REVIEW ARTICLE

Revealing the synergy of Sn insertion in hematite for next-generation solar water splitting nanoceramics

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Abstract
Hematite nanoceramics is considered as one of the most promised materials for photoelectrochemical (PEC) water splitting due to its remarkable characteristics such as low band gap, earth abundant composition and stability. In general, the hematite design over fluorine-doped tin oxide (FTO) glass substrate involve high thermal treatment to promote its surface activation. As consequence, Sn from FTO substrate is commonly found migrating through the hematite layer. This unintentional Sn species diffusion is often associated with improvements on the photoelectrochemical response. The role played by Sn migrating from FTO against intentionally incorporated during the synthesis process into hematite to boost its performance remain unclear. In this perspective, the complexity of these matters was discussed to reveal the contribution and limiting aspects of each effect on the hematite manufacture. Indeed, a deep comprehension and latest advances on Sn diffusion and incorporation role on hematite led us to find synergistic characteristics between them, indicating economically viable alternatives to design active hematite nanoceramics. Regardless of its morphology, the key direction is based on external modifications which reduce energetic barriers on interfaces to favor electron carrier dynamics.

KEYWORDS
annealing temperature, hematite nanoceramics, interfaces, Sn diffusion, water oxidation

1 | INTRODUCTION

Solar water splitting–driven hydrogen fuel production is very attractive due to positive aspects as higher energy density and a renewable energy source arising from water and sunlight.¹ Despite these remarkable overall strengths, sustainable large-scale clean hydrogen production is quite far from being available, in particular by the lack of efficient and economically viable electrodes for photoelectrochemical (PEC) cells. These devices involve two redox electrochemical reactions: hydrogen evolution on the cathode and oxygen evolution on the anode, where one or more photosensitive material can be enforced in the device design.² It is worth mentioning that oxygen evolution reaction (OER) is the rate-determining step of the photoelectrochemical water splitting, because of the four-electron reaction mechanism of water oxidation, which
requires a large overpotential and has associated sluggish kinetics. Therefore, studies devoted to this area are relatively trivial, in which earth-abundant metal oxides such as ZnO, TiO₂, SiO₂, and Fe₂O₃ are usually exploited in the development of new electrodes for sunlight-assisted water splitting. Among them, hematite nanoceramics (α-Fe₂O₃) stands out when it is desired to have cheap and efficient electrodes for PEC, being the focus of several works and review papers.

The abundance of iron minerals in the Earth’s crust is well known, and in particular, Brazil is the second largest producer of iron ore in the world due to its mineralogical aspects, exporting to several countries. The presence of natural mineral reserves and mining activity represents an advantage if hematite is used in PEC photoanodes, since the demand could be supplied by the countries that explore iron sources. To overcome well-known intrinsic deficiencies of hematite associated with their electronic limitation that make the real response fall short of the predicted theoretical efficiency into solar to hydrogen conversion, different elements, such as: Ti, V, Sh, P, Cr, B, Ge, and Sn have been highlighted as a potential modifier for this semiconductor polycrystalline ceramic, since it has been reported as able to improve the separation of photogenerated charges, achieving the highest photocurrent values among hematite photoanodes with different morphologies.

However, in addition to these aspects, there is still some ambiguity and lack of consensus regarding the Sn presence in hematite. The different contributions of this element have been reported to depend on the methodology, the hematite morphology, and the thermal treatment employed. Thus, all Sn-hematite preparation steps generate a large number of experimental variables related to the final response. To exemplify such complexity involved in assigning the role of Sn into hematite nanoceramics, some points can be introduced taking into account materials engineering. Among these, the manufacturing process is normally carried out by nanstructured morphology grown over a commercial conductive glass substrate composed of fluorine-doped tin oxide (FTO), where regardless of exposure time at high temperature, the diffusion of Sn through the hematite nanoceramic layer will occur. The discussion where Sn-diffused will “compete” or work in synergy with other elements intentionally incorporated becomes a paradox. Understanding and split the real role of each element intentionally or unintentionally incorporated is quite a challenge in this field. Therefore, we believe that an appropriate discussion is capable of directing future studies from a perspective on the development of more efficient hematite nanoceramic-based devices. A critical analysis of this interdependence can lead to the development of figures of merit and achieve a convergence point revealing a promisor direction on how to synthesize or incorporate Sn in hematite system. In parallel, the findings can be expanded to other hematite modifying elements, incorporating the promising advantages for the commercialization project of hematite photoanodes.

In this regard, Sn presence on hematite can be classified in: (a) unintentional Sn introduction on hematite nanoceramics caused by tin diffusion from glass substrate (FTO) during the annealing process or (b) intentional Sn addition, which is associated with the hematite precursors or in a subsequent step of the hematite modified synthesis. Unintentional Sn addition is very common and inevitable for certain thermal treatment conditions, such as exposure for long periods and/or high temperature (usually above 600°C). As a consequence, bare hematite does not always refer to Sn-free material and both strategies have been often reported as Sn doping methodologies. Based on these aspects, some controversial points have been disseminated, mainly by the indiscriminate use of the word “doping” referring to any Sn addition on hematite able to change the photoelectrochemical performance. Moreover, tin incorporation into hematite has been reported as capable of occurring in crystalline structure, on the surface or at grain boundaries, not necessarily replacing Fe³⁺ by Sn⁴⁺ in a site. Given the complexity of the issue, all these points will be properly discussed on the next sections, with the pertinent experimental basis, aiming to solve possible confusions about doping, segregation, and the effects of unintentional and intentional Sn presence on hematite or even on heterointerfaces.

In this perspective, we intend to find figures of merit based on the literature to elucidate the roles associated with Sn diffused and Sn incorporated on hematite regarding the overall system impacts. Since Sn-hematite can have the contribution of both diffused and incorporated Sn, the uncertainty about which one is responsible for the photoanodes characteristics needs to be considered. To provide the reader a complete view on the subject, the text was divided into sections, initially covering the temperature effect on the FTO-glass substrate regarding its properties impairment, followed by the importance of temperature and Sn diffusion for the hematite photoelectrochemical response, finishing with a deep analysis about the Sn intentionally incorporated to hematite. Through a critical and comprehensive view of the literature, including recent reports, we critically reviewed and discussed the points of convergence in the works presented in the state-of-the-art to provide a path for the reader, giving a new direction that should be pursued toward the nanoceramics design. The great challenge in this perspective is to present the difficulty in assigning those responsible for the majority response, where all the parameters analyzed play important
roles. Thus, we propose to understand the importance and the limits in each parameter leading to a step by step in the construction of knowledge.

2 | TEMPERATURE EFFECTS ON TCO SUBSTRATE

Nanostructured hematite photoanodes are commonly prepared by depositing the material over conductive substrates, among which fluorine-doped tin oxide (FTO) glass is commonly used to support the hematite structure due to its cost-benefit. The main material on FTO substrate is SnO₂, which is almost insulating at room temperature, especially if it is completely stoichiometric.⁴³ Due to such characteristics, there is a need to increase conductivity to make the substrate suitable for optoelectronic applications, such as PEC devices and, doping the semiconductor is an alternative to improve the carrier density and decrease the resistivity. Fluorine doping stands out since it provides a decrease system resistivity while maintaining transparency, which favors the application of FTO as a substrate for optical-electronic devices.⁴⁴,⁴⁵ However, it is known that the FTO homogeneity, stability, morphology, optical and electrical properties are dependent on processing conditions such as precursors concentration and temperature, at commercial scale and homemade.⁴³,⁴⁶ The knowledge of this dependence is fundamental to understand that similar effects may occur during the annealing of hematite. Therefore, we believe that before properly discussing any effect related to the Sn presence on hematite, a previous step is necessary to address information regarding the effect of annealing temperature on the FTO and answer the first question: What are the impacts caused by the relatively high-temperature exposure of the glass conductive substrate on which hematite is supported?

The commonly employed methods to obtain FTO substrates involve chemical reactions on glass substrate, which can be heated and/or subjected to an additional thermal treatment step to produce fluorine-doped tin oxide. Chemical precursors like SnCl₄, SnCl₂, C₄H₈SnC₁₃ and NH₄F, CF₃COOH have been used as tin and fluoride source in chemical spray pyrolysis, ultrasonic spray pyrolysis, atmosphere pressure chemical vapor deposition, electrochemical deposition at atmospheric pressure, not exclusively.⁴⁴,⁴⁶ Considering that the precursors can be prepared in aqueous, acid, organic solutions and a mixture of them, hydrogen interaction is facilitated on the hydrophilic surface of silicate-based glass substrates, on which O⁻ ions, [glass](OH)⁻, acts as nucleation sites for heterogeneous surface reactions. Those solvents are capable of coordinate with tin cations and the adequate heating decompose/evaporate these ligands and secondary products, promoting tin adhesion onto substrate surface as [glass] Sn(OH)₃³⁻ and its conversion to [glass]SnO₂, represented by the reaction (1). It was reported that lateral growth can occur from the attachment of OH⁻ ions onto as-formed tin oxide, resulting in nanomorphology of the layer.⁴⁸

\[
[\text{glass}] \text{Sn(OH)}_3^{3-} + 3\text{OH}^- \rightarrow [\text{glass}] \text{SnO}_2 + 2\text{H}_2\text{O(↑)} \quad (1)
\]

Concomitantly, the process of fluorine doping also occurs, considering F substitution on oxygen site of SnO₂ lattice, as described by the reaction (2).

\[
[\text{glass}] \text{Sn(OH)}_3^{3-} + 4\text{NH}_4\text{F} + 3\text{OH}^- \rightarrow [\text{glass}] \text{SnF}_4 + 4\text{H}_2\text{O(t)} + 4\text{NH}_3(↑) \quad (2)
\]

Ammonium fluoride decomposes in NH₃ and HF at 100°C, also enabling the fluorine doping from the reaction of the HF cloud that surrounds the SnO₂ being formed.⁴⁶ In both processes, the dopant concentration and temperature have an important role on the FTO deposition rate. In general aspects and considering the usually employed chemicals, the global reaction for FTO deposition onto glass substrate submitted to a temperature able to promote thermal decomposition of byproducts can be expressed as:⁴⁷

\[
\text{SnCl}_4 + 4\text{NH}_3\text{F} + 2\text{H}_2\text{O} \rightarrow \text{F}: \text{SnO}_2 + 3\text{HCl(t)} + \text{NH}_4\text{Cl(t)} + \text{HF(↑)} \quad (3)
\]

To elucidate the influence of processing parameters on the final properties of FTO, Figure 1 displays the dependence of electrical properties regarding the F concentration and the annealing temperature. As can be observed in Figure 1A, electrical properties are strictly influenced by the fluorine concentration which increases the mobility and charge density while decreases the resistivity. The fluorine concentration from 10% in the precursor solution contributes to the F atoms occupying oxygen sites in the SnO₂ structure that are sufficient to decrease few orders of magnitude in resistivity. Nevertheless, for the F/Sn ratio above 60% there was a decreasing in mobility and charge density, which led to an increment in resistivity. This and findings of similar works⁴⁹ make it clear that there is a limit for beneficial contribution to the substrate conductivity from fluorine doping and an optimal inflection point should be achieved to guarantee the electrical properties on this substrate.

Indeed, the increase in resistivity with high dopant concentrations has been investigated and even attributed to fluorine interstitial (Fᵢ). However, Fᵢ formation is claimed to be energetically unfavorable on the SnO₂ structure and, therefore, is the subject of in-depth studies. From density functional theory (DFT) calculations and related theories, it was pointed out that fluorine atom occupying substitutional oxygen sites in SnO₂ is most stable in the configuration (Fₐ⁻), which can bind with the Fᵢ forming the complex (F₂)₀, with both fluorine atoms sharing the oxygen site. This (F₂)₀ was related to a compensation derived from the increase in the dopant concentration, capable to reduce the
charge density. Another work investigated the effects of $F_i$ from Hall measurements and DFT calculations associating them to X-ray photoemission spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Distinct fluorine configurations were studied considering Sn-rich and O-rich conditions, chemical potentials associated to standard enthalpy of formation for SnO$_2$ ($-5.98 \text{ eV}$) and for SnF$_4$ ($-12.14 \text{ eV}$). The results evidenced delocalization of electron density when fluorine substitutes oxygen ($F_O$) and localization when $F_i$ occupies interstitial position, estimating two $F_O$ donors to one $F_i$ acceptor. From SIMS, it was confirmed that there are approximately three F atoms than the free electron density ($n$) on the FTO, responsible for reducing mobility by a third over the theoretical value ($120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $n$ close to $4 \times 10^{-20} \text{ cm}^{-3}$) in a self-compensation effect.

Despite the electrical parameters influenced by the fluorine concentration and its possible configuration on tin oxide, it is important considering the effects of thermal treatment on the fluorine-doped tin oxide chemical stability, since fluorine loss can be stimulated by certain conditions. In this regard, Luangchaisri et al demonstrated that, in addition to temperature, the exposure time can be decisive for the FTO properties, increasing the charge mobility by increasing the grain size which contributes to decrease grain boundary losses. In the medium-temperature regime, changes in resistivity and charge mobility in the FTO are observed. Above $200^\circ\text{C}$, the exposure time at the desired temperature becomes a determining factor contributing to decrease internal resistance, which can be related to several factors of the structure accommodation (crystallinity, grain growth, etc.). However, the charge density decreases by five times compared to the bare substrate, as shown in Figure 1B. This result is a strong indication of the correlation between temperature and the fluorine losses, which would cost a decrease in the FTO charge density and even result in substrate inefficiency for further applications.

Furthermore, higher temperature is often used during FTO preparation and some works report its influence on the functional properties. One of these exploited the atmosphere pressure chemical vapor deposition (APCVD) technique for prepare FTO in an industrial production line, maintaining the glass surface at $600^\circ\text{C}$ at nitrogen flow during the deposition and submitted the as-prepared samples to air annealing at temperatures from 200 to $650^\circ\text{C}$ for 20 minutes. Lower mobility and carrier concentration were obtained for the annealing above $400^\circ\text{C}$. In addition, there was a reduction of the grain sizes for temperatures above $580^\circ\text{C}$, which can be associated with more grain boundaries. As a consequence, the sheet resistance was increased for these substrates, being almost six times higher for the one annealed at $650^\circ\text{C}$ in relation to the others.

By using the APCVD method to prepare FTO coated glass, but varying the deposition temperature between 580 and $640^\circ\text{C}$, Yates et al observed a decrease on carrier concentration and a resistivity increment of $\sim 2.5$ with increasing temperature. Considering the same deposition method (maintaining the substrate temperature at $650^\circ\text{C}$) and postannealing the samples from 600 to 720$^\circ\text{C}$ during 150 to 300 s, important results were revealed considering that the glass tempering process above $700^\circ\text{C}$ is often used in the industry. Indeed, this temperature proved to be critical to preserving the substrate properties, since the resistivity increases gradually from $5.99 \times 10^{-4}$ for 150 s to $9.00 \times 10^{-4} \Omega \text{ cm}$ for 260 s, and to $36.7 \times 10^{-4} \Omega \text{ cm}$ for 300 s, as a result of the lower mobility and carrier density, as expected. Based on these reports, it is clear that high temperature and exposure time have considerable impacts on the final electrical properties of FTO coated glass substrates. As demonstrated, few seconds of annealing may have a high influence on...
substrate conductivity, so it is necessary to consider whether the changes resulting from thermal treatment of thin films are due to the deposited material or the substrate itself.

In addition, other concepts involving FTO substrates preparation are important to be considered. In the solar-driven water splitting field is widely reported the nanosstructure growth over FTO substrate and, it is well known the PEC device efficiency is limited by interfaces. In this sense, back-contact quality has an important role and can be decisive in the charge collecting process through the external circuit. Once the nanostructures are supported on a conductive substrate, the ohmic contact between the substrate-nanostructure is expected to be satisfactory to maintain efficiency in the charge transport. As a heterojunction, the influence of thermal treatment on the FTO is a good approach to analyze the impacts on the photoelectrochemical performance of photoanodes supported onto this substrate.

Another aspect to mention is the possible variation of glass quality onto which the FTO is coated, considering that is commonly used as a commercially developed substrate. This aspect turns the discussion more complex in terms of annealing temperature and conductive layer properties, interconnecting issues that limit the selection of the subsequent temperature to which the system will be subjected, avoiding the glass melting and the possible diffusion of unwanted impurities.

In most works presented in the literature, the manufacturing process and the effects on the substrate conductivity due to temperature exposure are suppressed by the characteristics of the photoactive material that is supported on it, bringing the discussion to the background. Nonetheless, it is known that the thermal treatment can provoke effects that range from: (a) relieving tension due to lattice mismatches, (b) modifying the surface energy and/or morphology, (c) improving crystallinity, and (d) particles adherence to the substrate. Despite the morphological, structural, and optical impacts associated with temperature, annealing processes can lead to the ion diffusion between deposited layers and the conductive substrate that need to be considered.

For instance, a barrier layer can be coated on the glass substrate before depositing FTO for further investigation about a possible diffusion region at glass-FTO interface and its influence on final properties. By using this strategy and depositing the FTO layer by APCVD onto a SiO$_2$-glass substrate (at 650°C), Yang et al studied the elements distributions with sputtering time (0-800 s) and post-treatment at 700°C for 202 and 262 s. The Si atomic content remained insignificant until sputtering time of 490 s, when it began to increase gradually along with the gradual Sn decrease, corresponding to a diffusion region between SiO$_2$-layer until FTO surface. From this point, the relative concentration [O]/[Sn] increased with the sputtering and annealing time, while the fluorine content was negligible during all the time period employed.

Moreover, the chemical states distribution in the XPS spectra was changed from the as-prepared FTO films to those annealed, mainly referring to the Sn3d$_{5/2}$ and Si2p, which were influenced by oxygen-deficient states and lattice mismatch in the diffusion layer caused by thermal treatment. As expected, the electrical properties were affected and, comparing the as-prepared and annealed FTO film at 262 s, the charge density decreased from $6.98 \times 10^{20}$ to $1.39 \times 10^{20}$ cm$^{-3}$ and the resistivity increased from $3.13 \times 10^{-4}$ to $4.73 \times 10^{-4}$ Ω cm.$^{49}$

In view of the limiting aspects presented here, related to the use of temperature in transparent glass conducting substrates, some delimitation is necessary to be carried out preliminarily to the nanostructures design. In the wide range of temperatures to which the substrate is subjected to obtain thin films, the literature shows that, even at medium temperatures, no positive effects regarding the improvement of electronic conductivity can be observed. Conversely, such improvements have been achieved with high temperature, especially when considering usual annealing of the hematite supported on FTO. This raises many questions regarding whether the temperature influence on the glass-FTO electrical parameters, fluoride loss, and ion diffusion through the interfaces can be cumulative, not only in the preparation of the FTO layer but also during the deposition of materials on it and subsequent thermal treatments. In this case, a balance to preserve the TCO properties as much as possible, reducing the resistance to the charge transport with minimal fluorine losses and avoiding the glass melting are extremely necessary.

Despite the knowledge of the problems previously mentioned and investigated in several papers focused on decreased conductivity and increased resistance of the substrate caused by inherent changes resulting from temperature and exposure time, we understand that it can be complicated to control and identify these effects at high temperatures. Broadly speaking, all the aspects covered here are fundamental to the following topics, to understanding the maintenance of the overall system efficiency regarding the substrate properties. Especially on the hematite-based photoanodes field, there are a large number of papers reporting benefits and harms of annealing at high temperature, ranging from the ion diffusion between the layers to the stoichiometry loss on the conductive layer changing electrical properties, favoring or not the final performance.$^{56-59}$ It has to be admitted that given the various works in this area, each one pointing out specific effects for the annealing step, it is sometimes difficult to establish a trend or common effect between them. Notwithstanding the lack of agreement, our idea is elucidating these temperature-dependent topics in the next section following the discussion initiated here, with great emphasis on the unintentional Sn diffusion from the FTO substrate through the deposited layer over it, seeking to discuss its effects and whether they are beneficial or not to final application.
3  |  Sn-MODIFIED HEMATITE PHOTOANODES

3.1  |  Sn diffusion from FTO to hematite

The annealing process is a common step involved in hematite photoanode manufacturing, considering the different methods that can be used to achieve the hematite phase. As an example, the widely used wet-based or environmentally friendly routes capable to produce different morphologies generally involve the synthesis of an intermediate phase (such as β-FeOOH/akaganeite), for which annealing step is necessary to obtain the photoactive phase.23,60 According to the iron oxide phase diagram, the α-Fe₂O₃ phase can be thermodynamically stabilized at the temperature around 390°C, confirmed by thermogravimetric and X-ray diffraction analysis.56,61 Thus, annealing treatment at temperature above 400°C is commonly reported and, as previously discussed, it can induce modifications in the conductive substrate and, consequently, in the layers deposited on it. Among the observed impacts associated with temperature, Sn diffusion from FTO to hematite has been widely observed, mainly for high-temperature annealing which is commonly also named as activation process for hematite photoanodes. This associated activation has been related to improvements on the hematite photoelectrochemical properties when compared to the ones do not submit to additional annealing process or annealed at lower temperature.62 In this respect, in order to better understand the key effects on hematite nanoceramics, we need to answer important questions: How far do the benefits of unintentional Sn diffusion in hematite photoanodes extend?

To answer these questions and provide a proper direction to the field, Figure 2 can help to develop initial understanding. On this, we have tried to summarize the photoelectrochemical responses as a function of wide range of temperature that hematite has been subjected, considering different synthesis method and morphologies such as nano-columns,63 mesoporous wormlike,64 nanorods,65 nanowires, and nanocorals,66 obtained from atomic layer deposition, colloidal solution, and hydrothermal treatments. It can be observed from three distinct regions regarding hematite photoanode response according to temperature: the first one comprises low temperature range (400-650°C), in which the current state was similar to dark scans, in other words, representing hematite nanocermics with no photoelectroactivity; the second region corresponds to annealing temperatures of 700-800°C, responsible for the greater reported current densities in the literature; and the third includes 1000°C and the highest photocurrent obtained for Sn self-diffusion.

It is necessary to mention that hematite photoanodes performances have not shown any previous normalization, and looking at this way, photoelectrochemical response seems to be directly proportional to the temperature increment. Furthermore, a critical view must be directed to the maximum point, which will be discussed ahead, but refers to a hematite deposited onto a FTO-quartz substrate. This work is extremely important for fundamental study, but does not represent a realistic region for commercial purposes, considering the cost of using a suitable substrate to withstand high temperature and possible changes in the FTO interface. As aforementioned, at high annealing temperature the enhancement on hematite properties is commonly related to the presence of tin diffused from the substrate. In these aspects, reports in the literature have associated the performance to different effects as: morphological, optical, structural, and/or electronic properties.

In terms of morphological modifications, it was investigated hematite nanowires (NWs) obtained from hydrothermal conditions and two-step annealing at 550°C for 30 minutes and 800°C for 20 minutes.31 This annealing process promoted a NWs diameter increment from 60 to 150 nm and a length reduction from 700 to 370 nm, associated respectively with higher probability of charge recombination and lower light absorption. By chemical vapor deposition process at 400°C for 10 hours, with subsequent treatments at 700 or 800°C for 20 minutes, it was observed a particle size increase from 30 nm for the hematite treated at 400°C, to 60 and 75 nm for hematite annealed at 700 and 800°C, respectively.64 Regarding the hydrothermal preparation, different hematite nanocermics synthesized at 0.25, 2, 6, 10 and 24 hours at 100°C and, subsequently annealed at 390°C for 1 hour or 750°C for 30 minutes, demonstrated that high temperature enabled the rod growth preferentially on the (110) plane which is associated with the best electronic transport on hematite structure.56

By the colloidal method, an increase of two orders of magnitude was obtained in the optical properties and, the particle
growth was associated with an improvement in the photovoltaic efficiency of the hematite, correlated it with the incorporation of doping ions (Sn⁴⁺). Temperature deserves to be highlighted as a determining factor at this point, since low temperature promoted photocurrent values with few orders of μA cm⁻², while hematite treated at high temperature (800°C) reached 0.56 mA cm⁻². At intermediate temperature (700°C), it was observed a photocurrent value corresponding to that observed for 400°C.

Analytically, the photocurrent associated with material absorption (J_{abs}) and overall efficiency (η_{global}) was calculated for these different heat treatment conditions presented (Equations 4 and 5). The correspondence between η_{global} for hematite photoanodes annealed at different temperatures is presented in Figure 3 to gain insights on its influence on real performance.

\[ J_{abs} = -q\varphi (\eta_{LH}) \quad \eta_{LH} = 1 - e^{-\int J_{abs}\, dz} \]  

\[ J_{photo} = J_{abs} \cdot \eta_{global} \]

where \( q \) is the elementary charge, \( \varphi \) is the photon flux in the AM 1.5 G and \( \eta_{LH} \) is the light harvesting.

Estimated \( J_{abs} \), a critical analysis can be made, from which it is noticed that the absorption efficiency follows the described trend increasing linearly from 6.52, 8.63 to 9.21 (mA cm⁻²), following the temperature increase of 400, 700, and 800°C, respectively. However, the photoelectrochemical response does not follow that obtained by \( J_{abs} \). According to the previous section, tin diffusion is expected to be increased at high temperatures (700 and 800°C). However, in Figure 3, analyzing in terms of \( \eta_{global} \) we were able to isolate the optical effect associated with the increment of Sn ions into hematite structure, showing that the tin role goes beyond the change in optical property. Clearly, the effect might be different, for example crystallographic, as we observe a contradictory tendency in the absorption efficiency: the 700°C presented an absorption efficiency ~1.5 times greater than 400°C, but an approximate global efficiency, which is far from the observed for 800°C.

Aware of this tendency, it was evaluated the sintering effect at 1000°C for 4 minutes to investigate the effects of annealing under limited temperature conditions, concerning hematite annealed at 550°C for 10 minutes. Both hematite nanoceramics were obtained from magnetite nanocrystal deposition process (CND) growth onto FTO-quartz substrate. It was also noted a grain growth induced by the high temperature, from 20 to 60 nm. The more elongated hematite grains along the [110] axis contribute to electronic conductivity, facilitating the charge separation process that culminated in a photocurrent density of 1.8 mA cm⁻² at 1.23 V RHE. Moreover, scanning transmission electron microscopy (STEM) and dispersive X-ray spectroscopy (EDS) analysis revealed that an interdiffusion layer (~100 nm) was formed at FTO–hematite interface, where Sn cations diffuse toward hematite over a length of 40 nm and Fe cations at 60 nm in length into FTO.

From this and other results showing a tin/iron mixture near to the FTO–hematite interface, where Sn cations diffuse toward hematite over a length of 40 nm and Fe cations at 60 nm in length into FTO.

In the knowledge that hematite nanoceramics with a layer thickness of a few hundred nanometers, the tin diffused from the FTO rarely dives through the entire bulk and up to the surface, making it difficult to say that Sn-diffused alone is capable of causing direct changes in the OER. As it was not possible to perform normalization in terms of \( \eta_{global} \) for all the results in Figure 3, based on the points with a photocurrent density above 1.0 mA cm⁻², it is important to mention that the hematite layer thickness for them was ~700 nm. Whereas the results refer to measurements at front-side illumination, the unintentional Sn benefits are completely indirect for the photoelectrochemical performance. Especially to the 1000°C annealing, it is difficult to affirm whether the higher photocurrent density can be attributed to the diffusion process of Fe and Sn species in the vicinity of the hematite–FTO interface or if the temperature has a greater impact on beneficial modifications, such as elimination of defects in a polycrystalline material, when compared to treatment at 700-800°C. Considering that ion mobility tends to increase with increasing temperature at the same time that changes in crystallinity and adhesion are more likely to occur, postannealing properties of hematite nanoceramics can be the result of a synergy between these aspects, opening an opportunity for an important line to be investigated.
In this vein, the tin diffusion length limit has been studied by different research groups. For instance, ionic exchanges can be observed in Figure 4A, where the behavior of Sn diffusion in the semiconductor matrix was detailed by the line profile obtained from cross-section TEM-EDS analysis (Figure 4B) of hematite nanoceramics.

With the annealing, the Sn ions from FTO are concentrated between the lower limit of the film (improving the solid/solid interface) up to approximately 100 nm,unchanging the bulk, as evidenced by the Figure 4C. Analyzing analytical transmission electron microscopy data for in situ incorporation of Sn, it was observed that Sn atoms are incorporated into the hematite lattice without additional phase formation or tin oxide clusters. However, the spatial distribution indicates that Sn is preferably arranged in the near-surface regions of the hematite photoanodes, resulting in a shell-like structure. It can be noted that unintentional Sn addition is not responsible for performance improvement of hematite photoanodes thicker than tin diffusion. The diffusion and ions exchanges are thermodynamically unquestionable, and regardless of the method, hematite properties are altered. However, an important fundamental question arises: Are the observed improvements strictly related to the tin itself?

To address this question, we can contribute in this topic by analyzing the presence of underlayers to block the diffusion process of the substrate, maintaining its properties preserved as much as possible. Similarly to discussed in the previous section about a possible mismatch between FTO and glass interface, analogous process can occur between FTO-hematite interface, resulting in a dead layer, most damaging for thin films. On this, intermediate defect states can be formed, hindering the photogenerated current due to charge recombination process. To overcome these effects, ultrathin underlayer or also called blocking layer of metal oxide such as Nb2O5, SiO2, Ga2O3, and TiO2 is deposited onto FTO to support the further hematite layer. The underlayers have the possibility to interfere with the hematite growth, improving their conductivity by reducing the recombination of charges. Notwithstanding, the underlayer also is a potential by dopant source to be disseminated and incorporated in different regions during thermal treatment.

Considering the wide utilization of TiO2 as underlayer and to give an overview about the ion diffusion process, investigations were conducted on mesoporous TiO2 deposited onto a FTO layer of ~700 nm and sintering at 450-600°C for 30-90 minutes. EDS maps revealed considerable Sn diffusion (~80%) from FTO for both underlayer and glass regions with increasing the temperature and annealing time. However, tin diffusion coefficient varied from $3.2 \times 10^{-5}$ to $59 \times 10^{-5} \, \mu m^2 s^{-1}$ in TiO2 layer and from $2.5 \times 10^{-5}$ to $25 \times 10^{-5} \, \mu m^2 s^{-1}$ in glass substrate, attributed to diffusion through grain boundaries. As the Sn diffusion on glass proved to be more difficult, it can be inferred that its activation energy barrier is higher than the one for TiO2, corresponding to $75 \pm 13 \, kJ \, mol^{-1}$, claimed to be lower than the correspondent for multivalent cation diffusion related to Arrhenius model. Apart from these achievements, it can be noted again the importance of the time and temperature to which the substrate is submitted, demonstrating that the Sn diffusion can occur even with a reasonably thick layer of FTO and TiO2. Nevertheless, this possibility is not always considered.

As shown in the literature, using a compact layer of TiO2 prevents the diffusion of Sn, where notoriously the blocking layer over FTO reduces the overall resistance. At 800°C, the Ti4+ incorporation was favored and the photocurrent increases from 0.8 to 1.28 mA cm$^{-2}$ for FTO/Fe2O3 and FTO/ 

**FIGURE 4** Line profile obtained from TEM-EDS analysis of Sn-hematite nanoceramics (A), cross-sectional TEM micrograph after FIB cutting (B) and schematic representation of the diffusion of Sn ions from FTO to hematite (C). Sn-hematite nanoceramics was prepared from pulse reverse electrode-position for iron coating, and annealed at 800°C for 13.5 min. (Adapted and reproduced with permission. Copyright 2016, The Royal Society of Chemistry)
accompanied by this, an evident increase in the charge separation culminating in a greater photon-to-current efficiency was observed. In addition, at lower temperature (550°C) which is known to have a photo-response close to dark scan values, in the presence of TiO$_2$ protective layer the photocurrent increased to $<0.5$ mA cm$^{-2}$ at 1.23 $V_{RHE}$.

Likewise, a SiO$_2$ thin layer (~3 nm) on the FTO before depositing hematite, shows an increase of 0.17 to 0.58 mA cm$^{-2}$ for photoanodes treated at 550°C classified as a reduction of electron-hole recombination on FTO-hematite interface. In this perspective, the presence of blocking layers prevent the Sn diffusion process, however, relative photoelectrochemical responses are observed with values equivalent to those presented for hematite in the presence of Sn-diffused.

Furthermore, the chemical atmosphere of the thermal treatment can influence the Sn diffusion degree. In this vein, recent work exploiting annealing of hematite at 600 and 750°C in air or low oxygen (LO) atmosphere demonstrate that Sn diffusion is promoted by the LO environment and high temperature. Interestingly, the best photocurrent was obtained for the hematite annealed at 600°C—LO ($n$ of 4.88 $\times$ $10^{19}$ cm$^{-3}$), followed by the 750°C—air, 750°C—LO and 600°C—air ($n$ of 4.86 $\times$ $10^{18}$ cm$^{-3}$), with more pronounced differences at higher potentials. Comparing the photoelectrochemical performances, it was evidenced that annealing at lower temperature and shorter time is an effective way to ensure the conductivity and stability of the substrate, especially at LO atmosphere which also is able to create oxygen vacancies at hematite structure that can act as shallow donors and improve the conductivity. Based on these findings, we can classify that the diffusion process goes beyond the improvements made, in which Sn is not the determinant to obtain hematite with a high photocurrent value, but apparently, the results obtained are more linked to a process of accommodation of the structure or adhesion.

Indeed, most studies addressing the Sn diffusion to hematite revealed an enhancement in the photocurrent density values with increasing temperature. Concomitantly, it is often remembered that the selected temperature range should be analyzed carefully to avoid the glass melting, indiscriminate ion diffusion, besides adhesion impairment and reduced FTO conductivity. Therefore, the role of unintentional Sn incorporation is not properly clarified by the literature, which identifies it with a nonconsensual perspective and, the answer to the question initially asked about the real contribution of Sn diffusion to the final hematite performance even remains incomplete.

At this point, diving deeper into evidence shown on the effects of Sn diffusion on hematite, it was noted that the gain with diffusion is limited, for which the maximum reached in the literature was 1.8 mA cm$^{-2}$ at 1000°C, being strictly necessary to use the temperature-resistant substrate (quartz) for this condition. Clearly, this is a limitation for technological application in two aspects: cost-benefit of the substrate and the maximum observed value is still far from the theoretically predicted (~12 mA cm$^{-2}$) to make the device commercially available. Moreover, it has been found in different studies that there is a limit for the ion diffusion between the layers, which is hundreds below the thickness necessary to photon absorption needed to achieve the maximum efficiency on light harvesting and conversion.

It is widespread that hematite photoanodes need a thermal activation step, which has a duality that can cause destructive or constructive effects on the overall properties, as we have shown. However, for hematite deposited on FTO in commercial glass substrates and subjected to annealing between 600 and 800°C for a short time of exposure, the problems that may be caused to the substrate properties tend to be minimized in relation to the benefits arising from the Sn diffusion. Based on the literature and critical analysis of the results, we know that this benefit is limited, leading to an average improvement in hematite performance to values close to 0.7 mA cm$^{-2}$ for the commonly used annealing temperatures (650-800°C). In summary, both for the usual annealing conditions and for the fundamental study at 1000°C, the photocurrent density values obtained for the hematite photoanodes are still 85% far from the theoretical prediction and the experimentally expected according to $J_{abs}$.

From which has been presented so far, it is worth noting that great photoelectrochemical efficiencies have never been observed in pure hematite nanoceramics as photoanodes, confirmed by different techniques. Hence, the guarantee of improved hematite photoelectrochemical performance is not strictly associated with Sn-diffused and the chosen temperature for annealing process should not be justified by it. In this way, although ion diffusion can improve adhesion, conductivity, interfaces, and so on, it is not the unintentionally Sn incorporated that dictates or majoritally controls what happens on photo-induced process, showing a minimal effect on overall hematite efficiency. This leads us to conclude that despite the beneficial aspects promoted by Sn diffusion, they are insufficient to make hematite competitive commercially so that intentional modification is necessary to achieve better performances. In fact, some studies focused on unintentional Sn incorporation, which was the first step to show that tin is a good element for improving the hematite photoelectrochemical performance. From this prior knowledge, opportunities were opened for the emergence of studies involving even the intentional Sn incorporation. Thus, in the next section we intend to address the challenges and understandings surrounding the ex situ Sn incorporation, unraveling the role of this modification on different hematite properties.

### 3.2 Sn incorporation

As presented in the previous sections, it was possible to systematically analyze the role played in each stage on...
| Hematite preparation | Precursor | Method                  | Together hematite precursor | After hematite precursor | Annealing                      | Morphology     | $E_{\text{onset}}$ (V_RHE)$^A$ | $J$ (mA cm$^{-2}$)$^B$ | Ref. |
|----------------------|-----------|-------------------------|----------------------------|--------------------------|-------------------------------|----------------|--------------------------------|----------------------|------|
| Magnetic field-assisted dip coating | Tin(IV) tert-butoxide (1 mM) | Dip coating              | X                           | 850°C for 3 min           | Wormlike                     | 0.80/1.05     | 2.7                            | 89                   |      |
| Hydrothermal         | SnCl$_4$  | Dip coating              | X                           | 800°C for 10 min          | Nanorods                     | 0.75/0.97     | 1.03                           | 85                   |      |
| Hydrothermal         | SnCl$_2$ (9 mM) | Dipping                  | X                           | 550°C for 2 h and 750°C for 15 min | Nanorods                     | 0.78/0.80     | 1.26                           | 32                   |      |
| Hydrothermal         | SnCl$_2$ (9 mM) + SnCl$_4$ (9 mM) | Dipping + spin coating    | X                           | 550°C for 2 h and 750°C for 15 min + 300°C for 30 min | Nanorods                     | 0.78/0.80     | 1.54                           | 32                   |      |
| Hydrothermal         | SnCl$_4$  | Dip coating              | X                           | 500°C for 2 h 800°C for and 20 min | Nanorods                     | 0.74/0.68     | 1.35                           | 111                  |      |
| Hydrothermal         | SnCl$_4$ (2 mg mL$^{-1}$) | Dropping                 | X                           | 350°C for 5 min and 800°C for 20 min | Nanowires                    | 0.82/0.92     | 1.36                           | 31                   |      |
| Hydrothermal         | SnCl$_4$ (0.05 mol L$^{-1}$) | Dropping                 | X                           | 550°C (8.75°C min$^{-1}$) for 2 h and 750°C (25°C min$^{-1}$) in Ar for 20 min | Nanorods                     | ~1.0/1.0      | 1.6                            | 29                   |      |
| Hydrothermal         | SnCl$_4$ (20 mM) | Dropping                 | X                           | 750°C (4°C min$^{-1}$) for 30 min | Nanorods                     | 0.8/0.9       | 1.62                           | 95                   |      |
| Hydrothermal         | SnCl$_4$ (20 mM) | Dip coating              | X                           | 750°C for 30 min in N$_2$ | Nanorods                     | 0.80/0.93     | 1.01                           | 27                   |      |
| Hydrothermal         | SnCl$_4$ (10 mg mL$^{-1}$) | In hydrothermal          | X                           | 550°C for 4 h and 800°C for 10 min | Nanocorals                   | 0.80/1.0      | 0.73                           | 104                  |      |
| Hydrothermal         | SnCl$_4$ (5 mM) | Dipping                  | X                           | 550°C for 4 h and 800°C for 10 min x   | Nanorods                     | 0.80/1.0      | 1.0                            | 104                  |      |
| Hydrothermal         | SnCl$_4$ (10 mg mL$^{-1}$) | Dropping                 | X                           | 800°C for 3 min           | Nanorods                     | 0.80/0.90     | 0.93                           | 35                   |      |
| Hydrothermal         | Tetrakis(dimethylamido) tin (IV) | ALD                    | X                           | 650°C for 2 h            | Nanorods                     | 0.84/0.90     | 3.12                           | 84                   |      |
| Hydrothermal         | SnCl$_4$ (5 mM) | Dipping                  | X                           | 800°C for 10 min          | Nanorods                     | 0.72/0.92     | 1.0                            | 110                  |      |
| Pulse reverse electrode position | SnCl$_4$ (1 mM) | Dipping                  | X                           | 800°C for 13.5 min        | Planar (ellipsoid)           | 0.80/0.83     | 0.69                           | 72                   |      |
| Spin coating from polymeric solution | SnCl$_4$ (1%) | Spin coating             | X                           | 550°C for 30 min and 750°C under N$_2$ for 30 min | Planar                       | 0.90/0.98     | 0.52                           | 93                   |      |

(Continues)
nanoceramics manufacturing toward the evolution of material efficiency. From then on, it was evident that the thermal activation process linked to the Sn diffusion from FTO to the deposited layers is not able to promote significant benefits in the hematite photoanodes for the sunlight driven water splitting efficiency. With this in mind, we can consider that the previous steps served as a platform for further modifications, which will present effective contributions to the overall performance of hematite photoanodes. Thus, the need to add external modifiers seems to be mandatory to increase the photogenerated charges and photoelectroactivity of hematite photoanodes.

In this scenario, simultaneous strategies aimed at increasing the probability of photogenerated minority carriers to reach the semiconductor-electrolyte interface are required. Different morphological designs (including nanostructuring, crystal size and shape, crystal edge orientation toward incident light, porosity, crystalline disorder and specific surface area) as well as increasing the majority carrier conductivity by doping/insertion have been successfully implemented to overcome hematite drawbacks.81 Among the various elements used to improve hematite properties, the Sn incorporation from chemicals has been one of the most relevant. However, the manner it changes hematite and the effects resulting from its insertion result in a wide and relatively controversial discussion presented in the literature. In general, the Sn insertion has been reported to alter different hematite parameters, such as morphology, optical properties, charge density, that contribute to improving the photoanode performance.31,64,82 Nevertheless, it has not been clarified how Sn incorporates in the hematite structure, whether it acts as a doping agent, modifier or in some other way. When analyzing the literature, which is quite broad and shows a great dependence on how Sn is incorporated, for example, directly in the synthesis, overlaid on hematite structure, with or without additional annealing process, some questions arise: Is Sn⁴⁺ really a dopant? What does the presence of intentional Sn cause in the hematite properties? In what aspect is the change most significant (optical, electronic, chemical)? Then, in this section we will conduct a critical analysis of the literature to present new perspectives on the role of Sn addition, seeking to answer these questions and elucidating the Sn incorporation effect constantly present in most works.

Considering the existence of many aspects behind the Sn incorporation on hematite, to address the proposed questions, we conducted a critical analysis of the literature, intending to minimize the ways to explain the role of Sn modification, in terms of which parameters are affected by it, seeking points of convergence that help to reveal the incompatibilities found in the state-of-art. Thus, we intend to discuss the correlation between hematite photoanodes of different morphologies modified with Sn and their photocatalytic activity, since recent reports have demonstrated contrasting ideas for that.
It is desired to take into account, among other factors, single-crystallinity with minimal charge trapping defects, high interconnectivity between the nanostructures, nonisotropic morphology and choosing an efficient strategy for Sn incorporation, which will be evaluated from the works summarized in Table 1.

As can be noted, hydrothermal-based synthesis is often adopted as an initial step to produce hematite nanoceramics. The mild conditions of hydrothermal process are well-documented, and temperature lower than 200°C is habitually employed. As mentioned in the previous section, an intermediate akaganeite phase is obtained from this condition and thermal treatment is necessary for the conversion into hematite phase. For such conversion, one or two-steps annealing process are used and Sn incorporation can happen before or after any thermal treatment. Uncomplicated strategies for Sn modification of hydrothermally designed photoanodes are often reported, among which the dropping/immersion of akaganeite in a Sn-based solution followed by high-temperature annealing process is one of the simplest. Different reports in the literature presented similar results using the iron oxyhydroxide immersion in Sn⁴⁺ precursor solution, either in aqueous or ethanol-based solution. From SEM images, in most cases, the annealing step necessary to phase conversion reveals considerable changes showing a less well-defined morphology, with grain coalescence, defects and the thick layer of SnO₂ on the nanorods' (NRs) surface.

In another way, Sn-dip coated over akaganeite NRs were investigated using an approach with a concentration range of 0.025, 0.05, 0.1, 0.2, and 0.3 mol L⁻¹ SnCl₄ solutions and a subsequent annealing at 550°C for 2 hours and at 750°C for 20 minutes, in air. From focused ion beam scanning electron microscopy (FIB-SEM) and field-emission transmission electron microscopy (FE-TEM) was revealed the diameter and length of bare hematite and Sn-modified hematite were 80 and 750 nm, respectively. It was not observed any modification on morphology, surface or the size of nanorods, besides a Sn concentration > 1% over the entire NRs length determined by secondary ion mass spectrometry (SIMS). The fast top-down diffusion of Sn⁴⁺ ions (with an ionic radius and Pauling electronegativity similar to Fe³⁺ ions) in hematite lattices without modifying its morphology or decreasing its crystallinity is usually achieved by ex situ (co)doping methodologies and annealing at high temperatures. The same consensus has not yet been reached for the Sn insertion during the hematite synthesis (Sn-precursor included on iron-based solution), since the effect on morphology has been related to the method of tin incorporation and to the thermal treatment and, may have a considerable impact on the PEC response.

Nevertheless, crystalline wormlike, nanorods, nanowires and nanotubes hematite are often identified as morphologies that exhibit highly conductive basal planes (001) perpendicular to the substrate, increasing the conductive capacity of these morphologies which may adjust the flat band potential, band bending and surface states, along with directional charge transport properties and short charge diffusion distances to the electrolyte. For this reason, methodologies to produce hematite in these morphologies are generally employed to combine their advantages with those of Sn addition. As can be observed in Table 1, few works obtained photocurrent densities lower than 0.60 mA cm⁻² using Sn-modified hematite nanoceramics with such morphologies, while a considerable number of studies reached values higher than 1.0 mA cm⁻², including performances close to 3.0 mA cm⁻². Especially the discussion of the latter may help to understand the positive points arising from the Sn incorporation on hematite.

Combining Sn addition (together with hematite precursor) by localized interdiffusion in hematite photoanode with columnar grains, a pronounced 2.7 mA cm⁻² photocurrent was exhibited in a mesoporous morphology, representing a 93% increase in relation to undoped hematite. It is possible that this good performance is justified by the high electron-hole separation efficiency η₁(λ) due to a “planar” hematite with a low recombination rate, following a higher light harvesting efficiency η₂(λ), since there is slight light scattering or internal reflection. This hypothesis can be structured by the external quantum efficiency EQE(λ) of light-driven water oxidation equation:

$$\text{EQE}(\lambda) = \eta_1(\lambda) \cdot \eta_2(\lambda) \cdot \eta_{\text{trans}} \quad (6)$$

Which depends on the product of the efficiencies of light harvesting, η₂(λ), charge separation, η₁(λ) and hole-transfer to the electrolyte, η₁(λ). Indeed, Sn⁴⁺ cations segregated during the annealing process, mitigated the grain growth and promoted the formation of an interface free of unfilled space, due to the rearrangement of grains of smaller sizes, culminating in: (a) improvement of the hematite/substrate contact, (b) higher surface area, (c) surface energy reduced, when compared to bare hematite. Thus, the substantial enhancement in PEC efficiency resulted from a synergistic effect of increasing the light harvesting efficiency promoted by the highly anisotropic morphology, combined with an improved interdiffusion process at the solid/solid interface, besides the smaller charge transfer resistance on solid/liquid interface.

The higher photocurrent density value present in Table 1 was obtained from ex situ Sn incorporation by atomic layer deposition (ALD) on the surface of akaganeite nanorods. This strategy allowed the thickness of the SnO₂ layer had considerable precision and homogeneity, reducing surface defects, interfacial recombination and also acting as a passivating layer. Added to this, the akaganeite phase compared to hematite, allows easier tin diffusion in the semiconductor lattice during
annealing. Thus, the as-prepared nanorods consisted of a hematite matrix with small amounts of embedded Sn, protected by a Sn-rich surface shell. The Sn incorporation in the hematite lattice ensured superior injection and low bulk recombination of the minority carriers, resulting in better charge mobility throughout the nanorod structure. Simultaneously, the presence of the thin SnO\textsubscript{x} layer in a favorable band alignment from the heterojunction indicated that a larger fraction of holes was injected into the electrolyte.\textsuperscript{84} Here, again we note the importance of synergistically improving the parameters of Equation (6) to increase Sn-hematite performance. Still concerning the hematite morphology aligned to (001) plane, it was recently reported that Sn/P co-doped hematite showed a high PEC performance compared to pristine one, owing to a positive synergistic effect between the tubular morphology and the introduction of metal and nonmetal ions.\textsuperscript{36} The preparation consisted in soaking the akaganeite nanotube prepared by wet chemical route in a tin precursor solution, followed by annealing in air and subsequently in PH\textsubscript{3} atmosphere. It is important to mention that the uniform incorporation of Sn\textsuperscript{4+} and P\textsuperscript{5+} did not introduce additional surface trap states, instead increased the carrier density for each modifier element added. Thus, the width of the depletion layer of the Sn/P-hematite was reduced by almost 8-fold when compared to the pure hematite, promoting better photogenerated charge separation.\textsuperscript{36} Evidently, this work demonstrated that there is an element able to act in synergy with Sn to improve hematite performance, but it also reveals a study line to be explored, since the photocurrent obtained was 0.9 mA cm\textsuperscript{-2}, still below the desired. Recent findings regarding spin-coating method to prepare hematite nanoceramics from Pechini solution, with outstanding OER performance among similar works reported until date,\textsuperscript{90} allowed to develop Sn-modified hematite from a single Sn-Pechini solution. Figure 5 shows the top-view morphology of bare and 3\% Sn-hematite prepared by our group, followed by thermal treatment at 450\textdegree{}C in air atmosphere and 750\textdegree{}C in N\textsubscript{2} atmosphere, both for 30 minutes. It can be seen that there are larger grains in pure hematite (Figure 5A), with morphological differences and apparently fused together at some points. Conversely, Sn addition proved to be able to suppress grain growth (Figure 5B), resulting in smaller grain size and greater uniformity when compared to pure hematite. Although studies correlate smaller grains with possible doping of the hematite structure,\textsuperscript{35} the grain size modification is an indicative that Sn\textsuperscript{4+} do not enter the crystalline lattice, but rather segregate on the hematite surface.

Figure 5C showed the proposed Sn distribution on hematite photoanodes surface for two distinct morphology configurations. It is necessary to keep in mind that, from we have discussed so far, even the Sn-hematite nanoceramics intentionally modified have some contribution of Sn diffused from FTO promoted by the annealing treatment. Therefore, the nanocolumnar Sn-coated hematite usually show tin species covering the entire surface, with more uniform Sn distribution for the thinner hematite nanoceramics, as the produced by ALD.\textsuperscript{91} Additionally, regarding the thickness of hematite layer and the method used for Sn incorporation, it can exist a greater Sn concentration on top/surface that diffuses to the bulk during the thermal treatment and, some Sn species may be found in hematite region close to FTO interface as a result of self-diffusion.\textsuperscript{32,35} In return, planar hematite structures like the obtained by us often have a different mechanism of Sn incorporation. In this case, Sn species can accumulate on grain boundary rather than hematite structure, since the last process is more difficult and Sn accumulation on surface or grain boundary is favored.\textsuperscript{92} Nonetheless, such accumulation on grain boundaries contributes to smaller grain size that can help to improve the electrochemical response of the hematite photoanodes, compared to the bare hematite, as observed in.

**Figure 5** Top-view SEM images of bare hematite (A), 3\% Sn-modified hematite nanoceramics (B), both obtained from spin-coated of Pechini solution nonmodified and modified with SnCl\textsubscript{4} on the FTO substrate. Comparison of Sn intentionally added to the system, accompanied by Sn diffusion from the substrate represented by the green arrow, for columnar and planar hematite structures, where the green points represent unintentional Sn species and purple points the incorporated Sn ones (C)
our Pechini-based ones and related to better charge separation efficiency.93

In fact, the experimental variables related to Sn addition on hematite can lead to distinct aspects, as evidenced by the works previously discussed. A groundbreaking work used atomic layer deposition (ALD) to selectively dope hematite with Sn on top (top-Sn), on the subsurface (surf-Sn) and throughout the entire hematite layer (bulk-Sn).94 The ALD allowed deposit intercalated layers of hematite and SnO_x with a final thickness close to 16 nm, after a slow air thermal treatment at 600°C. The atom probe tomography (APT) of the top-Sn hematite indicated a short-range Sn diffusion to the more favorable surface sites. XRD patterns of top-Sn and undoped hematite were similar, while the bulk-Sn showed the lowest crystallinity due to a Sn segregation at grain boundaries, attributed in this work to the creation of recombination centers that impair charge transfer efficiency and photoelectrochemical performance.

A more recent work of this group investigated different Sn concentrations of 6, 14 and 32 mol% on hematite prepared by ALD and annealed at 600°C (3.2°C min⁻¹) for 30 minutes. The increased Sn concentration caused the diminution of crystallinity, grain size and optical absorption, reducing the band gap. From density functional theory calculations with a Hubbard U parameter (DFT + U), these aspects were related to an enhancement of Fe²⁺ concentration that provoked modifications on lattice constants and grain boundaries. In general, photocurrent values were close to 0.4 mA cm⁻² and suffer a reduction for the hematite nanoceramics with Sn concentration above 6 mol%. The authors attributed this poor photoelectrochemical performance to the lower optical absorption and crystallographic defects, among which higher grain boundary density was suggested as possible trap states that have impaired electronic movement.91

Contrary to these above negative effects of grain boundary increment on Sn-modified hematite, a late work of Soares et al92 revealed that Sn cations segregation on grain surfaces are extremely important to the improvement of the electron conductivity in hematite, based on a set of morphological and electronic characterization techniques. For this investigation, hematite modified with 2.0 wt% SnO_x was prepared in high-density pellet, which was sliced and polished to obtain samples with different number of grains (n) for comparison. The J–E curves normalized by n demonstrated a resistivity reduction to higher n values due to low back-to-back Schottky barrier, also evidenced by Nyquist plots in terms of reduction of total and grain boundary resistance (R_{gb}). Interestingly, grain resistance (R_g) remained unchanged with different number of grains and both showed similar values, implying the existence of preferential paths for electron transport, which were not observed for bare hematite (Figure 6). This was evidenced by the conductivity atomic force microscopy topographic images, in which the great current and bright area represents grain boundary region with high conductivity for Sn-hematite about the unmodified one. Considering that Sn addition preferentially segregates in the high-angle grain boundary, the surface and defects chemistry is altered, resulting in lowering of interfacial energy that facilitates the conductivity, as represented in Figure 6C.92

In summary, we can understand that orderly Sn-hematite architectures with a unidirectional electric channel for the transport of photogenerated electrons are commonly more

![FIGURE 6](http://example.com/image6.png)  
Conductivity atomic force microscopy topographic images for bare hematite nanoceramics (A), Sn-hematite nanoceramics (B) and different pathways for electronic current flow (C).92 (Adapted and reproduced with permission)
efficient that complex morphologies, which can hinder electron transport and affect the efficiency of charge separation, as seen in the low photocurrent densities listed in Table 1. Furthermore, as shown by the previously discussed works, the grain growth suppression resulted from Sn incorporation is responsible to generate more interfaces, which have been reported as possible recombination centers, now deserve to be seen as important electronic transport pathways just promoted by the Sn addition. As we have presented so far, there is a great challenge based on the different types of tin incorporation with respect to the interconnection parameters between the results. However, despite the morphological issues and reduced interface energy, regarding the nonconsensual reports in literature on hematite-based photoanodes, it is clearly observed that the best photoelectrochemical responses are majority observed for Sn-hematite system. In fact, the incorporation of this donor element, in general, reflects in significant photocurrents with average values around ~1 mA cm⁻² at 1.23 V_RHE. By colloidal nanocrystal deposition method, the Sn incorporation presented one of the record values in the literature for Sn-hematite thickness of 250 nm, reaching photocurrent values of 2.7 mA cm⁻² at 1.23 V_RHE with a pronounced plateau at high applied potentials, achieving at least 4 mA cm⁻² which represents the saturation in the photoanode response.⁸⁹

Aligning with the different modifications caused by the Sn presence in the photoanodes, it was observed that the hematite surface becomes superhydrophilic in the presence of Sn⁴⁺.⁹⁵ The same behavior was also recently reported for ex situ Sb⁵⁺ incorporation on hematite. ²¹ The principal advantage of having a more hydrophilic surface lies in a better interaction with electrolyte used in the photoelectrochemical processes. Consequently, high photocurrent values were observed for Sn-modified hematite photoanode with high wettability due to a greater affinity with the electrolyte and more active surface for oxygen evolution reaction, when compared with unmodified material. Despite the important contact angle measurements not be routinely explored, we can infer that the improved wettability due to the Sn incorporation probably occurs in several other Sn-hematite nanocermics as photoanodes, positively affecting their performance.

On the other hand, returning to the discussion highlighted in the previous section, it was raised by reports in the literature that the Sn presence in hematite photoanodes results in the distortion on hematite lattice, provoking a 2-fold increase in the optical absorption coefficient.⁶⁴ In the case of Sn intentionally incorporated, most studies do not present great variations in the hematite absorption spectrum. In fact, results showed that there is no change on direct transitions in the optical band gap, which reveals the presence of optical transitions mostly related to hematite.⁹⁶ However, the energy decrease in the indirect transitions is strictly associated with the increase on Sn concentration, revealing intermediate states due to the formation of sub-band gap states.⁹⁷ The shallow states apparent in this scenario contribute minimally to the light harvesting efficiency.

After addressing the Sn incorporation effects on different hematite nanocermics, in general, the Sn contribution in the overall hematite enhancement can be addressed by two different main effects: (a) reducing the energetic barrier between

**FIGURE 7** Three electrode PEC configuration for Sn-hematite nanocermics as photoanode under illumination and photoelectrochemical response (dark gray: bare hematite and red: Sn-hematite) revealing the charge transport mechanism.
the homojunctions, decreasing the built-in resistances and/or (b) enhancing the electrical field on the solid-liquid interface which lead with an increment on the band bending (improving the charge separation). Figure 7 summarizes the charge transport impacts on designed hematite photoanodes. In fact, a commonly obtained result all over the literature (as shown in the current density) presented an increment on photocurrent for Sn-modified photoanodes. The process (a) highlights the enhancement on charge transport which is addressed to a clear increase on the current density well-defined at higher applied potential. This process deals with a reduced energetic barrier at the bulk structure that favors the electron transport to the back contact. In another hand, process (b) shows that the Sn addition can, at the same time, increase the surface trapping states, which contributes to slowing the oxygen evolution reaction kinetic. In this case, the current density shows a displacement on the turn-on voltage to positive potentials.

As the process (a) of pronounced slope in the photocurrent curve remains similar in most studies and it is one of the main reasons that lead to the choice of Sn as a modifier, it is interesting to investigate the aspects of hematite that have been modified behind this improvement. In this case, more sophisticated techniques to investigate carrier transport and transfer might be necessary to understand the role of Sn addition on hematite PEC response. To thoroughly investigate the determining parameters, resulting from the Sn incorporation, which help to overcome hematite disadvantages, one of the techniques most applied to analyze the intrinsic carrier kinetic properties is electrochemical impedance spectroscopy (EIS). Under certain conditions, the space charge capacitance ($C_{SC}$) can be calculated from the EIS plots employing the Mott-Schottky analysis, according to the Equation (7):69,98,99

$$\frac{1}{C_{SC}^2} = \frac{2}{e_0 \varepsilon_0 N_D} \left[ (V - V_{fb}) - \frac{kT}{e_0} \right]$$

where: $e_0$ is the electron charge, $\varepsilon$ is the dielectric constant of hematite, $\varepsilon_0$ is the permittivity of vacuum, $N_D$ is the donor density, $V$ is the potential difference across the semiconductor space charge region, $V_{fb}$ is the flatband potential, and $kT/e_0$ is a temperature-dependent correction term.

When $1/C^2$ is zero, the x-intercept is equal to the flat band potential, and the donor density ($N_D$) can be calculated using the slope obtained from the graphic. Furthermore, it is well known that the amount of charges transferred from the electrode surface to the electrolyte solution and the donor density are directly related to the potential distribution and the width ($W_{SC}$) of the space charge layer, which can be determined by Equation (8):

$$W_{SC} = \sqrt{\frac{2ke_0 V_{fb}}{qN_D}}$$

For intentional Sn incorporations, in different researches a common tendency is not observed, in some cases, comparing the doped with the bare hematite, the $N_D$ increases significantly,35,41 representing a displacement of hematite Fermi level closer to the conduction band position. However, in other situations, $N_D$ technically does not variate.32,89,100

This discussion makes it difficult to discuss Sn doping, as suggested in several published reports, as there is no coherent trend in the results. It is known that for a semiconductor, doping involves directly pronounced alterations in charge density, demonstrating changes in the localized charge distributions in the crystalline arrangement. In this way, it is difficult to associate the Sn as a substitutional dopant in hematite structure, once the closed-packed structure and the electronic investigations do not reinforce the possibility for that. Moreover, new trends showed that Sn incorporation on hematite can lead to its segregation on grain boundaries; besides that only some doping of superficial hematite sites may also occur. Thus, the final effect is no-dominant change on the density or conductivity; that is, the final contribution is a weak dopant behavior.27,38,94

The Sn-doped hematite defect equilibrium diagram shows that the temperature and oxygen partial pressure ($pO_2$) control if the vacancies are produced on Fe or O sites.42 In counterpart of the commonly presented literature results, the hematite Sn-doping process is not a simple task. A substitutional Fe$^{3+}$/Sn$^{4+}$ doping is described by the following reaction:

$$2SnO_2 \rightarrow Fe^{3+}_O, 2Sn^{4+}_Fe + 3O^{x-}_O + 2e^- + \frac{1}{2}O_2 \quad (9)$$

where: Sn and $O^{x-}_O$ correspond to tin incorporation in the iron site and an oxygen ion at an oxygen site, respectively. Replacing an iron ion by tin involves high temperatures and high-pressure conditions, which turns the discussion of doping unfeasible as regularly presented by several researchers and corroborates the findings related to Sn segregation.

According to what has been discussed so far, it is notable that the effects of Sn incorporation is more complicated than expected and EIS can show another panorama by analyzing the $W_{SC}$: some studies showed that the $W_{SC}$ decreases when Sn is added to the hematite. Duan et al16 suggested that the high and uniform doping and the thinner depletion layer are producing a greater band bending that induces an internal electrical field capable to separate the $e^-h^+$ pairs more efficiently. However, varying %Sn on hematite photoanodes showed a constant $N_D$, but they observed a $W_{SC}$ decrease, associated with a band bending reduction, which results in more potential being dropped across the Helmholtz layer rather than across the depletion layer.73

By employing an equivalent circuit to fit the impedance spectra and calculate the different capacitances
and resistances involved in the charge transfer process, it was observed that for the best Sn-hematite nanoceramics (low Sn concentration), a reduction in the charge transfer resistance, as well as the bulk resistance were achieved, without major changes in the electronic properties. Conversely, as long as Sn concentration increases, it was favored an increase on the solid-liquid interface resistance, which can be associated with some resistive phases deposited on it. Interestingly, the authors reported the reduction of the hematite nanorod size after Sn incorporation,29 which, in line with the electrochemical characterizations, supports the possibility of Sn segregation at the nanostructure surface (preventing growth in temperature conditions). Moreover, another sensitive parameter is the flat band potential ($V_{fb}$), estimated from Mott-Schottky plot, which can be altered in the presence of tin-modified hematite photoanodes for higher values. The $V_{fb}$ is closely connected with the electric field (promoting the band bending) on the surface of the nanostructure, with a fundamental role in the charge separation. However, this trend does not always happen, and seems to be related to different synthesis conditions.

Other alternative technique that gives a general panorama about the carrier kinetics at the semiconductor/electrolyte interface is the transient absorption spectroscopy (TAS), however, different studies showed contrast ideas: an earlier study reported in 2011 by Ling et al.66 showed that, in picosecond scale, the Sn diffused cannot reduce the rapid loss of the photoexcited electrons through different decay process, concluding that tin only improves the electrical conductivity (the classical interpretation). A few years later, it was exposed that, according to their results, the tin diffusion does not alter the primary electron-hole recombination on scale faster than miliseconds.101 However, they observed that tin diffusion increases the electron mobility that is associated with electron extraction. On the other hand, the intentional Sn incorporation on hematite, showed an improved applied bias photon-to-current efficiency (APBE) compared to phase pure photoanodes. Also, their transient decay associated with the trapped photoholes (575 nm) is slower, indicating a slower hole-electron pair recombination. This implies that Sn is modifying the surface processes.102 As it is observed, despite TAS being a powerful tool to analyze the electrode/electrolyte interface, there are still different explanations about the Sn influence.

Following the same line, intensity modulated-photocurrent spectroscopy (IMPS) has been employed by different groups to analyze the carrier kinetics on the electrode. This technique helps to deconvolute the transfer and surface recombination constant due to the light variation that modulates the carrier concentration at constant band bending.103 Although IMPS was developed several years ago, its use on PEC systems is still limited. There are few studies that apply IMPS for study the charge carrier behavior on the Sn-system, however, they showed an agreement. Mostly, an electrocatalyst can improve the material PEC response by enhancing the charge separation, reducing the surface recombination or accelerating the charge transfer rates; according to IMPS.36,73 Sn surface incorporation does not alter the surface recombination rates, it influences positively the transfer rate, becoming it faster. Also, the shape of the IMPS spectra (Figure 8A) indicates that charge separation (related to the intercept at
medium frequencies) was enhanced compared to hematite spectra.

In fact, these studies showed that, even if there was a transfer rate improvement, surface recombination (associated with the presence of an upper semicircle) is still present in the electrode and restricts its PEC performance. Figure 8B schemes the different effects that Sn can provoke on hematite in terms of charge carrier dynamics. Undoubtedly, Sn incorporation is a great strategy to improve the hematite performance drawbacks, however, charge transfer studies suggest a limiting surface. To achieve highly efficient Sn-modified hematite photoanodes by engineering their charge kinetics, it is necessary to find the optimal conditions that guarantee the spontaneity in the photooxidation process. However, the mostly observed effect of Sn addition is related to onset behavior, in which is evident that the efficiency in collecting photogenerated charges on the surface of Sn-modified hematite photoanodes is impaired, regardless of morphological issues. Figure 9 summarizes the main Sn incorporation impacts related to the ideal photocurrent state and the limiting charge dynamics processes for the hematite-based system.

Ideally, the current density onset should be equal to the flat band potential (Figure 9A). However, the onset potential ($E_{\text{onset}}$) is associated with the charge kinetics on the surface, taking into account the accumulation of charges at the semiconductor-electrolyte interface. The Sn-hematite curve illustrates a common behavior for the photoanodes intentionally modified with tin. For example, more positive onset potentials (at least 100 mV) were obtained for Sn-hematite prepared by hydrothermal treatment with subsequent dip coating in water-based SnCl$_4$ solution, dropping and dipping in ethanol-based SnCl$_4$ solution. Furthermore, from the correlation between the capacitance of surface states ($C_{ss}$), charge transfer resistance ($R_{ct}$), and the photocurrent onset displayed in Figure 9B, it is revealed that turn-on voltage is mediated by intermediate states on the surface, in other words, associated with their charging process.100

In fact, taking a look on the state-of-the-art there is a tendency to increase the onset with the Sn addition, as summarized on Figure 10. It is possible to analyze that independent of Sn addition method or hematite structure, there is a notable increase in the $E_{\text{onset}}$ with an average of 0.95 V RHE for Sn-modified hematite.

Interestingly, according to the general solid-state basis, doping effect essentially must change the electronics parameters and do not to become a surface limiter which should not involve shifting the $E_{\text{onset}}$. In this case, again there is a strong indication of Sn segregation at hematite boundaries changing the surface chemistry. The correlation of tin addition and the onset displacement at more positive potentials is considered an evidence of a deficient charge transfer mechanism in the solid-liquid interface by the incorporation of surface states reducing OER kinetics. In counterpart, it was revealed that, despite the thermodynamic cost on the surface, Sn modification brings beneficial effects by reducing built-in resistances improving the bulk conductivity, as well as increasing the band bending which provides an efficient charge separation.

The positive effects of the Sn intentionally incorporated in hematite easily outweigh the negative ones. Aiming to reach better global efficiency, the hinder in surface kinetics can be controlled by coupling a solar cell system that provides the necessary overpotential using a completely solar-based arrangement. This is a desired design system that preferentially trends to spontaneous reactions, like artificial

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**FIGURE 9** PEC performance representation for theoretical, bare and Sn-hematite nanoceramics as photoanodes showing the limiting charge dynamics and onset behavior (A).12 (Reproduced by permission of The Royal Society of Chemistry) Schematic band diagram for hematite and Sn-hematite and surface states charging dependency of onset potential (B) (Reprinted (adapted) with permission from100. Copyright (2012) American Chemical Society)
leaf model. Currently, cocatalyst materials showed an alternative to collect the photogenerated charge at low potentials by partially passivating the low kinetic surface states acquired by Sn intentional modification.\textsuperscript{29,31} As already discussed in the literature and also by our group,\textsuperscript{1,106} there is a great prospect in selecting a suitable cocatalyst that can act synergistically with Sn to decrease the \( E_{\text{onset}} \) maintaining the satisfactory charge transport efficiency, as it has been achieved.

In this scenario, despite the sometimes incoherent denomination of Sn doping being constantly attributed as a fundamental factor for the improvement of hematite performance, deep investigations have arisen with important results for the area. From the findings highlighted in this perspective, we hope that they will be helpful for further works and for a better comprehension of the Sn role on hematite, which may be extended to other modifiers. In sum, the way Sn is distributed in the hematite structure is closely related to the \( E_{\text{onset}} \) shift and to significant changes in the crystalline lattice and electrochemical parameters like charge density. In other words, if \( E_{\text{onset}} \) is modified by Sn incorporation, there is a high probability of tin species being on the hematite surface, since the kinetic on solid/liquid interface is affected. Considering the difficulty of inserting Sn\textsuperscript{4+} in a Fe\textsuperscript{3+} site, but not excluding this possibility, it must be taken into account if the altered electronic parameters are not due only to a superficial hematite doping or iron vacancy. These observations suggest that Sn segregation is quite plausible to be present in Sn-modified hematite photoanodes and that, regardless of how many aspects tin may affect, we can understand that its main role is to change the interfaces and associated energies. Furthermore, we can consistently confirm that the Sn modification on hematite is strictly associated to enhance charge transport efficiency. From these experimental results, a new opportunity has now been created based on the possibility of not using only columnar hematite structures, expanding the possible morphologies that can be studied in interface engineering, seeking a joint improvement of the parameters that govern the global performance of hematite photoanodes.

4 \ | \ OVERALL SUMMARY AND OUTLOOK

Throughout the discussions presented in the previous sections, it is notable that much effort has been devoted to improving the hematite nanoceramic properties for photoanodes design. Herein, we have shown a detailed follow-up of the literature, in which we have collected knowledge step by step revealing the limiting and determining factors in the global performance of hematite-based nanoceramics. Unquestionably, the first limiting factor permeates the discussion of the thermal activation process on hematite photoanodes, often giving great prominence to the diffusion of Sn\textsuperscript{4+} species into hematite structure. It was revealed that the temperature-dependent changes can result in irreparable impairments on FTO substrate, ranging from changes in chemical stoichiometry, reduction in the electrical conductivity to interdiffusion of species between deposited layers, caused mainly by the increase in temperature and exposure time in the annealing process, contributing to the accumulation of losses during the nanostructure manufacturing process which can hardly influence the final product.

The great role given to the diffusion of Sn over the years often does not address the synergy to be maintained between the diffusion of species and preserving the substrate nature while seeking to improve the properties of nanoceramics. Analytically, for further clarification, we have selected photocurrent responses at different temperatures, which varied from approximately 0.12 to 1.24 mA cm\textsuperscript{-2} in the range of 650-800°C. However, for most hematite nanocermics as photoanodes, high-temperature activation results in responses below 1.0 mA cm\textsuperscript{-2}, besides that the limit for the Sn/Fe interdiffusion has been found to be < 100 nm. In fact, the Sn-diffused contribution from the conductive substrate is minimal with characteristics that apparently are better associated with the structure.
accommodation and/or to the reduction of stress between layers. In the state-of-the-art, the best photoreponse to hematite was obtained using FTO-quartz substrate and annealed at 1000°C, however, the photocurrent density obtained was 85% distant from the theoretically expected (~12 mA cm⁻²). Therefore, it is not possible that hematite photoanodes prepared on FTO-common glass and submitted to high temperatures (up to 800°C), even with the presence of diffused Sn, are suitable for commercial purposes. Thus, the thermal treatment process aligned with Sn diffusion is a step that must be analyzed with caution, aware that Sn diffusion alone is unable to obtain economically competitive photoanodes.

In view of the limitations presented by the indiscriminate use of temperature in line with the interdiffusion of ions between layers, intentional modification strategies stand out as ways to overcome the deficiencies presented. Among the various chemical elements studied, Sn has been frequently used and associated with improvements on charge separation process on hematite, where the major challenges presented are related to find out convergence points in the different Sn incorporation methods, from physical techniques and chemical routes. In this regard, many works have mainly addressed the Sn intentionally as doping in Fe sites. An important discussion arises here regarding the doping attribution for any presence of Sn atoms in the hematite photoanodes. The Sn⁴⁺ insertion on hematite crystal structure is not trivial, since it involves adding a larger cation in the lattice that causes changes in structural parameters. Moreover, doping is accompanied by changes in the electronic structure, which is not an agreement in the literature, where contradictory results are often presented in this regard. Based on these aspects, it is reasonable to use the Sn-doped expression appropriately only when experimental evidence shows that doping has occurred at a certain level.

Perhaps, the comprehension about the Sn distribution on hematite and its effects may help the researchers to find new methods to synthesize more efficient devices. According to preliminary work carried out in 2002, the scientific view of the time was focused on the development of oriented hematite structures with no grain boundaries to improve the electron transport. Actually, this concept has endured over the years, as a material with more interfaces was considered to be susceptible to have more trapping sites. Meanwhile, recent studies contributed to explaining different roles of tin insertion on hematite nanocermics, opening new perspectives and understanding for results in the area. The main point was clarified from Sn-hematite with manipulated number of interfaces, demonstrating that tin segregation was responsible to decrease the grain boundary resistance, favoring the electron flow through preferred pathways due to minimization of high-energy interfaces. Moreover, defect equilibrium models applied for undoped and Sn-doped hematite nanopowders annealed in different atmospheres showed a dependence on O₂ pressure, from which Sn⁴⁺ donors are compensated by iron vacancies rather than electrons, even at lower pressures.

All the new contributions are essential to assist the development of researches involving interface engineering and the search for elements that behave similarly to Sn. According to the literature review and recent studies, new perspectives showed complementary results that opportunities to future works focused on Sn⁴⁺ presence on the grain boundaries of hematite crystals, promoting preferential pathways for higher electronic conductivity. The others unoccupied contours may have high or low energy, but do not contributed to conductivity. Within the framework of these criteria, a mapping aiming to identify the contours/interfaces from in situ techniques is a useful tool that can be applied to define the best methodology for modifying elements on hematite. Probably, the great challenge is synthesize a hematite sample, in which the grain boundaries or interfaces between the crystals can be identified, especially those responsible for favoring the flow of electrons without trapping or recombination.

Furthermore, after years of research aimed at understanding the effects of intentional Sn addition on hematite, it can be seen that, in many cases, Sn addition creates surface states on solid/interface that positively shift the Eₜₚₜ, hindering the reaction kinetics because it demands greater overpotential. Despite being indicative that substitutional doping did not occur, this disadvantage resulting from the Sn incorporation is controllable by using co-doping elements with distinct roles or cocatalysts that negatively shift the Eₜₚₜ, making water oxidation more spontaneous and optimizing the photoelectrochemical process. In this way, modifying the hematite nanocermics to manipulating the complex parameters that govern the global photocurrent (Jₜₚₜ, ηₑₑₑ, and ηₖₑ) is a way of overcoming its limitations.

Taken together, the findings described in this perspective can help future works to prepare more efficient hematite nanocermics to be applied as photoanode, exploiting synergistically an annealing temperature and time that active the material promoting controlled Sn diffusion without damage for the FTO-glass substrate and, that make it possible to use the advantages of elements like Sn, which act by modifying the interface energies between hematite crystals. In this respect, some elements such as Sb²¹, Nb¹⁰⁸,¹⁰⁹ and so on, have shown similar characteristics to Sn, arising high photocurrent values and showing their poten-tial application on PEC devices. These new evidence and similarities found in the literature and addressing by us show that the interface engineering can be manipulated to improve charge separation and charge transport process, rather than creating trapping sites. Through the physicochemical insights of the hematite photoanodes presented in this perspective, as different researchers have presented
similar conclusions, we believe that the direction to be followed should be much more than worrying about doping effects. The focus on working with morphology and interface engineering stands out as the great perspective and necessary achievement for the advance on hematite-based PEC cells area, seeking for elements that segregate to reduce the barriers energy on homo and/or heterointerfaces without forming a resistive phase and capable of increasing the overall performance.

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