

The Influence of Annealing on the Sb Layer in the Synthesis of [001]-Oriented Sb_2Se_3 Film for Photoelectrochemical Hydrogen Gas Generation

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This work reports a new thermal treatment approach to obtain [001]-oriented Sb_2Se_3 film, which consists of preliminary annealing of the Sb layer before its selenization. Among the different Sb annealing temperatures assessed, the one at 200 °C followed by selenization (Sb_2Se_3 (Sb-A200)) results in a considerably high texture coefficient at the [001] direction, whereas the Sb_2Se_3 film obtained only by selenization of the non-annealed Sb film (Sb_2Se_3 (Sb-NA)) features preferential orientation at the $[hk0]$ direction. In terms of photoelectrochemical (PEC) performance for H_2 generation, the Sb_2Se_3 (Sb-A200)/CdS/TiO₂/Pt film delivers a substantial photocurrent density of -5.65 mA cm^{-2} at 0 V_{RHE} , which is 10 times higher compared to the Sb_2Se_3 (Sb-NA)/CdS/TiO₂/Pt film. Additionally, the employment of the Sb annealing step results in stable PEC performance of the Sb_2Se_3 film over 7000 s, meaning that the photocorrosion is minimized. The improved PEC performance of the Sb_2Se_3 film is attributed to better crystallinity and composition closer to the stoichiometric condition, as well as the preferential orientation at the [001] direction that favors charger carriers' transportation. At last, the findings of this work feature an innovative thermal treatment approach to obtain [001]-oriented Sb_2Se_3 film to further improve H_2 generation from PEC water splitting.

renewable energy sources that can potentially replace them. More worrying is that fossil fuel resources contribute about 90% of global energy consumption, which impacts the increase in the emission of carbon dioxide (CO_2) into the atmosphere.^[1] Although CO_2 is an essential gas for the maintenance of life, the ever-growing release of this gas into the atmosphere, from fossil fuel combustion, can considerably contribute to the intensification of the greenhouse effect and climate changes, and these can cause an increase in the average temperature of the planet and affect the entire existing ecosystem.^[2] To circumvent these problems, sunlight has become one of the most promising alternative energy resources due to being abundant and environmentally friendly, ease of usage/harvest, less overall cost, and versatile.^[3,4] Additionally, solar energy can be converted to thermal energy via solar water heaters, or electrical and chemical energy via photovoltaic and PEC devices, respectively.^[5] The conversion of solar

energy into chemical energy consists of storing energy in the bonds of hydrogen gas (H_2) molecules, and this molecule is known as a dense energy carrier. H_2 has heat capacity and energy density much higher than batteries,^[6,7] and the energy yield

1. Introduction

The concern of depletion of energy resources based on fossil fuels has led lately to a considerable increase in the search for

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of H_2 is 2.75 times higher compared to that of hydrocarbon fuels.^[8] One way to obtain H_2 is via solar water splitting, which can be carried out in PEC cells or photovoltaic panels coupled to electrolyzers.^[7]

To drive solar water splitting into PEC cells, a variety of semiconductor materials have been under investigation, and among those antimony(III) selenide (Sb_2Se_3) thin film has stood out as a promising photocathode owing to its adequate intrinsic optoelectronic properties, earth-abundant elements, and low toxicity.^[9,10] To exemplify the optoelectronic properties of Sb_2Se_3 , this material has a high absorption coefficient, α , in the ultraviolet and the visible region of the solar spectrum ($\alpha > 10^5 \text{ cm}^{-1}$),^[11] suitable optical bandgap energy, E_g , of 1.1–1.3 eV,^[12–14] high mobility ($\approx 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for minority carriers),^[15] long carrier lifetime ($\approx 60 \text{ ns}$),^[15] and appropriate energy band position to drive hydrogen evolution reaction (HER) under illumination.^[14,16,17] In addition, Sb_2Se_3 has a single orthorhombic crystalline phase composed of quasi-1D (Q1D) parallel ribbons of $(Sb_4Se_6)_n$ in one spatial direction.^[18,19] These Q1D $(Sb_4Se_6)_n$ ribbons present covalent Sb–Se bonds along the [001] direction, and the ribbons are stacked along the [100] and [010] directions, which are held together by van der Waals forces.^[20] The different orientation growth of the $(Sb_4Se_6)_n$ ribbons enables the existence of anisotropic crystallographic behavior, meaning that any preferred orientation in the [001] direction (ribbons vertically oriented to the substrate) favors the charge transport, as the charge carriers travel more easily along the ribbon-like structure. On the other hand, the $(Sb_4Se_6)_n$ ribbons featuring [100] and [010] directions (ribbons horizontally oriented to the substrate) result in difficulty for charge carriers transport due to the hopping mechanism, that is, charge carriers must hop from one $(Sb_4Se_6)_n$ ribbon to another.^[20] Such an anisotropic charge carriers' transportation suggests that a properly textured Sb_2Se_3 film (i.e., featuring [hk1] direction) is the ideal condition for solar energy conversion applications.^[20–22] Additionally, the combination of all these properties makes Sb_2Se_3 a very promising semiconductor material to be used as a photocathode for PEC cells when compared to other semiconductors.^[23–25]

Although Sb_2Se_3 has been extensively demonstrated to be an excellent alternative as a photocathode for solar-driven water splitting,^[26,27] the electron-hole recombination process in bulk, and the presence of interfacial defects are recurrent issues^[18] that limit to reach satisfactory PEC performance of this material for commercial application.^[28] To overcome these issues, the improvement of crystallinity and the control of elemental composition of Sb_2Se_3 have been attributed as the main factors to enhance the PEC performance of Sb_2Se_3 photocathode.^[29,30] Regarding, particularly the elemental composition effect, Caño et al.^[31] have recently shown that nonstoichiometric Mo/ Sb_2Se_3 film gives rise to secondary phases, that is, Se-rich Mo/ Sb_2Se_3 film leads to the formation of $MoSe_2$ and Se phases, whereas the Sb-rich condition favors the occurrence of Sb_2O_3 and m-Sb phases. In another recent study, Lian et al.^[32] identified the presence of deep-level defects in Sb-rich Sb_2Se_3 film, which, based on experimental results, were characterized as amphoteric Sb_{Se} defects. Moreover, according to the authors, the amphoteric defects in this material can trap both electrons and holes, resulting eventually in a recombination process. It was also shown that Se-rich Sb_2Se_3 films have relatively less defect concentration as well as a reduced num-

ber of shallow energy levels. Besides the elemental composition effect, another limiting factor is that the [hk1]-oriented Sb_2Se_3 , which is the ideal condition for PEC and photovoltaic cells, is not thermodynamically favorable compared to that of [hk0] orientation, as the [hk0] leads to the formation of Sb_2Se_3 crystal facets with a lower formation energy.^[33]

To tackle this issue, studies have recently shown that [hk1]-oriented Sb_2Se_3 film can be obtained by optimizing the selenization temperature of either the Sb or Sb_2Se_3 film.^[34,35] It is often reported that the employment of molybdenum (Mo) as the back-contact to grow [hk1]-oriented Sb_2Se_3 film during the selenization step, however, Liang et al.^[36] demonstrated that the in situ surface selenization of tungsten (W) can be used as a back-contact to enable the obtainment of Sb_2Se_3 film featuring [hk1] preferred orientation. Furthermore, the authors reported that the thin layer of WSe_2 behaves as a hole transport layer, which means that this material can collect the photogenerated holes and block the photogenerated electrons from transferring to the back-contact, hindering the electron-hole recombination process.

Herein, it is considered an alternative thermal treatment approach to obtain [001]-oriented Sb_2Se_3 film. For this study, a new methodology was developed consisting of preliminary annealing of the Sb layer before the selenization step. Particularly, it was aimed to investigate the influence of the different annealing temperatures of the Sb layer and the different selenization conditions (i.e., temperature and dwelling time) of the annealed Sb layer to produce [001]-oriented Sb_2Se_3 film. It was also targeted to assess how the crystallinity and elemental composition of the [001]-oriented Sb_2Se_3 film directly affect the PEC performance for H_2 production via solar-driven water splitting. As will be shown in the Results and Discussion section, compared to the Sb_2Se_3 film obtained only via selenization, the annealing of the Sb layer before selenization led to the formation of Sb_2Se_3 film with preferential crystallographic orientation to the [001] direction, better crystallinity, and suitable elemental composition. It will also be demonstrated that the Sb_2Se_3 film obtained via annealing of Sb before selenization delivers a substantial improvement of PEC activity and stability for H_2 generation from the water splitting reaction. All in all, the annealing step developed in this work provides an alternative approach to considerably enhance PEC activity and stability of [001]-oriented Sb_2Se_3 film for H_2 production.

2. Results and Discussion

2.1. Characterization of Single-Layered Films

2.1.1. Selenization of Non-Annealed Sb

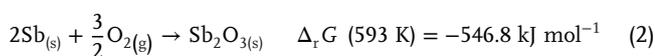
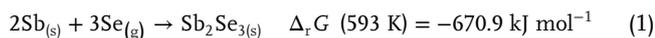
In this regard, the elemental composition of the Sb_2Se_3 (Sb-NA) film submitted to selenization at 320 °C for 30 min was analyzed by XRF. According to Figure S3a, Supporting Information, the elemental composition of the film was Se-rich, presenting a maximum atomic percentage ratio of $3[Sb\%]/2[Se\%] \approx 0.67$, which is far from the stoichiometric value ($3[Sb\%]/2[Se\%] = 1$, corresponding to 60 at.% Se and 40 at.% Sb). A brief investigation was performed over the range of selenization temperatures of $320 \pm 20 \text{ }^\circ\text{C}$ (i.e., 300 and 340 °C for 30 min), however, the films continued to present a Se-rich composition. Se-rich Sb_2Se_3 films have also been reported as an effective stoichiometric condition

for photovoltaic cell application due to the presence of benign defects, that is, Se_{Sb} antisites (shallow acceptors) and the difficulty of detrimental defects formation, such as selenium vacancies and Sb_{Se} antisites (deep donors).^[37–39]

2.1.2. Annealing Temperature Effect of Sb

In the attempt to find out the reason for obtaining Se-rich Sb_2Se_3 (Sb-NA) films, XRD measurements were performed for the as-deposited Sb film not subjected to annealing step (labeled as Sb-NA), as well as for those annealed at 150, 200, and 250 °C for 30 min (labeled as Sb-A150, Sb-A200, and Sb-A250, respectively). As shown in Figure S3b, Supporting Information, it was identified weak reflections for the (003), (006), and (202) planes of the Sb-NA film, which were assigned to the rhombohedral Sb phase (Powder Diffraction File (PDF) no. 35–732). These peaks featured low intensity, suggesting poor crystallinity of the Sb-NA film. That may have prevented the formation of a more stoichiometric Sb_2Se_3 film and affected its composition during the selenization process. However, the results for the as-deposited Sb films annealed at the highest temperatures, namely, Sb-A200 and Sb-A250 films, showed strong reflections and therefore more crystalline films compared to those of the Sb-NA and Sb-A150 films, which have weak reflections.

As additional evidence of the annealing effect, it can be observed that a decrease of up to 21.5% of the full width at half maximum (FWHM) values for the (006) plane (Figure S3c, Supporting Information), indicating an increase in the size of the Sb crystallite as the annealing temperature increases. Interestingly, the Sb-A200 and Sb-A250 films featured a secondary phase of Sb_2O_3 (PDF no. 75–1565) as noted by the peaks indexed to the (111), (222), and (444) planes, which are indicated by circled regions in the XRD patterns (cf. Figure S3b, Supporting Information). Although the annealing was performed under Ar atmosphere, this result indicates that the Sb films underwent thermal oxidation at annealing temperatures higher than 200 °C. Despite the presence of the Sb_2O_3 secondary phase, the selenization process (performed at 320 °C) can convert all oxidized phases into Sb_2Se_3 . According to Equations (1) and (2), which consider the reaction between $\text{Sb}_{(\text{s})}$ and $\text{Se}_{(\text{g})}$, and the reaction of $\text{Sb}_{(\text{s})}$ and $\text{O}_{2(\text{g})}$ both at 320 °C (corresponds to 593 K),^[40,41] the formation of Sb_2Se_3 is thermodynamically more favorable than Sb_2O_3 and the selenization also allows any oxide residues to be converted into the Sb_2Se_3 . Furthermore, elementary Se has a melting point of 221 °C,^[42] and high vapor pressure,^[43] which contributes to the chalconization in the absence of oxygen gas. The reader is referred to the Supporting Information (SI) for details about the calculation of the values of the molar Gibbs energy of reaction at 593 K ($\Delta_r G(593 \text{ K})$) for the reactions in Equations (1) and (2).



2.1.3. Selenization of Sb Annealed at Different Temperatures

The as-deposited Sb films annealed at different temperatures were subsequently submitted to selenization and assessed their

elemental composition by the XRF analysis (Figure 1a). It is possible to observe that the annealing of the Sb improved the stoichiometry of the Sb_2Se_3 films, allowing the $3[\text{Sb}\%]/2[\text{Se}\%]$ atomic ratio of these films to increase compared to those of the Sb_2Se_3 films obtained without annealing the Sb. This is indicative that more crystalline Sb films may lead to better formation of Sb_2Se_3 phase in the selenization process. The best annealing condition before selenization was at 200 °C, as favored a maximum $3[\text{Sb}\%]/2[\text{Se}\%]$ atomic ratio of ≈ 0.8 . The improvement of adjusted chemical composition might be attributed to a lesser extent elemental Se condensation over the surface of the Sb_2Se_3 (Sb-A) films compared to those of Sb_2Se_3 (Sb-NA) films. The elemental Se condensation may have occurred during the selenization process of the Sb-A and Sb-NA films.^[44] The presence of elemental Se on the Sb_2Se_3 (Sb-A) films' surface was verified by XPS analysis (see discussion further). The minimized condensation of elemental Se for the Sb_2Se_3 (Sb-A) films might be associated with the crystal structure of the [001]-oriented Sb-A films (see discussion of Figure 1b,c) that possibly favors diffusion of sublimated Se atoms into the [001]-oriented crystal lattice of the Sb-A film that can subsequently react to form [001]-oriented Sb_2Se_3 .^[45]

The Sb_2Se_3 films obtained via selenization of annealed Sb, as well as the Sb_2Se_3 (Sb-NA) film, were also characterized by XRD measurements (see Figure 1b). All the diffractograms featured diffraction peaks indexed to the (020), (120), (220), (230), (211), (221), (301), (311), (240), (231), (141), (411), (002) and (061) planes, and these peaks were assigned to the orthorhombic Sb_2Se_3 phase (PDF no. 89–821). The diffraction peaks labeled with asterisks (*) are attributed to the Mo-coated glass substrates (PDF no. 42–1120). Furthermore, it was not identified the diffraction peaks of the secondary phase of Sb_2O_3 , proved the efficacy of the method of fully converting the Sb and Sb_2O_3 phases into the Sb_2Se_3 phase during selenization, as shown in Equations (1) and (2). Another interesting aspect from Figure 1b is that all the Sb_2Se_3 films obtained via selenization of the annealed Sb showed strong reflections for the (002) plane compared to those of the Sb_2Se_3 (Sb-NA) film, indicating better crystallinity and preferential orientation in the [001] direction. To better understand the preferred orientation of the crystallographic planes of the Sb_2Se_3 films, the texture coefficient for a given (hkl) plane, $\text{TC}(hkl)$, was calculated using Equation (3),^[27] and the results are displayed in Figure 1c.

$$\text{TC}(hkl) = \frac{I_{(hkl)}}{I_{0(hkl)}} \left\{ \frac{1}{N} \sum_{i=0}^N \frac{I_{(hkl)}}{I_{0(hkl)}} \right\}^{-1} \quad (3)$$

where $I_{(hkl)}$ and $I_{0(hkl)}$ are the diffraction peak intensities for a given (hkl) plane measured from the XRD and the database of XRD (Sb_2Se_3 PDF no. 89–821) patterns, respectively, and N is the number of planes considered for the calculation (10 planes in that diffractogram).

According to Figure 1c, the TC for the (120), (301), (221), and (211) planes featured similar values and were lower than 1, meaning no preferential crystal orientation for these planes. However, $\text{TC}(230) > 1$ was achieved for the Sb_2Se_3 (Sb-NA) and Sb_2Se_3 (Sb-A150) films, suggesting that the crystal of Sb_2Se_3 has a preferential growth orientation parallel to the substrate ([100] and/or [010] orientation), which is not efficient for photogenerated charge

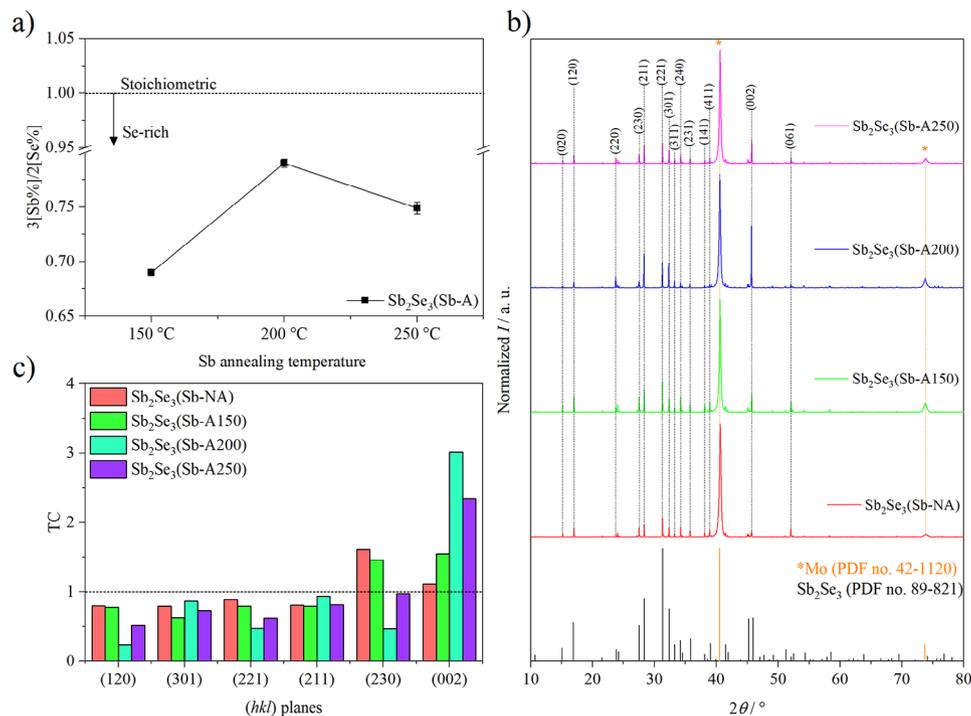


Figure 1. a) Atomic percentage ratio obtained from the XRF analysis, b) XRD patterns, and c) TC(*hkl*) values of the Sb₂Se₃ (Sb-NA) and the Sb₂Se₃ (Sb-A) films. XRD patterns of the PDF database for the orthorhombic Sb₂Se₃ (PDF no. 89–821) and the cubic Mo (PDF no. 42–1120) phases are displayed as vertical lines at the bottom of the diffractograms. The diffraction peaks labeled with * were assigned to the Mo back-contact.

carriers transportation due to inter-ribbons hopping mechanism. For the (002) plane, the Sb₂Se₃ (Sb-A200) film featured the highest TC(002) value (i.e., ≈ 3), indicating the ribbons of the Sb₂Se₃ are vertically grown to the substrate ([001] orientation), which favor efficient photogenerated charge carriers transportation owing to the transport of the carriers alongside the ribbons. It was also noted that the Sb₂Se₃ (Sb-A200) film has the lowest value for the TC(120), indicating low contribution of the parallel orientation to the substrate. This preferential growth of the [001] direction for the Sb₂Se₃ has likely occurred due to the influence of the improved intensity of the diffraction peaks for the (003) and (006) planes ([001]-oriented Sb) of the Sb-A200 and Sb-A250 films compared to those of the Sb-A150 and Sb-NA films (cf. Figure S3b, Supporting Information). The (003) and (006) planes enable continuous diffusion of sublimated Se to react with [001]-oriented Sb and form column growth of [001]-oriented Sb₂Se₃.^[45] To better understand this phenomenon in terms of a possible selenization mechanism, the change in temperature during the annealing process directly influences the vapor pressure of Se atoms and their kinetic energy. At a given selenization temperature, the sublimated Se atoms may adsorb on the [001]-oriented Sb film surface with sufficient energy to react and form a Sb₂Se₃ crystal nucleus. The sublimated Se atoms may continue to diffuse to the [001]-Sb/[001]-Sb₂Se₃ interface along the van Waals gaps of Sb₂Se₃ to extend the length of the [001]-Sb₂Se₃ preferential growth.^[34,46]

However, despite the Sb-A250 film featuring the highest intensity of the Sb's diffraction peaks for the (003) and (006) planes, the presence of the Sb₂O₃ phase may have minimized its preferential orientation in the [001] direction compared to that of the

Sb₂Se₃ (Sb-A200) film. Therefore, the experimental condition for the preparation of Sb₂Se₃ (Sb-A200) film was chosen as the optimum condition.

Additional characterization of the Sb₂Se₃ (Sb-NA) and the Sb₂Se₃ (Sb-A) films was achieved by Raman spectra, as shown in Figure 2. The main vibrational modes of Sb₂Se₃ are represented by well-defined bands within a range of 50 – 300 cm⁻¹.^[44] The bands located at 210 and 190 cm⁻¹ are related to the A_g mode of the Sb–Se–Sb bending vibrations of the Sb₂Se₃, while the small band ≈ 154 cm⁻¹ is assigned to the A_{2u} vibration mode of the Sb–Sb bond. The observed bands at 120 and 80 cm⁻¹ are attributed to the Se–Se bending.^[44,47] It is important to mention that none of the samples displayed the characteristic bands of the Sb₂O₃ secondary phase in the Raman spectra (corresponding to the main bands at 254 and 450 cm⁻¹),^[44] however, all the samples presented low-intensity bands at 98 and 250 cm⁻¹ assigned to the presence of Se₆ ring (rhombohedral Se).^[44,48] It has also been reported that Se-rich chalcogenide film can provide rhombohedral Se signals in that region, which arise from the excess of Se deposited on the samples' surface.^[49,50] The Raman spectra in this work suggest that the selenization process may have contributed to the occurrence of elemental Se on the surface of all the samples, and this agrees with the XRF analysis, which indicates that the Sb₂Se₃ are Se-rich (cf. Figure 1a). Nevertheless, it was not identified Se phase in the XRD data (cf. Figure 1b), probably indicating that Se phase may be present in small quantities.

Figure S4a,b, Supporting Information show the Tauc plots as $(\alpha h\nu)^{1/2}$ versus E_{ph} (indirect transition) and $(\alpha h\nu)^2$ versus E_{ph} (direct transition), respectively.^[51] For an indirect and a direct transition, the linear extrapolation to the baseline rendered optical E_g

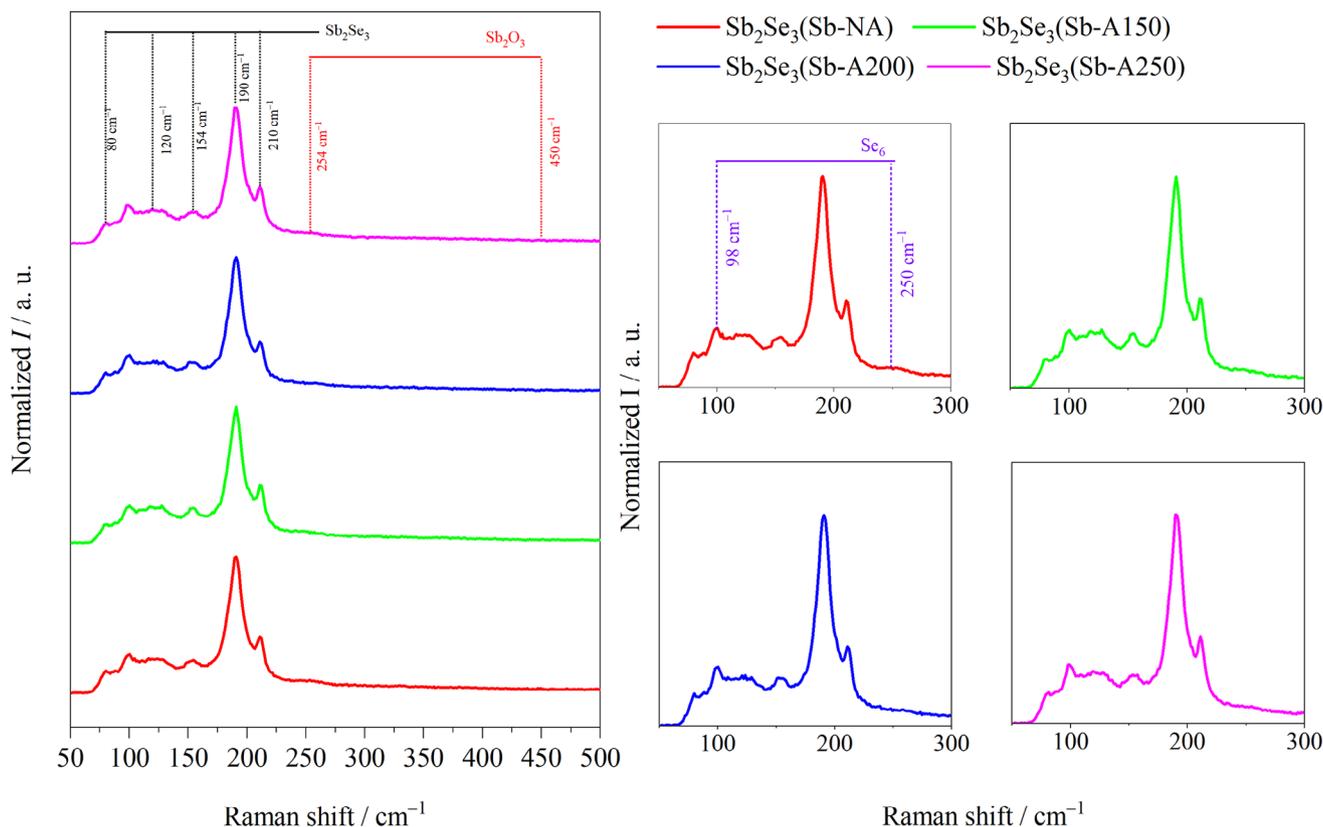


Figure 2. (on the left) Raman spectra and their corresponding (on the right) expanded region of the spectra encompassing the main bands of Sb_2Se_3 for the Sb_2Se_3 (Sb-NA) and the Sb_2Se_3 (Sb-A) films.

values of 1.33 and 1.34 eV, respectively, for all the samples. These results are slightly higher than those reported in the literature (i.e., 1.1–1.3 eV^[12–14]), however, it is also reported that Sb_2Se_3 with higher optical E_g for nanorod^[52,53] or nanowires^[54] morphologies. In addition, it was also assessed the E_u of the films, which characterizes the structural disorder of the semiconductor.^[55] An increase of E_u value represents an enlargement of the width of the bands' edges tail, which means a more pronounced structural disorder in the semiconductor. This parameter can be understood as the width of the tail of the conduction and valence band edges associated with the localized defect states within the E_g . Additionally, the presence of the bands' edges tailing corresponds to transitions between extended states of the valence band and localized states of the conduction band.^[56] According to Figure S4c, Supporting Information, it can be seen a narrow linear region in the inset of the E_u plot before the E_g values, which the E_u was estimated from the inverse of the slope of the straight lines in the graphs. Unlike the optical E_g value in which there was no difference in comparison with the different samples, the E_u has shown a slight difference in their values. The lowest value of the E_u was 0.21 eV for the Sb_2Se_3 (Sb-A200) film compared to those of the other films. This indicates that the annealing at 200 °C of the Sb film has contributed to the decrease of the structural disorder and the localized defects in the band edges of the Sb_2Se_3 (Sb-A200) film. On the other hand, the Sb_2Se_3 (Sb-A250) film featured the highest value of the E_u (i.e., 0.32 eV), indicating that this film has a higher num-

ber of localized defects in its band edges compared to the other films.^[57]

The Sb_2Se_3 (Sb-A200) film, that is, representing the optimum condition, was chemically assessed by the XPS measurements, and the spectra are displayed in Figure 3. As shown in Figure 3a, the survey spectrum exhibits the main peaks of Sb, Se, O, and C elements, corresponding to Sb 4p, Sb 3d, Sb 4s, Sb 4d, Se 3s, Se 3p, Se 3d, O 1s, and C 1s core levels, respectively. Regarding the high-resolution XPS spectra (Figure 3b), the spectrum of the Sb 3d core level features two Sb 3d doublets: the first one with peaks at 529 (Sb 3d_{5/2}) and 538.34 eV (Sb 3d_{3/2}) are assigned to the Sb–Se bonds in Sb_2Se_3 , whereas the second one having peaks at 530 (Sb 3d_{5/2}) and 539.34 eV (Sb 3d_{3/2}) are attributed to the Sb–O bonds.^[58] Since XPS is a highly surface-sensitive technique, the presence of an Sb–O signal is a result of the sample being exposed to air before the XPS analysis,^[59] and this has also been reported in the literature.^[60–62] The presence of Sb–O signal (possibly Sb_2O_3) might be beneficial as it could passivate defects (i.e., Se vacancies) on the surface of Sb_2Se_3 films.^[62] Moreover, bearing in mind that XPS is surface-sensitive (penetration depth of 10 nm or less^[63]), despite the possibility of superficial formation of Sb_2O_3 , the bulk properties of Sb_2Se_3 films remain unaltered, as can be verified from the discussion of XRD (cf. Figure 1) and Raman (cf. Figure 2). Still regarding Figure 3b, The O 1s peak at 531.7 eV is assigned to the adventitious oxygen weakly adsorbed on the surface, which could also be a result of atmospheric CO_2 physisorption on the photoelectrode surface.^[64] Concerning the

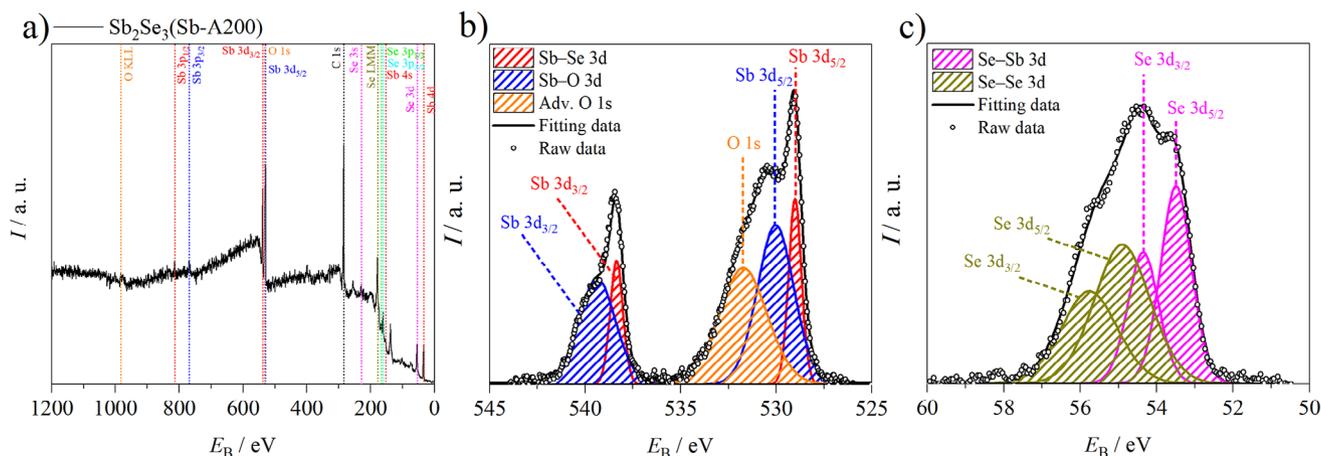


Figure 3. a) The survey and high-resolution XPS spectra of b) Sb 3d and c) Se 3d core levels for Sb_2Se_3 (Sb-A200) film.

high-resolution spectra of the Se 3d core level (Figure 3c), one notices the presence of two Se 3d doublets: the first one containing peaks at 53.5 (Se $3d_{5/2}$) and 54.36 eV (Se $3d_{3/2}$) are assigned to the Se–Sb bonds in Sb_2Se_3 , and the second one with peaks at 54.9 (Se $3d_{5/2}$) and 55.76 eV (Se $3d_{3/2}$) are attributed to the Se–Se bonds in elemental selenium.^[58] As shown in the discussion of the Raman spectra (cf. Figure 2), the presence of elemental selenium arises from the excess of Se in the form of Se_6 rings on the samples' surface during the selenization process or even as a side-product of the Sb_2Se_3 air oxidation.

Besides the chemical assessment, it has employed SEM analyses (Figure 4) to characterize the morphology on the surface and at the cross-section of the Sb_2Se_3 (Sb-NA) and the Sb_2Se_3 (Sb-A) films. As indicated in Figure 4a, it is possible to observe the formation of rod-like structures with lengths of more than 1 μm , which are randomly oriented in all directions on the surface of the Sb_2Se_3 (Sb-NA) film. The presence of these rod-like structures may indicate a preferential orientation of the Sb_2Se_3 crystal. Since the Sb_2Se_3 (Sb-NA) film featured preferential orientation to the (230) plane (cf. Figure 1c), this implies that the rod structures might be associated with the existence of $(\text{Sb}_4\text{Se}_6)_n$ ribbons oriented at the $[hk0]$ direction (i.e., ribbons horizontally oriented to the substrate).^[33] For the Sb_2Se_3 (Sb-A) films (cf. Figure 4a), the Sb_2Se_3 (Sb-A150) film features a mix of morphologies on its surface, ranging from microrods to round-shaped structures. The morphology of the Sb_2Se_3 (Sb-A200) film mostly consists of compacted irregular structures, whose contours are well-defined. On the other hand, the morphology of the Sb_2Se_3 (Sb-A250) film presents a less-defined shape, including elongated and misshapen grains. The cross-section micrographs in Figure 4b showed differences in the films' morphology. The Sb_2Se_3 (Sb-NA) and Sb_2Se_3 (Sb-A150) films show less-defined grains, whereas the Sb_2Se_3 (Sb-A250) film displays voids between the Sb_2Se_3 and the tri-layer Mo. For the Sb_2Se_3 (Sb-A200) film, one notices the presence of homogeneous and well-defined grains vertically grown on the tri-layer Mo with no voids between them. The formation of these vertically oriented structures for the Sb_2Se_3 (Sb-A200) film suggests formation of [001]-oriented $(\text{Sb}_4\text{Se}_6)_n$ ribbons,^[33] as was also observed by the highest TC(002) value of ≈ 3 (see Figure 1c). All the morphological features of

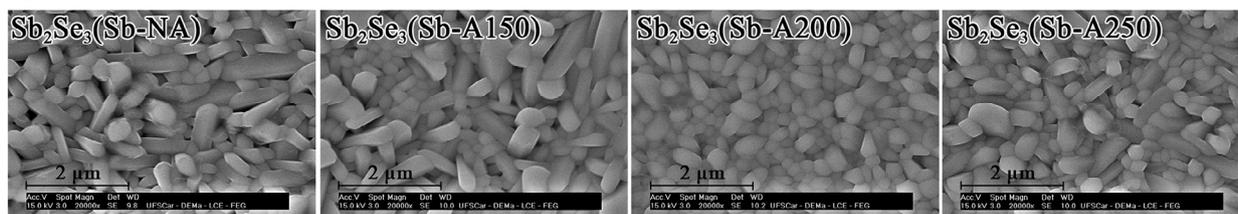
the Sb_2Se_3 (Sb-A200) film can be better observed in the micrographs zoomed out of the surface and cross-section (Figure 4c). Regarding the thickness of the films, although it is not possible to accurately measure the thickness due to the non-uniformity, one notices that the thickness of the Sb_2Se_3 (Sb-A) films is higher compared to that of Sb_2Se_3 (Sb-NA) film (cf. Figure 4b). This apparent increase in thickness of the Sb_2Se_3 (Sb-A) films is probably due to enlarged crystallite size of Sb-A films upon the annealing process, which can be observed by the decrease of up to 21.5% of the FWHM values for the (006) plane (Figure S3c, Supporting Information), representing an increase in ≈ 11 nm (according to the Scherrer equation) of the Sb crystallite size.

2.1.4. Optimizing Selenization of Annealed Sb

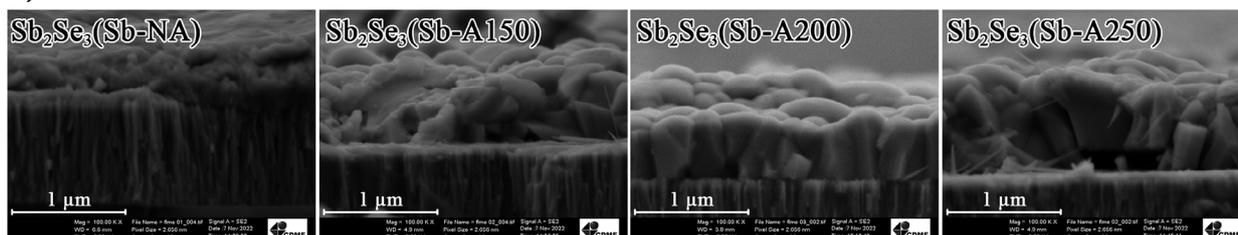
According to the results that have been presented so far, the optimum thermal treatment condition corresponded to the sample labeled as Sb_2Se_3 (Sb-A200). Aiming to further evaluate the thermal treatment approach of the Sb_2Se_3 films, it has also been assessed the effect of the selenization on the Sb-A200 films at different temperatures (i.e., 280, 300, 320, and 340 $^\circ\text{C}$) and dwelling times (i.e., 30 and 60 min). The Sb-A200 films selenized at different temperatures and times were characterized in terms of their elemental composition, crystal structure, and photoelectrocatalytic performance toward HER, as presented as follows.

From the XRF analysis (Figure 5a), one notices that the Sb-A200 films selenized at the lowest temperature and time (i.e., 280 $^\circ\text{C}$ and 30 min, respectively) featured the highest atomic ratio of 0.81, which is reasonably close to the expected stoichiometric value. Additionally, the Se-rich condition became more pronounced for the Sb-A200 films selenized at the highest temperature and time (i.e., 340 $^\circ\text{C}$ and 60 min, respectively), leading to a minimum value of atomic ratio of 0.69. Based on these results, one can infer that longer dwelling times and higher temperatures can lead to a sublimated Se-rich atmosphere and significantly affect the composition of the samples. This result means that the employment of the annealing step for the Sb film and the simple

a) Surface



b) Cross-section



c) Sb₂Se₃(Sb-A200)

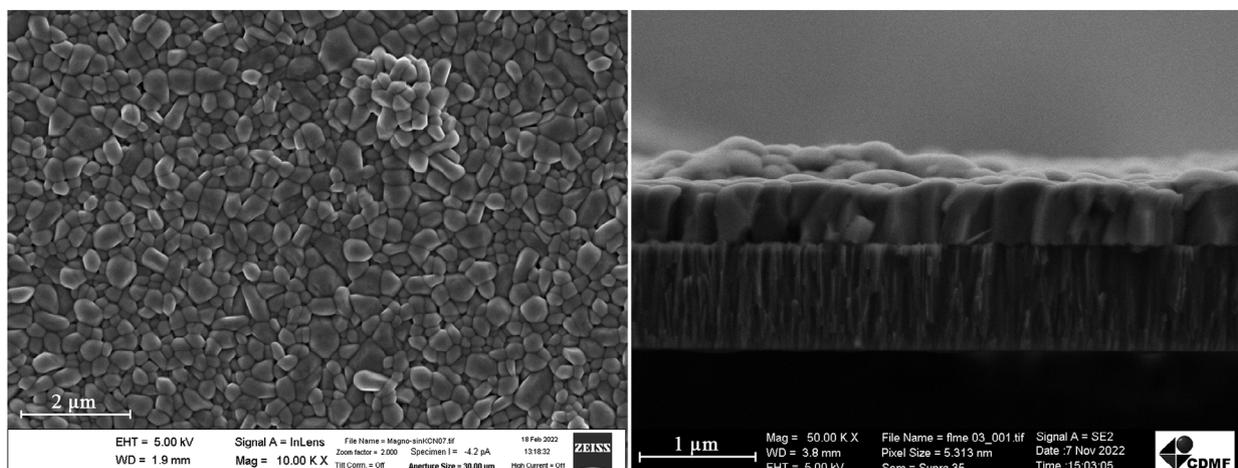


Figure 4. FEG-SEM micrographs of the a) surface (20k times magnification) and b) the cross-section (100k times magnification) for the Sb₂Se₃(Sb-NA) and the Sb₂Se₃(Sb-A) films. c) FEG-SEM micrographs zoomed out of the surface (10k times magnification) and cross-section (50k times magnification) of the Sb₂Se₃(Sb-A200) film.

adjustment of the selenization temperature and time play an important role in improving the stoichiometry of the Sb₂Se₃ films.

Concerning the XRD analysis (Figure 5b), the diffraction peaks of all the samples were assigned to the orthorhombic Sb₂Se₃ phase (which follows the PDF no. 89–821), and no secondary phase, such as elemental Se and Sb₂O₃, was detected. Additionally, all the samples have shown strong reflections in the diffraction peak indexed to the (002) plane as the most intense one, indicating better crystallinity and preferential orientation of the Sb₂Se₃ crystal to the [001] direction. As additional analysis from the XRD patterns, it was also calculated the mean of crystallite size, *D*, from the diffraction peak positions via Equation (4)^[65] for the Sb₂Se₃(Sb-A200) films selenized at different temperatures and dwelling times.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

where *K* is the shape factor (0.9, considering the orthorhombic nature of Sb₂Se₃^[65,66]), λ is the X-ray wavelength (1.54 Å for Cu *K*_{α1} radiation), β is the FWHM for a given diffraction peak, and θ is the diffraction peak position.

As shown in Figure 5c, a slight tendency was noted for the *D* values of the samples selenized at different temperatures and dwelling times. For the dwelling time of 60 min, *D* presented values ranging from 107.85 to 116.41 nm with increasing selenization temperature, suggesting an increase in the grain size as the temperature increases. This increase of *D* may indicate that the crystallinity and grain size of the Sb₂Se₃ film are affected upon selenization. Since the film becomes Se-rich as the selenization temperature increases, the atoms of Se may incorporate into the Sb₂Se₃ structure^[66] and increase its size. Conversely, for the dwelling time of 30 min, *D* presented a maximum value of 112.61 nm for the selenization temperature of 300 °C and then this value decreased for higher selenization

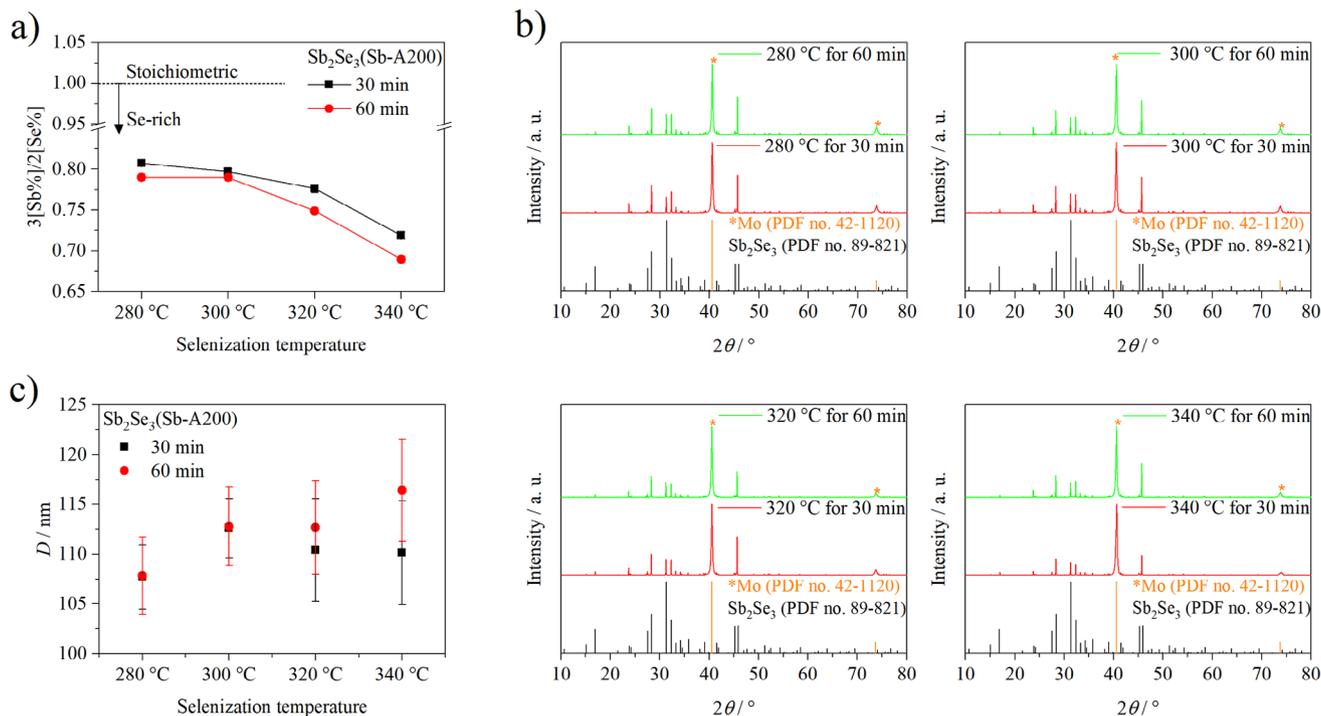


Figure 5. a) Atomic percentage ratio obtained from the XRF analysis, b) XRD patterns, and c) D values for the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ films selenized at different temperatures and dwelling times. XRD patterns of the PDF database for the orthorhombic Sb_2Se_3 (PDF no. 89–821) and the cubic Mo (PDF no. 42–1120) phases are displayed as vertical lines at the bottom of the diffractograms. The diffraction peaks labeled with * were assigned to the Mo from the Mo back-contact.

temperatures. This decrease in the D values of the Sb_2Se_3 at selenization temperatures > 300 °C is probably related to the partial decomposition of the Sb_2Se_3 crystallites, as Sb_2Se_3 can undergo thermal decomposition and/or structural rearrangement under high temperatures.^[47,67]

2.2. Characterization of Multi-Layered Films

Aiming to obtain a multilayer photocathode for the H_2 generation via solar-driven water splitting, the surface of the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ film was initially etched with the KCN solution followed by the sequential deposition of the CdS and the TiO_2 layers onto their films' surface to obtain the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})/\text{CdS}/\text{TiO}_2$ films. Regarding the morphological analysis of the multilayer films, Figure S5 shows the surface micrographs obtained by FEG-SEM at 20k times magnification for each of the layers present in the sample. The surface of the back-contact (tri-layer Mo) presented a worm-like morphology, whereas the Sb-A200 layer, which was deposited onto this back-contact, exhibited a morphology of irregular grains closely packed. For the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ film, obtained by selenizing the Sb-A200 film at 320 °C for 30 min, one notices that the particles featured irregular shape and once the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ film was etched with the KCN solution, the irregular shape of the particles was drastically affected by the etching process, suggesting a slight dissolution of the particles of this layer.^[18] For the CdS layer, which was deposited over the KCN-etched $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ film, it was noted the presence of vertically grown plate-like structures and the occurrence of clus-

ters distributed throughout the CdS film's surface. For the upper layer, that is, TiO_2 , one notices the presence of a compact layer covering the whole film's surface.

As additional SEM image analyses, it was also obtained the cross-section micrograph of the SLG/Mo/ $\text{Sb}_2\text{Se}_3(\text{Sb-A200})/\text{CdS}/\text{TiO}_2$ film to measure the thickness of the layers (Figure 6a). The tri-layer Mo exhibited a total thickness of ≈ 0.9 μm , which was comprised of the denominated Mo_A (≈ 0.6 μm , lower region of the back-contact), and $\text{Mo}_B + \text{Mo}_A$ (≈ 0.3 μm), corresponding to the porous (intermediate region of the Mo layer) and the sacrificial (upper region of the Mo layer) layers, respectively. It is worth mentioning that the difficulty in differentiating the porous and the sacrificial layers does not allow a proper distinction between them, however, the morphological characteristics of these layers are very similar to that reported in the literature.^[68] It is also worth pointing out that the denomination of the layers in the tri-layer Mo (i.e., SLG/ $\text{Mo}_A/\text{Mo}_B/\text{Mo}_A$) was based on the work developed by Lopez-Marino et al.,^[68] who reported the tri-layer Mo was comprised of the Mo_A layer (back-contact), deposited at high power and low pressure, Mo_B (resistant to selenization), deposited at low power and high pressure, and the Mo_A layer (sacrificial layer). The Mo_A layer is more compact and has excellent electrical properties, but it is easily overselenized, whereas the Mo_B layer is more porous and has higher shunt resistance. The presence of a thin Mo_A layer on the upper region acts as a sacrificial layer for the formation of MoSe_2 , and the interior selenization of the back-contact is prevented by the Mo_B layer, leading thus the thick Mo_A layer on the lower region unselenized, which acts as the back-contact for

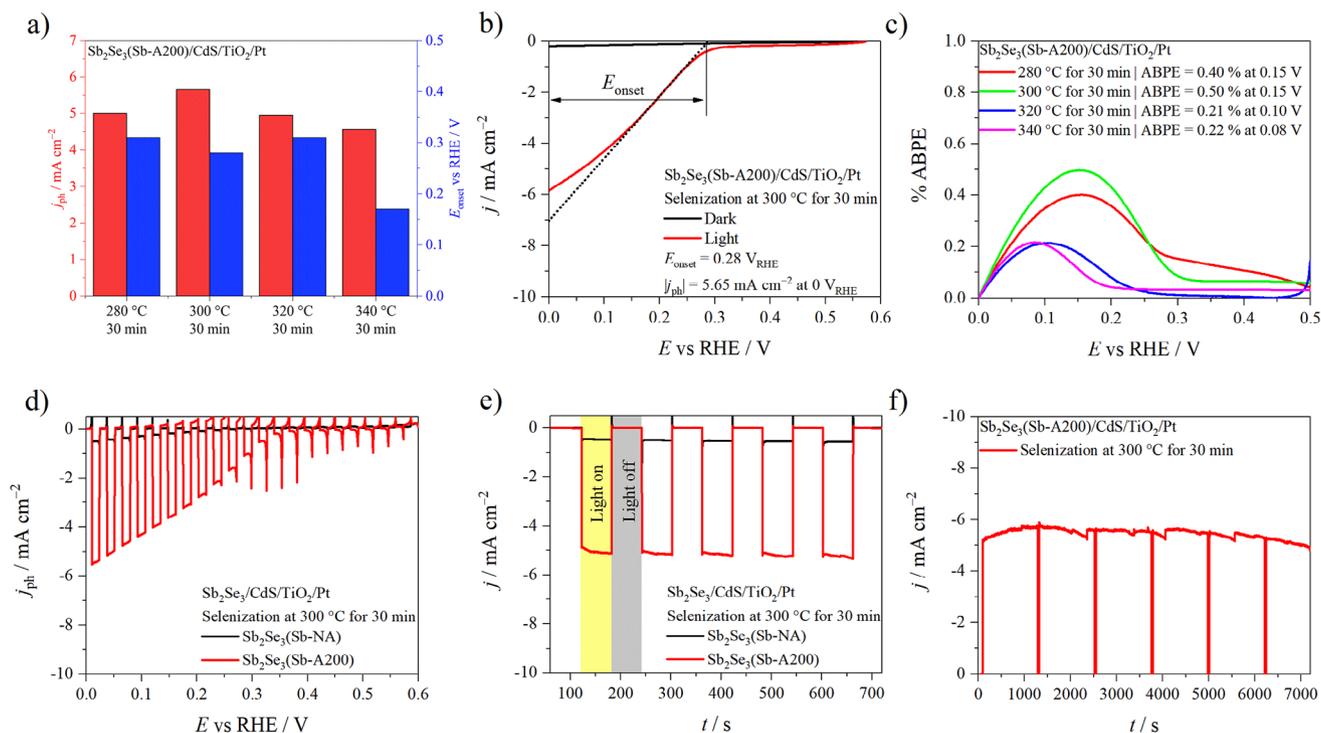


Figure 7. a) Summary of j_{ph} at 0 V_{RHE} and E_{onset} values, b) LSVs (featuring E_{onset} extrapolation) at a scan rate of 5 mV s^{-1} in the dark and under solar illumination (100 mW cm^{-2}), c) ABPE plots, d) LSV measurement under chopped illumination (100 mW cm^{-2}), e) short-term stability, and f) long-term stability at 0 V_{RHE} for the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})/\text{CdS}/\text{TiO}_2/\text{Pt}$ films in different conditions. The electrolyte was a N_2 -saturated solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ $\text{pH} \approx 0.3$.

temperatures and dwelling times has been investigated. For this analysis, the selenized films were in a multilayer configuration, that is, $\text{Sb}_2\text{Se}_3(\text{Sb-A200})/\text{CdS}/\text{TiO}_2/\text{Pt}$. The PEC experiments consisted of recording LSV curves in the dark and under solar illumination in a potential range between $0.6 \text{ V}_{\text{RHE}}$ and 0 V_{RHE} , as shown in Figure S7, Supporting Information.

For all the selenization conditions, the samples exhibited negative values of the current density, j , under illumination, as an indication of the cathodic current associated with the light-driven HER. This attribution is thermodynamically feasible, as the conduction band edge potential of the light absorber layer (Sb_2Se_3) is more negative than the potential of HER,^[72] and that enables the transfer of the photogenerated electrons in the conduction band of the semiconductor to reduce H_3O^+ to produce H_2 . From the LSV curves, one can obtain the photocurrent density, j_{ph} , by subtracting at a given potential the j under solar illumination from the j obtained in the dark (i.e., $j_{\text{ph}} = j_{\text{light on}} - j_{\text{light off}}$), and the j_{ph} values at 0 V_{RHE} are exhibited inside the graphs. As shown in Figure S7, Supporting Information, the different selenization temperatures did not significantly affect the j_{ph} responses of the samples, however, the dwelling time had a considerable influence on the j_{ph} values. The highest values of j_{ph} at 0 V_{RHE} were for the multilayer $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ films selenized for 30 min. The very low values of j_{ph} for film selenized for 60 min are probably associated with the atomic ratio far from the stoichiometric condition.

In addition to the j_{ph} analysis, it has also employed the LSV curves to assess the onset potential, E_{onset} , which is defined as the potential at which a specific reaction starts.^[73] The E_{onset} was

estimated from the so-called tangent method, which consists of a linear extrapolation of the line tangent to the j curve (i.e., LSVs under illumination) until it intercepts the baseline,^[73] wherein the interception corresponds to an approximate value of the E_{onset} . It is important to mention that the E_{onset} obtained represented an estimated value to be used for making comparisons between the different samples in this work. For a more accurate determination of the E_{onset} value, studies in literature recommend the use of mass-activity or specific-activity of a material,^[73] however, this is out of the scope of this work. Regarding the estimated E_{onset} from the LSVs (Figure S7, Supporting Information), for each selenization temperature, the E_{onset} for the HER of the samples selenized for 30 min presented higher values than those selenized for 60 min. This result means that short selenization times can result in the obtainment of films with improved photoelectrocatalytic activity for the HER.

To ensure the reliability of the [001]-oriented Sb_2Se_3 film, LSVs were also performed on the $\text{Sb}_2\text{Se}_3(\text{Sb-A150})$ and $\text{Sb}_2\text{Se}_3(\text{Sb-A250})$ films in the same previous conditions, and the result can be assessed in the Figure S8, Supporting Information. It is possible to notice a huge improvement in both j_{ph} and E_{onset} of the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ film when compared with the $\text{Sb}_2\text{Se}_3(\text{Sb-A150})$ and $\text{Sb}_2\text{Se}_3(\text{Sb-A250})$. These results are evidence that the Sb annealing before the selenization approach employed in this work can improve the performance of solar-driven water splitting.

To summarize the PEC assessment, Figure 7a displays the j_{ph} and E_{onset} values of the multilayer $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ films having the Sb_2Se_3 layer obtained from different selenization

temperatures for 30 min. The j_{ph} values exhibited a slight trend as a function of the selenization temperature, and the maximum photoresponse for the HER was $j_{\text{ph}} = -5.65 \text{ mA cm}^{-2}$ and $E_{\text{onset}} = 0.28 \text{ V}_{\text{RHE}}$ for the selenization temperature of $300 \text{ }^{\circ}\text{C}$ (Figure 7b). Additional PEC analysis was conducted in terms of evaluating the efficiency of the PEC performance at the photocathode|electrolyte interface via ABPE. The highest value of ABPE was 0.50% at $0.15 \text{ V}_{\text{RHE}}$ for the multilayer Sb_2Se_3 (Sb-A200) film obtained via selenization at $300 \text{ }^{\circ}\text{C}$, whereas the ones selenized at 320 and $340 \text{ }^{\circ}\text{C}$ featured the lowest efficiencies, that is, 0.21% and 0.22%, respectively. Considering these results, the optimum selenization condition of the Sb_2Se_3 (Sb-A200) films for PEC water splitting application is $300 \text{ }^{\circ}\text{C}$ for 30 min.

It was also made a comparison of the PEC performance of the Sb_2Se_3 (Sb-A200) and Sb_2Se_3 (Sb-NA) films, both selenized under the same conditions (i.e., $300 \text{ }^{\circ}\text{C}$ for 30 min), and these films also featured a multilayer configuration. For such, LSV measurements under chopped illumination were performed. The LSVs results (Figure 7d) show that the annealing step of the Sb film before selenization resulted in a huge increment of the j_{ph} values for the HER, that is, the multilayer configuration featuring the Sb_2Se_3 (Sb-A200) film presented a tenfold increase of the j_{ph} at 0 V_{RHE} compared to that of multilayer configuration having the Sb_2Se_3 (Sb-NA) film. This increase of j_{ph} is probably assigned to the preferential growth of the Sb_2Se_3 crystal to the [001] direction, which facilitates the transportation of the photogenerated carriers for the occurrence of the light-driven HER, and their stoichiometric characteristics compared to the Sb_2Se_3 (Sb-NA) film. It is also important to make an attempt comparison of the PEC performance obtained in this work with the studies in literature, however, one should bear in mind that is rather difficult to make a fair/systematic comparison due to the different synthesis methods, power of the lamps used, and the variability of surface characteristics of the Sb_2Se_3 film (i.e., surface defects, dangling bonds, impurities, etc.). The results of j_{ph} and E_{onset} values described in this work are compared below to those reported in the literature,^[74] nevertheless, the uniqueness of this work was the development of a simple and effective alternative method to improve the stoichiometry, crystallinity, and preferential orientation to the [001] direction of the Sb_2Se_3 film via employing the annealing of the Sb layer before their selenization.

In addition to the evaluation of the PEC activity, it has also assessed the short-term stability of both samples described previously. This experiment was performed by chronoamperometries, and the films were polarized at 0 V_{RHE} for 10 min under chopped illumination (each light on and light off conditions spanned 60 s). As shown in Figure 7e, it was observed that a steady j_{ph} with no noticeable decay during the time analyzed for both films, indicating good PEC stability for the light-driven HER. Additionally, the chronoamperometry measurements also displayed a tenfold increase of the j_{ph} value for the multilayer configuration containing the Sb_2Se_3 (Sb-A200) film compared to that of the Sb_2Se_3 (Sb-NA) film, which follows the LSV measurements. This result confirms the efficacy of annealing of the Sb layer before selenization to improve PEC performance. It has also performed long-term stability measurement for the multilayer Sb_2Se_3 (Sb-A200) film (Figure 7f), and one notices a stable j_{ph} with a value of $\approx -5 \text{ mA cm}^{-2}$ at 0 V_{RHE} during 7000 s, sug-

gesting thus no noticeable photocorrosion of the films during the light-driven HER.

2.4. Efficiency Analysis

Since there was a huge difference in the PEC performance between the multilayer configuration having the Sb_2Se_3 (Sb-A200) and the Sb_2Se_3 (Sb-NA) films, efficiency analysis was employed to better understand the main loss mechanism occurring in both samples. The reader is referred to SI for details about the calculation of the efficiency analysis. Based on the integration of the curve in Figure 8a by employing Equation S8, Supporting Information, it was obtained a maximum photocurrent density, $j_{\text{ph,max}}$, for the Sb_2Se_3 semiconductor of 39.9 mA cm^{-2} (for its corresponding E_{g} of 1.2 eV), as reported in the literature.^[27] Conversely, the absorption photocurrent density, $j_{\text{ph,abs}}$, was calculated from the employment of Equation S15, Supporting Information, and is displayed in Figure 8b. It notices $j_{\text{ph,abs}}$ values of 29.8 and 27.1 mA cm^{-2} for the Sb_2Se_3 (Sb-A200) and the Sb_2Se_3 (Sb-NA) films, respectively. These results did not represent significative differences between them for these films, and this is due to the E_{g} values being very similar to both films. This means that the decrease in the PEC performance of the Sb_2Se_3 (Sb-NA) film compared to that of the Sb_2Se_3 (Sb-A200) film is not due to loss of light absorption in the Sb_2Se_3 .

As additional analyses to determine the nature of the limiting factor(s) for the PEC performance of the films, the transfer ($\eta_{\text{transf.}}$) and separation ($\eta_{\text{sep.}}$) efficiencies were calculated from the Equations (7) and (8),^[75–77] and the results are shown in Figure 8c,d. For this analysis, it was used as an electron scavenger,^[78] a solution of $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_8$ dissolved in the electrolyte.

$$\eta_{\text{transf.}} = \frac{j_{\text{ph}}}{j_{\text{ph}(\text{Na}_2\text{S}_2\text{O}_8)}} \quad (7)$$

$$\eta_{\text{sep.}} = \frac{j_{\text{ph}(\text{Na}_2\text{S}_2\text{O}_8)}}{j_{\text{ph,abs}}} \quad (8)$$

The $\eta_{\text{transf.}}$ of the Sb_2Se_3 (Sb-A200) and Sb_2Se_3 (Sb-NA) films did not provide a relevant difference between their values (57% and 43% at 0 V_{RHE} , respectively), whereas the $\eta_{\text{sep.}}$ of these films differed drastically in 29% (i.e., 33% and 4% at 0 V_{RHE} , respectively). Bearing in mind that the $\eta_{\text{sep.}}$ represents the fraction of minority charge carriers reaching the surface of the semiconductor, while the remaining carriers recombine in the bulk.^[79] Although the $j_{\text{ph,abs}}$ of the Sb_2Se_3 (Sb-A200) and the Sb_2Se_3 (Sb-NA) films did not significantly change, the $\eta_{\text{sep.}}$ values suggest that a significant portion of the photogenerated charge carriers in the Sb_2Se_3 (Sb-NA) film undergo recombination before reaching the surface of the photoelectrode. In other words, the influence of annealing of Sb film before its selenization not only improved the crystallinity and preferential orientation to the [001] direction and stoichiometry but also directly resulted in a decrease in bulk recombination of the electron-hole pairs. Overall, these factors mentioned above featured a substantial improvement in the PEC performance toward light-driven HER due to the annealed Sb films submitted to selenization.

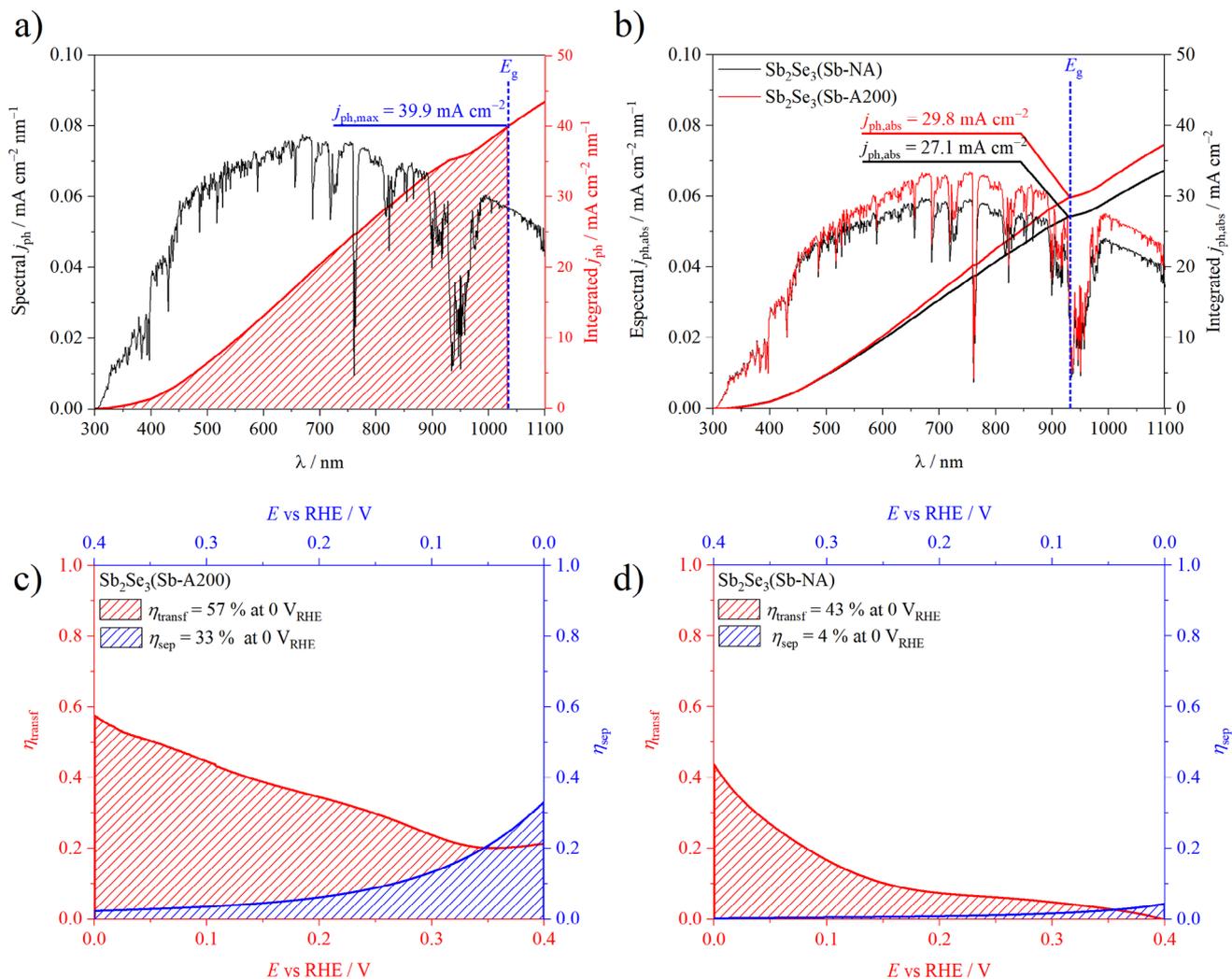


Figure 8. a) $j_{\text{ph,max}}$ for ideal Sb_2Se_3 semiconductor and b) $j_{\text{ph,abs}}$ for the Sb_2Se_3 films. η_{transf} and η_{sep} for c) the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})$ and d) the $\text{Sb}_2\text{Se}_3(\text{Sb-NA})$ films. The electrolyte was a N_2 -saturated solution of $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ pH $\approx 0.3 + 0.5 \text{ mol L}^{-1} \text{Na}_2\text{S}_2\text{O}_8$.

3. Conclusions

In the final analysis, the employment of an annealing step of the Sb film before selenization is utterly important to obtain Sb_2Se_3 film featuring high crystallinity, suitable stoichiometry, and preferential [001] orientation, which is required to favor charge carrier transportation to ultimately boost PEC H_2 generation. The crystal orientation was assessed by the $\text{TC}(hkl)$ calculated from the XRD data, which showed $\text{TC}(002) \gg 1$ for the optimized condition, indicating that the annealing of the Sb film favored the formation of highly oriented Sb_2Se_3 crystals in the [001] direction during the selenization step. Annealing the Sb film resulted in the formation of Sb film crystallographically oriented to the [001] direction, which might have ultimately contributed to obtaining [001]-oriented Sb_2Se_3 during the selenization process. The Sb_2Se_3 film obtained only by selenizing the non-annealed Sb film displayed $\text{TC}(230) > 1$, meaning that the Sb_2Se_3 crystal is oriented to the $[hk0]$ direction, which hinders charge carriers' transportation. The Sb annealing approach was also beneficial

for improving the crystallinity degree and the atomic ratio of the Sb_2Se_3 films as verified by the XRD and XRF analyses, respectively. In terms of PEC performance for the HER, the $\text{Sb}_2\text{Se}_3(\text{Sb-A200})/\text{CdS}/\text{TiO}_2/\text{Pt}$ film resulted in delivering a considerable $j_{\text{ph}} = -5.65 \text{ mA cm}^{-2}$ at 0 V_{RHE}, representing a tenfold increase compared to that of the $\text{Sb}_2\text{Se}_3(\text{Sb-NA})/\text{CdS}/\text{TiO}_2/\text{Pt}$ film. The Sb_2Se_3 film synthesized from the optimized condition also displayed stable photoelectroresponse for the HER over 7000 s of continuous experiment, and a higher value of efficiency for the photogenerated charge carriers' separation. Based on all these results, the improved PEC performance of the Sb_2Se_3 film, obtained from selenization of the annealed Sb, was due to the preferred Sb_2Se_3 crystal growth in [001] direction, improvement of crystallinity and stoichiometry, and reduced occurrence of the electron-hole recombination process. Last, this work contributes with an alternative approach to obtain [001]-oriented Sb_2Se_3 film and paves the way for future studies to further modify this material to

achieve even higher PEC activity for H₂ generation via water splitting.

4. Experimental Section

Fabrication of SLG/Mo Substrate: Soda-lime glass (SLG) plates, with dimensions of 2 cm × 2 cm, were cleaned with glassware detergent and then ultrasonicated with acetone, isopropanol, and deionized water for 10 min in each solvent, followed by drying with argon (Ar) gas. Subsequently, the SLG plates were coated with a tri-layer structure of molybdenum (Mo) with ≈900 nm of thickness by employing a DC-magnetron sputtering (Alliance Concept AC450) and used as substrate (SLG/Mo, where the metal acts as back-contact) for the deposition of the Sb₂Se₃ film.^[80] Each of the tri-layer Mo configurations was obtained at different sputtering deposition conditions, that is, power and pressure, which are described somewhere else.^[68] The tri-layer Mo configuration has been employed in this way to minimize its overselenization (formation of a thick layer of MoSe₂) during the thermal treatment process, which could be detrimental to the performance of the solar energy conversion devices. Additionally, the tri-layer Mo deposited on the SLG has been used to improve efficiency and enhance the performance of photovoltaic devices.^[68] The SLG/Mo was omitted in the sample labels (presented in the following section) and will be indicated when it is essential for the discussion of the results.

Synthesis of Sb₂Se₃ Film: The Sb layer (thickness of ≈250 nm) was deposited on the substrate via thermal evaporation (MBraun MBEvap) using Sb beads as the material source (Sigma-Aldrich 99.999%) placed on a Mo boat. The pressure of the system was set at 1 × 10⁻⁵ mbar, the deposition rate was ≈10 Å s⁻¹, and the holder rotation was 5.5 RPM.^[37] The as-deposited Sb layer on the substrate was subjected afterward to the annealing process in a three-zone tube furnace (Nabertherm). For the thermal treatment experiment, four approaches were investigated: a) selenization of non-annealed Sb, b) annealing temperature effect of Sb, c) selenization of annealed Sb at different temperatures, and d) optimizing selenization of annealed Sb. The first approach consisted of selenizing the non-annealed Sb film at 320 °C for 30 min (labeled as Sb₂Se₃ (Sb-NA)). The second one concerned the annealing temperature effect of the Sb films without selenization, which were annealed at 150, 200, and 250 °C for 30 min, and the samples were labeled as Sb-A150, Sb-A200, and Sb-A250, respectively, or Sb-A as a general label. The third approach consisted of selenizing the annealed Sb films in the same previous conditions, that is, the as-deposited Sb films were annealed at different temperatures, namely, 150, 200, and 250 °C for 30 min, followed by selenization at 320 °C for 30 min and the samples were labeled as Sb₂Se₃ (Sb-A150), Sb₂Se₃ (Sb-A200), and Sb₂Se₃ (Sb-A250), respectively, or Sb₂Se₃ (Sb-A) as a general label. The fourth approach encompassed the optimization of the selenization temperatures (i.e., 280, 300, 320, and 340 °C) and times (i.e., 30 and 60 min) for the annealed Sb. The sample was placed in a Petri dish inside the three-zone tube furnace and then submitted to an inert Ar atmosphere (internal pressure of 500 mbar). For the selenization experiments, 10 mg of Se powder (ThermoScientific) was placed inside the Petri dish. For all the approaches, the thermal treatment was performed under an Ar atmosphere and employed a heating rate of 10 °C min⁻¹; the cooling process was done naturally to room temperature. These thermal treatment approaches developed in this work are summarized in Figure S1, Supporting Information for a better overview.

Etching with KCN: The samples thermally treated were subsequently placed facing up in a Petri dish filled with a 2% m/v KCN solution for the etching process. The samples were etched for 40 min at room temperature and then washed extensively with ultrapure water (Milli-Q) and dried with N₂.^[18] According to the literature, KCN etching has been widely used in photovoltaic absorbers, such as CZTS,^[81] CIGSSe,^[82] CZTSSe,^[83] and Sb₂Se₃,^[18] as it has a positive impact on the electronic structure and superficial chemical composition of these materials. According to Jiménez-Guerra et al., etching Sb₂Se₃ film with KCN solution produces very Sb-rich surfaces, without affecting the bulk property, and inverts Sb₂Se₃'s polarity,

creating thus a buried junction with CdS, which improves the fill factor of the photovoltaic device.^[18]

Deposition of CdS Film: CdS film, which is an n-type semiconductor commonly used as an electron transport layer,^[84] was immediately deposited on the KCN-modified Sb₂Se₃ film by chemical bath deposition to form the Sb₂Se₃/CdS heterostructure. This aimed to protect Sb₂Se₃ films from any formation of superficial oxides as well as to further improve PEC performance. For this experiment, it was employed a total volume of 200 mL of CdS bath solution, and the preparation consisted of heating 100 mL of ultrapure water to 75 °C and then sequentially adding 55 mL of 0.1 mol L⁻¹ Cd(NO₃)₂, 30 mL of 1 mol L⁻¹ Na₃C₆H₅O₇, and 5 mL of NH₄OH (adapted from Vigil-Galán et al.^[85]). The samples were affixed onto a 4 cm × 4 cm plate glass using Kapton tape and placed vertically on a PTFE support. This system was immersed in the CdS bath solution and waited ≈5 min for stabilization, followed by the addition of 10 mL of 1 mol L⁻¹ (NH₂)₂CS. At this point, the chemical bath solution was kept under continuous stirring for 40 min, which was the deposition time. After that, the samples were removed from the bath, exhaustively rinsed with ultrapure water, and dried with Ar gas.

Deposition of TiO₂ Film: Aiming to protect the Sb₂Se₃/CdS heterojunction against photocorrosion, a protective layer of TiO₂ was deposited, which is a stable material even in aqueous media.^[86] The layer was deposited over the Sb₂Se₃/CdS film by the thermal atomic layer deposition (ALD, Veeco Savannah 200) technique. The samples were heated at 175 °C, and the deposition was performed using tetrakis(dimethylamino)titanium(IV) (TDMAT) as Ti precursor source and H₂O as an oxidant agent. The TDMAT precursor was heated at 75 °C during the deposition process, and the H₂O cylinder was set at room temperature. It employed 600 cycles for the deposition of the TiO₂ layer, and each cycle corresponded to exposing the samples to the TDMAT for 0.1 s followed by a 10 s purge of N₂, and then exposing the samples to H₂O vapor for 0.02 s with a subsequent purge with N₂ for 10 s. The growth rate of the TiO₂ film was 0.43 Å/cycle, resulting in a layer with a thickness of ≈26 nm.

Processing Photoelectrodes for PEC Measurements: To avoid losses of photoresponse signal of the photoelectrodes during the PEC measurements, it is utterly important to ensure a good electrical contact in the region where the connector is clipped onto the photoelectrode's back-contact. In this sense, an indium-based (In-based) solder was used to deposit a melted In layer on the upper region of the substrate (Figure S2a, Supporting Information). Then, the edges of the Sb₂Se₃/CdS/TiO₂ layers were properly removed to minimize potential border defects and to circumvent shunt resistance issues.^[87] Subsequently, a highly chemically stable and electrically insulating epoxy resin was used to cover the exposed edges of the Mo film (Figure S2a,b, Supporting Information), which cannot be in contact with the supporting electrolyte during the PEC measurements. The epoxy resin was allowed to dry for 24 h to ensure complete removal of the dispersing solvent from the polymer. The films' geometrical area delimited by the epoxy resin was determined from their photographs, which were taken close to a caliper, and using the ImageJ software.^[88] The geometrical area of the films was typically in the range of 0.1 – 0.2 cm².

Photoelectrodeposition of Pt Nanoparticles: Since Pt is highly electrocatalytic for the HER and can easily transfer electrons at the photoelectrode|electrolyte interface,^[89] it was photoelectrodeposited Pt nanoparticles over the film surface to further boost the HER. As a Pt precursor source, it was employed a solution containing 1.0 mmol L⁻¹ H₂PtCl₆·xH₂O in 0.1 mol L⁻¹ phosphate-buffered solution (PBS) at pH 6.5 and 0.1 mol L⁻¹ Na₂SO₄ (Sigma-Aldrich), which was previously deaerated for 15 min with N₂ flow before the Pt deposition on the samples. Pt photoelectrodeposition was carried out in a three-electrode cell with a quartz window and using a potentiostat/galvanostat (Biologic VSP). The counter electrode was a Pt plate with a geometric area of ≈1 cm², while the reference electrode was an Ag/AgCl/Cl⁻_(sat. KCl), that is, all the potential values presented in the text are referenced against the Ag/AgCl/Cl⁻_(sat. KCl) electrode, unless the reversible hydrogen electrode (RHE) is specified. The working electrode was the Sb₂Se₃/CdS/TiO₂ film. The Pt deposition was performed in galvanostatic mode, applying a current density of -0.05 mA cm⁻² for 10 min, and under a solar light simulator (Newport LSH-7320

LED, 100 mW cm⁻²).^[90] Figure S2c, Supporting Information summarizes all the steps involved in the fabrication of the complete device, which will be employed as photoelectrode for the PEC measurements.

Physical and Chemical Characterization: The crystalline structure of the Sb₂Se₃ was characterized by X-ray powder diffraction (XRD, Bruker D8 Advance) with Cu Kα₁ radiation of 1.54 Å and a scan rate of 0.02° s⁻¹ in a 2θ range between 10 and 80°. The vibrational modes of Sb₂Se₃ were investigated by Raman spectroscopy (Renishaw Raman microscope) under a 532 nm excitation laser. Morphological characterization and cross-section measurements were performed via high-resolution field emission scanning electron microscopy (FE-SEM, Neon40 Crossbeam, and Philips XL30 FEG) operating with 15 kV and using an in-lens detector. The chemical composition was assessed employing X-ray fluorescence (XRF, Fischer-science X-ray). The elemental mapping of the top surface and cross-section of the samples was carried out on a FE-SEM (Jeol JSM-7200F) equipped with an energy-dispersive X-ray spectrometer (EDS, Bruker XFlash 6|60 detector). It was also evaluated the superficial chemical composition of the Sb₂Se₃ film via X-ray photoelectron spectroscopy (XPS, Scienta Omicron ESCA 2SR) with Al Kα₁ radiation (1486.7 eV), which was the excitation source. All the XPS spectra were adjusted by setting the C 1s peak at 284.5 eV and employing the Gaussian-Lorentzian function (30%) for the peak adjustment and the Tougaard function for the background. The XPS spectra processing was done with the CasaXPS software.^[91] The optical E_g was estimated from the diffuse reflectance spectra recorded on a UV–vis–NIR spectrophotometer (Cary 5E) and calculated via Kubelka-Munk function, $f(R)$, and Tauc plots (Equations (9) and (10)^[92,93]).

$$f(R) = \frac{a}{s} = \frac{(1-R)^2}{2R} \quad (9)$$

$$(ah\nu)^n = A_0 (h\nu - E_g) \quad (10)$$

where s is the scattering coefficient, which was considered to be wavelength independent and that means that $f(R)$ can be used instead of a ,^[51] R is the absolute diffuse reflectance, h is the Planck constant (6.626 × 10⁻³⁴ J s), n assumes the values of 2 or 2/3 for direct transition (allowed and forbidden, respectively) and 1/2 or 1/3 for indirect transition (allowed and forbidden, respectively), A_0 is a constant, and ν is the frequency of radiation.

Urbach energy, E_u , which describes the occurrence of band tail energy within the E_g ,^[56] was calculated from Equation (11):^[94]

$$a = a_0 \exp\left(\frac{E_{ph}}{E_u}\right) \quad (11)$$

where the a_0 is a constant and E_{ph} is the photon energy, and such is defined in Equation (12):

$$E_{ph} = h\nu \quad (12)$$

The values of E_u can be determined from the inverse of the slope in the linear region (below the optical E_g) of the $\ln a$ versus E_{ph} graphs.

Photoelectrochemical Characterization: The PEC experiments were carried out in the same cell configuration and solar simulator as described previously. The supporting electrolyte was a solution containing 0.5 mol L⁻¹ H₂SO₄ pH ≈ 0.3 (measured pH), and this solution was deaerated with N₂ flow for 15 min before the PEC experiments. To evaluate the PEC activity for the H₂ generation, it was employed linear sweep voltammetry (LSV) in the dark and under illumination, as well as under chopped illumination. The LSVs were recorded at a scan rate of 5 mV s⁻¹ and were scanned from the open-circuit potential to the thermodynamic potential of the HER at pH 0.3. The potential values recorded against the Ag/AgCl/Cl⁻ (sat. KCl) electrode were converted to potential values relative to the RHE by using Equation (13).^[95,75,76]

$$E \text{ (versus RHE)} = E_{\text{appl.}} \text{ (versus Ag/AgCl/Cl}^-_{\text{(sat. KCl)})} + \text{pH} \times 0.059 + 0.197 \quad (13)$$

Chronoamperometry measurements were employed to check the short-term stability of the samples, and this experiment was conducted by polarizing the samples at 0 V_{RHE} for 660 s under chopped illumination (pulses of 60 s for each light on and light off conditions (Thorlabs SHB1T diaphragm shutter)). It was also performed long-term stability tests for 2 h under chopped illumination (pulsed light, alternating 20 min of light on and 30 s of light off) for the samples polarized at 0 V_{RHE}. The current values, obtained from the LSVs and chronoamperometries, were normalized by the geometric area. The geometric area was obtained from the photograph processing of the photoelectrodes, as described previously. The applied bias photon-to-current efficiency (ABPE) of the photocathodes was calculated from Equation (14).^[51] It is worth noting that the PEC experiments performed to obtain this efficiency were conducted in a three-electrode cell configuration (i.e., bias was applied between the working and reference electrodes). This means that the ABPE values obtained in this work represent the efficiency of the PEC performance at the photocathode|electrolyte interface and not the efficiency of an entire PEC device.^[51] Despite this, the ABPE results are valuable in providing insights about the semiconductor material and its interface properties.

$$\text{ABPE} = \left[\frac{j_{\text{ph}} [E_{\text{appl.}} \text{ (versus RHE)} - 0] \eta_F}{I} \right]_{\text{AM1.5G}} \quad (14)$$

where $E_{\text{appl.}}$ (versus RHE) is the applied potential relative to the RHE, j_{ph} is the photocurrent density at a given $E_{\text{appl.}}$ (versus RHE) value, which was obtained from the LSVs, η_F is the faradaic efficiency (considered 100% for this study), and I is the solar simulator irradiance on the photocathode (100 mW cm⁻²).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

hydrogen, photoelectrochemical water splitting, preferential orientation, Sb₂Se₃, solar energy

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