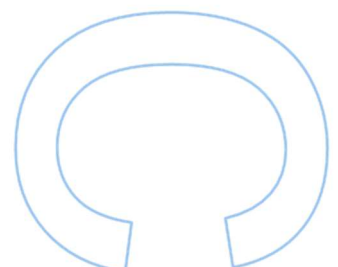
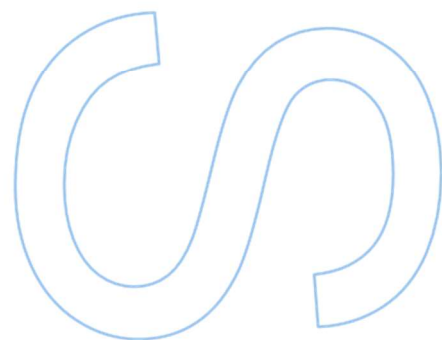
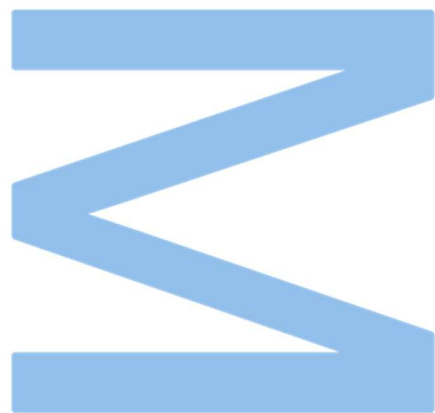


Incorporating Au plasmonic nanoparticles into hematite nanowires for improved solar water splitting

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Master in Engineering Physics
Department of Physics and Astronomy
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2024



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Resumo

Com o crescimento populacional e industrial observado ao longo dos anos, a procura pela energia assim como o seu consumo tem aumentado. Torna-se assim necessário implementar e maximizar a eficiência dos métodos de produção de energia renovável de modo a suprir as necessidades da população mundial, reduzindo a emissão dos gases de efeito estufa.

O hidrogénio ao longo dos últimos anos tem-se destacado como uma fonte de energia. Contudo, grande parte do hidrogénio produzido ainda é de origem fóssil. As células fotoeletroquímicas surgem como um método de energia limpo alternativo capaz de produzir hidrogénio verde. Estas células operam segundo o princípio da eletrólise da água. Um semiconductor, utilizado como um dos elétrodos e imerso em água, absorve a luz solar incidente e gera pares eletrão-lacuna. Esses pares participam nas reações redox da água, levando à clivagem da molécula de água e à geração de O_2 e H_2 .

A hematite é um óxido semiconductor que se destaca como um candidato promissor para células PEC devido à sua abundância na Terra, não toxicidade, e hiato de energia estreito, o que potencialmente permite uma grande eficiência teórica de 16,7%.

Esta dissertação foca-se em melhorar o desempenho fotoeletroquímico de fotoânodos de hematite através de estratégias de nanoestruturação. Nanofios de hematite foram implementados e combinados com nanopartículas de metais plasmónicos e camadas de passivação para melhorar o desempenho fotoeletroquímico e a eficiência de conversão solar-para-hidrogénio.

A integração de nanopartículas metálicas plasmónicas em fotoânodos de hematite pode melhorar significativamente o desempenho de células fotoeletroquímicas, otimizando a separação e transferência de cargas, aumentando a absorção de luz visível e prolongando os tempos de vida dos excitões. Essa melhoria ocorre porque, sob radiação solar, a oscilação coletiva dos eletrões de condução nas nanopartículas metálicas dá origem a um efeito de ressonância de plasmões de superfície localizada (LSPR), que amplifica o campo eletromagnético e localiza a absorção de luz nas proximidades das nanopartículas.

Fotoânodos de nanofios de hematite (configuração 1D) com nanopartículas de ouro incorporadas foram sintetizados pelo método hidrotérmico, utilizando três abordagens distintas. As estratégias usadas incluem a incorporação de nanopartículas plasmónicas de ouro (Au) em diferentes estágios do processo de síntese hidrotérmica dos nanofios de

hematite: (1) após a síntese completa (crescimento de FeOOH e tratamento térmico de alta temperatura para conversão em hematite) dos nanofios de hematite; (2) a meio do processo (depositando ouro logo após a preparação dos nanofios de FeOOH); e (3) antes do crescimento dos nanofios (depositando ouro por sputtering diretamente nos substratos).

Para além de alterar os locais de deposição das nanopartículas de ouro, o seu tamanho e dispersão também foram ajustados através da variação do método de síntese, especificamente o tempo de sputtering de ouro (30 s, 120 s e 300 s).

O impacto destas diferentes estratégias de fabrico foi minuciosamente analisado e estudado. Os fotoânodos desenvolvidos, à base de nanofios de hematite e partículas de ouro, foram caracterizados quanto às suas propriedades morfológicas, óticas e estruturais, usando Microscopia Eletrónica de Varrimento (SEM), espectroscopia UV-Vis e Difração de Raios-X (XRD), respetivamente.

Na série 1, foram obtidos fotoânodos com nanopartículas de ouro, cujos diâmetros médios foram de 15,1 nm, 49,0 nm e 61,9 nm, em função dos tempos crescentes de sputtering de ouro (30 s, 120 s e 300 s, respetivamente). Na série 2, fotoânodos com nanopartículas de ouro de diâmetros médios de 21,2 nm e 50,0 nm foram obtidos para tempos de deposição de ouro de 30 s e 120 s. Nanopartículas de ouro não foram detetadas na série 3, uma vez que o ouro foi depositado diretamente sobre o substrato antes do crescimento dos nanofios de hematite.

A análise da porosidade superficial revelou tendências diferentes dependendo da estratégia utilizada. Na série 1, foi observada uma diminuição na porosidade com tempos de sputtering mais longos, de 26,5% para 22,3%, e os nanofios estavam bem distribuídos. Na série 2, foi observado um comportamento oposto, com os nanofios a tornarem-se mais agregados e a porosidade a aumentar, formando caminhos livres mais largos (de 25,3% para 26,7%). Na série 3, a porosidade foi semelhante entre todas as amostras sintetizadas e a hematite pura (17,4% - 18,3%). A porosidade da hematite pura obtida foi de 17,3%.

A avaliação do desempenho PEC envolveu o uso de curvas de densidade de fotocorrente-comprimento de onda ($j-\lambda$) a um potencial de 1.45 V vs. eletrodo de referência, espectroscopia de impedância eletroquímica (EIS) e curvas de densidade de fotocorrente-potencial ($j-v$) para investigar a excitação plasmónica, as propriedades de transferência de carga e o comportamento fotoeletroquímico geral, respetivamente.

Observou-se que os fotoânodos contendo nanopartículas menores (diâmetro em torno de

15/20 nm), correspondendo a tempos de sputtering de 30 segundos, apresentaram densidades de corrente melhoradas em comparação com aqueles com tempos de deposição mais longos. Esta tendência foi observada tanto na estratégia (1) com nanopartículas na superfície da hematite, quanto na estratégia (2), com nanopartículas na superfície do β -FeOOH.

Foi observado um deslocamento catódico consistente no V_{Onset} em todas as amostras com nanopartículas de ouro em relação à hematite pura. Isto significa que a cinética da reação de oxidação da água foi melhorada, requerendo um potencial de início mais baixo. Este deslocamento catódico é sustentado pela redução da resistência à transferência de carga superficial, observada nas medições de espectroscopia de impedância eletroquímica (EIS). Além disso, a razão entre os valores de intensidade dos picos (110) e (104) dos difratogramas de XRD mostra a mesma tendência, com uma suave diminuição com o potencial de início.

É de notar que a amostra em que o ouro foi depositado (por sputtering durante 30 s) na fase FeOOH antes do recozimento térmico em duas etapas demonstrou um deslocamento catódico notável no potencial de início, alcançando um valor de 0,67 V, em comparação com 0,81 V para a hematite pura. Concluiu-se que o ouro efetivamente acelera a reação de oxidação da água.

A amostra com ouro depositado, também por 30 s, antes da formação da hematite exibiu a maior densidade de fotocorrente ($j = 0,74 \text{ mA/cm}^2$), um aumento de cerca de 10% comparativamente à hematite pura, e o menor hiato de energia, destacando a eficácia desta abordagem.

Por fim, uma camada de TiO_2 foi depositada nas amostras configuradas na estratégia 1, entre a hematite e o ouro, e na estratégia 2, entre o FeOOH e o ouro. Estas amostras foram selecionadas devido aos melhores resultados obtidos em termos de comportamento plasmónico de superfície. O objetivo da deposição da camada de TiO_2 foi mitigar a corrosão da hematite e minimizar os estados superficiais. No entanto, este passo adicional não resultou numa melhoria nas propriedades fotoeletroquímicas, levando a um deslocamento anódico do potencial de início e a uma redução da densidade de fotocorrente.

Palavras-chave: hematite, fotoss separação da água, nanofios, hidrogénio verde, nanopartículas de ouro plasmónicas

Abstract

With the population and industrial growth observed over the years, the demand for energy as well as its consumption has increased. It has thus become necessary to implement and maximize the efficiency of renewable energy production methods to meet global needs while reducing greenhouse gas emissions.

Over recent years, hydrogen has emerged as a prominent energy source, however, a significant portion of the hydrogen produced is still derived from fossil fuels. Photoelectrochemical cells have emerged as an alternative clean energy method capable of producing green hydrogen. These cells operate on the principle of water electrolysis. A semiconductor, used as one of the electrodes and immersed in water, absorbs incident solar light, and generates electron-hole pairs. These pairs participate in the redox reactions of water, leading to the splitting of water and generation of both O_2 and H_2 .

Hematite is a semiconductor oxide that stands out as an appealing candidate for PEC cells due to its earth abundance, non-toxicity, and narrow band gap, which potentially allows for a large theoretical efficiency of 16.7%.

This dissertation focuses on enhancing the photo-performance of hematite photoanodes through nanostructuring strategies. Hematite nanowires were implemented and combined with plasmonic metal nanoparticles and passivation layers to improve the photoelectrochemical performance and the solar-to-hydrogen efficiency.

The integration of plasmonic metal nanoparticles into hematite photoanodes can significantly enhance the performance of photoelectrochemical cells by optimizing charge separation and transfer, increasing visible light absorption, and extending exciton lifetimes. This improvement occurs because, under solar radiation, the collective oscillation of conduction electrons in the metal nanoparticles gives rise to a localized surface plasmon resonance (LSPR) effect, which amplifies the electromagnetic field and localizes light absorption near the nanoparticles.

Hematite nanowire photoanodes (1D configuration) with incorporated gold nanoparticles were synthesized by hydrothermal method using three distinct approaches.

The strategies used includes the incorporation of plasmonic gold nanoparticles (Au) at different stages of the hydrothermal synthesis process of hematite nanowires: (1) after the full synthesis (FeOOH growth and high temperature annealing to convert in hematite) of the hematite nanowires; (2) in the middle of the process (depositing gold right after the as-prepared FeOOH nanowires); and (3) before the growth of the nanowires (depositing

gold by sputtering directly on the substrates).

Furthermore, in addition to modifying the deposition locations of the gold nanoparticles, their size and dispersion were also adjusted by varying the synthesis method, specifically the gold sputtering time (30 s, 120 s, and 300 s).

The impact of these different fabrication strategies was thoroughly analysed and studied. The developed hematite nanowires-gold particles based photoanodes were characterized for their morphological, optical, and structural properties using Scanning Electron Microscopy (SEM), UV-Vis spectroscopy and X-Ray Diffraction (XRD), respectively.

In series 1, photoanodes with gold nanoparticles, with average diameters of 15.1 nm, 49.0 nm, and 61.9 nm, were obtained based on increasing gold sputtering times (30 s, 120 s, and 300 s, respectively). In series 2, photoanodes with gold nanoparticles of average diameters of 21.2 nm and 50.0 nm were obtained for gold deposition times of 30 s and 120 s. Gold nanoparticles were not detected in series 3, as gold was deposited directly onto the substrate before the growth of the hematite nanowires.

The analysis of surface porosity revealed different trends depending on the strategy used. In series 1, a decrease in porosity was observed with longer gold sputtering times from 26.5% to 22.3%, and the nanowires were well distributed. In series 2, an opposite behaviour was noted, with the nanowires becoming more aggregated and porosity increasing, forming wider free paths (25.3% to 26.7%). In series 3, the porosity was similar among all synthesized samples and the bare hematite (17.4%-18.3%). The porosity of bare hematite obtained was 17.3%.

The evaluation of PEC performance involved the use of photocurrent density-wavelength (j - λ) curves at a potential of 1.45 V vs. reference electrode, electrochemical impedance spectroscopy (EIS), and photocurrent density-potential (j - v) curves to investigate plasmonic excitation, charge transfer properties, and overall photoelectrochemical behaviour, respectively.

It was observed that photoanodes containing smaller nanoparticles (diameter around 15/20 nm), corresponding to sputtering times of 30 seconds leads to improved current densities compared to those with longer deposition times. This trend is observed either with strategy (1) nanoparticles on the surface of hematite or (2) nanoparticles on the surface of β -FeOOH.

A consistent cathodic shift in V_{Onset} was observed in all samples with gold nanoparticles relative to pure hematite. This means that the kinetics of the water oxidation reaction is

improved, requiring a lower onset potential. This cathodic shift is supported by reduced surface charge transfer resistance observed in electrochemical impedance spectroscopy (EIS) measurements. Furthermore, the ratio of intensity values of (110) and (104) peaks from the XRD diffractograms show the same trend, a smooth decrease with the onset potential is observed.

Notably, the sample where gold was deposited (by sputtering for 30 s) on the FeOOH phase prior to two-step annealing demonstrated a remarkable cathodic shift in onset potential, achieving a value of 0.67 V compared to 0.81 V for pure hematite. It was concluded that gold effectively accelerates the water oxidation reaction.

The sample with gold deposited, also for 30 s, before hematite formation exhibited the highest photocurrent ($j = 0.74 \text{ mA/cm}^2$), an increase of about 10% compared to pure hematite, and the lowest band gap, highlighting the effectiveness of this approach.

Finally, a TiO_2 layer was deposited on the samples configured in strategy 1, between hematite and gold, and in strategy 2, between FeOOH and gold. These samples were selected because they exhibited the best results in terms of plasmonic surface behaviour. The objective of depositing the TiO_2 layer was to mitigate hematite corrosion and minimize surface states. However, this additional step did not lead to an improvement in the photoelectrochemical properties, resulting in an anodic shift in the onset potential and a reduction of photocurrent density.

Keywords: water splitting, hematite, nanowires, green hydrogen, gold plasmonic nanoparticles

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Symbols

ΔG Change in Gibbs free energy (kJ/mol)

e^- Electron

ν Frequency (Hz)

h^+ Hole

j Photocurrent density (mA/cm²)

c Speed of light (m/s)

λ Wavelength (nm)

List of Abbreviations

ALD Atomic Layer Deposition

BSE Backscattered electrons

CCS Carbon Capture System

CPE Constant Phase Element

D_{XRD} Crystallite size

EDS Energy Dispersive X-ray Spectroscopy

E_g Energy gap

EIS Electrochemical Impedance Spectroscopy

FTO Fluorine-doped Tin Oxide

FWHM Full Width at Half Maximum

H_2 Hydrogen

HEI Hot Electron Injection

HER Hydrogen Evolution Reaction

IBD Ion Beam Deposition

IPCE Incident Photon-to-Current Efficiency

L Thickness

LSPR Localized Surface Plasmon Resonance

NHE Normal Hydrogen Electrode

OER Oxygen Evolution Reaction

PEC Photoelectrochemical

PIRET Plasmon-Induced Resonance Energy Transfer

PV Photovoltaic

RE Reference Electrode

RHE Reversible Hydrogen Electrode

SE Scattered electrons

SEM Secondary Electron Microscopy

SERS Surface-Enhanced Raman Spectroscopy

STH Solar to Hydrogen

V Potential

UV-Vis Ultraviolet-Visible

XRD X-ray Diffraction

WE Working Electrode

1. Introduction

Over the centuries, a huge evolution in the energy sector has allowed a significant improvement in people's quality of life and greater economic development.

Energy plays a crucial role in today's society. It is present everywhere in the form of electricity, powering our alarm clocks, the refrigerator used to store food and providing light when natural light is insufficient. Additionally, electricity has a significant impact on sustaining the equipment and machines in industrial and hospital sectors, which are essential for economic growth and quality healthcare.

Despite enormous progress in the energy sector, it is estimated that there are still 745 million people in the world without access to electricity [1]. Projections made by the United Nations represented in figure 1.1 indicate that the world population will increase from 8 thousand million people in 2022 to 9.7 thousand million people in 2050 [2].

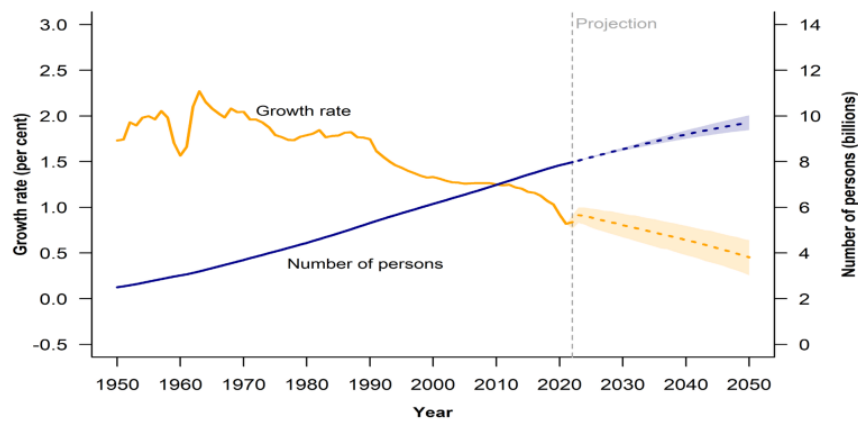


Figure 1.1: Global population size and annual growth rate: estimates, 1950-2022, and medium scenario with 95 percent prediction intervals, 2022-2050. (Extracted from [2]).

In 2022, 61.26% of electricity produced in the world came from fossil fuels (35.63%, 22.48% and 3.15% from coal, gas and oil, respectively), 9.18% of nuclear energy and 29.56% of renewable origin, with hydro energy being the most dominant [3]. Unfortunately, most of the electricity produced in the world continues to be of nonrenewable origin. Although the share of electricity in final energy consumption was 20% in 2022, the electricity and heat sector represented around 40% of total energy-related CO₂ emissions [4], which leads to a significant increase in greenhouse gases emissions. These gases trap the heat from the sun and cause a gradual rise in the temperature of the Earth's atmosphere, contributing to global warming. It is essential to reduce the carbon footprint by

reducing the percentage of energy coming from fossil fuels to avoid the worsening and potentially irreversible effects of climate change.

Figure 1.2 shows that the projected global GHG emissions based on nationally determined contributions before the United Nations Climate Change Conference in 2021 (COP 26) make it likely that warming will exceed 1.5°C and will also make it more difficult, after 2030, to limit warming to below 2°C . It is necessary to reduce approximately 43% of greenhouse gas emissions by 2030, compared to 2019 emissions, so that the global average temperature in 2100 does not exceed the pre-industrial period temperature by more than 1.5°C [5]).

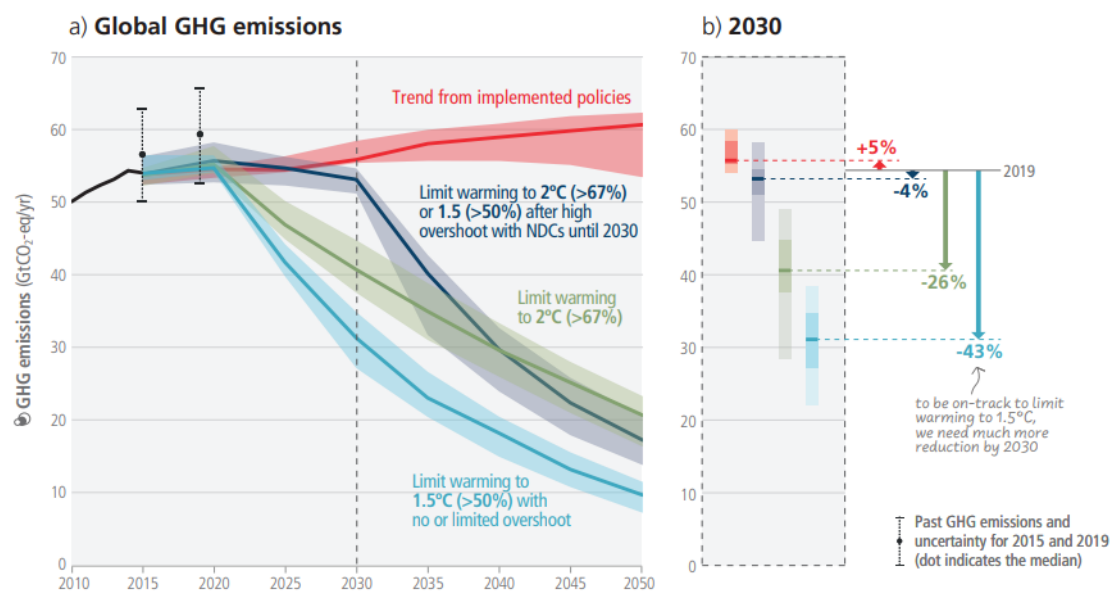


Figure 1.2: a) Greenhouse gases emissions in different policies scenarios; b) Projected emissions results from short-term policy assessments to 2030. (Extracted from [5]).

It is important to focus on the 1.5°C path rather than the 2°C path, since an additional 0.5°C will lead to more severe and devastating effects [5, 6]. With an increase in global temperature of 2°C , 36.9% of the world's population is expected to face a heat wave every 5 years, around 23.3% more than for 1.5°C . The balance of ecosystems and food chains would be strongly impacted by 2°C warming, considering that 8%, 16% and 6% of vertebrate, insect and plant species, respectively, would lose more than half of their geographical distribution determined by the climate, while per 1.5°C of warming, this percentage is reduced by two thirds for insects and by half for plants and vertebrates [5]. Also it is known that the ocean has absorbed about 30% of anthropogenic carbon dioxide, which helps reduce global warming. However, ocean acidification is occurring, putting marine ecosystems at risk. The warming and acidification of the oceans, corresponding

to 2°C of global warming, would have a huge impact on several marine creatures. For example, 99% of the coral reefs that currently exist would disappear [7].

Furthermore, the increase in temperature would cause significant changes in the agricultural, fishing and aquaculture systems [8, 9].

At COP 28 [6] an agreement and commitment were established for all countries involved to strengthen their environmental policies and innovations due to the need to triple renewable energy capacity and double energy efficiency by 2030, in order to keep in target the limit of temperature increase to 1.5°C above pre-industrial levels by the end of this century.

It is imperative to adopt measures that aim to maximize the production and use of energy from renewable sources, with the aim of meeting the needs of the entire world population, without harming the environment.

Renewable energies will play a crucial role in the clean energy transition. The use of renewable energy for electricity production, for the transport and industrial sectors will make a difference and contribute significantly to the reduction of greenhouse gas emissions.

However, it is fundamental to consider that this energy transition must be carried out consciously, consistently and without putting at risk the population's energy demand. It is essential to assess which renewable solutions are most suitable for each geographic region and to provide these regions with the necessary infrastructure for storing and transporting these technologies.

Research and development work on renewable energy must continue to achieve energy that is lower in cost, more sustainable and more efficient than fossil fuels.

In recent years, there has been growing interest in the production of green hydrogen which consists in hydrogen produced through renewable energy [10, 11]. This energy carrier can be used in various applications, both in the transport [12], industrial [13] and energy sectors [14], contributing to their decarbonization [15], which will be explored in the next section.

To produce green hydrogen, the conventional method involves using electrolyzers powered externally by energy from renewable sources, such as photovoltaic solar panels (PV-electrolysis devices). In this approach, the solar panels generate electricity, which is then used to drive the electrolysis process.

Photoelectrochemical cells represent an innovative alternative. They combine the solar light absorption and water splitting into a single module [16].

In this thesis, we aim to optimize one of the electrodes of the PEC cell, specifically the

photoanode, to enhance its performance in solar water splitting for the production of green hydrogen.

This thesis is motivated by the ambition of having a world without anthropogenic greenhouse gas emissions, with efficient, low-cost, sustainable renewable energies capable of providing energy throughout the world. This way, future generations will be able to have a promising future.

1.1. The Hydrogen Revolution

Hydrogen is the lightest and most abundant chemical element in the universe. At room temperature, it is a gaseous, colorless, odorless, non-toxic, and highly combustible substance.

Besides these characteristics, hydrogen is widely acknowledged as an energy carrier and vector, capable of storing and transporting energy.

Its energy density per unit mass is notably high, around 120 megajoules per kilogram (MJ/kg), roughly three times greater than that of gasoline (≈ 44 MJ/kg). However, hydrogen's volumetric energy density is relatively low, meaning it occupies much more space than conventional fossil fuels under normal temperature and pressure conditions. Therefore, hydrogen is typically compressed to 700 bar or liquefied for more efficient storage and transportation, though liquefaction at 22 K is costly and energy intensive.

Hydrogen finds diverse applications, with various production techniques developed over last decades. With growing environmental awareness in businesses and society at large, significant efforts are underway to produce hydrogen using renewable energies. Various production methods and their applications are detailed in the following subsection.

1.1.1 Hydrogen Synthesis and Applications

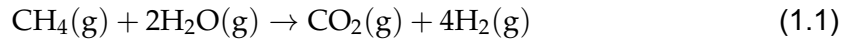
Hydrogen can be produced through various processes, often categorized by colors to differentiate the synthesis methods used.

Most hydrogen is derived from fossil fuels, known as gray hydrogen, primarily through processes like steam methane reforming (SMR) or coal gasification. These methods generate significant CO₂ emissions, which hinder the transition to net-zero emissions [17].

Steam methane reforming is the most common thermochemical process for hydrogen production, using natural gas, primarily methane, as the fossil fuel source. This process involves reacting methane with steam at high temperatures (800-1000°C), producing a synthesis gas composed of carbon dioxide and hydrogen. Subsequently, a water-gas

shift reaction occurs, where carbon monoxide in the synthesis gas reacts with steam to produce additional hydrogen and carbon dioxide [15].

The overall chemical reaction in this process is:



Despite the efficiency of this technique in producing hydrogen, the significant CO₂ emissions associated with this method present a challenge for sustainable development and the reduction of global greenhouse gas emissions.

To minimize the emissions of CO₂ during the production of hydrogen from fossil fuels, new technologies have been developed that allow for the capture and storage of the carbon dioxide generated. However, it is important to note that these systems are unable to capture all of the CO₂ produced. These technologies, known as Carbon Capture and Storage (CCS), represent a significant step toward reducing the environmental impact of hydrogen produced from fossil sources, but there are still technical and economic challenges to overcome in achieving higher and more consistent capture rates. This type of hydrogen is classified as blue color.

Turquoise hydrogen uses natural gas as raw material without generating CO₂ emissions. Through the pyrolysis process, the carbon present in methane is transformed into solid carbon black. This carbon black has an established market, providing an additional source of revenue. Furthermore, carbon black can be stored more easily and safely than gaseous CO₂ [17, 18].



In this reaction, one molecule of methane (CH₄) is thermally decomposed (pyrolysis) to produce solid carbon black (C) and two molecules of hydrogen (H₂). This is the basis of the process that characterizes turquoise hydrogen, where carbon is separated from hydrogen without emitting carbon dioxide (CO₂) during production, unlike conventional steam methane reforming (SMR). In pyrolysis, methane is thermally decomposed at high temperatures (generally above 700 °C), in the absence of oxygen or with a limited amount of oxygen [18].

Green hydrogen represents the most sustainable option for an energy transition, as it uses renewable energy sources for its synthesis. The most commonly used method is water electrolysis, in which water is split into hydrogen and oxygen by applying an electric

current sourced from renewable energies, such as solar or wind power.

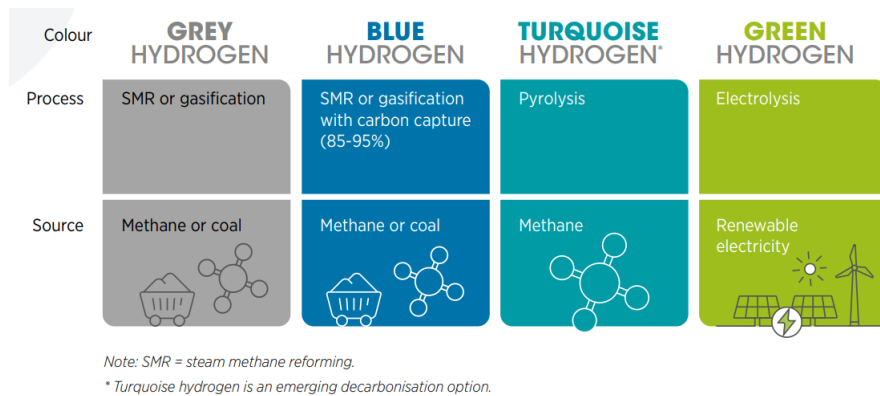


Figure 1.3: Main hydrogen colours depending on synthesis method. (Extracted from [17]).

In steel production, hydrogen can replace coal as a reducing agent, thereby reducing CO₂ emissions [19]. In refineries, hydrogen is used in hydro processing to remove impurities and produce cleaner liquid fuels from crude oil [20]. In the chemical industry, hydrogen is used to produce ammonia, which is essential for the manufacture of fertilizers needed for agriculture [13].

Hydrogen is used in fuel in Fuel Cell Electric Vehicles (FCEVs). In these cells, hydrogen is converted into electricity to power an electric motor, emitting only water as a byproduct. Additionally, it can be used in modified internal combustion engines to burn hydrogen instead of fossil fuels.

For residential and industrial heating, hydrogen can be burned in boilers to provide heat without CO₂ emissions. Hydrogen heating systems are a promising alternative to traditional natural gas heating systems, especially in areas where electrification of heating is challenging or economically unfeasible [21].

In power generation, hydrogen can be used in power plants to produce electricity, either through fuel cells or by direct burning in hydrogen-adapted gas turbines [14, 22]. Hydrogen fuel cells are highly efficient and generate electricity with water as the only byproduct. Moreover, hydrogen can be stored and used to generate electricity during periods of high demand or when renewable energy sources such as solar and wind are unavailable, thereby helping to stabilize the electrical grid.

In summary, hydrogen holds significant potential to decarbonize various industries and sectors, offering a cleaner and more sustainable alternative to traditional fossil fuels.

1.2. Photoelectrochemical cell

Photoelectrochemical (PEC) cells for water splitting emerge as a promising method to obtain green hydrogen by converting solar energy into chemical energy using water and sunlight. These cells directly utilize solar energy to produce hydrogen. The photoelectrochemical water splitting approach using solar energy, in a simplistic way, consists of the dissociation of water into hydrogen and oxygen, using electric current generated by a sunlight-absorbing semiconductor material in the presence of an electrolyte solution.

The photoelectrochemical cell consists of two electrodes: a semiconductor working electrode, which can be n-type (designated as a photoanode) or p-type (designated as a photocathode), and a counter electrode (usually a metal like platinum) immersed in an water-based electrolyte solution (acidic or basic).

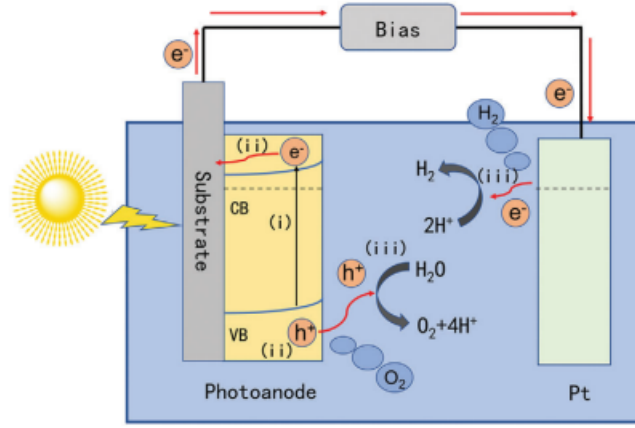
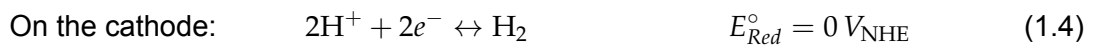
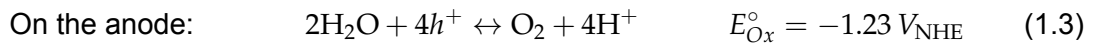
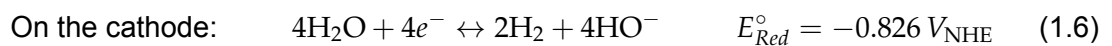
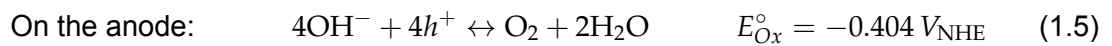


Figure 1.4: Diagram illustrating the fundamental principles of water splitting in a photoelectrochemical cell featuring an n-type semiconductor photoanode for oxygen evolution, and a counter electrode (Pt) for hydrogen evolution. (Extracted from [23]).

For an acidic electrolyte, the water oxidation and reduction reactions in reference of normal hydrogen electrode (NHE) may be represented as follows [24, 25]:



In basic electrolyte, the reactions for water oxidation and reduction can be expressed as follows:



The overall reaction of photoelectrochemical water splitting is:



It can be seen from equations (1.3-1.7), under standard conditions that this reaction is endothermic and not spontaneous. For every 1 mol of water involved in the reaction, the standard Gibbs free energy change is 237 kJ. During the reaction, 1.23 eV of energy is consumed for every electron transferred [26]. This means that, theoretically, the minimum potential required for water splitting is 1.23 V at 25 °C.

In this thesis, an n-type semiconductor was used, and the mechanism discussed focuses on its application as a photoanode.

When an n-type semiconductor photoanode absorbs photons from incident solar radiation with energy equal to or greater than the semiconductor's band gap, necessary to inject electrons from the valence band to the conduction band of the semiconductor, electron-hole pairs ($e^- - h^+$) are generated. The spatial separation of photogenerated electrons and holes is facilitated by the electric field established across the space charge layer (SCL). This field arises from the Fermi level equilibrium process between the semiconductor and the electrolyte Fermi levels. It is established by the flow of charge between the semiconductor and the electrolyte, which is crucial for maintaining electronic equilibrium. The photoexcited electrons are transferred through an external circuit to the counter electrode, where they participate in the reduction reaction of the hydrogen evolution reaction (HER), reducing water to produce H_2 . Meanwhile, the photoexcited holes migrate to the photoanode surface, where they facilitate the oxidation of water molecules at the photoanode surface in the oxygen evolution reaction (OER), resulting in the production of O_2 [26–28].

Under solar irradiation, H_2 is produced at the metal electrode and O_2 at the anode. This configuration is advantageous because it allows the production of oxygen and hydrogen to occur at separate electrodes of the cell, facilitating their separation and collection. Due to the bias between the electrodes, the probability of electron-hole recombination is reduced in these PEC systems, thereby improving the solar-to-hydrogen efficiency. However, the fact that it is necessary to apply a minimum bias of 1.23 V for water splitting poses a challenge and requires the incorporation of a power supply or a photovoltaic panel into the PEC cell to provide this additional bias.

The choice of semiconductor material is extremely important because the semiconductor needs to have the valence band edge slightly below the water oxidation potential and the conduction band edge slightly above the water reduction potential to minimize the need for bias input [28].

Semiconductor requirements will be discussed in the next subsection.

1.2.1 Semiconductor photoanode materials

The choice of semiconductor photoanode is crucial for the success of a photoelectrochemical cell. Although the theoretical minimum potential required for water splitting is 1.23 eV, it is necessary to account for thermodynamic losses (0.3–0.4 eV) and the overpotentials needed to initiate the reaction (0.4–0.6 eV) [29]. Therefore, an ideal semiconductor should have a bandgap of at least 1.9 eV and ensure effective coverage of the energies required for both hydrogen and oxygen evolution reactions as mentioned before. This will maximize the performance of the PEC cell and reduce the need for an external bias. The semiconductor must exhibit strong absorption in the visible light spectrum to maximize photon capture from incident solar radiation.

Furthermore, the semiconductor should be abundant in the Earth's crust, non-toxic, chemically stable in aqueous media and under illumination, efficient, low-cost, and scalable to be effectively integrated and deployed in the energy sector.

The figure illustrates a variety of semiconductors used in photoelectrochemical cells.

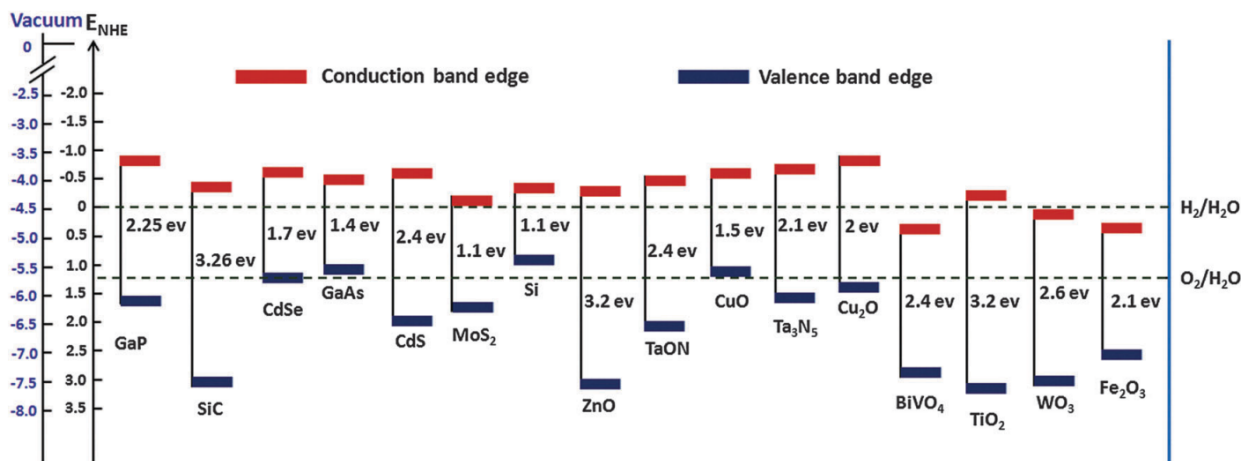


Figure 1.5: Conduction and valence band edges positions for several semiconductor materials in contact with the aqueous electrolyte at pH = 0, relative to the Normal Hydrogen Electrode (NHE) and the vacuum level. The HER (upper dashed line) and OER (lower dashed line) redox potentials are included for reference.(Extracted from [28]).

Although some of these semiconductors cover the chemical potentials of water oxidation and reduction, the wide band gap limits the capture of visible sunlight.

So far, no semiconductor has been found that meets all the necessary criteria mentioned before. This requires thorough research to optimize both the synthesis and configuration of the material, aiming to improve the conversion of solar energy to hydrogen. It is important to note that photoelectrochemical cells require an efficiency of 10% to be commercially viable.

Among the various presented photoelectrode materials, Hematite ($\alpha\text{-Fe}_2\text{O}_3$), Tungsten Trioxide (WO_3), Titanium Dioxide (TiO_2) and Bismuth Vanadate (BiVO_4) are the target of extensive research due to their low cost, stability, and large-scale production.

This thesis focuses on the development of hematite photoanodes to improve the PEC cells performance, using strategies such as nanostructuring and the incorporation of plasmonic nanoparticles, employing low-cost and scalable synthesis methods.

The fact that hematite has a theoretical maximum efficiency for solar-to-hydrogen conversion of around 16%, corresponding to 12.6 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ [30], which exceeds the STH benchmark efficiency of 10% required for real applications, and has a bandgap between 1.9 and 2.3 eV makes hematite an attractive material for photo water splitting.

In the following subsection, the physical and chemical properties of hematite will be discussed.

1.2.1.1 Hematite and their properties

Iron is the fourth most abundant element in the Earth's crust, and it is easily oxidized in the air to its ferrous (Fe^{2+}) and ferric (Fe^{3+}) states. The resulting iron oxides, which exhibit distinctive reddish-brown colours, demonstrate a significant ability to absorb solar radiation. Due to these properties, iron oxides, being non-toxic, abundant, and efficient in light absorption, are particularly attractive for use in photoelectrochemical cells. Among the existing iron oxides, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and magnetite (Fe_3O_4), hematite stands out as the most common and thermodynamically stable crystalline form at room temperature [30].

Crystalline structure

Hematite crystallizes in the rhombohedral crystal system (or trigonal), similar to the crystal

structure of corundum (α - Al_2O_3). Hematite has trigonal-hexagonal scalenohedral symmetry and belongs to the space group R-3c. Its lattice parameters are $a = 5.0356 \text{ \AA}$ and $c = 13.7489 \text{ \AA}$. The unit cell of hematite contains six formula units, which include 12 iron atoms and 18 oxygen atoms.

The O^{2-} anions are arranged in a hexagonally close-packed lattice along the [001] direction, and the Fe^{3+} cations occupy two-thirds of the octahedral interstices in the basal (001) planes [30, 31].

Analysing the preferential orientation of hematite's crystal planes through X-ray diffraction is essential, as hematite exhibits strongly anisotropic carrier-transport properties, which significantly influence the material's conductivity and PEC cell performance [32]. Materials with more than one preferential orientation typically led to lower photocurrents.

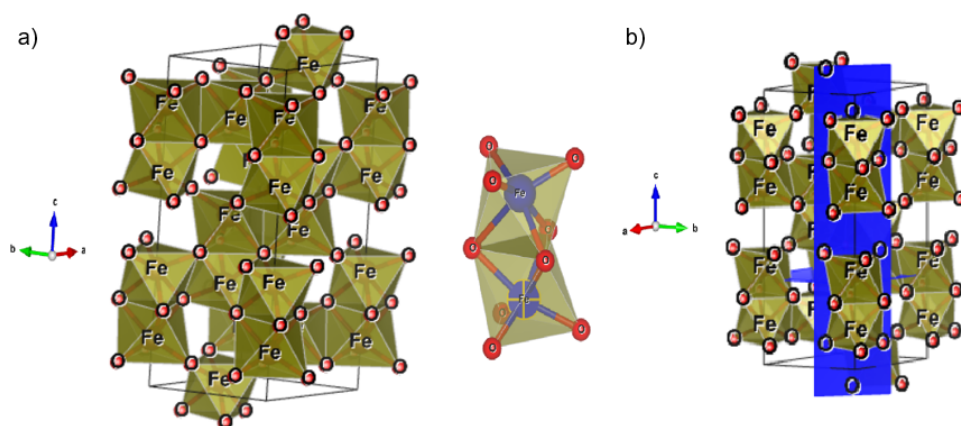


Figure 1.6: a) Visualization of the hematite unit cell using VESTA software, based on CIF file 9000139 from the Open Crystallographic Database. The magnification represents one face-sharing dimer (Fe_2O_9). b) The (100) crystalline plane is highlighted in blue in the unit cell representation, as this preferential orientation is associated with enhanced conductivity.

Optoelectronics properties

The characteristic red-brown colour of hematite results from its strong absorption of photons in the wavelength range from ultraviolet (315–400 nm) to yellow (approximately 570–590 nm), and its transmission of photons in the wavelength range from orange (590–620 nm) to near-infrared (beyond 700 nm) [31].

The indirect band gap of hematite ranges from 1.9 eV to 2.2 eV, corresponding to wavelengths of approximately 650 nm and 560 nm, respectively.

When the incident radiation has a wavelength longer than the band gap of hematite, meaning that the photons have energies lower than the band gap energy of the semiconductor, electron-hole pairs cannot be generated, inhibiting the production of photocurrent. Therefore, it is essential that the incident photons have energies greater than the band gap of

the material to generate photocurrent effectively. A reduced band gap, associated with higher crystallinity degrees and lower concentration of defects, enables the absorption of a broader range of the solar spectrum, thus enhancing the efficiency of photocurrent generation.

Hematite is an n-type semiconductor where electrons are the majority charge carriers responsible for electrical conductivity.

At room temperature, $\alpha\text{-Fe}_2\text{O}_3$ presents poor conductivity ($10^{-14} \Omega^{-1} \text{cm}^{-1}$), short diffusion length (2–4 nm), very short excited-state lifetime (3–10 ps) and low carrier mobility ($10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) [33, 34].

The low electrical conductivity is attributed to the *hopping* mechanism of polarons. Polarons are charge carriers that are coupled with a local distortion of the crystal lattice. In hematite, conductivity is influenced by the valence alternation between the iron ions Fe^{2+} and Fe^{3+} which have different oxidation states. Electrons tend to remain localized in specific 3d orbitals, and the movement of polarons is not spontaneous, which limits the mobility of charge carriers and, consequently, the material's conductivity [31].

As an electron moves through the crystal lattice, it causes distortion in the atoms surrounding the iron ion. This distortion is particularly pronounced when an Fe^{3+} ion gains an electron and is reduced to Fe^{2+} , due to the increase in its ionic radius. The larger size of the Fe^{2+} ion exacerbates the lattice distortion, making it more difficult for polarons to move and increasing the energy required for charge transport.

The need to overcome the activation energy for polaron hopping limits the mobility of charge carriers. Additionally, the lattice distortion caused by the increased size of the Fe^{2+} ion restricts the free movement of charge carriers, resulting in low conductivity and short diffusion lengths.

These conditions contribute to high electron-hole recombination rates and decreased efficiency in PEC cells.

1.3. Strategies to improve PEC performance

To overcome the drawbacks and enhance the performance of hematite photoanodes, various strategies are being developed and continuously refined. These include nanostructuring, doping, the use of passivation layers, plasmonic metal nanoparticles, and co-catalysts, all aimed at improving the efficiency of photoelectrochemical cells.

Nanostructuring of hematite significantly increases the surface area of the interface with

the electrolyte, which enhances charge collection and transport. By creating nanostructured surfaces, the effective path length for light absorption is increased, and the recombination of electron-hole pairs is reduced, leading to better photocurrent generation [35, 36].

Doping hematite with elements such as tin (Sn) and titanium (Ti) can effectively increase the charge carrier concentration and electrical conductivity [36–38]. Doping introduces additional energy levels within the band gap [39] which can serve as charge carriers or enhance the mobility of electrons and holes, thus improving the overall photoresponse of the material.

The incorporation of plasmonic metal nanoparticles, such as gold or silver, into hematite can significantly boost its light-harvesting capabilities. These nanoparticles exhibit localized surface plasmon resonances that enhance the local electromagnetic field, increasing the light absorption cross-section of the hematite and thereby reducing charge recombination [40, 41].

The application of passivation layers helps in reducing the recombination of surface states in the semiconductor. These layers, often composed of thin films of metal oxides like aluminium oxide (Al_2O_3) or titanium dioxide (TiO_2), act as a protective barrier that mitigates surface defects and traps, leading to improved stability and enhanced photoelectrochemical performance [42, 43].

The use of co-catalysts for the oxygen evolution reaction (OER) on the surface of hematite promotes the kinetics of water oxidation at lower potentials. Co-catalysts such as cobalt phosphate [44] or nickel-based compounds [45] facilitate the formation and release of oxygen, effectively lowering the overpotential required for the reaction and increasing the overall efficiency of the photoelectrochemical process.

1.3.1 Nanostructuring

The morphology of hematite photoanodes is crucial to their photoelectrochemical performance in solar cells. Various nanostructured photoanodes (seen in figure 1.7), including nanorods, nanowires, nanotubes, dendrites, cauliflowers, and nanosheets, have been developed using different synthesis methods, each demonstrating significant improvements in photoelectrochemical cell performance.

Nanostructured hematite photoanodes enhance the active surface area in contact with electrolyte and reduce the migration distance of photogenerated carriers from the bulk

phase of $\alpha\text{-Fe}_2\text{O}_3$ photoelectrodes to their surface reaction sites. This reduction in migration distance leads to lower recombination rates of charge carriers, thereby enhancing charge collection efficiency and light absorption, which improves overall photoelectrochemical performance. Consequently, this approach mitigates some of the limitations associated with hematite, such as low charge carrier mobility and short hole diffusion lengths.

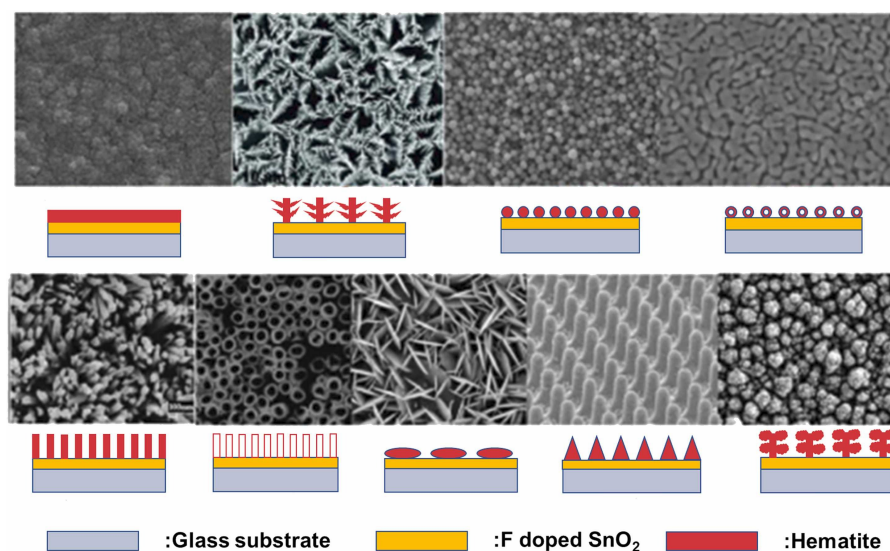


Figure 1.7: Scanning electron microscope (SEM) images and corresponding schematic representations of different nanostructured $\alpha\text{-Fe}_2\text{O}_3$ photoanodes grown on FTO-coated glass substrates. (Extracted from [28]).

In this thesis, hematite nanowires (1D nanostructures) were synthesized to enhance performance by providing more efficient pathways for charge transport and improving electron percolation. The hydrothermal method was chosen for synthesizing these photoanodes due to its simplicity, low cost, and capability to produce photoanodes with high crystallinity.

1.3.2 Plasmonic nanoparticles

Integrating plasmonic metal nanoparticles into hematite photoanodes can substantially enhance photoelectrochemical cell performance by improving charge separation and transfer, enhancing excitation lifetime as well as increasing visible light absorption [46]. Metals like gold and silver can be tailoring to efficiently absorb light making them attractive for use in photoelectrochemical cells for water splitting.

Plasmonic metal nanoparticles can alter the location of charge carrier generation in a semiconductor by acting as an antenna that localizes optical energy and transfers it to the semiconductor, within approximately 10 nm from the metal, promoting optical conversion

in the semiconductor above and below the band gap [24, 47]. These nanostructures enhance light-harvesting capacity and minimize the charge recombination due to their localized surface plasmon resonance (LSPR) features.

The energy from plasmonic metal nanoparticles can be transferred to semiconductors in two ways: direct electron transfer (DET) and plasmon-resonance energy transfer (PRET). In DET, plasmons generate hot electrons that are injected into the semiconductor's conduction bands, enhancing photoelectrochemical performance. In PRET, the nanoparticles amplify the electric field at the semiconductor's surface, increasing light absorption and generating electron-hole pairs. This improves photocatalytic activity by extending the diffusion of carriers and reducing recombination [27, 48].

Localized Surface plasmon resonance (LSPR) occurs due to the interaction of conduction electrons in metallic nanoparticles with photons from incident solar light. This interaction induces a collective oscillation of the electrons in the metallic nanoparticles, causing the plasmonic nanoparticles to resonate at a specific wavelength that matches the incident solar radiation. This resonance significantly enhances the electromagnetic field. This near field absorption enhancement can be used to confine light absorption to the proximity of metal nanoparticles and improve the performance of PEC cells [49, 50]. The optical properties of metal LSPR are influenced by several factors, including particle size, morphology, composition, and the surrounding medium.

The contact between noble metal nanoparticles and n-type semiconductors forms a Schottky junction, which creates an internal electric field in the space-charge region near the metal/semiconductor interface. This junction facilitates enhanced charge separation and transfer by driving electrons and holes to move in opposite directions upon their generation. Additionally, the metallic component facilitates efficient charge transfer by providing a low-resistance pathway and its surface acts as a charge trap, offering additional active sites for photoreactions. The nanoparticles also improve light absorption due to their size and morphology, effectively covering visible and near-infrared (NIR) wavelengths.

When light strikes the semiconductor, it generates charge carriers that release energy through radiative and non-radiative processes. The presence of plasmonic metal nanostructures plays a crucial role by extending the lifetime of these carriers and modulating their recombination (figure 1.8). This enhancement is achieved through mechanisms such as hot electron injection (HEI) and plasmon-induced resonance energy transfer (PIRET).

Together with the Schottky junction, the efficient charge transfer pathways, and the improved light absorption, these plasmonic effects work synergistically to suppress electron-hole recombination and significantly boost the overall efficiency of the photoelectrochemical system [46, 49].

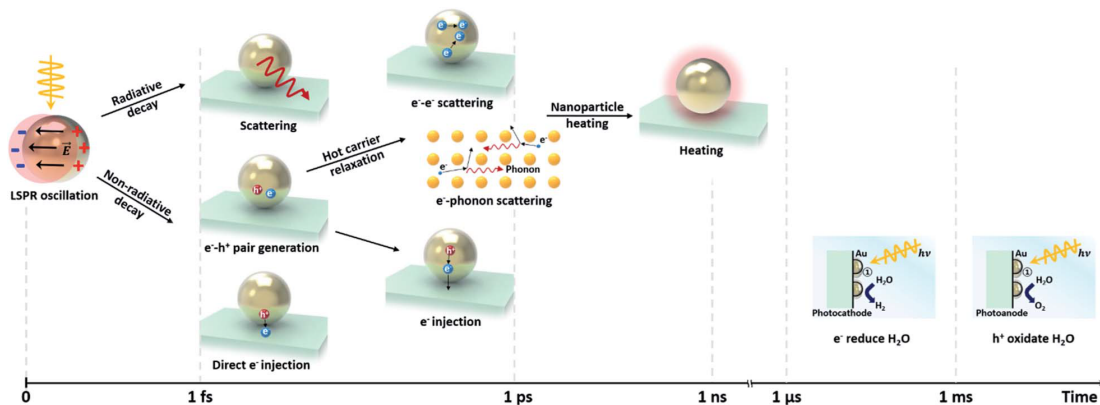


Figure 1.8: Schematic of the time scale of different plasmon decay processes induced by LSPR-excitation in a plasmonic NP/semiconductor system. (Extracted from [51]).

Extending the lifetime of charge carriers provides more time for them to be separated and collected before recombination occurs, which improves the efficiency of charge separation and collection. At the same time, more solar energy can be converted into electricity, reducing energy losses associated with the recombination of excitons. This, in turn, enhances the overall energy conversion efficiency in solar cells.

The Hot Electron Injection (HEI) mechanism involves the generation and transfer of high-energy electrons from plasmonic metal nanoparticles to an adjacent semiconductor. When light strikes these nanoparticles, it excites charge carriers, resulting in the generation of hot electrons through localized surface plasmon resonance (LSPR). These hot electrons possess energy greater than the metal's Fermi level.

After their generation, hot electrons can be transferred to a nearby semiconductor through the Schottky barrier formed at the metal-semiconductor interface. The efficiency of this transfer depends on the kinetic energy of the electrons and the alignment of the Fermi levels between the metal and the semiconductor. When the Fermi level of the semiconductor is higher than that of the metal, a Schottky barrier is created, allowing hot electrons with sufficient energy to overcome this barrier and inject into the semiconductor. Once in the semiconductor, these electrons contribute to generating electric current and driving photocatalytic reactions [24, 49, 51].

Plasmon-Induced Resonance Energy Transfer (PIRET) is a non-radiative process where

energy from plasmons in metallic nanoparticles is transferred to nearby semiconductor nanoparticles without requiring direct contact. The efficiency of PIRET depends on factors such as the distance between the particles and the spectral overlap between the localized surface plasmon resonance (LSPR) absorption of the metallic nanoparticles and the absorption band of the semiconductor. PIRET enables light absorption and charge separation in a semiconductor at energies below the band edge [24, 48, 49].

However, to fully leverage these benefits, it is essential to carefully optimize and balance various factors such as nanoparticle size, position, shape, stability, band bending and the interface properties between the metal and the semiconductor.

The location where plasmonic metal nanoparticles are placed on the photoanode is crucial and uniquely enhances the efficiency of solar cells. When positioned at the interface between the semiconductor and the electrolyte, the generation of charge carriers is enhanced. Placing the particles at the back interface, such as between the substrate and the semiconductor, can improve the transport capacity of the majority carriers in the semiconductors[50].

The interaction of light with photoanodes comprising semiconductors and gold nanoparticles results in various plasmonic mechanisms that can enhance the performance of photoelectrochemical cells. Figure 1.9 illustrates several hematite photoanodes with gold nanoparticles and the mechanisms that contribute to increased efficiency. Among the mechanisms mentioned in these studies are the Schottky junction and localized surface plasmon resonance (LSPR), hot electron injection (HEI) and plasmon-induced resonance energy transfer (PIRET) previously detailed.

Yanming and co-workers [52] synthesized a photoanode consisting of hematite nanorods with gold nanoparticles, demonstrating an increase in current density from 0.25 mA/cm^2 to 0.4 mA/cm^2 after the addition of the gold nanoparticles due to the reduced bulk recombination. This represents a 1.6-fold increase compared to pure hematite. Initially, the hydrothermal method was employed to grow $\beta\text{-FeOOH}$ films onto fluorine-doped tin dioxide substrates. The substrates with the solution were heated in an autoclave for 24 hours at 100°C . Subsequently, gold nanoparticles were deposited on the $\beta\text{-FeOOH}$ films using the sputtering deposition technique. The films were annealed at 750°C for about 30 minutes, with a heating ramp of 25°C/min to obtain $\alpha\text{-Fe}_2\text{O}_3/\text{Au}$. Various sputtering deposition times were explored, and it was determined that a nanoparticle size of 15 nm, obtained via sputtering, maximized the photocurrent.

Tonafallo et al. [53] synthesized a nanorod hematite photoanode with gold nanoparticles via the hydrothermal method for 1 hour at 100°C. The samples in the β -FeOOH (akaganeite) phase were then annealed at 750°C for 30 minutes with a heating ramp of 3°C/min to convert them into hematite nanorods. Subsequently, Au nanoparticles were incorporated via a dip coating method at different concentrations. Electrochemical tests revealed that lower concentrations of gold, corresponding to nanoparticles of 20 nm, led to higher photocurrents. These photoanodes showed an increase in current density from 0.82 mA/cm² to 1.2 mA/cm² after the addition of the gold nanoparticles. This improvement was attributed to the Schottky contact and Fermi level equilibration.

Another study by Khan et al. [54] revealed an improvement in the performance of a hematite nanorod photoanode with gold nanoparticles on its surface. There was an increase in photocurrent from 0.42 mA/cm² for bare hematite to 0.63 mA/cm² for hematite with gold, indicating a 1.5-fold improvement compared to pristine hematite. The onset potential of α -Fe₂O₃/Au was cathodically shifted by 70 mV compared to that of pristine hematite. The hydrothermal method was used for 6 hours at 95°C, followed by a two-step annealing process: 550°C for 1 hour, followed by another annealing at 800°C for 20 minutes to obtain hematite films. Gold was incorporated onto the surface of the photoanodes via photodeposition.

The results of these studies have demonstrated that the size of gold nanoparticles is a critical factor in improving photoelectrochemical performance. However, the impact of incorporating gold nanoparticles at different stages of hematite synthesis on photoelectrochemical performance, including onset and surface kinetics, requires further research. Therefore, these studies inspired us to develop photoanodes consisting of porous hematite nanowires with gold nanoparticles incorporated at different stages of the hydrothermal synthesis method.

The PVD sputtering technique was used to introduce gold nanoparticles into the photoanodes. Three series of photoanodes were fabricated:

- The first series involved the standard synthesis of hematite, followed by the incorporation of gold nanoparticles on the surface of the photoanode.
- The second series incorporated gold nanoparticles into the samples during the akaganeite phase, followed by a two-step annealing process.
- The third series involved depositing gold directly on the FTO substrate before proceeding with the usual hydrothermal procedure.

In all series, sputtering depositions were conducted for duration of 30 seconds, 120 seconds and 300 seconds.

This approach was designed to study how the structural order of applying the metal and semiconductor, as well as the size of the nanoparticles, influences the photoelectrochemical performance, specifically the onset potential and current density. The goal was to identify the configuration that best exploits the plasmonic characteristics.

By developing an efficient light-harvesting method capable of generating surface plasmons that intensified light absorption and the local electric field, this strategy aimed to boost the efficiency of the PEC cell.

1.3.3 Passivation layer

The use of passivation layers on hematite (as TiO_2 , and Al_2O_3) is a employed strategy to reduce the surface states of hematite that can act as electron recombination centres, thereby decreasing the recombination of electron-hole pairs at the surface states of hematite. This improves the efficiency of charge separation and transfer at the semiconductor-electrolyte interface and enhances the photoelectrochemical performance of solar cells [55].

Fu et al. reported that the addition of a TiO_2 layer by Pulsed Laser Deposition (PLD) on the surface of hematite nanowires facilitated the diffusion of hydroxyl ions (OH^-) to the electrolyte, improved the injection of holes into the electrolyte for the water oxidation reaction, reduced surface recombination, and allowed for an increase in current density from approximately 0.25 mA/cm^2 to approximately 0.5 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$.

Another study by Ahmed et al. also reported the beneficial effect of depositing a thin TiO_2 layer on top of hematite nanowires. It was observed that the photocurrent density increased from 0.27 mA/cm^2 from pristine hematite to 1.2 mA/cm^2 with the addition of TiO_2 overlayer. This improvement is attributed to the fact that TiO_2 passivates the surface states of hematite, thus reducing the probability of electron-hole recombination at these surface states and enhancing charge transfer.

Based on these studies, a new strategy was devised involving the deposition of a 5 nm TiO_2 layer directly onto surface of the ($\beta\text{-FeOOH}$) or ($\alpha\text{-Fe}_2\text{O}_3$) phase to investigate the effects of surface passivation through ion beam deposition. Additionally, gold nanoparticles were added to the surface to simultaneously passivate the hematite and leverage

the benefits of the gold nanoparticles, aiming to enhance solar absorption, inhibiting bulk and surface recombination.

Sample										Photoelectrochemical Performance					Reference
Photoanode	Gold position on photoanode	Nanostructure	Gold size (nm)	Mechanism	Hematite treatment		Gold treatment		Electrolyte	Plateau current (mA/cm ²)	On-set potential (V vs. V _{ref})	Illuminated area (cm ²)			
					Type	Time/ Temperature	Type	Time/ Temperature							
α-Fe ₂ O ₃ /Au	Surface of Hematite	Nanorod	≈ 20	Schottky contact and Fermi level equilibration	Hydrothermal (HT)	HT 1h at 100°C; Annealing 750°C 30 min	Dip coating (1%)	_____	1 M NaOH	1.2 at 1.23 V vs. V _{ref}	≈ 0.7	_____	doi.org/10.1021/acs.jpcc.9b11966		
α-Fe ₂ O ₃ /Au	Surface of Hematite	Nanorod	_____	_____	Chemical bath	HT 6h at 95°C; β-FeOOH layers sintered at 550°C 1h and calcinated for 20 min 800°C	Au photo-deposition	from 1.0 mmol/L HAuCl ₄ aqueous solution in 90 min at pH 3.0 under white led illumination	1 M NaOH	0.63 at 1.23 V vs. V _{ref}	≈ 0.83	0.25	_____		
α-Fe ₂ O ₃ /PI/Au	Surface of α-Fe ₂ O ₃ /PI	Nanorod	_____	SPR and high density of accumulated holes	Chemical bath and PI dipping	Hematite films modified with PI layer by dipping them in 0.5 M phosphate buffer solution for 60 min at pH=5.8; Annealing 350°C 1h	Au photo-deposition	from 1.0 mmol/L HAuCl ₄ aqueous solution in 90 min at pH 3.0 under white led illumination	1 M NaOH	1.32 at 1.23 V vs. V _{ref}	≈ 0.81	0.25	doi.org/10.1016/j.apscata.2022.18373		
α-Fe ₂ O ₃ /CoOx/Au	Surface of α-Fe ₂ O ₃ /CoOx	Nanoflower	≈ 10	SPR of gold and action of CoO _x as co-catalyst	Hydrothermal	HT with 0.01 M Co(NO ₃) ₂ ·6H ₂ O precursor solution 10h at 110°C; Note: The substrate is Nickel foam. Annealing 500°C 2h	Electrochemical reduction deposition	Electrodes immersed in the mixed solution of 8 mmol/L HAuCl ₄ and 0.1 mol/L KCl	1 M KOH	3.88 at 1.23 V vs. V _{ref}	_____	_____	doi.org/10.1016/j.jphotochem.2021.04.097		
α-Fe ₂ O ₃ /Au	Surface of β-FeOOH	Nanorod	15	Inhibited bulk recombination	Hydrothermal	HT 100°C 24 h to obtain β-FeOOH	Sputtering	100 s Au sputtering Annealing at 750 °C for 0.5 h with heating rate of 25°C/min	1 M NaOH	0.4 at 1.23 V vs. V _{ref}	≈ 0.8	0.785	_____		
α-Fe ₂ O ₃ /Au/TiO ₂	Surface of β-FeOOH	Nanorod	15	Reconstructed interfaces	Hydrothermal	HT 100°C 24 h; TiO ₂ overlayer was deposited using pulsed laser deposition (PLD) after gold sputtering	Sputtering	100 s Au sputtering Annealing at 750 °C for 0.5 h with heating rate of 25°C/min	1 M NaOH	1.05 at 1.23 V vs. V _{ref}	≈ 0.8	0.785	doi.org/10.1016/j.jphotochem.2019.118206		
Ti-Fe ₂ O ₃ /Au	Surface of Ti-Fe ₂ O ₃	Nanorod	10-50	Direct contact, SPR	Hydrothermal	HT 100°C 12h; Annealing 550°C 2h	Sodium citrate reduction; Drop penetration	Sodium citrate reduction method, Au NPs were dropped onto Ti-Fe ₂ O ₃ photoanodes. Annealing at 350°C 0.5h.	1 M NaOH	0.6 at 1.23 V vs. V _{ref}	0.8	0.28	_____		
Ti-Fe ₂ O ₃ /Al ₂ O ₃ /Au	Surface of Ti-Fe ₂ O ₃ /Al ₂ O ₃	Nanorod	10-50	Passivation / PIRET and SPR	Hydrothermal	HT 100°C 12h; Annealing 550°C 2h; ALD: 15 cycles at 200°C Al ₂ O ₃ Annealing 550° 0.5h	Sodium reduction; Drop penetration	Sodium citrate reduction method, Au NPs were dropped onto Ti-Fe ₂ O ₃ /Al ₂ O ₃ photoanodes. Annealing at 350°C 0.5h	1 M NaOH	1.5 at 1.23 V vs. V _{ref}	0.8	0.28	doi.org/10.1002/cssc.201701679		
α-Fe ₂ O ₃ /Au	Surface of α-Fe ₂ O ₃	Nanorod	20-50	PIRET	Hydrothermal	HT 100°C 6h; Annealing 800°C 20 min	Electrodeposition	Electrodeposition using a HAuCl ₄ solution	1 M NaOH	≈ 1 at 1.23 V vs. V _{ref}	≈ 0.78	_____	_____		
α-Fe ₂ O ₃ /Au/FeOOH	Surface of α-Fe ₂ O ₃	Nanorod	20-50	PIRET	Hydrothermal	After gold electrodeposition the photoanode was immersed in a heated (100°C) solution of FeCl ₃ ·6H ₂ O and 1 M NaNO ₃	Electrodeposition	Electrodeposition using a HAuCl ₄ solution	1 M NaOH	2 at 1.23 V vs. V _{ref}	≈ 0.7	_____	doi.org/10.1016/j.jphotochem.2024.103737		
α-Fe ₂ O ₃ /Au	Embedded	Compact film	48	_____	Spray pyrolysis	Pre-heated 550°C; Sprayed 30 mL of solution; Annealing 450°C 5 min	Citrate reduction of HAuCl ₄ ; Flame Aerosol	Thermoporesis deposition	1 M NaOH	≈ 0.08 at 1.23 V vs. V _{ref}	≈ 1	_____	doi.org/10.1021/nl1022354		
α-Fe ₂ O ₃ /Au	Surface of α-Fe ₂ O ₃	Platelets	45	_____	Spray pyrolysis	Pre-heated 540°C; Sprayed 8 hours	Flame Aerosol	Thermoporesis deposition	1 M NaOH	≈ 0.95 at 1.23 V vs. V _{ref}	≈ 0.84	_____	_____		
Fe ₂ O ₃ /Au/Al ₂ O ₃	Surface of α-Fe ₂ O ₃	Nanowires	10	LSPR; Surface passivation by Al ₂ O ₃ ; Schottky junction	Electrodeposition; Atomic layer deposition (ALD)	Electrodeposition of Fe on FTO; Annealing 150°C 2h; Annealing 520°C 4h heating ramp of 2°C/min ALD of Al ₂ O ₃	Sputtering	Sputtering; Annealing 300°C 1h	1 M KOH	≈ 0.55 at 1.23 V vs. V _{ref}	≈ 1	_____	doi.org/10.1186/s11671-015-10772-y		
α-Fe ₂ O ₃ /Au	Surface of α-Fe ₂ O ₃	Nanoflake	5-10	SPP modes in the Au NPs and improvement of electrical contacts	Thermal Oxidation iron foil	Thermal Oxidation iron foil (500°C 10-15 min in air)	Preparation of solution of gold chloride hydrate (HAuCl ₄); Dip	Immersion of photoanode in HAuCl ₄ aqueous solution 6 h	1 M KOH	1 at 1.23 V vs. V _{ref}	0.6	_____	doi.org/10.1002/cssc.201403013		
α-Fe ₂ O ₃ /Au	Surface of α-Fe ₂ O ₃	Columnar thin films	8-40	LSPR; Better surface charge transfer	Electron beam evaporation	Evaporating Fe metal under O ₂ environment ontoFTO; Annealing 600°C 4h heating ramp 5°C/min	Drop casting; Spin coating	Drop casting of HAuCl ₄ ·H ₂ O (5 mM) onto hematite films; Spin coating 500 rpm 30 s and 2000 rpm 1 min; Annealing 60°C 1 min/ 200°C 10 min	1 M NaOH	1.75 at 1.23 V vs. V _{ref}	0.62	_____	doi.org/10.1002/cssc.201802860		

Figure 1.9: State of the art of Hematite with gold nanoparticles.

2. Experimental and Characterization techniques

This chapter presents the materials, synthesis techniques, and characterization methods used for the photoanodes synthesized throughout this thesis. First, the materials employed in the synthesis of the photoanodes are described, followed by a detailed explanation of the synthesis methods utilized. Subsequently, the characterization techniques applied to analyze the morphology, optical properties, structure, and photoelectrochemical performance of the photoanodes are discussed.

2.1. Materials

Two types of transparent conductive oxide (TCO) substrates from Solaronix company were used for sample synthesis:

- Glass substrates coated with fluorine-doped tin oxide (FTO), with a thickness of 2.2 mm and a resistivity of $7 \Omega/\text{sq}$, were used for calibrating the size of gold nanoparticles synthesized by sputtering.
- FTO coated glasses substrates with a thickness of 1.1 mm and a resistivity of $10 \Omega/\text{sq}$ were employed in the synthesis of hematite photoanodes, as they can resist the higher temperatures required for hematite synthesis.

For cleaning the substrates, the following chemical products were used:

- CH_3COCH_3 , Acetone (Fisher Scientific, $\geq 99.8\%$);
- $\text{C}_2\text{H}_6\text{O}$, Ethanol (Fisher Scientific, $\geq 99.8\%$);
- Detergent (Labkem).

The following reagents were used for hydrothermal synthesis of $\alpha\text{-Fe}_2\text{O}_3$:

- $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Iron (III) Chloride Hexahydrate (Acros Organic, $+99\%$);
- FeCl_3 , Iron (III) Chloride (Sigma-Aldrich, 97%);
- NaNO_3 , Sodium Nitrate (Sigma-Aldrich, $\geq 99.0\%$);
- HCl , Hydrochloric Acid (Fisher-Scientific, 37%).

For the gold sputtering, a target of gold with a diameter of 73 mm and a thickness of 0.1 mm was used.

2.2. Synthesis Methods

For the successful synthesis of photoanodes, washing, cleaning, and pre-treatment of the fluorine-doped tin oxide (FTO) glass substrates are essential.

The FTO substrates, measuring 1.23 cm x 2.5 cm, are first scrubbed and washed with acetone, followed by detergent. They are then placed in an ultrasonic bath with detergent for 10 minutes, rinsed with deionized water, and cleaned again in pure ethanol using ultrasonic cleaning for 10 minutes. This process is repeated with detergent and pure ethanol, each followed by rinsing in deionized water. Finally, the substrates undergo a 20-minute ultrasonic bath in deionized water to ensure complete residue removal.

After the washing was completed, the samples were placed vertically on top of laboratory paper, supported in a small beaker, and covered with a larger beaker to allow them to dry while avoiding potential contamination.

Following the substrates are properly cleaned and dried, Kapton tape is applied to completely cover the non-conductive part of the glass FTO substrate and the upper edge of the conductive part (1.23 cm x 0.5 cm), ensuring that the FTO maintains good electrical contact for subsequent electrochemical measurements. In this way, the samples are ready for both hydrothermal synthesis and sputtering techniques described in the upcoming subsections.

2.2.1 Hydrothermal Method

The hydrothermal method is often used as a hematite synthesis method because it is cost-effective, user-friendly, and scalable technique. In this approach, a solution containing a precursor is prepared with the addition of salts or other ionic compounds to enhance the solution's ionic strength [56]. The pH of the solution is adjusted to minimize premature precipitation of the precursor. The prepared solution is then transferred into a Teflon container, which is covered by a stainless-steel sealed autoclave, and subjected to high temperatures and pressures in a heating chamber. Under these conditions, the substances that are poorly soluble or insoluble under normal circumstances can be dissolved and recrystallized effectively [57].

In this thesis, different precursors were used at different times. Initially, hematite photoanodes were synthesized using the precursor iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). However, due to the depletion of this reagent and the difficulty in obtaining more in useful time, the synthesis of photoanodes continued using the precursor iron (III) chloride

(FeCl₃).

Two TCO substrates (1.1 mm thick, 10 Ω/sq), after being thoroughly cleaned, dried, and having Kapton tape properly applied, are then positioned at an angle such that their lower edges touch at the central axis of the container and their upper edges are in opposite walls, with the conductive surfaces facing the walls of the Teflon container. This orientation is favourable to the formation of hematite nanowires due to the movement of convection currents within the container. The teflon container was filled with 20 mL of a chemical solution composed of 0.15 M FeCl₃ · 6H₂O and 1 M NaNO₃.

Sodium nitrate salt (NaNO₃), which has high ionic strength, was used in the solution to increase the surface charge density and reduce the interfacial tension between the solution and the crystals being formed. When FeCl₃ · 6H₂O was substituted for FeCl₃, the concentration of FeCl₃ was adjusted to 0.15 M by accurately calculating the required mass of FeCl₃, accounting for the difference in molar masses between the two compounds.

The solution was adjusted to pH 1.5 using 56 µl of hydrochloric acid (HCl at 37%) as described by Quiterio et al. to reduce iron precipitation.

Finally, the Teflon container was sealed within the autoclave, which was then placed in a heating chamber at 95°C for 4 hours to synthesize the akaganeite phase (β-FeOOH) on the substrate, following the protocols outlined by Quiterio et al. and Ling et al..

The temperature gradient created inside the autoclave generates convection currents that facilitate the transport of dissolved ions or molecular groups in the hydrothermal solution. As the solution is heated, the metallic precursor, being denser, settles at the bottom of the autoclave [60]. The thermal gradient dissolves the metallic solute in the hotter region and transports the solution by convection currents to the cooler upper region. In this cooler region, the solubility of the solute decreases, resulting in the formation of a supersaturated solution. Due to this supersaturation, the solute begins to crystallize, forming small crystalline nuclei. As ions or molecules reach the growth interface, they are adsorbed and incorporated into the crystal structure, contributing to the formation and growth of additional crystals [57].

In the next subsection, the thermal annealing required for the synthesis of hematite (α-Fe₂O₃) nanowires will be discussed.

2.2.2 Thermal Annealing

Annealing treatments are widely used to induce structural changes in materials such as semiconductors. Precise control of the annealing temperature and time promotes the formation of new phases, improves the crystallinity of the materials, and can also lead to the formation of controlled defects [27].

In the case of synthesizing hematite photoanodes deposited on FTO-coated glass substrates, thermal annealing is crucial for converting the intermediate (β -FeOOH) phase, which forms during the hydrothermal method, into the final crystalline (α -Fe₂O₃) phase. Additionally, the high temperature (750-800°C) promotes the diffusion of Sn⁴⁺ ions into the hematite. This diffusion increases the donor electron density [58], which enhances the material's electrical properties and reduces surface defects. Consequently, this helps to minimize surface recombination, improving the overall efficiency of the photoanodes.

In this thesis, two ovens were used (fig. 2.1) with different specifications due to the initial oven being damaged. As a result, adjustments were made to the heating ramps to accommodate the characteristics of the second oven, ensuring the continuation of the photoanode synthesis.

The differences between the samples prepared with each oven are clearly documented and identified throughout the thesis. Given the variations in sample characteristics and applied thermal treatments, the specific experimental procedures will be detailed in the following chapter.

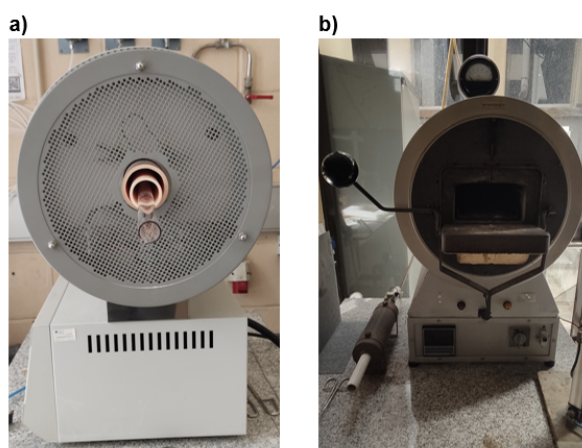


Figure 2.1: a) Initial and b) second furnace for thermal annealing.

2.2.3 Sputtering

Sputtering is a physical vapor deposition technique based on the bombardment of atomic particles resulting from the ionization of an inert gas, typically argon, to strike a target and eject several target atoms, which will then deposit onto a substrate. This gas is used because it is inert, meaning it does not chemically react with the target material.

For incorporating gold nanoparticles into the samples synthesized throughout the thesis, gold ion sputtering was used with a BOC Edwards Scancoat Six Sputter Coater, coupled with an Edwards RV3 Rotary Vane Vacuum Pump. In this process, argon was used, and the working pressure was maintained at approximately 2.3 bar. Sputtering was performed only after the chamber was properly evacuated. All depositions were conducted with a current of around 20 mA and a voltage of approximately 1 kV.

2.2.4 Ion Beam Deposition (IBD)

The IBD process is an efficient method for the fabrication of thin films, allowing the use of various materials for both the target and the substrate. In IBD, an ion source generates a beam of ions, typically argon, which is collimated and accelerated within the vacuum chamber and directed at the target. This ion beam collides with the atoms from the target and removes them, which are then deposited onto the substrate. The plasma generated is primarily confined to the ion gun, preventing direct exposure of the substrate and ensuring precise control of the ion energy. This results in the formation of homogeneous thin films with precise and controlled thicknesses, in an environment free from unwanted chemical reactions.

For this study, a 5 nm layer of titanium (Ti) was deposited onto the surfaces of β -FeOOH and α -Fe₂O₃ photoanodes at room temperature using a CEMUP-MNTEC deposition system from Commonwealth Scientific Corporation. The deposition took place in an ISO-7 clean room, maintaining a base pressure of less than 5×10^{-7} Torr. The deposition process was performed under an argon (Ar) flow of 5 standard cubic centimetres per minute (sccm) and a deposition pressure of 1.4×10^{-4} Torr.

2.3. Characterization techniques

The photoanodes were characterized in terms of their morphology, optical properties, structural properties, and photoelectrochemical performance.

2.3.1 Morphological characterization: Scanning Electron Microscopy

The Scanning Electron Microscope (SEM) is a powerful tool for high-resolution morphological analysis of nanostructures. It provides detailed topographic imaging and cross-sectional views through the detection of secondary electrons (SE) and backscattered electrons (BSED), enabling comprehensive surface and compositional characterization.

The SEM operates under high vacuum conditions to prevent the electrons from scattering due to interactions with air molecules, ensuring high-resolution images. An electron source generates electrons, which are then accelerated using a specific voltage. These high-energy electrons are concentrated into a fine beam by magnetic lenses and are meticulously aimed at a small area on the surface of the sample. This electron beam scans the surface of the specimen [61]. The interaction of the electron beam with the sample results in the emission of electrons and photons from the surface. These emitted signals are collected by detectors, and the intensity of these signals is used to construct the SEM image. Variations in brightness and contrast in the image correspond to different surface features and characteristics of the sample. Secondary electrons, which have energies less than 50 eV, are emitted due to inelastic collisions between the primary beam electrons and those on the surface of the sample [62]. These electrons are useful for analysing the surface layer of the sample, typically within a depth of about 1 to 10 nm. In contrast, backscattered electrons (BSED), with energies above 50 eV, result from elastic collisions between the primary electrons and the atomic nuclei of the sample [62–64]. These backscattered electrons images are highly sensitive to the atomic numbers of the elements within the sample. Elements with higher atomic numbers, having more positively charged nuclei, scatter more electrons, resulting in increased brightness in the image and providing better contrast for variations in sample composition.

In this study, SEM was employed to characterize samples using both top view mode with secondary and backscattered electrons, as well as cross-sectional views to determine the thickness of photoanodes. The analysis was conducted with a FEI Quanta 400 FEG high-resolution scanning electron microscope at the Materials Centre of the University of Porto (CEMUP). To prepare the samples for SEM, a piece of carbon tape was placed on

the side of the sample without hematite to minimize charge accumulation on the surface, which could otherwise cause image drift. The top view mode utilizing secondary electrons was used to measure the diameter of nanowires, while the backscattered electron mode was employed to assess the diameter of gold nanoparticles. This approach leverages the fact that gold (atomic number $Z = 79$) has a significantly higher atomic number than iron in hematite ($Z = 26$), enhancing the contrast between the elements in the photoanodes and making gold nanoparticles more visible in this mode. Measurements of the obtained images were conducted using ImageJ software.

2.3.2 Optical characterization: UV-Vis Spectroscopy

To investigate the optical properties of the developed photoanodes, the reflectance and transmittance percentages were measured using a UV-Vis spectrometer in the range of 250 to 700 nm. Measurements were performed with two different instruments: the UV-VIS T-70 spectrometer and the Jasco V-650 spectrometer.

For transmittance measurements with the UV-VIS T-70, it was necessary to create a custom sample holder so that the sample could fit into the original motorized sample compartments of the equipment. For reflectance measurements, it was required to replace the transmittance device with the MR181-1 specular reflectance measurement device. However, this device is only suitable for smooth, polished surfaces as it measures only the light reflected in the same direction as the incidence angle, which in this case is 5° . Given that the samples consist of nanostructured thin films with rough surfaces, it is crucial to collect light reflected in all directions. Therefore, using an integrating sphere is more appropriate than a specular reflectance optical measurement device. To address this issue, the UV-VIS Jasco spectrometer was used, which allows for accurate measurement of both reflection and transmission spectra.

Reflectance (R) and Transmittance (T) were measured for the photoanodes as well to the FTO. The Absorbance (A) was calculated by the following formula:

$$A = 100 - T - R \quad (2.1)$$

The absorbance of photoanodes was corrected by subtracting the contribution of the FTO substrate. These measurements were also used to evaluate the optical band gap properties of the semiconductor materials, derived from Tauc plots, with the assistance of

cross-sectional measurements obtained via SEM:

$$\alpha h\nu = B \cdot (h\nu - E_g)^n \quad (2.2)$$

where h is the Plank's constant, $h\nu$ is the incident photon energy (in eV), α is the absorption coefficient, E_g is the optical band gap energy (in eV), and B and n are constants dependent on the type of electronic transition.

The absorption coefficient can be obtained by manipulating the Beer-Lambert law, resulting in the equation:

$$\alpha = \frac{2.303 \times A}{t} \quad (2.3)$$

where t is the thickness of photoanode and A is the absorption. For direct allowed transitions $n = 1/2$ and for indirect allowed transitions $n = 2$ [65]. In hematite, indirect transitions are considered to determine its band gap.

2.3.3 Structural characterization: X-Ray Diffraction

X-ray diffraction (XRD) is a nondestructive materials characterization technique used to obtain detailed information about the crystalline structure of a sample. It enables the identification of crystalline phases, determination the preferred orientation of the crystals, calculation of the degree of crystallinity, the size of crystallites, the microstrain and the lattice parameters of the unit cell [66]. From XRD, it is possible to obtain the diffraction pattern of a crystalline material, which is unique and can be used to crystalline phase identification.

When x-ray beams interact with electrons in the sample, interference and diffraction of the beams occurs. If the interference is destructive, no diffraction peaks are observed. However, if the interference is constructive, diffraction peaks will appear at specific angles (θ), which are determined by the distance between the crystalline planes of the sample (d_{hkl}). This relationship is described by Bragg's Law:

$$n \lambda = 2d_{hkl} \sin (\theta) \quad (2.4)$$

where λ is the wavelength of the X-ray, d_{hkl} is the distance between the crystal planes, θ is the angle of incidence (and diffraction), and n is an integer representing the order of

diffraction.

The X-ray diffraction (XRD) analysis was conducted to structurally characterize the synthesized photoanodes using a SmartLab Rigaku® diffractometer. The setup involved a copper Cu K α radiation with a wavelength (λ) of 1.540593 Å, and the anode x-ray tube was operated at 45 kV and 200 mA. The diffractometer was set to operate in parallel beam mode with a grazing incidence angle to minimize the FTO substrate's contribution to the final diffractogram. A scan was performed in the 2 θ mode with a range from 20° to 80°, using a step size of 0.02°. The acquisition time was set to 0.5°/min to reduce signal noise and obtain higher detail in the diffraction patterns.

2.3.4 Photoelectrochemical characterization

Photoelectrochemical measurements (***j*-V curves**) were conducted at room temperature on hematite nanowires photoanodes, with and without gold deposition, using a cappuccino-type photoelectrochemical cell with an illuminated surface area of 0.528 cm². Measurements were carried out both in the dark and under simulated sunlight equivalent to 1 sun (100 mW/cm²), using a 150 W xenon lamp from Oriel, Newport, calibrated with a silicon photodiode (c-Si).

In the three-electrode configuration, the photoanode was used as the working electrode, a platinum wire was used as the counter electrode, and an Ag/AgCl electrode saturated with KCl was used as the reference electrode (RE). All the electrodes were submerged in a 1.0 M NaOH electrolyte solution (pH = 13.6). The measurements were made in front-illumination mode, with the hematite nanowires oriented towards the light source. Data acquisition was performed with Zennium potentiostat, using Thales software, at the Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE). The potential was scanned at a rate of 10 mV/s. A higher current density (*j*) is associated with a greater rate of hydrogen generation, while a lower onset potential (V_{Onset}) indicates that less energy is required to initiate the redox reactions. This can improve the efficiency of the photoelectrochemical cell, reducing reliance on a high-power external energy source. The measured potentials were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E_{Ag/AgCl}^0 \quad (2.5)$$

where E_{RHE} is the converted potential vs. RHE, pH is the pH of the electrolyte, $E_{Ag/AgCl}$ is the potential measured experimentally against the reference Ag/AgCl electrode and $E_{Ag/AgCl}^0 = 0.1976$ V at 25 °C.

Since the software already accounts for the $E_{Ag/AgCl}^0$ value, the potential referenced to the reversible hydrogen electrode (RHE) was calculated by adding the value read from the Thales software to $0.059 \times pH$.

Additionally, **photocurrent density-wavelength (j - λ) curves at a fixed potential** were performed to evaluate how the incorporation of gold in the different strategies employed affected the photoresponse in the wavelength range corresponding to the plasmonic resonance of gold. These measurements were carried out using a 150 W continuous-wave xenon lamp, in conjunction with a computer-controlled monochromator from the Aminco Bowman Series 2 luminescence spectrometer [67]. Scanning was conducted over wavelengths ranging from 300 nm to 700 nm, with a scanning speed rate of 10 nm/s. Measurements were performed at a potential of 1.45 V vs. V_{RE} . During the measurements, a three-electrode configuration was also used, and the electrolyte was also 1 M NaOH.

Electrochemical Impedance Spectroscopy and Photoelectrochemical Impedance Spectroscopy measurements were performed under dark and simulated sunlight conditions, respectively, to evaluate the electrical properties of the photoanodes. An anodization cell with a three-electrode configuration was used. The anodization cell contained 1 M NaOH electrolyte. The working electrode was connected to the base of the anodization cell, the counter-electrode was the upper pin of the anodization cell, and the Ag/AgCl reference electrode had a portion submerged in the 1 M NaOH electrolyte. The BioLogic SP-150 potentiostat (Bio-Logic, Seyssinet-Pariset, France) was used for the measurements, which were conducted at 1.45 V versus the reference electrode (RE). A sinusoidal perturbation with an amplitude of 10 mV was applied, and the frequency range was swept from 0.1 Hz to 1 MHz. The magnitude of the modulation signal was 10 mV. An electrical equivalent circuit was then fitted to the EIS spectra using EC-Lab software.

3. The role and optimization of plasmonic gold nanoparticles at different stages of hematite synthesis

In this chapter, we investigated how the different sizes and deposition locations of gold nanoparticles on hematite photoanodes affect their photoelectrochemical performance. We explored how the plasmonic effect of gold enhances photocurrent, as gold can alter light interaction on the photoanode surface.

3.1. Gold calibration

Initially, a study was conducted to calibrate gold deposition by sputtering onto FTO in order to obtain gold nanoparticles of different sizes by varying the deposition time: 30, 60, 90, and 120 seconds. Figure 3.1 represents the calibration study of gold deposition by sputtering.

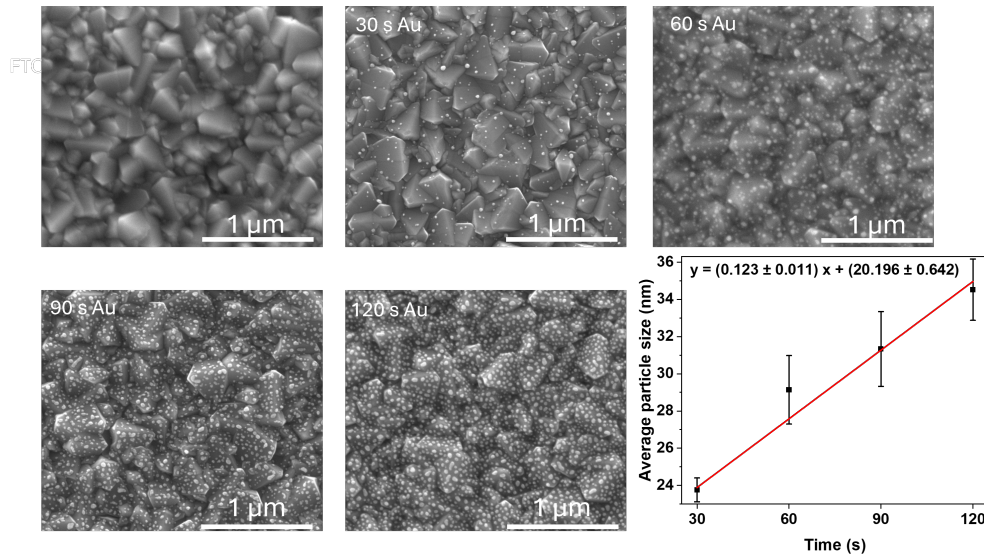


Figure 3.1: Secondary electron images used to calibrate the gold nanoparticle size via sputtering.

Due to the minimal variation observed in the size of gold nanoparticles, ranging from 23.76 nm for 30 seconds to 34.52 nm for 120 seconds, it was decided to extend the gold deposition time to 300 seconds. Tuning the gold particle size is important because, with the increase in particle size from 20 to 80 nm, the SPR shifts from 520 to 550 nm, resulting in a redshift that contributes to the increased absorption of solar light [68].

This change was made with the aim of achieving a more precise control over the morphology of the gold, whether as nanoparticles or continuous films, allowing for a more detailed study of the impact of different deposition times on the morphology of gold deposited onto the transparent conductive oxide (TCO) substrate. The study aims to understand how increasing the deposition time alters the morphology of gold and the resulting properties of the films or nanoparticles.

Therefore, deposition times of 30, 120, and 300 seconds were chosen to apply a post-thermal annealing of 370°C. This thermal annealing was performed to promote the formation and coalescence of gold nanoparticles, as the increased atomic mobility during annealing allows gold atoms to diffuse and reorganize into energetically favourable configurations, such as spherical shapes [69–71].

Observing the SEM images in figure 3.2 it was concluded that the addition of 370°C 1 hour annealing induces significant differences in the dispersion of the gold. The gold nanoparticles with annealing aggregated and coalesced, resulting in increase in their size with longer sputtering deposition times.

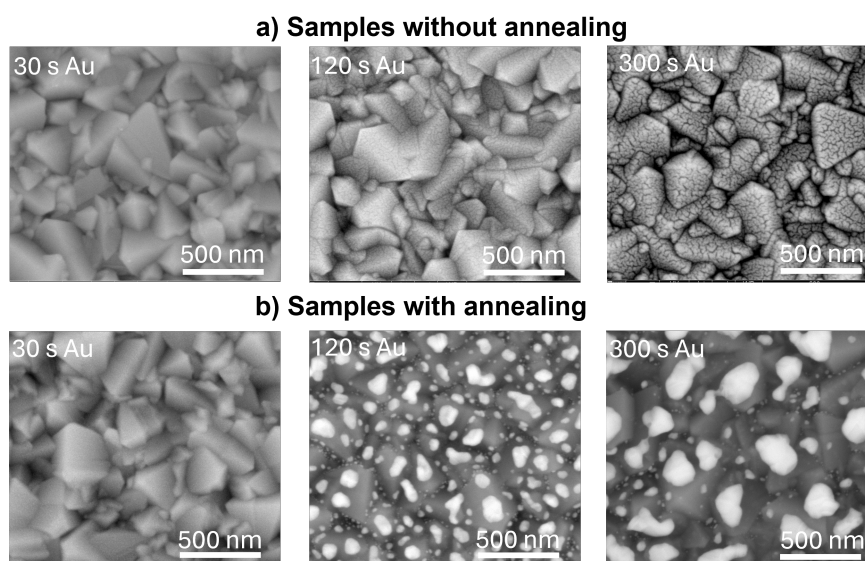


Figure 3.2: SEM (Secondary electron) images used to calibrate the gold nanoparticle size via Au sputtering for different times (30, 120, and 300 seconds): a) before and b) after annealing. This annealing process enables the formation of gold nanoparticles.

3.2. Experimental details on the fabrication of photoanodes using different approaches of integrating Au nanoparticles

With the aim of exploring the functional properties of gold nanoparticles of different sizes, incorporated at distinct stages of the synthesis of hematite nanowires for photoanodes, distinct synthesis methods were developed. For each method, three photoanodes were fabricated, each utilizing a different gold deposition time by sputtering (30, 120, and 300

seconds). All the synthesized photoanodes are based on FTO substrates (1.1 mm thick, 10 Ω/sq) that were duly washed and cleaned, with Kapton tape applied to ensure that, at the end of the synthesis, the electrical contact of the FTO was preserved, which is essential for electrochemical analyses, as described in chapter 2.

In **Series 1** the samples were subjected to the hydrothermal process as described in chapter 2. The first step of hydrothermal process resulted in $\beta\text{-FeOOH}$. The precursor used in the synthesis of these photoanodes was $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. These samples were then two-step thermally annealed in furnace 1 at 550°C for 2 hours with a heating ramp of 10°C/min, followed by a rise to 800°C at 8°C/min for 20 minutes to obtain the hematite nanowires. After that, gold was sputtered onto the hematite nanowires.

In **Modified Series 1** the hydrothermal treatment was performed as in series 1 using FeCl_3 as precursor. The two-step thermal annealing was performed using furnace 2 with a heating ramp of 5°C/min. Then gold was sputtered onto the hematite nanowires. An additional annealing at 370°C for 1 hour at a heating rate of 5°C/min was conducted to create and increase the gold nanoparticles size (as previously observed in figure 3.2). This additional annealing was also applied to improve gold adhesion to hematite [41] and prevent the disaggregation of gold nanoparticles on the surface, observed during electrochemical measurements in a 1 M NaOH solution without this thermal treatment.

Samples from Series 2 and 3 were also prepared using FeCl_3 as the reagent and subjected to thermal annealing in Furnace 2.

In **Series 2** the gold was incorporated in the $\beta\text{-FeOOH}$ phase by sputtering, followed by a two-step thermal annealing to form hematite nanowires.

In **Series 3** the gold was directly incorporated onto the substrates by sputtering. After that, these samples were subjected to the hydrothermal method previously mentioned, followed by a two-step thermal annealing.

Bare Hematite	H
Series 1 (Hematite/Au)	H/30 s Au H/120 s Au H/300 s Au
Modified Series 1 (Hematite/Au + Annealing 370°C 1h)	H/30 s Au H/120 s Au H/300 s Au
Series 2 ($\beta\text{-FeOOH}$ /Au + 2 step annealing)	FeOOH/30s Au FeOOH/120s Au FeOOH/300s Au
Series 3 (Au/ Hematite)	30 s Au/H 120 s Au/H 300 s Au/H

Figure 3.3: Nomenclature of photoanodes synthesized according to the strategies outlined in the previously described series.

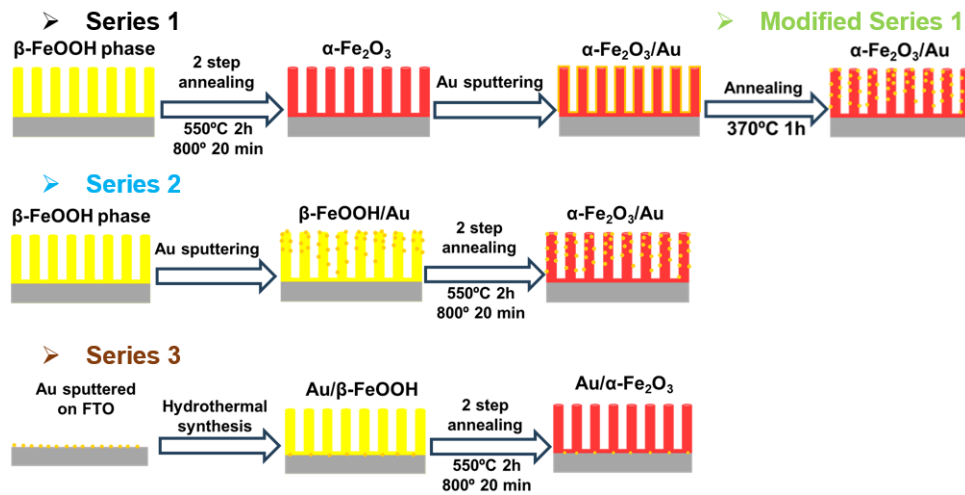


Figure 3.4: Scheme with the different proposed synthesis strategies.

3.3. Results and Discussion

3.3.1 Morphological characterization

SEM analysis was used to study the morphology of the different photoanodes produced. Figure 3.5 shows significant differences between series 1, without thermal annealing after sputtering gold deposition, and modified series 1, which was subjected to thermal annealing at 370°C for 1 hour after gold deposition.

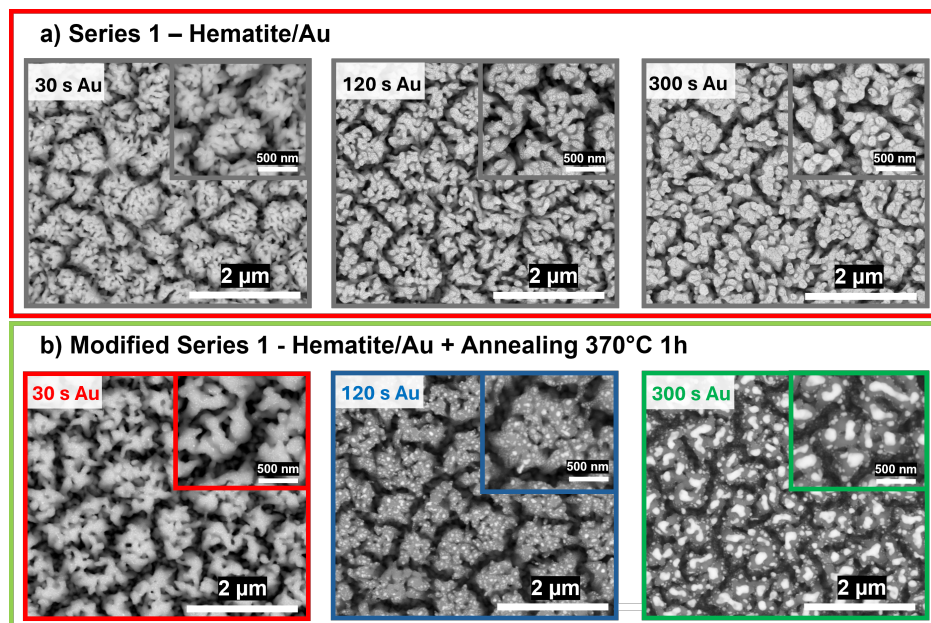


Figure 3.5: SEM (backscattered electron) images of series 1 and modified series 1 ($\alpha\text{-Fe}_2\text{O}_3/\text{Au}$) photoanodes. a) Images of synthesized photoanodes without gold post-annealing; and b) after annealing, for the different samples with different gold sputtering time. Insets provide a magnified view of the photoanode morphology.

In Series 1, we observed images of three samples after gold deposition at different times: 30, 120, and 300 seconds. All the samples exhibited uniform hematite nanowires. For the shortest sputtering time (30 seconds), only a few widely spaced nanoparticles were formed. With longer sputtering times, the hematite nanowires were uniformly covered by thin, highly “granular” gold films.

In modified Series 1, we observed images of three samples after the same time deposition intervals of gold, followed by thermal annealing of the gold. After this post-annealing treatment of gold, we observed the formation of Au nanoparticles due to film coalescence. These nanoparticles aggregated, coalesced, and increased in size with longer deposition times. The contrast between the gold nanoparticles and the hematite nanowires is evidenced by the increased brightness of the gold nanoparticles.

From this point in the thesis, the analyses and characterizations focused on the modified Series 1, Series 2, and Series 3 samples.

In figure 3.6 we verified that in modified series 1 (Hematite/Au + annealing 370°C 1h) with increasing sputtering deposition time the size of the gold nanoparticles increases considerably from 15.1 ± 5.5 nm for 30 s of gold deposition to 61.9 ± 43.8 nm for 300 s of gold deposition. Additionally, a rise in the standard deviation is observed, indicating a greater dispersion in the size of the gold particles with increasing sputtering time.

For the series 2 (β -FeOOH/Au + 2 step annealing), the same trend is observed: increasing the sputtering time from 30 to 120 seconds the nanoparticles average size also increases, from 21.2 ± 6.9 nm to 50.0 ± 16.4 nm, respectively.

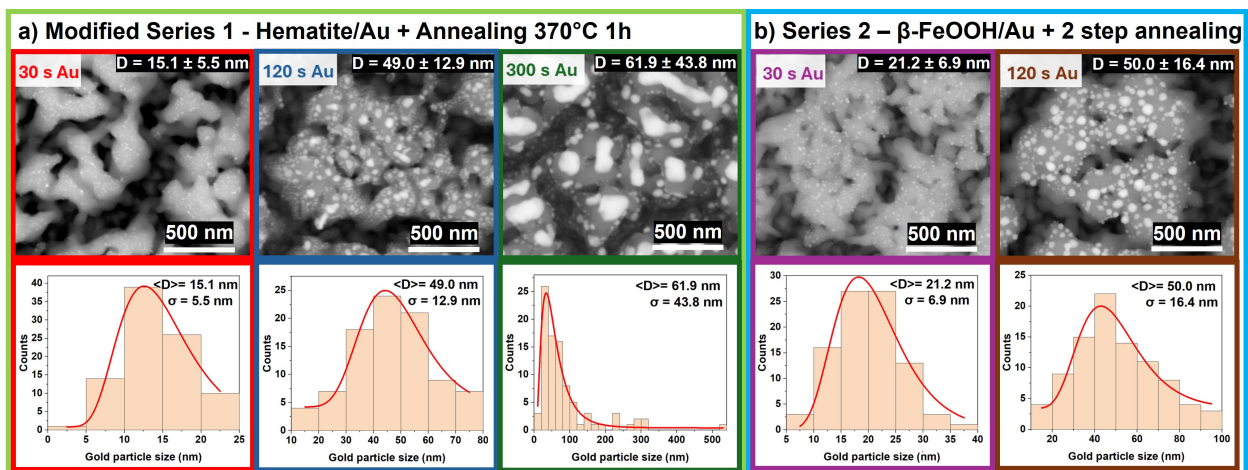


Figure 3.6: High-magnification SEM (backscattered electron) images of the photoanodes belonging to: a) modified series 1 (Hematite/Au + Annealing 370°C 1h); and b) series 2 (β -FeOOH/Au + 2 step annealing), for different gold sputtering times. Statistical analysis of the size distribution of gold nanoparticles in each sample is presented, along with histograms, lognormal distribution fitting, and the resulting average size.

We can conclude that regardless of whether the nanoparticle deposition strategy is applied using modified series 1 or series 2, the size of the nanoparticles is approximately the same. Since the samples from Series 3 do not have gold on their surface, they are not included in figure 3.6, as it is not possible to observe gold nanoparticles using SEM.

The surface porosity of the synthesized photoanodes was estimated by performing SEM image processing analyses with ImageJ software [72, 73], using secondary electron mode images in top view at 50000x magnification (see figure 3.7). The porosity (%) was obtained by determining the fraction of the area corresponding to the empty spaces present on the surface of the photoanodes. Details of this method are found in appendix A.

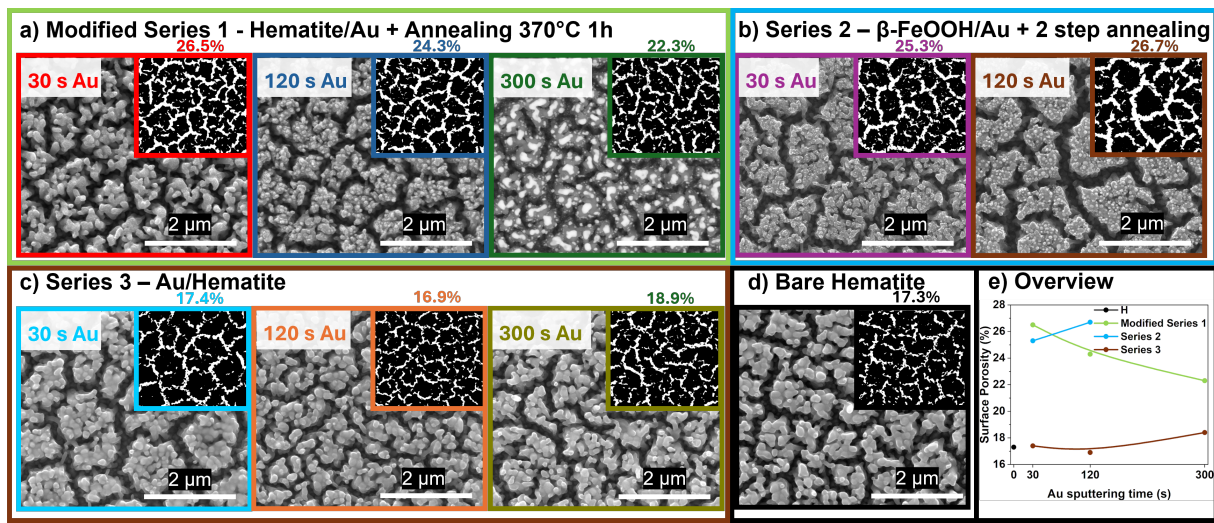


Figure 3.7: SEM (secondary electron) images at a magnification of 50000 times of a) modified series 1 (α -Fe₂O₃/Au) photoanodes; b) series 2 (β -FeOOH/Au + 2 step annealing) photoanodes; and c) series 3 (Au/ α -Fe₂O₃) photoanodes, for different gold sputtering times; and d) bare hematite photoanode. Image e) represents the behavior of porosity as a function of gold sputtering time. Insets show threshold-adjusted images for determining porosity, with white areas indicating porous regions as well as the respective percentage of porosity.

Compared to the bare hematite sample used as a control, it is observed that gold deposited on the surfaces of both the α -Fe₂O₃ phase (modified Series 1) and the β -FeOOH phase (Series 2) increases the voids present in the samples, whereas gold deposited underneath the hematite does not increase surface porosity. The morphology of the nanowires synthesized using Method 3 is similar to that of the bare hematite, with small clusters of dispersed nanowires. The 30 s sample from this series visually exhibits more concentrated agglomerates and wider pathways between different nanowires agglomerates, but without an increase in porosity.

When analysing Series 1 and 2, distinct behaviours are observed. In Series 1, as the gold deposition time increases, the number of voids decreases, resulting in a reduction in

surface porosity from 26.5% (1.5 times higher than the bare hematite) to 22.3% (1.3 times higher than the bare hematite). In all these samples, the nanowires are well distributed; however, there is a slight increase in nanowire agglomeration. The sample Hematite/30s Au stands out due to the higher number of interstitials between the nanowires. In Series 2, porosity increases with sputtering time, from 30 s to 120 s of gold deposition, showing increments of 1.43 and 1.52 times compared to the bare hematite. The sample of series 2 with 120 s of gold exhibits larger nanowire agglomerates and wider pathways. Nanowires coalesce with increased gold sputtering time.

Therefore, it is concluded that the synthesis method of series 2 promotes greater nanowire aggregation, and thus a lower photocurrent response is expected, despite the increased porosity.

3.3.2 Optical Characterization: UV-Vis Spectroscopy

Figure 3.8 shows the absorption spectra of hematite nanowire photoanodes incorporating gold nanoparticles, which were prepared using the different methodologies outlined in the experimental section: modified series 1 (Hematite/Au + Annealing 370°C 1h), series 2 (β -FeOOH/Au + 2 step annealing) and series 3 (Au/Hematite). A bare hematite photoanode is also included as a reference.

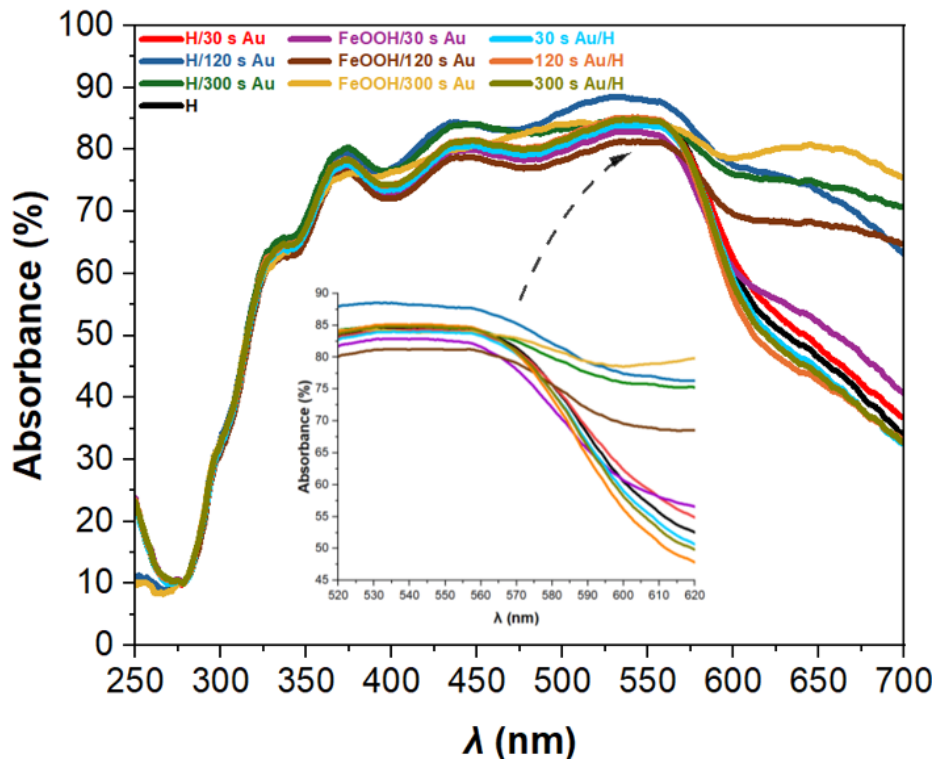


Figure 3.8: UV-Vis spectrum of hematite of all nanowires.

Analysing this overall image, it is observed that all the obtained spectra display the characteristic features of hematite nanowires, with peaks around 375, 440, and 535 nm. In the synthesized photoanodes, the maximum absorption peak is situated in the range of 531 to 546 nm. A redshift is observed in the samples containing gold on the surface, particularly in those with longer gold deposition times, indicating a positive contribution of the gold, as previously observed in [41].

With a closer examination of each series, it is possible to obtain more relevant information of gold influence.

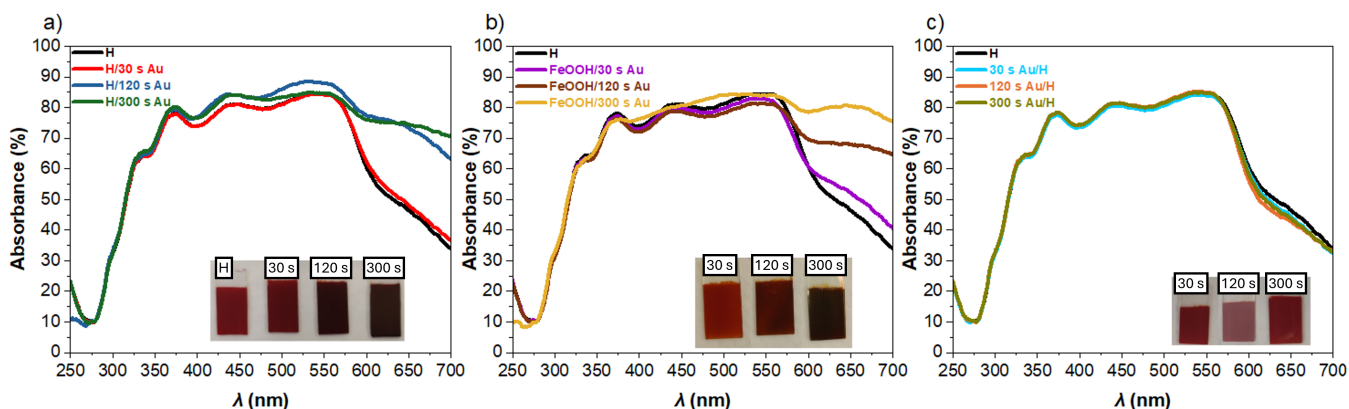


Figure 3.9: UV-Vis spectrum of photoanodes from a) modified series 1; b) series 2 and c) series 3. The macroscopic image of each photoanode is provided.

Observing the macroscopic images of the photoanodes presented in figure 3.9, it can be concluded that with the increase in gold deposition time on the surfaces of β -FeOOH or α -Fe₂O₃, the samples become visibly darker. This indicates an increase in the amount of gold present, which is supported by the increase in the average size of the gold nanoparticles observed in the SEM analysis. However, regarding Series 3, no visible impact of gold addition directly onto the substrate is observed, both in the macroscopic images and in the SEM results.

For the modified series 1, as the gold sputtering time increases from 30 seconds to 120 seconds and 300 seconds, higher absorption is observed starting at 375 nm compared to the bare hematite used as a reference, with a more pronounced increase after 600 nm. The phenomenon of localized surface plasmon resonance (LSPR) is evident for the 120 s and 300 s Au samples from modified series 1, within the wavelength range corresponding to gold (520-580 nm), with increased light absorption in this region, as seen in the spectra. The increase in absorption and the broadening of absorption peaks with longer sputtering times can be explained by the greater variability in nanoparticle sizes resulting from the increase in the amount of gold and the coalescence of particles

during the thermal annealing [40].

Regarding series 2, it is concluded that this methodology, involving gold sputtering for 30 and 120 seconds followed by two thermal annealing, is not beneficial, as the absorptions are lower than that of bare hematite across most of the visible light spectrum. The sample $\beta\text{-FeOOH}/300\text{ s Au}$ stands out from the others due to its very broad and poorly defined peaks. Beyond 600 nm, absorption becomes more significant with the increased gold sputtering time. Despite the similarity in the size of the gold nanoparticles for 30 s and 120 s sputtering times in both modified series 1 and series 2 samples, the absorption in series 2 samples is worse. The decreased absorption in series 2 samples may be attributed to the fact that the nanowires in this series are more agglomerated, which reduces light capture in the interstices of the nanowires.

Finally, in series 3, it can be seen that the spectra obtained are quite similar to that of bare hematite, indicating that gold deposited directly onto the substrate before the hematite does not induce changes in the absorption of the hematite.

The band gap values for all samples, except for those with 300 seconds of gold deposition, were determined from the Tauc plots, according to equation 2.2. The absorption coefficient was calculated considering the thicknesses of the hematite nanowires obtained from the cross-sectional images of the scanning electron microscope (SEM) shown in appendix figure A.2. Graphs of $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ were created to extract the band gap values (see figure 3.10).

The results presented in table 3.1 show that the band gap energy tends to increase with the increase in gold sputtering time across all series, with this effect being more pronounced in the modified Series 1. This suggests that the sputtering time and the strategy of incorporating gold into the photoanodes are the factors that most influence the band gap energy.

The strategy of depositing gold before hematite resulted in photoanodes with smaller thickness and a lower band gap compared to pure hematite, which may lead to an increase in current density. This is because a smaller photoanode thickness reduces the distance that electrons need to travel to the charge collector, thereby decreasing the probability of recombination.

Optical analysis of the photoanodes in Series 2 suggests that this methodology does not favour an increase in either the band gap or absorption, which may result in lower photocurrent densities. In contrast, Series 1 showed a significant increase in both band gap and absorption with the increase in gold deposition time.

The incorporation of gold nanoparticles on top of hematite seems to be the most beneficial configuration for enhancing absorption.

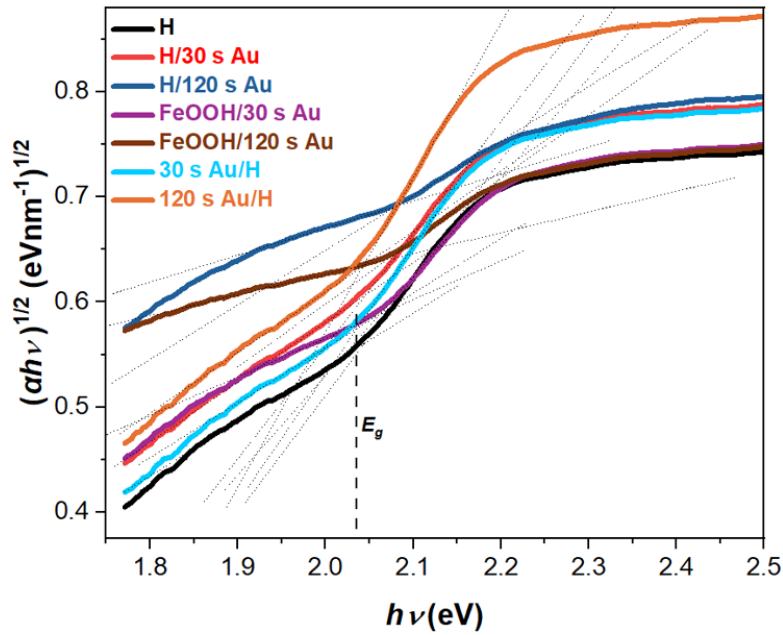


Figure 3.10: Tauc plots of photoanodes considering the indirect allowed transitions of hematite. E_g corresponds to the band gap energy of photoanodes.

Samples	H	Modified series 1 (H/Au)		Series 2 (FeOOH/Au)		Series 3 (Au/H)	
Au sputtering time	0 s	30 s	120 s	30 s	120 s	30 s	120 s
L (nm)	843 ± 23	749 ± 47	779 ± 60	814 ± 32	803 ± 32	753 ± 87	615 ± 58
Band gap (eV)	2.044	2.046	2.080	2.063	2.071	2.036	2.042
Absorbance (%)	84.454	84.285	88.492	82.904	81.268	83.969	84.823

Table 3.1: Au sputtering time, absorbance at 535 nm, thickness (L), and Band gap for the hematite nanowires from 3 series of samples and the reference hematite bare.

These results highlight the importance of choosing the deposition strategy and the gold sputtering time in optimizing the optical properties of the photoanodes, directly influencing their performance in photoelectrochemical cells.

3.3.3 Structural characterization: X-Ray Diffraction

The identification and characterization of the crystalline structure of the synthesized samples were carried out using X-ray diffraction. Figure 3.11 presents the diffractograms of pure hematite (H), hematite with 30 seconds of gold deposition (modified series 1), samples with 30 and 120 seconds of gold deposition from series 2 (with gold deposited during the FeOOH phase), and the sample that underwent gold sputtering for 30 seconds directly onto the FTO, followed by the conventional hematite synthesis process (series 3).

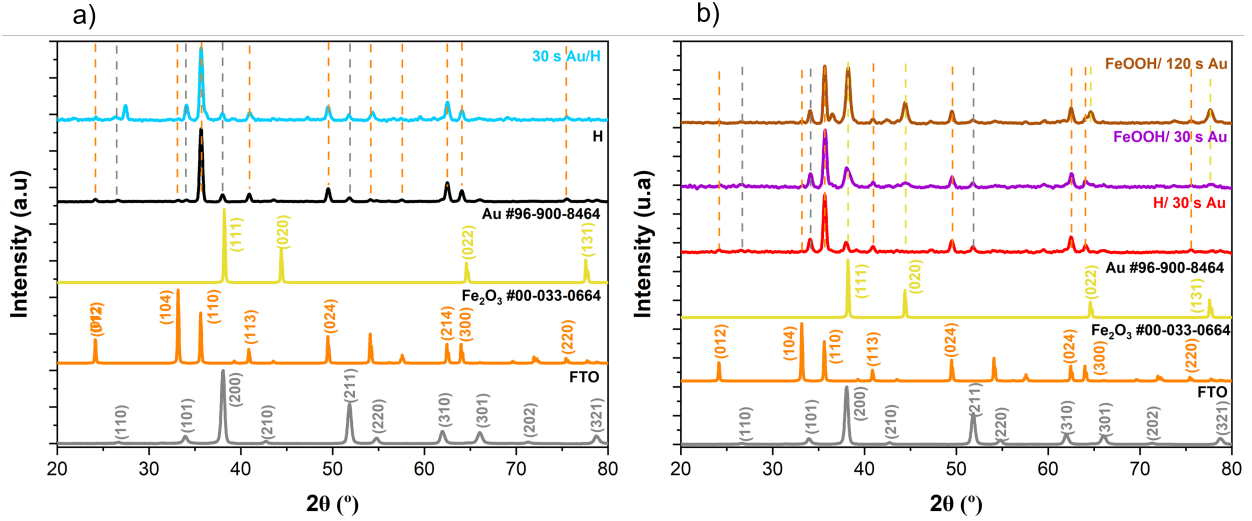


Figure 3.11: a) X-ray patterns of bare hematite and the sample with gold before hematite. b) X-ray patterns of samples with gold on surface of hematite and akaganeite phase. The first 3 layers are the reference patterns.

The diffractograms show characteristic peaks of hematite, corresponding to its rhombohedral crystal phase, belonging to the R3c space group (group 167), according to the JCPDS 00-033-0664 standard. These results confirm the presence of the expected crystal phase, demonstrating the structural stability of hematite under the different gold deposition conditions.

In the samples containing gold, characteristic peaks of gold in the face-centred cubic (FCC) phase were also observed, belonging to the Fm3m space group (group 225), according to the COD 96-900-8464 standard.

This indicates that gold crystallized in this phase with a preferred (111) orientation, regardless of the deposition conditions.

It is observed that the intensity of the gold peaks is higher when gold is deposited during the FeOOH phase and subjected to a two-step thermal treatment, compared to direct deposition onto the hematite surface followed by thermal treatment at 370°C.

Furthermore, with increased deposition time, the peaks associated with gold become more intense, as evidenced by the comparison between the FeOOH/30 s Au and FeOOH/120 s Au samples.

This suggests a greater amount of gold deposited and larger gold nanoparticles (verified by SEM) in the structure with longer deposition time.

In all samples, the predominant peak of hematite corresponds to the (110) plane, indicating a preferred crystallographic orientation in this direction. This peak is particularly relevant for the electrical conductivity of the samples. Previous studies have shown

that hematite exhibits significant electrical anisotropy, with electron conductivity along the [110] direction being up to four times greater than in the perpendicular directions [59, 74]. This preferred orientation may, therefore, positively impact the photoelectrochemical performance of the samples.

The ratio between the peaks corresponding to the (110) and (104) planes is also of extreme importance. The (104) peak is associated with crystallographic orientations where O_2^- groups are predominant. In these orientations, oxygen vacancies act as electron traps or surface defects, impairing charge transport efficiency and, consequently, photoelectrochemical performance [75]. Thus, a higher ratio between the (110) and (104) peaks may indicate a lower density of defects related to oxygen vacancies, favouring the efficiency of the synthesized samples.

In addition to the (110) plane of hematite, other planes of lower intensity were observed, such as (012), (104), (113), (024), (214), (300), and (220). These additional planes provide further details about the crystal structure of the samples, corroborating the presence of different orientations and confirming the complexity of the crystal structure of hematite.

The (104), (110), (113), (024), (214), and (300) peaks of hematite were fitted using the Pseudo-Voigt function to obtain the peak positions and the Full Width at Half Maximum (FWHM), which were then used in the Scherrer equation to determine the crystallite size.

$$D_{XRD} = \frac{k\lambda}{\beta \cos(\theta)} \quad (3.1)$$

where $\lambda = 1.540593 \text{ \AA}$, $k = 0.94$ is a Scherrer constant, β is the FWHM and θ is the Bragg peak divided by 2.

The crystallite size (D_{XRD}) obtained for hematite was $24.3 \pm 0.3 \text{ nm}$. For hematite with 30 seconds of gold deposition, the crystallite size was $22.6 \pm 1.5 \text{ nm}$. For the Series 2 samples, the crystallite sizes were $20.7 \pm 2.0 \text{ nm}$ for 30 seconds and $20.9 \pm 3.7 \text{ nm}$ for 120 seconds of gold deposition. For the sample of series 3 with 30 seconds (30 s Au/H), the crystallite size was $22.6 \pm 1.5 \text{ nm}$.

Reduction in crystallite size is observed with the inclusion of gold nanoparticles, particularly for samples where gold is deposited onto the β -FeOOH phase. This indicates that the presence of gold in this phase may inhibit the growth of hematite crystallites. Specifically, the gold nanoparticles might act as growth inhibitors or nucleation sites that disrupt the normal growth process, leading to smaller crystallite sizes of hematite.

This effect is more pronounced in samples where the gold is deposited directly onto the

β -FeOOH phase, suggesting that the interaction between gold and β -FeOOH significantly influences the crystallite size reduction. It's important to note that in samples of series 2, the reduction in crystallite size becomes more pronounced.

This conclusion is supported by the X-ray diffraction spectra, where the intensities of the gold peaks, particularly the (111) peak, are more pronounced compared to those for the H/30 s Au sample. This increase in gold peak intensity may contribute to a decrease in photocurrent density.

3.3.4 Photoelectrochemical performance

The photoelectrochemical performance of the synthesized hematite photoanodes was evaluated using photocurrent density - voltage (j - V) curves, current density - wavelength (j - λ) curves, and EIS measurements.

The j - λ curves shown in 3.12 allowed us to conclude that the photoanodes following the synthesis strategy of series 3 (Au/H) exhibit higher photocurrent density than the other series, being the only one that surpasses the performance of bare hematite. As for the other series, the performance is worse, with series 2 (FeOOH/Au) showing the poorest performance.

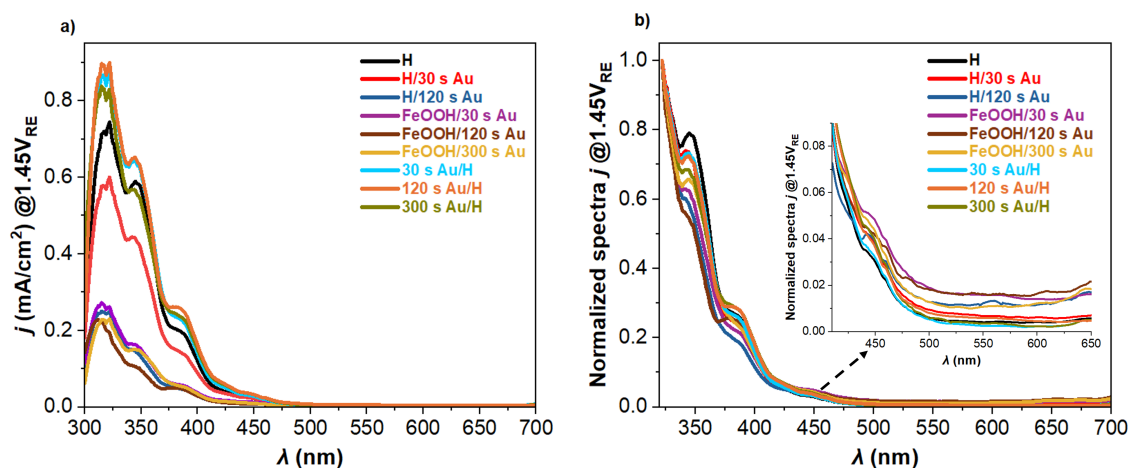


Figure 3.12: a) j - λ curves for the synthesized photoanodes and b) normalized spectra by the value at 322 nm. The inset represents a zoom in the area where the plasmonic gold effect can be observed.

Based on these results, it can be inferred that the synthesis method 3 is the most suitable for improving photocurrent and, consequently, hydrogen production. All samples show a maximum peak around 322 nm. To examine the relative impact of the localized surface

plasmon of gold on the spectral response of the photoanodes, the spectra were normalized by their respective values at 322 nm, which is the wavelength corresponding to the maximum current density for the photoanodes [52, 76].

Although series 2 had the lowest photocurrent densities overall, when we normalize all the spectra of the different series by the value at 322 nm, in the series 2 samples there is a specific region of the light spectrum where the response was better than expected. A higher response was observed in the region of spectral overlap with the plasmon resonance. This phenomenon suggests an enhancement due to the coupling between the localized surface plasmon and the semiconductor. Regarding series 1, the H/120s sample showed a better performance compared to the H/30s sample. This result indicates that 120 seconds of gold deposition provides more favourable locations for surface plasmon resonance to occur.

As expected, in series 3, the plasmonic effect of gold is not observed, and the curves show the typical behaviour of bare hematite. This is because the gold was deposited between the FTO and the hematite, rather than on the surface of the hematite. Additionally, the photoelectrochemical measurements were conducted in front illumination mode, where light directly illuminates the upper layer of hematite. Since the gold is positioned beneath this layer, it does not interact with the light and cannot contribute to the plasmonic effect that might enhance the photocurrent.

In summary, positioning the gold on the β -FeOOH surface is the configuration that best utilizes the plasmonic effect of gold although the improvement is not significant.

To confirm this trend and gain further insights, $j - V$ curves were measured under both dark and sunlight illumination for bare hematite and a sample from each series with a 30-second gold deposition time. The results corroborate the $j - \lambda$ measurements.

Photoelectrochemical measurements in the dark revealed negligible photocurrents for all photoanodes. Measurements under simulated solar illumination revealed considerable photocurrents.

The sample where gold was deposited directly onto the photoelectrode before the hydrothermal synthesis of hematite exhibited a photocurrent of 0.74 mA/cm^2 at $1.45 \text{ V}_{\text{RHE}}$ and $V_{\text{Onset}} = 0.74 \text{ V}$, representing an increase of approximately 10% compared to the value obtained for bare hematite (0.67 mA/cm^2) (see figure 3.13) with a $V_{\text{Onset}} = 0.81 \text{ V}$. In contrast, the hematite sample that underwent 30 seconds of gold sputtering followed by annealing at 370°C for 1 hour displayed a photocurrent density of 0.51 mA/cm^2 at

1.45 V_{RHE} , which corresponds to a decrease of approximately 24%, $V_{\text{Onset}} = 0.73$ V. Finally, the sample where gold was deposited in the β -FeOOH phase and subsequently subjected to a two-step annealing process exhibited a photocurrent of 0.39 mA/cm^2 with a $V_{\text{Onset}} = 0.68$ V, indicating a reduction of around 42% compared to bare hematite. It was observed that the incorporation of gold reduces the onset potential required for the reaction to commence, thereby decreasing the external energy needed. Additionally, the sample where gold was deposited prior to hematite (30 s Au/H) exhibited the highest photocurrent.

It is important to note that the determination of the onset potential is not standardized, and there are different methods for determining V_{Onset} , which influences the results obtained as well as the comparison of these results with previous ones [77]. There are complex methods, such as using the derivative of current density in function of potential and the point where j reaches 0.2 mA/cm^2 . Here, V_{Onset} was determined by the intersection of the tangent of the rising photocurrent curve with the horizontal line of the dark current.

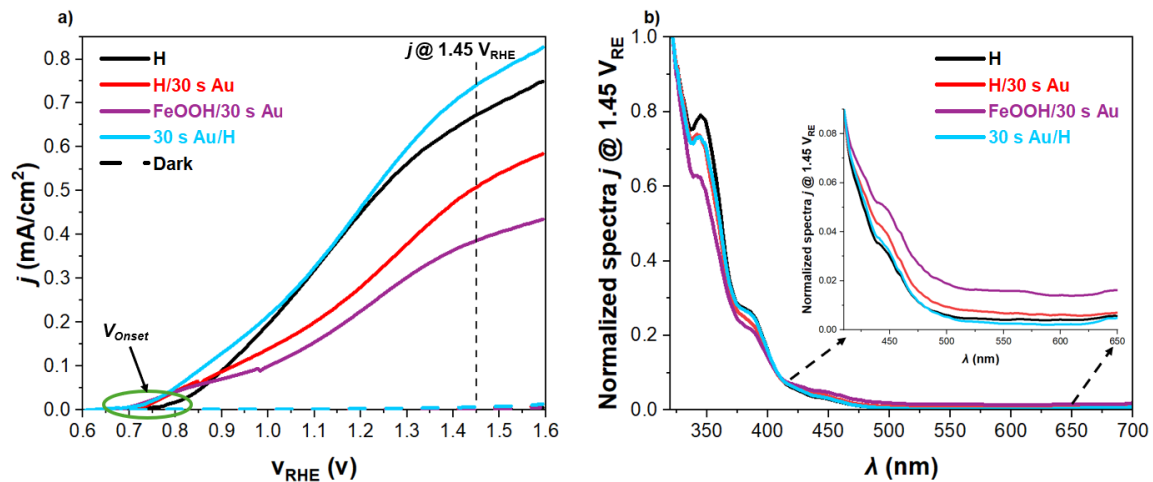


Figure 3.13: a) $j - V$ curves for the bare hematite photoanode and photoanodes of 3 series with 30 seconds of gold sputtering and b) normalized spectra by the value at 322 nm. The inset represents a zoom in the area where the plasmonic gold effect can be observed.

These results are in line with the morphological characterization that was carried out and expressed previously. The sample that presented the best photocurrent performance depending on the applied potential was the one with the smallest band gap while the one that had the worst result was the one with the largest band gap and the greatest aggregation of nanowires.

A correlation between porosity and photocurrent density is also observed. Lower porosity leads to higher photocurrent densities (see figure 3.14).

A cathodic shift in V_{Onset} observed for the photoanodes with gold can be related to the higher intensity of the Bragg peak at the (104) plane compared to what is observed for bare hematite. This enhancement can be attributed to the ability of gold to trap photogenerated holes at the hematite surface, making them available near the electrolyte for water oxidation reactions, thus accelerating the water oxidation process [30]. In general, a correlation is observed between the higher intensity ratio I_{110}/I_{104} and higher photocurrent. The fact that the sample with gold deposited before the hematite shows a lower ratio compared to the bare hematite (H) and the hematite with 30 seconds of gold deposition (H/30s Au) while exhibiting higher photocurrent suggests that the placement of gold affects the photoelectrochemical performance.

This may be due to gold's placement before the hematite layer, which could facilitate faster charge transfer to the surface without change in the morphology of hematite. Thus, in addition to the intrinsic structure of hematite, the location of gold deposition influences the intensity ratio of hematite peaks, potentially due to distortions induced in the crystal lattice.

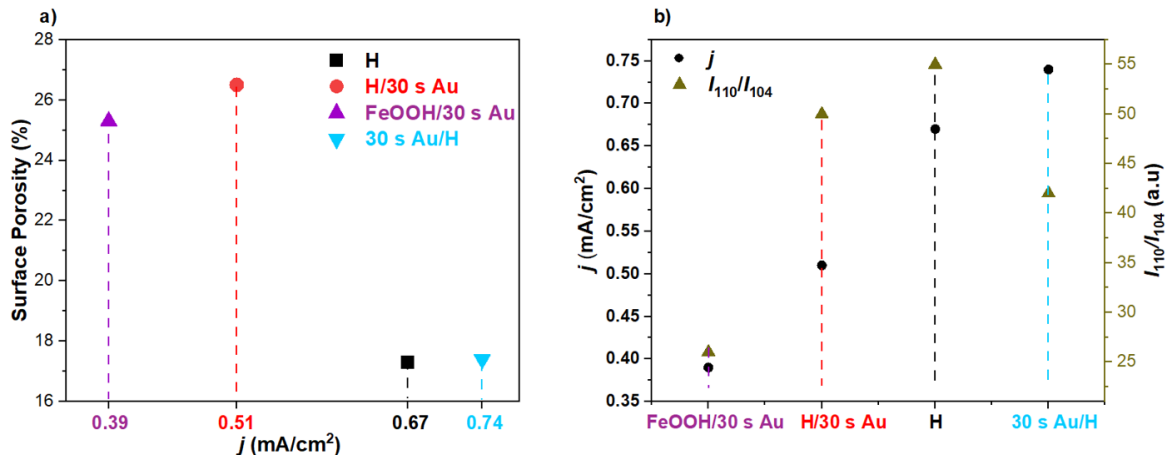


Figure 3.14: Correlation between surface porosity from SEM and ratio between I_{110}/I_{104} from XRD analysis with photocurrent density.

The electrochemical impedance spectroscopy (EIS) measurements, represented as Nyquist plots in figure 3.15, were fitted using the equivalent circuit model depicted in the same figure.

This circuit includes a series resistance, R_{Series} , which accounts for the resistance from the FTO substrate and the electrical connections in the experimental setup. Additionally, the model incorporates a bulk resistance, R_{Bulk} , which is associated with the recombination of electron-hole pairs within the bulk of the material. This resistance is in parallel with a constant phase element, CPE_{Bulk} , which represents charge accumulation in the bulk.

Furthermore, the circuit includes a charge transfer resistance, R_{Ct} , which corresponds to the resistance associated with charge transfer processes at the electrode/electrolyte interface. This resistance is also paired with its respective constant phase element CPE_{Ct} . Since these photoanodes are made of nanostructured hematite, the capacitors do not exhibit ideal behaviour due to the non-uniform current distribution in the heterogeneous material [78]. Consequently, constant phase elements (CPEs) are used to represent this non-ideal capacitance.

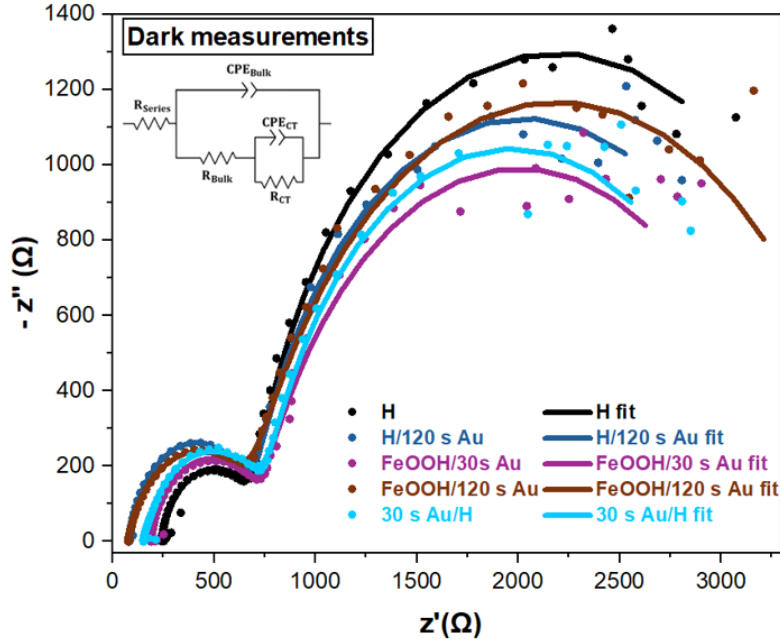


Figure 3.15: Nyquist diagrams obtained at 1.45 V_{RE} for different photoanodes synthesized with respective fits.

The Nyquist plots reveal the presence of two distinct semicircles. The semicircle observed at high frequencies is associated with the resistance within the bulk material, while the low-frequency semicircle corresponds to the resistance at the interface between the semiconductor and the electrolyte. It is also important to note that some visible noise appears in the Nyquist plots at low frequencies. This noise may be attributed to the use of a reference voltage of 1.45 V_{RE} instead of 1.45 V_{RHE} , which might have introduced slight inaccuracies in the low-frequency range.

Samples	$R_{Series}(\Omega)$	CPE_{Bulk}	$a1$	$R_{Bulk}(\Omega)$	CPE_{Ct}	$a2$	$R_{Ct}(\Omega)$
H	239.90	1.06E-05	0.882	502.0	1.57E-04	0.909	2961
H/120 s Au	82.07	4.81E-06	0.864	644.3	3.13E-06	0.843	2653
FeOOH/30 s Au	188.10	4.92E-06	0.832	563.7	1.61E-04	0.829	2556
FeOOH/120 s Au	75.29	1.09E-05	0.762	710.1	1.60E-05	0.863	2854
30 s Au/H	150.60	8.89E-06	0.787	661.9	1.43E-04	0.898	2404

Table 3.2: Electrochemical impedance spectroscopy results for dark conditions.

A decrease in charge transfer resistance is observed for photoanodes modified with gold nanoparticles, with this reduction being more pronounced in the sample where gold was deposited between the FTO and hematite (30 s Au/H). This significant decrease in charge resistance may be the reason for the improvement in photocurrent, as the photogenerated holes are more easily transferred from the electrode surface to the electrolyte, facilitated by the presence of gold as a conductive intermediate layer.

The reduction in charge transfer resistance (R_{Ct}) and the lower onset potential observed in gold-modified samples compared to bare hematite suggest that gold enhances the water oxidation reaction. The lower R_{Ct} indicates improved charge transfer efficiency lowering the charge recombination rate [79], while the lower onset potential means that gold facilitates the reaction at lower potentials [80].

Together, these results imply that gold modification effectively catalyses the water oxidation process, as observed in other studies [41, 76, 81].

PEIS measurements also revealed a decrease in surface charge transfer resistance with the incorporation of gold, consistent with the observations from EIS. The results are detailed in the appendix B.

To optimize electrochemical performance, it is essential to develop photoanodes that simultaneously minimize both surface and bulk resistance.

3.4. Conclusion

In this chapter, the impact of gold on hematite was investigated through three distinct deposition approaches. Each approach had a significant effect on the morphology, optical properties, and photoelectrochemical performance of the resulting materials.

The samples were analysed based on the gold deposition method: after the formation of hematite (Series 1), during the akaganeite phase (Series 2), and directly onto the FTO substrate before the hydrothermal synthesis of hematite (Series 3). Morphological analysis revealed that the size of the gold nanoparticles increases with the sputtering time, but did not vary significantly based on the deposition surface. Series 2 showed more aggregated nanowires compared to Series 1, indicating that the deposition method affects the aggregation of the nanowires and surface porosity.

Optical analysis showed that the presence of gold on the surface of the samples increased absorption for wavelengths above 600 nm, except in Series 3, where the absorption followed the pattern of pure hematite. This suggests that the distribution and configuration

of gold influence the material's absorption capability.

Band gap analysis revealed that longer sputtering times result in a slightly increased band gap, reducing the efficiency of electron-hole pair generation.

Series 3, with gold deposited directly onto the FTO before hematite formation, exhibited the best photocurrent ($j = 0.74 \text{ mA/cm}^2$) and a reduction in onset for all gold-containing samples compared to bare hematite. The decrease in onset was associated with an increase in the I_{104} peak in X-ray diffraction, suggesting an improvement in conductivity. Photocurrent and EIS analysis confirmed that lower porosity and better dispersion of the nanowires contribute to higher photoelectrochemical efficiency.

In conclusion, gold effectively catalyses the water oxidation reaction, and the time and configuration of gold deposition plays a crucial role in optimizing photoelectrochemical performance.

It is essential to avoid excessive aggregation of the nanowires and ensure that gold does not negatively interfere with light absorption by hematite. The results show that depositing gold directly onto the FTO before the formation of hematite (Series 3) offers the best overall performance.

4. Effect of Ti passivation layer on hematite nanowires prior to incorporation of gold nanoparticles

In this chapter, the role of TiO_2 as a passivation layer and its synergistic effect with hematite and gold nanoparticles were investigated. Based on the findings from the previous chapter, the TiO_2 layer was incorporated to passivate the surface states of hematite, with the aim of improving photoelectrochemical performance. The deposition times and configurations of the best-performing samples from the previous chapter, in terms of surface plasmon resonance and photocurrent, were employed in this study. In all samples, TiO_2 was deposited prior to the gold layer.

4.1. Experimental details

Four photoanodes were synthesized taking advantage of the plasmonic properties of gold mentioned in the previous chapter and the capability of titanium to passivate the surface states of hematite.

Two of these photoanodes were made of hematite, synthesized using the same method as the bare hematite described in the previous chapter. The other two photoanodes were in the $\beta\text{-FeOOH}$ phase, prior to annealing into the final hematite phase.

All samples underwent ion beam deposition to apply a thin layer of 5 nm of titanium onto their surfaces. To ensure titanium oxidation to titanium dioxide, all samples were subjected to annealing at 550°C for 2 hours. The heating rate used was $5^\circ\text{C}/\text{min}$ until the desired temperature was reached, with a 2-hour hold at this temperature before cooling to room temperature.

One of the hematite samples with TiO_2 served as a reference (H/TiO_2). Gold was deposited onto the other hematite sample by sputtering for 30 seconds on the surface of the photoanode, followed by annealing at 370°C for 1 hour to improve adhesion (method A). The name of this sample is ($\text{H}/\text{TiO}_2/30\text{ s Au}$).

For the remaining two samples in the $\beta\text{-FeOOH}/\text{TiO}_2$ phase, gold was deposited for 30 seconds on one sample and for 120 seconds on the other, followed by a two-step annealing process: 550°C for 2 hours and 800°C for 20 minutes to achieve the hematite phase (method B).

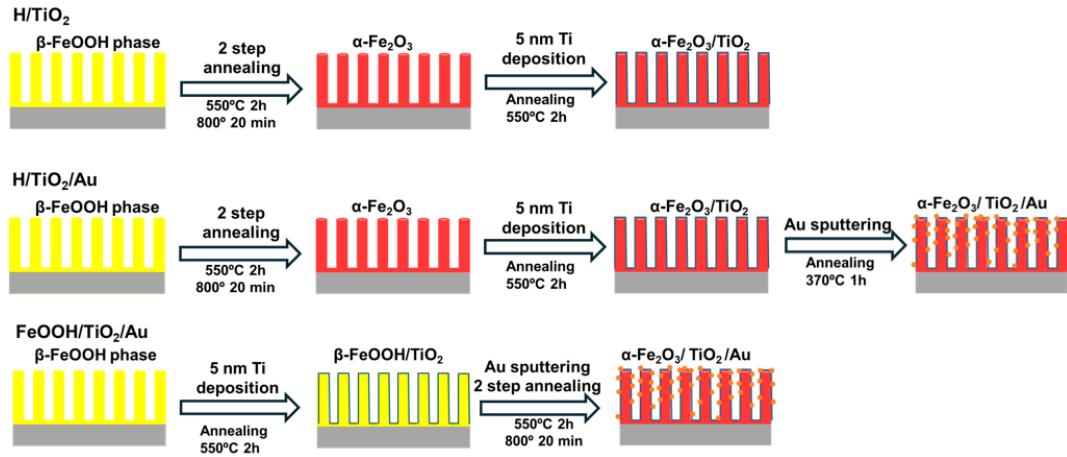


Figure 4.1: Scheme with the different proposed synthesis strategies.

4.2. Results and Discussion

4.2.1 Morphological characterization

The morphology of the developed photoanodes was examined using top-view SEM images in both secondary electron and backscatter electron modes.

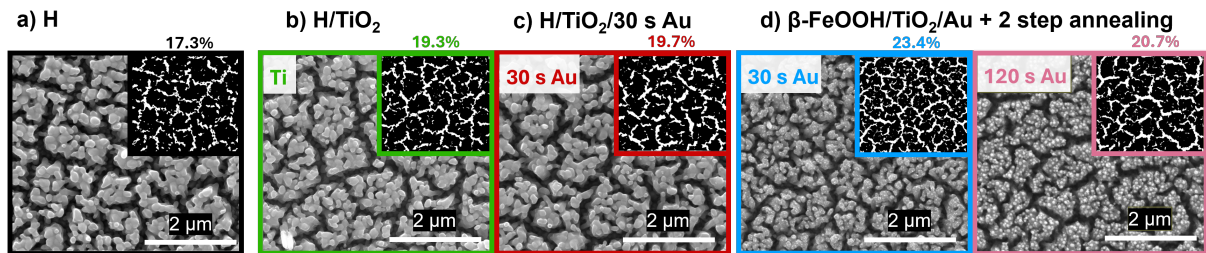


Figure 4.2: SEM (secondary electron) images of the synthesized photoanodes. a) Bare hematite; b) hematite with a titanium dioxide layer; c) hematite with titanium dioxide and gold nanoparticles on the surface, followed by annealing at 370°C for 1 hour (Method A); and d) photoanodes synthesized using method B. Insets show threshold-adjusted images for determining porosity, with white areas indicating porous regions as well as the respective percentage of porosity.

Figure 4.2 shows that the hematite nanowires were successfully synthesized, although titanium is not detected by SEM. However, complementary Energy Dispersive X-ray Spectroscopy (EDS) analysis confirms the presence of titanium in the samples (see appendix figure A.4). The average diameters of the bare hematite and the hematite with a 5 nm Ti layer after annealing were measured, showing that the 5 nm Ti layer does not significantly alter the nanowire dimensions. The average diameter of the bare hematite is 155.9 ± 55.6 nm, while for the hematite with TiO_2 , it is 149.1 ± 37 nm (all uncertainties are reported as standard deviations).

The sample shown in Figure 4.1-c) was expected to display visible gold on its surface, but neither SEM nor EDS detected it. This suggests that the gold may have disaggregated

after annealing or during the photoelectrochemical measurements, as this sample was analysed in the SEM afterward.

For the samples synthesized using Method B, gold deposition was successful. The backscattered images, provided as supplementary material (figure A.3), show that the average size of the gold nanoparticles for both the 30 s and 120 s deposition times is similar to that observed in Chapter 3, where gold was directly deposited onto both the β -FeOOH and hematite phases. The sample with 30 s of gold sputtering produced particles with an average size of 22.0 ± 3.5 nm, while the sample with 120 s of sputtering resulted in particles with an average size of 48.9 ± 18.8 nm. The observed increase in gold nanoparticle size is consistent with longer gold sputtering times.

Through the measurement of surface porosity of the photoanodes using the method detailed in the attachment, it is observed that the porosity among the bare hematite, hematite with TiO_2 , and hematite with TiO_2 and 30 s of Au is similar, with the titanium-containing samples exhibiting about 2% higher porosity compared to bare hematite. These samples show a homogeneous distribution of nanowires, which are clustered in small aggregates. For the samples where TiO_2 and Au were deposited onto the FeOOH phase and then subjected to a two-step thermal annealing process, a decrease in porosity is observed with increasing sputtering time, and the nanowires become more aggregated with longer gold deposition times. The sample following methodology B with 30s of Au shows the most dispersed nanowires throughout the image.

Comparing the images obtained from these samples with those in Figure 3.6, where gold was directly deposited on the FeOOH phase in Chapter 3, it is observed that the nanowires presented in this chapter are less aggregated, and that porosity decreases rather than increases with longer gold sputtering times. This reduced aggregation suggests that the Ti layer incorporated into the akaganeite phase forms a protective film, allowing for efficient nanowire growth and preventing the gold from interfering with their normal development.

4.2.2 Structural characterization: X-Ray Diffraction

The X-ray diffraction patterns presented in figure 4.3 were obtained using a parallel beam configuration, with the grazing incidence angle adjusted to minimize the intensity of the characteristic peaks of the FTO substrate.

All the diffraction patterns obtained align with JCPDS 00-033-0664 pattern, confirming the presence of hematite phase. The (110) peak is the most intense, indicating a preferential

growth orientation, which is typically associated with higher electrical conductivity [59, 74]. Peaks from planes (012), (104), (024), (214), (300) and (220) were also identified. No peaks associated to titanium were identified due to amorphous structure and/or smaller particle size than the diffraction limit.

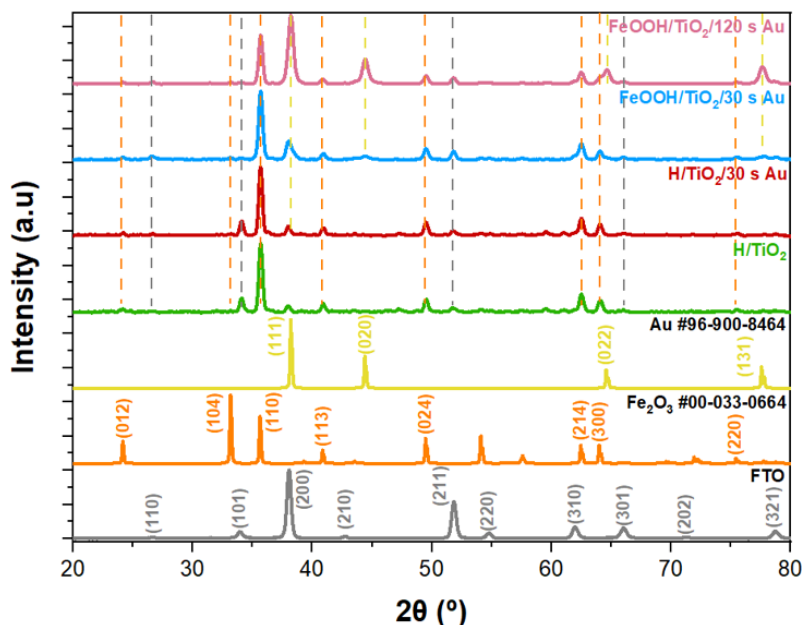


Figure 4.3: X-ray diffraction patterns of photoanodes with TiO_2 following the method A and B described in experimental section.

The hematite sample with titanium dioxide and 30 seconds of gold sputtering did not reveal any peaks related to gold, corroborating the absence of gold nanoparticles observed in the SEM images. The gold nanoparticles likely disaggregated at some stage of the process.

For the samples following B methodology, in which Ti and Au are deposited directly onto the β -FeOOH phase and subsequently subjected to a two-step thermal annealing process, diffraction peaks corresponding to the (111), (020), and (131) planes of gold were observed. Additionally, the sample with 120 seconds of gold sputtering also exhibited the (022) peak. There is a correspondence with the COD 96-900-8464 standard, confirming that gold crystallizes with a preferential orientation in the (111) plane.

It is also noted that the intensity of the gold peak in the sample with 120 seconds of deposition is higher than the maximum peak of hematite, which may affect the behaviour of the photoanode.

The crystallite diameter was determined using the Scherrer equation, with the pseudo-Voigt fits of the hematite peaks observed in the XRD spectra. The obtained results are summarized in the following table.

Samples	Crystallite Size (nm)
H/TiO ₂	25.3 ± 5.7
H/TiO ₂ /30 s Au	22.1 ± 3.0
FeOOH/TiO ₂ /30 s Au	20.9 ± 3.2
FeOOH/TiO ₂ /120 s Au	21.7 ± 1.7

Table 4.1: Estimated crystallite sizes obtained using the Scherrer equation applied to XRD data.

The crystallite sizes are within the range of standard deviation, indicating that the different synthesis methods do not appear to significantly alter the crystallite size.

4.2.3 Photoelectrochemical characterization

The photoelectrochemical performance of the synthesized hematite photoanodes was assessed using photocurrent density versus voltage (j - v) curves under simulated sunlight and dark conditions.

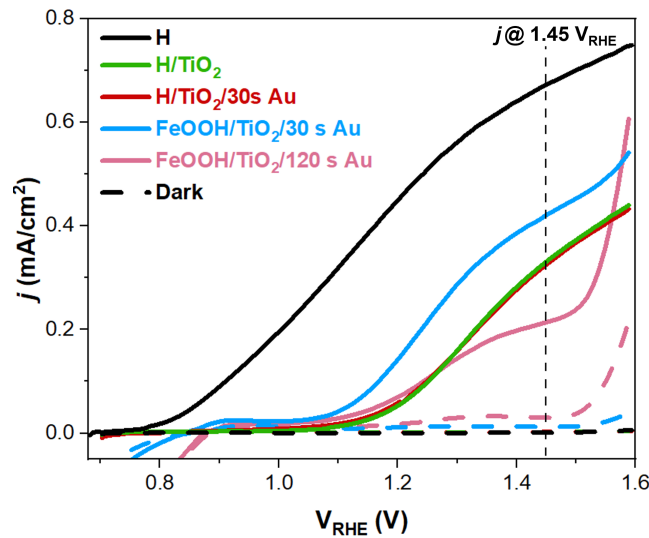


Figure 4.4: Photocurrent density-voltage curves under dark and solar simulated sunlight.

Contrary to expectations, the addition of the TiO₂ layer, instead of passivating the surface states of hematite and increasing the photocurrent, resulted in a decrease. Additionally, an anodic shift in the onset potential V_{Onset} was observed, which was more pronounced in the samples where both Ti and Au were incorporated in the surface of hematite.

Samples	Photocurrent Density (j at 1.45 V_{RHE})	Onset Potential (V)
H/TiO ₂	0.33	1.09
H/TiO ₂ /30 s Au	0.32	1.11
FeOOH/TiO ₂ /30 s Au	0.42	0.84
FeOOH/TiO ₂ /120 s Au	0.22	0.88

Table 4.2: Summary of photocurrent density and onset potential for the samples.

This suggests a reduction in the kinetic efficiency required to initiate the photoelectrochemical reaction. Although the TiO_2 layer is only 5 nm thick, it appears to interfere with the efficient absorption of sunlight by the hematite nanowires. The anodic shift in the photocurrent onset potential may be related to Ti diffusion, promoted by the thermal treatments to which the material was subjected [82]. Furthermore, the TiO_2 layer appears to be too thick, hindering the efficiency of photogenerated hole transfer and blocking light from reaching the inner hematite layer, impairing the transport of holes between Fe_2O_3 and the electrolyte needed to participate in the water oxidation reaction [83, 84].

When gold and titanium are incorporated into the β - FeOOH phase, a cathodic shift is observed compared to the samples where titanium is deposited directly on the surface of hematite. This shift may be attributed to the role of gold as an accelerator of the reaction kinetics. However, despite these modifications, the photocurrent density and onset potential do not surpass those of bare hematite.

These strategies have proven to be inefficient and necessitate further investigation into the annealing temperature and the thickness of the photoanode.

4.3. Conclusions

In this chapter, the impact of depositing a 5 nm titanium layer between the β - FeOOH phase and gold, or between hematite and gold, was investigated. The goal was to assess whether the photoanode could benefit from both the surface passivation provided by titanium and the plasmonic properties of gold, which enhance light absorption, reduce recombination rates, and increase photocurrent density. A decrease in photocurrent and an increase in the onset potential relative to bare hematite were observed, which can be explained by the blockage of incident light and reduced charge carrier transfer. The sample prepared by method B with 30 seconds of gold deposition showed a higher photocurrent ($0.42 \text{ mA}/\text{cm}^2$), compared to the other samples. This can be attributed to a more dispersed distribution of nanowires, observed by SEM images, providing more free interstices for electrolyte interaction, thereby enhancing the photocurrent. The smaller gold nanoparticle size compared to the 120-second deposition sample resulted in a higher photocurrent, indicating that a smaller gold size is beneficial for photoelectrochemical performance. This is because the dark current becomes significantly high in the photoanode subjected to 120 seconds of sputtering. Optimizing the thickness of the TiO_2 layer is crucial for improving photoelectrochemical performance.

5. Conclusions and Future Work

This thesis focused on optimizing the solar performance of hematite nanowires integrated with gold nanoparticles, using hydrothermal synthesis for hematite and the sputtering technique for gold deposition.

Initially, hematite nanowires were synthesized using the hydrothermal method. To improve their efficiency, we focused on the strategy of incorporating gold nanoparticles at distinct stages of the nanowire hydrothermal synthesis. The plasmonic gold nanoparticles were incorporated after the complete synthesis of the hematite nanowires (Series 1); in the middle of the hematite synthesis process (onto the as-prepared FeOOH nanowires - Series 2), prior to the two-step thermal annealing; and directly onto the substrate before the hydrothermal synthesis of the hematite nanowires (Series 3). The gold deposition time was varied to assess its impact on the size and dispersion of the nanoparticles. Each series is composed of 3 photoanodes corresponding to deposition times of 30 s, 120 and 300 s. A morphological analysis made it possible to verify evidence between the increase in the size of gold nanoparticles with longer sputtering times in series 1 and 2 and that the phase of the hydrothermal method of synthesis of hematite nanowires in which gold is deposited has no influence on the size of the nanoparticles obtained. Regarding series 3, the same cannot be concluded, since the gold was deposited directly on the substrate. The analysis of surface porosity revealed different trends depending on the strategy used. In Series 1, a decrease in porosity was observed with longer gold sputtering times, and the nanowires were well distributed. In Series 2, an opposite behaviour was noted, with the nanowires becoming more aggregated and porosity increasing, forming wider free paths. In Series 3, the porosity was similar among all synthesized samples and the bare hematite. A redshift was observed through UV-Vis analysis for series 1 and 2 photoanodes for wavelengths greater than 600 nm, indicating a positive contribution from the plasmonic effect of gold in these configurations. As, in series 3, the gold is below the hematite, the observed behaviour of these photoanodes was similar to that of bare hematite. A slight increase in band gap was observed for all series with longer deposition times. The sample of series 3 with 30 seconds of sputtering gold time showed the lowest band gap.

Photoelectrochemical performance measurements, obtained from photocurrent density versus voltage curves and photocurrent versus wavelength curves, showed the same

trend. The samples synthesized by method 3 showed the best performance while series 2 showed worse performance. The sample with gold deposited prior to hematite formation exhibited the highest photocurrent ($j = 0.74 \text{ mA/cm}^2$) and the lowest band gap, underscoring the efficacy of this approach. However, it is important to highlight that although the samples from series 1 and 2 have lower photocurrent, analysing the photocurrent density curves as a function of wavelength it is verified that in series 1 (H/30 s Au) and series 2 the surface plasmon effect is observed, being more significant in the series 2, meanwhile no plasmonic effect in series 3. A consistent cathodic shift on V_{Onset} was observed in all cases. This cathodic shift is supported by reduced surface charge transfer resistance observed in electrochemical impedance spectroscopy (EIS) measurements and a decrease in the I_{110}/I_{104} ratio from X-ray diffraction analysis. Notably, the sample where gold was deposited on the FeOOH phase prior to a two-step annealing and 30 seconds of gold showed a remarkable onset potential of 0.67 V, compared to 0.81 V for bare hematite, which could be related to the increased evidence of surface plasmon resonance. It is therefore concluded that gold works as a catalyst for the water oxidation reaction, that the strategy of incorporating gold directly into the substrate before hematite synthesis is the one that exhibits the best photoelectrochemical performance and that the series in which gold is incorporated into the β -FeOOH phase prior two step annealing is the one with the most evident surface plasmonic effect.

The samples that had the best performance in relation to surface plasmonic behaviour were selected and new photoanodes were created in which TiO_2 was incorporated into the interface between hematite or β -FeOOH and gold in order to passivate the surface states of the hematite and simultaneously benefit from the gold plasmonic effect. This strategy proved to be less effective from a photoelectrochemical standpoint. The current density decreased significantly compared to bare hematite and hematite with 30 seconds of gold deposition, along with an anodic shift in the onset potential. However, this part of the study revealed that placing TiO_2 at the β -FeOOH-gold interface resulted in a smaller anodic shift compared to its placement on the surface of hematite. The results highlight the critical role of gold in enhancing the photoelectrochemical performance of hematite nanowires and provide valuable insights into optimizing deposition methods and conditions for future applications in solar energy conversion.

Based on the results obtained in this dissertation, several approaches can be pursued to further improve the performance of the photoanodes. First, performing Surface-Enhanced Raman Spectroscopy (SERS) is required to investigate whether the presence of gold on

the photoanodes enhances the electric field at wavelengths corresponding to localized surface plasmon resonance (LSPR). This would help confirm the plasmonic effects that gold nanoparticles may have on the photoactivity of hematite.

Additionally, it is important to repeat the measurement of photocurrent density (j) as a function of wavelength at a potential of 1.45 V_{RHE} to confirm the trends observed. These measurements would then allow for accurate determination of the Incident Photon-to-Current Efficiency (IPCE), providing a more comprehensive understanding of the device's efficiency under different wavelengths of light. The samples were not measured at the reversible hydrogen electrode potential of 1.45 V due to an experimental configuration error that was not detected in a timely manner. As the contribution of the dark current is more significant at higher potentials, there may be discrepancies in the results obtained. The synthesis of a photoanode combining the strategies of series 2 and series 3, with gold applied directly to the substrate and placed after the as-prepared FeOOH nanowires, prior to the 2-step thermal annealing, would be worth studying. This approach would combine the best plasmonic behaviour and lower onset potential (observed in the series 2 samples) with the higher photocurrent density found in the series 3 samples.

Relative to the deposition of the Ti layer, its thickness should be optimized to not block the solar light. Additionally, adopting Atomic Layer Deposition (ALD) instead of Ion Beam Deposition (IBD) may offer better control over the TiO₂ layer morphology, as ALD provides highly uniform and conformal coatings even on complex nanostructured surfaces, which could improve the overall performance of the photoanode.

The deposition of a catalyst based on FeCo, as FeC₂O₄, on top of the photoanodes should also be explored to further reduce electron-hole recombination and improve the kinetics of the water oxidation reaction boosting the overall photocurrent.

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A. Appendix - Morphological Characterization

The diameter of the nanowires was estimated using ImageJ by taking 50 measurements per sample, and the results were analysed using a log-normal distribution. To estimate the average size of the gold nanoparticles on each photoanode, ImageJ was again used to measure particle dimensions, with 90 measurements taken per photoanode to ensure robust statistical confidence. The diameter of the nanowires and the size of the gold nanoparticles were measured along the longest axis of their respective morphologies. The data were then analysed using Origin software, where a log-normal distribution fit was applied to each dataset, providing an accurate determination of the mean size and standard deviation of the gold nanoparticles.

To assess whether the hematite nanowires were successfully synthesized using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a reagent, and with subsequent annealing following the hydrothermal method with a heating ramp of $10^\circ\text{C}/\text{min}$ up to 550°C and $8^\circ\text{C}/\text{min}$ up to 800°C , using the initial furnace mentioned in Chapter 2, as well as using FeCl_3 as a reagent and the furnace 2 from Chapter 2 with heating ramps of $5^\circ\text{C}/\text{min}$ to reach both 550°C and 800°C , SEM was used.

It was found that the hematite nanowires were synthesized correctly, although there were some differences in morphology regarding the arrangement and diameter of the hematite nanowires.

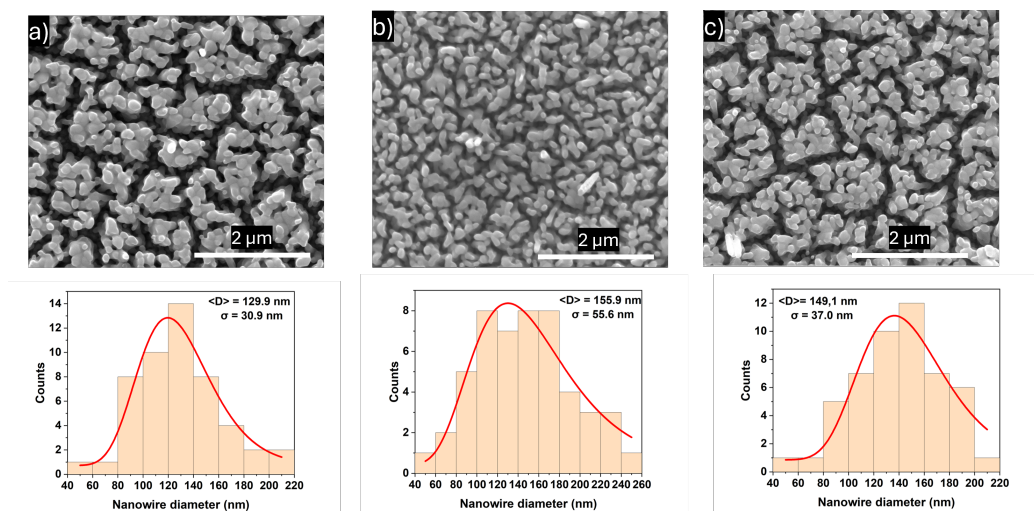


Figure A.1: SEM (secondary electron) images of the following photoanodes: a) $\alpha\text{-Fe}_2\text{O}_3$ synthesized with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and annealed in furnace 1; b) $\alpha\text{-Fe}_2\text{O}_3$; and c) $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$, both synthesized with FeCl_3 and annealed in furnace 2. Below each figure are the histograms and the corresponding lognormal distributions of $\alpha\text{-Fe}_2\text{O}_3$ nanowires.

For the hematite synthesized with the first reagent and the heating characteristics of furnace 1, an average diameter of 129.9 ± 30.9 nm. For the hematite synthesized using the second method, the average diameter was 155.9 ± 55.6 nm. The hematite with titanium dioxide presents an average nanowire diameter of 149.1 ± 37.0 nm. The size of the hematite nanowires does not vary significantly with the change of reagent or the addition of a 5 nm layer of TiO_2 on the surface of the hematite.

To perform the surface porosity analysis, the secondary electron image in top view was converted to 8-bit gray-scale binary mode on ImageJ software. Then, the scale was adjusted correctly, and the threshold was applied and adjusted so that all empty spaces were correctly selected. In the "Set Measurements" menu, the "Fraction Area" option was selected, and, subsequently, the "Measure" option was chosen, thus allowing the surface porosity of the photoanodes to be determined.

The following figure presents cross-sectional images of the photoanodes synthesized, as detailed in Table 3.1 of Chapter 3. The images were obtained using backscatter electron mode.

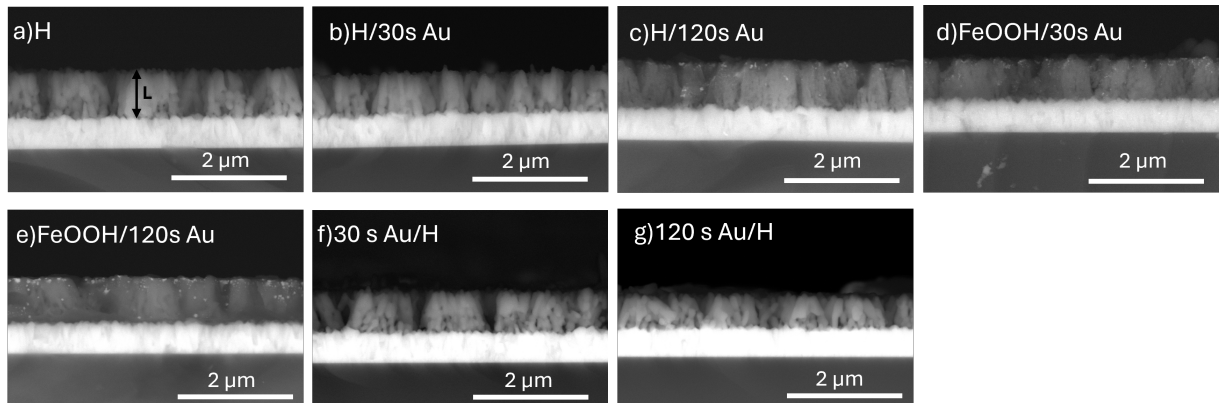


Figure A.2: Cross-sectional images of various photoanodes: a) bare hematite; b) and c) samples from modified series 1; d) and e) samples belonging to series 2; and f) and g) samples corresponding to series 3.

BSED images of samples from chapter 4 with gold:

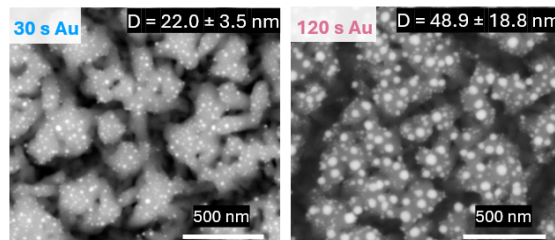


Figure A.3: BSED images from samples $\text{FeOOH}/\text{TiO}_2/\text{Au}$ after two step thermal annealing. The average gold nanoparticle size is indicated in each figure.

EDS (Energy Dispersive X-ray Spectroscopy) images of samples H/TiO₂ and H/TiO₂/30 s Au:

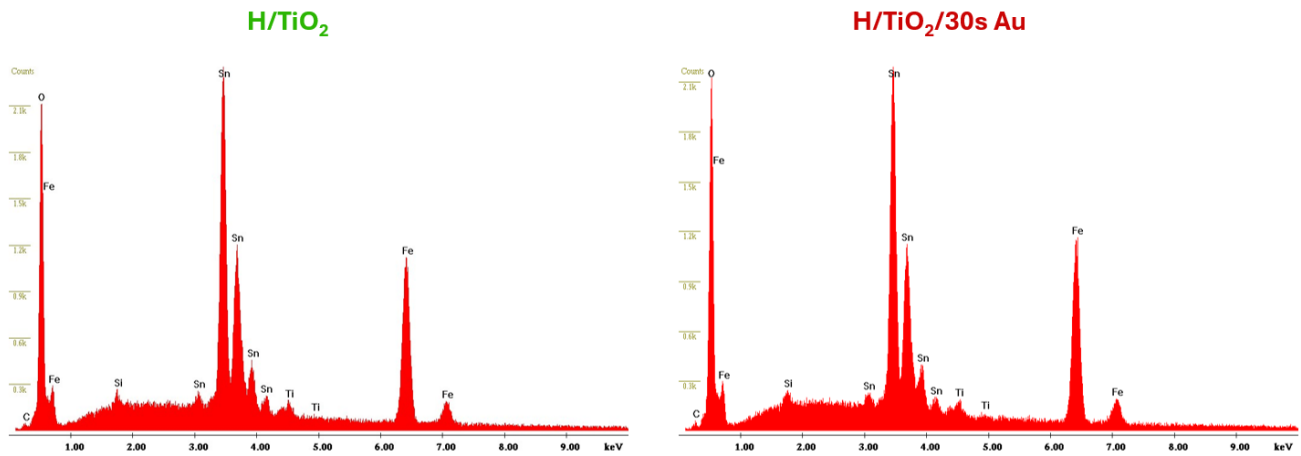


Figure A.4: EDS images from samples H/TiO₂ and H/TiO₂/30 s Au confirming the presence of Ti in their composition.

B. Appendix - Photoelectrochemical impedance spectroscopy

Samples	$R_{Series}(\Omega)$	CPE_{Bulk}	$a1$	$R_{Bulk}(\Omega)$	CPE_{Ct}	$a2$	$R_{Ct}(\Omega)$
H	220.50	6.74E-06	0.874	1226.0	2.15E-04	0.675	4579
H/120 s Au	82.41	3.73E-06	0.894	905.4	1.90E-04	0.756	3741
FeOOH/30 s Au	188.40	4.32E-06	0.851	782.3	1.97E-04	0.749	3688
FeOOH/120 s Au	78.28	8.60E-06	0.795	1015.0	1.75E-04	0.777	3355
30 s Au/H	158.50	6.47E-06	0.837	2104.0	1.95E-04	0.766	3446

Table B.1: Electrochemical impedance spectroscopy results under solar conditions.

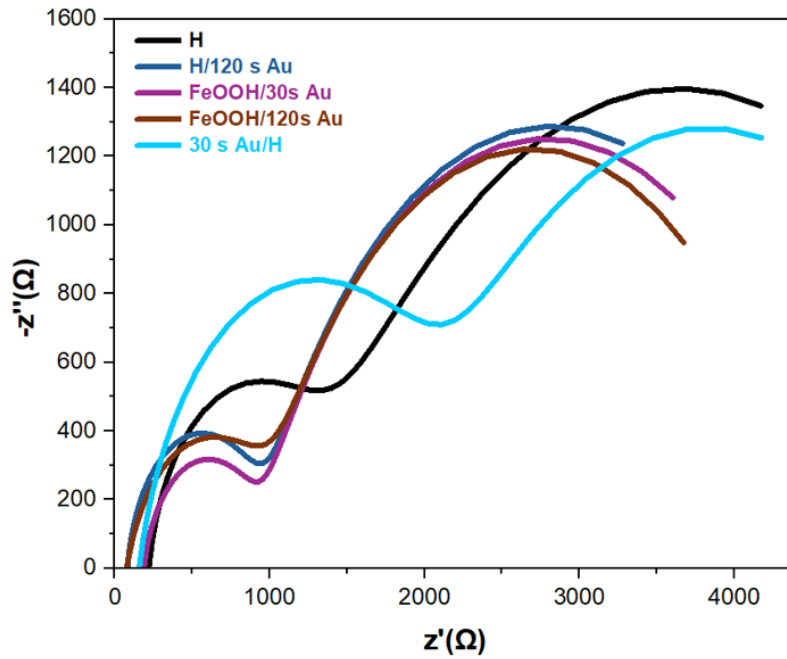


Figure B.1: Nyquist fits plots obtained at 1.45 V_{RE} for different photoanodes synthesized under solar conditions.

