

Article

Synthesis, Characterization, and Application of CeO₂, TiO₂, ZrO₂, and SnO₂ Oxides in Dye-Sensitized Solar Cells (DSSCs)

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Abstract

Dye-sensitized solar cells (DSSCs), belonging to the third generation, are highlighted for their low production cost compared to other photovoltaic technologies. These cells are composed of a cathode, an electrolyte, and an anode, commonly using TiO₂. This work aims to produce and characterize CeO₂, SnO₂, and ZrO₂ oxides as substitutes for TiO₂ in DSSCs. The semiconductor oxides were synthesized using the Pechini methodology and applied as the anode of the system. The device was assembled in a sandwich configuration, with an anode and cathode (graphene), an active area of 0.2 cm², and an electrolyte containing the I₃[−]/3I[−] redox pair. The techniques employed included scanning electron microscopy (SEM), dynamic light scattering (DLS), X-ray diffraction (XRD), UV-Vis spectroscopy, open-circuit potential curves and electrochemical impedance spectroscopy (EIS). The oxides exhibited good crystallization with non-defined morphology. The obtained band gap values were 2.8 eV, 3.0 eV, 3.1 eV, and 4.8 eV for CeO₂, TiO₂, SnO₂, and ZrO₂, respectively. In DSSCs, these oxides showed photosensitivity, generating potential when exposed to light with TiO₂-based cell exhibited the lowest charge transfer resistance (R_{ct} = 57.8 kΩ). This comparative framework establishes a preliminary screening of the intrinsic interfacial charge transfer and recombination kinetics of alternative standalone photoanodes, serving as a baseline for future device optimization.

Keywords: renewable energies; Pechini; semiconductor oxides; photovoltaic systems



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1. Introduction

Global warming is caused by the accumulation of polluting gases, such as carbon dioxide and methane, in the atmosphere. These gases interrupt the natural carbon cycle, which includes the release of CO₂ by volcanoes and its absorption by plants and organisms [1].

The use of fossil fuels accelerates this cycle, releasing carbon stored at the bottom of the oceans and increasing the concentration of CO₂ in the atmosphere, which contributes to the increase in global temperature. Although the shift from oil to alcohol, in recent years, represents progress, more investment in research and development of alternative and sustainable sources is still necessary to address current challenges related to climate change [2].

The search for sustainable energy alternatives has led to the development of renewable technologies. Among them, solar cells stand out for their ability to convert sunlight into electricity in a clean and efficient way [3]. First-generation solar cells, made of monocrystalline and polycrystalline silicon, are widely used and offer high efficiency, reaching up to 30% in solar energy conversion. However, these cells have a higher manufacturing cost [4,5].

Second-generation solar cells, such as CIGS (copper, indium, gallium, and selenium), CdTe (cadmium telluride), and amorphous silicon, have a lower production cost but an average efficiency of about 20%. These technologies represent an advance compared to first-generation cells, offering a balance between cost and performance [6,7].

Third-generation solar cells, which include QDSSCs (quantum dot solar cells), PSCs (perovskite solar cells) [8], and DSSCs (dye-sensitized solar cells) [9], are particularly promising, since they present easier production and lower costs compared to the others. The DSSC operates as follows: when sunlight strikes the device, electrons from the dye are injected into the conduction band of a semiconductor, thus generating a flow of charges and consequently an electric current. These charges move toward the counter electrode, which subsequently regenerates the oxidized species due to the diffusion of the electrolyte [3]. TiO_2 is the main material used in DSSCs (as a scaffold oxide) due to its high chemical stability, low toxicity, and excellent electrical and optical conductivity, which ensure efficiency and durability in the devices. However, TiO_2 has limitations in terms of cost and maximum light absorption efficiency, especially in the visible region of the spectrum. Therefore, there is increasing interest in finding substitutes that can offer better performance and lower cost, as recently demonstrated in the literature [10,11]. The replacement of TiO_2 with other semiconductor oxides, such as CeO_2 , SnO_2 , and ZrO_2 , is promising, since these alternative materials can potentially improve efficiency and reduce the production costs of DSSCs [9,12,13].

As reported in the literature, other semiconductor oxides have also been explored in third-generation solar cells, although to a lesser extent, including SnO_2 , CeO_2 , etc. [4]. Such materials can be synthesized through various synthetic routes, such as the Pechini method, which has been used for the synthesis of these materials, providing an efficient and low-cost approach [14]. This method allows the production of nanoparticles and metal oxides with high purity and uniform size, facilitating the development of solar cells with advanced characteristics. The Pechini method is highly valued for its low synthesis cost and its outstanding ability to generate nanostructured ceramic materials, which is crucial for the fabrication of third-generation solar cells [15]. In this perspective, the Pechini route stands out significantly compared to other liquid phase techniques, such as the hydrothermal methodology. While the hydrothermal approach typically demands specialized high-pressure reactors (autoclaves) and precise temperature controls to achieve phase-pure ceramic oxides, the polymeric precursor method offers a simpler, safer, and highly reproducible benchmark that ensures excellent molecular-level homogeneity without the need for sophisticated or costly infrastructure [16–18].

This work aims to synthesize, via the Pechini methodology, characterize, and apply the metal oxides TiO_2 , CeO_2 , ZrO_2 , and SnO_2 in third-generation photovoltaic systems. Instead of targeting advanced optimization, this study is designed as a fundamental, comparative screening. By isolating the oxides under identical synthesis and deposition conditions, we aim to systematically investigate how their intrinsic energy band alignments, optical bandgaps, and charge transfer resistance influence the initial photoresponse and open-circuit potential kinetics, establishing a baseline for alternative standalone anodes.

2. Materials and Methods

The metal oxides CeO_2 , TiO_2 , ZrO_2 , and SnO_2 were synthesized through the Pechini method using ethylene glycol and citric acid, using the respective metal salts: cerium nitrate hexahydrate (Neon), titanium isopropoxide (Aldrich, Cajamar, Brazil), zirconium chloride (Êxodo, Sumare, Brazil), and tin chloride (Synth, Diadema, Brazil).

For the synthesis, 300 mL of ethylene glycol and 79.2 g of citric acid were used, dissolved at a temperature of up to 70 °C in a 600 mL beaker. The temperature was monitored during the dissolution. After the complete dissolution of citric acid, 6.22 g of the metal salt was added, carried out individually for each oxide, forming a metal citrate. The mixture was then heated until the liquid reached 100 °C, forming a polyester, followed by resting for 12 h [19].

Subsequently, the polymer was calcinated in a muffle furnace to eliminate all organic matter, in two steps: the first at 400 °C for two hours and the second at 650 °C for four hours. After calcination, the metal oxides corresponding to each metal salt were obtained. Films were prepared using 3 g of Triton X, 0.1 mL of acetylacetone, 0.1 mL of polyethylene glycol and 3 mL of deionized water [20]. These films were deposited onto conductive FTO (fluorine-doped tin oxide) substrates using the doctor blading method (with thickness in the range of approximately 20–25 μm as reported in previous work [21]) and, afterward, calcination was carried out at 450 °C for 30 min, to perform photoanode preparation, as shown in Figure 1 [20].

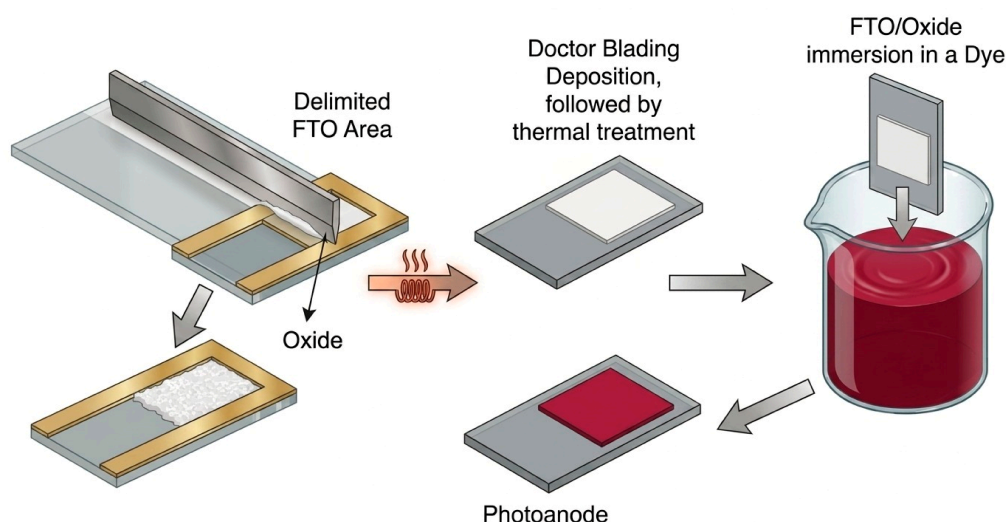


Figure 1. Production of the working electrode onto the FTO substrate through the doctor blading method.

After the calcination of the films, the produced plates were immersed for 24 h in a solution of a specific dye, the N719 dye (bis (tetrabutylammonium)-cis-dithiocyanato-bis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II)), used in photovoltaic cells and systems, in a concentration of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ ethanol solution. Subsequently, the plates were assembled in the sandwich configuration, where the anode consisted of the synthesized film impregnated with the dye, and the cathode was made of graphene supplied by the company HCLG Soluções em Grafeno LTDA. The system also included an electrolyte liquid (I^-/I_3^-) responsible for electron regeneration and for establishing contact between the poles, as described by Tractz and co-workers [20].

The synthesized metal oxides CeO_2 , TiO_2 , ZrO_2 , and SnO_2 were characterized using several methodologies to evaluate their properties. Scanning electron microscopy (SEM) was employed to examine the morphology of the oxides with high resolution. Dynamic

light scattering (DLS) was used to analyze the particle size distribution and particle aggregation, in water, without the addition of any chemical dispersants or surfactants and without undergoing any ultrasonic treatment. X-ray diffraction (XRD) allowed the identification of the crystalline phases present and the determination of the crystalline structure of the oxides through Rietveld analysis. In addition, UV-Vis spectroscopy was applied to investigate the optical properties and determine Egap value using Tauc plots [22]. All these tests were carried out at the Federal University of Technology—Paraná (UTFPR), at the Londrina campus. The photovoltaic cells, in turn, were electrochemically analyzed using open-circuit potential techniques in a Zhenium Zahner potentiostat, under a standard light intensity of 100 mW cm^{-2} , at the Electrochemistry Research Group of UNICENTRO. The deposited films were also analyzed through electrochemical impedance spectroscopy, in a frequency range of 10 kHz – 0.1 Hz and amplitude of 10 mV , in a three-electrode cell (Pt as counter electrode and Ag/AgCl as reference electrode and $\text{KCl } 0.1 \text{ mol L}^{-1}$ as supporting electrolyte), with Nyquist plots fitted using Nova Software (2.1.8).

3. Results and Discussions

In Figure 2A–H the micrographs for all powder synthesized using the Pechini methodology are depicted.

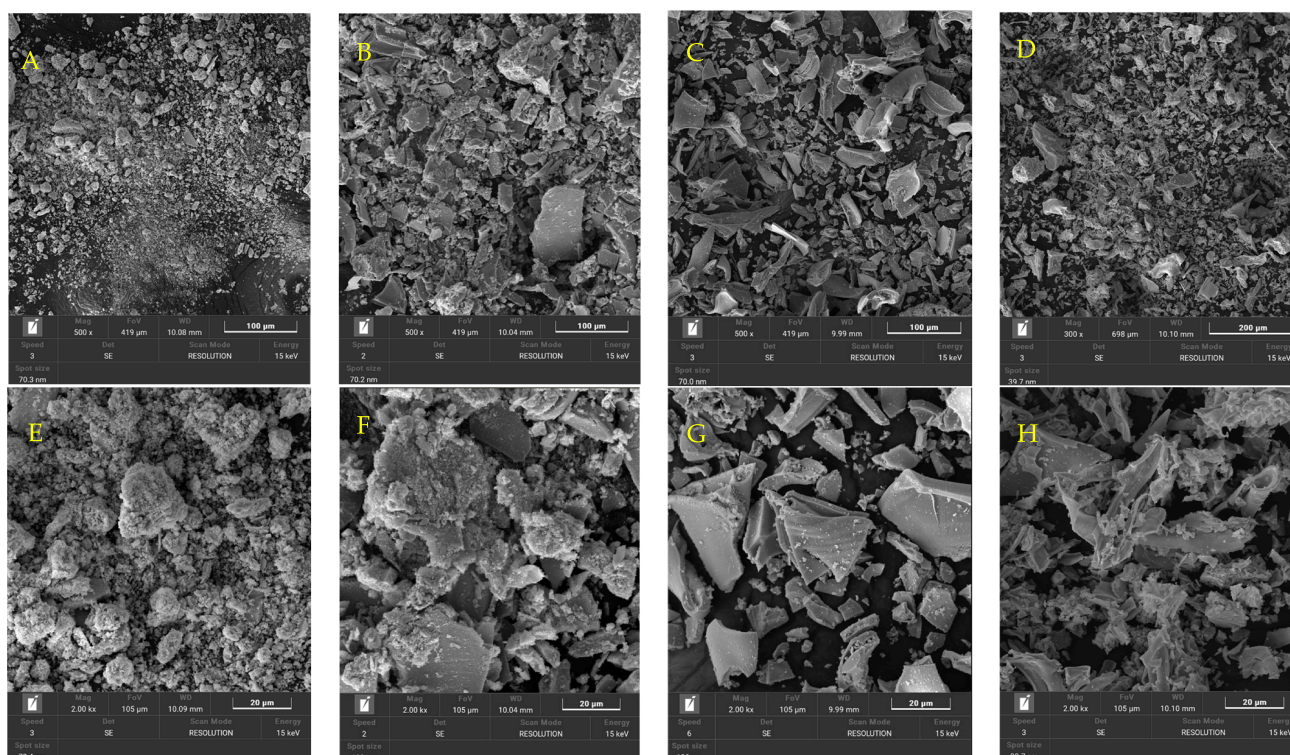


Figure 2. (A–H). Scanning electron microscopy (SEM) images of the synthesized metal oxides at different magnifications. (A,E) CeO_2 ; (B,F) SnO_2 ; (C,G) TiO_2 ; (D,H) ZrO_2 . (A–D) $500\times$ magnification; (E–H) $2k\times$ magnification.

The scanning electron microscopy (SEM) micrographs of the synthesized metal oxides revealed a predominantly non-uniform morphology with particles lacking a defined shape across all samples (Figure 2). This structural heterogeneity and irregularity are expected characteristics inherently originating from the Pechini synthesis method [23]. At lower magnification ($500\times$), the CeO_2 (Figure 2A) and SnO_2 (Figure 2B) particles displayed irregular distributions with coarse agglomerates, which were confirmed at $2k\times$ magnification (Figure 2E,F) as severely polydisperse matrices with varied sizes. Similarly, the ZrO_2

(Figure 2D,H) and TiO_2 (Figure 2C,G) particles also exhibited this lack of defined shape and typical non-uniformity. However, the TiO_2 sample at $2k\times$ magnification (Figure 2G) stood out by presenting a noticeably smoother particle surface and fewer dense agglomerates. This specific surface refinement is consistent with Tractz et al. (2021), who reported that the high organic load of the titanium precursor improves steric hindrance and spacing between nuclei, preventing severe agglomeration during pyrolysis without suppressing the characteristic irregular morphology of the method [21,24].

Furthermore, the highly irregular and interconnected morphology observed in SEM micrographs is a direct consequence of the Pechini polymeric precursor route. During the calcination stage, the rapid thermal decomposition and pyrolysis of the organic resin matrix release a significant volume of volatile gases. Consequently, this gas-induced porosity directly dictates the interfacial dynamics of DSSCs. The smaller pore voids drastically enhance the effective internal surface area available for the chemical anchoring (dye loading) of N719 molecules, which is critical for efficient photon harvesting [15]. Simultaneously, the larger macroscopic pathways formed by the escaping gases ensure unhindered infiltration and mass transport of the liquid electrolyte through the photoanode thickness. As observed in Figure 2G, the characteristic non-uniformity and the presence of fewer dense agglomerates are expected to positively influence the TiO_2 porosity. This behavior is directly attributed to the use of titanium isopropoxide as the starting precursor, which introduces a significantly higher intrinsic organic load that acts as an in situ expanding agent during the pyrolysis process [21].

In Figure 3, the X-ray diffraction patterns of the synthesized oxides are presented with Rietveld refinement.

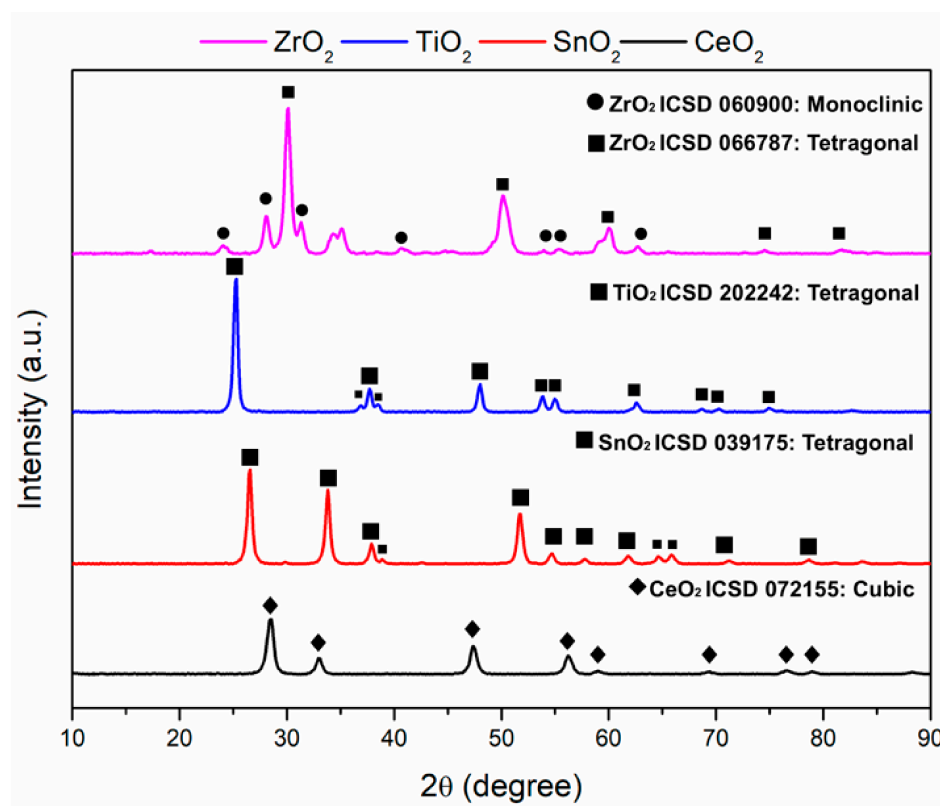


Figure 3. X-ray diffraction (XRD) patterns of the synthesized metal oxides CeO_2 , SnO_2 , TiO_2 , and ZrO_2 .

By observing the XRD patterns, it is possible to see narrow and well-defined peaks with different intensities for the analyzed materials, including CeO_2 , TiO_2 , SnO_2 , and

ZrO₂. This result indicates the crystalline nature of the particles, which is an extremely important parameter for the development of efficient photovoltaic systems. The calcination temperature and time appear to have been effective for promoting crystal growth, since all produced materials presented good crystallinity [25].

All samples exhibited narrow, well-defined diffraction peaks with prominent intensities, confirming the highly crystalline nature of the powders produced via the Pechini route. For the CeO₂ sample, the characteristic peaks located at $2\theta = 28.5^\circ$, 33.1° , 47.5° , 56.3° , correspond respectively to the (111), (200), (220), and (311) crystalline planes of the cubic fluorite structure, showing flawless agreement with the ICSD 072155 standard pattern. The SnO₂ diffractogram revealed major reflections at $2\theta = 26.6^\circ$, 33.9° , 37.9° , and 51.8° , assigned to the (110), (101), (200), and (211) planes of the tetragonal cassiterite phase (ICSD 039175). For TiO₂, the intense peaks at $2\theta = 25.3^\circ$, 36.9° , 37.8° , 38.6° , 48.0° , 54.3° and 55.1° match the (101), (103), (004), (112), (200), (105) and (211) reflections of the standard tetragonal anatase polymorph (ICSD 202242). Lastly, the ZrO₂ profile displayed a unique dual-phase crystalline assembly; the distinct splitting and positioning of the reflections between $2\theta = 24.0^\circ$, 28.2° , and 31.5° confirm the coexistence of both the monoclinic phase (ICSD 060900), highlighted by the (110), ($\bar{1}11$), and (111) planes, the tetragonal phase (ICSD 066787) highlighted by the (101), (110) and (112) planes corresponding to $2\theta = 30.2^\circ$, 35.3° and 50.2° [26].

The Rietveld refinement (Figure S1) of the synthesized oxides showed agreement between the experimentally obtained diffractograms and diffraction patterns obtained from the Inorganic Crystal Structure Database (ICSD). Furthermore, the refinement revealed that under the experimental conditions used, ZrO₂ exhibited the formation of two phases: monoclinic and tetragonal, with the monoclinic phase being more abundant at a relative content of 61.2%, while the tetragonal phase showed a relative content of 38.8%. The other oxides presented a single phase (TiO₂ and SnO₂ tetragonal phase and CeO₂ cubic phase). The stabilization of this dual-phase structure at lower calcination temperatures is particularly interesting for several technological applications, including photocatalysis [27]. In these fields, the controlled coexistence of monoclinic and tetragonal phases within the same matrix is widely recognized as a promising feature, as the structural interfaces between different polymorphs can act as strategic sites to enhance overall materials performance compared to conventional single-phase systems [17,27].

The refinement also shows no significant differences between the network parameters, volume, and density (Tables S1 and 1) of the synthesized oxides when compared to the patterns obtained from the ICSD, thus corroborating the accuracy of the experimentally obtained data.

Table 1. Synthesized powder oxides with crystal system and crystalline size obtained through XRD.

Scaffold Oxide	Crystal System		Crystalline Size (nm)
ZrO ₂	Monoclinic (61.8%)	Tetragonal (38.8%)	14.17
TiO ₂	Tetragonal (100%)		19.53
SnO ₂	Tetragonal (100%)		13.32
CeO ₂	Cubic (100%)		13.14

Table 1 also shows that the crystallite size of the synthesized oxides is in the range of 13–20 nm. These values are similar to those found in the literature for oxides synthesized via alternative synthetic routes, such as the sol–gel method, yielding crystallite sizes around 10 nm [28], the hydrothermal approach, with sizes of approximately 20 nm [29], and the Pechini methodology, resulting in sizes larger than 20 nm [30]. Crystalline size is an

important property when dealing with DSSC, as this factor influences dye adsorption, which directly reflects the efficiency of solar energy conversion into electrical energy [9,31], so that the smaller the crystallite size, probably greater the area for dye adsorption [31]. Therefore, it can be said that the obtained oxides have potential for application in not only in DSSC, but in several electrochemical areas.

Since not only particle shape and crystallinity, but also particle size, can interfere with the photovoltaic parameters of the device, dynamic light scattering was performed, as shown in Table 2.

Table 2. Hydrodynamic radius, polydispersity index (PDI), and zeta potential of the synthesized metal oxides (CeO₂, SnO₂, TiO₂, and ZrO₂), obtained through dynamic light scattering (DLS).

Particle	Hydrodynamic Radius	Polydispersity Index	Zeta Potential
CeO ₂	1083.50 nm	0.121	−3.1 mV
SnO ₂	3908.83 nm	0.271	−5.1 mV
TiO ₂	935.97 nm	0.489	−9.4 mV
ZrO ₂	946.52 nm	0.201	−6.1 mV

The results obtained through the dynamic light scattering (DLS) technique indicate the average hydrodynamic radius of 1083.50 nm for CeO₂, 3908.83 nm for SnO₂, 935.97 nm for TiO₂, and 946.52 nm for ZrO₂. The DLS data must be interpreted carefully, since the values obtained generally correspond to the hydrodynamic diameter of agglomerates rather than to the primary crystallite size. The average hydrodynamic radius obtained for CeO₂, SnO₂, TiO₂, and ZrO₂ suggest the formation of relatively large aggregates, especially in the case of SnO₂. This result is consistent with the work of Viomar et al. (2016), because the Pechini methodology, although low-cost and easy to perform, tends to generate significant agglomeration [23]. According to the same authors, variations in calcination time and temperature, the use of microwaves, and processing in a ball mill are possible strategies to reduce these sizes.

In this context, the particle size values obtained through DLS are important because they may influence interfacial phenomena and directly affect charge transfer kinetics and mass transport processes in electrochemical systems [32]. Particularly, in photovoltaic systems, electrochemical sensors, and hydrogen production applications, larger aggregates can reduce the effective surface area and limit the number of active sites, whereas a better particle dispersion can improve interfacial reactions and overall device performance. Furthermore, the presence of agglomerates can also affect the crystalline phase composition observed using X-ray diffraction, since particle growth during calcination may favor phase transformations and increase crystallite size. Therefore, the correlation between DLS, XRD, and morphological analysis is essential for a more accurate interpretation of the structural and functional properties of the materials.

For zeta potentials, all values obtained were negative, ranging from −3.1 mV for CeO₂ to −9.4 mV for TiO₂. These relatively low absolute values suggest limited electrostatic stabilization of the suspensions, indicating a tendency for particle agglomeration [33,34]. This behavior is consistent with both the SEM observations and the large hydrodynamic radii obtained using DLS. In general, suspensions with zeta potential values greater than ± 30 mV are considered electrostatically stable, while lower values indicate insufficient repulsive forces to prevent particle aggregation [33]. The low zeta potential values observed in this study may be associated with the calcination process and the absence of dispersing agents during the DLS measurements.

The synthesized oxides were also analyzed by ultraviolet–visible spectroscopy in the solid state, and the wavelength and reflectance data were used to calculate the band gap, as shown in Table 3.

Table 3. Egap extrapolation in the Tauc plot from the Kubelka–Munk function.

Oxide	Egap (eV)
CeO ₂	2.8
TiO ₂	3.0
SnO ₂	3.1
ZrO ₂	4.8

The analysis of the UV-Vis data, using the band gap calculation method based on the Kubelka–Munk equation (Equation (1)), allowed the determination of approximate forbidden band widths for the studied materials: 2.8 eV for CeO₂, 3.0 eV for TiO₂, 3.1 eV for SnO₂, and 4.8 eV for ZrO₂ [22].

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

These gap values are in agreement with those typically reported in the literature for these oxides, confirming the successful formation of the expected semiconductor phases. Slight deviations may be associated with several factors, such as particle size, structural disorder, and the presence of defects, including oxygen vacancies, which are commonly introduced during calcination processes [35]. It is important to note that the optical bandgap values themselves play a foundational role in predicting the charge transport and conductivity within these matrices. In third-generation photovoltaic systems, the optimal semiconductor bandgap typically ranges between 3.0 and 3.2 eV [15]. Materials within this ideal threshold, such as the synthesized TiO₂ (3.0 eV) and SnO₂ (3.1 eV), provide an appropriate balance: they ensure high transparency to the visible solar spectrum, preventing competitive photon absorption with the anchored dye molecules, while sustaining proper electronic mobility.

The band gap results are particularly relevant because they affect the electronic structure of the materials and, consequently, their behavior in photoelectrochemical applications. However, the position of the conduction band is even more decisive in determining the voltage that a device can produce. As reported by Longo et al. (2003), the V_{OC} of a cell is determined by the difference between the conduction band of the oxide and the redox potential of the electrolyte [3]. Since the same electrolyte was used in all cells, the observed variations in potential values are related to shifts in the conduction band toward more positive or less positive values. In this sense, the open-circuit potential results provide important insight into the electronic behavior of the different oxides studied.

It is important to note that the open-circuit potential measurement, showed in Figure 4, provided electrical potential values for the different materials studied.

It was observed in Figure 4 that all systems presented a response to illumination, since when sunlight reached the device, the current increase was instantaneous. In Figure 4, TiO₂ presents a potential close to 0.7 V and higher than the others. In addition, ZrO₂ shows the most similar potential value to titanium dioxide, with a value close to 0.6 V.

The V_{OC} results show that all systems were capable of generating a photoresponse, indicating that the devices were successfully assembled and sensitive to illumination [36,37]. Among the tested materials, TiO₂ exhibited the highest potential, close to 0.7 V, which is consistent with its well-known performance in dye-sensitized solar cells. ZrO₂ showed a potential close to 0.6 V, making it the material most similar to TiO₂ in terms of electrical

potential. This behavior is likely related to the position of the conduction band of zirconium dioxide, which is suggested to be close to that of TiO_2 , reinforcing the idea that ZrO_2 may behave as an alternative material with comparable electrical potential characteristics, as demonstrated in schematic overview of Figure S2 [38].

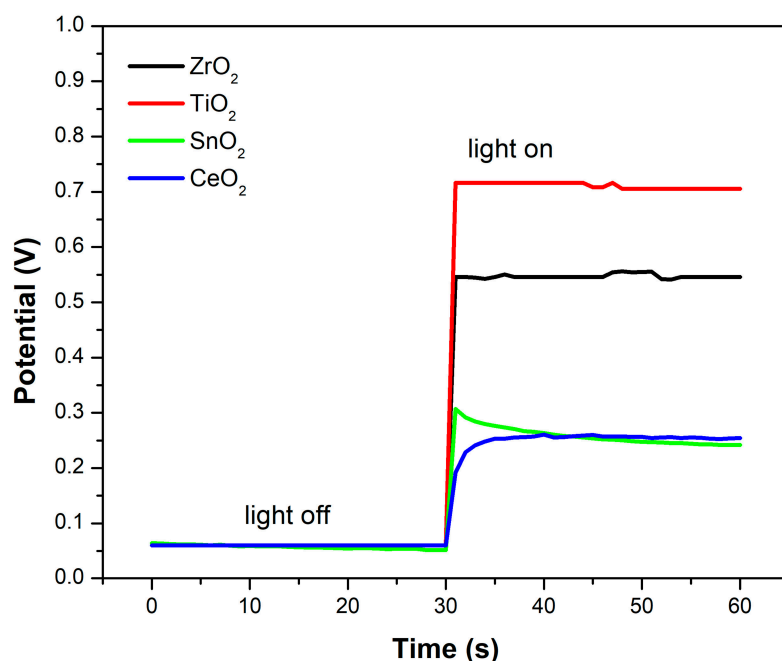


Figure 4. Open-circuit potential (V_{oc}) as a function of time for devices based on ZrO_2 , TiO_2 , SnO_2 , and CeO_2 . The measurements were performed under dark conditions (light off) and upon illumination (light on).

Nevertheless, ZrO_2 , CeO_2 , and SnO_2 , when used as standalone materials in dye-sensitized solar cells, present intrinsic limitations that reduce their photovoltaic performance. Although ZrO_2 has a favorable conduction band position for electron injection, its very wide band gap, as previously reported in E_{gap} determination, and insulating character limit light absorption and electron transport [15]. CeO_2 may suffer from increased charge recombination due to defect states associated with the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox pair and oxygen vacancies. SnO_2 , despite its high electron mobility, has a more positive conduction band position, which can reduce V_{oc} and favor recombination [39].

To further investigate the charge transport properties of the synthesized oxides, electrochemical impedance spectroscopy (EIS) measurements were performed in 0.1 mol L^{-1} KCl solution (Figure 5). The obtained charge transfer resistance (R_{ct}) values were $57.8 \text{ k}\Omega$ for TiO_2 , $72.6 \text{ k}\Omega$ for SnO_2 , $283 \text{ k}\Omega$ for CeO_2 , and $305 \text{ k}\Omega$ for ZrO_2 (Figure S3). These results indicate significant differences in the electron transfer behavior of the investigated materials.

Among the analyzed oxides, TiO_2 exhibited the lowest charge transfer resistance, confirming its excellent electronic properties and reinforcing its widespread use as a photoanode material in dye-sensitized solar cells. SnO_2 presented a similarly low R_{ct} value, which is consistent with its high electron mobility reported in the literature ($1.21 \times 10^{-3} \text{ V}^{-1} \text{ s}^{-1}$) [40]. Although SnO_2 generally exhibits faster electron transport than TiO_2 , its more positive conduction band position may limit the photovoltage generated in DSSC devices, explaining the lower open-circuit potential observed in comparison with TiO_2 [15].

In contrast, CeO_2 and ZrO_2 showed considerably higher charge transfer resistance values. For CeO_2 , the elevated R_{ct} may be associated with the presence of defect states related to the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple and oxygen vacancies, which can act as electron

trapping sites and hinder charge transport through the material [39]. Although such defects may be advantageous in catalytic and photocatalytic applications, they tend to increase recombination processes and reduce electron mobility in photovoltaic systems.

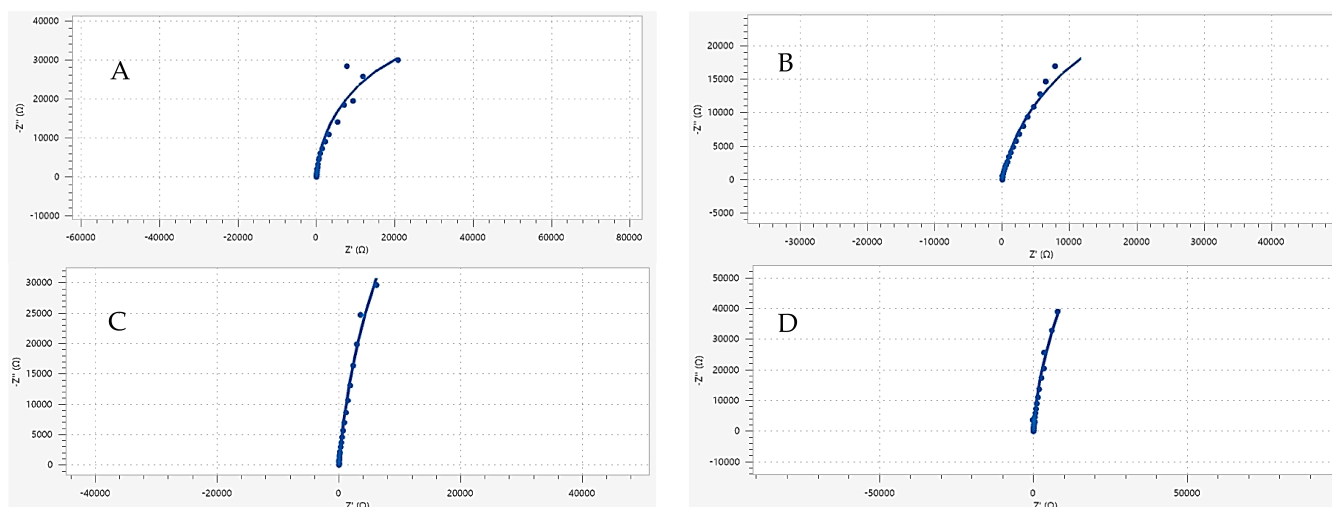


Figure 5. (A–D) EIS fit to photoanodes produced using SnO₂ (A), TiO₂ (B), CeO₂ (C) and ZrO₂ (D) onto the FTO through doctor blading.

ZrO₂ exhibited the highest charge transfer resistance among the studied oxides. This behavior can be attributed to its wide band gap (4.8 eV) and intrinsically insulating character, which limit the concentration and mobility of charge carriers. Interestingly, despite presenting the highest R_{ct} value, ZrO₂ generated an open-circuit potential close to that observed for TiO₂. This result demonstrates that the photovoltage generated by a semiconductor is not exclusively determined by its electrical conductivity, but is strongly influenced by the relative position of its conduction band with respect to the redox potential of the electrolyte [15].

The combined analysis of V_{OC} and EIS results provides important insights into the electronic behavior of the synthesized oxides. While the V_{OC} measurements are primarily associated with the energetic alignment between the semiconductor conduction band and the electrolyte redox potential, the charge transfer resistance reflects the efficiency of electron transport across the semiconductor/electrolyte interface [41,42]. Consequently, materials such as ZrO₂ may exhibit relatively high photopotentials while simultaneously presenting poor charge transfer characteristics. On the other hand, TiO₂ combines favorable band alignment with low charge transfer resistance, which contributes to its superior performance in DSSC applications. Therefore, while these oxides show potential, their most effective use is generally reported in doped systems or in combination with TiO₂, where improvements in charge separation and overall device efficiency can be achieved [43].

It is important to emphasize that while Open-Circuit Potential (V_{oc}) transients and Electrochemical Impedance Spectroscopy (EIS) provide valuable insights into the thermodynamic band alignment and electronic transport kinetics across the semiconductor/electrolyte interface, they do not depict full device power conversion efficiency (PCE) or spectral quantum efficiency (IPCE). Nevertheless, as a preliminary screening framework, isolating these parameters under standardized conditions allows a direct evaluation of the electronic limitations of each standalone material—such as the insulating behavior of ZrO₂ or the recombination pathways in CeO₂, without the geometric interferences of film thickness variations. Consequently, these findings serve as a fundamental stepping stone.

Overall, the results demonstrate that the Pechini methodology is an effective and versatile route for synthesizing metal oxides with potential application in photoelectro-

chemical systems. Although some materials presented limitations when used as standalone photoanodes in DSSC devices, the obtained photopotentials indicate that these oxides may still be promising for other applications where high V_{OC} or suitable band alignment is required, such as photoelectrochemical hydrogen production, sensors, and hybrid systems [44,45]. In this context, the control of synthesis parameters, particle dispersion, and electronic structure becomes essential to tailor the materials for specific functionalities. Therefore, beyond DSSC applications, the materials synthesized in this study show potential for broader use in energy conversion and environmental technologies, especially when employed in composite or doped configurations.

4. Conclusions

The Pechini methodology proved to be efficient in the fabrication of metal oxides. The structural analysis through X-ray diffraction confirmed the crystalline nature of the synthesized materials and showed good agreement with the expected reference phases. ZrO_2 presented a mixed-phase composition, with monoclinic and tetragonal contributions, while TiO_2 was obtained as a single tetragonal phase, SnO_2 as a tetragonal cassiterite phase, and CeO_2 as a cubic fluorite phase. In addition, the narrow and well-defined diffraction peaks indicated satisfactory crystallinity, reinforcing the effectiveness of the synthesis route. Despite this, the morphology of the oxides was not fully uniform, with the presence of agglomerates, resulting in average radius values of 1083.50 nm for CeO_2 , 3908.83 nm for SnO_2 , 935.97 nm for TiO_2 , and 946.52 nm for ZrO_2 .

The determination of the band gap values for the metal oxides CeO_2 , TiO_2 , SnO_2 , and ZrO_2 , with results of 2.8 eV, 3.0 eV, 3.1 eV, and 4.8 eV, respectively, demonstrated that all materials presented photosensitive characteristics when applied in a DSSC. The formation of an electrical potential was observed when light was incident on the device, confirming the photoresponse of the systems; however TiO_2 exhibited a lower R_{ct} value (57.8 k Ω). Overall, the results indicate that the synthesized oxides possess structural and optical properties consistent with their intended application, showing that the Pechini methodology is a viable route for the production of functional semiconductor materials.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr14142327/s1>, Figure S1: X-ray diffractograms of the experimentally synthesized oxides and calculated using the Rietveld refinement method: (a) ZrO_2 , (b) TiO_2 , (c) SnO_2 , and (d) CeO_2 . Table S1: Network parameters obtained through Rietveld refinement for the synthesized oxides. Figure S2: Schematic overview of band energy alignment of synthesized oxides in a dye-sensitized solar cells. Figure S3: Electric circuit for scaffold oxide/electrolyte interface obtained through EIS measurement with KCl as supporting electrolyte to TiO_2 , SnO_2 , CeO_2 and ZrO_2 respectively.

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Abbreviations

DSSC	Dye-Sensitized Solar Cell
SEM	Scanning Electron Microscopy
DLS	Dynamic Light Scattering
XRD	X-Ray Diffraction
ICSD	Inorganic Crystal Structure Database (ICSD).
EIS	Electrochemical Impedance Spectroscopy
Rct	Charge Transport Resistance
Voc	Open-Circuit Potential
PCE	Photoconversion Energy Efficiency
IPCE	Incident Photon to Current Efficiency
Egap	Energy Gap Value

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