is, thermodynamically, the best candidate to be used in a photoelectrochemical cell. However, Cu_xS and Cu_xS/TiO₂ have a narrower band gap. In the latter case, since its conduction band is in higher energy, it is thermodynamically more feasible for it to reduce water.



Figure 34. Band diagrams of BiVO4 materials and Cu based materials photocathodes

The cell used for testing the photoelectrodes for photoelectrochemical water splitting was previously described in the experimental section and Figure 11. Figure 35 shows the current response of the system when Xe light was irradiated. The current observed is due to the electrons that pass from the BiVO₄ or e-BiVO₄ photoanodes to the CuO photocathode. For this experiment, during the first 600 seconds, the light was intermittent on the surface for intervals of 5 seconds. The inset plots show that the current turns back to the original value before and after the sample is irradiated, indicating stability and fast kinetics. Capacitive currents are observed in both cases; nevertheless, it is higher in the photoelectrochemical cell composed by e-BiVO₄/CuO. As it was observed in the linear polarization under interrupted light (Figure 17), this behaviour is more prominent in the region of -100 mV to 200 mV of the modified BiVO₄, which is the actual potential region where the PEC is operating. Aforementioned, the high capacitive current under irradiation

is likely due to the accumulation of charge on the surface. After the chopped light response, the light was maintained constant for the remaining time. In both cases, the current remains stable for 2700 s. The increase in photocurrent with the modified material can be attributed to the higher kinetic performance shown in the IPCE measurements (Figure 19) and the straddling of the conduction band of e-BiVO₄ with the CuO valence band as shown in Figure 34. With the maximum current, the solar to hydrogen efficiency (STH) was estimated using Eq. (12) by assuming no parasitic reactions (faradaic efficiency of 100%). Hence, for the cell made from the modified BiVO₄ and CuO, the STH calculated is $0.013 \pm 0.01\%$ and for the pristine BiVO₄ and CuO a value of $0.0098 \pm 0.0014\%$. It is, therefore, demonstrated that the BiVO₄ improvement is retained when it is used in a photoelectrochemical cell.



Figure 35. Transient photoresponse of photoelectrochemical cell at $E_{app}=0.0$ V vs photoanode of BiVO₄ as photoanode and CuO as photocathode a) and e-BiVO₄ as photoanode and CuO as photocathode. From t = 60 s to t=690 s the light was chopped in intervals of 5 s. After t=750 s the light was irradiating continuously until t=2500 s

Solar-to-hydrogen hereby presented was achieved by using earth abundand materials in both anode and cathode sides and a home-made photoelectrochemical cell. Even though STH values were low, unassisted water splitting is not a simple task and has not to be achieved by many research groups. Table 2 shows some examples of bismuth-based materials from recent literature where STH was directly measured or theoretically estimated. By simple inspection, it is clear that some of the photoelectrodes -either anode or cathode- employed are expensive (as IrO_x/ZnO [109]) or implied the use of several layers which increases its complexity (Pt/P3HT/PEDOT [110]). Some of the examples, make use of applied potential (ref [110] and [111]) which implies the use of a more complex cell. It has to be considered also that, the STH evaluations presented in Table 2 were carried out under a solar simulator. The latter means that the contribution of photons of 350 and 750 nm (visible region) is higher than in the case of the Xe light used in this work. By using a solar simulator, the STH obtained in this thesis work could be yield higher since BiVO4 and CuO absorbs mostly in the 350 and 750 nm region.

Anode	Cathode	Efficiency	year	Ref	
		(STH) %			
FeOOH/TiO ₂ /BiVO ₄	Cu ₂ O	0.46	2019	[69]	
IrO _x /ZnO	Pt/P3HT/PEDOT	0.12	2017	[109]	
BiVO ₄	CuBi ₂ O ₄	0.04	2019	[51]	
W-doped BiVO ₄ /Bi ₄ V ₂ O	BiVO4/Bi4V2O/Pt	0.95	2018	[87]	
W:BiVO ₄ -Co	Au/Cu ₂ O/AlZnO/T iO ₂ /RuO	0.5	2015	[112]	
AlGaAs/Si	RuO ₂ /Pt	21.2	2000	[113]	
FeOOH/Mo:BiVO ₄	Si-cell/Ni	2.5	2014	[50]	
NiFeOx/B- C ₃ N ₄ /Mo-BiVO ₄	Pt/P3HT/PEDOT	2.67 @ 0.54 V	2019	[110]	
Mo:BiVO ₄ /Fe(Ni)O OH	Pt	6.2 @ 1.23 V	2016	[111]	

Table 2. Solar-To-Hydrogen (STH) efficiency from recent literature

In this work, the conditions used for water splitting were mild (room temperature, pressure, and neutral pH). Previous studies show that there is little difference in the efficiency of water oxidation on BiVO₄ when the pH is varied between 4 and 10 [86], [114]. Appreciable currents and

improvement in the performance are observed at neutral pH (Figure 17 and Figure 19). However, the position of the bands is influenced by the pH value [115], [116]. The latter observation needs to be considered if further modifications are intended on e-BiVO₄ (e.g., the addition of FeOOH or CoPi catalysts). [117] Furthermore, this would also influence the overlap of bands with CuO. This thesis was focused on the improvement after the synthesis of BiVO₄. However, optimizing other parameters prior to the electrochemical treatment, i.e. during the synthesis, such as film

thickness and morphology (as mentioned in 3.2.5) could yield improved performance.

A comparison of unassisted water splitting hereby presented with a photovoltaic (PV) + electrolysis system is illustrated schematically in Figure 36. Silicium solar cells have an efficiency (η_{PV}) in the 14-19% range [3] and water electrolysis units have energy efficiencies of about (η_E) 60-80% [5]. The efficiency of the combined PV+electrolyzer system using commercially available components is close to 12% ($\eta_T=\eta_{PV*}\eta_E$). The latter value is consistent with more a thorough analysis carried out by Bilgen (ref [118]). The efficiency value of hydrogen stored for the case of the PEC cell is directly $\eta_{T=\eta_{PEC}}$. Therefore, there are no efficiency loosses. Nevertheless, the efficiency obtained in this work ($\eta_{PEC} = 0.013$ %) is far below the PV+electrolysis system. Notably, the photoelectrochemical cell assembly presented in this work is still far from being relevant to high-scale hydrogen production. However, the unassisted photoelectrochemical experiment presented here demonstrates the concept. Only a few attempts have achieved water splitting with earth-abundant materials (see Table 2). Moreover, very few reports have demonstrated the photoanode improvement compared to pristine materials. We submit that the next logical step for the present work could include the proper design and manufacture of an improved photoelectrochemical cell, which could highly increase the STH.

In 1995, Allen Bard proposed an STH of 10% as the ultimate goal in photoelectrochemistry [119]. While the research outcomes presented here are is still far from this value, the proposed electrochemical modifications yielded a significant improvement from work reported previously.



Figure 36. Comparison between the photoelectrochemical cell presented in this work with photovoltaic (PV)+Electrolysis process for hydrogen production

Chapter 4: Conclusions

The modified BiVO₄ photoanode exhibited higher performance in the oxygen evolution reaction under irradiation than pristine BiVO₄. This improvement was achieved through a dynamic polarization as a post-synthetic technique on the BiVO₄ photoanode. The increase in photocurrent is notable in a range of potentials tested from -0.1 and 1.0 vs Ag/AgCl (KCl_{sat}). The highest improvement was observed at 1.0 vs Ag/AgCl (KCl_{sat}) with an increase of 80%.

The Incident Photon-to-Electron Conversion Efficiency (IPCE) study showed that most of the increase in photocurrent is found mainly within two regions of the light spectrum: between 350-550 nm (blue region) and 600-800 nm (yellow-red) without the use of a hole scavenger. The highest increase found was 20% at 450 nm and 700 nm. Diffuse Reflectance spectroscopy showed an increase in light absorption of the modified BiVO₄ on the 600-800 nm (yellow-red) region.

The stability test showed a stable response of both $BiVO_4$ and modified $BiVO_4$ during 40 min under irradiation and applied potential of 1.0 vs Ag/AgCl (KCl_{sat}). A decay in photocurrent of 16% was observed at the end of the test owed intrinsic detriment of the material.

The capability of BiVO₄ as a photoanode was demonstrated in a photoelectrochemical cell. Using CuO as a photoanode in a tandem arrangement, unassisted water splitting was achieved. The impact of dynamic polarization on the performance of BiVO₄ was also observed in the photoelectrochemical cell. The Solar-To-Hydrogen efficiency (STH) increase using a PEC cell made of e-BiVO₄//CuO was 33% in comparison to BiVO₄//CuO cell.

On the structural characterization, XRD and SEM did not show significant changes in the lattice structure and the surface of BiVO₄ after the dynamic polarization.

The electrochemical treatment provoked an irreversible change in the $BiVO_4$ which is explained by the increase in the concentration of V⁴⁺ and the insertion of hydrogen into the lattice. The hydrogen insertion forms OH groups within the BiVO₄ structure. The dynamic polarization causes the filling of trap states which provides better electron-hole separation and charge transfer. In general, the dynamic polarization post-synthetic treatment is an option that yields favorable results to improve oxygen evolution and overall unassisted water-splitting through photoelectrochemical process. Since electrochemical post-treatment processes on photoanodes are a new field, there is great room for improvement in each step of the procedure for future work.

4.1 Future work

The work presented in this thesis work is a novel area for a new generation of post-synthetic modifications. Thus, the specific objectives of this thesis work were limited to achieving the improvement of the BiVO₄ photoanode for photoelectrochemical unassisted water splitting using an electrochemical technique. For this reason, there is still room for further improvement. Some suggestions for further enhancement are presented in Future Work. Moreover, some experiments are suggested to have a better understanding of the changes occurring in BiVO₄.

On the BiVO₄ synthesis, the first step used consisted of bismuth electrodeposition using a bismuth salt (Bi(NO₃)₃), which is insoluble in water unless a low pH is achieved. Nevertheless, the films are not stable at low pH as hereby presented. The pulsed electrodeposition of bismuth on FTO glass could be tested in an aqueous electrolyte solution using KI, Bi(NO₃)₃, and HNO₃. This would improve the mass transport of Bi ions and the conductivity over the FTO glass. Consequently, a more uniform and reproducible film can be obtained. Moreover, the use of the aqueous solution is better than the organic solvent used in this thesis work (DMSO) in terms of environmental impact. The thickness of the bismuth film could be optimized to provide a better IPCE efficiency. Additionally, the calcination temperature after adding VO(acac)₂ was fixed to

400 °C under air atmosphere. The temperature at which $BiVO_4$ is calcinated impacts the density of defects induced, therefore on the photoelectrochemical performance. By testing calcination at different temperatures, performance could also be optimized. It is also suggested that annealing is tested under an inert atmosphere (N₂ or Ar) to study only the influence of defects caused by the impact of the electrochemical modification.

On the modification of BiVO₄, dynamic polarization was carried out using the KClO₄ electrolyte. Other electrolytes could be used to test the influence of the anion and counter-ion. Furthermore, additional potential window ranges should be investigated.

The addition of elements as electrocatalysts is often necessary to achieve high currents due to their effect on the kinetics of the oxygen evolution reaction. As it was observed in this thesis work, some charge is accumulated in the interface. Thus, for further efficiency enhancement, a catalyst layer can be put on the BiVO₄ film for the oxygen evolution reaction. Moreover, more studies are required to optimize and further improve the dynamic polarization with BiVO₄. However, it needs to be considered that the PEC cell tested in this thesis work for water splitting was a tandem cell. This electrode arrangement irradiates the photoanode from the front. The catalyst layer may block the incident light. Therefore, a parallel cell arrangement could be used in this case.

More attention should be put on the photocathode as this is a limiting factor for STH, as shown in this thesis work. CuO was used as a photoanode due to its relative stability, low cost and simplicity of synthesis. However, as it was observed, its IPCE values and photocurrents are poor. For future research, it is highly encouraged to try Cu_xS and improve its stability. It is highly likely that this will improve STH. During the STH tests, it was assumed a faradaic efficiency of 100%. It is suggested that this assumption is verified by measuring O_2 and H_2 gasses produced during irradiation. A sealed cell is needed to take a gas sample from the head-space. Overall, a well-engineered photoelectrochemical cell needs to be designed to improve the charge transport in the solution.

Lastly, an important factor to consider for future experiments is the light source. The lightbulb employed for photoelectrochemical experiments was a Xe arc lamp. The arc produced between the electrodes for the light irradiation diffuses and flickers as a consequence of natural decay and heating during operation. However, the lamp employed had a very short lifetime which limited the long-term experiments for testing stability. The decay of lamp performance can be caused by inadequate cooling or poor lamp quality. Moreover, the lamp generates ozone (a hazardous chemical), which limited the long-term stability experiments to 40 min or less. Thus, adequate ventilation is needed to be considered for future stability tests. In short, it is suggested to improve the cooling of the lamp during operation or try different a lightbulb quality.

Although Xe arc lamps are the most common light sources employed in photoelectrochemical experiments, another option that can be considered is the use of a different type of light source. The Xe light source employed had an initial power of 175 W. The estimated power density of the light irradiated on the samples after going through the monochromator was 3.75 mWcm⁻². The photocurrent produced under this irradiation power was in the order of 10⁻⁹A for the area of electrode employed (0.45 cm²). A common light bulb with a power output of approximately 100 W would yield smaller currents and larger errors in the measurements. This option could be feasible only if higher electrode areas are employed. Alternatively, projector lamps produce more than 150 W and have been employed in prior work. Hence, this option could be feasible for the size of the electrodes.

In summary, given that the experimental setup for PEC experiments is well installed and functional in the laboratory, the first step suggested would be to improve the cooling system. Secondly, different light quality could be tested. Lastly, a projector lamp would be a better option over the common light bulb. For testing unassisted water splitting, it is recommended the use of a solar simulator (AM 1.5 G 1000 W/m²) to take into account the solar spectrum and improve the estimation of cell performance.

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Appendix A: 2019 Young Electrochemist Symposium poster

